The Environmental Behavior of Ethylene Dibromide and 1,2-Dichloroethane in Surface Water, Soil, and Groundwater

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Regulatory and Scientific Affairs Department

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Executive Summary

This report reviews the available environmental fate literature for two compounds, ethylene dibromide (EDB) and 1,2,-dichloroethane (1,2-DCA). The purpose of this report is to serve as a reference for environmental professionals evaluating potential risks at former leaded gasoline fueling sites where EDB or 1,2-DCA is detected in groundwater.

EDB was previously used as a soil fumigant and as a leaded gasoline additive while 1,2-DCA is currently produced in large quantities as a commercial chemical. 1,2-DCA was also used as a leaded gasoline additive. EDB and 1,2-DCA were added to the lead mix in order to prevent the build-up of solid lead oxides on spark plugs and exhaust values in piston engines. The sale of leaded fuel for use in on-road vehicles was banned in 1996, although fuel containing lead can still be used for off-road uses including in aircraft, racing cars, farm equipment, and marine engines.

The current presence of 1,2-DCA in air, surface water, and groundwater samples can be attributed mainly to its high production volume. EDB is not typically found in recent air or surface water samples since its use as a soil fumigant is no longer permitted and because of limited use of leaded fuels. However, EDB and 1,2-DCA have been reported in groundwater and soil samples at some sites where leaded gasoline was previously dispensed.

The physical/chemical similarities of the two compounds indicate that they will behave similarly in the environment. Both compounds are volatile, have relatively high water solubilities, and are soluble in organic solvents. Transport data show that they readily volatilize from water and soil surfaces as pure compounds and have low Koc values. This indicates that they have the potential to leach through soil to groundwater, although studies also indicate that a residual amount remains trapped in soil by absorption or in residual NAPL. Hydrolysis half-lives are slow, on the order of 1 to 10 years for EDB and tenfold longer for 1,2-DCA.

Biotic degradation is reported for both compounds under aerobic and anaerobic conditions in laboratory studies. Based on these data, 1,2-DCA appears to be more resistant to biodegradation than EDB. Evidence for the anaerobic biodegradation of 1,2-DCA in the field includes the presence of biodegradation products in groundwater and changes in 13C/12C ratios of 1,2-DCA as the groundwater moves downgradient from the source area. More limited field data exist for EDB. The field study data collected for 1,2-DCA and EDB are typically reported as disappearance rate constants, particularly for aquifer studies. The use of these values as biodegradation half-lives is not appropriate, as loss due to other processes (both transport and abiotic degradation processes) is included in this rate constant.

Fuel hydrocarbons present at leaded fuel release sites may also slow the biodegradation of 1,2-DCA and/or EDB in the environment. Laboratory studies for both EDB and 1,2-DCA were nearly always run using a single compound. Reported biodegradation rates are slower for these compounds in the presence of fuel-contaminated groundwater.

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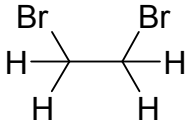
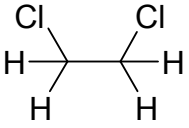
I. Introduction

The following document reviews the available environmental fate literature for two compounds, ethylene dibromide (EDB) and 1,2-dichloroethane (1,2-DCA). While these particular names suggest that these two compounds have different structures, EDB and 1,2-DCA are structurally similar (Table 1). Neither compound contains a double bond despite the common names of ethylene dibromide and ethylene dichloride. The two structures differ only with the presence of either bromine or chlorine substituents.

Table 1. A comparison of structure and nomenclature for the lead scavengers ethylene dibromide and 1,2-DCA

Chemical name used in report	EDB	1,2-DCA
Chemical structure		
CAS registry number	106-93-4	107-06-2
Molecular formula	$C_2H_4Br_2$	$C_2H_4Cl_2$
SMILES notation	BrCCBr	ClCCCl
CAS-9CI name	Ethane, 1,2-dibromo-	Ethane, 1,2-dichloro-
Synonyms	Ethylene dibromide 1,2-Dibromoethane 1,2-Ethylene dibromide DBE	Ethylene dichloride 1,2-Dichloroethane 1,2-Ethylene dichloride EDC

EDB was previously used as a soil fumigant and as a leaded gasoline additive while 1,2-DCA is currently produced in large quantities as a commercial chemical (nearly 8.2 billion kilograms in the mid-1990s) with most of this, >96%, used as a chemical intermediate. 1,2-DCA was also used as a leaded gasoline additive. The current presence of 1,2-DCA in air, surface water, and groundwater samples can be attributed mainly to its high production volume. EDB is not typically found in recent air or surface water samples since its use as a soil fumigant and leaded gasoline additive are no longer permitted by the U.S. EPA. However, it has been reported in groundwater and soil samples affected by historical uses.

The following sections provide a review of environmental fate data for both compounds as well as monitoring data from sites where direct release occurred and from larger monitoring studies where concentrations cannot be attributed to a single release. Section II briefly describes the literature search process. Section III contains all available environmental information for EDB while Section IV contains the available information for 1,2-DCA. Within Sections III and IV, transport processes are considered initially, followed by abiotic and biotic transformation processes, and then monitoring data. While EDB and 1,2-DCA are considered separately, the environmental processes relevant for each compound are expected to be similar. For example, the physical trapping of pure EDB by soil samples was well studied because of its use as a soil fumigant. Similar studies were not conducted for 1,2-DCA; however, based on the mechanism reported for EDB and the structural similarity of the two compounds, it is likely to be important for 1,2-DCA as well. In such cases, the reader is referred back to the relevant section of the report where the original data are reported.

II. Technical Approach

The literature search began with an electronic search of two files in SRCs Environmental Fate Data Base (EFDB), DATALOG, and BIOLOG, as sources of information on abiotic and biotic transformation processes, environmental transport, physical/chemical properties, and environmental concentrations. In particular, DATALOG contains a citation index catalogued by environmental process (e.g., adsorption, biodegradation, hydrolysis, photooxidation) as well as field and ecosystem studies, physical/chemical properties (e.g., Henry's Law constant, vapor pressure, water solubility), and environmental concentrations in multiple media (e.g., air, water, soil, sediment). Because DATALOG only catalogues mixed culture studies, BIOLOG was also queried as a source of information on pure culture or defined/enrichment culture biodegradation studies. Both EDB and 1,2-DCA were well-represented in the available literature. A Chemical Abstracts search was also conducted using a combination of degradation and media keywords for citations published during and after year 2000.

In addition to the in-house literature searches and the references cited in the Request for Proposal (RFP), SRC searched the reference section of every identified paper for additional relevant articles. This was particularly effective in identifying recent papers from less well known sources, such as those from conference proceedings. Online searches using GOOGLE were used to identify field study data and recent monitoring data that may not have been published. Recent articles such as those by Falta and Bulsara (2004), Burton (2005b) and Miner (2005) published online by LUSTLine were also located using this approach. Relevant presentations from the Annual Clemson University Hydrogeology Symposium, as well as government sites for ATSDR Health assessments, and Record of Decision documents for Superfund sites were also located from online sources.

III. Ethylene Dibromide (EDB)

A. Historical and Current Use Patterns

EDB was first produced in 1923 (Scheibe and Lettenmaier, 1989). The major historical uses of EDB were as a soil fumigant and as an additive to leaded gasoline and aviation fuel. Small amounts of EDB were used as an intermediate in the synthesis of dyes and pharmaceuticals and as a solvent for resins, gums, and waxes (Fishbein, 1979; U.S. EPA, 1977). EDB is currently used as a chemical intermediate particularly for manufacturing vinyl bromide (a flame retardant used in modacrylic fibers), as a nonflammable solvent for resins, gums, and waxes (U.S. DHHS, 2005), in the treatment of felled logs for bark beetles and control of wax moths in beehives (ATSDR, 1992), and as a lead scavenger in leaded fuels for off-road uses such as in aircraft, racing cars and marine engines (Burton, 2005b; U.S. EPA, 1996). Monitoring data indicating the presence of very low concentrations of EDB in ocean water and ocean air suggest that EDB also may be formed naturally in ocean environments due to growth of macro algae (Class and Ballschmiter, 1988; Laturnus, 1995).

The total annual U.S. production of EDB peaked in 1974 at 150.9 million kilograms and by 1983, production was only 70.5 million kilograms (U.S. ITC, 1970–1984) (Figure 1). This decrease can be attributed to two events: the cancellation of EDBs registration for use as a pesticide in 1983/1984 and more importantly, the widespread installation of catalytic converters on passenger cars and light trucks for U.S. distribution in model year 1975 due to tightened emission standards (U.S. EPA, 1996) and the subsequent phase-out of leaded gasoline beginning in 1978. IUR (Inventory Update Reporting) CUS production volumes for EDB are available for the following years: 1986, >45.5M to 227M (millions of kilograms); 1990, >22.7M to 45.5M; 1994, >4.5M to 22.7M, 1998 and 2004 both >0.45M to 4.5M (U.S. EPA, 2007).

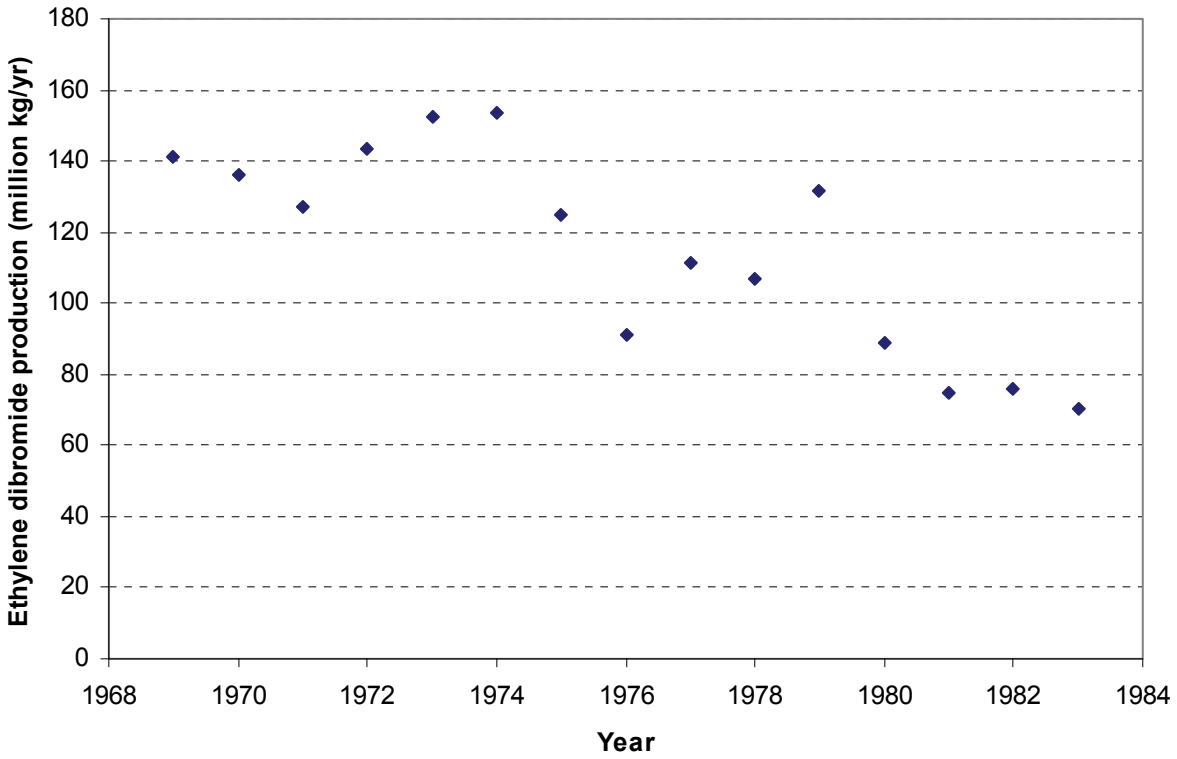


Figure 1. Annual U.S. production of EDB from 1969 to 1983 (U.S. ITC, 1970–1984)

EDB was registered as a pesticide, mainly for the control of soil nematodes, in 1948 and was typically sold as a liquid mixture with petroleum solvents. EDB was also used in spot fumigations of grain milling machinery and flour mills, post-harvest fumigation of grain, and in the control and prevention of infestations in fruits and vegetables (Alexeeff et al., 1990). Minor uses included the control of mountain pine bark beetles, moths in vault-stored furniture and clothing, termites, Japanese beetles, and wax moths (Alexeeff et al., 1990; U.S. EPA, 1977). The discovery of EDB in stored grain and in well water in 1983 resulted in an EPA ban on agricultural uses (U.S. EPA, 1977). In the 1983 Federal Register notice cancelling EDBs registration for use as a soil fumigant, it is noted that based on the "geographic range of contaminated groundwater sites and reports of leaching of EDB through the soil column in the west and southwest… that EDB will leach wherever it is applied" (U.S. EPA, 1983). In 1984, the registration of EDB for use as a fumigant on grains and grain milling machinery was cancelled.

In 1975, approximately 3–4% of the total 1975 EDB production was used as a pesticide (U.S. EPA, 1977). By 1983, nearly 10 million kg EDB active ingredient was applied to ~400,000 ha of a variety of crops in the U.S. (11% of the total EDB production for that year) (Pignatello and Cohen, 1990). In contrast, in 1983, an estimated 111 million kg/yr EDB was used as a lead scavenger in leaded gasoline and aviation fuel (Pignatello and Cohen, 1990).

The commercial sale of leaded gasoline began in 1923 (Burton, 2005a). EDB was added to leaded motor fuel as of 1925 (Burton, 2005a). EDB and 1,2-DCA were added to the lead mix in order to prevent the build-up of solid lead oxides on spark plugs and exhaust values in the piston engine (Burton, 2005b). The volatile lead bromide and lead chloride formed during the engine combustion process were then released to the air. The amount of EDB added to leaded gasoline is dependent on the concentration of lead. Leaded fuels from 1942 to present day contain 1.0 mole 1,2-DCA and 0.5 mole of EDB per mole of alkyl

lead (Falta, 2005; U.S. EPA, 1984). Prior to 1942, varying molar ratios of EDB to 1,2-DCA were used (Falta, 2005). Aviation fuel which contains only EDB (at 1.0 mole EDB per mole of alkyl lead) has twice as much EDB as leaded gasoline.

Lead concentrations in gasoline have varied considerably since lead was shown to reduce spark knock in engines in the early 1920's. Initially, a maximum limit of 3.17 g lead/gallon was recommended by the federal government in 1926. This was increased in 1959 to 4.23 g lead/gallon due to increased compression ratios and octane requirements of engines at this time (Gibbs, 1990). Lead concentrations actually reached historic average highs of only 3.0 g lead/gallon and 2.5 g lead/gallon for premium and regular gasolines, respectively, in the late 1960s (Gibbs, 1990). By the 1970s, improvements were made in refining processes resulting in higher octane base gasoline (Gibbs, 1990) and the U.S. EPA enacted regulations that systematically limited lead concentrations in the U.S. gasoline pool. These regulations are covered by Gibbs (1990) in some detail. By 1979, the average lead content for large refiners (producing >50,000 barrels daily) was set at 0.8 g lead/gallon and 2.65 g lead/gallon for small refiners (for leaded and unleaded gasoline together). After several further changes, a maximum limit of 0.5 g lead/gallon was set across all leaded gasoline manufactured by each refinery in 1985. By 1988, an average of 0.1 g lead/gallon was reached for all U.S. leaded gasoline.

In 1995, leaded fuel made up only 0.6% of total gasoline sales in the U.S. (U.S. EPA, 1996). The sale of leaded fuel for use in on-road vehicles was banned in 1996, although fuel containing lead can still be used for off-road uses including in aircraft, racing cars, farm equipment, and marine engines (U.S. EPA, 1996). For example, EDB is still found in several leaded aviation gasoline products: Avgas 80, Avgas 100, and Avgas 100LL (low lead) (Burton, 2005b). Avgas 100LL is the most commonly used aviation fuel for spark-ignition internal combustion engines (e.g., single piston airplanes) (Florida Department of Environmental Protection, 2006). The typical composition of the TEL-CB tetraethyl lead package currently produced by Ethyl Corporation for use in leaded fuels (61.49% tetraethyllead, 17.86% EDB, 18.81% 1,2-DCA) is similar to the classic formulation of ethyl fluid. A second package, TEL-B, contains 61.49% tetraethyllead and 35.73% EDB which is similar to the formulation used for Avgas (Burton, 2005b).

B. Physical Properties

Physical/chemical properties for EDB are presented in Table 2. EDB has relatively high vapor pressure and water solubility values. Based on its vapor pressure, EDB is expected to volatilize in dry soils which is the basis of its use as a soil fumigant. Its Henry's Law constant indicates that EDB will volatilize readily from water surfaces.

EDB is miscible in many organic solvents. If released to the environment in a fuel mixture, it will move with the light non-aqueous phase liquid (LNAPL) by gravity through the vadose zone potentially to groundwater. The dissolution of a single compound from a mixture such as gasoline in contact with water is different than its dissolution as a pure compound. For the release of a pure compound such as EDB, water-phase concentrations at the NAPL-water interface are at the solubility limit in water. However, for a compound in a gasoline mixture at the NAPL-water interface, the maximum concentration in the water phase is estimated as the effective solubility. This can be presented as a retardation coefficient (total concentration/fraction in mobile-water phase) in a saturated soil matrix.

In soil the retardation coefficient, R_i, is:

$$R_i = \frac{[\theta_w + \rho_s \cdot f_{oc} \cdot K_{oc,i}]}{\theta_w} = 1 + \frac{\rho_s \cdot f_{oc} \cdot K_{oc,i}}{\theta_w} \qquad \text{Eq. (1)}$$

With an immobile residual oil phase (gasoline) present, based on presumed ideal Raoult's law partitioning

$$R_i = \frac{\left(\theta_w + \rho_s \cdot f_{oc} \cdot K_{oc,i} + \frac{\theta_o \cdot \rho_o}{S_i} \cdot \frac{MW_i}{MW_o}\right)}{\theta_w} = 1 + \frac{\rho_s \cdot f_{oc} \cdot K_{oc,i}}{\theta_w} + \frac{\frac{\theta_o \cdot \rho_o}{S_i} \cdot \frac{MW_i}{MW_o}}{\theta_w} \qquad \text{Eq. (2)}$$

Equivalently, for a measured gasoline to water partition coefficient

$$R_i = \frac{\left(\theta_w + \rho_s \cdot f_{oc} \cdot K_{oc,i} + \theta_o \cdot \rho_o \cdot K_{gw,i}\right)}{\theta_w} = 1 + \frac{\rho_s \cdot f_{oc} \cdot K_{oc,i}}{\theta_w} + \frac{\theta_o \cdot \rho_o \cdot K_{gw,i}}{\theta_w} \qquad \text{Eq. (3)}$$

With θ_w (cm^3-water/cm^3-soil) volumetric moisture fraction in soil matrix, equal to the total soil porosity in saturated soil; ρ_s (g-soil/cm^3-soil) is the soil dry bulk density; f_{oc} (g-oc/g-soil) is the mass fraction of organic carbon in soil; and $K_{oc,i}$ (cm^3-water/g-oc) is the chemical-specific organic carbon-water partition coefficient. MW_i is the molecular weight of the chemical, S_i is the pure chemical aqueous solubility limit. With the chemical of interest as a small fraction of the total residual phase, values of θ_o (cm^3-oil/cm^3-soil), ρ_o (g-oil/cm^3-oil), and MW_o (which is a function of oil mixture composition) will be relatively constant and the factor R_i will be independent of the total oil mixture concentration in soil.

The gasoline to water partition coefficient can be estimated from the octanol to water partition coefficient as:

$$K_{gw} = K_{ow} \cdot \frac{MW_{octanol}}{MW_o} \qquad \text{Eq. 4}$$

EDBs gasoline-water partition coefficient (Table 2) indicates that once in contact with groundwater, it will dissolve more rapidly out of the LNAPL in the groundwater than will benzene (benzene has a gasoline:water partition coefficient of 350) (Cline et al., 1991; Falta, 2004b). Based on EDBs gasoline:water partition coefficient, Pignatello and Cohen (1990) reported that groundwater in contact with gasoline LNAPL at lead levels present in 1990, will contain approximately 80 µg/L EDB. Falta (2004b), however, reported a potential maximum concentration of 1900 µg/L for EDB near a residual or LNAPL gasoline source determined from EDBs gasoline:water partition coefficient. If EDB is released alone or as a spill of grain bin fumigant (e.g., mixtures of EDB with carbon tetrachloride and/or 1,2-DCA), the EDB would be expected to move through the vadose zone potentially to the groundwater as a dense non-aqueous phase liquid (DNAPL) based on its density compared to water. Once EDB is dissolved in groundwater, it is not expected to markedly change the water density; therefore, EDB will move with the bulk of the groundwater flow (Pignatello and Cohen, 1990).

Table 2. Physical/chemical properties for EDB

Property	Ethylene dibromide	Reference
CAS Registry Number	106-93-4	
Structure	$CH_2Br—CH_2Br$	
Physical description	Colorless, heavy non-flammable liquid	U.S. EPA (1977)
Molecular weight	187.86 g/mol	
Melting point (°C)	9.97	SRC (2007)
Boiling point (°C)	131.6	SRC (2007)
Solubility	Water: 3910 mg/L at 25 °C Octanol: miscible Organic solvents: miscible	Horvath et al. (1999) Johns (1976) Alexeeff et al. (1990)
Vapor pressure	11.2 mm Hg at 25 °C	Daubert and Danner (1985)
Octanol-water partition coefficient	91.2	Hansch et al. (1995)
Henry's Law constant	$6.5x10^{-4}$ atm-m^3/mol at 25 °C 0.029 (dimensionless)	Rathbun (1998) Falta and Bulsara (2004)
Gasoline-water partition coefficient (dimensionless)	152	Pignatello and Cohen (1990)
Specific gravity (liquid)	2.179 at 25 °C	Alexeeff et al. (1990)
Specific gravity (vapor)	6.5 at 25 °C	Alexeeff et al. (1990)
Equilibrium aqueous concentration	1900 µg/L	Henderson (2005)
Diffusion coefficient in dry air	0.0813 cm^2/sec (20 °C) 0.0708 cm^2/sec (0 °C)	Pignatello and Cohen (1990)
Diffusion coefficient in water	$1.0x10^{-5}$ cm^2/sec (25 °C, estimated)	Pignatello and Cohen (1990)
Density	2.701 at 25 °C	van Agteren et al. (1998)
Vapor density relative to air	6.1; density of EDB saturated air is 1.08 (air = 1)	U.S. EPA (1977)
Heat of vaporization	+53 cal/gm at 25 °C	U.S. EPA (1977)
Percent in saturated air	At saturation, the concentration of EDB is 1.3% by volume at 25 °C	U.S. EPA (1977)
Conversion factors	1 ppm = 7.68 mg/m^3 in air 1 mg/m^3 = 0.13 ppm in air 1 mg/L = 130 ppm at 25 °C/760 mm Hg	U.S. EPA (1977)

C. Transport Processes

1. Transport from Water Surfaces

The release of EDB to water results in rapid volatilization. Overall mass transfer coefficients for the volatilization of EDB from water are dependent on wind speed (Rathbun and Tai, 1987). Both gas-film and liquid film coefficients are important in determining EDBs resistance to volatilization from water (Rathbun and Tai, 1986). Lyman et al. (1982) estimated liquid- and gas-phase exchange coefficients of 16 and 1400 cm/hr, respectively, and a mass transfer coefficient of 11.4 cm/hr. Based on these values, a volatilization half-life of 4 hours can be estimated using a wind speed of 3 m/sec and a water speed of 1 m/sec (Lyman et al., 1982). Rathbun and Tai (1987) measured gas-film coefficients for the volatilization of EDB from water of 286 and 533 m/d (1192 and 2221 cm/hr, respectively) for low (0.1 m/sec) and high (2.0 m/sec) windspeeds, respectively, at 25 °C (Rathbun and Tai, 1987). Hsieh et al. (1993) measured mass-transfer coefficients of EDB at varying impeller speeds (150 to 500 rpm). Mass transfer coefficients of 0.14, 0.53, 1.05, and 1.30 hr^{-1} were reported for 150, 200, 400, and 500 rpm,

respectively. Gas film constants of 0.68 and 0.410 are reported by Hsieh et al. (1993) and Rathbun and Tai (1987), respectively. A water-film reference substance parameter of 0.633 indicates that the water-film mass-transfer coefficient for the volatilization of EDB will be 63.3% that of the reaeration coefficient for the absorption of oxygen by a stream (Rathbun, 1998). An air-film reference-substance parameter of 0.393 indicates that the air-film mass-transfer coefficient for the volatilization of EDB from a stream will be 39.3% that of the mass transfer coefficient for the evaporation of water (Rathbun, 1998).

Mackay and Yeun (1983) measured volatilization rates of EDB in a 6 m long, 0.61 m deep, and 0.60 m wide wind-wave tank. Overall mass transfer coefficients of 23.6, 45.3, 54.7, and 77.2 $x10^{-6}$ m/sec were measured for windspeeds of 5.96, 8.57, 10.31, and 77.2 m/s, respectively. Based on their results, a water evaporation half-life of 4.26 hours can be calculated (windspeed of 8.57 m/sec, 0.61 m depth) (Mackay and Yeun, 1983). The authors state, however, that laboratory-derived mass transfer coefficients are generally expected to be higher than those that would be measured in the environment at the same windspeed. An evaporation half-life in water of 6.4 minutes was reported by Chiou et al. (1980) at 23.1°C, an initial concentration of 0.1 ppm, 1.6 cm depth, and stirring speed of 100 rpm. In still air, the evaporation rate of EDB from water is $1.24x10^{-5}$ g/cm^2-sec (Chiou et al., 1980). Volatilization data from spill sites for 1,2-DCA (Section IV, C.1) confirm that volatilization of these small molecules from water surfaces is rapid.

2. Transport in Soil

The movement of a chemical in the vadose zone is dependent on both transport and adsorption processes. Based on different release scenarios, EDB in the vadose zone can be found dissolved in solution, as a vapor, as pure compound adsorbed to soil, as free NAPL, or as residual NAPL. Dissolved EDB will move with the infiltrating water to the water table via advection while vapor-phase EDB will move by diffusion through the soil (Pignatello and Cohen, 1990). EDB present in an LNAPL (such as a mixture of leaded gasoline) or DNAPL (such as a grain fumigant spill) will move mainly downward with the NAPL through the pores of the soil due to gravitational and capillary forces. If only a small quantity of NAPL is released, it may be contained in the vadose zone by the soil. However, if the amount of NAPL is sufficiently large, the bulk of the NAPL can move through the vadose zone to the groundwater table. An LNAPL will accumulate at the groundwater table, while a DNAPL will continue to migrate downward until it encounters a sufficient confining stratum. The NAPL's movement in the soil is determined by many factors including soil porosity, soil permeability, and capillary pressure. During movement downwards, NAPL can become "trapped" within the soil matrix due to capillary forces leaving residual NAPL behind in the soil (Rixey, 1996). This residual saturation may represent a long-term source of soluble NAPL components to the environment (Garg and Rixey, 1999; Rixey, 1996).

Sorption of vapor-phase EDB to soil has been studied by Thomason and McKenry (1974) and Sawhney and Gent (1990). In soil chamber studies, EDB was injected into dry soil (montmorillonite silty clay loam soil, 13:62:25% sand:silt:clay, 1.1% organic matter, 7.7% w/w water) at a depth of 30.5 cm and at an application rate of 47 L/ha commercial product (Thomason and McKenry, 1974). EDB diffused radially outwards from the point of injection. A vapor-phase concentration of $4.5x10^{-7}$ moles/L (0.05 ppm) at 90 cm depth was reached within 7 days. Loss of EDB to the atmosphere was measured in a sandy loam soil (68:22:15% sand:silt:clay, 0.6% organic matter). Injection was at a depth of 30.5 cm and air was passed over the soil surface at 0.80 km/hr. After 14 days, approximately 1% of the total was lost to the atmosphere. Under field conditions, it was anticipated that this value would be greater (Thomason and McKenry, 1974). The results from Thomason and McKenry (1974) differ from volatilization half-lives of 0.4 and 3.4 days at 1 and 10 cm depths, respectively, estimated by Jury et al. (1984).

The sorptive capacity of vapor-phase EDB to two different soils, the sandy loam and the silty clay loam described above was measured under different conditions of temperature and soil moisture (Thomason

and McKenry, 1974). At moisture tensions >15 bars, the sorptive capacity was greatly increased in both soils. The sorptive capacity was greater for the sandy loam soil than the silty clay loam and for soil incubated at 15 °C over soil at 25 °C. A mass balance in soil at 15 °C found approximately 24, 24, 50, and 2% of the initially-added EDB in the soil water phase, unaccounted for, in the soil particle phase and in the soil vapor phase, respectively, by day 7 post-treatment. Mass balance measurements on day 15 post-treament found 20, 40, 38, 1, and 1% of the initially-added EDB in the soil water phase, unaccounted for, in the soil particle phase, in the soil vapor phase, and lost naturally to the atmosphere, respectively (Thomason and McKenry, 1974). Sawhney and Gent (1990) measured the vapor-phase sorption of EDB to a series of clay minerals. The rate of EDB sorption was high initially but slowed considerably over the remaining study period; 3, 5, 6, and 9% EDB by weight was sorbed to columns filled with pyrophyllite, kaolinite, illite, and smectite, respectively. Sorption was not correlated with BET (Brunauer, Emmett, Teller) surface areas. EDB desorption from the columns was also initially rapid but again became slower as the study proceeded.

Results from early studies show linear sorption isotherms for aqueous-phase EDB (Call, 1957; Phillips, 1964). Phillips (1964) reported that EDB sorption to a sand loam (34.2: 45.5: 7.7: 7.4% coarse sand, fine sand, silt, and clay, respectively, 4.15% organic matter), a silt loam (0.5: 68.7: 10.0: 10.9% coarse sand, fine sand, silt, and clay, respectively, 3.28% organic matter), and a peaty soil (6.4: 9.5: 7.8: 30.9% coarse sand, fine sand, silt, and clay, respectively, 30.6% organic matter) was linear for each soil. The moisture content of soils affects the sorption of EDB with drier soils showing greater adsorption. The transition point for this observation is reported to be between 5 and 20% water/dry weight soil (Pignatello and Cohen, 1990).

Recent studies have suggested that the sorption of EDB may also be affected by the presence of other compounds (Pignatello, 1990a). The sorption of EDB to granular activated carbon was measured as a single solute and as a mixture with five other compounds (chloroform, chlorodibromomethane, bromoform, trichloroethene, tetrachloroethene) at varying concentrations (Crittenden et al., 1985). As a single solute, EDB had a K_p value of 0.4808 over a concentration range of 32 to 1750 μg/L. In the presence of other compounds, the sorption of EDB decreased significantly over the entire concentration range due to competitive interactions. The K_p of EDB decreased by a factor of 3.1 (from 0.77 to 0.25) when sorbed trichloroethene (TCE) concentrations of 0 to 120 mg/kg, respectively, were present (Pignatello, 1990a). In the presence of o-dichlorobenzene, the K_p of EDB decreased by a factor of 1.4 (from 0.77 to 0.55) at sorbed o-dichlorobenzene concentrations of 0 to 240 mg/kg, respectively (Pignatello, 1990a). Using a peat (BET surface area of 1.4 m^2/g, organic-carbon content of 49.3%) and a mineral soil (BET surface area of 11.2 m^2/g, organic-carbon content of 1.26%), Chiou and Kile (1998) measured the sorption of EDB in both single-solute and binary-solute systems. In single-solute systems, EDB showed non-linearity at low relative concentrations of EDB in water but the sorption isotherm became linear at medium to high relative concentrations of EDB for both soils. The apparent non-linear capacity of EDB on the peat and mineral soils is 0.18 mg/g and <0.008 mg/g, respectively, with apparent saturation when the ratio of solute concentration to solute solubility is approximately 0.010 to 0.015 (Chiou and Kile, 1998). This non-linearity was attributed to the presence of "high surface area carbonaceous material" (HSACM) which becomes saturated at higher relative concentrations of EDB (Chiou and Kile, 1998; Chiou et al., 2000). In preparations of a humic acid fraction free of HSACM and a fraction enriched in HSACM, the non-linear behavior of EDB was enhanced in the enriched fraction over the HSACM free fraction (Chiou et al., 2000). Log K_{oc} values for the linear portions of the EDB isotherms are 1.28 and 1.23 for the peat and mineral soils, respectively. The presence of TCE (at 370 mg/L), 3,5-dichlorophenol (at 1400 mg/L), or phenol (at 5900 mg/L) suppresses the non-linearity reported for EDB on both soils (Chiou and Kile, 1998).

