

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

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

Regulatory and Scientific Affairs Department

API PUBLICATION 4774
DECEMBER 2008

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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 valves 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 widespread 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 K_{oc} 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.

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 inhibit 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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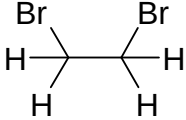
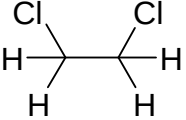
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I. Introduction

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 ₂ H ₄ Br ₂	C ₂ H ₄ Cl 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 widespread 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; Laternus, 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).

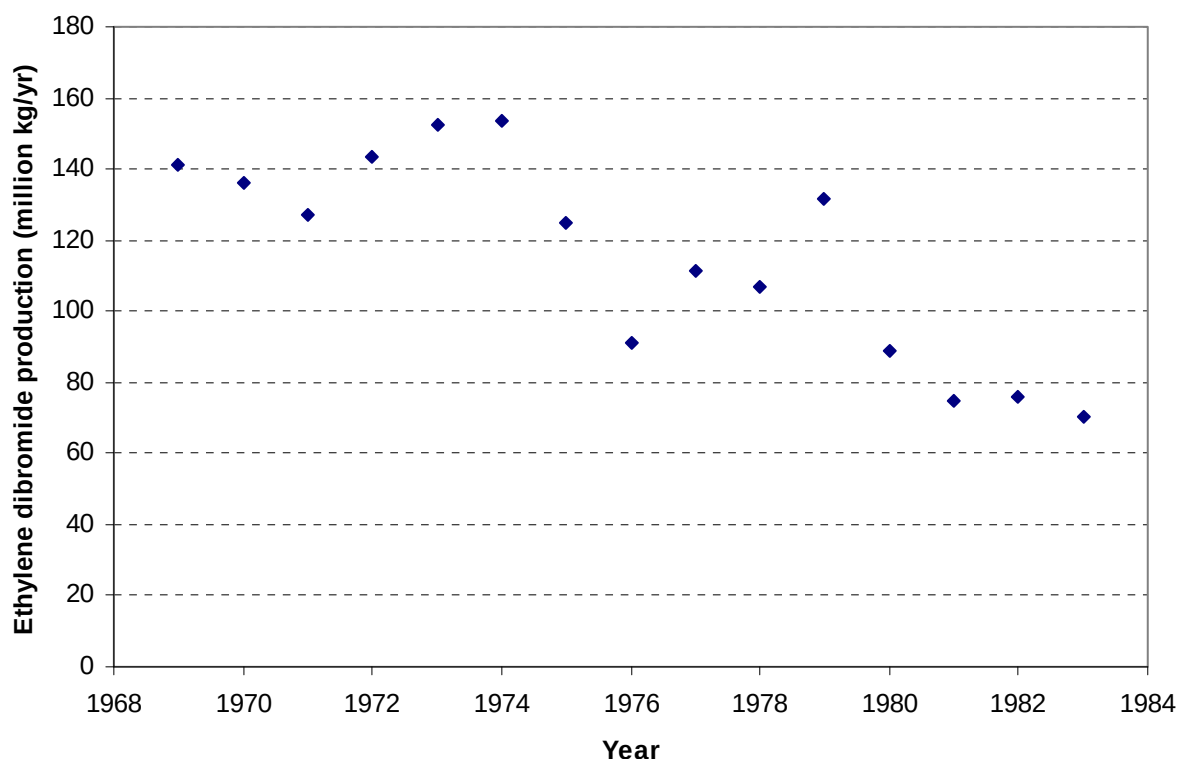


Figure 1. Annual U.S. production of EDB from 1969 to 1983 (U.S. ITC, 1970–1984)

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 valves 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:

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

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

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

Equivalently, for a measured gasoline to water partition coefficient

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

With 2_w ($\text{cm}^3\text{-water}/\text{cm}^3\text{-soil}$) volumetric moisture fraction in soil matrix, equal to the total soil porosity in saturated soil; Δ_s ($\text{g-soil}/\text{cm}^3\text{-soil}$) is the soil dry bulk density; f_{oc} ($\text{g-oc}/\text{g-soil}$) is the mass fraction of organic carbon in soil; and $K_{oc,i}$ ($\text{cm}^3\text{-water}/\text{g-oc}$) 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 2_o ($\text{cm}^3\text{-oil}/\text{cm}^3\text{-soil}$), Δ_o ($\text{g-oil}/\text{cm}^3\text{-oil}$), 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:

