Natural Attenuation of Lead Scavengers EDB and 1,2-DCA

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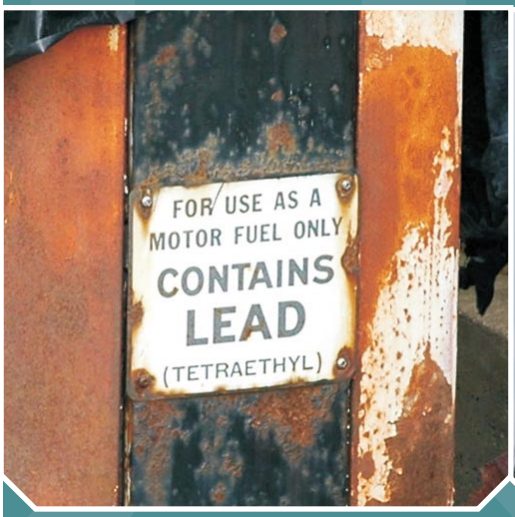

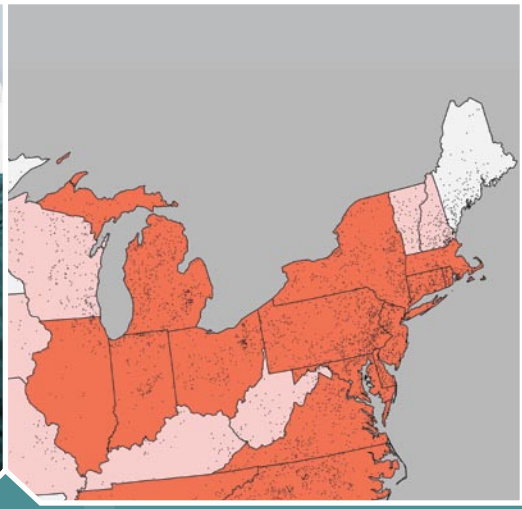

Office of Research and Development
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Notice

The U.S. Environmental Protection Agency through its Office of Research and Development funded portions of the research described here. Mention of trade names and commercial products does not constitute endorsement or recommendation for use. All research projects making conclusions and recommendations based on environmentally related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project was conducted under a Quality Assurance Project Plan for Task 5857. Work performed by U.S. EPA employees or by the U.S. EPA on-site analytical contractor followed procedures specified in these plans without exception. Information on the plans and documentation of the quality assurance activities and results are available from Cherri Adair or John Wilson.

Front Cover photos:

Courtesy of: Ron Falta and John Wilson

#1 Warning on a dispenser for leaded gasoline.

#2 Examining a water sample from a monitoring well to see if the sample has been collected properly.

#3 Vulnerability of shallow ground water wells to contamination with EDB.

Foreword

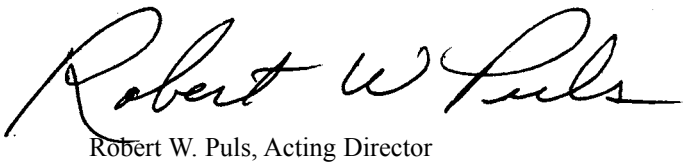
The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

Tetra-ethyl lead was widely used in leaded automobile gasoline from 1923 until 1987. To prevent lead deposits from fouling the engine, 1,2-dibromoethane (EDB) and 1,2-dichloroethane (1,2-DCA) were added to the gasoline to act as lead scavengers. These compounds reacted with lead in the engine to make volatile compounds that were discharged in the exhaust. If leaded gasoline is spilled to ground water from a leaking underground storage tank, there is a potential for EDB and 1,2-DCA to partition from the spill and contaminate ground water. The Maximum Contaminant Levels (MCLs) for EDB and 1,2-DCA are 0.05 and 5.0 µg/L respectively. The concentrations of EDB and 1,2-DCA that would be expected in ground water in contact with unweathered leaded automobile gasoline are 1,900 and 3,700 µg/L respectively.

Lead was effectively banned in gasoline in the USA before the underground storage tank program was fully implemented. As a result, only a portion of the state agencies that implement the federal UST program routinely monitor for EDB and 1,2-DCA at gasoline spill sites. In many states, little is known of the risk from EDB and 1,2-DCA at old leaded gasoline spill sites. Monitored Natural Attenuation (MNA) is widely used by State Agencies to manage the risk from other fuel components, such as benzene, in ground water. The appropriate application of MNA requires a solid understanding of the behavior of the contaminants in ground water.

To provide a technical basis for application of MNA, this report reviews the current knowledge of the transport and fate of EDB and 1,2-DCA in ground water. This report also provides information on the distribution of EDB and 1,2-DCA at motor fuel release sites that was collected during a survey of sites coordinated by the U. S. EPA Office of Underground Storage Tanks and the Association of State and Territorial Solid Waste Management Officials (ASTSWMO) and evaluates the associated chance of contaminating ground water.



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Acknowledgment

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Executive Summary

The lead scavengers Ethylene Dibromide (EDB) and 1,2-Dichloroethane (1,2-DCA) were added to leaded motor gasoline to prevent the buildup of deposits of lead oxide inside internal combustion engines. Recent studies demonstrate that lead scavengers may persist for long periods of time in certain ground water environments. Although lead and lead scavengers were phased out in conventional motor gasoline by the end of the 1980s, the lead scavengers from old releases may continue to contaminate ground water at many gasoline service station sites. In addition, aviation gasoline (Avgas) contains lead scavengers, and gasoline containing lead scavengers is still used for certain off-road applications such as automobile racing. There is a significant possibility that lead scavengers from releases of leaded gasoline pose an ongoing risk to ground water quality.

Domestic ground water wells and certain small public water supply wells that are in close proximity to sites where leaded gasoline may have been released should be of particular concern. These wells often produce ground water from shallow aquifers, which makes them more vulnerable to contamination than larger municipal water supply wells which usually produce water from deeper aquifers.

EPA has formed a team with the Association of State and Territorial Waste Management Officials to determine the scope and magnitude of the occurrence of lead scavengers at leaking UST sites. The team developed a three-phased approach to this problem: (1) developing an understanding of the magnitude of the potential problem by compiling existing background information, (2) assessing gaps in current knowledge, based on the findings of Phase 1, and implementing appropriate measures to fill the gaps, and (3) determining an appropriate response based on evaluation of the results of Phases 1 and 2.

Phase 1 culminated in development of a document entitled Lead Scavengers Compendium: Overview of Properties, Occurrence, and Remedial Technologies (U.S. EPA, 2006). Phase 2 consisted of collecting and analyzing ground water samples from 102 old gasoline release sites spread across the 19 states that chose to participate in the investigation. This report *Natural Attenuation of the Lead Scavengers 1,2-Dibromoethane (EDB) and 1,2-Dichloroethane (1,2-DCA) at Motor Fuel Release Sites and Implications for Risk Management* represents the culmination of Phase 2. It fills some of the data gaps on the expected distribution of lead scavengers at gasoline release sites, it discusses mechanisms for abiotic transformation and biodegradation of EDB and 1,2-DCA, and it provides new tools to recognize and use natural transformation and degradation of EDB and 1,2-DCA as part of a risk management strategy.

The survey found that significant concentrations of EDB continue to persist at many old leaded gasoline spill sites. Both EDB and 1,2-DCA were present at concentrations above their respective Maximum Concentration Level (MCL) at a significant number of sites; EDB was detected above its MCL of 0.05 µg/L at 42% of the sites sampled, and 1,2-DCA was detected above its MCL of 5.0 µg/L at 15% of the sites sampled. Benzene (with an MCL of 5.0 µg/L) was present at 100% of the sites sampled and was the primary risk driver at 75% of the sites where both benzene and EDB were present in ground water; EDB was the primary risk driver in the remaining 25% of sites.

The persistence of EDB at UST spill sites is consistent with its expected behavior in ground water. Simple physical weathering of EDB and 1,2-DCA from residual gasoline is a slow process that may require decades to centuries to reduce high concentrations of EDB or 1,2-DCA to their MCLs. At some sites, anaerobic biodegradation can provide substantial reductions in the concentrations of EDB and 1,2-DCA. At some sites, abiotic degradation caused by reaction with Iron(II) sulfide minerals in aquifer material can also produce substantial reduction in the concentration of EDB, particularly in ground water at neutral pH.

Although it is theoretically possible that anaerobic biodegradation or abiotic degradation will remove EDB at a particular site, it is frequently difficult to prove that degradation is occurring based on conventional monitoring data. Compound Specific Isotope Analysis (CSIA) can be useful to recognize biodegradation and

abiotic transformation of EDB ground water. Degradation is recognized and documented by a change in the ratio of stable isotopes of carbon in the molecules of EDB that remain in the ground water after degradation. The change in the ratios can put a conservative boundary on the extent of degradation that has occurred in the ground water sampled by a particular well. This makes CSIA a useful tool to prove that degradation has happened at field scale at a particular site.