Soil-water partition coefficients (K_{oc} values) for EDB in the solution phase range from 12 to 160 (Table 3) but average about 50 to 65. The available K_{oc} values indicate that EDB is not significantly adsorbed to soil. Based on EDBs K_{oc} values and its relatively high water solubility, EDB can and, based on available monitoring data, does leach through the vadose zone to groundwater. Aquifer environments typically have low concentrations of organic carbon. After 24 hours, there was no detectable sorption of EDB to unconsolidated aquifer fines (0.1% organic carbon) with a limit of determination of 0.1 L/kg (Pignatello et al., 1990). With a K_p of 0.1 L/kg, a retardation factor of 2 can be estimated (Pignatello and Cohen, 1990). This value has not been independently verified for EDB in the field however. Groundwater retardation factors of 1.17 and 2.65 were estimated for an aquifer with an f_{oc} of 0.001 and an f_{oc} of 0.01, respectively (Falta et al., 2005a).

Table 3. Soil adsorption data for EDB

Soil type	K_p (L/kg)	f_{oc}[1]	K_{oc} (L/kg)	Soil characteristics	Reference
Silt loam	0.57	0.008	71	26% clay, 3.3% sand, 69% silt, pH 6.8; K_{oc} assumption that organic matter is 50% organic carbon	Chiou et al. (1979)
Peat soil		0.0493	19.1	BET surface area of 1.4 m^2/g	Chiou and Kile, 1998
Mineral soil		0.00126	17.0	BET surface area of 11.2 m^2/g	Chiou and Kile, 1998
2 soils			39.7, 40.0		Cohen et al. (1984)
Soil			69		Hassett et al. (1983)
Pond sediment	2.0				Jafvert and Wolfe (1987)
Soil			44		Kenaga and Goring (1980)
Several soils		0.00290–0.126	36–160		Mingelgrin and Gerstl (1983)
Sandy loam	0.25–0.45	0.021	12–21	Assumption that organic matter is 50% organic carbon	Phillips (1964)
Peaty loam	5.0	0.153	33	Assumption that organic matter is 50% organic carbon	Phillips (1964)
Aquifer fines (<100 um diameter)	<0.1	0.0012–0.0013	<83		Pignatello et al. (1990)
Soil	1.49, 2.08, 1.70	0.011 0.0161 0.0165	135 129 103		Steinberg et al. (1987)
Silt loam	1.31	0.026	50	1% sand, 31% clay, CEC[2] = 17, pH 5.6	Rogers and McFarlane (1981)
Silt loam	1.49	0.018	83	15% sand, 34% clay, CEC[2] = 29, pH 7.8	Rogers and McFarlane (1981)
Silt loam	0.856	0.0149	57.4	pH of 4.97	Walton et al. (1992)
Sandy loam	0.303	0.0066	45.9	pH of 4.43	Walton et al. (1992)

[1] f_{oc} = fraction of organic carbon
[2] CEC = cation exchange capacity, mequiv/100 g

The adsorption studies above measure the partitioning of EDB between the solid and solution phases in soil or sediment. In these studies, sorption to soil is based on weak chemical bonds (van der Waals) that are formed and broken between the soil and EDB (Pignatello, 1990c). The K_{oc}/K_p values reported in Table 3 and the sorption isotherm experiments typically use study protocols where equilibrium is assumed to have been reached within 24 hours. While EDB added to soil is expected to adsorb/desorb in a rapidly reversible process based on this premise, it has been shown that a portion of the added EDB behaves in a "non-equilibrium" manner during the desorption phase. This has been attributed to the physical "trapping" of EDB within the soil matrix. This process is considered separately from the "trapping" of residual NAPL as discussed earlier in this section.

Similar to other small, low molecular weight halocarbons, EDB can become physically trapped within the soil matrix possibly due to tortuosity or constriction in pore structure and that release is determined by diffusion processes characterized by very slow kinetics and a large temperature dependence (Pignatello, 1990a, 1990b; Steinberg et al., 1987). Pulverization of EDB-residual soil results in the complete release of the trapped EDB (Steinberg et al., 1987). Studies specifically investigating the entrapment of EDB in soil are provided below.

K_p values from three soils (soil 1, 1.11% organic carbon; soil 2, 1.61% organic carbon; soil 3, 1.65% organic carbon) fumigated up to 20 years previously (170, 230, 300 mL/g) were two orders of magnitude greater than K_p values determined from 24-hour equilibration periods (1.49, 1.70, 2.08 mL/g) (Steinberg et al., 1987). This indicates that the desorption of residual, trapped EDB is extremely slow with an estimated 50% equilibrium reached in 23–31 years at 25 °C, assuming a diffusion rate law (in a 1:2 soil-water suspension with mild agitation) (Pignatello et al., 1987).

EDB was added to Cheshire soil at a concentration of 100 μM (18.8 mg/kg) in aqueous solution (Pignatello, 1990c). After a sorption period of 1.8 and 7 days and a desorption phase using adsorbent beads in the soil suspension, 0.564 and 0.921 mg/kg (3 and 4.9 μM), respectively, remained as a slow-desorbing residual fraction (quantified using a hot solvent extraction procedure) (Pignatello, 1990c). The structural characteristics of the soil matrix involved in this non-equilibrium sorption were further studied (Pignatello, 1990c). Overall, the amount of EDB residual was reported to be greater with increasing concentrations of organic carbon, although not linearly (Pignatello, 1990c). The EDB residual concentration for each particle size fraction of an Agawam soil (36:8% silt:clay, 2.57% organic carbon) was measured. The majority of residual EDB was found in the silt and coarse sand fractions following a 7-day sorption phase (34.2, 19.1, 41.5, and 5.3% of residual in the medium to very coarse sand, very fine to fine sand, silt, and clay fractions, respectively) (Pignatello, 1990c). On an organic carbon basis, 9.94, 59.0, 23.8, and 3.49 mg/kg EDB was found in the medium to very coarse sand, very fine to fine sand, silt, and clay fractions, respectively (Pignatello, 1990c). From these results, the authors attributed non-equlibrium desorption of EDB to the slow diffusion of EDB from "remote sites in the soil organic matter matrix". The distribution of EDB between different soil size fractions in two different soils was reported by Steinberg et al. (1987). EDB concentrations of 69, 142, 111, and 21 μg/kg were reported for diameter ranges of 106–250, 53–106, 2–53, and 0–2 μm, respectively, for one soil. EDB concentrations of 104, 164, 66, and 34 μg/kg were reported for the second soil, respectively. Concentrations were highest for the very fine sand fraction (53–106 μm) and lowest in the clay fraction (<2 μm) (Steinberg et al., 1987). Steinberg et al. (1987) cited "extremely tortuous or sterically hindered diffusion paths through microporous structures" as the reason for diffusion-limited desorption of EDB.

The entrapment of EDB, reported in soil, has been shown to occur in aquifer sediments as well (Pignatello and Cohen, 1990). A residual of 18 μg/kg reported in aquifer sediment following incubation for 4 days with a solution of 10 mg/L EDB was attributed to the trapping of EDB in the soil/aquifer material pore structure (Pignatello et al., 1990). In addition, Pignatello et al. (1990) reported higher EDB

concentrations in soil cores from a contaminated aquifer than would have been predicted based on K_p and EDB concentrations in the water.

This trapped residual may represent a potential low-level, slow-release source to these environments (Pignatello and Cohen, 1990) or a mechanism for plume retardation over decades or longer. Mayer et al. (1991) studied the effects of temperature and precipitation on EDB groundwater concentrations from an 11-meter deep domestic well located in Whatcom county, Washington, an area that historically used EDB as a soil fumigant. The initial concentration of EDB was 1.69 µg/L although the concentration varied over the next 27 months from a low of 0.94 to a high of 2.29 µg/L. Concentrations were negatively correlated with precipitation. The authors suggest that the infiltration of water from precipitation initially dilutes the EDB in the aquifer followed by slow EDB infiltration from overlying soils working to reestablish the EDB concentrations prior to the precipitation event (1 to 3 months were required to reestablish EDB levels).

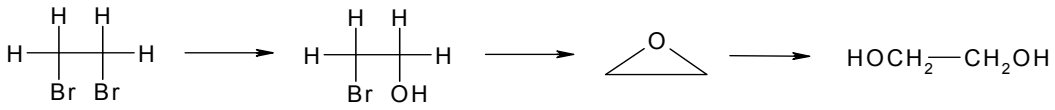
D. Transformations

1. Abiotic Transformations

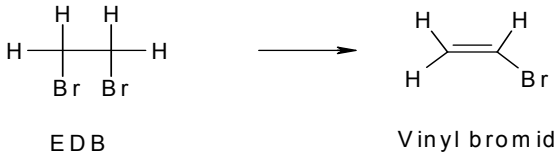
a. Hydrolysis

EDB is slowly hydrolyzed with published half-lives ranging from approximately 1 to 15 years (Table 4). The attack of EDB by H_2O can occur at the carbon atom giving the substitution product 2-bromoethanol and then further to ethylene glycol via ethylene oxide or at the α-hydrogen leading to the elimination product vinyl bromide (Pignatello and Cohen, 1990).

1. S_N2 (substitution) hydrolysis reaction of EDB in water:



2. E_2 (elimination) reaction of EDB in water:



The hydrolysis of EDB is primarily S_N2 with conversion to ethylene glycol based on results from several studies (Table 4). Vogel and Reinhard (1986) are the only authors reporting vinyl bromide as a major reaction product during nucleophilic attack. Their data suggest that the elimination reaction and not S_N2 substitution may be the most important reaction mechanism in some cases. This study was criticized by others because the product identification method may not have been able to identify ethylene glycol, and buffer effects were not addressed (Pignatello and Cohen, 1990). In addition, it was suggested that the EDB concentration used by Vogel and Reinhard (1986), 100 ppm, was not typical of groundwater contamination by EDB. Moye and Weintraub (1988) suggest that at lower concentrations, as might be found in groundwater (10–100 µg/L), ethylene glycol and bromide ions account for nearly complete degradation of EDB. However, as the rates of both elimination and substitution processes are first order

with respect to organic reactant, the product distribution is not expected to change with different initial concentrations of EDB. Given an initial concentration of 100 µg/L EDB, 30 µg/L ethylene glycol is expected via hydrolysis and 6 µg/L vinyl bromide via elimination (Reinhard and Vogel, 1988). The elimination reaction is reportedly 9 to 12 times slower than the substitution reaction (Barbash and Reinhard, 1989; Reinhard and Vogel, 1988). Pseudo first-order rate constants for EDB for S_N2 and E_2 reactions between EDB and H_2O at 25 °C are $3.7x10^{-4}$ day^{-1} and $3.1x10^{-5}$ day^{-1}, respectively (Barbash and Reinhard, 1989).

The hydrolysis of EDB is independent of pH in the environmental pH range of 5 to 9 (Jeffers and Wolfe, 1996; Roberts et al., 1993). Jeffers and Wolfe (1996) studied the neutral and alkaline hydrolysis of EDB in distilled water. The hydrolysis of EDB is dominated by neutral hydrolysis. The reaction at pH 9 is responsible for only 10% of the total observed hydrolysis (K_b of $2.5x10^{-10}$ $M^{-1}min^{-1}$).

Haag and Mill (1988) studied the effect of aquifer materials on the hydrolysis rate of several haloalkanes (isopropyl bromide, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane). The sediment was collected from Lula, Oklahoma at a depth of 5.4 to 6.4 meters and had a total organic carbon content of 0.02%, a total surface area of 11 m^2/g, a cation-exchange capacity of 2.5 meq NH_4^+/g, a porosity of 0.36, and a bulk mass density of 1.59 g/mL. Based on both product and kinetic analysis, the authors state that there was no significant difference in the hydrolysis rate of these compounds in distilled water versus in the presence of aquifer materials. The hydrolysis of EDB in Florida groundwater was studied by Weintraub et al. (1986). Groundwater from shallow wells in Florida was fortified with 10 or 100 ppb EDB and incubated at temperatures ranging from 40 to 80 ºC. Extrapolated half-lives of 259 and 435 days for Polk county groundwater (10 and 100 ppb EDB, respectively), 772 and 308 days for Highlands county groundwater (10 and 100 ppb, respectively), and 659 and 369 days for Jackson county groundwater (10 and 100 ppb, respectively). A half-life of 323 days was reported in deionized water at 10 and 100 ppb at 22 °C. Reaction products included bromide ion and ethylene glycol supporting an S_N2 mechanism.

Table 4. Hydrolysis half-lives reported for EDB

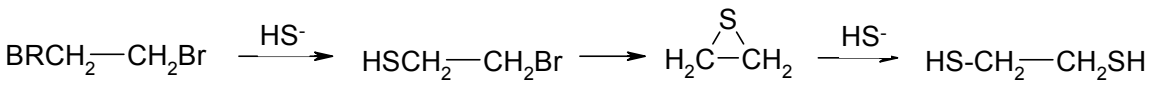
$T_{1/2}$ (years)	Temp. (°C)	Comments	Reaction products	Reference
pH Independent Reactions				
4.6	25	Extrapolated to zero buffer from 0.05M phosphate buffer data. Proceeds primarily via S_N2 mechanism.	7.7% vinyl bromide	Barbash and Reinhard (1989)
14	20	Neutral hydrolysis, $k = 7.2x10^{-4}$ hr^{-1}		Ehrenberg et al. (1974)
15	20	Half-life at pH 7		Ellington (1987)
4.1	25	Measured in unbuffered distilled water at 60 and 100 °C.	Ethylene glycol (major, 91% of total product at 100 °C), vinyl bromide (minor; 12% at 60 °C)	Haag and Mill (1988)
6.4	25	Measured in unbuffered distilled water. $k_H = 2.1x10^{-7}$ min^{-1} at 25 °C $K_b = 2.5x10^{-10}$ min^{-1} at 25 °C		Jeffers and Wolfe (1996)
8	20	Measured in aqueous buffer, $T_{1/2}$ for pH 7. $k = 0.00189$ hr^{-1} (pH 5); 0.00187 hr^{-1} (pH 7); 0.00197 hr^{-1} (pH 9). Authors noted that the rate of hydrolysis is increased in the presence of buffer.	Bromide ion. Speculate that the major hydrolysis product was ethylene glycol. Vinyl bromide present at minor amounts, <2%.	Jungclaus and Cohen (1986)
1.1	25	Measured at pH 7.		Rathbun (1998)
8, 2.2	25	Measured at pH 7.		Rathbun (1998)
2.5	25	Measured in aqueous buffer, pH 7.5. Buffer effects not addressed by study authors.	Vinyl bromide reported as the major product indicating dehydrobromination as the main mechanism. Product identification method could not detect ethylene glycol however.	Vogel and Reinhard (1986)
1.5–2.0	22	Florida groundwater, pseudo-1st order kinetics followed between 40 to 70 °C.	Bromide ion, ethylene glycol	Weintraub et al. (1986)
Base-Promoted Reactions				
1154	25	$k_{OH} = 1.91x10^{-4}$ $M^{-1}sec^{-1}$	E_2 product (~95% at 30 °C)	Hine and Langford (1956)
$2.0x10^{+4}$	20	$k_{OH} = 4.0x10^{-2}$ $M^{-1}hr^{-1}$		Ehrenberg et al. (1974)
5035	25	$k_{OH} = 4.4x10^{-5}$ $M^{-1}sec^{-1}$		Roberts et al. (1993)

b. Reaction with Sulfur Nucleophiles

Data for the reaction of EDB with sulfur nucleophiles are given in Table 5. H_2S and HS^- are typically found in anaerobic groundwater and in wetland/estuarine environments due to the microbial reduction of sulfate (Pignatello and Cohen, 1990). Typical concentrations in a salt marsh are 0.07 mM polysulfides, 0.2 mM sulfite, 0.5 mM thiosulfate, and 5 mM HS^- (Barbash and Reinhard, 1989). HS^- is the dominant sulfur nucleophile at pH values above 7 (>50% dissociation of H_2S based on a pK_a of H_2S of 7.01) while at lower pH values, sulfite may be more important. Total sulfide concentrations in a SO_4^{-2} reducing groundwater (typical pH values of 6 to 8) range from 10^{-6} to 10^{-3} M (Barbash and Reinhard, 1989).

HS^- can react with primary bromoalkanes forming various thiols and thioethers (Schwarzenbach et al., 1985). This reaction is considerably faster than the hydrolysis of EDB in water alone (Barbash and Reinhard, 1987). They reported the disappearance of EDB in the presence and absence of HS^- (at 0.060 mM) at 25 °C. First-order rate constants were 3.6 times greater when HS^- was present [8.6×10^{-3} day^{-1} (k_{H2O}) versus 6×10^{-3} $M^{-1}sec^{-1}$ (k_{HS-})] (Barbash and Reinhard, 1987). Rate constants for the S_N2 and E_2 reactions of EDB and HS^- at 25 °C are 23 $M^{-1}day^{-1}$and 9.6 $M^{-1}day^{-1}$, respectively (Barbash and Reinhard, 1989). The half-life for the reaction of EDB with H_2S-containing water was only slightly affected by pH changes between 6.5 and 8.5 (Weintraub and Moye, 1987).

The reaction of EDB with HS^- results in the formation of 1,2-ethanedithiol and a second minor peak that is thought to be vinyl bromide. Barbash and Reinhard (1989) proposed a reaction pathway of EDB to 2-bromoethanethiol, followed by intramolecular displacement forming cyclic thiirane, and finally attack by another HS^- to open the ring.



In the presence of 0.05 M phosphate buffer and 067 mM Na_2S, <5% vinyl bromide was measured over a temperature range of 37.5 to 87.5 °C (Barbash and Reinhard, 1989). While in laboratory studies, half-lives indicate that reaction with sulfur nucleophiles may be an important process in sulfate-reducing or even possibly FeS-containing groundwaters (Wilson et al., 2007), the significance of this process has not been verified in the field.

Table 5. Half-lives for the reaction of EDB with sulfur nucleophiles

$T_{1/2}$ (days)	Temp. (°C)	Comments	Reaction products	Reference
19–21 46–60 104–134	25 25 25	Three $T_{1/2}$ ranges correspond to H_2S concentrations of 2.27 mM, 0.758 mM, and 0.147 mM (5–100 ppm), respectively. Initial EDB concentration of 7.94 µM.	Tentatively reported as saturated rings of 1, 2, or 4 ethylene units and 2, 3, or 4 sulfur atoms, positive identification of 1,4-dithane.	Weintraub and Moye (1987)
70	25	EDB with sulfur (0.005 M phosphate buffer + 0.758 mM Na_2S), pH 6.9.	Propose ethylene glycol, and 1,2-ethanedithiol as major products with vinyl bromide as a minor product (<10%).	Barbash and Reinhard (1987)
37	25	Reaction with HS^- at pH 9 in the presence of phosphate buffer. The measured rate constant (overall, including both nucleophilic substitution S_N2 plus dehydrohalogenation E_2 reactions) is 34.0 $M^{-1}day^{-1}$.	1,2-Ethanedithiol (56%) and a second minor peak believed to be vinyl bromide.	Barbash and Reinhard (1989)
	25	$k_{HS-} = 4.13x10^{-4}$ $M^{-1}sec^{-1}$ at pH 9. Reaction with HS^- at 88 mM. Calculated maximum reaction rates of EDB with this species is 256 times faster than reaction with water.		Haag and Mill (1988)
	25	$k_{SO3-2} = 4.13x10^{-4}$ $M^{-1}sec^{-1}$ at pH 10.2. Reaction with SO_3^{-2} at 1000 mM. Calculated maximum reaction rates of EDB with this species is 6 times faster than reaction with water.		Haag and Mill (1988)
	20	$k_{S2O3-2} = 9.61x10^{-5}$ $M^{-1}sec^{-1}$ at pH 7. Reaction with $S_2O_3^{-2}$ at 1000 mM. Calculated maximum reaction rates of EDB with this species is 6 times faster than reaction with water.		Haag and Mill (1988)

c. Photolysis

EDB is not susceptible to direct photolysis (Jaber et al., 1984; Ollis, 1985). It can indirectly photolyze in the presence of OH radicals in the atmosphere. Several rate constants for this reaction are available in the literature: $2.50x10^{-13}$ cm^3/molecule-sec, at 23 °C (Howard and Evenson, 1976), $2.25x10^{-13}$ cm^3/molecule-sec at 24 °C, and $1.86x10^{-13}$ cm^3/molecule-sec at 22 °C (Atkinson, 1994). Using the rate constant of Howard and Evenson (1976), an atmospheric half-life of 43 days can be estimated based on an OH radical concentration of $1.5x10^{+6}$ OH radicals/cm^3 and a 12-hour day. Products of this reaction include formyl bromide, $CHOCH_2Br$, $CBr(O)CH_2Br$ (Kao, 1994), formaldehyde, bromoethanol, and hydrogen bromide (Spicer et al., 1993). The bromide ion released during EDBs photochemical oxidation can react with ozone thereby contributing to the greenhouse effect (van Agteren et al., 1998).

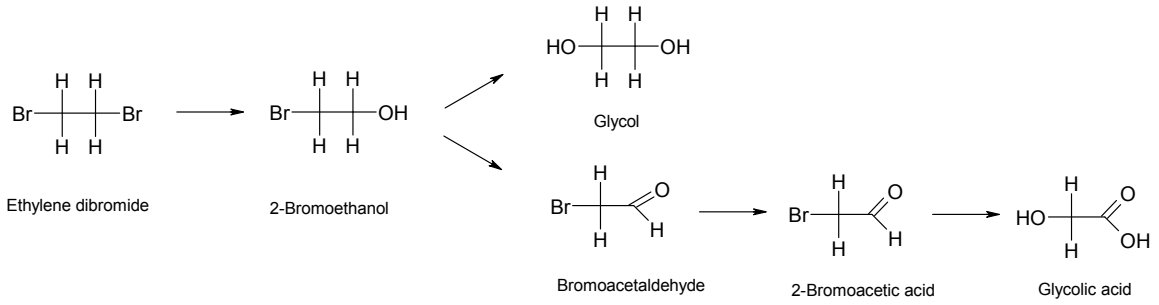
2. Biotic Transformations

The biodegradation of EDB can occur in the environment via anaerobic dehalogenation, aerobic catabolism, and aerobic co-metabolism (Hoyle and Arthur, 2000; Stensel and Bielefeldt, 2000). Reaction mechanisms for the biodegradation of EDB include the elimination of hydrogen bromide or the substitution of the bromide groups to H (reductive pathway), OH (hydrolytic pathway), or to thio groups (Neilson, 1990). Because oxygen is not necessary in the elimination pathway, both aerobic and anaerobic microorganisms can potentially use this pathway (Neilson, 1990).

a. Pure Culture Studies

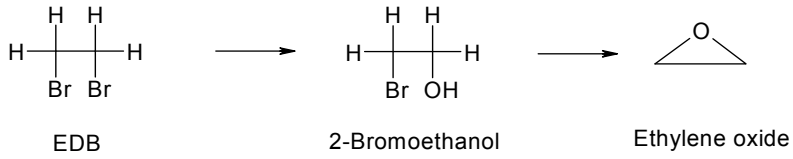
Based on the reaction pathway information from the pure culture studies summarized in Table 6, the aerobic and anaerobic biodegradation of EDB has been reported to proceed via several pathways.

1. An aerobic cometabolic pathway of degradation for EDB is given in van Agteren et al. (1998). EDB is debrominated to 2-bromoethanol via a haloalkane dehalogenase which then yields either glycol (via a second, different haloalkane dehalogenase) or bromoacetaldehyde via an alcohol dehydrogenase. Bromoacetaldehyde is then degraded further to 2-bromoacetic acid and then glycolic acid (van Agteren et al., 1998). A purified dehalogenase isolated from *Arthrobacter* strain HA1 (chlorohexane halidohydrolase) converted EDB to 2-bromoethanol which was then slowly dehalogenated to glycol (Hanson and Brusseau, 1994; Scholtz et al., 1987). An ammonium monooxygenase enzyme has been reported to mediate the cometabolic biodegradation of EDB by *Nitrosomonas europaea* although products of this reaction were not identified (Vannelli et al., 1990).

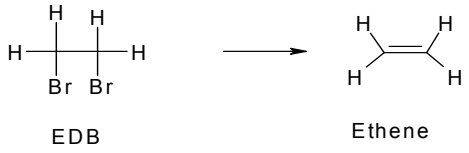


2. A second aerobic biodegradation pathway was proposed based on work by Poelarends et al. (1999). A pure culture of *Mycobacterium* sp. Strain GP1, able to use EDB as its sole carbon and energy source, degraded EDB to 2-bromoethanol using a hydrolytic haloalkane dehalogenase. A haloalcohol dehalogenase then mediated the degradation of 2-bromoethanol to ethylene oxide. Ethylene oxide can be

incorporated into the Kreb's cycle via 2-hydroxy-ethyl-CoM, acetal-CoM, and finally acetyl CoA (Henderson, 2005).

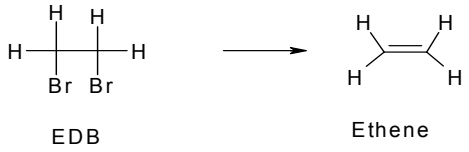


3. The aerobic microbial reductive elimination of EDB to ethene was reported by Castro et al. (1989) for *Pseudomonas putida* PpG-780. The enzyme responsible for this reaction was a P-450 cam heme protein. This pathway does not necessarily mirror the dihaloelimination reaction seen for anaerobic pure culture studies.



Two pathways for the anaerobic biodegradation of EDB have been proposed.

1. Belay and Daniels (1987) reported the anaerobic biodegradation of EDB via vicinal reduction (i.e., dihaloelimination) resulting in the formation of ethene for a set of methanogens. If ethene concentrations reach 1 to 5%, inhibition of methanogenesis can occur (Belay and Daniels, 1987). Ethene can also be potentially formed through a combination of reduction and elimination steps and not necessarily via vicinal reduction (Kuhn and Suflita, 1989). No pure culture data were available to support this pathway under nitrate-, iron-, or sulfate-reducing conditions.



2. A second, more complex pathway was proposed by Henderson (2005). Here EDB can be degraded to bromoethene, then ethene, and ethane. Other options include EDB to ethene and then ethane or EDB to bromoethane and then to ethane.

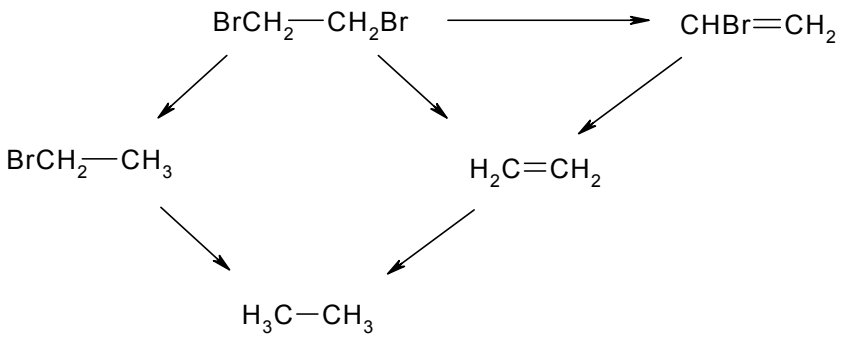


Table 6. Pure culture strains studied for their ability to degrade EDB

Strain	Aerobic or anaerobic	Notes	Reference
Xanthobacter autotrophicus GJ10	Aerobic	Aerobic nitrogen-fixing autotroph. 1,2-Dichloroethane-degrading culture. Cometabolic degradation of EDB. Lack of growth on EDB attributed to accumulation of toxic bromoacetaldehyde (lack of bromoacetaldehyde dehydrogenase) (Janssen et al., 1994; van Agteren et al., 1998). Purified haloalkane dehalogenase from this strain readily degrades EDB showing bromide release (Keuning et al., 1985).	Janssen et al. (1985)
Ancylobacter aquaticus	Aerobic	Cannot degrade EDB, attributed to lack of a bromoacetaldehyde dehydrogenase and accumulation of toxic bromoacetaldehyde.	Van der Ploeg et al. (1995)
Acinetobacter sp. GJ70	Aerobic	Currently described as a gram-positive actinomycete-like organism, not an *Acinetobacter* strain (Hanson and Brusseau, 1994). Cometabolic biotransformation of EDB. Resting cells converted EDB to 2-bromoethanol via a haloalkane dehalogenase, then to 2-bromoacetaldehyde (toxic product). A 2-bromoethanol resistant mutant strain of GJ70 (GJ70M4) was able to dehalogenate EDB to 2-bromoethanol, ethylene glycol and bromide ions	Janssen et al. (1987)
Mycobacterium sp. GP1	Aerobic	Isolated from an enrichment culture described by Freitas dos Santos et al. (1996). Used EDB as its sole carbon and energy source. Pathway proceeds via ethylene oxide using a hydrolytic haloalkane dehalogenase and a haloalcohol dehalogenase, avoiding toxic intermediates 2-bromoethanol and 2-bromoacetaldehyde.	Poelarends et al. (1999)
Nitrosomonas europaea	Aerobic	Aerobic obligate chemolithotrophic nitrifying autotroph. Microbe depends on oxidation of ammonia for growth. Cometabolically degraded EDB via an ammonium monooxygenase.	Vannelli et al. (1990)
Arthrobacter sp. Strain HA1	Aerobic	Isolated by enrichment on 1-chlorohexane. The chlorohexane halidohydrolase from this strain converts EDB to bromoethanol which is then slowly dehalogenated to give 1,2-dihydroxyethane.	Scholtz et al. (1987)
Pseudomonas putida PpG-780	Aerobic	Used EDB as its sole carbon and energy source. Reaction proceeds via reductive elimination to ethene.	Castro et al. (1989)
Methanobacterium thermoautotrophicum ΔH	Anaerobic	Methanogen. Cells grown on H_2-CO_2. Degrades EDB to ethene via vicinal reduction.	Belay and Daniels (1987)
Methanococcus deltae ΔLH	Anaerobic	Methanogen. Cells grown on H_2-CO_2. Degrades EDB to ethene via vicinal reduction.	Belay and Daniels (1987)
Methanococcus thermolithotrophicus	Anaerobic	Methanogen. Cells grown on H_2-CO_2. Degrades EDB to ethene via vicinal reduction.	Belay and Daniels (1987)

b. Enrichment Culture, Defined Culture, and Sewage Studies

Freitas dos Santos et al. (1996, 1997) isolated an enrichment culture that was able to completely degrade EDB at quantities of up to 1 g/L to CO_2, bromide and biomass under aerobic conditions. This culture also rapidly degraded bromoethanol, bromoacetate, and bromoethane. Based on this result, the authors suggested a degradation pathway from EDB to bromoethanol, bromoacetaldehyde and then bromoacetate. Under aerobic conditions, EDB was degraded by a sludge inoculum to a highly water-soluble, non-volatile product (i.e., not ethene) within days (Jex et al., 1983; Weintraub et al., 1986). However, in aerobic batch culture experiments by Bouwer (1983), EDB was not biodegraded. Details of the test conditions for this experiment were not available for comparison with the preceding studies.

Cometabolic aerobic biodegradation of EDB by methylotrophs has been explored in experiments by Leeson and Bouwer (1989) and Hartzell et al. (2001). In a series of batch reactor studies, EDB, at an initial concentration of 150 µg/L, was transformed by an enrichment culture of methanotrophs (Leeson and Bouwer, 1989). Methane was present as a carbon donor. A rate constant of 7.5 L/g-day was provided and a half-life of 9.2 days based on a cell density of 10^{+7} cells/mL. Reaction products were followed by ^{14}C-radiolabel and included CO_2 and several unidentified compounds. Hartzell et al. (2001) isolated bacterial consortia from soil using propane, methane, or natural gas to selectively enrich for methylotrophic populations. These consortia were then used to inoculate batch reactors to study the degradation of EDB. In batch reactors containing additional propane, EDB at an initial concentration of 200 µg/L was completely degraded (<0.029 µg/L) within 4 days (primary biodegradation) via cometabolic degradation. In methane batch reactors, EDB was completely degraded (>99%) after 6 days incubation and in natural gas batch reactors, >99% loss of EDB was reported after 6 days.