$$K_{gw} = K_{ow} \cdot \frac{MW_{oc \tan ol}}{MW_o} \quad \text{Eq. 4}$$

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 $\mu\text{g}/\text{L}$ EDB. Falta (2004b), however, reported a potential maximum concentration of 1900 $\mu\text{g}/\text{L}$ 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	$\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$	
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	6.5×10^{-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	1.0×10^{-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 77.2×10^{-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 1.24×10^{-5} g/cm²-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 4.5×10^{-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-treatment 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 m²/g, organic-carbon content of 49.3%) and a mineral soil (BET surface area of 11.2 m²/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 carbon²CEC = 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 μ M (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 μ M), 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-equilibrium 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 μ g/kg were reported for diameter ranges of 106–250, 53–106, 2–53, and 0–2 μ m, respectively, for one soil. EDB concentrations of 104, 164, 66, and 34 μ g/kg were reported for the second soil, respectively. Concentrations were highest for the very fine sand fraction (53–106 μ m) and lowest in the clay fraction (<2 μ m) (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 μ g/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 $\mu\text{g/L}$ although the concentration varied over the next 27 months from a low of 0.94 to a high of 2.29 $\mu\text{g/L}$. 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).

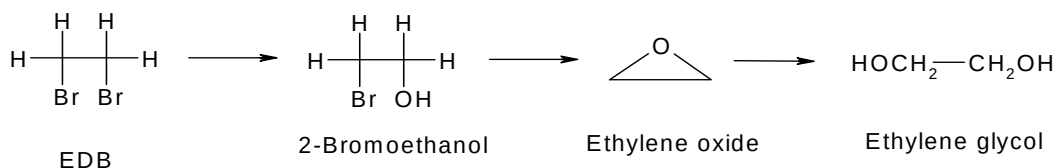
D. Transformations

1. Abiotic Transformations

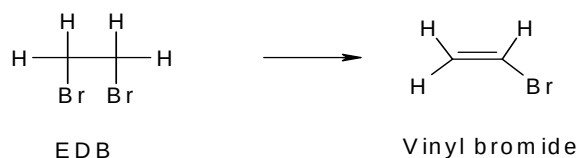
a. Hydrolysis

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. $\text{S}_\text{N}2$ (substitution) hydrolysis reaction of EDB in water:



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



The hydrolysis of EDB is primarily $\text{S}_\text{N}2$ 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 $\text{S}_\text{N}2$ 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 $\mu\text{g/L}$), 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 $3.7 \times 10^{-4} \text{ day}^{-1}$ and $3.1 \times 10^{-5} \text{ day}^{-1}$, 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 $2.5 \times 10^{-10} \text{ M}^{-1} \text{ min}^{-1}$).

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 °C. 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

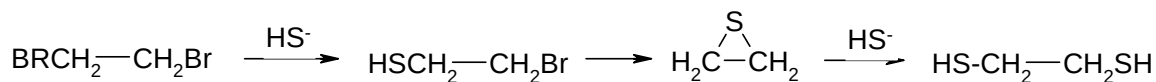
T_{1/2} (years)	Temp. (°C)	Comments	Reaction products	Reference
pH Independent Reactions				
4.6	25	Extrapolated to zero buffer from 0.05M phosphate buffer data. Proceeds primarily via S _N 2 mechanism.	7.7% vinyl bromide	Barbash and Reinhard (1989)
14	20	Neutral hydrolysis, $k = 7.2 \times 10^{-4} \text{ hr}^{-1}$		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. $k_H = 2.1 \times 10^{-7} \text{ min}^{-1}$ at 25 °C $K_b = 2.5 \times 10^{-10} \text{ min}^{-1}$ at 25 °C		Jeffers and Wolfe (1996)
8	20	Measured in aqueous buffer, T _{1/2} for pH 7. $k = 0.00189 \text{ hr}^{-1}$ (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-1 st order kinetics followed between 40 to 70 °C.	Bromide ion, ethylene glycol	Weintraub et al. (1986)
Base-Promoted Reactions				
1154	25	$k_{OH} = 1.91 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$	E ₂ product (~95% at 30 °C)	Hine and Langford (1956)
2.0×10^{-4}	20	$k_{OH} = 4.0 \times 10^{-2} \text{ M}^{-1} \text{ hr}^{-1}$		Ehrenberg et al. (1974)
5035	25	$k_{OH} = 4.4 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$		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 [$8.6 \times 10^{-3} \text{ day}^{-1}$ ($k_{\text{H}_2\text{O}}$) versus $6 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ (k_{HS^-})] (Barbash and Reinhard, 1987). Rate constants for the $\text{S}_{\text{N}}2$ and E_2 reactions of EDB and HS^- at 25 °C are $23 \text{ M}^{-1} \text{ day}^{-1}$ and $9.6 \text{ M}^{-1} \text{ day}^{-1}$, 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 0.67 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 ₂ S 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 ₂ S), 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 _N 2 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 ₂ O 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: 2.50×10^{-13} cm³/molecule-sec, at 23 °C (Howard and Evenson, 1976), 2.25×10^{-13} cm³/molecule-sec at 24 °C, and 1.86×10^{-13} cm³/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 1.5×10^6 OH radicals/cm³ and a 12-hour day. Products of this reaction include formyl bromide, CHOCH₂Br, CBr(O)CH₂Br (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).