If the concentrations of EDB and 1,2-DCA in ground water in the source area of plumes do not attenuate, the hazard associated with these contaminants will persist indefinitely. MNA is most cost effective as a remedy when the concentrations of contaminants attenuate to their MCLs in a reasonable period of time. The concentrations of EDB and 1,2-DCA that would be expected in ground water in contact with unweathered leaded automobile gasoline are 1,900 and 3,700 µg/L respectively. To bring these initial concentrations to their MCL within 20 years, the first order rate of attenuation in concentration in the most contaminated well at a site should be 0.5 per year or greater for EDB and 0.33 per year or greater for 1,2-DCA. At certain sites, and under some circumstances, rates in excess of 0.5 per year for EDB or 0.33 per year for 1,2-DCA can be attained through anaerobic biodegradation or by abiotic reactions. To apply MNA at a specific site, rate constants for attenuation over time should be extracted from site-specific data and should be verified and validated by continued long-term monitoring.

Monitoring for concentrations of EDB in ground water can be a major cost of risk management at gasoline spill sites. The MCL for EDB is one hundred fold lower than the MCLs for Benzene or 1,2-DCA. Because the MCL for EDB is so low, not all analytical methods can detect EDB when it is present at its MCL. The EPA Method that is most commonly used to analyze for gasoline constituents in ground water (Method 8260B) has a detection limit for EDB of approximately 3.0 µg/L, which is sixty fold higher than the MCL. As a result, Method 8260B cannot be used to document that ground water is free of contamination from EDB. In contrast, EPA Method 8011 has a method detection limit for EDB of approximately 0.01 µg/L, which is sufficiently sensitive to measure EDB at its MCL.

Method 8260B would have only discovered 40% of the survey sites with concentrations of EDB above its MCL. At sites where benzene is the primary risk driver, Method 8260B would be appropriate to monitor the quality of ground water during active remediation. However, to determine if the site has reached the MCL for EDB, it is necessary to use Method 8011 or its equivalent.

Keywords: EDB, 1,2-dibromoethane, DCA, 1,2-DCA, 1,2-dichloroethane, ground water, UST, underground storage tank, MNA, Monitored Natural Attenuation

1.0 Introduction

This section reviews the use of the lead scavengers 1,2-dibromoethane (also called ethylene bromide or EDB) and 1,2-dichloroethane (1,2-DCA) in leaded motor fuel , and briefly describes the regulatory framework developed to protect ground water resources from releases of leaded motor fuel[1] stored in underground storage tanks. Also, this section describes two investigations of EDB and 1,2-DCA at motor fuel release sites. Finally, this section describes the scope and intended purpose of this report.

1.1 Use of EDB and 1,2-DCA in Leaded Motor Fuel

Internal combustion engines burn a mixture of fuel and air to create mechanical energy that turns a crankshaft. The most common automotive engine operates on a four-stroke cycle: intake, compression, combustion, and exhaust. During the compression cycle, a mixture of air and fuel vapor is compressed by a piston moving upward in its cylinder. Ideally, at the height of the compression cycle, the mixture is ignited by a spark from the spark plug, thus initiating the "combustion" stroke, whereby the piston is pushed downward in the cylinder producing the mechanical energy that turns a crankshaft. During the next upstroke of the piston, exhaust gases are expelled from the cylinder. Sometime during the combustion stroke, pockets of unburned fuel outside the advancing flame front within the cylinder are heated and pressurized leading to sudden ignition ("detonation") resulting in engine "knock". Engine knock is damaging to the mechanical parts of the engine and it wastes fuel.

To reduce the tendency to knock, various additives have been used to increase the octane of the motor fuel. These additives have included tetra-ethyl lead (TEL) since the 1920s, and since the 1960s tetra-methyl lead (TML), tri-methyl-ethyl lead (TMEL), di-methyl-di-ethyl lead (DMDEL), and methyl-tri-ethyl lead (MTEL). The additives to increase octane also included methyl tertiary-butyl ether (MTBE) and ethanol.

Tetra-ethyl lead was widely used in motor gasoline from 1923 to 1987 (Falta, 2004). Lead oxide deposits produced during the combustion of leaded motor fuel can accumulate and damage the engine. To make the lead volatile and thus reduce the accumulation of lead deposits, the lead scavengers EDB and 1,2-DCA were added to gasoline along with the TEL. With these additives, the lead forms lead dihalides which are volatile and can be expelled from the engine.

Starting in 1975, automobiles in the U.S. were fitted with catalytic converters to treat the exhaust gas and allow the vehicles to meet U.S. EPA standards for emissions to control air pollution. Because lead in motor fuel can poison the catalyst and ruin the catalytic converter, in 1973 EPA (a) required that one grade of unleaded gasoline be available to protect catalytic converters that were to appear on new cars in 1975, and (b) re-proposed annual reductions in lead content of all other grades of gasoline to protect public health[2]. Figure 1.1 presents estimates of gasoline consumption in the U.S. that were collected and collated by Falta (2004). It also estimates the consumption of EDB and 1,2-DCA in gasoline, based on the estimates of Falta (2004) for lead consumed in gasoline, and his observation "Since the early 1940s, leaded automotive gasoline has contained EDB and 1,2-DCA in proportion to the amount of tetraalkyllead with a molar ratio of Pb:Cl:Br of 1:2:1..."

The proportion of EDB and 1,2-DCA consumed each year to the total gasoline consumed each year changed little from 1949 to 1972. The peak years for use of EDB and 1,2-DCA were 1969 through 1972. After 1972, the total amount of EDB and 1,2-DCA consumed in automobile gasoline declined as the content of lead declined in gasoline. After 1988, much less EDB and 1,2-DCA were added to conventional automobile gasoline in the

1 "Leaded motor fuel" is a more inclusive term that includes leaded gasoline for automobiles plus aviation gasoline, which still contains lead and a lead scavenger package, and some grades of racing fuel. Where this report refers more specifically to "gasoline" it is because the data and information pertain to leaded gasoline for automotive purposes.

2 Even though leaded gasoline has not been used for on-road automobiles for nearly two decades, leaded gasoline (which also contains lead scavengers) is still in use in aviation gasoline (avgas) and in some off-road applications such as racing fuel.

United States because leaded gasoline had largely been phased out.

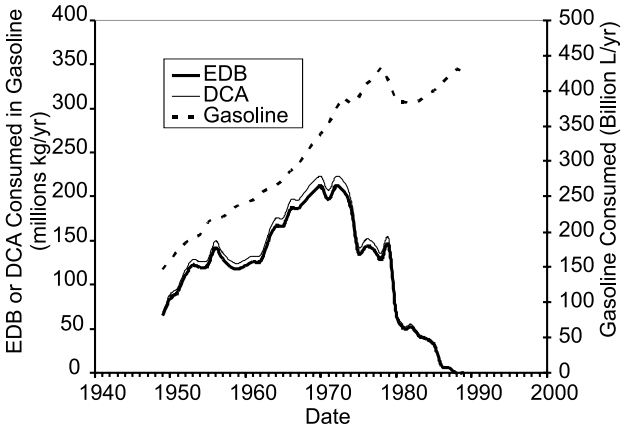

Figure 1.1. Consumption of leaded motor fuel, EDB, and 1,2-DCA in the United States from 1949 through 1989.

Although lead and lead scavengers were phased out in conventional motor gasoline by the end of the 1980s, the lead scavengers from old releases may continue to contaminate ground water at many gasoline service station sites. In addition, aviation gasoline (Avgas) contains lead scavengers, and gasoline containing lead scavengers is still used for certain off-road applications such as automobile racing (Aronson and Howard, 2008).

A portion of the EDB produced in the US was used as pesticide and fumigant (Aronson and Howard, 2008), and ground water contamination continues in certain agricultural areas from the past use of EDB as an agricultural chemical. EDB was used on citrus crops, on vegetables, on grain crops, and to protect golf courses (U.S. EPA, 2006). In 1977 approximately 136 million kilograms of EDB was produced in the USA; 127 million kilograms was used in fuel, approximately 8 million kilograms was used as a soil fumigant, and approximately 0.9 million kilograms was used to fumigate stored grain and grain milling machinery, and quarantined citrus and other tropical fruits (U.S. EPA, 2006).

1.2 Regulation of Motor Fuel Storage to Protect Ground Water and Drinking Water

In 1974, Congress passed the Safe Drinking Water Act, which required U.S. EPA to determine safe levels of hazardous chemicals in drinking water. These safe levels are called Maximum Contaminant Level Goals or MCLGs. Because of the difficulty in achieving MCLGs, MCLs (Maximum Contaminant Levels) have been established for most contaminants; MCLs are a compromise based on best available treatment technology, limitations of analytical methods, and cost. In 1989, U.S. EPA promulgated MCLs for benzene and for 1,2-DCA of 5 µg/L. In 1992, U.S. EPA promulgated an MCL of 0.05 µg/L for EDB.