Tandol et al. (1994) studied the anaerobic biodegradation of EDB by an enrichment culture capable of dechlorinating high concentrations of tetrachloroethylene (PCE). This culture, in the presence of methanol as a carbon donor, rapidly degraded EDB at an initial concentration of 50 µmoles/100 mL to 100% ethene within 7 hours via dihaloelimination. In a second study, EDB was converted almost completely to ethene, again by dihaloelimination, over a 2-month period using a mixed microbial culture enriched for DBCP degraders (mainly *Pseudomonas* and *Flavobacteria* species) (Castro and Belser, 1968). 0.5% glycerol was added to the culture. The redox conditions present during this study are not clear. Although the authors did not flush the study bottles with N_2, saturated soils left unagitated over the 2-month study period could form anaerobic pockets.

Studies using a sewage inoculum suggest that EDB is biodegraded under methanogenic and sulfate-reducing conditions but is resistant to biodegradation under nitrate-reducing conditions. ^{14}C-EDB (at 25–90 µg/L) in methanogenic batch cultures was nearly completely degraded in 2 weeks (Bouwer and McCarty, 1985). At 2, 4, 14, and 17 weeks, ^{14}C-hydrocarbons (described as highly volatile and non-halogenated, believed to be ethene) represented 41, 27, 31, and 19% of the total radioactivity, respectively, while an unidentified fraction (described as non-volatile, hydrophilic, cited as possibly bromoethanol by the authors) represented 59, 73, 69, and 81% of the total radioactivity at the same timepoints, respectively. Complete oxidation to CO_2 was not seen over the study period. In nitrate-reducing batch transformation studies in the presence of added ethanol and a sewage inoculum, low concentrations of EDB (10-30 µg/L) were not biodegraded over an 8-week period as monitored by GC results and ^{14}C activity (Bouwer and McCarty, 1983).

EDB was degraded in continuous-flow biofilm columns with added acetate as the primary substrate (Bouwer and Wright, 1986; Bouwer and Wright, 1988). The detention time of the columns was 2.5 days. Under methanogenic conditions, >99% EDB removal (20 µg/L influent) was reported following a 2-week acclimation period while 63% removal of EDB (19 µg/L influent) with an acclimation period of <2 weeks was observed under sulfate-reducing conditions. Under nitrate-reducing conditions up to 23% EDB

removal (30 µg/L influent) was reported (Bouwer and Wright, 1986). The authors concluded that the nitrate-reducing data were inconclusive and that loss may have been due to sorption or volatilization losses. In a series of short-term experiments (1.0 hour detention time) using the same columns, ^{14}C-radiolabeled EDB was added to identify the transformation products of EDB. In the methanogenic column, <1, 100, 13, and <2% of the radiolabel was found as EDB, ^{14}C-volatile products, $^{14}CO_2$, and unknown products, respectively, as reported by the authors. In the sulfate-reducing column, 42, 24, 21, and 13% of the radiolabel was found as EDB, ^{14}C-volatile products, $^{14}CO_2$, and unknown, respectively. The authors suggest that the volatile product reported in the methanogenic and sulfate-reducing column experiments is most likely ethene. 100% of the ^{14}C-radiolabel was recovered as EDB following passage through the nitrate-reducing column (Bouwer and Wright, 1988).

^{14}C-Radiolabel experiments by Weintraub et al. (1986) indicate that EDB degrades readily in methanogenic sewage sludge suspensions. Nearly complete degradation was observed in 60 days at initial concentrations of 1 to 2 ppm EDB. Ethene was the only radioactive product. Similar results were noted for a sewage sludge inoculum known to contain a rich population of facultative microorganisms.

c. Microcosm Studies

Aerobic and anaerobic microcosm studies for EDB are summarized below in Tables 7 and 8, respectively. The data from these studies indicate that under environmentally-relevant laboratory conditions, EDB is biodegradable under oxygenated and reducing environments. The rate of biodegradation is typically lower in anaerobic studies when compared to studies run under aerobic conditions. Primary biodegradation of aerobic samples showed half-lives from days to weeks with mineralization studies showing somewhat longer half-lives (typically several months). Available anaerobic studies measured primary biodegradation only and half-lives were typically weeks to months in length. In most cases, specific redox conditions were not reported for the anaerobic studies. Therefore, a comparison of EDB biodegradation under nitrate-reducing, iron-reducing, sulfate-reducing, or methanogenic conditions cannot be made.

Reaction products were monitored in several studies. In radiolabel experiments using aerobic soil, 41–45% of the radiolabel was incorporated into CO_2, 6–17% remained as EDB, 6.9–4.1% was found as unextractable ^{14}C in culture filtrate, and 23–33% was unextractable ^{14}C bound to solids after 13 days (Pignatello, 1986a). The presence of nearly equal amounts of $^{14}CO_2$ and unextractable ^{14}C solids data indicate that EDB is a substrate for both growth and energy under aerobic conditions (Pignatello, 1986b). Under anaerobic conditions, ethene is reported as a product of biodegradation by Jafvert and Wolfe (1987).

Concentration effects have been reported by Pignatello (1986a, 1986b) in aerobic and anaerobic soil studies. At low concentrations (6 to 8 µg/L), EDB rapidly degraded in two different soils but at concentrations of 15 to 18 mg/L, biodegradation proceeded more slowly. LC_{50} values for microbial toxicity of 100 and 50 mg/L for EDB in soil indicate that the effects seen at higher EDB concentrations were not due to toxic effects (Pignatello, 1986a). A second study showed that EDB concentrations up to 1000 µg/kg had no effect on the CO_2 production of two different soils over a 6-day period (Walton et al., 1989). Aelion et al. (1989) reported that the rate of EDB mineralization was not affected by varying concentrations from 1 to 139 µg/L. Using the same soils as Pignatello (1986a), Pignatello (1986b) measured the biodegradation of EDB under anaerobic conditions. Biodegradation was rapid in both sand and muddy soils at EDB concentrations of 6–8 µg/L (complete degradation in <1 week) but at initial concentrations of 15–18 mg/L, EDB was only slowly degraded with an initial lag phase of weeks and slow loss once the concentration dropped to hundreds of µg/L.

Several studies have shown that physically trapped residues of EDB are not bioavailable to microbial populations. ^{14}C-EDB was added to soil from a former soil fumigation site in Connecticut in a 1:1 ratio with water (Pignatello, 1987b). Freshly-added EDB was rapidly degraded with complete degradation in weeks (for 2 soils) while the field residue EDB was not degraded at all over the 24 to 38 day period. The freshly added EDB was converted to CO_2 (45%) and unextractable ^{14}C associated with solids (thought to be cell material, 55%). The field residue EDB did not chemically exchange with the ^{14}C-EDB but pulverization of the soil enhanced its release to both aqueous and vapor phases with release following diffusion kinetics (Pignatello, 1987b). Biodegradation of freshly-added ^{14}C-radiolabeled EDB in surface soils from the Simsbury, Connecticut site (historic application of EDB fumigant) occurred rapidly with nearly complete degradation within 22 days (Pignatello et al., 1990). Major products were CO_2 and ^{14}C-unextractable residues. Two topsoil samples containing historic EDB at concentrations of 32 and 21 µg/kg were shaken with water over 20 days. No detectable residues of EDB were released over this time indicating that the EDB in these soils is not available for leaching or biodegradation (Pignatello et al., 1990).

Very limited data exist in the literature measuring the biodegradation of EDB in the presence of fuel hydrocarbons (Tables 7 and 8) (Henderson et al., 2007; Reiss, 2000). Groundwater and soil samples from the Clemson Tiger Mart, a site contaminated with leaded gasoline due to leaking tanks, were incubated for 284 to 380 days in closed bottles without shaking (Henderson et al., 2007). At initial concentrations of ~200–300 µg/L, a concentration theoretically similar to the source area of a contamination plume, a lag period of ~80 days was reported with a final EDB concentration of approximately 50 µg/L by day 380. After day 120, very little further biodegradation of EDB was observed through day 380. At an initial concentration of 10 µg/L, a concentration similar to what might be found mid-gradient in a contaminant plume, a lag period of approximately 60 days was noted with a final EDB concentration of approximately 0.25 µg/L by day 380. Half-lives are reported in Table 8. The redox condition for this study was not available but is assumed to be mainly anaerobic since the bottles were filled and left to sit for many months.

Table 7. Aerobic biodegradation microcosm studies for EDB

Sample type	M/P[1]	Initial concn.	Study period (days)	Rate constant (day^{-1})	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Aquifer sediment	M	14 µg/kg	100	1.11% day^{-1}		CO_2	Uncontaminated site. Maximum respiration was 25%. Initially rapid rate of respiration over the first 25–30 days, leveling off after this period.	Aelion et al. (1987)
Aquifer sediment	M	166 µg/kg	100	0.93% day^{-1}		CO_2	Uncontaminated site. Maximum respiration was 20%. Initially rapid rate of respiration over the first 25–30 days, leveling off after this period.	Aelion et al. (1987)
Aquifer sediment	M	1 µg/g	150		250	CO_2	Uncontaminated site. Lula aquifer sample 9KK4. Maximum respired is 16% by day 120 (1 µg/L) and 13% respired by day 120 (139 µg/L). Low biodegradation rate when compared with rates seen for 2 other aquifer samples from the same site (9HH11 and 9OO1).	Aelion et al. (1989)
Aquifer sediment	M	48 µg/kg	21		53	CO_2	Uncontaminated site. Lula aquifer sample 9OO1. Biodegradation rates similar for sample 9HH11 at 6 and 110 ng/g. Maximum respired is 18% with 6% cellular incorporation on day 21.	Aelion et al. (1989)
Soil	P	6–8 µg/L	7	0.84	<1		Site overlies an EDB-contaminated aquifer (0.1 to 11 µg/L). Soil composed of mainly sand taken from a stream bed (0.24% total organic carbon by weight). 2 replicates. Complete loss by first time point (7 days) by both.	Pignatello (1986a)
Soil	P	6–8 µg/L	35	0.38	2		Site overlies an EDB-contaminated aquifer (0.1 to 11 µg/L). Soil composed of organic carbon-rich muddy soil from an area of groundwater upwelling. Only 6.4 and 7.5% remained by day 7 (2 replicates).	Pignatello (1986a)

Table 7. Aerobic biodegradation microcosm studies for EDB

Sample type	M/P[1]	Initial concn.	Study period (days)	Rate constant (day^{-1})	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Soil	P	15,000–18,000 µg/L	99	0.0028	247		Site overlies an EDB-contaminated aquifer (0.1 to11 µg/L). Soil composed of mainly sand taken from a stream bed (0.24% total organic carbon by weight). 4 replicates. 68% EDB remained by day 99 (90% remained in the control).	Pignatello (1986a)
Soil	P	15,000–18,000 µg/L	108	0.0074	94		Site overlies an EDB-contaminated aquifer (0.1 to11 µg/L). Soil composed of organic carbon-rich muddy soil from an area of groundwater upwelling. 4 replicates. 24% EDB remained by day 108 (50% remained in the control).	Pignatello (1986a)
Soil	M	65 µg/L	13	0.046	15	CO_2	Site overlies an EDB-contaminated aquifer (0.1 to 11 µg/L). Soil composed of organic carbon-rich muddy soil from an area of groundwater upwelling. 2 replicates. 41 and 45% of radiolabel found as CO_2 after 13 days (20 and 33% after 5.7 and 8.8 days).	Pignatello (1986a)
Soil	P	80 µg/kg	36	0.52	1.3		Hamden, CT. Farm site contaminated with EDB. Freshly added ^{14}C-EDB was rapidly degraded with half-life given in table. However, native EDB field residues from the farm soil were not degraded at all unless the soil was pulverized.	Pignatello (1987b)
Soil	P	85 µg/kg	24	0.104	7		Warehouse Point, CT. Farm site contaminated with EDB. Native EDB field residues from the farm soil were not degraded unless the soil was pulverized.	Pignatello (1987b)
Soil	P	0.5 and 5.0 µg/kg	380	0.0093	75		Wells tapping aquifer site and stream fed by groundwater containing up to 11 µg/L EDB. Windsor Locks, CT samples. Approximately 100, 75, 60, 40, 35, 5% remaining after 0, 50, 100, 140, 200, and 280 days, respectively (0.5 µg/kg initial concentration).	Pignatello (1987a)

Table 7. Aerobic biodegradation microcosm studies for EDB

Sample type	M/P[1]	Initial concn.	Study period (days)	Rate constant (day^{-1})	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Soil	P	0.7 µg/kg	133	0.0083	83	CO_2	Former tobacco farm with last agricultural application of EDB in 1967 (concentrations of 2 µg/L or less of EDB). Simsbury, CT samples. Air-saturated conditions (11 mg/L). 34% of the ^{14}C label as CO_2, 17% as solid bound ^{14}C, and 16% as water soluble ^{14}C after 133 days.	Pignatello (1987a)
Soil	P	9.3–11.7 µg/kg	22	0.136	5	CO_2	Simsbury CT farm site. Topsoil 1. 43% as CO_2 in 22 days, only 5% EDB remaining.	Pignatello et al. (1990)
Soil	P	9.3–11.7 µg/kg	22	0.16	4	CO_2	Simsbury CT farm site. Topsoil 2. 49% as CO_2 in 22 days, only 3% EDB remaining.	Pignatello et al. (1990)
Soil	P	9.3–11.7 µg/kg	22	0.16	4	CO_2	Simsbury CT farm site. Topsoil 3. 50% as CO_2 in 22 days, only 3% EDB remaining.	Pignatello et al. (1990)
Aquifer	P		110		39		Previously contaminated with EDB and 1,2-DCA, remediation completed. Half-life given by author, preliminary batch reactor studies. No further study details.	Reiss (2000)
Aquifer	P		110		87		Uncontaminated site. Half-life given by author, preliminary batch reactor studies. No further study details.	Reiss (2000)
Aquifer sediment	M	108 µg/kg	11	0.0127–0.018	38.5–55	CO_2	Uncontaminated site. Lula aquifer sample 9JJ3. Vials filled, no headspace. Only oxygen present is in the water. Maximum recovered as CO_2 is 13–18% by day 11. Addition of inorganic salts (N, P) or glucose, or amino acids does not increase mineralization.	Swindoll et al. (1988)
Aquifer sediment	M	108 µg/kg	11	0.014–0.017	41–51	CO_2	Uncontaminated site. Lula aquifer sample 9MM1. Vials filled, no headspace. Only oxygen present is in the water. Maximum recovered as CO_2 is 14–17% by day 11. 10–12% mineralization reported by day 5.	Swindoll et al. (1988)

[1] Primary biodegradation (P) or mineralization (M) was measured as the endpoint.

Table 8. Anaerobic biodegradation microcosm studies for EDB

Sample type	M/P[1]	Initial concn.	Study period (days)	Rate constant (per day)	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Pond sediment	P	56.3 µg/L	5	0.30	2.3	Ethene	Samples were collected from 5.0 to 7.5 cm of bottom pond sediment. Half-life and rate constant reported by the authors. Reduction via vicinal dehalogenation is indicated as the major loss process.	Jafvert and Wolfe (1987)
Aquifer	P	250 µg/L	380	0.0042	238		Source zone simulation, high concentration. Fuel hydrocarbons present. Aquifer sediment/groundwater collected from a former gasoline station. UST site (Former Clemson Tiger Mart, SC). Presumed anaerobic although not stated, not shaken during study period, small headspace left in 2L bottles. Lag period of 80 days.	Henderson et al. (2007)
Aquifer	P	10 µg/L	284	0.0138	72.5		Mid-gradient zone simulation, low concentration. Fuel hydrocarbons present. Aquifer sediment collected from a former gasoline station. UST site (Former Clemson Tiger Mart, SC). Presumed anaerobic although not stated, not shaken during study period, small headspace left in 2L bottles. Lag period of 60 days.	Henderson et al. (2007)
Soil	P	6–8 µg/L	7		<1, <7		Two soils. Soil S1 was composed of mainly sand taken from a stream bed (0.24% total organic carbon by weight) degraded to below the detection limit in 7 days. Soil S2 was composed of organic carbon-rich muddy soil from an area of groundwater upwelling and EDB was degraded to below the detection limit in a few hours. Site overlies an EDB-contaminated aquifer (0.1 to 11 µg/L).	Pignatello (1986a)

Table 8. Anaerobic biodegradation microcosm studies for EDB

Sample type	M/P[1]	Initial concn.	Study period (days)	Rate constant (per day)	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Soil	P	15,000–18,000 µg/L					Two soils. Soil S1 was composed of mainly sand taken from a stream bed (0.24% total organic carbon by weight) and Soil S2 was composed of organic carbon-rich muddy soil from an area of groundwater upwelling. Degradation was preceded by a lag phase and EDB concentrations were reduced to the several hundred ppb range where they slowly declined over many weeks. Respiking reduced the lag period but total removal below the ~100 ppb persisted. Site overlies an EDB-contaminated aquifer (0.1 to 11 ug/L).	Pignatello (1986a)
Soil	P	0.7 µg/kg	133	0.0062	112 (35–350 day range)	CO_2	Former tobacco farm with last agricultural application of EDB in 1967. Low O_2 conditions (0.1 mg/L). 18% of the ^{14}C label as CO_2, 17% as solid bound ^{14}C, and 21% as water soluble ^{14}C after 133 days.	Pignatello (1987a)
Soil	P	400 µg/L	210	0.0024	285	Possibly ethene	40% biodegradation was reported after 7 months incubation. No CO_2 was produced. Reaction products were volatile, suggesting ethene.	Weintraub et al. (1986)
Aquifer	P	194 µg/L	112	0.033	21		Methanogenic conditions. pH 7.3, Eh -50 mV. By 7 weeks incubation, only 27% EDB remained and by 16 weeks, EDB concentrations were below the limit of detection.	Wilson et al. (1986)

[1] Primary biodegradation (P) or mineralization (M) was measured as the endpoint.

d. Field Studies

Despite the evidence in Tables 7 and 8 that this compound is biodegradable under both aerobic and anaerobic conditions in environmentally-relevant laboratory studies, data from field sites suggest otherwise. For example, sites where EDB was applied as a soil fumigant decades ago still contain residual EDB in topsoils and plumes of EDB are found in the underlying aquifers. Nearly 50% of UST sites in South Carolina (Falta et al., 2005a) and a 17-state area survey (Wilson et al., 2007) had EDB concentrations above the maximum contaminant level (MCL) in groundwater samples despite the fact that most of these releases occurred decades earlier.

Only 2 field studies have been published reporting the loss of EDB in the environment (Table 9). One is a soil fumigation study (Frink and Bugbee, 1989) and the other is a study of a former gasoline site (Mayer, 2005). The authors report their data as disappearance rate constants. These are based on measuring the concentration of a chemical at a specific location over time. The disappearance rate constant does not remove the effect of other processes such as advective loss and adsorption separately so it is not the same as a degradation rate constant (Washington and Cameron, 2001). Loss in the environment, especially in groundwater, may be due not only to degradation processes (abiotic and biotic) but also to transport processes such as dilution, dispersion, sorption, and advection.

Below, the release of EDB to the environment is considered separately for a soil fumigation site and a leaded gasoline spill site. While EDB was also used in grain bin fumigants, insufficient data were available to support a more detailed account of their loss in the environment from this source. Grain bin sites are discussed in the following monitoring data section. Brookhaven National Laboratory is an example of low-level EDB contamination from historic soil fumigation practices and the well-studied Massachusetts Military Reservation is an example of a spill of aviation fuel complete with an LNAPL phase at one site.

Table 9. Disappearance half-lives for EDB in field studies							
Sample type	**M/P[1]**	**Initial concentration**	**Study period (days)**	**Rate constant (day^{-1})**	**$T_{1/2}$ (days)**	**General comments**	**Reference**
Soil	P	5000 µg/kg	500		1st yr $T_{1/2}$ = 26 2nd yr $T_{1/2}$ = 115–200	Soil fumigation study. 1987 study. Non-1st order biodegradation. Soil type: Cheshire fine sandy loam 60% sand, 34% silt, 6% clay, 16.5 g/kg organic carbon. Injected at rate of 82 kg/ha. Concentrations decreased from 5000 to 500 to 102 µg/kg on day 0, 75, and 500, respectively. Soil extraction with hexane.	Frink and Bugbee (1989)
Soil	P	1000 µg/kg	525		1st yr $T_{1/2}$ = 36 2nd yr $T_{1/2}$ = 115–200	Soil fumigation study. 1986 study. Non-1st order biodegradation. Soil type: Cheshire fine sandy loam 60% sand, 34% silt, 6% clay, 16.5 g/kg organic carbon. Injected at rate of 82 kg/ha. Concentrations decreased from 1000, 200, 100, and 90 µg/kg on day 0, 50, 125, and 325 respectively. Soil extraction with hexane.	Frink and Bugbee (1989)
Aquifer	P	3400 µg/L	4015	0.0015	460	Former gasoline station site. Estimated plume extent ~76+ m. Data reported from 1993 to 2004 for a monitoring well located near the source area. Clayey soils at this site are found near the surface and are underlain by sandy silts and silty sands. The groundwater velocity ranges between 2.1 to 6.4 m/year.	Mayer (2005)
Aquifer	P	280 µg/L	4015	0.000926	750	Former gasoline station site. Estimated plume extent ~76+ m. Data reported from 1993 to 2004 for a monitoring well located approximately 45-55 meters down-gradient from the source area. Clayey soils at this site are found near the surface and are underlain by sandy silts and silty sands. The groundwater velocity ranges between 2.1 to 6.4 m/year.	Mayer (2005)

[1] Primary biodegradation (P) or mineralization (M) was measured as the endpoint.

1. Soil Fumigant Use

Frink and Bugbee (1989) studied the loss of EDB following its field application as a soil fumigant (Table 9). They noted that EDB does not follow first order decay except during the initial period of loss. Half-lives of 36 and 26 days were reported for the first year of the field studies in 1986 and 1987, respectively, while in the second year after fumigation the apparent half-life decreased to 115 to 200 days. These study results support the conclusions of Steinberg et al. (1987), Pignatello (1987b), and Pignatello et al. (1990); when EDB is physically trapped within the soil matrix, bioavailability correspondingly decreases. A field study in Whatcom county, Washington followed concentrations of EDB in groundwater from a private well for over 18 years. From 1980 to 1986, concentrations of approximately 6 μg/L were reported. In 1987 to 1989 and 1991 to 1994, concentrations of 3 to 3.5 μg/L and approximately 2 μg/L were measured, respectively, with final concentrations of <0.5 μg/L reported as of 1998 (Duff, 2000).

EDB was used to fumigate the "Biology Fields" at Brookhaven National Laboratories (BNL) during the late 1960–1970s. EDB leached through the soil to the groundwater and is now found as a separate plume ~457 m in length south/southeast of the fields at a depth of 27.4–39.6 meters below ground surface (bgs). Sediments found beneath Brookhaven National Laboratory consist of unconsolidated sediments [Upper Glacial aquifer, 39.6–60 m thick, mainly unconfined, sandy, gravelly permeable glacial outwash deposits, the water table is about 5 m or less bgs] (ATSDR, 2005b), followed by the Gardiner's clay confining unit (0.61 to 4.6 m thick, permeability of approximately 12.2 liters/day/m^2) (Paquette et al., 2002) that separates the upper aquifer from the underlying Magothy aquifer. The clay deposits may not be continuous and may lead to direct hydraulic connection between the Upper Glacial and the Magothy aquifers. The Magothy aquifer is about 244 to 271 m thick composed mainly of coarse sand and gravel with estimated flow velocities of 0.91 to 4.3 cm/day. The Magothy aquifer is mainly confined where the Gardiner's clay overlies it and semi-confined/unconfined where it is absent (Paquette et al., 2002). Groundwater preferentially flows through the more permeable Upper Glacial aquifer (measured porosity of 0.18 to 0.36, average of 0.25) (ATSDR, 2005b). Groundwater flow velocity was estimated as 23 cm/day (but as high as 44 cm/day) (Paquette et al., 2002). Based on modeling results, including time for vertical transport, EDB has been moving southward at 100 to 125 m/year (ATSDR, 2005b). EDB was first detected in groundwater samples in 1986 as a set of 7 underground pools. EDB is currently moving as a "pocket" of contaminated groundwater. Initial pump and treat efforts to remove EDB were unsuccessful. By 1995, 5 EDB plumes were shown to be moving off of the southern boundary of the biology fields. Phytoremediation was attempted and was considered unsuccessful because most plants did not take up the EDB through their root systems (Swenson, 1999). Pump and treat remediation at the site from 1997 through 2004 (75,700,000 liters water treated) and in 2005 (596,770,000 liters water treated) is estimated to have removed less than 0.45 kilogram of EDB for each period (Dorsch et al., 2007). Soil sampling at the Biology Fields area was undertaken from 1994–1995. EDB was not detected in any sample. Groundwater samples prior to 1993 were collected from on-site wells and a maximum concentration of 0.21 μg/L was reported. As of 1993, a monitoring well network was established to determine the vertical and horizontal extent of the EDB plume (ATSDR, 2005b). EDB detected near the source area is found at shallow depths (6 to 13.7 m bgs) while EDB concentrations further from the source area at the BNL site boundary are found at greater depths (15.2 to 44.2 m bgs). Concentrations measured in on-site groundwater from 1994–1995 ranged from 0.04 to 0.78 μg/L (at depths of 4.6 to 21 m bgs). Concentrations of EDB were reported as a maximum of 1.2–3.5 μg/L at a depth of 27.4 to 39.6 m bgs in off-site wells in 1993 to 1995 (ATSDR, 2005b). Maximum EDB concentrations of 6 and 3.6 μg/L were measured in 1998 and 1999, respectively (Brookhaven National Laboratory, 2000). Projections in 2000 estimated that it would require a period of 40 years for natural attenuation to return groundwater concentrations to the drinking water standard (Brookhaven National Laboratory, 2000).

2. Leaded Fuel Release Sites

The available field site data for EDB at gasoline spill sites indicate that this compound can persist in groundwater environments with disappearance half-lives ranging from several months to more than a year, depending on the site. Falta (2004a) estimated disappearance rate constants for 65 wells in South Carolina that were impacted by the release of leaded gasoline. Their data indicate that while a reduction in concentration may be seen at a given site, frequently an increase in concentration is seen with time (Table 10). Increasing concentrations may be due to the LNAPL source still containing EDB or to water table fluctuations (Falta et al., 2005b).

Table 10. 1st Order disappearance rate constants for EDB for 65 wells at LUST sites in SC (Falta, 2004a)

1st order disappearance $T_{1/2}$ days)	k value (per day)	Number of wells
	<-0.01	6
	-0.0081 to -0.01	0
	-0.0061 to -0.008	3
	-0.0041 to -0.0060	5
	-0.0021 to -0.0040	5
	-0.0001 to -0.0020	13
>347	0 to 0.0020	8
173–347	0.0021 to 0.0040	6
116–173	0.0041 to 0.0060	2
87–116	0.0061 to 0.0080	2
69–86	0.0081 to 0.0100	0
<69	>0.0100	5

Disappearance rate constants and half-lives for EDB and 1,2-DCA were estimated by Mayer (2005) for a gasoline service station (Speedway #60) in Gaston county, North Carolina operated between 1964 and 1992 (Table 9). Clayey soils at this site are found near the surface and are underlain by sandy silts and silty sands. The groundwater velocity ranges between 2.1 to 6.4 m/year. Redox conditions at this site were not reported, however, monitoring data were available for EDB, 1,2-DCA, benzene, and MTBE over a number of years. The current plume extent of EDB and 1,2-DCA at this site is estimated to be ~76.2 and ~87 m, respectively. Samples were collected from 2 wells (MW-1, approximately 3 to 6 meters from the source area, and MW-7, approximately 45 to 55 meters downgradient from the source area) between 1993 and 2004 and samples from a third well (MW-10, located approximately 60 to 70 meters downgradient from the source area) were collected from 1996 to 2004. Benzene concentrations at MW-1, MW-7, and MW-10 were 29,000, 10,000, and 4200 μg/L, respectively, in 1993/1996 and 100, 110, and 3.9 μg/L, respectively, in 2004. Disappearance rate constants of 0.695, 0.426, and 0.843 per year were reported from these concentrations (MW-1, MW-7, and MW-10) corresponding to half-lives of 1.0, 1.63, and 0.82 years, respectively. 1,2-DCA concentrations at MW-1, MW-7, and MW-10 were 3800, 1700, and 860 μg/L, respectively, in 1993/1996 and 9.3, 65, and 220 μg/L, respectively, in 2004. Based on these concentrations, disappearance rate constants of 0.577/yr, 0.233/yr, and 0.128/yr and half-lives of 1.20, 2.97, and 5.41 years can be estimated for MW1, MW7, and MW10, respectively. Concentrations of EDB were reported for MW-1 and MW-7 only. EDB concentrations at MW-1 and MW-7 were 3400 and 280 μg/L, respectively, in 1993 and 6.3 and 3.3 μg/L, respectively, in 2004. Based on these concentrations, disappearance rate constants of 0.549/yr and 0.338/yr and half-lives of 1.26 and 2.05 years can be estimated for MW-1 and MW-7, respectively. From these data, the author concluded that EDB is as mobile as benzene and more resistant to degradation while 1,2-DCA is the most resistant to degradation and is more mobile than both benzene and EDB.

Based on information from the EPA Superfund Record of Decision (U.S. EPA, 2006), the Massachusetts Military Reservation (Camp Edwards and Otis Airfield) (MMR) first opened in 1911. Most onsite activity occurred between 1940 to 1946 and 1955 to 1970. The site geology consists of "stratified outwash sand underlain by silty glaciolacustrine sediment". There is a single, primarily unconfined aquifer, approximately 64 m thick, with a mainly horizontal flow gradient of 0.00025 to 0.0006 m/m (Kavanaugh et al., 1999). The water table elevation is approximately 20.4 m msl (mean sea level) ±0.3 to 1.2 m annual fluctuation. In 1972, a pipeline break spilled an estimated 265,000 liters of aviation gasoline. The plume from this spill was first detected in 1990 and is currently designated as FS-12. A remedial investigation in 1992 found NAPL above the water table, identified as a diesel-like fuel that contained BTEX but not EDB. The plume was approximately 1463 m long, 609.6 m wide, and 18.3 to 39.6 m thick and was defined by any contaminant exceeding its MCL. Groundwater samples collected during the investigation contained high concentrations of EDB and benzene (maximum concentrations of 597 and 1600 µg/L, respectively). Groundwater contamination was reported 1524 m downgradient from the source as of 1992. Remedial action was undertaken in 1995 with a combination of air sparging and soil vapor extraction. By 1998, 11% of the residual hydrocarbons had been removed by this action and it was stopped. Further remedial action consisting of extraction at the leading edge of the plume began in 1997. As of 2005, the plume was 670 m long, 427 m wide, and up to 38 m thick. The maximum EDB concentration in the plume in 2003 and 2005 was 27 and 12.8 µg/L, respectively (U.S. EPA, 2006). 1,2-DCA is also present in FS-12 with maximum concentrations of 1.7 and 0.115 µg/L on off-base and on-base locations, respectively (U.S. EPA, 2006). Falta (2004b) has estimated a rough half-life of approximately 18 years based on the removal of 38% of the originally released EDB during remediation procedures in 1997 (i.e., after 25 years, 38% of the originally spilled EDB was still present). Two other EDB-contaminated plumes, FS-1 and FS-28 are located on the Massachusetts Military Reservation. The sources of both are believed to be fuel spills. FS-28 was first discovered in 1992. The plume was described as 3200 m long, with a maximum width of 305 m and thickness of up to 30.5 m (AFCEE, 1998, 2003). The maximum concentration of EDB in the FS-28 plume was 16 µg/L (AFCEE, 1998). Remediation began in 1997. The source of FS-1 was an aircraft fuel dump area from 1955–1970 (Falta, 2004b). The plume was described as 1990 m long, 366 m wide and up to 55 m thick (AFCEE, 2003). EDB was not detected at the source area, although toluene was still present, but was measured in cranberry bogs one mile away at 1.4 µg/L (Falta, 2004b). This detached plume was delineated with wells in 1998 and a maximum EDB concentration of 10 µg/L was reported (Falta, 2004b). Remediation of this site began in 1999. A fourth plume (2400 m long, 360 m wide and 30 m thick) was detected in 1997/1998 with concentrations up to 10 µg/L and was found to discharge directly into the Quashnet River (Falta, 2004b). Three of the 4 plumes at the MMR site have detached from both the source area and from the BTEX contaminant plume, however, it is not known if this is typically seen at other locations (Falta et al., 2005b).