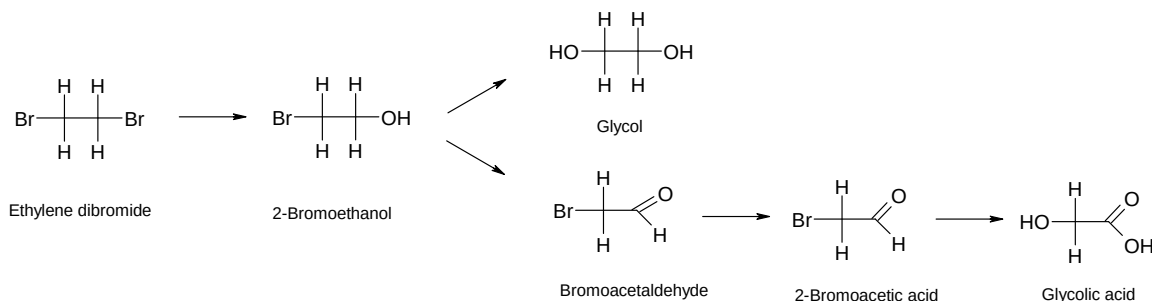
2. Biotic Transformations

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

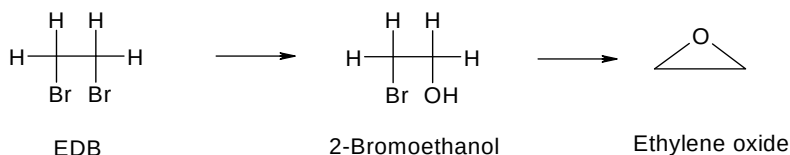
Based on the reaction pathway information from the pure culture studies summarized in Table 6, the aerobic and anaerobic biodegradation of EDB has been reported to proceed via several pathways.

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 halohydrilase) 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).

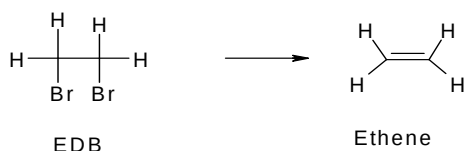


2. A second aerobic biodegradation pathway was proposed based on work by Poelarends et al. (1999). A pure culture of *Mycobacterium* sp. Strain GP1, able to use EDB as its sole carbon and energy source, degraded EDB to 2-bromoethanol using a hydrolytic haloalkane dehalogenase. A haloalcohol dehalogenase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

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

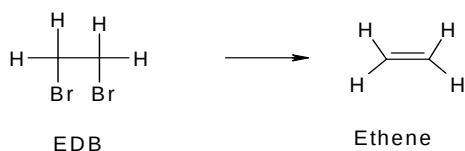


3. The aerobic microbial reductive elimination of EDB to ethene was reported by Castro et al. (1989) for *Pseudomonas putida* PpG-780. The enzyme responsible for this reaction was a P-450 cam heme protein. This pathway does not necessarily mirror the dihaloelimination reaction seen for anaerobic pure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