In 1984, Congress added Subtitle I to the Resource Conservation and Recovery Act (RCRA), which required U.S. EPA to develop a regulatory program for underground storage tank systems (USTs) that contained petroleum or certain hazardous substances (collectively referred to as "regulated substances"). The federal underground storage tank program is administered by the Office of Underground Storage Tanks (OUST), within the Office of Solid Waste and Emergency Response (OSWER). Subtitle I of the Resource Conservation and Recovery Act (RCRA) allows state UST programs approved by EPA to operate in lieu of the federal program. The U.S. EPA has granted State Program Approval to most of the states and the others implement their own program under cooperative agreements with EPA.

Most USTs are used for the storage of motor fuel (gasoline and diesel fuel) and the regulated substance that escaped from most leaking USTs was gasoline. The primary petroleum-derived contaminants of concern in gasoline are the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes (collectively referred to as "BTEX"). Most state programs treat the individual MCLs for the BTEX compounds as the concentration below which the compounds are not a concern at gasoline release sites. Even today ground water monitoring at gasoline release sites is focused on BTEX.

Most state agencies have not routinely monitored for EDB or 1,2-DCA in ground water. This may have been due to the fact that lead in gasoline, and therefore EDB and 1,2-DCA, was being phased out, or was altogether banned, at the time the state agencies put their monitoring programs in place. The South Carolina Department of Health & Environmental Control (SDHEC) was an exception.

Beginning in 2001, SDHEC started collecting data on the concentrations of EDB in monitoring wells at gasoline service stations that were in existence at a time when leaded gasoline was still available in the USA. EPA Methods 8260 or 8021, which are conventionally used for analysis of BTEX compounds and fuel oxygenates such as MTBE, do not have adequate sensitivity to determine concentrations of EDB at its MCL (0.05 µg/L).

The SDHEC required that analyses for EDB be performed by EPA Method 8011, which has a method detection limit that is near 0.01 µg/L.

1.3 Investigations of EDB and 1,2-DCA at Motor Fuel Release Sites

1.3.1 Evaluation of Data from South Carolina Performed at Clemson University

Professor R.W. Falta and his students at Clemson University evaluated the monitoring data on the distribution of EDB in ground water in South Carolina, and found that many gasoline release sites had concentrations of EDB that far exceeded the MCL (Falta, 2004; Falta et al., 2005). They analyzed the data available as of December 2004, and found that 537 underground storage tank sites had ground water with concentrations in excess of the MCL (Falta et al., 2005). Figure 2 of Falta et al., (2005) presented a frequency distribution of the maximum concentration of EDB in any well at each individual site. Figure 1.2 plots the data from Falta et al., (2005). The concentrations of EDB followed a log-linear distribution with approximately half of the sites having concentrations of EDB that exceed the MCL. The median concentration of EDB in sites where EDB was detected was 4.3 µg/L and the maximum concentration was 6,550 µg/L. These results were unexpected and surprised many ground water scientists and engineers. Staff in EPA's Region 4 office in Atlanta, GA, brought Dr. Falta's findings to the attention of the Office of Underground Storage Tanks (OUST) at EPA's headquarters in Washington, DC.

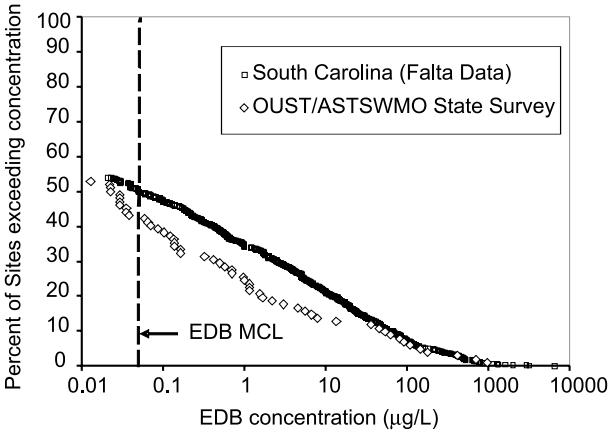

Figure 1.2. Distribution of EDB in ground water from monitoring wells at gasoline release sites in South Carolina, and in sites in the EPA/ASTSWMO Study.

1.3.2 EPA/ASTSWMO Lead Scavengers Team

The U.S. EPA's OUST and Office of Research and Development's National Risk Management Research Laboratory (NRMRL) in association with the Association of State and Territorial Solid Waste Management Officials (ATSWMO) formed a team to determine what problems, if any, these lead scavengers pose to public health and the environment. The team's mission statement outlines an investigation comprised of the following three phases:

1. Develop an understanding of the potential problem as it exists today by:
   a. Compiling existing background information: toxicological data; historical usage information; and occurrence in drinking water supplies;
   b. Evaluating selected state databases and case files for information on sampling, monitoring, and remediation at LUST sites;
   c. Conducting a study on the effectiveness and cost of treatment and remediation technology; and
   d. Assess whether or not there are any gaps in our current knowledge, based on the results of Phase 1. If so, develop and implement appropriate measures to fill the gaps.
2. Identify next steps by evaluating the results of Phases 1 and 2.

Phase 1 culminated in production of a compendium of information entitled *Lead Scavengers Compendium: Overview of Properties, Occurrence, and Remedial Technologies* (U.S. EPA, 2006). The compendium represents EPA's state of knowledge on lead scavengers (through 2005) relating to historical usage, physical and chemical properties, analytical methods, environmental fate and transport, toxicology, occurrence in drinking water supplies, presence at leaking UST sites, and the effectiveness and cost of treatment technologies. In compiling information for the compendium, some gaps in knowledge were identified, including the lack of information on the occurrence of lead scavengers in domestic (private) wells, the effectiveness of remediation and treatment technologies, and the magnitude of the occurrence of lead scavengers in ground water at leaking UST sites. Filling in this last data gap became the focus of Phase 2 of the investigation.

To develop information on the distribution of EDB and 1,2-DCA in ground water at leaking UST sites in states that did not routinely monitor for

these contaminants, EPA offered to provide free analysis of samples collected by the states (or their contractors) from sites that met certain criteria:

- sites that were used for storage and/or dispensing of leaded gasoline whether or not they were currently in use (i.e., sites where USTs were located in 1989 and earlier) or
- sites where leaded aviation gasoline (AvGas) or leaded racing fuel was used or is still being used (i.e., airports, automobile race tracks) and
- sites that had existing monitoring wells on-site and were regularly scheduled for monitoring (this was done to minimize the burden on states and their contractors; however, no sites offered as candidates for sampling were turned down).

Sites meeting the criteria above that were also within close proximity to a private well or small community well were of particular interest because such wells are more vulnerable to contamination than larger municipal water supply wells.

States that volunteered to participate in the investigation were provided with a sampling kit for each candidate site. Typically the kit was shipped to the contractor that routinely sampled the wells at the site. Sample vials were filled by the contractor at the time the wells were sampled for normal compliance monitoring, and the samples were returned to NRMRL at the R.S. Kerr Environmental Research Center in Ada, Oklahoma, for analysis of EDB by Method 8011, and benzene and 1,2-DCA by Method 8260. Details of sampling, preservation, shipment, storage, and analysis are presented in Appendix A. Samples were provided between October 2005 and July 2007. A total of 19 states provided samples from a total of 802 monitoring wells spread over 102 sites (Table 1.1).

Table 1.1. Occurrence of EDB in ground water provided by the state agencies that participated in the EPA/ASTSWMO State Study.

State	Number Samples	Number Sites	Number Sites	Number Sites
			EDB detected	EDB>MCL
Arizona	12	1	1	1
Colorado	107	9	4	2
Georgia	12	2	1	1
Maryland	27	3	2	2
Minnesota	29	4	3	3
Missouri	16	8	2	2
Mississippi	28	2	2	2
Montana	31	11	5	3
North Carolina	25	6	6	6
North Dakota	34	6	2	0
New Hampshire	63	4	3	3
New Mexico	15	1	1	1
Oklahoma	57	10	6	5
South Carolina	50	5	5	5
South Dakota	67	5	2	0
Tennessee	90	7	3	1
Utah	37	5	3	3
Vermont	19	3	1	1
Wisconsin	83	10	2	2
Total	**802**	**102**	**54**	**43**

1.4 Purpose and Scope of This Report

This report represents the culmination of Phase 2 of the EPA/ASTSWMO study. It fills some of the data gaps on the expected distribution of EDB at gasoline release sites, it identifies a previously unsuspected role of iron(II) sulfides in the abiotic transformation of EDB in ground water, and provides new tools to recognize and use natural transformation and degradation of EDB and 1,2-DCA as part of a risk management strategy.