E. Monitoring Data

Because of EDBs direct release to the environment as a soil fumigant, emissions from its use as an additive to motor fuels, or spills of EDB-containing leaded motor and aviation fuels, it has been detected widely in ambient air, groundwater, and soil. The available monitoring data has been divided into sites contaminated by EDB purposefully (as a fumigant) or due to a spill and those studies where broader baseline-type sampling has been undertaken.

1. Release Site Data

Monitoring data in this section have been separated into sites affected by the release of leaded fuels, soil fumigation sites, and sites affected by grain bin fumigants (Table 11). Many of these sites have undergone remediation efforts to prevent movement of the contaminant plume to nearby residences that

may use groundwater as a water source and the data reported over time cannot be used to determine natural attenuation rates.

The presence of EDB at UST (underground storage tank) sites has come under more intense scrutiny in recent years (Falta, 2004a, 2004b, 2005; Falta and Bulsara, 2004; Falta et al., 2005a; Wilson et al., 2007). The South Carolina Department of Health and Environmental Control maintains a database of the approximately 7200 documented petroleum release sites in that state. 1100 UST sites have been tested for EDB from the early 1990s on with 537 of these sites reporting concentrations above the MCL (approximately 50% of sites). The median EDB concentration is about 5 µg/L but concentrations of 50 µg/L or more are found at more than 20% of these sites and concentrations >200 µg/L occur at 10% of these sites (Falta et al., 2005a). At 47, 71, 84, 52, and 14 sites positive for EDB (268 sites total), maximum concentrations of 0.05 to 0.5, 0.5 to 5, 5 to 50, and 500 to 5000 µg/L were reported, respectively (Falta and Bulsara, 2004). One site had an EDB concentration of 6550 µg/L (Miner, 2005). Concentrations of EDB ranged from not detected to 8200 µg/L at 7 LUST sites in Kansas, 0.013 to 1140 µg/L (4% of these were above the MCL) for 31 sites in South Carolina, and from 0.084 to 65 µg/L for 8 sites in Santa Barbara county, California (Burton, 2005a). A recent study by Wilson et al. (2007) reported similar results to those published by Falta and Bulsara (2004) and Falta et al. (2005a). 54% of 79 UST sites in 17 states, had detectable concentrations of EDB and 43% of the total sites had concentrations of EDB greater than the MCL (132 positive detections out of 736 samples; 11% of the EDB detections had concentrations greater than the MCL). The distribution, based on maximum concentration reported at each site was similar to that reported by Falta and Bulsara (2004) in South Carolina.

As a follow-up to the work by Falta and Bulsara (2004) in South Carolina, 104 sites in this state, representing 14 counties with 9 of these counties in the coastal plane (composed mainly of sediments) and 5 counties in the piedmont province (metamorphic rock and saprolite) were analyzed further to determine whether geological/surficial features affected the behavior of EDB at these sites (Miner, 2005). Not all sites contained LNAPL. Benzene and EDB concentrations did not appear to be correlated with each other. EDB plume lengths were <30.5, 30.5–76.2, 76.3–152.4, 152.5–243.8, and >243.8 (up to 853.4 m) m at 64, 25, 6, 4, and 1 site, respectively. In comparison with the BTEX plume at each site, approximately 50% were similar in length, 44% BTEX plumes were longer than the EDB plume, and only 6% of EDB plumes were longer than the BTEX plume. Yet EDB has a higher gasoline:water partition coefficient when compared to benzene (i.e., it will partition more easily into water than benzene), has low retardation, and is slowly degraded, particularly under anaerobic conditions. Miner (2005) suggests that monitoring limitations may be responsible for the results seen in South Carolina. Longer EDB plumes are described as "very narrow, cigar-shaped features …. that commonly dive with increasing distance from the source" (Miner, 2005). These features can make it difficult to locate an EDB plume, particularly when only a shallow well network is installed. In addition, some UST site results may be complicated by multiple releases of both leaded and unleaded gasoline at different times.

While field study data implicating cometabolic degradation of EDB were not located, several pure culture studies for EDB specifically, and enriched culture, and microcosm studies for the structurally-similar 1,2-DCA (see section IV, D2a-c) indicate that cometabolism by methanotrophs may occur in the environment. The release of residual gasoline to soil and groundwater will provide a large hydrocarbon source that is likely to result in a localized area of highly reduced, methanogenic conditions in the residual source area. Methanogens in the anaerobic source area will produce methane during the anaerobic biodegradation of gasoline components which may encourage the growth of methanotroph populations in the surrounding aerobic soil zone. Potentially, this may result in the cometabolic biodegradation of EDB present in a leaded gasoline mixture. While data specific to gasoline releases are not available, cometabolic biodegradation of other compounds has been reported in the field. An increase in the methanotroph population and corresponding cometabolic biodegradation of trichloroethylene was reported in the presence of methane and nutrients during a groundwater biostimulation demonstration in

the field (Brigmon, 2001). In addition, the biodegradation of VOCs, including several chlorinated ethanes, by methanotrophs has been reported in soil microcosms incubated under methane/air conditions similar to that of a landfill soil cover (Scheutz et al., 2004). In this study, biodegradation occurred in parallel with methane oxidation suggesting that the VOCs were degraded via cometabolic processes.

Table 11. EDB monitoring data for release sites

Site location	History	Hydrogeology	Concentration in soil	Concentration in groundwater (date of sampling)	Other Concentrations	Remediation efforts	Reference
Leaded gasoline release							
Massachusetts Military Reservation (MMR)	Military site. Leaded fuel spills.	Site geology consists of "stratified outwash sand underlain by silty glaciolacustrine sediment". There is a single, primarily unconfined aquifer, approximately 64 m thick, mainly horizontal flow gradient of 0.00025 to 0.0006 m/m. Water table elevation is ~20.4 m msl.		FS-12: Max = 597 µg/L (1992) Max = 27 µg/L (2003) Max = 12.8 µg/L (2005) FS-28: Max = 16 µg/L (1992) FS-1: Max = 10 µg/L (1998)	Surface water affected by groundwater (Coonamessett and Quashnet Rivers) Max = 1.69 µg/L	FS-12: 1995–1998, combination of air sparging and soil vapor extraction. Extraction at the leading edge of the plume began in 1997. FS-28: remediation began in 1997. FS-1: remediation began in 1999.	Xia and Rice (2001); Kavanaugh et al. (1999); U.S. EPA (2006); AFCEE (1998, 2003); Falta (2004b)
Camp Lejuene Campbell Street Fuel Farm, NC	Military site. JP-5 and aviation gasoline were stored in 8 USTs that were replaced with ASTs in 1985.	Undifferentiated layers of sand, silt, and clay to ~12.2 m below land surface. Hydraulic conductivity: 4.3–14.0 cm/day.		Max = 3.5 µg/L (1996/1999)		Seven UST sites were excavated and contaminated soil removed, 1 was filled with sand and left.	Radian International (2000)

Table 11. EDB monitoring data for release sites

Site location	History	Hydrogeology	Concentration in soil	Concentration in groundwater (date of sampling)	Other Concentrations	Remediation efforts	Reference
Fort Wainwright, AK	Military site. Undocumented leaded fuel spills, refueling area, pipelines.	Heterogeneous mixture of coarser and finer soil lenses of relatively small size, unconfined aquifer, depth to water table = 3-4.6 m bgs, average linear velocity of 30.5–45.7 cm/day, horizontal hydraulic conductivity = 38.1–121.9 m/day, vertical hydraulic conductivity 1/20th of the horizontal.		Range = 0.02–0.46 µg/L (1989–1994)			U.S. EPA (1999)
Fort Randall, Cold Bay, AK	Former military site (1940–1950), aviation fuel spills and releases from 38 under-ground storage tanks as well as several pipelines.	Soils described as either glacial till or silty sands and sandy silts. Groundwater levels are about 3.0 to 6.1 m bgs. Hydraulic conductivity ranges from $3.0x10^{-5}$ to $2.0x10^{-1}$ cm/sec.	Range = 0.309–17 µg/kg (5/134 samples positive; 2004)	Range = 1.35–10 µg/L (4/6 samples positive; 2004)		Cleanup activity at this site began in 1985 including removal of drums, contaminated soil, construction of an HVE system.	Jacobs Engineering Group, Inc. (2002, 2005)

Table 11. EDB monitoring data for release sites

Site location	History	Hydrogeology	Concentration in soil	Concentration in groundwater (date of sampling)	Other Concentrations	Remediation efforts	Reference
Orangeburg, SC	Former gasoline station (1953–1987)	Underlain by clays and silts, water table depth is 4.6–6.1 m. Groundwater velocity: 1.5–6.1 m/yr. Not much movement of EDB off site, ~45.7 m.		Max = 189 µg/L (1999)		Original tanks from 1953 abandoned in 1971 and removed in 2003. New tanks in place in 1971 and removed in 1987.	Falta (2004b)
Soil fumigant use							
Fort Hall Indian Reservation, ID	Soil fumigation use.	Sandy to loamy soils and coarse gravelly material 51–102 cm below the surface, hydraulic conductivity 100–150 µmeter/sec, hydraulic gradient 0.38 m/km. Most soils have a low water holding capacity with a relatively shallow depth to groundwater.		Range = 0.02–16 µg/L (109 wells positive; 1996)			ATSDR, 2005a; IDHW, 2002; USDA and NRCS, 2006
Connecticut	Three farms. Low concen-tration from soil last fumigated in 1973.	Organic carbon content of 11.1, 16.1, and 16.5 g/kg, respectively.	40, 89, 124.5 µg/kg (1980s)				Sawhney et al. (1988)

Table 11. EDB monitoring data for release sites

Site location	History	Hydrogeology	Concentration in soil	Concentration in groundwater (date of sampling)	Other Concentrations	Remediation efforts	Reference
North Whatcom County, WA	Soil fumigant use.	The Sumas-Blaine aquifer is composed of permeable sand and gravel glacial outwash ranges up to 23 m thick with the water table less than 3 m bgs (Duff, 2000) and has an average hydraulic conductivity of 283 m/day (Berg et al., 2001). It is unconfined.		Average = 0.3 µg/L Max = 6.1 µg/L (1984–1999; 126/444 samples positive; 98/444 samples above MCL)			Duff (2000)
Whatcom County, WS	Soil fumigant use.			Range = <0.02–6.17 µg/L (18/107 wells positive; 1986–1991)			Mayer et al. (1991)
Pattison Lake, Lake St. Clair Thurston County, WA	Soil fumigant use. Drinking water well samples.			Average = 0.34 µg/L Max = 1.2 µg/L (1984–2001; 63/195 samples positive; 52/195 samples above MCL)			Berg et al. (2001)

Table 11. EDB monitoring data for release sites

Site location	History	Hydrogeology	Concentration in soil	Concentration in groundwater (date of sampling)	Other Concentrations	Remediation efforts	Reference
Connecticut	Soil fumigant use; last fumigated in 1967.	Glacial deposits of sand, gravel, and silt from 6.1–12.2 m thick, water table at 1.8–4.3 m, hydraulic conductivity, hydraulic gradient, estimated porosity, and calculated water velocity are 79.9–5290 m/yr, $2.5x10^{-2}$ m/m, 0.30, and 100 m/yr, respectively for the shallow aquifer and 24.5–327 m/yr, $1.34x10^{-2}$ m/m, 0.1, and 33 m/yr, respectively for the bedrock aquifer.	Range = 1–32 µg/kg Mean = 5.1 µg/kg (58 positives; 1980s)	Range = 0.02 to 1.2 µg/L (1980s)			Marin and Droste (1986); Pignatello et al. (1987)
Grain bin fumigant site							
Hilton grain bin site, KS	Grain bin site; on-site well contained 910 µg/L CCl_4 and 2.9 µg/L EDB			2.9 µg/L (1992)			Kansas Department of Health and Environment (2007)

Table 11. EDB monitoring data for release sites

Site location	History	Hydrogeology	Concentration in soil	Concentration in groundwater (date of sampling)	Other Concentrations	Remediation efforts	Reference
Hastings, NE	FAR-MAR-CO site stored and handled grain for over 30 years. Groundwater upgradient of this site does not contain detectable EDB.	The upper aquifer consists of sand, silt, and gravel units extending from a depth of about 36.6 to 68.6 m bgs. Groundwater flow rates are estimated to be 15–45.7 cm/day.	Max = 1200 µg/kg (1986)	Range = ND–6.8 µg/L (1985–1987) ~460 µg/L (Sept 1997) 740 µg/L (Sept 1999 (pump and treat system suspended for 1 year), 360 to 220 µg/L (Sept 2000 to Sept 2002).		In 1990, a pilot SVE study removed >1200 lbs (>545 kg) of CCl_4 and EDB from soil. In 1997, a full SVE system was added and after 2.5 years, EDB concentrations in soil were 0.0016 µg/L. Pump and treat has been in place since 1997 to handle the CCl_4 and EDB groundwater plume moving from the site.	U.S. EPA (1988, 2003)
Scoular Elevator site, Salina, KS	Spill of 1140–2300 liters grain fumigant in 1963. CCl_4 and chloroform found in plume.			Plume extends for 0.5 mile, relatively stable over time.		Pump and treat with air stripping.	Kansas Department of Health and Environment (2007)
McShares, Inc. Salina, KS	Grain fumigant formulating facility. 1,2-DCA also found in contaminant plume.			Plume extends for 1 mile down-gradient.			Kansas Department of Health and Environment (2007)

Table 11. EDB monitoring data for release sites

Site location	History	Hydrogeology	Concentration in soil	Concentration in groundwater (date of sampling)	Other Concentrations	Remediation efforts	Reference
Latimer Agri-Services facility, Latimer, KS	CCl_4 and EDB found in contaminant plume.	A succession of shale aquitards and limestone aquifers.		0.24–24.0 µg/L (1998). Plume extends for approximately 0.5 miles downgradient.			ATSDR (2002); Kansas Department of Health and Environment (2007)
Kansas, Nebraska, Iowa, Missouri	USDA grain bin project. Private wells in a 1-mile radius of identified site sampled.			1 of 829 sites positive (negative upon retest)			Field (2007)

2. Non-site Based Environmental Monitoring

Monitoring data are presented below for surface water (Table 12), groundwater (Table 13), outdoor air (Table 14), and indoor air (Table 15). While soil concentrations were measured in a few soil fumigant studies, EDB concentrations in soil are given in the section above on transport in soil and are not reported here. EDBs use as a soil fumigant (up to the 1980s) and as a component of leaded fuel has led to its environmental release and the resulting detection of EDB in outdoor air samples from the 1970s–1980s and in groundwater surveys up to the present day. Because of its high Henry's Law constant, EDB is rapidly volatilized from surface waters. The few studies from the 1970s and 1980s where EDB was measured in surface waters indicate that EDB was found either at very low concentrations or was below the detection limit (Table 12). EDB is reported in groundwater at low concentrations (typically less than 1 μg/L). A survey of 2110 community water systems from 12 northeastern and mid-Atlantic states (from 1993–1998) found that 1.7% of the water systems (36 community systems) had detectable levels of EDB in their finished drinking water (Grady and Casey, 2001). Water from 27% of the positive systems also contained 1,2-DCA suggesting that the source of EDB to those water systems may be from leaded gasoline (Falta, 2004b).

EDB was reported in outdoor air samples from studies in the 1970s and 1980s at concentrations typically less than 1 $\mu g/m^3$. More recent studies from the 1990s report that EDB is not detected or report its presence at average concentrations <0.1 $\mu g/m^3$. Indoor and outdoor air concentrations were monitored for 35 residences in the Kanawha Valley of West Virginia in the mid-1980s. While 29% of indoor air samples collected from these residences contained detectable concentrations of EDB [limit of detection (LOD) of 8.5 $\mu g/m^3$], none of the outdoor air samples had measurable concentrations of EDB (Cohen et al., 1989). A second study measured indoor and outdoor air concentrations of EDB at 75 residences in Ottawa, Canada during the winter of 2002 and 2003 (Zhu et al., 2005). EDB was not detected in 75 indoor and 74 outdoor air samples based on a detection limit of 0.01 $\mu g/m^3$ (Zhu et al., 2005).

Table 12. Surface water concentrations for EDB

Concentration	Number of positive samples/total samples	Location	Date of sampling	Notes	Reference
Median = 0 µg/L Max = 0.2 µg/L	11/175	New Jersey	1977–1979		Page (1981)
Not detected	0/42	Ten locations, Great Lakes	1982–1983	Detection limit of <0.1 µg/L	Otson (1987)
Mean = 0.02 ng/L	NR[1]	North and South Atlantic ocean	1985	Baseline concentrations in seawater.	Class and Ballschmiter (1988)

[1] NR = Not reported

Table 13. Groundwater concentrations for EDB

Concentration	Number of positive samples/total samples	Location	Date of sampling	Notes	Reference
Median = 0 µg/L Max = 48.8 µg/L	34/421	New Jersey	1977–1979		Page (1981)
Range = 0.001–15,772.4 µg/L	2918/20221	U.S.	1971–1991	Pesticides in Groundwater database (U.S. EPA). Biased data as some geographic areas have been more intensively studied than others.	Hoyle and Arthur (2000)
0.058, 0.075, 0.100, 0.190 µg/L	NR[1]	Pearl Harbor aquifer, Waipahu, Oahu	1983–1984	Maximum concentrations reported for samples collected from 4 water pumps.	Oki and Giambelluca (1987)
Not detected (<0.2 µg/L)	0/292	U.S.	1985–1995	Urban wells. Untreated ambient groundwater study as part of NAWQA.	Squillace et al. (1999)
Median = 0.9 µg/L Range = 0.3–1.4 µg/L	5/1798	U.S.	1985–1995	Rural wells. 0.3% of wells exceed MCL of 0.05 µg/L. Untreated ambient groundwater study as part of NAWQA.	Squillace et al. (1999)
Median = 0.72 µg/L (positives)	2/2851	U.S.	1985–2001	National assessment of groundwater from various types of wells representing almost 100 different aquifer studies (regionally extensive aquifers of aquifer systems). Detections were in shallow aquifers in rural areas.	Zogorski et al. (2006)

Table 13. Groundwater concentrations for EDB

Concentration	Number of positive samples/total samples	Location	Date of sampling	Notes	Reference
Median (positives) = 0.55 µg/L	4/2085	U.S.	1985–2001	National assessment of groundwater from domestic wells representing almost 100 different aquifer studies (regionally extensive aquifers of aquifer systems).	Zogorski et al. (2006)
Median (positives) = <0.2 µg/L	0/462	U.S.	1985–2001	National assessment of groundwater from public wells representing almost 100 different aquifer studies (regionally extensive aquifers of aquifer systems).	Zogorski et al. (2006)
Max = 1.1 µg/L	23/302	Fresno/Clovis, California	1988–1993	Thirteen active and 10 closed wells contained detectable concentrations of EDB; 10 wells exceeded the MCL of 0.02 ppb.	Kloos (1996)
Max = 1.40 µg/L	5/1831	U.S.	1992–1996	Wells representative of 20 major hydrologic basins in NAWQA program study. Mainly recently recharged shallow groundwater systems.	Kolpin et al. (2000)
0 of 36 positive samples had concentrations >0.02 µg/L	36/876	Kansas	1998–1999	Finished water from public water supply wells.	Kansas Dept Health and Environment (2000)
Not detected	0/518	U.S.	1996–2002	National water-quality assessment program of USGS. Shallow groundwater in new residential/commercial areas (median well depth, 10 m).	Squillace et al. (2004)
2 of 3 positive samples had concentrations >0.02 µg/L	3/220	Kansas	2002–2005	Untreated water from 29 different wells.	Kansas Dept Health and Environment (2006)
8 of 38 positive samples had concentrations >0.02 µg/L.	38/1347	Kansas	2002–2005	Finished water from public water supply wells.	Kansas Dept Health and Environment (2006)

[1] NR = Not reported

Table 14. Outdoor air concentrations for EDB

Concentration	Number of positive samples/total samples	Location	Date of sampling	Notes	Reference
Mean = 0.081 µg/m^3 Range = <DL (DL not reported)–0.28 µg/m^3	32/32	Arctic atmosphere	March and April 1983	Whole air-grab samples taken from aircraft and ground. Investigation of Arctic haze.	Berg et al. (1984)
Monthly average range = 0.0077–0.015 µg/m^3	NR[1]	Barrow, AK	1983	Authors believed the source was from polluted air transported from industrial mid-latitude sources.	Rasmussen and Khalil (1984)
Mean = 0.0023 µg/m^3	NR	Open Atlantic Ocean (30° S to 40 °N)	1985	Concentrations from in the boundary layer.	Class and Ballschmiter (1988)
Mean = 0.00077 µg/m^3	NR	Open Atlantic Ocean (30° S to 40 °N)	1985	Concentrations from above the boundary layer.	Class and Ballschmiter (1988)
Mean = 0.00077–0.0038 µg/m^3	NR	Open Atlantic Ocean (30° S to 40 °N)	1985	Air concentration with coastal input.	Class and Ballschmiter (1988)
Range = 0.069–0.110 µg/m^3	NR	Phoenix, AZ; Los Angeles, CA; Seattle, WA	Early 1970s	Samples collected along urban roadways in three western U.S. cities (high traffic loads, near gasoline stations).	Johns (1976)
Range = 4.2–115 µg/m^3 (manufacturing sites) Range = 0.23–1.65 µg/m^3 (oil refinery)		Arkansas (manufacturing site) Kansas City (oil refinery)	Early 1970s		Going and Long (1975)
Range = 0.001–0.17 µg/m^3	NR	London, England	1976	Ambient air samples taken from Exhibition Road, London (1500 vehicles/hr).	Leinster et al. (1978)
Range = 0.07–1.26 µg/m^3	NR	London, England	1979	Exhibition Road, London, urban site.	Tsani-Bazaca et al. (1981)
Mean = 0.025 µg/m^3 Range = 0.041–1.4 µg/m^3	NR	Los Angeles, CA	April 1979		Singh et al. (1981a)
Mean = 0.31 µg/m^3 Range = 0.018–1.57 µg/m^3	NR	Phoenix, AZ	April/May 1979		Singh et al. (1981a)

Table 14. Outdoor air concentrations for EDB

Concentration	Number of positive samples/total samples	Location	Date of sampling	Notes	Reference
Mean = 0.12 µg/m^3 Range = 0.018–0.65 µg/m^3	NR	Oakland, CA	June/July 1979		Singh et al. (1981a)
Mean = 0.78 µg/m^3 Range = <0.038–3.2 µg/m^3	52/61	Downey, CA	February 1984		Singh et al. (1987)
Mean = 2.25 µg/m^3 Range = <0.038–24.4 µg/m^3	104/106	Houston, TX	March 1984		Singh et al. (1987)
Mean = 0.94 µg/m^3 Range = <0.038–4.6 µg/m^3	98/99	Denver, CO	April 1984		Singh et al. (1987)
Mean = 0.16 µg/m^3 Range = <0.038–3.3 µg/m^3	144/147	Philadelphia, PA	April 1983		Singh et al. (1987)
Mean = 0.15 µg/m^3 Range = 0.061–0.31 µg/m^3	58/58	Staten Island, NY	May 1983		Singh et al. (1987)
Average = 1.33 µg/m^3 Max = 42.2 µg/m^3	74/222	6 locations, New Jersey	1979	39/222 samples contained trace concentrations EDB, 35/222 samples had quantifiable levels.	Harkov et al. (1981)
Geometric mean = <0.02 µg/m^3	12/111	New Jersey	July/August 1981	Three urban locations in New Jersey (Newark, Elizabeth, Camden).	Harkov et al. (1984)
Geometric mean = <0.02 µg/m^3	11/105	New Jersey	January/February 1981	Three urban locations in New Jersey (Newark, Elizabeth, Camden).	Harkov et al. (1984)
Mean = 0.015 pptm Range = 0.00–0.10 pptm	NR/175	Silwood Park, England	1982	Rural site	Clark et al. (1984)
Mean = 0.05 pptm Range = 0.009–0.26 pptm	NRR/198	Toddington, England	1982	Motorway site.	Clark et al. (1984)
Mean = 0.03 pptm Range = 0.01–0.13 pptm	NR/256	London, England	1982	Exhibition Road, London, urban site.	Clark et al. (1984)

Table 14. Outdoor air concentrations for EDB

Concentration	Number of positive samples/total samples	Location	Date of sampling	Notes	Reference
Average = 0.057 µg/m^3	153/511	El Monte, Los Angeles, Dominguez, and Riverside, CA	January 1983–May 1984	CARB data. All values below the reporting limit (5 ppt) were considered to be 2.5 ppt for the calculation of the average.	California EPA (2003)
Mean = 1.80 µg/m^3 Range = 0–231 µg/m^3	603/2120	U.S.	1976–1987	National ambient VOCs database (data from Shah and Heyerdahl, 1988). 64 urban to suburban locations.	Kelly et al. (1993)
Not detected (detection limit 0.38 µg/m^3)		Columbus, OH	June/July 1989	Six sites were sampled in metropolitan Columbus, OH.	Spicer et al. (1996)
Average = 0.038 µg/m^3 Range = <0.077–0.15 µg/m^3	2/451	California	1989	CARB sampling program. Only 2 samples were above the LOD (limit of detection) of 0.01 ppb.	Loscutoff and Poore (1993)
Average = 0.054 µg/m^3 Range = <0.077–0.54 µg/m^3	14/575	California	1990	CARB sampling program. Only 14 samples were above the LOD of 0.01 ppb.	Loscutoff and Poore (1993)
Not detected (<0.78 µg/m^3)	0/81	Lima, OH	1990–1991		Kelly et al. (1993)
Median = 0.02 µg/m^3 Mean = 0.04 µg/m^3 Maximum = 14.68 µg/m^3	NR/3650	Minnesota	1991–1998	Data collected at 25 sites across Minnesota for up to 8 years.	Pratt et al. (2000)
Not detected	0/2201	U.S.	1962–1992	Survey of ambient measurements of HAPS. Analyzed for but not detected at 65 locations.	Kelly et al. (1994)

[1] NR = Not reported

Table 15. Indoor air concentrations for EDB

Concentration	Number of positive samples/total samples	Location	Date of sampling	Notes	Reference
Mean = 6.06 µg/m^3 Median = 3.94 µg/m^3 Max = 23.53 µg/m^3	29/35	Kanawha Valley, WV	1980s	35 residences, 3-week integrated sample. LOD (limit of detection) of 8.5 µg/m^3.	Cohen et al. (1989)

F. Fugacity Estimates

The EPIWIN Level III fugacity model was used to model the environmental fate and persistence of EDB under different release scenarios (Tables 16 and 17) (U.S. EPA, 2007b). This is a diffuse model and does not contain a groundwater component. The Level III fugacity model assumes that EDB is being continually released to the environment and that steady state conditions are reached. EDB can be removed from this system by either advection (the movement of undegraded chemical out of the geographical boundaries of the model) or degradation within the compartments (air, water, soil, and sediment) of the model environmental media (based on a user-supplied degradation half-life). Equilibrium between environmental media is not assumed in the Level III fugacity model. Input data to the model included relevant physical/chemical properties reported in Table 2, an aerobic biodegradation half-life in water and soil of either 7 (results reported in Table 16) or 70 (results reported in Table 17) days based on aerobic microcosm biodegradation data (Table 7) and an atmospheric half-life of 43 days as reported in the photolysis section for EDB in this report. Emission scenarios were varied as given below in Tables 16 and 17 as this can affect the distribution and persistence of a compound in the environment. The model was also run with advection on and with advection turned off. With advection off, EDB cannot be removed from the model environment undegraded, giving a "global" perspective of the environmental fate of EDB where loss due to degradation becomes most important in determining the persistence of EDB in the environment.

For highly volatile chemicals such as EDB, the overall persistence time may be very short when advection is considered since the advection lifetime in air is very short. This does not necessarily mean that the chemical has low persistence, however; in many cases it simply means the chemical has been removed from the model environment undegraded and exists in some other location beyond the boundaries of the model. This is exemplified by comparing the overall persistence time for EDB with advection on and with advection off. The first two columns of Table 16 illustrate the results of the model run where EDB is emitted solely to the air compartment. With advection on, the overall persistence time of EDB in the model environment is only 89.3 hours; however, almost 90% of the loss is through advection processes. When advection is not considered, the overall persistence time of the chemical is 706 hours and all the loss is through degradation processes. Comparable results are observed for each emission scenario. Tables 16 and 17 also indicate that when advection is considered, almost all the advective loss of mass occurs through the air compartment.

A similar pattern is also observed using the longer half-lives (70 days in water and soil and 280 days in sediment) (Table 17). Comparing the results of Tables 16 and 17 for each emission scenario: (1) a higher percentage of chemical is advected when longer half-lives are considered (assuming advection is on); (2) a higher percentage of chemical is reacted in air when longer half-lives are considered (assuming advection is off). (3) the overall persistence time increases when longer half-lives are considered irregardless of whether or not advective processes are used in the model; (4) similar distributions of EDB between the environmental media are observed.

Table 16. Fugacity estimates for EDB (7-day half-life in water and soil, 28-day half-life in sediment)

	1000 kg to air only (advection off)	1000 kg to air only (advection on)	1000 kg to water only (advection off)	1000 kg to water only (advection on)	1000 kg to soil only (advection off)	1000 kg to soil only (advection on)	1000 kg each to air, water, and soil (advection off)	1000 kg each to air, water, and soil (advection on)
Mass amount in air (%)	97.4	97.7	54.7	13.6	50.9	11.9	74.4	29.3
Mass amount in water (%)	2.2	1.9	45	86.1	2.3	2.0	13.5	32.9
Mass amount in soil (%)	0.4	0.4	0.2	0.05	46.8	86.1	12.1	37.7
Mass amount in sediment (%)	0	0	0.1	0.2	0	0	0.04	0.08
% Advected (air)	0	87.3	0	22.8	0	23.8	0	44.6
% Advected (water)	0	0.2	0	14.4	0	0.4	0	5.0
% Advected (soil)	0	0	0	0	0	0	0	0
% Advected (sediment)	0	0	0	0	0	0	0	0
% Reacted (air)	92.4	11.7	28.2	3.0	25.3	3.2	48.6	6.0
% Reacted (water)	6.6	0.7	71.4	59.6	3.5	1.7	27.2	20.7
% Reacted (soil)	1	0.1	0.3	0	71.2	71	24.2	23.7
% Reacted (sediment)	0	0	0	0	0	0	0	0
Persistence time (hr)	706	89.3	385	168	369	200	487	152
Reaction time (hr)	706	711	385	267	369	264	487	302
% Reacted	100	12.6	100	62.7	100	75.8	100	50.4
% Advected	0	87.4	0	37.3	0	24.2	0	49.6

Table 17. Fugacity estimates for EDB (70-day half-life in water and soil, 280-day half-life in sediment)

	1000 kg to air only (advection off)	1000 kg to air only (advection on)	1000 kg to water only (advection off)	1000 kg to water only (advection on)	1000 kg to soil only (advection off)	1000 kg to soil only (advection on)	1000 kg each to air, water, and soil (advection off)	1000 kg each to air, water, and soil (advection on)
Mass amount in air (%)	93.2	94.9	54.6	13.6	51.2	11.9	63.4	20
Mass amount in water (%)	5.8	4.1	44.6	85.9	5.9	4.2	19.9	33.2
Mass amount in soil (%)	1.0	1.0	0.6	0.1	42.8	83.8	16.5	46.7
Mass amount in sediment (%)	0	0.02	0.2	0.4	0.03	0.02	0.1	0.15
% Advected (air)	0	87.7	0	49.3	0	67.8	0	68.3
% Advected (water)	0	0.4	0	31.2	0	2.4	0	11.3
% Advected (soil)	0	0	0	0	0	0	0	0
% Advected (sediment)	0	0	0	0	0	0	0	0
% Reacted (air)	97.8	11.8	79.7	6.6	77.4	9.1	85	9.2
% Reacted (water)	1.9	0.16	20	12.9	2.7	1.0	8.2	4.7
% Reacted (soil)	0.3	0	0.25	0	19.9	19.6	6.8	6.5
% Reacted (sediment)	0	0	0	0	0	0	0	0
Persistence time (hr)	781	93.2	1090	363	1120	568	998	341
Reaction time (hr)	781	772	1090	1860	1120	1900	998	1700
% Reacted	100	12	100	19.5	100	29.8	100	20.4
% Advected	0	88	0	80.5	0	70.2	0	79.6

IV. 1,2-Dichloroethane (1,2-DCA)

A. Historical and Current Use Patterns

1,2-DCA was first manufactured commercially in the U.S. in 1922 (U.S. DHHS, 2005). It is currently produced at approximately 15.5 billion kg/yr (SRI, 2005, 2006). Unlike EDB, 1,2-DCA has numerous current economic uses and the source of this compound to the environment is not as clearly determined. 1,2-DCA is used as a chemical intermediate principally in the production of vinyl chloride, but also vinylidene chloride, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, aziridines, and ethylene diamines (ATSDR, 2007, 1,2-DCA profile). In addition, 1,2-DCA was used in paints, coatings, and adhesives, as a solvent and as a dispersant, as a grain, household, and soil fumigant, in varnish and finish removers, in soaps and scouring compounds, in metal degreasers, in ore flotation, in textile and PVC cleaning, and in organic synthesis for extraction and cleaning purposes (Fishbein, 1979; U.S. DHHS, 2005; U.S. EPA, 1984). The annual use of 1,2-DCA in grain fumigants was approximately 870 to 1570 Mg from 1976 to 1979 (U.S. EPA, 1984). In these formulations, 1,2-DCA at up to 70% was typically mixed with carbon tetrachloride and/or EDB (U.S. EPA, 1984). 1,2-DCA does not have any known natural sources.