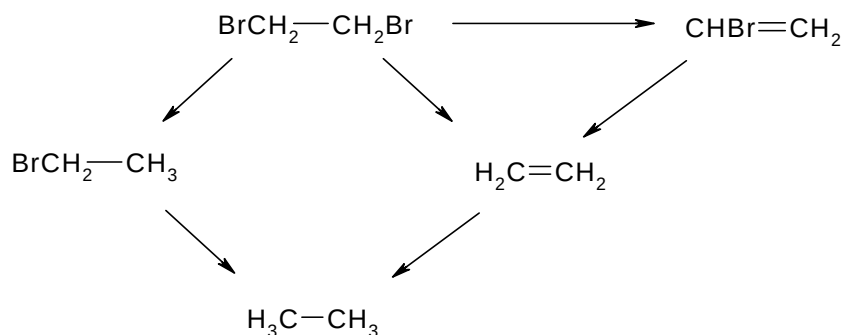


Table 6. Pure culture strains studied for their ability to degrade EDB

Strain	Aerobic or anaerobic	Notes	Reference
<i>Xanthobacter autotrophicus</i> 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)
<i>Ancylobacter aquaticus</i>	Aerobic	Cannot degrade EDB, attributed to lack of a bromoacetaldehyde dehydrogenase and accumulation of toxic bromoacetaldehyde.	Van der Ploeg et al. (1995)
<i>Acinetobacter</i> sp. GJ70	Aerobic	Currently described as a gram-positive actinomycete-like organism, not an <i>Acinetobacter</i> 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)
<i>Mycobacterium</i> 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)
<i>Nitrosomonas europaea</i>	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)
<i>Arthrobacter</i> 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)
<i>Pseudomonas putida</i> PpG-780	Aerobic	Used EDB as its sole carbon and energy source. Reaction proceeds via reductive elimination to ethene.	Castro et al. (1989)
<i>Methanobacterium thermoautotrophicum</i> JH	Anaerobic	Methanogen. Cells grown on H ₂ -CO ₂ . Degrades EDB to ethene via vicinal reduction.	Belay and Daniels (1987)
<i>Methanococcus deltae</i> LH	Anaerobic	Methanogen. Cells grown on H ₂ -CO ₂ . Degrades EDB to ethene via vicinal reduction.	Belay and Daniels (1987)
<i>Methanococcus thermolithotrophicus</i>	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 CO₂, 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 ¹⁴C-radiolabel and included CO₂ 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 N₂, 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. ¹⁴C-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, ¹⁴C-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 CO₂ 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 Φg/L) were not biodegraded over an 8-week period as monitored by GC results and ¹⁴C 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, ¹⁴C-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, ¹⁴C-volatile products, ¹⁴CO₂, 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, ¹⁴C-volatile products, ¹⁴CO₂, 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 ¹⁴C-radiolabel was recovered as EDB following passage through the nitrate-reducing column (Bouwer and Wright, 1988).

¹⁴C-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 CO₂, 6–17% remained as EDB, 6.9–4.1% was found as unextractable ¹⁴C in culture filtrate, and 23–33% was unextractable ¹⁴C bound to solids after 13 days (Pignatello, 1986a). The presence of nearly equal amounts of ¹⁴CO₂ and unextractable ¹⁴C 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. LC₅₀ 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 CO₂ 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 $\mu\text{g}/\text{kg}$ 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 $\sim 200\text{--}300\text{ }\mu\text{g}/\text{L}$, 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 $50\text{ }\mu\text{g}/\text{L}$ by day 380. After day 120, very little further biodegradation of EDB was observed through day 380. At an initial concentration of $10\text{ }\mu\text{g}/\text{L}$, 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 $0.25\text{ }\mu\text{g}/\text{L}$ 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/P¹	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 to 11 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 to 11 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. Respirography reduced the lag period but total removal below the ~100 ppb persisted. Site overlies an EDB-contaminated aquifer (0.1 to 11 µg/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		1 st yr T _{1/2} = 26 2 nd yr T _{1/2} = 115–200	Soil fumigation study. 1987 study. Non-1 st 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		1 st yr T _{1/2} = 36 2 nd yr T _{1/2} = 115–200	Soil fumigation study. 1986 study. Non-1 st 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/m²) (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)

1 st 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 Φ g/L, respectively, in 1993/1996 and 100, 110, and 3.9 Φ g/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 Φ g/L, respectively, in 1993/1996 and 9.3, 65, and 220 Φ g/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 Φ g/L, respectively, in 1993 and 6.3 and 3.3 Φ g/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) $\pm$ 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 $\mu\text{g/L}$, 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 $\mu\text{g/L}$, respectively (U.S. EPA, 2006). 1,2-DCA is also present in FS-12 with maximum concentrations of 1.7 and 0.115 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ (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 $\mu\text{g/L}$ (Falta, 2004b). This detached plume was delineated with wells in 1998 and a maximum EDB concentration of 10 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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.