2.0
Transport and Fate of EDB and 1,2-DCA at Motor Fuel Release Sites

This section is intended for technical personnel who will conduct a risk evaluation for EDB or 1,2-DCA at specific motor fuel release sites, and for the technical staff of regulatory agencies that review the risk evaluations and make decisions concerning risk management and cleanup of the contamination.

The implementation of Monitored Natural Attenuation (MNA) as part of a program of risk-based corrective action for contaminants in ground water requires a robust understanding of the exposure to the contaminant, which in turn requires a robust understanding of the transport and fate of the contaminant from the point of release to the receptor. This section presents a conceptual model for the behavior of a release of EDB and 1,2-DCA in leaded gasoline into the subsurface environment. It discusses the available information on the attenuation of EDB and 1,2-DCA caused by weathering of the original mass of gasoline released, and the relationship between weathering and the persistence of EDB and 1,2-DCA in source areas at motor fuel release sites. This section also discusses the effect of sorption on the attenuation of concentrations of EDB and 1,2-DCA along a flow path in ground water, and it also presents new information on the rate of abiotic degradation caused by sulfide in solution in ground water, or by FeS mineral phases precipitated in the aquifer matrix as a result of sulfate reducing activity. This section also discusses prospects for biodegradation of EDB and 1,2-DCA, and provides data on the rate of anaerobic biodegradation of EDB and 1,2-DCA in ground water at gasoline spill sites. It also describes the application of Compound Specific Isotope Analysis (CSIA) for documenting the degradation of EDB and 1,2-DCA.

2.1 Conceptual Model of a Motor Fuel Release in the Subsurface

Gasoline released from an underground storage tank seeks the water table. If it is released above the water table it drains downward by gravity. If it is released below the water table it rises by buoyancy. Gasoline can act as a wetting phase for particles in the unsaturated zone. As a consequence, it tends to move into the capillary fringe just above the water table where it is held by capillary attraction. Over time, capillary attraction will re-distribute the gasoline in a roughly circular or oval shape just above the water table. As the re-distribution continues, the area contaminated with liquid phase gasoline gets larger and the concentration of liquid phase gasoline declines until the gasoline can no longer maintain a continuous wetting phase on the aquifer solids. At this point the gasoline breaks into discrete droplets that are no longer in contact with each other, the redistribution of gasoline stops or slows, and the gasoline is said to be at residual saturation.

There are several ways that soluble contaminants from gasoline can enter the ground water. Soluble contaminants can diffuse from the gasoline in the capillary fringe down into the ground water. Recharge water draining down through the unsaturated zone can perfuse the gasoline and carry soluble contaminants to the ground water. Finally, variations in the elevation of the water table can inundate the residual gasoline, allowing soluble contaminants to partition directly into the ground water. At most sites, the elevation of the water table will vary a few inches to a few feet in a year's time. As the water table moves up and down, the gasoline in the capillary fringe moves up and down, creating a "smear zone" that contains gasoline at residual saturation. Under typical conditions, the lower portion of the smear zone is below the average elevation of the water table.

The most contaminated wells at a site are usually screened in material that has gasoline at residual saturation. Over time, residual gasoline tends to accumulate in the geological material with the finest texture: silt and clays rather than sands or gravels. This is probably because the material with

finer texture has a higher capillary attraction for the residual gasoline.

The concentration of soluble contaminants in ground water produced by the wells is controlled by equilibrium partitioning of the contaminants between the ground water and residual gasoline. As a consequence, the rate of attenuation of concentrations of EDB over time in monitoring wells in the source area of releases is controlled by the rate at which EDB dissolves from the residual gasoline into the flowing ground water and is either flushed away by ground water flow, or destroyed by biodegradation or abiotic transformation.

The rate of attenuation over time in sediment contaminated with residual gasoline determines how long a release of gasoline can continue to contaminate ground water. Once a contaminant enters the flowing ground water and moves away from the residual fuel in the source area, the concentration of the contaminate can be attenuated by processes such as dilution and dispersion, sorption to native organic matter, biodegradation by aerobic or anaerobic microorganisms, by neutral hydrolysis, or by non biological reactions with either sulfide in solution, or with sulfide minerals. The rate of removal in the flowing ground water will determine how far the plume of contamination can reach.

2.1.1 Mathematical Description of Rates of Attenuation

The exposure assessment that is conducted as part the RBCA processes usually incorporates a mathematical description of the behavior of the contaminants at a site. This can be as simple as a few calculations with equations that describe the transport and fate of the contaminants, or it can require the calibration of a computer model to describe the behavior of the plume of contaminated ground water in time and space. In any case, the RBCA process requires a quantitative understanding of the behavior of the contaminant. The following section reviews the mathematics typically used to describe the behavior of organic contaminants in ground water, identifies rates of removal that are needed for MNA to be a practical alternative for EDB and 1,2-DCA at many sites, and reviews the literature on the rates of attenuation of EDB and 1,2-DCA over time in the source area of plumes in ground water at gasoline spill sites.

2.1.2 Relationship between a First Order Rate Constant and a Half Life

Attenuation processes that follow a first order rate law can be described with either a half life or a pseudo first order rate constant. Readers that are familiar with these relationships can skip to the next section.

When the rate of reaction is proportional to the concentration of the contaminant, the progress of the reaction can be described by equation 2.1;

$$\frac{C_t}{C_o} = e^{kt} \qquad (2.1)$$

where t is the time elapsed during the reaction, C_t is the concentration after time t, C_o is the original concentration, and k is the first order rate constant for the instantaneous rate of change in concentration over time. When k has a negative value, concentrations are declining over time. The rate constant for the rate of attenuation, the rate of abiotic transformation, or the rate of biodegradation is the negative of the rate constant for the rate of change (k) in Equation 2.1. The solution of Equation 2.1 for k yields Equation 2.2.

$$k = \ln\left(C_t / C_o\right) / t \qquad (2.2)$$

The half life corresponds to the value of t where one half of the contaminant has been destroyed, as described in Equation 2.3.

$$t_{1/2} = \ln\left(0.5\right) / k = -0.693 / k \qquad (2.3)$$

A half life can be converted to a first order rate constant or vice versa by dividing one parameter into -0.693 to calculate the other parameter. The unit for a half life is time (e.g. years), and the unit for a first order rate constant is reciprocal time (per year).

Most readers have an intuitive grasp of a half life, and as a consequence, microbiologists and other life scientists commonly describe first order processes with a half life. Engineers tend to describe first order processes with a first order rate constant for two important reasons. The rate of change is directly related to the constant. In addition, if several first order processes are operating simultaneously, such as hydrolysis and biodegradation, the rate constant for the combined effect is simply the sum of the individual rate constants. This property is particularly convenient when calibrating transport and fate models because several processes can be combined into one calibration parameter. The remainder of this report will describe first order processes using first order rate constants. For readers who are more comfortable with half lives, and do not have access to a calculator, Figure 2.1 can be used to convert first order rate constants in units of per year to half lives in days, weeks or years.

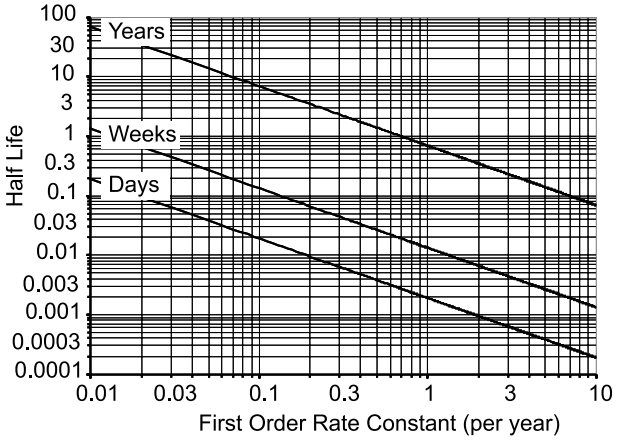

Figure 2.1. Relationship between a first order rate constant in units of per year and half-lives in units of days, weeks, and years.

2.1.3 A Definition of a "Generally Useful" Rate of Attenuation

To put a rate of attenuation into context for natural attenuation, it is necessary to define a rate that might be useful for MNA. Any determination of "useful" is site specific depending on the hydrological context of a particular release, and the proximity of receptors. On a site-specific basis, the useful rate of attenuation is the rate that will achieve the remedial objectives within a reasonable time frame (U.S. EPA, 1999). If the degradation follows first order kinetics, then the first order rate constant (k) for a "useful" rate of removal is defined by the relationship in Equation 2.4.

$$k = -\frac{Ln\left(\text{MCL}/\text{Current Concentration}\right)}{\text{Time Available}} \qquad (2.4)$$

Any release of conventional leaded gasoline is at least 20 years old. For the purposes of discussion and comparison, we will arbitrarily define a "generally useful" rate as the rate that will bring the concentration of EDB or 1,2-DCA that would be expected in ground water in contact with unweathered leaded gasoline to the MCL for EDB or 1,2-DCA within an additional 20 years.