In 1979, 85, 3.2, 2.6, 2.3, 1.7, and 1.6% of produced 1,2-DCA was used as an intermediate for vinyl chloride, ethylene amines, tetrachloroethylene, vinylidene chloride, trichloroethylene and used as a lead scavenger, respectively (Letkiewicz et al., 1982). By 1989, 90, 7, and 3% of total 1,2-DCA production was used in vinyl chloride monomer, exports, and miscellaneous (including chlorinated solvents and ethyleneamines), respectively (ICIS Chemical Business Americas, 1974–2006). As of 2005, 1,2-DCA is nearly completely used as a chemical intermediate, predominately for the production of vinyl chloride monomer (96%), but also for the production of ethyleneamines (2%), C_2 chlorinated solvents (1%), and for miscellaneous uses (1%) (ICIS Chemical Business Americas, 1974–2006).

The amount of 1,2-dichloroethane used as a lead scavenger for leaded gasoline was never greater than 1–3% of its total production (ICIS Chemical Business Americas, 1974–2006). As of 1971, 1977, 1980, 3, 3, and <2% of total 1,2-DCA production was used as a lead scavenger, respectively (ICIS Chemical Business Americas, 1974–2006). In 1979, 85% of the total production of 1,2-DCA was used in the production of vinyl chloride (Letkiewicz et al., 1982). Only 1.6% of the total production in 1979 was used as a lead scavenger (Letkiewicz et al., 1982). While this is only a small percent of the total production, it is comparable to the amount of EDB used as a lead scavenger because the annual production value of 1,2-DCA is so high. In 1978, 0.36 million metric tons/yr (363 million kg) was used for lead scavenging purposes (Singh et al., 1981a).

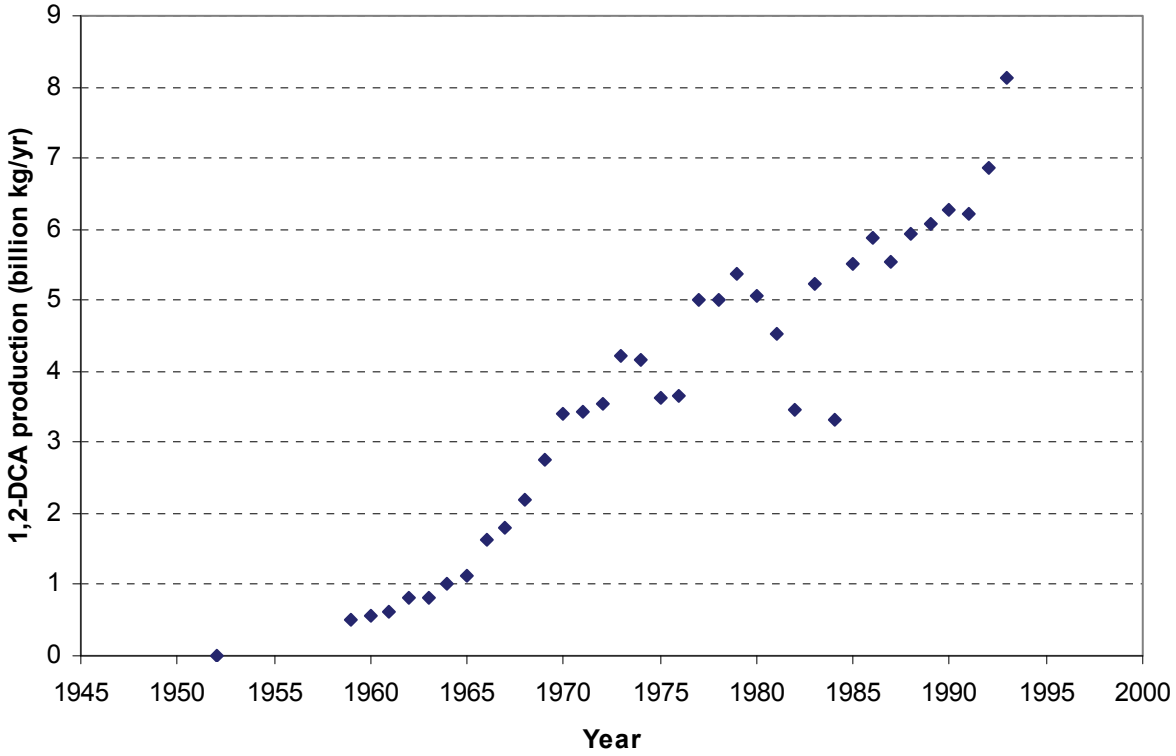


Figure 2. Annual U.S. Production of 1,2-DCA from the years 1952 to 1994 (U.S. ITC, 1953–1995)

The commercial sale of leaded gasoline began in 1923 (Burton, 2005a). While EDB was added to leaded motor fuel as of 1925, 1,2-DCA was added to the lead/EDB mixture used for motor fuel in the 1940s (Burton, 2005a). These compounds were added to the lead mix in order to prevent the build-up of solid lead oxides on spark plugs and exhaust values in the piston engine (Burton, 2005b). The volatile lead bromide and lead chloride formed during the engine combustion process were then released to the air. The amount of 1,2-DCA added to leaded gasoline is dependent on the concentration of lead. Leaded fuels from 1942 to present day contain 1.0 mole 1,2-DCA and 0.5 mole of EDB per mole of alkyl lead (Falta, 2005; U.S. EPA, 1984). Unlike EDB, 1,2-DCA was not used in aviation fuel.

Lead concentrations in gasoline have varied considerably since lead was shown to reduce spark knock in engines in the early 1920's. Initially, a maximum limit of 3.17 g lead/gallon was recommended by the federal government in 1926. This was increased in 1959 to 4.23 g lead/gallon due to increased compression ratios and octane requirements of engines at this time (Gibbs, 1990). Lead concentrations actually reached average highs of only 3.0 g lead/gallon and 2.5 g lead/gallon for premium and regular gasolines, respectively, in the late 1960s (Gibbs, 1990). In the 1970s, improvements were made in refining processes resulting in higher octane base gasoline (Gibbs, 1990). In addition, the U.S. EPA enacted regulations to systematically limit lead concentrations in the U.S. gasoline pool. These regulations are covered by Gibbs (1990) in some detail. By 1979, the average lead content for large refiners (producing >50,000 barrels daily) was set at 0.8 g lead/gallon and 2.65 g lead/gallon for small refiners (for leaded and unleaded gasoline together). After several further changes, a maximum limit of 0.5 g lead/gallon was set across all leaded gasoline manufactured by each refinery in 1985. By 1988, an average of 0.1 g lead/gallon was reached for all U.S. leaded gasoline.

In 1995, leaded fuel made up only 0.6% of total gasoline sales in the U.S. (U.S. EPA, 1996). The sale of leaded fuel for use in on-road vehicles was banned in 1996, although fuel containing lead can still be used for off-road uses including in aircraft, racing cars, farm equipment, and marine engines (U.S. EPA, 1996). The typical composition of the TEL-CB tetraethyl lead package currently produced by Ethyl Corporation for use in leaded fuels (61.49% tetraethyllead, 17.86% EDB, 18.81% 1,2-DCA) is similar to the classic formulation of ethyl fluid (Burton, 2005b).

B. Physical Properties

Physical/chemical properties for 1,2-DCA are presented in Table 18. Like EDB, 1,2-DCA has relatively high vapor pressure and water solubility values. Based on its vapor pressure, 1,2-DCA is expected to volatilize in dry soils. Its Henry's Law constant indicates that 1,2-DCA will readily volatilize from water surfaces.

1,2-DCA is miscible in many organic solvents. If released to the environment in a fuel mixture, it will move with the light non-aqueous phase liquid (LNAPL) by gravity through the vadose zone, potentially to groundwater. The dissolution of a single compound from a mixture such as gasoline in contact with water is different than its dissolution as a pure compound. For the release of a pure compound such as EDB, water-phase concentrations at the NAPL-water interface are at the solubility limit in water. However, for a compound in a gasoline mixture at the NAPL-water interface, the maximum concentration in the water phase is estimated as the effective solubility. This can be presented as a retardation coefficient (total concentration/fraction in mobile-water phase) in a saturated soil matrix.

In soil the retardation coefficient, R_i, is:

$$R_i = \frac{[\theta_w + \rho_s \cdot f_{oc} \cdot K_{oc,i}]}{\theta_w} = 1 + \frac{\rho_s \cdot f_{oc} \cdot K_{oc,i}}{\theta_w} \qquad \text{Eq. (5)}$$

With an immobile residual oil phase (gasoline) present, based on presumed ideal Raoult's law partitioning

$$R_i = \frac{\left(\theta_w + \rho_s \cdot f_{oc} \cdot K_{oc,i} + \frac{\theta_o \cdot \rho_o}{S_i} \cdot \frac{MW_i}{MW_o}\right)}{\theta_w} = 1 + \frac{\rho_s \cdot f_{oc} \cdot K_{oc,i}}{\theta_w} + \frac{\frac{\theta_o \cdot \rho_o}{S_i} \cdot \frac{MW_i}{MW_o}}{\theta_w} \qquad \text{Eq. (6)}$$

Equivalently, for a measured gasoline to water partition coefficient

$$R_i = \frac{\left(\theta_w + \rho_s \cdot f_{oc} \cdot K_{oc,i} + \theta_o \cdot \rho_o \cdot K_{gw,i}\right)}{\theta_w} = 1 + \frac{\rho_s \cdot f_{oc} \cdot K_{oc,i}}{\theta_w} + \frac{\theta_o \cdot \rho_o \cdot K_{gw,i}}{\theta_w} \qquad \text{Eq. (7)}$$

With θ_w (cm^3-water/cm^3-soil) volumetric moisture fraction in soil matrix, equal to the total soil porosity in saturated soil; ρ_s (g-soil/cm^3-soil) is the soil dry bulk density; f_{oc} (g-oc/g-soil) is the mass fraction of organic carbon in soil; and $K_{oc,i}$ (cm^3-water/g-oc) is the chemical-specific organic carbon-water partition coefficient. MW_i is the molecular weight of the chemical, S_i is the pure chemical aqueous solubility limit. With the chemical of interest as a small fraction of the total residual phase, values of θ_o (cm^3-oil/cm^3-soil), ρ_o (g-oil/cm^3-oil), and MW_o (which is a function of oil mixture composition) will be relatively constant and the factor R_i will be independent of the total oil mixture concentration in soil.

The gasoline to water partition coefficient can be estimated from the octanol to water partition coefficient as:

$$K_{gw} = K_{ow} \cdot \frac{MW_{octanol}}{MW_o} \qquad \text{Eq. (8)}$$

1,2-DCAs gasoline-water partition coefficient indicates that once in contact with groundwater, it will dissolve more rapidly out of the LNAPL in the groundwater than will benzene (benzene has a gasoline:water partition coefficient of 350) (Cline et al., 1991; Falta, 2004b). Based on 1,2-DCAs gasoline:water partition coefficient, Falta (2004b) reported a potential maximum concentration of 3700 µg/L for 1,2-DCA near a residual or LNAPL gasoline source. When 1,2-DCA is released alone or as a spill of grain bin fumigant (e.g., typically mixtures of 1,2-DCA with carbon tetrachloride and/or EDB), it will move through the vadose zone potentially to the groundwater as a DNAPL based on its density compared to water. Based on its similar physical/chemical characteristics to EDB, dissolved 1,2-DCA is not expected to change the water density much, therefore, 1,2-DCA is also expected to move with the bulk of the groundwater flow.

Table 18. Physical/chemical properties for 1,2-DCA

Property	1,2-Dichloroethane	Reference
CAS Registry Number	107-06-2	
Structure	$CH_2Cl—CH_2Cl$	
Physical description	Colorless liquid	Verschueren (2001)
Molecular weight	98.96 g/mol	
Melting point (°C)	-35.5	SRC (2007)
Boiling point (°C)	83.5	SRC (2007)
Solubility	Water: 8600 mg/L at 25 °C Ethanol, chloroform, diethyl ether, most organic solvents: miscible	Horvath et al. (1999) IARC (1999)
Vapor pressure	78.9 mm Hg at 25 °C	Daubert and Danner (1985)
Octanol-water partition coefficient	31	Hansch et al. (1995)
Henry's Law constant	1.18×10^{-3} atm-m^3/mol at 25 °C 0.050 (dimensionless)	Leighton and Calo (1981) Falta and Bulsara (2004)
Gasoline-water partition coefficient (dimensionless)	1,2-DCA = 84	Falta (2004b)
Specific gravity (liquid)	1.25	Verschueren (2001)
Specific gravity (vapor)	NA[1]	
Equilibrium aqueous concentration	3700 µg/L	Henderson (2005)
Diffusion coefficient in dry air	NA[1]	
Diffusion coefficient in water	NA[1]	
Density	1.25 at 20 °C	van Agteren et al. (1998)
Vapor density relative to air	3.42	van Agteren et al. (1998)
Heat of vaporization	NA[1]	
Percent in saturated air	11.5% at 25.5 °C	Christain and Moorehead (1985)

Table 18. Physical/chemical properties for 1,2-DCA

Property	1,2-Dichloroethane	Reference
Conversion factors	1 ppm = 4.43 mg/m^3 in air 1 mg/m^3 = 0.24 ppm in air	Verschueren (2001)

[1]NA = No data available.

C. Transport Processes

1. Transport from Water Surfaces

The release of 1,2-DCA to water results in rapid volatilization. Lyman et al. (1982) estimated liquid- and gas-phase exchange coefficients of 22 and 1900 cm/hr, respectively, and a mass transfer coefficient of 17.1 cm/hr. Based on these values, a volatilization half-life of 6.1 hours can be estimated using a wind speed of 3 m/sec and a water speed of 1 m/sec (Lyman et al., 1982). A water-film reference substance parameter of 0.643 indicates that the water-film mass-transfer coefficient for the volatilization of 1,2-DCA will be 64.3% that of the reaeration coefficient for the absorption of oxygen by a stream (Rathbun, 1998). An air-film reference-substance parameter of 0.529 indicates that the air-film mass-transfer coefficient for the volatilization of 1,2-DCA from a stream will be 52.9% that of the mass transfer coefficient for the evaporation of water (Rathbun, 1998). Goss (1997) measured a gas-phase adsorption coefficient for 1,2-DCA of 1.01×10^{-6} M for a water surface at 20 °C.

Several laboratory studies have measured evaporation half-lives in water for 1,2-DCA. Scherb (1978) measured an evaporation half-life in flowing water of 1 to 4 hours. Experimental evaporation half-lives of 28.4, 28.2, and 27.5 minutes were reported by Dilling (1977) using a 1 ppm aqueous solution at a depth of 6.5 cm with stirring at 200 rpm. An evaporation half-life in water of 5.3 minutes was reported by Chiou et al. (1980) at 23.1°C, an initial concentration of 0.1 ppm, 1.6 cm depth, and stirring at 100 rpm. In still air, the evaporation rate of 1,2-DCA from water is 5.20×10^{-5} g/cm^2-sec (Chiou et al., 1980).

Field data for 1,2-DCA confirm that volatilization occurs very rapidly and is the major fate process for this compound in surface waters. In March 1982, a spill of 628,720 liters of 1,2-DCA (0.79 million kilograms), and 223,230 liters ethylene glycol occurred due to a train derailment near the Thompson River in British Columbia, Canada (Christian and Moorehead, 1985). At the time of the spill, the water temperature was 4 °C, air temperature was 10 °C, wind speed was 4 m/sec, the flow of the river was approximately 25.2 m^3/sec with an average depth of 1.5 m and a velocity of 0.3 m/sec (Neely and Lutz, 1985). In addition, up to 50% of the river surface was covered with ice. Concentrations of 1,2-DCA at the site decreased over the following days from 22, 7, 3.6, and 3.2 mg/L on days 7, 8, 9, and 14 post-derailment, respectively. At 38 km from the spill site, concentrations of 1,2-DCA in river water were 3.9, 3, 2 mg/L, and not detected on days 6, 8, 9, and 14 post-derailment, respectively. At 51 km from the spill site, 1,2-DCA concentrations were 3, 2, 1.7 mg/L, and not detected on days 6, 8, 9, and 14 post-derailment, respectively (Neely and Lutz, 1985). At 135 miles downstream from the spill site, 1,2-DCA concentrations were not detected until day 8 post-derailment; on days 8, 9, 10, 13, 15, and 20, concentrations were 1.3, 1.3, 0.85, 0.110, 0.090, 0.011 ppm (w/w), respectively (Christian and Moorehead, 1985). Initial reductions in concentration were due to dilution and dispersion, the major fate process important in the removal of 1,2-DCA from the river was volatilization although, based on modeling results it was considered possible that pools of 1,2-DCA (up to 80–85% of the initial material) formed on the bottom of the water column and were protected by the flow of the river. The 1,2-DCA was then solubilized over a few days post-spill and resulted in a residual tail that contributed 1,2-DCA to the river flow even after the initial 1,2-DCA front had moved downstream. Using this scenario and comparing it to measured concentrations downstream, the authors estimated a half-life of 57 hours for 1,2-DCA under these winter conditions. If the water temperature is increased to 20 °C, as might be

normal under summer conditions, the half-life for the loss of 1,2-DCA is estimated to be 41 hours (Neely and Lutz, 1985).

In June 1986, 10,000 kg of 1,2-DCA was accidentally released into the Rhine River, Germany (Bruggemann et al., 1991). Again, because the flow time from Basel to the North Sea is only 10 days, and because 1,2-DCA is not rapidly degraded or adsorbed onto particulates, volatilization was considered to be the main fate process. As the 1,2-DCA front moved downstream, concentrations of 1,2-DCA were ~73 µg/L on day 2 (~210 km downstream from the spill site), 30–35 µg/L (~250 km from the spill site) on day 2.5 to 3, and <10 µg/L (~450 km from the spill site) on day 3.5 to 4.

2. Transport in Soil

The movement of a chemical in the vadose zone is dependent on both transport and adsorption processes. Based on different release scenarios, 1,2-DCA in the vadose zone can be found dissolved in solution, as a vapor, as pure compound adsorbed to soil, as free NAPL, or as residual NAPL. Dissolved 1,2-DCA will move with the infiltrating water to the water table via advection while vapor-phase 1,2-DCA will move by diffusion through the soil (Pignatello and Cohen, 1990). 1,2-DCA present in an LNAPL (such as a mixture of leaded gasoline) or DNAPL (such as a pure compound spill) will move mainly downward with the NAPL through the pores of the soil due to gravitational and capillary forces. If only a small quantity of NAPL is released, it may be contained in the vadose zone by the soil. However, if the amount of NAPL is sufficiently large, the bulk of the NAPL can move through the vadose zone to the groundwater table. An LNAPL will accumulate at the groundwater table, while a DNAPL will continue to migrate downward until it encounters a sufficient confining stratum. The LNAPL's movement in the soil is determined by many factors including soil porosity, soil permeability, and capillary pressure. During movement downwards, NAPL can become "trapped" within the soil matrix due to capillary forces leaving residual NAPL behind in the soil. This residual saturation may represent a long-term source of soluble NAPL components to the environment (Garg and Rixey, 1999; Rixey, 1996).

Sorption of vapor-phase 1,2-DCA to soil has been studied by Raihala et al. (1999) and Cabbar et al. (1994). Raihala et al. (1999) studied the vapor-phase sorption of 1,2-DCA on dry Yolo silt loam soil [EGME surface area 80.6 m^2/g, 1.73% organic carbon, pH 7.3, 21.1 CEC (meq/100 g), 34:51:15% sand:silt:clay]. Following a desorption step, 9.7% of the 1,2-DCA remained adsorbed on the soil and was resistant to further desorption. If toluene, a compound with higher adsorption affinity when compared with 1,2-DCA, was then added to the column, much of the adsorbed 1,2-DCA was then desorbed (8.3% leaving 1.4% still adsorbed to the soil). Using dry soil pellets, Cabbar et al. (1994) measured an absorption rate constant of 4.9 cm^3/g-sec for vapor-phase 1,2-DCA in soil using pulse-response measurements (soil description: total porosity = 4.9 cm^3/cm^3, solid density = 2.97 g/cm^3, surface area = 23.9 m^2/g). 1,2-DCA has 2 stable forms, trans- and gauche- forms and the trans-form is 3 times more abundant in the vapor phase. In liquid phase, the gauche-form is slightly greater (1.3 times more common than the trans-form). The most stable form in the adsorbed state is the gauche configuration (Cabbar et al., 1994). Effective diffusion coefficients of 0.022 and 0.034 were reported for this soil using two different approaches.

Soil-water partition coefficients (K_{oc} values) for 1,2-DCA in the solution phase range from 14 to 164 (Table 19) but average about 45 to 60. The available K_{oc} values indicate that 1,2-DCA is not significantly adsorbed to soil. Based on 1,2-DCAs K_{oc} values and its relatively high water solubility, it can and does, based on monitoring data, leach through the vadose zone to groundwater. An adsorption isotherm for 1,2-DCA using a Willamette silt loam (1.6% organic matter, 26% clay, 3.3% sand, and 69% silt, pH 6.8) was linear (Chiou et al., 1979). The K_{oc}/K_p values reported in Table 19 and the sorption isotherm experiment reported by Chiou et al. (1979) are typically based on study protocols where equilibrium is assumed to have been reached within 24 hours. While the majority of 1,2-DCA added to soil is expected

to adsorb/desorb in a rapidly reversible process, it is expected that a portion of the added 1,2-DCA will behave in a "non-equilibrium" manner during the desorption phase as was seen for vapor-phase 1,2-DCA (Raihala et al., 1999). Similar to other small, low molecular weight halocarbons such as EDB, it is expected that pure 1,2-DCA can become trapped within the soil pores due to tortuosity or constriction in pore structure and release is determined by diffusion processes (Pignatello, 1989) (See Section III.C.2 for information on this process for EDB).

A soil retardation factor of <1.5 was measured for 1,2-DCA in a Lincoln fine sand (sand:silt:clay ratio of 92:5.9:2.1% respectively, organic carbon content of 0.087%) soil column experiment (Wilson et al., 1981). Several studies report higher values based on studies using aquifer sediments. Retardation factors of 5.2, 7.2, and 5.8 (average of 6.1) were measured in column studies using aquifer material from beneath the Gloucester landfill at velocities of 10, 45, and 90 cm/day, respectively (benzene had an average retardation factor of 12.2 in this study) (Priddle and Jackson, 1991). In a field study at the Gloucester landfill aquifer (composed of poorly sorted gravels, sands, and silts; f_{oc} range of 0.0035 to 0.01, average hydraulic conductivity of $1.1x10^{-4}$ m/sec and a groundwater velocity of 5 cm/day), the plume length was used to calculate a retardation factor of 7.6 (based on a comparison of the contaminant plume length with the chloride plume length) (Patterson et al., 1985). Benzene had a retardation factor of 8.8 in this study. Retardation factors for dichloroethane (1,1-DCA and 1,2-DCA combined) ranged from 1.1 to 1.3 at an aquifer underlying the KL Avenue Landfill, Kalamazoo, MI (Ravi et al., 1998a, 1998b). An aquifer beneath a former chemical manufacture site had a calculated retardation factor of 1.08 (Cox et al., 1998), Groundwater retardation factors of 1.05 and 1.53 were estimated for an aquifer with an f_{oc} of 0.001 and an f_{oc} of 0.01, respectively (Falta et al., 2005a).

Table 19. Soil adsorption data for 1,2-DCA

Soil Type	K_p (L/kg)	f_{oc} [1]	K_{oc} (L/kg)	Soil Characteristics	Reference
			41.7		Borisover and Graber (1997)
Silt loam	0.008	0.0093	32.4	26% clay, 3.3% sand, 69% silt, pH 6.8, 1.6% organic matter; K_{oc} assumption that organic matter is 50% organic carbon.	Chiou et al. (1979)
			14		Chu and Chan (2000)
Silt loam		0.0084	36		Hassett et al. (1980)
Pond sediment	1.3			12 replicates	Jafvert and Wolfe (1987)
Silty clay	0.71	0.0113	63	21.9:47.6:30.5% sand:silt:clay, surface area of 12 m^2/g, pH 5.8, 1.13% organic carbon	Valsaraj et al. (1999)
Clay soil	0.41	0.0025	164	22: 28.4: 49.4% sand:silt:clay, surface area of 45 m^2/g, pH 4.3, 0.25% organic carbon	Valsaraj et al. (1999)
Sand soil	0.09	0.0011	82	77.5:9.4:13.1% sand:silt:clay, surface area of 7 m^2/g, pH 7.4, 0.11% organic carbon	Valsaraj et al. (1999)

[1] f_{oc} = fraction of organic carbon

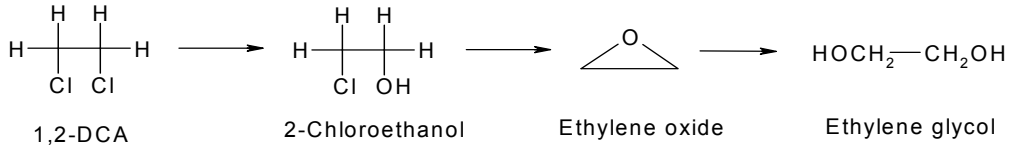
D. Transformations

1. Abiotic Transformations

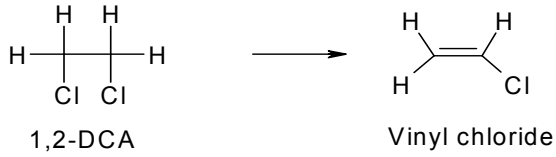
a. Hydrolysis

1,2-DCA is slowly hydrolyzed with published neutral half-lives ranging from approximately 70 to 44,000 years (Table 20). The attack of 1,2-DCA by H_2O or OH^- can occur at the carbon atom giving the substitution product 2-chloroethanol and then further to ethylene glycol via ethylene oxide or at the α-hydrogen leading to the elimination product vinyl chloride as was seen for EDB (Pignatello and Cohen, 1990) (See Section III.D.1.a for information on this process for EDB).

1. S_N2 (substitution) hydrolysis reaction of 1,2-DCA in water



2. E_2 (elimination) reaction of 1,2-DCA in water



The neutral hydrolysis of 1,2-DCA was shown to be mainly S_N2 with conversion to ethylene glycol based on results from Jeffers et al. (1989) (Table 20). Barbash and Reinhard (1989) report that vinyl chloride, produced via elimination, is a minor product.

The hydrolysis of 1,2-DCA is pH independent below pH 9 (the alkaline reaction at pH 9 is just 10% of the total observed hydrolysis) (Jeffers and Wolfe, 1996). Vinyl chloride was reported as a product from the alkaline hydrolysis of 1,2-DCA. In the presence of 50 mM phosphate buffer, 1.3% vinyl chloride was formed from the hydrolysis of 1,2-DCA. The amount of vinyl chloride appears to be reduced as the concentration of phosphate buffer is reduced (by a factor of 0.78 for phosphate buffer concentrations from 50 to 5 mM at 50 °C) (Barbash and Reinhard, 1989).

Table 20. Hydrolysis half-lives for 1,2-DCA

$T_{1/2}$ (years)	Temp. (°C)	Comments	Products	Reference
pH-independent hydrolysis				
64	25	Extrapolated to zero buffer from 0.05M phosphate buffer data.	1% vinyl chloride	Barbash and Reinhard (1989)
150	20	Rate constant = $5.4x10^{-7}$ hr^{-1}, measured at 20 °C.		Ehrenberg et al. (1974)
72	25	Rate constant = $1.83x10^{-8}$ min^{-1}	Ethylene glycol found as product during neutral hydrolysis.	Jeffers et al. (1989)
44,000	25			Mabey et al. (1981)
644	10			Washington (1995)
70.1	25	pH 5.6		Washington (1995)
644	10	pH 5.6		Washington (1995)
Base-promoted hydrolysis				
$4.9x10^{+4}$	15	Half-life reported for pH 9	At pH 12.94, 1,2-DCA formed vinyl chloride (93% conversion of 1,2-DCA; product yield of 98.4%)	Miyamoto and Urano (1996)
$4.8x10^{+4}$	25	$k_{OH} = 4.6x10^{-6}$ $M^{-1}sec^{-1}$	Vinyl chloride reported as a major product.	Okamoto et al. (1967)
$1.6x10^{+5}$	25	$k_{OH} = 1.35x10^{-6}$ $M^{-1}sec^{-1}$		Walraevens et al. (1974)
$6.1x10^{+5}$	20	$k_{OH} = 1.3x10^{-3}$ $M^{-1}hr^{-1}$		Ehrenberg et al. (1974)
$1.2x10^{+5}$	25	$k_{OH} = 1.04x10^{-11}$ min^{-1}, pH 7)	Product mass balance not reported. Vinyl chloride reported as a product.	Jeffers et al. (1989)
$8.8x10^{+4}$	25	$k_{OH} = 2.5x10^{-6}$ $M^{-1}sec^{-1}$		Roberts et al. (1993)

b. Reaction with Sulfur Nucleophiles

H_2S and HS^- are typically found in anaerobic groundwaters and in wetland/estuarine environments due to the microbial reduction of sulfate (Pignatello and Cohen, 1990). Typical concentrations in a salt marsh are 0.07 mM polysulfides, 0.2 mM sulfite, 0.5 mM thiosulfate, and 5 mM HS^- (Barbash and Reinhard, 1989). HS^- is the dominant sulfur nucleophile at pH values above 7 (>50% dissociation of H_2S based on a pK_a of H_2S of 7.01) while at lower pH values, sulfite may be more important. Total sulfide concentrations in a SO_4^{-2} reducing groundwater (pH range of 6 to 8) range from 10^{-6} to 10^{-3} M (Barbash and Reinhard, 1989).

HS^- has been reported to react with primary bromo- and chloroalkanes forming various thiols and thioethers (Schwarzenbach et al., 1985). This reaction is considerably faster than the hydrolysis of 1,2-DCA in water alone (Barbash and Reinhard, 1987) (Table 21). They reported the disappearance of 1,2-DCA in the presence and absence of HS^- (at 0.060 mM) at 25 °C with first-order rate constants of $3.0x10^{-5}$ day^{-1} (k_{H2O}) and 0.51 $M^{-1}sec^{-1}$ (k_{HS-}), respectively (Barbash and Reinhard, 1987). 1,2-Ethanedithiol is the main product of the reaction between HS^- and 1,2-DCA with yields of 79% (Barbash and Reinhard, 1989). The reaction of 1,2-DCA in the presence of 0.05 M phosphate buffer and 0.67 mM Na_2S produced 1.3% vinyl chloride over a temperature range of 37.5 to 87.5 °C (Barbash and Reinhard, 1989).