Falta (2004) used the average composition of gasoline and partitioning theory to estimate the concentration of EDB and 1,2-DCA, that would be expected in ground water in contact with unweathered leaded gasoline. The expected concentrations for EDB and 1,2-DCA, were 1,900 µg/L and 3,700 µg/L respectively. The first order rate of removal that would bring EDB from the maximum concentration expected (1,900 µg/L) to the MCL (0.05 µg/L) in 20 years is 0.5 per year, and the corresponding rate that would bring the maximum concentration of 1,2-DCA of 3,700 µg/L to 5 µg/L in 20 years would be 0.33 per year. Therefore the "generally useful" rate of degradation of EDB would be 0.5 per year or greater and the "generally useful" rate of degradation of 1,2-DCA would be 0.33 per year or greater.

2.2 Attenuation caused by physical processes

The flow of ground water through the residual gasoline should weather ("leach") EDB and 1,2-DCA from the residual source material. With each exchange of the pore water in contact with residual gasoline, some fraction of the total amount of EDB and 1,2-DCA would be flushed away from the source area. Typical values for the concentration of gasoline at residual saturation vary between 2,000 and 10,000 mg/kg of Total Petroleum Hydrocarbon (TPH). Appendix A provides equations that can be used to predict the distribution of EDB and 1,2-DCA between residual gasoline and ground water. At these typical values for TPH, the fraction of the total amount of EDB that is dissolved in ground water would vary between 30% and 7%, and the fraction of 1,2-DCA in ground water would vary from 40% and 12%. Because a relatively small proportion of EDB or 1,2-DCA is in the ground water, these contaminants would be expected to weather slowly from residual gasoline. This leads to two questions: How fast is EDB and 1,2-DCA weathered from gasoline? What are the expected concentrations of EDB and 1,2-DCA in the plume?

2.2.1 Physical Weathering from Fuel Present at Residual Saturation

The rate of exchange of pore water in contact with residual gasoline will depend on the seepage velocity of ground water and on the distance ground water must move to traverse the region with residual gasoline. The faster the ground water moves, the faster the EDB and 1,2-DCA should be removed, therefore, higher seepage velocities should be associated with lower concentrations of EDB. The average seepage velocity of ground water is usually calculated from an estimate of hydraulic conductivity that is acquired from a slug test on a monitoring well. Because most monitoring wells are screened across materials with different textures, the average seepage velocity may underestimate the local seepage velocity through the material contaminated with residual gasoline.

The South Carolina Dept. of Health & Environmental Control collected data on the hydrological characteristics of 150 MTBE plumes in South Carolina (Personal Communication, Read Miner, South Carolina Dept. of Health & Environmental Control). The seepage velocity at each plume was estimated by multiplying the hydraulic gradient by the hydraulic conductivity, then dividing by 0.3 as an estimate of the effective porosity. Figure 2.2 presents the frequency distribution of seepage velocity in the plumes. The median seepage velocity was 4 m/yr, and only 10% of plumes exceeded a velocity of 50 m/yr. Measurements in the same data set indicated that the median width of the source area for MTBE plumes was 100 feet or 30 meters.

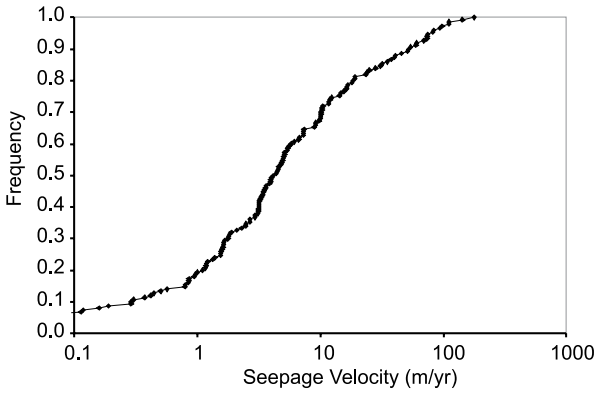

Figure 2.2. Distribution of seepage velocity in MTBE plumes in South Carolina (2002).

The following thought experiment is offered to put the rate of weathering of EDB and 1,2-DCA in context for risk management. Assume, following Falta (2004), that the initial concentrations of EDB and 1,2-DCA are 1,900 µg/L and 3,700 µg/L.

The distribution of EDB and 1,2-DCA between water and non-aqueous phase gasoline is controlled by the partitioning coefficient between water and gasoline, and by the relative proportions of pore water and gasoline in the aquifer. Appendix A derives equations that can be used to predict the distribution of EDB and 1,2-DCA based on the parameters. Assume that the concentration of residual gasoline is near 5,000 mg/kg, and that the total porosity is 30%. The equations in Appendix A would predict that 12% of EDB and 20% of 1,2-DCA is removed whenever one pore volume of ground water in contact with the residual gasoline is exchanged. The rate of exchange is the length of the region with residual gasoline divided by the seepage velocity of ground water.

Assume that the footprint of residual gasoline from releases of leaded gasoline had the same geometry as the releases of gasoline with MTBE, and that the length of the region with residual gasoline in the direction of ground water flow is equal to the width perpendicular to the flow. The assumed length is 30 meters.

Figure 2.3 projects the time course of concentrations of EDB and 1,2-DCA in ground water in contact with residual gasoline if the ground water seepage velocity is 4 m/yr (median velocity in South Carolina) or 50 m/yr (faster than 90% of sites). The year 1987 was taken as the last year for a plausible release of EDB from leaded gasoline in an underground storage tank. The EPA/ASTSWMO study was conducted twenty years later in 2006 and 2007.

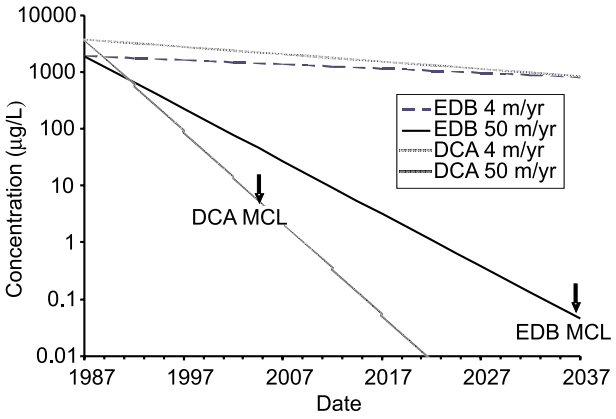

Figure 2.3. Thought experiment on the effect of the rate of ground water flow on the concentration of EDB and DCA in ground water in contact with residual leaded motor fuel. (Consult the text for assumptions in the comparisons.)

If the seepage velocity of ground water was 50 m/yr, the concentration of EDB in 2007 would be near 27 µg/L. While this represents a 70-fold reduction in concentration from the original concentration of EDB, the concentration is still 540-fold greater than the MCL. The concentration of EDB would not be expected to reach the MCL until 2037. If the seepage velocity were 4 m/year, the concentration of EDB would be reduced by less than 30% by 2007. It is reasonable to expect significant concentrations of EDB to remain in ground water at many releases of leaded gasoline.

In the case of 1,2-DCA, when the seepage velocity is 50 m/yr, concentrations of 1,2-DCA would be

expected to meet the MCL before samples were collected for the study in 2006 and 2007. If the seepage velocity was 4 m/yr, concentrations of 1,2-DCA would only be reduced to 50% of the original concentration. Because 1,2-DCA partitions to ground water more readily than EDB, it weathers more rapidly, but there is little practical difference in their behavior as it will take decades to centuries to reach their respective MCLs.

The survey conducted by the EPA/ASTSWMO Lead Scavengers Team provides a small data set that can be used to validate the thought experiment. Case workers in the state agencies were asked to review files on the sites, and provide either an estimate of the seepage velocity of ground water from the file, or data on the hydraulic gradient and hydraulic conductivity that could be used with a reasonable estimate of effective porosity to estimate the seepage velocity of ground water. Data are available from ten sites.

Figure 2.4 compares the average seepage velocity of ground water at the sites to the highest concentrations of EDB at each site in 2006. In general, the concentrations were lower than would be expected from the thought experiment. In eight of the ten sites, the maximum concentration of EDB was 1 µg/L or less, regardless of the seepage velocity of the ground water. This would indicate that some process other than leaching controlled the concentrations of EDB at these eight locations. The sites with the highest concentrations of EDB had seepage velocities of 11.5 and 71 meters per year. These velocities are relatively high, exceeding 72% and 92% of sites in South Carolina respectively (compare Figure 2.2). Despite these high seepage velocities, the concentrations of EDB were above 400 µg/L, consistent with the slow rates of physical weathering predicted by the thought experiment.