Table 21. Half-lives for the reaction of 1,2-DCA with sulfur nucleophiles

$T_{1/2}$ (years)	Temp. (°C)	Comments	Reaction products	Reference
6.1	25	1,2-DCA with sulfur (0.005 M phosphate buffer + 0.758 mM Na_2S), pH 6.9.	1,2-Ethanedithiol is reported as the major product of this reaction (79%).	Barbash and Reinhard (1987)

c. Photolysis

1,2-DCA is not susceptible to direct photolysis (Lyman et al., 1982). Several similar rate constants for the reaction of 1,2-DCA with atmospheric OH radicals are available in the literature: $2.20x10^{-13}$ cm^3/molecule-sec, at 23 °C (Howard and Evenson, 1976), $2.64x10^{-13}$ cm^3/molecule-sec at 24 °C (Arnts et al., 1987), $2.48x10^{-13}$ cm^3/molecule-sec at 19 °C, $2.09x10^{-13}$ cm^3/molecule-sec at 19 °C and $2.14x10^{-13}$ cm^3/molecule-sec at 22 °C (Atkinson, 1994). Using the rate constant of Howard and Evenson (1976), an atmospheric half-life of 49 days can be estimated based on an OH radical concentration of $1.5x10^{+6}$ OH radicals/cm^3 and a 12-hour day. Products of this reaction include ClHCHO, $H_2CClCOCl$, H_2CO, $H_2CClCHO$ (Cupitt, 1980), formyl chloride (Kao, 1994), formyl chloride, chloroacetyl chloride, hydrogen chloride, and chloroethanol (Spicer et al., 1993). In a study by Spence and Hanst (1978), 1,2-DCA was exposed to black lights (maximum intensity near 3650 angstroms) and sun lamps (maximum intensity of 3100 angstroms) in dry air in a glass reaction cell at 22.5 °C. Chlorine atoms were used to initiate the oxidation of 1,2-DCA in order to simulate hydroxyl radical attack in the atmosphere. After 4 minutes of irradiation, 3.5 ppm formyl chloride (40% of degraded 1,2-DCA) and 0.5 ppm chloroacetyl chloride were reported.

Wallington et al. (1996) studied the atmospheric fate of 1,2-DCA in detail. Based on their results, 1,2-DCA reacts with OH radicals giving $CH_2ClCHCl$ radicals that then react very quickly with O_2 to form the corresponding peroxy radicals ($CH_2ClCHClO_2$). These radicals react with NO forming NO_2 and $CH_2ClCHClO$ radicals (half-life of 7 minutes). In 1 atmosphere of air and 23 °C, 89% of the $CH_2ClCHClO$ radicals then decompose via HCl elimination giving HC(O)Cl while the remaining 11% of the radicals react with O_2 giving $CH_2ClC(O)Cl$.

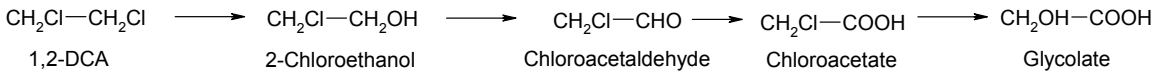
2. Biotic Transformations

The biodegradation of 1,2-DCA can occur in the environment via anaerobic dehalogenation, aerobic catabolism, and aerobic co-metabolism (Hoyle and Arthur, 2000; Stensel and Bielefeldt, 2000). Reaction mechanisms for the biodegradation of 1,2-DCA include the elimination of hydrogen chloride or the substitution of the chloride groups to H (reductive pathway), OH (hydrolytic pathway), or to thio groups (Neilson, 1990). Because oxygen is not necessary in the elimination pathway, both aerobic and anaerobic microorganisms can potentially use this pathway (Neilson, 1990).

a. Pure Culture Studies

Based on the reaction pathway information from the pure culture studies summarized in Table 22, the aerobic and anaerobic biodegradation of 1,2-DCA can proceed via several pathways.

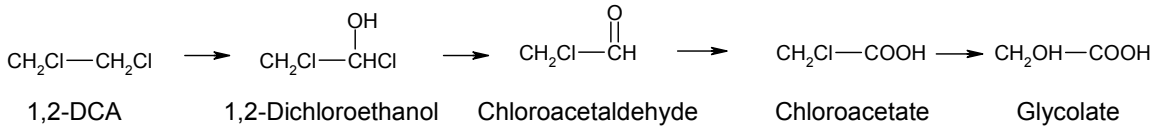
Under aerobic conditions, pure cultures of *Xanthobacter autotrophicus* GJ10 and *Ancylobacter aquaricus* initially degrade 1,2-DCA to 2-chloroethanol which is oxidized to chloroacetaldehyde, then chloroacetate and finally glycolate (Janssen et al., 1995; Pries et al., 1994). These strains are reported to use 1,2-DCA as a sole carbon source in the following reaction pathway:



The first step is mediated by a haloalkane dehalogenase, the second step by an alcohol dehydrogenase, the third step by an aldehyde dehydrogenase, and the fourth step via a haloacetate dehydrogenase (Janssen et al., 1995). Oxidation of the aldehyde during this reaction process is believed to be the critical step in the degradation of 1,2-DCA (Janssen et al., 1995).

This pathway was verified using the technique of carbon isotope fractionation using a pure culture of *X. autotrophicus* GJ10 (Hunkeler and Aravena, 2000). As a compound is biodegraded, the precursor typically becomes enriched in the heavier ^{13}C isotope over the lighter ^{12}C isotope. While non-degradative pathways such as adsorption and volatilization do not change the ratio of ^{13}C to ^{12}C, degradative pathways will because light isotopic bonds will react more quickly than heavier isotopic bonds (based on reaction rates and activation energies associated with breaking the bond). 1,2-DCA, at an initial concentration of 120 mg/L, was enriched by 10.6% in ^{13}C while inorganic carbon and biomass carbon were depleted in ^{13}C by -47.4 and -18.3%, respectively (overall carbon -30.9%), by 36 hours. The difference in the depletion of ^{13}C between inorganic carbon and biomass was explained by the reaction pathway. 1,2-DCA is degraded by this pure culture to 2-chloroethanol, 2-chloroaldehyde, chloroacetate, and glycolate. Glycolate is oxidized to glyoxylate and then to acetyl coenzyme A. There are two decarboxylation steps between glyoxylate and acetyl coenzyme A with the CO_2 coming from the carboxyl end of the glycolate. The carboxyl carbon is expected to be ~60% depleted in ^{13}C compared with the initial 1,2-DCA while the hydroxyl carbon has a ^{13}C content similar to the concurrent substrate. According to the authors, the strong enrichment of ^{13}C in the remaining 1,2-DCA occurs because the first step in the biodegradation of 1,2-DCA is an S_N2 nucleophilic substitution reaction.

A second aerobic biodegradation pathway was proposed based on work by Hage and Hartmans (1999). A pure culture of *Pseudomonas* sp. Strain DCA1, able to use 1,2-DCA as its sole carbon and energy source, oxidized 1,2-DCA to the unstable 1,2-dichloroethanol which spontaneously decomposed to give chloroacetaldehyde and then chloroacetic acid. This reaction was mediated by a monooxygenase enzyme.



Yokota et al. (1986) reported the cometabolic oxidative degradation of 1,2-DCA to 2-chloroacetic acid by obligate methylotrophic bacteria strains H-2 and 66-1. Using $^{18}O_2$, the authors were able to show that the molecular oxygen was the source of oxygen for this reaction.

Anaerobic biodegradation data for sulfate-reducing and methanogenic conditions indicate that biodegradation can proceed by dehalogenation via vinyl chloride and chloroethane and then further to ethene and ethane (Belay and Daniels, 1987; Egli et al., 1987). A second reaction pathway including the direct formation of ethene via dehaloelimination and two hydrogenolysis reactions forming chloroethane and ethane was reported by Holliger et al. (1990) in methanogenic bacteria.

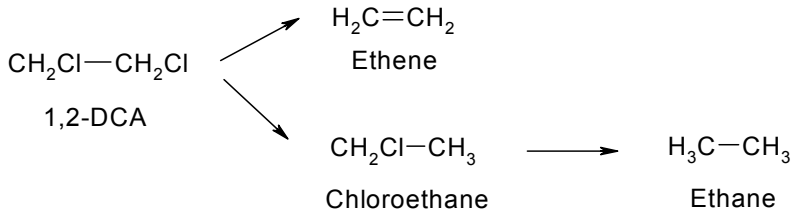


Table 22. Pure culture strains studied for their ability to degrade 1,2-DCA

Strain	Aerobic or anaerobic	Notes	Reference
Xanthobacter autotrophicus GJ10	Aerobic	Aerobic nitrogen-fixing autotroph. Grows aerobically with 1,2-DCA as its sole carbon and energy source. Degrades 1,2-DCA through 2-chloroethanol to glycolate. Haloalkane dehalogenase degrades both EDB and 1,2-DCA (Keuning et al., 1985). Described as facultative methylotroph in Janssen et al. (1995).	Janssen et al. (1985); Keuning et al. (1985)
Actinomycete-like organism strain GJ70	Aerobic	The purified dehalogenase was able to degrade both EDB and 1,2-DCA although the rate of EDB degradation was >10x higher than that for 1,2-DCA.	Janssen et al. (1988)
β-Proteobacterium JS666	Aerobic	Isolated by enrichment culture on cis-dichloroethene. 1,2-DCA is not used as a carbon source but can be cometabolically degraded by this culture when grown with cis-dichloroethene.	Coleman et al. (2002)
Ancylobacter aquaticus	Aerobic	Facultative methylotroph. Grows aerobically with 1,2-DCA as its sole carbon and energy source. Degrades 1,2-DCA through 2-chloroethanol to glycolate.	Janssen et al. (1995)
Ancylobacter aquaticus AD20 and AD25	Aerobic	Facultative methylotrophs. Degrade 1,2-DCA to 2-chloroethanol, then chloroacetaldehyde, then 2-chloroacetate, and finally to glycolate.	Van den Wijngaard et al. (1993)
Obligate methylotrophic strains H-2 and 66-1	Aerobic	Cometabolic degradation to 2-chloroacetic acid mediated via an oxygenase.	Yokota et al. (1986)
Methanotrophic strain CAC1	Aerobic	Shows product toxicity following cometabolism of 1,2-DCA.	Chang and Alvarez-Cohen (1996)
Methylosinus trichosporium OB3b	Aerobic	Methanotroph. Shows product toxicity following cometabolism of 1,2-DCA via methane monooxygenase.	Chang and Alvarez-Cohen (1996)
Methylosinus trichosporium OB3b	Aerobic	Methanotroph. Cometabolic degradation. Complete degradation with stoichiometric release of chloride via methane monooxygenase.	Oldenhuis et al. (1989)
Methanotroph, strain M	Aerobic	Type II obligate methanotroph. Degrades 1,2-DCA.	Uchiyama et al. (1989)
Bacterium DE2	Aerobic	Gram-negative, oxidase-positive motile rod. 1,2-DCA is used as its sole carbon and energy source. Degradation is thought to proceed to 1,2-dichloroethanol, then 2-chloroacetaldehyde, 2-chloroacetate and then glycolate.	Stucki et al. (1983)
Methylocystis sp. M	Aerobic	Methanotroph. Degrades 1,2-DCA. Further information not provided by authors.	Yagi et al. (1994)
Pseudomonas fluorescens PFL12	Aerobic	Uses 1,2-DCA as a sole carbon and energy source.	Vandenbergh and Kunka (1988)
Pseudomonas sp., strain DCA1	Aerobic	Uses 1,2-DCA as a sole carbon and energy source. Reaction pathway proceeds initially via oxidation to 1,2-dichloroethanol (via a monooxygenase) with spontaneous release of chloride giving chloroacetaldehyde, then chloroacetic acid, and then glycolic acid.	Hage and Hartmans (1999)
Pseudomonas sp., strain ENVPC5	Aerobic	Expresses a toluene p-monooxygenase (T4MO). Other toluene-oxidizing strains with a T2MO or T3MO did not degrade 1,2-DCA.	McClay et al. (1996)

Table 22. Pure culture strains studied for their ability to degrade 1,2-DCA

Strain	Aerobic or anaerobic	Notes	Reference
Pseudomonas mendocina KR1	Aerobic	Possibly expresses a toluene p-monooxygenase (T4MO). Other toluene-oxidizing strains with a T2MO or T3MO did not degrade 1,2-DCA.	McClay et al. (1996)
Nitrosomonas europaea	Aerobic	Autotrophic nitrifier. Degrades 1,2-DCA cometabolically through the action of ammonia monooxygenase. Chloroacetaldehyde reported as a product.	Rasche et al. (1991)
Dehalococcus ethenogenes strain 195	Anaerobic	Eubacterium. Not methanogenic, acetogenic, or sulfidogenic. H_2 is used as the electron donor. Used 1,2-DCA as an electron acceptor supporting growth. Products of ethene (99%) and vinyl chloride (1%).	Maymo-Gatell et al. (1997, 1999)
Methanobacterium thermoautotrophicum	Anaerobic	100% of the product yield was identified as ethane, a trace amount of chloroethane was also reported. Incubation at 60 °C.	Castro et al. (1994)
Methanobacterium thermoautotrophicum	Anaerobic	Autotrophic methanogen. No previous exposure to chlorinated solvents. 1,2-DCA is degraded to ethene via dihaloelimination.	Egli et al. (1987)
Methanobacterium thermoautotrophicum strain Marburg	Anaerobic	Autotrophic methanogen. H_2/CO_2 added, ethene (21 nmole; via dihaloelimination) and chloroethane (54 nmole; via hydrogenolysis) reported as degradation products. Chloroethane is dehalogenated to ethane but ethane production is inhibited by the presence of 1,2-DCA.	Holliger et al. (1990)
Methanosarcina barkeri	Anaerobic	Methanogen. Methanol added, ethene (4 nmole; via dihaloelimination) and chloroethane (34 nmole; via hydrogenolysis, substitution of the halogen with oxygen or with hydrogen) reported as degradation products. Chloroethane is dehalogenated to ethane but ethane production is inhibited by the presence of 1,2-DCA.	Holliger et al. (1990)
Methanococcus mazei	Anaerobic	Methanogen. Methanol added, ethene (3 nmole; via dihaloelimination) and chloroethane (107 nmole; via hydrogenolysis) reported as degradation products. Chloroethane is dehalogenated to ethane but ethane production is inhibited by the presence of 1,2-DCA.	Holliger et al. (1990)
Methanothrix soehngenii	Anaerobic	Acetoclastic methanogen. Acetate added, ethene (9 nmole; via dihaloelimination) and chloroethane (29 nmole; via hydrogenolysis) reported as degradation products. Chloroethane is dehalogenated to ethane but ethane production is inhibited by the presence of 1,2-DCA.	Holliger et al. (1990)
Methanobacterium thermoautotrophicum ΔH	Anaerobic	Methanogen. Degrades 1,2-DCA to ethene.	Belay and Daniels (1987)
Methanococcus deltae ΔLH	Anaerobic	Methanogen. Degrades 1,2-DCA to ethene.	Belay and Daniels (1987)
Methanococcus thermolithotrophicus	Anaerobic	Methanogen. Degrades 1,2-DCA to ethene.	Belay and Daniels (1987)

b. Enrichment Culture, Defined Culture, and Sewage Studies

Bioreactors were inoculated with a mixture of two pure cultures (strain GJ10 and DE1 (both are capable of mineralizing 1,2-DCA to HCl and CO_2) and fed with low conductivity medium representative of groundwater (700–1200 µS/cm) under aerobic conditions (Stucki et al., 1992). Initial concentrations of 20–25 mg/L 1,2-DCA were used and biodegradation at temperatures of 10 to 25 °C were studied. Up to 90% removal of 1,2-DCA was reported at all temperatures. These data do not agree with an aerobic batch culture study where 1,2-DCA was not biodegraded (Bouwer, 1983). Sun et al. (1992) examined the competition between biodegradation and volatilization processes in a model wastewater system using 1,2-DCA. Bench-scale activated sludge units were set up and provided with varying levels of air/oxygen (500 mL/min air and 75 mL/min of air for units 1 and 2, respectively). ^{14}C-1,2-DCA was added to each of the units and the radioactivity tracked over the study period. CO_2 production was measured as an indicator of biodegradation. Less than 0.5 mg/day $^{14}CO_2$ was produced in unit 1 while unit 2 produced up to 1.7 mg/d $^{14}CO_2$ over the 70-day period. The overall loss of 1,2-DCA in unit 1 was predominately due to volatilization with fractions of removal of 0.13 and 0.57 due to biodegradation in units 1 and 2, respectively. In two full-scale activated sludge units, however, biodegradation loss of 1,2-DCA was not significant when compared to loss due to air stripping. These results were similar to those reported by Stover and Kincannon (1983) in another bench-scale activated sludge treatment study.

Several studies where inocula have been enriched for methylotrophs report the cometabolic degradation of 1,2-DCA. A methane-grown enrichment culture was able to nearly completely degrade 1,2-DCA within 20 days; methane was required for growth of the consortium. Acetylene added to the enrichment culture inhibited the biodegradation of several halocarbons suggesting that methanotrophs are major components of this culture (Henson et al., 1989). 1,2-DCA in a mixture with 6 other chloroaliphatic compounds was added to 2 soil samples, one which was enriched for methanotrophs (previously exposed to methane over a 6-week period) and one which was not (Henson et al., 1988). The soil was incubated aerobically in the presence of added methane and after 6 days, 41 and 78% of the initially-added 1,2-DCA was removed from the non-enriched and enriched soil samples, respectively. Kim et al. (2000) studied the biodegradation of 1,2-DCA by a butane grown-enrichment culture. After 30 hours of incubation, 60% dechlorination of 1,2-DCA was reported. 1,2-DCA was degraded aerobically in a propane-fed bioreactor seeded with a TCE-degrading enrichment culture (<5 µg/L remaining after 21 days); controls showed no degradation over the same time period (Phelps et al., 1991).

An anaerobic sewage sludge enrichment culture degraded 1,2-DCA to chloroethane (20%; reductive dechlorination pathway) and ethene (10%; dichloroelimination pathway). There was an initial lag phase of 12 days with 40% loss reported by day 30 (initial rapid decline of 25% between days 12 to 14, followed by a much slower rate of loss). Chloroethane was first noted in the media on day 14 (Chen et al., 1996). An anaerobic enrichment culture obtained from creek sediment transformed 1,2-DCA to ethane with complete transformation reported within 2 weeks (initial 1,2-DCA concentration of 2 µmol) (Loffler et al., 1997). 1,2-DCA was biodegraded by an anaerobic enrichment culture that was reported to dechlorinate high concentrations of tetrachloroethene (PCE). Within 10–11 hours, 1,2-DCA at an initial concentration of 46 µmoles/100 mL was converted to 100% ethene via dihaloelimination (Tandol et al., 1994). An acetogenic enrichment culture grown with glucose and trichloroethene was able to dechlorinate 1,2-DCA to ethene (Wild et al., 1995). 1,2-DCA was not biodegraded during passage through an acetate-supported methanogenic biofilm column (2-day detention time, initial concentration of 22 µg/L) even after 4 months (Bouwer and McCarty, 1983). However, Bouwer and McCarty (1983) report that in a methanogenic batch culture study, ^{14}C-radiolabeled 1,2-DCA was degraded by 63% after 25 weeks. The main degradation product from this reaction was CO_2. Methane was not produced indicating that 1,2-DCA had been biooxidized.

c. Microcosm Studies

Aerobic and anaerobic microcosm studies for 1,2-DCA are summarized below in Tables 23 and 24, respectively. The data from these studies indicate that under environmentally-relevant laboratory conditions, 1,2-DCA can degrade under both aerobic and anaerobic environments. Aerobic half-lives vary widely from half-lives of less than a week to not biodegradable over a period of several months. For example, 1,2-DCA in one of 2 soils studied in a batch reactor system was not biodegraded over the 110-day study period (Reiss, 2000). The second soil degraded 1,2-DCA with a half-life of 96 days. Cox et al. (1998) reported half-lives of <1 day to 9 days using aquifer material from a contaminated site suggesting that acclimation of the microbial population had occurred. At another spill site, however, a half-life of several years was reported (Klecka et al., 1998). The concentration of 1,2-DCA in these studies is not expected to be toxic to aerobic microbial populations. IC_{50} microbial toxicity values of 700, 29, 25, and 470 mg/L were reported for 1,2-DCA for the Microtox assay, populations of *Nitrosomonas*, methanogens (anaerobic bacteria), and aerobic heterotrophs, respectively (Blum and Speece, 1991). Under anaerobic conditions, 1,2-DCA concentrations of 500, 100, 50, 10, 5, and 0.5 mg/L caused 97/96, 30/88, 25/44, 20/18, 15/10, and 13/6% inhibition of acetoclastic/hydrogenophilic populations in granular sludge, respectively (Colleran et al., 1992).

Hirschorn et al. (2004) were able to show that 1,2-DCA is degraded by two different enzymatic pathways in aerobic microcosm experiments from two different sites using stable isotopic analysis ($^{13}C/^{12}C$ ratio). Microcosms were constructed from aquifer sediment and groundwater from two 1,2-DCA-contaminated sites in Louisiana (East and West Louisiana). East and West Louisiana microcosms had mean enrichment factors of -4.8±0.5% and -25.7±0.5%, respectively, indicating that the West Louisiana sample had a much stronger enrichment in ^{13}C in the remaining 1,2-DCA. Enrichment cultures from the East Louisiana site initially had a mean enrichment factor of -3.4±0.5%. However, after a one-year incubation period in the presence of 1,2-DCA, the mean enrichment factor was reported as -23 ±1.5% suggesting that during this time, the dominant mechanism for degradation had changed. Pure cultures isolated from the East Louisiana enrichment cultures after the 1-year enrichment period had a mean enrichment factor of -31.4 ±0.8%. The authors also report enrichment factors of -32.3±1.8% and -32.1±1.7% for *X. autotrophicus* GJ10 and *A. aquaticus* AD20 (initial step in degradation pathway is via a hydrolytic dehalogenase, S_N2 reaction) and -3.0±0.2% for *Pseudomonas* sp. Strain DCA1 (initial degradation step is via a monooxygenase enzyme, oxidation reaction). The authors propose that the bimodal distribution of enrichment factors indicates that different degradation mechanisms are controlling the transformation of 1,2-DCA in these experiments and that the enrichment culture data suggest that the dominant degradation pathway may change with time.

The cometabolic biotransformation of 1,2-DCA was reported in several studies. The aerobic biodegradation of 1,2-DCA was measured in three different soils (Speitel and Closmann, 1991). Each soil had been enriched for methanotrophs over a 4–16 week period using a 1% methane in air mixture. Biodegradation was reported in each soil although the rate varied. 1,2-DCA at an initial concentration of 80 µg/L, was biodegraded in an aerobic aquifer column study in the presence of methane at 1.5 mg/L and a nutrient supplement with a half-life of over 300 days (Lanzarone and McCarty, 1990).

Anaerobic biodegradation half-life data, like the aerobic data for 1,2-DCA, vary widely (Table 24). A few studies report half-lives of approximately 2 weeks (Bosma et al., 1998; Hunkeler et al., 2002) while the remainder report half-lives from 50 to 600 days. The degradation of 1,2-DCA under redox conditions other than sulfate-reducing or methanogenic has not been reported. Based on data for EDB, it is likely that biodegradation rates are be slower under these less-reducing conditions. 1,2-DCA was biodegraded in soil and groundwater samples from two manufacturing sites known to be contaminated with 1,2-DCA (Plaquemine, Lousiana and Freeport, Texas) and from one site reported to be uncontaminated (Lula, Oklahoma) under both methanogenic and sulfate-reducing conditions (Klecka et al., 1995). Lag phases of

7 to 8 weeks were observed for material collected at the Oklahoma and Texas sites suggesting that microbial adaptation was occurring. No lag phase was observed in degradation of 1,2-DCA in the Louisiana samples that received 500 ppm sodium acetate. Degradation of 1,2-DCA in Louisiana microcosms that were incubated with 7 different organic chemicals (acetate, butyrate, lactate, ethanol, propylene glycol, glycerol, glucose) in addition to 1,2-DCA ranged from 50.6 to 71.3% loss versus only 4.8% loss in 14 weeks when only 1,2-DCA was present as a carbon source. Under anaerobic conditions, degradation was via reductive dehaloelimination (in a single step) resulting in the formation of ethene as the sole degradation product.

Hunkeler et al. (2002) studied degradation pathways in anaerobic microcosms constructed from aquifer materials collected at a former waste disposal site using stable isotope analysis. Vinyl chloride appeared at low concentrations for a short time during the degradation process; no ethane was detected during the study period. The major transformation product was ethene via dichloroelimination with a carbon isotopic enrichment factor for this reaction of -32.1%. Abiotic 1,2-DCA transformation over the study period was minimal.

Very limited data exist in the literature measuring the biodegradation of 1,2-DCA in the presence of fuel hydrocarbons in laboratory studies (Tables 23 and 24) (Henderson et al., 2007; Reiss, 2000). Groundwater and soil samples from the Clemson Tiger Mart, a site contaminated with leaded gasoline due to leaking tanks, were incubated for 284 to 380 days in closed bottles without shaking (Henderson et al., 2007). No biodegradation of 1,2-DCA was observed over the course of the experiment either at initial concentrations of ~200–300 µg/L, a concentration theoretically similar to the source area of a contamination plume, or at an initial concentration of 10 µg/L, a concentration similar to what might be found mid-gradient in a contaminant plume. The redox condition for this study was not available but is assumed to be mainly anaerobic since the bottles were filled and left to sit for many months.

Table 23. Aerobic microcosm/column biodegradation studies for 1,2-DCA

Sample type	M/P[1]	Initial concen.	Study period (days)	Rate constant (per day)	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Aquifer	M	10,000 µg/L	133		0.8–9.0	CO_2	Former chemical plant, currently Superfund site. Used aquifer materials and groundwater from 125 m downgradient from source area. Biodegraded via 2-chloroethanol to CO_2. 97% biodegradation in 6 days.	Cox et al. (1998)
Soil	P	250 µg/L	6		8		Uncontaminated site. 10 gm soil was added to 10 mL minimal salts medium. Methane added to headspace during experiment. Six other chloroaliphatic compounds also present.	Henson et al. (1988)
Aquifer	P	41,000 µg/L	126	0.00059	1175	CO_2	1,2-Dichloroethane spill site 3 to 43% of total radioactivity found as CO_2. No aerobic biodegradation was noted at the two other sites (Texas and Oklahoma) examined in this study after 180 days and no CO_2 was produced.	Klecka et al. (1998)
Aquifer	P	80 µg/L	170	0.0021	330		Contaminated, *in situ* biorestoration conducted on aquifer site. Aquifer column study in the presence of methane at 1.5 mg/L and a nutrient supplement. 30–35% degradation in 170 days.	Lanzarone and McCarty (1990)
Aquifer	P		110		96		Previously contaminated with EDB and 1,2-DCA, remediation completed. Preliminary batch reactor studies.	Reiss (2000)
Aquifer	P		110		NB[2]		Uncontaminated site. Preliminary batch reactor studies.	Reiss (2000)
Soil	P	10-250 mg/m^{-3}		64 µg g^{-1} soil h^{-1}			Soil from a landfill site. Methane oxidation conditions (15% methane, 35% oxygen, 50% nitrogen). Soil water content of 25% w/w. Zero-order rate constant, normalized to the dry soil mass, was reported by authors. Biodegradation occurred in parallel with methane oxidation suggesting that the added compounds were degraded via cometabolic processes.	Scheutz et al. (2004)
Soil	M	100 µg/g	22	1.31–1.39 µg/g soil-day	22	CO_2	Uncontaminated site. Sandy clay soil with added nutrients. Zero-order mineralization rate constant provided by authors. Enriched for methanotrophs over a 4–16 week period using a 1% methane in air mixture. Half-life based on primary biodeg and mineralization is 22 days.	Speitel and Closmann (1991)

Table 23. Aerobic microcosm/column biodegradation studies for 1,2-DCA

Sample type	M/P[1]	Initial concen.	Study period (days)	Rate constant (per day)	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Soil	M	100 µg/g	22	0.04–0.06 µg/g soil-day		CO_2	Uncontaminated site. Sandy clay soil without added nutrients (56:20:24% sand:silt:clay, pH 8.4, 0.1% organic matter). Enriched for methanotrophs over a 4–16 week period using a 1% methane in air mixture. Zero-order mineralization rate constant provided by authors.	Speitel and Closmann (1991)
Soil	M	100 µg/g	22	0.12–0.22 µg/g soil-day		CO_2	Uncontaminated site. Silty loam soil with added nutrients (20:54:26% sand:silt:clay, pH 8.2, 3.1% organic matter). Enriched for methanotrophs over a 4–16 week period using a 1% methane in air mixture. Zero-order mineralization rate constant provided by authors.	Speitel and Closmann (1991)
Soil	M	100 µg/g	22	0.81–0.83 µg/g soil-day		CO_2	Uncontaminated site. Sandy soil with added nutrients (88:4:8% sand:silt:clay, pH 7.7, 0.1% organic matter). Enriched for methanotrophs over a 4–16 week period using a 1% methane in air mixture. Zero-order mineralization rate constant provided by authors.	Speitel and Closmann (1991)
Soil	M	100 µg/L	28	0.0093	74	CO_2	Uncontaminated site. Sandy aridisol.	Watwood et al. (1991)
Soil	M	100 µg/L	28	0.0038	182	CO_2	Uncontaminated site. Riparian soil.	Watwood et al. (1991)
Soil	P	810 µg/L			NB[2]		Uncontaminated site. Soil column packed with 140 cm soil packed in the same relative position it occupied in the original soil. Average bulk density of 1.65 g/cm2. Saturated hydraulic conductivity of 120–190 cm/day. 14 cm water per day applied to the column. Soil properties: sand:silt:clay ratio of 92:5.9:2.1%, 0.087% organic carbon, pH 6.4, 5 halogenated hydrocarbons, 5 substituted benzenes, and bis(2-choroethyl)ether also present.	Wilson et al. (1981)

Table 23. Aerobic microcosm/column biodegradation studies for 1,2-DCA

Sample type	M/P[1]	Initial concen.	Study period (days)	Rate constant (per day)	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
Soil	P		56–112		NB[2]		Uncontaminated site. 3 microcosms, soil collected at different depths: 1.2, 3.0, and 5.0 m. No degradation reported at any depth. Soil at 5 m has sand:silt:clay content of 85:7:8%. Toluene, chlorobenzene, bromodichloromethane, 1,1,2-trichloroethane, TCE, and PCE also present.	Wilson et al. (1983)

[1]Primary biodegradation (P) or mineralization (M) was measured as the endpoint.
[2]NB = not biodegraded over the study period.

Table 24. Anaerobic microcosm biodegradation studies for 1,2-DCA

Redox[1]	Sample type	M/P[2]	Initial Concen.	Study period (days)	Rate constant (per day)	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
	Aquifer	P	5937 µg/L	43	0.05	14	25% recovered as ethene	Vinyl chloride production facility, spill site. Rapid degradation reported in microcosm constructed from materials from the pumping field. However, no biodegradation of 1,2-DCA was seen in microcosms constructed from test field materials. Field study half-lives estimated using APPROACH are considerably longer -from 1 to 30 years.	Bosma et al. (1998)
	Aquifer	P	500 µg/L	380		NB[3]		Gasoline station. 1,2-DCA was not biodegraded.	Henderson et al. (2007)
	Aquifer	P	20 µg/L	284		NB[3]		Gasoline station. 1,2-DCA was not biodegraded.	Henderson et al. (2007)
	Aquifer	P	200 µg/L	50	0.048	15	Ethene, vinyl chloride at low con-centra-tions	Former disposal site for liquid chlorinated hydrocarbons. Nearly complete degradation was reported by day 50. Ethane was not reported as a degradation product. Ethene was formed by direct dichloroelimination.	Hunkeler et al. (2002)
	Sediment	P	990 µg/L	35		NB[3]		Samples were collected at a depth of 5.0 to 7.5 cm from bottom pond sediment. No biodegradation was reported over the study period of 35 days.	Jafvert and Wolfe (1987)
METH	Aquifer	P		126	0.011	63	Ethene	1,2-Dichloroethane spill site. 500 ppm sodium acetate added. No lag phase. Concentrations of sand:silt:clay at shallow (0.6–0.9 m) and deep (3.4–4.6 m) were 95:2:3% and 38:46:16%, respectively. Organic carbon was 0.2 and 0.8%, respectively.	Klecka et al. (1998)

Table 24. Anaerobic microcosm biodegradation studies for 1,2-DCA

Redox[1]	Sample type	M/P[2]	Initial Concen.	Study period (days)	Rate constant (per day)	$T_{1/2}$ (days)	Biodeg. products	General comments	Reference
SO4	Aquifer	P	106,000 µg/L	168	0.003	230	Ethene	1,2-Dichloroethane spill site. Concentration of sand:silt:clay was 84:10:6%. Organic carbon was 0.3%. Groundwater temperature and pH were 27 °C and 6.8. On day 55, the color of soil changed from tan to black suggesting sulfate-reducing conditions established. Lag phase until day 55, then biodegradation proceeded. $T_{1/2}$ does not include lag phase. Stoichiometric conversion to ethene.	Klecka et al. (1998)
METH	Aquifer	P	29,000 µg/L	173	0.0049	141	Ethene	Adjacent to landfill site, no known history of 1,2-DCA exposure. Sampling location impacted by nearby landfill. Concentrations of sand:silt:clay at aerobic (0.5–1.0 m) and anaerobic (1.8–2.4 m) sites were 93:1:6% and 95:1:4%, respectively. Organic carbon was 0.2 and 0.1%, respectively. $T_{1/2}$ does not include ~50 day lag phase. 38–48% of initial radioactivity found as ethene by day 173.	Klecka et al. (1998)
	Aquifer	P	5000 µg/L	56		58	Ethane, ethene		Lee et al. (1999)
	Stream sediment	P			0.013	51.5		Organic carbon content of 6.4%.	Peijnenburg et al. (1998)
	Soil	M	100 µg/L	28	0.0012	568	CO_2	Uncontaminated site. Sandy aridisol.	Watwood et al. (1991)
	Soil	M	100 µg/L	28	0.0012	578	CO_2	Uncontaminated site. Riparian soil.	Watwood et al. (1991)

[1]Redox conditions: METH = methanogenic; SO4 = sulfate-reducing
[2]Primary biodegradation (P) or mineralization (M) was measured as the endpoint.
[3]NB = not biodegraded over the study period.