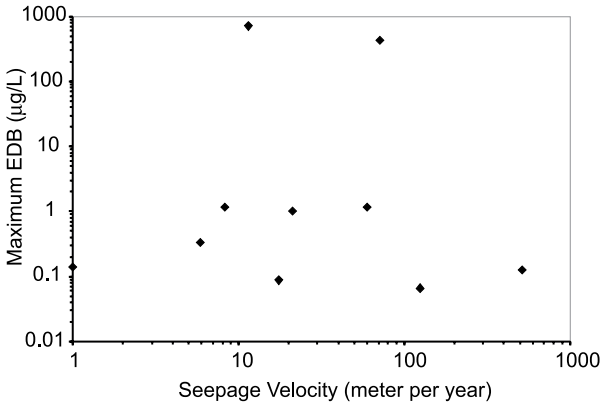

Figure 2.4. Association of concentrations of EDB in the most contaminated wells at each of ten sites with estimates of the seepage velocity of ground water at the sites.

2.2.2 Sorption on Native Organic Matter

As long as the ground water is in contact with residual gasoline, the concentration of EDB or 1,2-DCA is controlled by the concentration of EDB and 1,2-DCA in the gasoline. Once contaminated ground water moves away from the area with gasoline at residual saturation, the concentrations of EDB or 1,2-DCA are controlled by sorption to solids in the aquifer matrix, by biological degradation and abiotic transformation, and by dilution and dispersion in ground water.

Retardation due to sorption is not an important process contributing to natural attenuation of EDB or 1,2-DCA in ground water. Table 2.1 compares the retardation ratio of EDB, 1,2-DCA, MTBE, benzene, toluene, and xylenes that is expected from sorption of the contaminant to the native organic carbon in the aquifer. The retardation ratio is simply the rate of movement of water divided by the rate of movement of the contaminants. As discussed in Wiedemeier et al., (1999), the estimates of the retardation ratio in Table 2.1 are based on Equation 2.5;

$$R = 1 + \rho_b * K_{oc} * f_{oc} / \theta \qquad (2.5)$$

where R is the retardation ratio, ρ_b is the bulk density, K_{oc} is the partition coefficient of the organic contaminant between ground water and native organic matter, f_{oc} is the fraction organic carbon in the aquifer matrix material, and θ is the water filled porosity. In Table 2.1, values for K_{oc} are taken from Wiedemeier et al., (1999), except for the value of K_{oc} for EDB. Aronson and Howard (2008) concluded that "Soil-water partition coefficients (Koc values) for EDB in the solution

Table 2.1. Retardation in ground water due to sorption that is expected from the organic matter content of the aquifer solids.

		Fraction of Organic Carbon in sediment			
Compound	K_{oc} (L/kg)	0.01%	0. 1%	1%	10%
		Low for Aquifers	Median for Aquifers	High for Aquifers	Typical of soils
MTBE	12	1.0	1.1	1.6	7
Benzene	38	1.0	1.2	2.9	20
DCA	58	1.0	1.3	3.8	29
EDB	65	1.0	1.3	4.1	33
Toluene	135	1.1	1.7	7.6	68
Xylenes	240	1.1	2.2	13	120

phase range from 12 to 160 L/kg … but average about 50 to 65 L/kg." The calculation in Table 2.1 assumes a value of 65 L/kg for the K_{oc} of EDB.

The extent of sorption of EDB and 1,2-DCA is intermediate between the extent of sorption of benzene and toluene. At concentrations of organic carbon in the aquifer solids that are near 0.01%, there should be little retardation of EDB or 1,2-DCA. At concentrations of organic carbon in the aquifer solids near 0.1%, retardation of EDB and 1,2-DCA is of no practical consequence. These concentrations are typical of aquifers with low or average concentrations of organic matter in the aquifer solids. At relatively high concentrations of organic carbon in the aquifer solids near 1%, the expected retardation ratio for EDB and 1,2-DCA is near four to one.

Sorption can reduce concentrations in plumes that are expanding, but when a plume reaches steady state, sorption does not influence the concentration of the contaminant in ground water. As discussed in Section 1, the use of leaded gasoline for conventional motor gasoline was minimal after 1988. At the time of this writing, almost every plume of EDB or 1,2-DCA from a release of leaded gasoline from an underground storage tank at a conventional gasoline service station is at least twenty years old. In this time interval, it is reasonable to presume that most plumes of EDB or 1,2-DCA have reached (or are approaching) steady state. Sorption can not be an important mechanism that will bring high concentrations of EDB or 1,2-DCA to their MCLs.

2.2.3 Rate Constants for Physical Weathering of EDB and 1,2-DCA

There is very little data in the literature on trends of EDB concentrations in monitoring wells at gasoline release sites. Bulsara (2004) fitted first order rate constants for attenuation of EDB to monitoring data from 55 wells in South Carolina. The data are replotted in Figure 2.5. The rates varied widely, from approximately - 4 per year to + 4 per year. In 32 of the 55 wells, the rate constants were negative, indicating that the concentrations of EDB increased over time.

As a comparison, Figure 2.5 plots data for the attenuation of MTBE in monitoring wells at gasoline release sites (Wilson et al., 2005). At 6 out of 20 release sites, the rate constants were negative, indicating that concentrations of MTBE were increasing. However, the variation in rates of attenuation was less, from -0.52 to +0.75 per year. The range in rates of attenuation of MTBE was much less than the range in rates of attenuation of EDB. There is no obvious reason why this should be the case. The compounds have very similar physical properties.

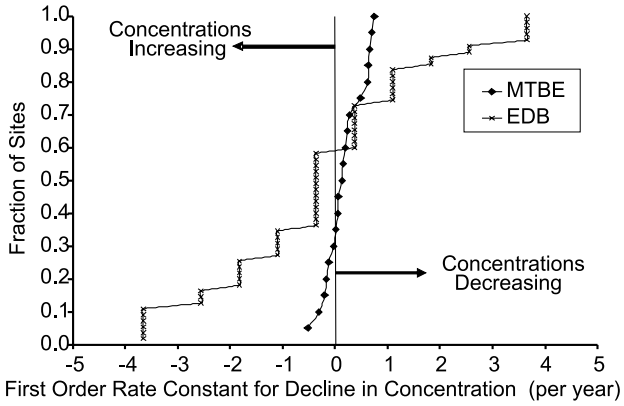

Figure 2.5. Rate of decline of concentrations of EDB over time in 55 monitoring wells in South Carolina (Bulsara, 2004). Rate of decline of concentrations of MTBE at 20 sites in the USA (Wilson et al., 2005) provided for reference.

Example data provided in Falta (2004) indicated that the rates for attenuation of EDB were extracted from three or four measurements extending over a monitoring period of one or two years. In contrast, the rates of MTBE attenuation were extracted from 6 to 34 measurements (mean of 14 measurements) extending over a minimum of two years. The comparison of the EDB rate constants to the MTBE rate constants suggests that rate constants extracted from small data sets collected over short time periods may have large uncertainty. If a rate constant extracted from monitoring data at a particular release site is used to estimate the time required for concentrations of EDB to decline below the MCL, the rate should be verified and validated by continued long term monitoring.

2.3 Attenuation Caused by Abiotic Transformation or Biodegradation

For many processes that destroy contaminants, the rate of the reaction is proportional to the concentration of the contaminant at any moment in time. This is particularly true for abiotic reactions such as hydrolysis or abiotic reactions with minerals. For biodegradation reactions at low concentrations, the diffusion of the contaminant to the organism, and association of the contaminant with the enzymatic machinery of the organism, is rate limiting. At these lower concentrations, the rate of reaction is proportional to the concentration of the contaminant. At higher concentrations, the processing of the contaminant by the enzymatic machinery becomes rate limiting, and the rate of reaction is proportional to the density of cells, not the concentration of the contaminant. This transition in the rate limiting step for anaerobic biodegradation of EDB should be near 1,000 µg/L. At typical concentrations at releases of leaded gasoline, the rate of EDB biodegradation should be proportional to the concentration of EDB, and the process can be described with first order kinetics.

2.3.1 Neutral Hydrolysis of EDB and 1,2-DCA

Both EDB and 1,2-DCA are slowly hydrolyzed in water. Barbash and Reinhard (1989) reported a half life for neutral hydrolysis of EDB of 22 years at 15 °C and 4.6 years at 25 °C. These half lives correspond to first order rate constants of 0.073 per year at 15 °C and 0.15 per year at 25 °C. The rate of neutral hydrolysis of 1,2-DCA was slower; the half life was 300 years at 15 °C and 64 years at 25 °C, corresponding to first order rate constants of 0.0023 per year at 15 °C and 0.0108 per year at 25 °C.