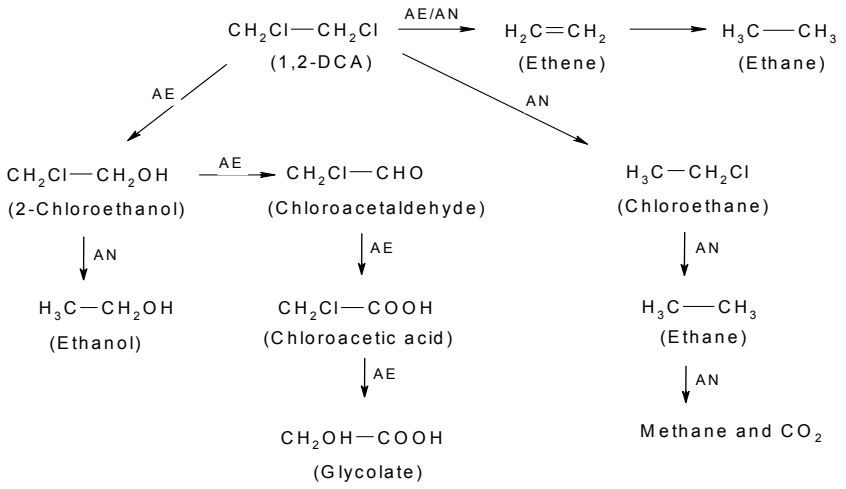
d. Field Studies

1,2-DCA has been observed to biodegrade under both aerobic and anaerobic conditions in the laboratory (Tables 23 and 24) although a considerable number of studies also report that this compound does not biodegrade over the study period. Similar results are seen in field studies (Table 25) (details on the site history, hydrogeological conditions, and remedial actions associated with these field studies are given in Table 26). In some studies, 1,2-DCA has been shown to degrade fairly readily (Cox et al., 1998; Lee et al., 1999). Other studies, such as Mayer (2005) and Ravi et al. (1998b) indicate that 1,2-DCA is very slow to degrade or even recalcitrant to biodegradation.

Loss in the available field studies is typically reported in terms of natural attenuation or disappearance rate constants. These are based on measuring the concentration of a chemical at a specific location over time. The disappearance rate constant does not remove the effect of other processes such as advective loss and adsorption separately so it is not the same as a degradation rate constant (Washington and Cameron, 2001). Loss in the environment, especially in groundwater, may be due not only to degradation processes (abiotic and biotic) but also to transport processes such as dilution, dispersion, sorption, and advection. Ravi et al. (1998b) were the only authors to correct their rate constants for these effects.

Three studies report degradation data for 1,2-DCA at field sites and in laboratory microcosm studies constructed using aquifer material from the field site (Bosma et al., 1998; Cox et al., 1998; Lee et al., 1999). The difference in laboratory and field half-lives can be quite large. Microcosm data from Bosma et al. (1998) indicate that 1,2-DCA will biodegrade under anaerobic conditions with a half-life of a few weeks, while estimated disappearance half-lives calculated from 1,2-DCA concentrations at the field site range from 336–2263 days. However, Cox et al. (1998) reported an anaerobic half-life of 58 days for a microcosm study using sediment from the lower aquifer with conversion of 1,2-DCA mainly to ethane and methane. At the field site, disappearance half-lives of 80 to 340 days were calculated for the lower aquifer.

The majority of the collected field data is from anaerobic sites. Degradation products of ethene and ethane are reported most frequently indicating reductive dechlorination and dihaloelimination reaction processes. Cox et al. (1998) and Lee et al. (1999) also report the presence of 2-chloroethanol. In several other studies, however, 2-chloroethanol was not detected. Hunkeler and Aravena (2000) have noted that aerobic biodegradation in a field site is harder to observe than anaerobic biodegradation because the end products of aerobic biodegradation (Cl^- and CO_2) are frequently present at high background concentrations while the anaerobic biodegradation products (ethene, ethane, etc.) are not and can be more easily followed. Lee et al. (1999) has provided a summary of the biodegradation pathways for 1,2-DCA.



In a field study at a former waste disposal site, degradation pathways of 1,2-DCA were studied using stable isotope analysis (Hunkeler et al., 2005). Hydrogeological conditions at the field site were generally anaerobic, with varying sulfate and high dissolved iron and manganese concentrations and the presence of methane. Source wells at the field site were used to monitor whether natural attenuation was occurring. Three separate aquifers are found below the waste site, separated by sandy clay and clay layers. Aquifer II is unconfined to semi-confined while aquifers III and IV are confined. 1,2-DCA concentrations at source wells in aquifer II and aquifer III were 490/2500 mg/L and 1500/2800 mg/L, respectively. Enrichment factors of -21.1/-22.2 and -21.9/-22.7 were also reported at the aquifer II and aquifer III source wells, respectively. Two wells 183 and 206 m downgradient from the aquifer II source wells had 1,2-DCA enrichment factors of -20.6 and -17.9% showing that enrichment of the heavier ^{13}C isotope was occurring (indicative of biodegradation processes). Wells downgradient from the aquifer III source wells (up to 457 m downgradient) had isotope ratios similar to the source wells suggesting that significant biodegradation was not occurring in this aquifer. Enrichment of ^{13}C in 1,2-DCA along with the detection of ethene depleted in ^{13}C in aquifer IV suggests that dichloroelimination of 1,2-DCA may be occurring at this location.

Sequential anaerobic and aerobic biodegradation of 1,2-DCA has been reported at one field site (Cox et al., 1998). The main contaminants at this site are chloroform and 1,2-DCA. The groundwater entering the site is mainly aerobic (dissolved O_2 of 7.3 mg/L) and oxidizing but becomes anaerobic (dissolved O_2 of 0.0 to 0.3 mg/L) and reducing at the source area. Downgradient from the source area the groundwater becomes aerobic again (320 m downgradient, dissolved O_2 of >4 mg/L). At the source area, high ethene concentrations (4978 and 5520 µg/L) are associated with high concentrations of 1,2-DCA (11,000 to 22,000 µg/L) and indicate that 1,2-DCA is undergoing biodegradation via dihaloelimination. The 1,2-DCA is not completely degraded in the source area, however, and concentrations of 2-chloroethanol in downgradient wells indicate aerobic transformation of the remaining 1,2-DCA.

Lee et al. (1999) studied the biodegradation of 1,2-DCA in the field following a pipeline spill in 1994. In this case, 1,2-DCA was essentially confined to upper surface layers and the 12 m sand layer beneath. Conditions at the site were predominately anaerobic (mainly methanogenic although sulfide and iron concentrations indicate their potential use as terminal electron acceptors). Recovery efforts focused on shallow NAPL removal and pump and treat of the groundwater over the next 3 years. Maximum concentrations of 1,2-DCA in wells in the surface layer and the sand layer were 8000 and 9200 mg/L, respectively, one year after the spill and 7700 and 7800 mg/L, respectively, 3 years after the spill. The detection limit for 1,2-DCA used in the investigation was 5 µg/L. Based on data collected from a series

of wells on site in 1995 and in 1997, first-order degradation half-lives were calculated for each well. A half-life of 3.3 years is reported for a well in the surface layer. Half-lives range from 0.21 to 4.2 years in the 12 m sand layer and from 0.22 to 0.93 years in the lower interbedded and Upper Chicot aquifer layers. Half-lives are considerably higher in those wells with high concentrations of 1,2-DCA as was reported by Bosma et al. (1997b) at another site. These half-lives do not consider the movement of 1,2-DCA in groundwater and assume that dilution is limited due to the slow groundwater flow rate. Highly contaminated wells in the surface layer and 12 m sand layer contain high concentrations of 2-chloroethanol (an aerobic degradation product) up to 130 and 160 mg/L, respectively, as well as ethene (7.7 and 44 mg/L, respectively) and ethane (0.79 and <0.74 mg/L, respectively [anaerobic products]). Ethanol was reported in 3 wells at concentrations of 5.0 to 7.6 mg/L. Chloroethane, chloroacetaldehyde, chloroacetic acid, and glycolate were not detected in groundwater at the site. Based on microcosm data from this site and data from the field study, the authors conclude that the main anaerobic degradation pathway at this site proceeds from 1,2-DCA to ethene and then ethane and that anaerobic degradation from 1,2-DCA to chloroethane, then ethane and methane and CO_2 plays only a minor role in the degradation of 1,2-DCA at this site. Aerobic degradation through 2-chloroethanol and ethanol is also important in the upper layers of the site.

The field study data reported by Kelley et al. (1998) and Mayer (2005) are for leaded gasoline release sites. The natural attenuation of 1,2-DCA in a fuel hydrocarbon mixture was reported by Kelley et al. (1998). The contaminant source for the predominately methanogenic groundwater was an LNAPL release that existed solely in the vadose zone. No DNAPL was found at the site. The 1,2-DCA contaminant plume was shown to be much smaller than expected and degradation products (ethene and ethane) were measured in areas where 1,2-DCA was present. Disappearance rate constants and half-lives for EDB, 1,2-DCA and benzene were estimated by Mayer (2005) for a gasoline service station (Speedway #60) in Gaston county, North Carolina that operated between 1964 and 1992. Clayey soils at this site are found near the surface and are underlain by sandy silts and silty sands. V_x ranges between 2.1 to 6.4 meters/year. The redox conditions at this site were not reported; however, monitoring data were available for EDB, 1,2-DCA, benzene, and MTBE over a number of years. The current plume extent of EDB and 1,2-DCA at this site is estimated to be ~76 and ~87 meters, respectively. Samples were collected from 2 wells (MW-1, approximately 3 to 6 meters from the source area, and MW-7, approximately 45 to 55 meters downgradient from the source area) between 1993 and 2004 and samples from a third well (MW-10, located approximately 60 to 70 meters downgradient from the source area) were collected from 1996 to 2004. Benzene concentrations at MW-1, MW-7, and MW-10 were 29,000, 10,000, and 4200 μg/L, respectively, in 1993/1996 and 100, 110, and 3.9 μg/L, respectively, in 2004. Disappearance rate constants of 0.695, 0.426, and 0.843 per year were reported from these concentrations (MW-1, MW-7, and MW-10) corresponding to half-lives of 1.0, 1.63, and 0.82 years, respectively. 1,2-DCA concentrations at MW-1, MW-7, and MW-10 were 3800, 1700, and 860 μg/L, respectively, in 1993/1996 and 9.3, 65, and 220 μg/L, respectively, in 2004. Based on these concentrations, disappearance rate constants of 0.577/yr, 0.233/yr, and 0.128/yr and half-lives of 1.20, 2.97, and 5.41 years can be estimated for MW1, MW7, and MW10, respectively. Concentrations of EDB were reported for MW-1 and MW-7 only. EDB concentrations at MW-1 and MW-7 were 3400 and 280 μg/L, respectively, in 1993 and 6.3 and 3.3 μg/L, respectively, in 2004. Based on these concentrations, disappearance rate constants of 0.549/yr and 0.338/yr and half-lives of 1.26 and 2.05 years can be estimated for MW-1 and MW-7, respectively. Based on these data, the author concluded that 1,2-DCA is more mobile and more resistant to biodegradation than either EDB or benzene.

While field study data implicating cometabolic degradation of 1,2-DCA were not located, several pure culture, enriched culture, and microcosm studies indicate that cometabolism of 1,2-DCA by methanotrophs may occur in the environment. The release of residual gasoline to soil and groundwater will provide a large hydrocarbon source that is likely to result in a localized area of highly reduced, methanogenic conditions in the residual source area. Methanogens in the anaerobic source area will

produce methane during the anaerobic biodegradation of gasoline components which may encourage the growth of methanotroph populations in the surrounding aerobic soil zone. Potentially, this may result in the cometabolic biodegradation of 1,2-DCA present in the gasoline mixture. While data specific to gasoline releases are not available, cometabolic biodegradation of other compounds has been reported in similar circumstances. An increase in the methanotroph population and corresponding cometabolic biodegradation of trichloroethylene was reported in the presence of methane and nutrients during a groundwater biostimulation demonstration in the field (Brigmon, 2001). In addition, Edwards and Cox (1997) reported that methane generated at a waste site from other materials was stimulating the cometabolic biodegradation of trichloroethylene also present at the site.

Table 25. Aquifer field studies for 1,2-DCA

Redox[1]	Initial concen.	Study period (days)	1st-order rate constant (day^{-1})	Biodeg $T_{1/2}$ (days)	Biodeg products	General comments	Reference
FE to METH	208–245,000 µg/L		$6.0x10^{-5}$–$1.18x10^{-4}$	336–2263	Ethene, vinyl chloride and ethane	Vinyl chloride production facility. Best case half-lives (assumes that degradation takes place within the 2 year travel time from source to pump and treat wells) estimated using APPROACH reported in table. Worst case half-lives (assumes that degradation has occurred over the 10 years since the first spill) of 4.6 to 30.8 years were also estimated Estimates assumed no loss of product via complete mineralization, dilution/dispersion processes affect the parent and transformation products similarly, and used concentrations of DCA, VC, ethene, and ethane to determine rate constants. The half-lives obtained from the well with a low concentration of 1,2-DCA ($T_{1/2}$ of 0.92 and 4.6 years for best and worst cases, respectively) are significantly lower than half-lives from those wells with higher concentrations of 1,2-DCA ($T_{1/2}$ of 2.2 to 6.2 and 10.8 to 30.8 years, for best and worst cases, respectively).	Bosma et al. (1997a, 1997b, 1998)
AE and AN (METH)	33,000 µg/L (max)				Ethene (AN), 2-chloro-ethanol to CO_2 (AE)	Former chemical plant. Chloroform also present at site. Groundwater entering site is aerobic and oxidizing but becomes anaerobic and reducing close to the source area with aerobic/oxidizing conditions downgradient from source (~320 m). At source area, 1,2-DCA concentrations of 11,000–22,000 µg/L are found in association with high concentrations of ethene (~5000–5500 µg/L) and methane. Complete degradation of 1,2-DCA does not occur in anaerobic zone and washout to the aerobic zone occurs. Low concentrations in the aerobic zone indicate that rapid biodegradation occurs at the aerobic/anaerobic interface at this site.	Cox et al. (1998)

Table 25. Aquifer field studies for 1,2-DCA

Redox[1]	Initial concen.	Study period (days)	1st-order rate constant (day^{-1})	Biodeg $T_{1/2}$ (days)	Biodeg products	General comments	Reference
AN (SO4, FE, MN, METH)	1400 µg/L				Ethene, ethane	Maintenance shop site. Found along with BTEX, 1,2-DCA suspected of being dissolved in the LNAPL. Maximum concentrations of 1,2-DCA, ethene, and ethane at one well were 1400, 37, and 13 µg/L, respectively. Chloroethane was not detected in any sample. Plume length of 94.5 meters (predicted >305 meters).	Kelley et al. (1998)
METH (lower aquifer)	9200 (max, upper aquifer); <5–50 µg/L (lower aquifer)	1095		77–1533 (upper aquifer) 80–150 (lower aquifer); Low concentration areas (<1000 mg/L): 77–340 High concentration areas (>1000 mg/L): 511–1533	2-Chloro-ethanol, ethanol, ethene, and ethane	1,2-DCA spill site. 1,2-DCA found as NAPL and dissolved-phase at site. 1st-order decay half-lives reported by the authors for the lower aquifer where 1,2-DCA is found at concentrations of <5–50 µg/L. Degradation products 2-chloroethanol, ethanol, ethene, and ethane were reported in the upper and lower aquifers. CO_2 is the major electron acceptor at the site.	Lee et al. (1999)
	3800 µg/L	4015	0.00158	438		Former gas station. Disappearance rate constant and half-life given by author. Estimated plume extent ~87+ meters. Data reported from 1993 to 2004. 1,2-DCA is washing out, concentrations downgradient from the original site are increasing. Data from the source area monitoring well.	Mayer (2005)

Table 25. Aquifer field studies for 1,2-DCA

Redox[1]	Initial concen.	Study period (days)	1st-order rate constant (day^{-1})	Biodeg $T_{1/2}$ (days)	Biodeg products	General comments	Reference
	1700 µg/L	4015	0.000638	1084		Former gas station. Disappearance rate constant and half-life given by author. Estimated plume extent ~87+ meters. Data reported from 1996 to 2004. 1,2-DCA is washing out, concentrations downgradient from the original site are increasing. Data from this monitoring well are 45-55 meters downgradient from the source area.	Mayer (2005)
	860 µg /L	4015	0.000351	1975		Former gas station. Disappearance rate constant and half-life given by author. Estimated plume extent ~87+ meters. Data reported from 1993 to 2004. 1,2-DCA is washing out, concentrations downgradient from the original site are increasing. Data from this monitoring well are ~60-70 meters downgradient from the source area.	Mayer (2005)
METH	>1000 µg/L	1095–1460	0.0031	225	Ethene, ethane, vinyl chloride	1,2-DCA production facility spill site. Concentrations of 1,2-DCA, vinyl chloride, ethene/ethane combined and methane were followed over a 3 to 4-year period in 5 monitoring wells. An average half-life was calculated by the authors for this site. Wells with high concentrations of 1,2-DCA also had high concentrations of ethene, vinyl chloride, and methane. Dihaloelimination reactions to ethene under methanogenic conditions appear to be important at this site. Air sparging at an anaerobic field site affected by a 1,2-DCA spill may have assisted methanotrophic populations to cometabolically degrade 1,2-DCA in the presence of methane and oxygen to CO2.	Nobre and Nobre (2004)

Table 25. Aquifer field studies for 1,2-DCA

Redox[1]	Initial concen.	Study period (days)	1st-order rate constant (day^{-1})	Biodeg $T_{1/2}$ (days)	Biodeg products	General comments	Reference
METH	18 µg /L	1095	0.00071–0.00074	937–976	Ethane	Landfill site. The authors calculated 1st order attenuation rate constants based on the chloride tracer correction method of Wiedemeier et al. (1996) and the method of Buscheck and Alcantar (1995) using discrete vertical profile sampling. At a distance 632.5 meters from the edge of the landfill, ethane was not detected suggesting that biodegradation is not occurring in this part of the plume. At 884 meters downgradient, ethane is measured at low concentrations when compared to 1,2-DCA concentrations. At 915 meters downgradient, biodegradation of 1,2-DCA to ethane is considerable in the shallow well while even further downgradient, 1,2-DCA concentrations are below detection and only ethane is measured in the shallow aquifer. Site is predominately methanogenic.	Ravi et al. (1998b)
	4,050,000 µg/L					Natural attenuation reported at site of 1,2-DCA spill based on elevated chloride concentrations and reduced O_2 levels where 1,2-DCA concentrations are high. Vinyl chloride present at site suggests possible abiotic hydrolysis.	Zhang et al. (1998)

[1] Redox conditions: METH = methanogenic; FE = iron-reducing; MN = manganese-reducing; SO4 = sulfate-reducing conditions

Table 26. Hydrogeological conditions for 1,2-DCA field studies discussed in text

Site location	Date of release	Type of release	Amount of release	Site geology/hydrogeology	Depth to groundwater	Groundwater velocity	NAPL present	Remediation at site	Reference
Vinyl chloride production facility, Rotterdam Harbor Area, the Netherlands	NR	Several spills, 1st spill 10 years prior to study	NR	The site is highly heterogeneous (sedimentation area). 4 m sand layer, 20 m clay layer with a confined aquifer at 20–30 m bgs. A sand pillar from the surface extending through the clay layer has allowed the DNAPL to reach the confined aquifer.			NR	Containment via pump and treat.	Bosma et al. (1997a, 1997b, 1998)
California Superfund site	1950s on	Drum storage site	NR	Interbedded silty, gravelly sand to depth of 12–14 m bgs, followed by a 3–7 m silty clay and well-cemented sandstone (confining layer). R_f = 1.08.	NR	110 m/yr	NR	NR	Cox et al. (1998)
Naval Air Station (NAS), Fallon NV	Start of operation in 1957	Source of contamination: maintenance shop	NR	Sandy soils cover site to 26.1 m bgs with intermittent silt/clay lenses (unconfined aquifer). At 6.1 m bgs, silt clay aquitard prevents further movement downward. f_{oc} at site = 0.09%. R_f = 1.06.	2.4 mbgs	Hydraulic gradient = 0.001 m/m; porosity 30% (estimated); hydraulic conductivity = 15.7 m/day (7.6, 11.3 m/day, other sites at NAS).	In vadose zone only, no DNAPL in aquifer.		Kelley et al. (1998)

Table 26. Hydrogeological conditions for 1,2-DCA field studies discussed in text

Site location	Date of release	Type of release	Amount of release	Site geology/hydrogeology	Depth to groundwater	Groundwater velocity	NAPL present	Remediation at site	Reference
Southern Gulf coastal region, U.S.	March 1994	Pipeline spill of 1,2-DCA alone	570,000 L	Low permeability, surficial peat, silt, and clay zone underlain by fractured clay, a confined 12 m deep sand groundwater flow zone, a confined 21 m deep interbedded fine sand zone followed by a deep 61 m Upper Chicot aquifer.	NR	Slow: 12.2 m sand layer: $1x10^{-5}$ to $1x10^{-4}$ cm/sec Interbedding layer: $1x10^{-5}$ to $3x10^{-5}$ cm/sec Upper Chicot aquifer: $9x10^{-5}$ cm/sec.	Yes	3-yr period, shallow free-phase NAPL recovery, groundwater pump and treat.	Lee et al. (1999)
Speedway #60 servic station, Gaston county, NC		Gasoline service station operated from 1964-1992		Clayey soils at this site are found near the surface and are underlain by sandy silts and silty sands.		V_x ranges between 2.1 to 6.4 meters/year.	Yes		Mayer (2005)
1,2-DCA production facility, NE Brazil			135 metric tons	30 m surficial deposits (11 m well-graded sand followed by a 4 m well-cemented sandstone with high organic fraction) above a silty clay layer followed by a massive limestone and a confined sandstone aquifer. 1,2-DCA contamination mainly confined to upper sandstone layer.	3.5–4.5 m	Hydraulic conductivity of surficial unit = 10^{-2} to 10^{-3} cm/sec, organic sand layer is 10^{-5} to 10^{-7} cm/sec. Hydraulic gradient of 0.5%.	Yes	Extraction wells, air sparging system, physical barrier (cement-bentonite wall).	Nobre and Nobre (2004)

Table 26. Hydrogeological conditions for 1,2-DCA field studies discussed in text

Site location	Date of release	Type of release	Amount of release	Site geology/hydrogeology	Depth to groundwater	Groundwater velocity	NAPL present	Remediation at site	Reference
KL Avenue Landfill, Kalamazoo, MI		Landfill site (open from 1960–1979)		The landfill is located above the Kalamazoo Moraine which is composed of 3 sets of alternating till and outwash deposits. There are 2 aquifers located beneath the landfill, a shallow unconfined aquifer about 30 m below ground surface and a deeper confined or semi-confined aquifer. R_f = 1.1–1.3 (1,1 and 1,2-DCA isomers combined).	30.5 m bgs	Shallow aquifer: groundwater table gradient of 0.006 m/m, seepage velocity of 21.9–39.6 cm/day, velocity varies from 22.9 to 30.5 cm/day based on chloride/time studies, hydraulic conductivity of 14.6 m/day.	NR		Ravi et al. (1998a, 1998b)
Fort Langley, British Columbia	February 1986	Spill	254,600 L	3–6 m silty sand/wood waste fill followed by a silt layer, then a sand and gravel aquifer (5–9 m thick) underlain by a silty clay aquitard up to 100 m thick.		Average hydraulic conductivity of the aquifer is $1.6x10^{-2}$ m/sec. Hydraulic gradient towards the river is $3x10^{-4}$ m/m. Average velocity of 0.7 to 1.3 m/day. Advective rate of transport ~1 m/day. Plume front moved ~2.5 m/day.	Yes	SVE from surface layers, pumping of DNAPL from bottom of aquifer, pump and treat of groundwater, air injection curtain.	Zhang et al. (1998); B.C. Ministry of Environment (2007)

E. Monitoring Data

The available monitoring data for 1,2-DCA have been divided into sites contaminated by 1,2-DCA because of industrial spills, leaking storage tanks, leaching from landfills, etc. (point source contamination) and those studies where broader baseline-type sampling has been undertaken.

1. Release Site Data

Monitoring data in this section have been separated into sites affected by the release of leaded fuels, chemical spill sites, and "other" sites affected by the release of 1,2-DCA (Table 27). 1,2-DCA has been reported in groundwater beneath numerous waste disposal and CERCLA sites. In data reviews by Plumb (1987, 1992), 1,2-DCA was found in groundwater at detectable concentrations at 14.2% of 178 CERCLA sites and at 82 of 500 disposal site investigations in the U.S. A literature review conducted by Roy (1994), found concentrations of 1,2-DCA ranged from below the detection limit to 11 mg/L in municipal landfill leachate. Spill sites reported above in the field study section report concentrations of 1,2-DCA at 10–100 mg/L levels.

The presence of EDB and 1,2-DCA at LUST sites has come under more intense scrutiny in recent years (Falta, 2004a, 2004b, 2005; Falta and Bulsara, 2004; Falta et al., 2005a; Wilson et al., 2007). While the South Carolina Department of Health and Environmental Control maintains a database of the approximately 7200 documented petroleum release sites in that state and testing has been conducted for EDB, measurement of 1,2-DCA concentrations at these sites has only begun since 2005 (Falta et al., 2005b). Based on field data from several UST sites in North Carolina, Falta et al. (2005b) report that 1,2-DCA concentrations are similar, if not higher, than those reported for EDB and that 1,2-DCA has traveled further from the source area than EDB. Wilson et al. (2007) recently surveyed the presence of 1,2-DCA in 12 states. 23% of 39 UST sites had detectable concentrations of 1,2-DCA. 15% of the total sites had concentrations of 1,2-DCA greater than the MCL (18 positive detections out of 293 samples; 3% of the 1,2-DCA detections had concentrations >MCL). In contrast, 54% of 79 UST sites in 17 states, had detectable concentrations of EDB and 43% of the total sites had concentrations of EDB greater than the MCL (132 positive detections out of 736 samples; 11% of the EDB detections had concentrations >MCL) (Wilson et al., 2007).

Table 27. 1,2-DCA monitoring data for release sites

Site location	History	Hydrogeology	Concentration in Soil	Concentration in groundwater (date of sampling)	Other concentrations	Remediation efforts	Reference
Leaded fuel release							
Orangeburg, SC	Former gasoline station (1953–1987)	Underlain by clays and silts, water table depth is 4.6–6.1 m. Groundwater velocity: 1.5–6.1 m/yr. Not much movement of EDB off site, ~45 meters.		Max = 111 µg/L (1999)		Original tanks from 1953 abandoned in 1971 and removed in 2003. New tanks in place in 1971 and removed in 1987.	Falta (2004b)
OU5, Fort Wainwright, AK		Unconfined aquifer, BTEX also present. Horizontal hydraulic conductivity 38.1–122 m/day, velocity of 30.5–45.7 cm/day, water table at 3–4.6 m bgs. 1,2-DCA plume overlaps NAPL and benzene plumes at site with an estimated depth of the plume of 6.1 m.		Range = 0.3–41 µg/L (9/19 wells positive, 1994)			U.S. EPA (1999)

Table 27. 1,2-DCA monitoring data for release sites

Site location	History	Hydrogeology	Concentration in Soil	Concentration in groundwater (date of sampling)	Other concentrations	Remediation efforts	Reference
McClellan AFB, Sacramento, CA	Management and repair of aircraft, electronics, and communication systems requiring use of solvents, fuel oils, lubricants, etc.	Soils and geology are a complex series of alluvial and fluvial deposits, limited in horizontal and vertical extent, rarely extend laterally more than 15.2 m. f_{oc} = 0.001–0.003; porosity = 0.35–0.45; bulk density = 1.2 to 1.3 g/cm^3. Hydraulic conductivity 0.85–9.4 m/day, transmissivity = 9–84 m^2/day (zone A). Groundwater table is 30.5 m bgs (drop of 18.3 m over last 50 yrs has led to a smear zone).	OU-C: Max = 360 µg/kg (1984/1985) OU-C/D: Not detected in soil gas samples (DL = 18 ppbv; 1987) OU-D vent: Max = 20.3 ppbv in soil gas (DL = 0.75 ppbv; 1991) Off-site residential sites near OU-D: Max = <80 ppbv in soil gas (1987, DL = 18 ppbv) Max = 1278 ppbv in soil gas (1991, DL = 0.75 ppbv, 7 samples)	Mean = 1.70 µg/L (9% detection; 1993) OU-D: Max = 2790 µg/L (1985) Max = 5900 µg/L (1989) Off-site residential wells: Max = 85 µg/L (1980) Max = 0.7 µg/L (1/6 positive; DL = 0.1 µg/L; 1991)	Off-site well heads (residential wells, 4 properties adjacent to OU-D): Max = 195.7 ppbv (1985) Off-site crawl space under four residences adjacent to OU-D: ND (DL = 0.9–12.3 ppbv; 1984/1985) ND in a 2nd study (1986/1987; DL of 0.593 ppbv) ND in 3rd study (Jan. 1992; DL of 1.19 ppbv) ND in 4th study (ambient air in yards, crawl spaces; June/Sept. 1992; DL = 0.2 ppbv)	Pump and treat with above ground air stripping. The treatment began in 1988, and was expanded in 1990.	ATSDR (1994b); Stone and Webster Engineering (1994)

Table 27. 1,2-DCA monitoring data for release sites

Site location	History	Hydrogeology	Concentration in Soil	Concentration in groundwater (date of sampling)	Other concentrations	Remediation efforts	Reference
Chemical spill site							
Cordova superfund site, Muskegon, MI	Organic chemical manufacturer. Chemical company used site from 1973. An explosion/on-site fire occurred in 1979, and site closure in 1983.			Max = 2200, 110,000, 21,000, 110,000 µg/L (1990s) shallow aquifer Max = 8 µg/L, lower semi-confined aquifer			U.S. EPA (1990)
Kalama Specialty Chemicals, SC	Organic chemical manufacturer. Plume also contains BTEX, methylene chloride.	Sand from land surface to 4.6–7.6 m separated by clay materials from a 2nd aquifer. Groundwater flow ~6–8.5 m/yr with leading edge of plumes about 1.5–2 times faster than this.		Well 1: Max = ~12,000 µg/L (1997) Max = 350 µg/L (2002) Well 2: Max = ~35,000 µg/L (1997) Max = 330 µg/L in (2002)		Soil removal and pump and treat (since 1997) used to remediate site.	U.S. ACE (2003)

Table 27. 1,2-DCA monitoring data for release sites

Site location	History	Hydrogeology	Concentration in Soil	Concentration in groundwater (date of sampling)	Other concentrations	Remediation efforts	Reference
Other release sites							
Bruno grain co-op, Butler county, NB	Leased by the USDA from 1947 to the 1960s for use as a Federal grain storage facility. Carbon tetrachloride and chloroform also present in groundwater.	Eight water supply wells in the town of Bruno were sampled.		Range of max values = ND–16 µg/L (1984–1988)			ATSDR (1994a)
Necco Park Landfill, Niagara Falls, NY	Industrial landfill owned by DuPont, process wastes.	Geology beneath the landfill consists of reworked till, sands, and silts, followed by a weathered, glacial till of silty sand or sandy silt and finally a fractured shale-limestone bedrock.		Maximum = 13.9–4255 µg/L			Lee et al. (1995)
Pristine, Inc. site, Reading, OH	Liquid waste disposal, liquid waste incinerator site. Upper and lower aquifers contain benzene, 1,2-DCA.	Soil units: fill, upper lake sediment (upper aquifer), glacial till, lower lake sediment, and lower outwash deposits (lower aquifer; flow velocity 67 cm/yr).	Surface soil: ND–110 µg/kg Subsurface soil: ND–3500 µg/kg Soil borings: ND–57,000 µg/kg	Upper aquifer: ND–150,000 µg/L Lower aquifer: ND–780 µg/L	Surface water: ND–6200 µg/L Sediment: ND–2400 µg/kg		Canter and Sabatini (1994)

Table 27. 1,2-DCA monitoring data for release sites

Site location	History	Hydrogeology	Concentration in Soil	Concentration in groundwater (date of sampling)	Other concentrations	Remediation efforts	Reference
Lackawanna Refuse site, PA	Coal strip mine used for refuse disposal, some industrial and hazardous waste dumping.			Max = 1500 µg/L (1983–1984)			ATSDR (1990)

2. Non-site Based Environmental Monitoring

Monitoring data are presented below for surface water (Table 28), groundwater (Table 29), outdoor air (Table 30), and indoor air (Table 31). 1,2-DCA is reported in surface (Table 28) and groundwater (Table 29) samples at low concentrations. In the U.S. STORET database (years 1975–1982), 7% of 7909 water samples (both surface water and groundwater) had detectable 1,2-DCA concentrations at a median value of <0.100 µg/L (Staples et al., 1985). A survey of 2110 community water systems from 12 northeastern and mid-Atlantic states (from 1993–1998) found that 1.9% of the water systems (36 community systems) had detectable levels of 1,2-DCA in their finished drinking water (Grady and Casey, 2001). Water from 27% of the positive systems also contained EDB suggesting that the source of 1,2-DCA to the water system in these cases may be from leaded gasoline (Falta, 2004b).

Mean concentrations of 1,2-DCA in outdoor (Table 30) and indoor (Table 31) air samples are low, typically less than 1 µg/m^3. Several studies are available that have measured both indoor and outdoor air concentrations of 1,2-DCA at residences during the 1980s. Indoor and outdoor air concentrations were monitored for 35 residences in the Kanawha Valley of West Virginia in the mid-1980s. Sixty-three percent of the samples contained detectable concentrations of 1,2-DCA, while only 29% of the outdoor air samples were positive detects for 1,2-DCA (Cohen et al., 1989). Indoor and corresponding outdoor air samples were collected from 20 residences in Greensboro, North Carolina (in 1980), 27 residences in Baton Rouge/Geismar, Louisana (1981), and 11 residences in Houston, Texas (1981) (Hartwell et al., 1984). 36.8, 100, and 40% of outdoor air samples (collected from the backyard of residences) in Greensboro, Baton Rouge, and Houston contained detectable concentrations of 1,2-DCA (median values of 0.025, 2.20, and 0.045 µg/m^3, respectively). Thirty, 88.9, and 18.2% of indoor samples from the same locations were positive for 1,2-DCA (median values of 0.025, 3.60, and 0.04 µg/m^3, respectively) (Hartwell et al., 1984). Indoor and corresponding outdoor air samples were collected from 25 residences in the Los Angeles community (winter 1984 and summer 1984), and from 10 residences in Antioch/W. Pittsburg, California (summer 1984) (Pellizzari et al., 1986). Fifty-four, 0, and 0% of outdoor air samples (collected from the backyard of residences) in winter Los Angeles, summer Los Angeles, and Antioch/W. Pittsburg contained detectable concentrations of 1,2-DCA (median values of 0.21, 0.02, and 0.03 µg/m^3, respectively). Sixty-four, 4.3, and 20% of indoor samples from the same locations were positive for 1,2-DCA (median values of 0.22, 0.03, and 0.12 µg/m^3, respectively (Pellizzari et al., 1986). 1987 TEAM study results show 1,2-DCA in 2.17, 82.4, 82.4, and 52.5% of breath, personal air, kitchen, and outdoor (backyard of residence) air samples. No concentrations are given (method quantifiable limit of 0.13 and 0.18 µg/m^3 for two different MS instruments) (Hartwell et al., 1992).

Table 28. Surface water concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Range = 50–210 ng/L	NR	Coastal stations, Gulf of Mexico	1977	Two of 3 coastal stations were affected by anthropogenic influences.	Sauer (1981)
Median = 0 µg/L Max = 304.9 µg/L	71/606	New Jersey	1977–1979		Page (1981)
9.51 ng/L	NR	Brazos River, U.S.	1981–1982		McDonald et al. (1988)
Mean = 50 ng/L Median = 18 ng/L Range = <5–647 ng/L	NR/108	Southern North Sea (Dutch coastal area)	1983/1984		van de Meent et al. (1986)
<3 µg/L	NR	Widnes West bank, Mersey estuary, U.K.	1989	Three bulk samples collected at the same location.	Rogers et al. (1992)
Range = 720–4020 ng/L	NR	Tees estuary, U.K.	1992	Samples collected close to a vinyl chloride monomer production facility.	Dawes and Waldock (1994)
<25 ng/L	NR	U.K.	1992	Sampling locations: Humber, Tyne, Wear, Poole, Southhampton Water, Tweed, Firth of Forth, Moray Forth, North Minch, Swansea Bay, Bristol Channel, Queens Channel, Falmouth, U.K. LOD (limit of detection) of 25 ng/L.	Dawes and Waldock (1994)
Range = <25–33.4 ng/L	NR	Liverpool, U.K. (Mersey estuary)	1992		Dawes and Waldock (1994)
4.9–9.8 ng/L	NR	Belgian continental shelf waters	1993		Dewulf and Van Langenhove (1995)
Median = 80 ng/L Range = 31–1270 ng/L	NR	Elbe River at Zollenspieker	1992	Location is upstream from Hamburg, Germany.	Gotz et al. (1998)
Median = 117 ng/L Range = 33–973 ng/L	NR	Elbe River at Seemannshoft	1992	Location is downstream from Hamburg harbor, Germany.	Gotz et al. (1998)
<0.1 µg/L (64 samples) >0.1 µg/L (26 samples) >1 µg/L (2 samples)	28/644	Portuguese surface waters	1999–2000	Surface waters (described as sea, estuarine, river water, and industrial effluents) were sampled across Portugal. Concentration levels typically between 0.1 and 0.7 µg/L when detected.	Martinez et al. (2002)

Table 28. Surface water concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Max range = 0.3–9.5 µg/L	NR	Rhine, Meuse, Northern Delta area, Westerscheldt, The Netherlands	1992–1997	Results given as maximum concentration reported in each of 4 surface waters. 13 samples/yr collected at each location.	Miermans et al. (2000)
Range = 0.1–3 µg/L	36/136	River and estuary water from Osaka, Japan	1993–1995	30 sites were sampled within the urban rivers and estuaries of Osaka.	Yamamoto et al. (1997)

Table 29. Groundwater concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Median = 0 µ/L Max = 36.5 µ/L	104/1066	New Jersey	1977–1979		Page (1981)
0.1, 1.8 µg/L	2/113	113 cities in the U.S.	1975	Results from the National Organics Monitoring Survey.	Cotruvo (1986)
trace, 4.8 µg/L	2/142	166 water supplies in the U.S.	1977–1981	Results from the National Screening Program.	Cotruvo (1986)
Median = 0.5 µg/L Max = 3.2 µg/L	18/466	U.S.	1982	Results from the 1982 Groundwater Supply Survey. 1000 drinking water supplies using groundwater as a source.	Cotruvo (1985)
Max = 250 µ/L	NR	U.S.	1980	Council on Environmental Quality study, data from EPA, 10 EPA regions, and several individual states.	Burmaster (1982)
>7 ug/L in 2 of 7 positive samples	7/1791	Wisconsin	1984	1174 community wells and 617 private wells were sampled.	Krill and Sonzogni (1986)
Max = 24 µg/L	36/7712	California	1984–1990	Water supply wells sampled under AB 1803 (large and small public water systems).	Lam et al. (1994)
Max = 0.90–1.6 µg/L	1/103	Kansas	1985/1986	103 farmstead wells were sampled across Kansas.	Steichen et al. (1988)
Median = 5.0 µg/L Max = 176 µg/L	NR/27	Finland	Late 1980s	Groundwater beneath 27 Finnish landfills was sampled for 1,2-DCA.	Assmuth and Strandberg (1993)

Table 29. Groundwater concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Median = 0.5 µg/L Range = 0.2–3.0 µg/L	7/351	U.S.	1985–1995	Urban wells. 0% of wells exceed MRL of 5 µg/L. Untreated ambient groundwater study as part of NAWQA.	Squillace et al. (1999)
Median = 0.3 µg/L Range = 0.2–2.9 µg/L	8/2449	U.S.	1985–1995	Rural wells. 0% of wells exceed MRL of 5 µg/L. Untreated ambient groundwater study as part of NAWQA.	Squillace et al. (1999)
Mean = 3.03 µg/L Median = 1.40 µg/L Range = 0.20–24.0 µg/L	45/11,686			43 of the 45 wells testing positive for 1,2-DCA had concentrations exceeding the MCL (Storm, 1994).	Storm (1994)
Median (positives) = 0.30 µg/L	21/3438	U.S.	1985–2001	National assessment of groundwater from various types of wells representing almost 100 different aquifer studies (regionally extensive aquifers of aquifer systems). Detections were in shallow aquifers in urban areas.	Zogorski et al. (2006)
Median (positives) = 1.3 µg/L	8/2383	U.S.	1985–2001	National assessment of groundwater from domestic wells representing almost 100 different aquifer studies (regionally extensive aquifers or aquifer systems).	Zogorski et al. (2006)
Median (positives) = 0.39 µg/L	7/1073	U.S.	1985–2001	National assessment of groundwater from public wells representing almost 100 different aquifer studies (regionally extensive aquifers or aquifer systems).	Zogorski et al. (2006)
Median = 0.4 µg/L Range = 0.1 to 33.4 µg/L	7/518	U.S.	1996–2002	National water-quality assessment program of USGS. Shallow groundwater in new residential/commercial areas (median well depth, 10 m).	Squillace et al. (2004)

Table 30. Outdoor air concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Average = 2.1 µg/m^3 Max = 27.9 µg/m^3	55/150	Rutherford, NJ	1978	Residential/industrial area. Average concentration of the quantifiable samples was 1.3 ppb.	Bozzelli and Kebbekus (1982)
Average = 0.53 µg/m^3 Max = 4.4 µg/m^3	5/18	Piscataway-Middlesex area, NJ	1978	Residential area. Average concentration of the quantifiable samples was 0.40 ppb.	Bozzelli and Kebbekus (1982)
Average = 2.9 µg/m^3 Max = 70.9 µg/m^3	49/110	Newark, NJ	1978	Industrial area. Average concentration of the quantifiable samples was 1.5 ppb.	Bozzelli and Kebbekus (1982)
Average = 0.035 µg/m^3 Max = 9.7 µg/m^3	29/263	Six locations, New Jersey	1979	27/263 samples contained trace concentrations 1,2-DCA, 2 samples had quantifiable levels.	Harkov et al. (1981)
Range = 0.48–2.14 µg/m^3	NR	London, England	1979	Exhibition Road, London, urban site.	Tsani-Bazaca et al. (1981)
Range = 0.15–0.5 µg/m^3	NR	Airedale valley, England	1979	Semi-rural site	Tsani-Bazaca et al. (1981)
Mean = 2.3 µg/m^3 Range = 0.76–6 µg/m^3	NR	Los Angeles, CA	1979		Singh et al. (1981a)
Mean = 1.0 µg/m^3 Range = 0.17–6.4 µg/m^3	NR	Phoenix, AZ	1979		Singh et al. (1981a)
Mean = 0.37 µg/m^3 Range = 0.17–3.7 µg/m^3	NR	Oakland, CA	1979		Singh et al. (1981a)
Mean concentration range = 0.22–1.3 µg/m^3 Max concentration range = 6.6–39.9 µg/m^3	NR/~1000	Three locations, The Netherlands	1980	Data were collected from a rural location, a small city, and a major city in The Netherlands.	Guicherit and Schulting (1985)
Mean = 6.7 µg/m^3 Range = 0.22–32.3 µg/m^3	NR	Houston, TX	May 1980		Singh et al. (1981b)
Mean = 0.55 µg/m^3 Range = 0.2–2.7 µg/m^3	NR	St. Louis, MS	May/June 1980		Singh et al. (1981b)

Table 30. Outdoor air concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Mean = 1.1 µg/m^3 Range = 0.24–9.3 µg/m^3	NR	Denver, CO	June 1980		Singh et al. (1981b)
Mean = 1.6 µg/m^3 Range = 63–2505 ppt	NR	Riverside, CA	July 1980		Singh et al. (1981b)
Mean = 1.1 µg/m^3 Range = 55–4312 ppt	NR	Staten Island, NY	March/April 1981		Singh et al. (1982)
Mean = 121 µg/m^3 Range = 0.24–1.0 µg/m^3	NR	Pittsburgh, PA	April 1981		Singh et al. (1982)
Mean = 0.86 µg/m^3 Range = 0.1–12.5 µg/m^3	NR	Chicago, IL	April 1981		Singh et al. (1982)
Mean = 0.45 µg/m^3 Range = 0.09–2.8 µg/m^3	45/45	Downey, CA	February 1984		Singh et al. (1987)
Mean = 2 µg/m^3 Range = <0.02–10.9 µg/m^3	47/48	Houston, TX	March 1984		Singh et al. (1987)
Mean = 0.1 µg/m^3 Range = <0.02–0.55 µg/m^3	31/38	Denver, CO	April 1984		Singh et al. (1987)
Geometric mean = <0.01 µg/m^3	0/111	New Jersey	July/August 1981	Three urban locations in New Jersey (Newark, Elizabeth, Camden)	Harkov et al. (1984)
Geometric mean = 0.044 µg/m^3 Max = 7.5, 8.4, 23.5 µg/m^3 (for 3 cities in notes, respectively)	28/105	New Jersey	January/February 1982	Three urban locations in New Jersey (Newark, Elizabeth, Camden)	Harkov et al. (1984)
Mean = 115 µg/m^3 Range = 22–346 µg/m^3	NR/256	London, England	1982	Exhibition Road, London, urban site.	Clark et al. (1984)
Mean = 9 µg/m^3 Range = 0–53 µg/m^3	NR/175	Silwood Park, England	1982	Rural site	Clark et al. (1984)
Mean = 9 µg/m^3 Range = 0.4–58 µg/m^3	NRR/198	Toddington, England	1982	15 miles from motorway site, countryside.	Clark et al. (1984)

Table 30. Outdoor air concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Mean = 0.8 µg/m^3	NR/310	Philadelphia, PA	1983/1984	Ten sites in Philadelphia county, sampled over a 4-month period.	Sullivan et al. (1985)
0.07–0.13 µg/m^3	NR	Lower troposphere, northern hemisphere	1984/1985	General baseline level reported – marine troposphere sampling on Atlantic Ocean.	Class and Ballschmiter (1986)
<0.018 µg/m^3	NR	Lower troposphere, southern hemisphere	1984–1985	General baseline level reported – marine troposphere sampling on Atlantic Ocean.	Class and Ballschmiter (1986)
<0.018 µg/m^3	NR	Above tradewind system, Bermuda Islands	1985	All values below the limit of detection (4 pptv).	Class and Ballschmiter (1986)
Arithmetic mean = 4.9 µg/m^3 Range = 0.12–30 µg/m^3	NR	Philadelphia, PA	1985	Urban air concentrations.	API (1988)
Mean = 77 ng/m^3 Range = 40–180 ng/m^3	NR	Asch, Germany	1985	Rural location.	Guthner et al. (1990)
Mean = 190 ng/m^3 Range = 50–660 ng/m^3	NR	Goppingen, Germany	1986	City of 50,000 people.	Guthner et al. (1990)
Mean = 0.09 µg/m^3	11/79	Kanawha Valley WV; Los Angeles CA; Houston TX	1986–1987	Data were collected from 3 separate programs – Kanawha Valley Toxics Evaluation; California Air Resources Board; Toxics Air Monitoring System station.	Pleil et al. (1988)
Range of annual means for 13 sites = 0.2 = 119 µg/m^3	NR	Hamburg, Germany	Mid-late 1980s	Four sites with annual mean concentrations >20 µg/m^3 – tend to be industrial or dense traffic areas. Annual mean for sites with industrial impact is 12.4 µg/m^3 (n = 250).	Bruckmann et al. (1988)
Mean = 1.61 µg/m^3 Median = 0.04 µg/m^3 Range = 0–74.7 µg/m^3	1136/2019	U.S.	1976–1987	National ambient VOCs database (data from Shah and Heyerdahl, 1988). 64 urban to suburban locations.	Kelly et al. (1993)
Range = ND–0.13 µg/m^3 Max = 2.78 µg/m^3	NR	Canada	1987–1990		Bunce and Schneider (1994)

Table 30. Outdoor air concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Average = 0.44 µg/m^3 Range = <0.9–1.3 µg/m^3	0/436	California	1989	CARB sampling program. No samples were above the LOD (limit of detection) of 0.2 ppb.	Loscutoff and Poore (1993)
Detected in 16% of all samples (detection limit 0.22 µg/m^3)		Columbus, OH	June/July 1989	Six sites were sampled in metropolitan Columbus, OH.	Spicer et al. (1996)
Mean = 0.16 µg/m^3 Range = <0.12–2.39 µg/m^3	48/298	Columbus, OH	1989		Kelly et al. (1993)
Mean = <0.16 µg/m^3 Range = <0.16–0.33 µg/m^3	1/349	11 U.S. cities	1990		Kelly et al. (1993)
Average = 0.44 µg/m^3 Range = <0.9–<0.9 µg/m^3	0/579	California	1990	CARB sampling program. No samples were above the LOD of 0.2 ppb.	Loscutoff and Poore (1993)
Range = 0.1–4.0 µg/m^3	NR	Toronto, Canada	1990	Data from 25 sampling sites in Toronto. Mean value reported for each site and range of means provided.	Campbell et al. (1995)
Not detected (<0.41µg/m^3)	0/81	Lima, OH	1990–1991		Kelly et al. (1993)
Median = 0.04 µg/m^3	NR/2747	U.S.	1962–1992	Survey of ambient measurements of HAPS. Analyzed for at 83 locations.	Kelly et al. (1994)
Average = 0.06 µg/m^3	NR/483	Berlin, Germany	1996	Average is the same for 3 sites, a street site in the inner city, an inner-city residential neighborhood, and a rural location outside of the city.	Thijsse et al. (1999)
<4.4 µg/m^3	NR	13 urban sites in the U.S.	1996–1997	Data from the Urban Air Toxics Monitoring program. All stations reported concentrations <1 ppbv.	Mohamed et al. (2002)
Median = 0.04 µg/m^3 Mean = 0.05 µg/m^3 Maximum = 3.15 µg/m^3	NR/3650	Minnesota	1991–1998	Data collected at 25 sites across Minnesota for up to 8 years.	Pratt et al. (2000)

Table 30. Outdoor air concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Mean = 0.13 µg/m^3 Range = 0.08–0.18 µg/m^3	NR	Chiba City, Japan	February 1999	7-day sampling method.	Uchiyama and Hasegawa (2000)
Arithmetric mean = 0.04 µg/m^3 Range = 0.01–0.69 µg/m^3	4/74	Ottawa, Canada	Nov. 2002–March 2003	Residential sites, samples collected on front porch or driveway (1.5 m from ground).	Zhu et al. (2005)

Table 31. Indoor air concentrations for 1,2-DCA

Concentration	Number of positives/total samples	Location	Date of sampling	General comments	Reference
Mean = 20.85 µg/m^3 Median = 17.30 µg/m^3 Max = 140.3 µg/m^3	29/35	Kanawha Valley, WV	1980s (exact year not specified)	35 residences, 3-week integrated sample. Limit of detection (LOD) = 8.5 µg/m^3.	Cohen et al. (1989)
Mean = 0.01 µg/m^3	NR/754	Canada	Fall 1991	1,2-DCA was not detected in any sample collected during the spring, summer, or winter sampling periods (1991) of the same residences.	Fellin and Otson (1994)

F. Fugacity Estimates

The EPIWIN Level III fugacity model was used to model the environmental fate and persistence of 1,2-DCA under different release scenarios (Tables 32 and 33) (U.S. EPA, 2007b). This is a diffuse model and does not contain a groundwater component. The Level III model assumes that 1,2-DCA is being continually released to the environment and that steady state conditions are reached. 1,2-DCA can be removed from this system by either advection (the movement of undegraded chemical out of the geographical boundaries of the model) or degradation within the compartments (air, water, soil, and sediment) of the model environmental media (based on a user-supplied degradation half-life). Equilibrium between environmental media is not assumed in the Level III fugacity model. Input data to the model included relevant physical/chemical properties reported in Table 18, an aerobic biodegradation half-life in water and soil of either 90 (results reported in Table 32) or 330 (results reported in Table 33) days based on aerobic microcosm biodegradation data (Table 23) and an atmospheric half-life of 49 days as reported in the photolysis section for 1,2-DCA in this report. Emission scenarios were varied as given below in Tables 32 and 33 as this can affect the distribution and persistence of a compound in the environment. The model was also run with advection on and with advection turned off. With advection off, 1,2-DCA is not able to be removed from the model environment undegraded, giving a "global" perspective of the environmental fate of 1,2-DCA where loss due to degradation becomes most important in determining the persistence of 1,2-DCA in the environment.

For highly volatile chemicals such as 1,2-DCA, the overall persistence time may be very short when advection is considered since the advection lifetime in air is very short. This does not necessarily mean that the chemical has low persistence, however; in many cases it simply means the chemical has been removed from the model environment undegraded and exists in some other location beyond the boundaries of the model. This is exemplified by comparing the overall persistence time for 1,2-DCA with advection on and with advection off. The first two columns of Table 32 illustrate the results of the model run where 1,2-DCA is emitted solely to the air compartment. With advection on, the overall persistence time of 1,2-DCA in the model environment is only 91.7 hours; however, almost 90% of the loss is through advection processes. When advection is not considered, the overall persistence time of the chemical is 874 hours and all the loss is through degradation processes. Comparable results are observed for each emission scenario. Tables 32 and 33 also indicate that when advection is considered, almost all the advective loss of mass occurs through the air compartment.

A similar pattern is also observed using the longer half-lives (330 days in water and soil and 1320 days in sediment) (Table 33). Comparing the results of Tables 32 and 33 for each emission scenario: (1) a higher percentage of chemical is advected when longer half-lives are considered (assuming advection is on); (2) a higher percentage of chemical is reacted in air when longer half-lives are considered (assuming advection is off); (3) the overall persistence time increases when longer half-lives are considered irregardless of whether or not advective processes are used in the model; (4) similar distributions of 1,2-DCA between the environmental media are observed.

Table 32. Fugacity estimates for 1,2-DCA (90-day half-life in water and soil, 360-day half-life in sediment)

	1000 kg to air only (advection off)	1000 kg to air only (advection on)	1000 kg to water only (advection off)	1000 kg to water only (advection on)	1000 kg to soil only (advection off)	1000 kg to soil only (advection on)	1000 kg each to air, water, and soil (advection off)	1000 kg each to air, water, and soil (advection on)
Mass amount in air (%)	96	97.3	61.7	15.5	70.4	39	74.3	34.6
Mass amount in water (%)	3.5	2.5	37.8	84.3	4.3	7.4	16.6	47.7
Mass amount in soil (%)	0.5	0.2	0.3	0	25.3	53.6	9.0	17.6
Mass amount in sediment (%)	0	0	0.2	0.2	0	0	0.8	0.12
% Advected (air)	0	89.2	0	54.5	0	84.2	0	76
% Advected (water)	0	0.2	0	29.6	0	1.6	0	10.5
% Advected (soil)	0	0	0	0	0	0	0	0
% Advected (sediment)	0	0	0	0	0	0	0	0
% Reacted (air)	98.9	10.5	85.6	6.4	89.7	9.9	91.4	9.0
% Reacted (water)	1.0	0.7	14.3	9.5	1.5	0.5	5.6	3.4
% Reacted (soil)	0.1	0	0.1	0	8.8	3.7	3.0	1.2
% Reacted (sediment)	0	0	0	0	0	0	0	0
Persistence time (hr)	874	91.7	1180	352	1080	216	1040	220
Reaction time (hr)	874	866	1180	2210	1080	1530	1040	1620
% Reacted	100	10.6	100	15.9	100	14.2	100	13.6
% Advected	0	89.4	0	84.1	0	85.8	0	86.4

Table 33. Fugacity estimates for 1,2-DCA (330-day half-life in water and soil, 1320-day half-life in sediment)

	1000 kg to air only (advection off)	1000 kg to air only (advection on)	1000 kg to water only (advection off)	1000 kg to water only (advection on)	1000 kg to soil only (advection off)	1000 kg to soil only (advection on)	1000 kg each to air, water, and soil (advection off)	1000 kg each to air, water, and soil (advection on)
Mass amount in air (%)	95.6	97.1	61.7	15.5	70.3	38.8	73.6	33.8
Mass amount in water (%)	3.9	2.7	37.7	84.3	4.7	7.9	17.4	48.8
Mass amount in soil (%)	0.5	0.2	0.4	0	25	53.2	9.0	17.2
Mass amount in sediment (%)	0	0	0.2	0.2	0	0	0.1	0.1
% Advected (air)	0	89.2	0	58.5	0	86.8	0	78.2
% Advected (water)	0	0.2	0	31.8	0	1.8	0	11.3
% Advected (soil)	0	0	0	0	0	0	0	0
% Advected (sediment)	0	0	0	0	0	0	0	0
% Reacted (air)	99.7	10.5	95.6	6.9	97	10.2	97.4	9.2
% Reacted (water)	0.3	0	4.3	2.8	0.5	0.2	1.7	1.0
% Reacted (soil)	0	0	0	0	2.6	1.0	0.9	0.3
% Reacted (sediment)	0	0	0	0	0	0	0	0
Persistence time (hr)	885	91.9	1310	378	1170	224	1120	231
Reaction time (hr)	885	872	1310	3900	1170	1960	1120	2190
% Reacted	100	10.5	100	9.7	100	11.4	100	10.5
% Advected	0	89.5	0	90.3	0	88.6	0	89.5

V. Conclusions/Recommendations for Further Study

The available environmental fate and monitoring data for EDB and 1,2-DCA are summarized in this report. This information will be useful when assessing the potential risks associated with EDB and 1,2-DCA at petroleum hydrocarbon sites.

A. Properties

The physical/chemical similarities of the two compounds indicate that they will behave similarly in the environment. Both compounds are volatile, have relatively high water solubilities, and are soluble in organic solvents. Transport data show that they readily volatilize from water and soil surfaces as pure compounds and have low Koc values indicating that they have the potential to leach through soil to groundwater, although studies also indicate that a residual amount remains trapped in soil by absorption or in residual NAPL. Hydrolysis half-lives are slow, on the order of 1 to 10 years for EDB and tenfold longer for 1,2-DCA. However, in the presence of sulfur nucleophiles, abiotic half-lives potentially of weeks to months are reported for EDB and on the order of several years for 1,2-DCA. This process has not been either studied or observed in the field.

B. Biodegradation

Biotic degradation is reported for both compounds under aerobic and anaerobic conditions in laboratory studies. Based on these data, 1,2-DCA appears to be more resistant to biodegradation than EDB. Evidence for the anaerobic biodegradation of 1,2-DCA in the field includes the presence of biodegradation products in groundwater and changes in 13C/12C ratios of 1,2-DCA as the groundwater moves downgradient from the source area. More limited field data exist for EDB. The field study data collected for 1,2-DCA and EDB are typically reported as disappearance rate constants, particularly for aquifer studies. The use of these values as biodegradation half-lives is not appropriate, as loss due to other processes (both transport and abiotic degradation processes) is included in this rate constant.

The field study results and monitoring data for contaminated sites do indicate, in some instances, that biodegradation rates reported in laboratory studies may not be in good agreement with what is actually seen in the field. The best documented example of this is data from several groundwater plumes at the Massachusetts Military Reservation. The FS12 plume at this site resulted from a 1972 spill of 265,000 liters of aviation gasoline. When it was first detected in 1990, nearly 20 years later, concentrations of EDB up to 597 g/L were reported in the groundwater. One rough estimate of EDB's halflife at this site, based on the mass of EDB recovered during remediation procedures in the 1990s, was 18 years (Falta, 2004b). However, EDB disappearance half-lives calculated for 65 wells in South Carolina were clustered around values of 6 months to >1 year (Falta, 2004a), values that are in better agreement with laboratory studies.

High concentrations of fuel hydrocarbons present at leaded fuel release sites may also slow the biodegradation of 1,2-DCA and/or EDB in the environment. Laboratory studies for both EDB and 1,2-DCA were nearly always run using a single compound. A recent laboratory study by Henderson et al. (2007) suggests that biodegradation rates are slower for these compounds in the presence of fuel-contaminated groundwater.

C. Occurrence and Persistence at Field Sites

Information about the occurrence and persistence of EDB and 1,2-DCA at petroleum hydrocarbon release sites is emerging. Wilson et al. (2007) surveyed the presence of EDB in 17 states. 54% of 79 UST sites

had detectable concentrations. 43% of the total sites had concentrations of EDB greater than the MCL (132 positive detections out of 736 samples; 11% of the EDB detections had concentrations >MCL). In contrast, 23% of 39 UST sites in 12 states had detectable concentrations of 1,2-DCA. 15% of the total sites had concentrations of 1,2-DCA greater than the MCL (18 positive detections out of 293 samples; 3% of the 1,2-DCA detections had concentrations >MCL). One should be careful when drawing conclusions about the relative frequency of occurrence between EDB and 1,2-DCA. The MCLs for EDB and 1,2-DCA are 0.05 µg/L and 5µg/L, respectively. Detection limits for EDB (Method 8011) and 1,2-DCA (Method 8260) are 0.01 µg/L and approximately 0.1 µg/L, respectively. Comparisons of occurrence between EDB and 1,2-DCA should consider the differences in their MCLs, detection limits and reporting limits.

When evaluating the environmental significance of EDB and 1,2-DCA at a given site, it is important to evaluate their risk relative to other compounds of concern at the site. For example, Wilson et al. (2007) compared the relative risk associated with EDB and benzene in samples by dividing the measured concentration of EDB or benzene by their respective MCL. At only approximately 25% of the sites with the highest EDB concentrations, is the relative risk of EDB higher than benzene.

Recent papers have begun to explore plume morphology at different sites and to look at geological and surface features that may affect the behavior of EDB in the environment (Miner, 2005). Similar studies are not available for 1,2-DCA. While 1,2-DCA and EDB have been reported to react with sulfur nucleophiles, no studies are available examining whether this occurs in sulfate-reducing groundwater or whether it is possible to observe this degradation pathway in the field sites. In addition, very little information is available on the effect of different electron acceptors on the rate of anaerobic biodegradation for these two compounds.

Additional fieldwork is needed to confirm the factors which cause EDB to form relatively long plumes in some sites and not at others. One hypothesis is that there are significant residual NAPL source areas at sites with persistent plumes. Soil type may also play a role. Relative to coarser grained soils, EDB flux from fine-grained soils would be lower and it would take a longer time before levels would fall below its very low MCL. Groundwater bypassing of significant amounts of residual NAPL (Rixey, 1996) could also contribute to plume longevity at some sites.

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