Hydrolysis of EDB can produce either 2-bromoethanol or vinyl bromide (Pignatello and Cohen, 1990; Aronson and Howard, 2008), with 2-bromoethanol being the dominant product. Similarly, 1,2-DCA hydrolyzes to 2-chloroethanol (Jeffers et al., 1989) and vinyl chloride with vinyl chloride being a minor product (Barbash and Reinhard, 1989).

Both EDB and 1,2-DCA can undergo base catalyzed hydrolysis; however, the rate of the base catalyzed hydrolysis is not important at the pH of natural ground waters. At pH 9, the base catalyzed reaction represents only 10% of the total hydrolysis reaction (Jeffers and Wolfe, 1996).

2.3.2 Abiotic Transformation of EDB and 1,2-DCA by Iron(II) Sulfide

Both EDB and 1,2-DCA can also react with sulfide as H_2S and HS^- to produce various thiols and thioethers (Schwarzenbach et al., 1985). Barbash and Reinhard (1989) compared the expected rates of hydrolysis and reaction with sulfide at 15 °C and 25 °C. In Figure 2.6, the combined rate constants for hydrolysis and reaction with sulfide are used to project the effects of the concentration of total sulfide at pH 7 on the rate of removal of EDB and 1,2-DCA. In general, the rate of reaction of EDB is approximately ten times the rate of reaction of 1,2-DCA (compare the scales of the vertical axes in Figure 2.6). The reaction of both EDB and 1,2-DCA is sensitive to temperature; rates at 25 °C are approximately five fold faster than at 15 °C. Reactions with sulfide only become important at concentrations above 0.2 mg/L for EDB and 1 mg/L for 1,2-DCA.

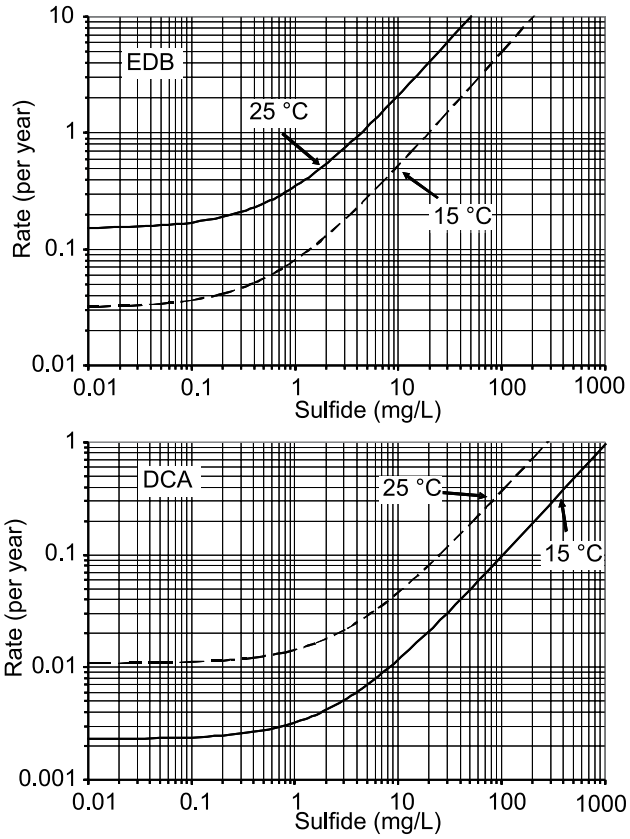

Figure 2.6. Effect of concentrations of sulfide at pH 7 on the rate of abiotic transformation of EDB and DCA.

Depending on temperature, the "generally useful" rate of EDB degradation of 0.5 per year is attained at concentrations between 2 and 10 mg/L total sulfide at pH 7. The "generally useful" rate for 1,2-DCA of 0.33 per year is attained at concentrations between 90 and 400 mg/L of sulfide.

Sulfide produced as the end product of sulfate reduction can react with iron(III) minerals in the aquifer matrix to produce various mineral phases of iron(II) sulfide according to the following reactions (Shen and Wilson, 2007).

$$4H_2 + SO_4^{-2} \rightarrow S^{-2} + 4H_2O$$

$$2Fe^{+3} + 3S^{-2} \rightarrow 2FeS + S^0$$

$$FeS + S^0 \rightarrow FeS_2$$

The overall reaction consumes three moles of sulfate to produce one mole of FeS and one mole of FeS_2.

$$12H_2 + 3SO_4^{-2} + 2Fe^{+3} \rightarrow FeS + FeS_2 + 24H_2O$$

The transformation of chlorinated hydrocarbons such as TCE and *cis*-DCE by FeS and FeS_2 is well documented in the literature (Butler and Hayes, 1999; Butler and Hayes, 2001; Shen and Wilson, 2007; Liang et al., 2007). Shen and Wilson (2007) reported abiotic transformation of TCE in four laboratory columns constructed with river sand and shredded plant mulch. Sulfate reduction supported by the plant mulch produced sulfide, which reacted with Fe(III) minerals in the river sand to produce non crystalline or poorly crystalline FeS. Two of the columns were supplemented with hematite to encourage precipitation of FeS in the columns. In these two columns, the first order rate constant for reaction of TCE with the FeS varied from 0.53 to 2.3 per day per mole of FeS in contact with a liter of pore water.

The EPA/ASTSWMO Lead Scavengers Team conducted an experiment to determine whether EDB or 1,2-DCA could be degraded by FeS. To evaluate the capacity of biogenic FeS to degrade EDB and 1,2-DCA, the column described by Shen and Wilson (2007) as the Column with Mulch and Hematite was frozen, cut into sections while frozen, and then the sections were allowed to thaw under an oxygen free atmosphere in a glove box. To remove the confounding effects of sorption to the plant mulch on concentrations of contaminants, the sections were sieved to remove the plant mulch. The sediment and pore water were transferred to 20 ml serum vials, dosed with solutions of EDB or 1,2-DCA, and incubated at room temperature. Experimental details are provided in Appendix B.

The removal of EDB and 1,2-DCA followed first order kinetics without a lag, indicating that removal was an abiotic process that did not require acclimation of an active biological process (Figure 2.7). The removal of EDB was more rapid than the removal of 1,2-DCA. The first order rate constants for degradation of EDB or 1,2-DCA were extracted from the data as the slope of a linear regression of the natural logarithm of concentration on time of incubation. The rate constants are presented in Table 2.2. At the end of the incubation, the concentration of Acid Volatile Sulfide or AVS was measured in each of the vials (mg/kg dry sediment). The AVS was taken as an estimate of FeS in the sediment. The water content of the wet sediment was determined by drying the sediment. The concentration of AVS in each vial was expressed as the millimoles AVS exposed to each liter of pore water. Finally, the rate of removal was normalized to the millimoles AVS exposed to the pore water.

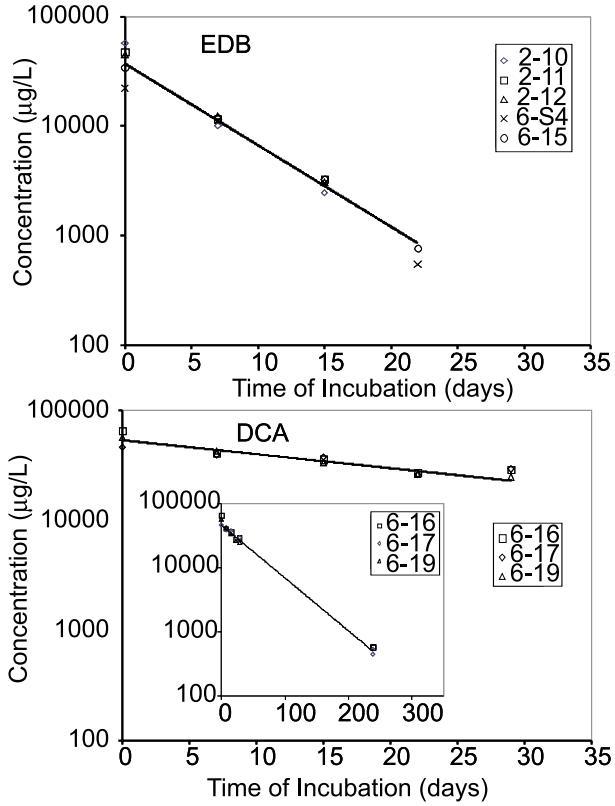

Figure 2.7. Removal of EDB or DCA in the presence of biogenic FeS in batch experiments at pH near 7.

The normalized rate constants for transformation of EDB were consistent between the experimental vials. The average normalized rate for EDB degradation was 0.285 ± 0.091 per year per millimole AVS exposed to a liter of water at 95% confidence. The rate of transformation of EDB was in the same range as the rates of abiotic transformation of TCE in the original column. The rate of 1,2-DCA degradation was an order of magnitude lower at 0.0263 per year per millimole AVS exposed to a liter of water.

Analysis of acid volatile sulfide is simple to perform, and is commercially available. Figure 2.8 presents the rate of abiotic degradation of EDB and 1,2-DCA that would be expected if the kinetics of degradation follow the rates of degradation presented in Figure 2.7. The detection limit for the analysis is near 2 to 3 mg/kg. The rates of abiotic degradation of EDB are "generally useful" at concentrations of AVS near 10 mg/kg. Concentrations of AVS must approach 100 mg/kg to provide "generally useful" rates of transformation of 1,2-DCA.

Table 2.2. Comparison of the rate of transformation of EDB and DCA by iron(II) sulfide to the rate or removal of TCE.

Compound	Experimental unit	Rate of Removal	Concentration FeS as AVS*	Rate of Removal
		yr^{-1}	mM**	$yr^{-1}mM^{-1}$
EDB	2-10	76.4	198	0.386
EDB	2-11	65.1	272	0.239
EDB	2-12	64.9	278	0.233
EDB	6-15	62.6	381	0.164
EDB	6-s4	94.8	236	0.402
DCA	6-16	10.2	293	0.0348
DCA	6-17	6.7	140	0.0479
Data from Table 1 of Shen and Wilson (2007)				
TCE	Entire Column Day 383	80	138	0.584
TCE	Entire Column Day 578	193	230	0.840
TCE	Entire Column Day 793	55	283	0.193

*Acid Volatile Sulfide
** millimoles AVS in contact with 1.0 liter pore water.

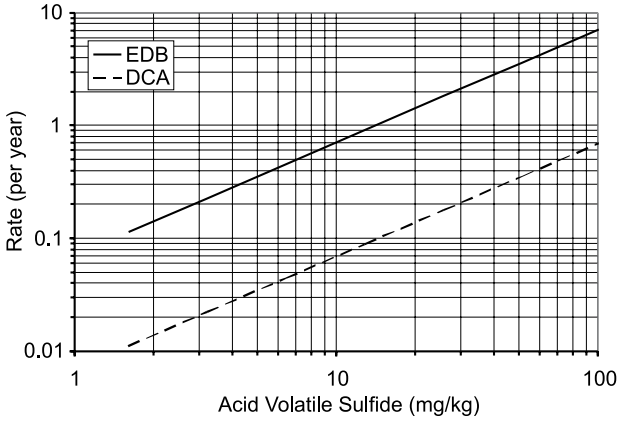

Figure 2.8. Expected rates of abiotic transformation of EDB or 1,2-DCA by FeS in aquifer sediment, assuming a water-filled porosity of 25%, and pH near 7.

The abiotic reaction of EDB or 1,2-DCA occurs on the surface of the solid iron(II) sulfide. As a result, the rate of the reaction should be proportional to the surface area and not to the mass of the iron(II) sulfide, and the reaction rate will be faster if the iron(II) sulfide is finely divided. The rate of abiotic transformation of EDB and 1,2-DCA has only been determined for this one preparation of biogenic iron(II) sulfide. It is not known at present if the properties of biogenic iron(II) sulfide in aquifer sediments vary from site to site. The projections in Figure 2.8 are provisional until more data can be obtained from field sites.

Butler and Hayes (2001) found that the rate of transformation of TCE on iron(II) sulfide decreased as the pH decreased. There is no information on the effect of pH on the rate of transformation of EDB and 1,2-DCA. However, it is possible that the rates will be substantially lower at pH less than 6.5. Based on sustained concentrations of sulfide in ground water and the temperature, reactions with sulfide can make a major contribution to removal of EDB and 1,2-DCA in ground water, once the water moves away from the area of the plume with residual gasoline.

2.3.3 Biodegradation of EDB and 1,2-DCA

Both EDB and 1,2-DCA can be rapidly degraded if oxygen is available (Aronson and Howard, 2008). Oxygen may be available in the far down gradient portion of the plume where metabolism of the petroleum hydrocarbons is complete, and diffusion and dispersion have mixed oxygen from un-impacted ground water into the plume. However, the oxygen demand of the petroleum hydrocarbons make it unlikely that oxygen will be available in the source area of a plume from a release of leaded gasoline, or in the mid gradient portions of the plume.

Methane producing bacteria can co-metabolize EDB and 1,2-DCA to ethylene when the cells are grown on molecular hydrogen and carbon dioxide (Belay and Daniels, 1987). The reaction does not support growth of cells, and the halogenated compounds can be harmful to the methane producing bacteria. Concentrations of EDB near 1,300 µg/L inhibit growth of the methane producing bacteria by 90%. In contrast, 1,2-DCA has less effect; higher concentrations of 1,2-DCA near 11,000 µg/L are required to inhibit growth.

Bacteria in the *Dehalococcoides* group can use EDB or 1,2-DCA as a substrate. These bacteria grow with molecular hydrogen as a source of reducing power, and use EDB or 1,2-DCA as the electron acceptor, basically as something to breathe. Strain *Dehalococcoides* BAV1 (He et al., 2003a) can grow while metabolizing EDB to ethylene, and *Dehalococcoides* ethanogenes 195 can grow on 1,2-DCA (Maymó-Gatell et al., 1999) and metabolize either EDB or 1,2-DCA to ethylene (Maymó-Gatell et al., 1997).

No information is available in the literature on the effect of concentrations of EDB on the rate of EDB degradation by *Dehalococcoides* strains. The effect is usually described by the half saturation constant, the concentration at which the rate is one-half of the maximum possible rate. This is the concentration where the rate of degradation becomes dependent on the density of active organisms instead of the concentration of the substrate. He et al., (2003b) published half saturation constants for degradation of vinyl chloride, *cis*-DCE, and *trans*-DCE by the mixed culture from which *Dehalococcoides* BAV1 was isolated. The values were 5.8, 8.9, and 8.5 µM for vinyl chloride, *cis*-DCE, and *trans*-DCE respectively. Cupples et al., (2004) determined half saturation constants for vinyl chloride and *cis*-DCE in a mixed culture containing the bacterium VS strain of *Dehalococcoides*. The values of the half saturation constant were 2.6 and 3.3 µM for vinyl chloride and *cis*-DCE respectively.

The value of the half saturation constant is controlled in part by the affinity of the substrate for microbial tissue, and for the active site of the enzyme. The affinity is inversely related to the water solubility of the substrate. The water solubility of EDB, vinyl chloride, and *cis*-DCE are 4,300 mg/L, 2,700 mg/L and 800 mg/L respectively.

The closest match to EDB is vinyl chloride. If the half saturation constant of vinyl chloride is considered the best estimate of the half saturation constant for EDB, the constant would vary between 5.8 millimolar and 2.6 millimolar, or 1,100 to 490 µg/L.

Considering the effect of EDB on the growth of methane producing bacteria along with the half saturation constant for *Dehalococcoides* strains, a value of 1,000 µg/L can be considered an upper boundary where biodegradation of EDB can be described by a first order rate law.

2.3.3.1 Rate Constants for Biodegradation of EDB and 1,2-DCA

Table 2.3 compares the first order rate constants for removal of EDB, 1,2-DCA, and benzene that were extracted from laboratory studies using anaerobic aquifer sediment. The table is restricted to data from sites that were actively methanogenic and would reflect the geochemical environment in the area of a release of leaded gasoline that had residual gasoline, as well as, the area in the plume that is immediately down gradient of the area with residual gasoline where BTEX compounds persisted in the ground water. The rates of degradation of EDB, 1,2-DCA, and benzene in the laboratory microcosm studies all had a fairly narrow range, extending from 17 per year to 0.3 per year.

In three different studies, the rate of anaerobic biodegradation of EDB was equivalent to the rate of biodegradation of benzene. The rate constants attained in the laboratory studies meet the arbitrary criteria established earlier for "generally useful" rate constants for applications to MNA (0.5 per year for EDB and 0.33 per year for 1,2-DCA). Anaerobic biodegradation can make an important contribution to MNA of EDB and 1,2-DCA in contaminated ground water, particularly under methane producing conditions.

Table 2.3 also compares rate constants that were extracted from the distribution of contaminants along the flow path in the aquifer. In Table 2.3, the rate constant was calculated from data provided in Mayer (2006) by multiplying the first order rate constant for attenuation of concentrations with distance along the flow path by the upper value of the range of the ground water seepage velocity at the site.

Washington and Cameron (2001) warn that field scale rates of attenuation include the effects of sorption and dispersion and dilution. Data in Table 2.3 are from old releases that have reached their maximum extent and are stable. They have likely reached sorptive equilibrium. The length of plumes reported by Henderson et al., (2008) and Mayer et al., (2006) is relatively short compared to the likely width of the source area. The rate constants reported by Ravi et al., (1998) are corrected for dispersion and dilution. In the data from Table 2.3, it is most likely that attenuation at field scale is dominated by biodegradation, which would explain the reasonable correspondence between the field scale rates and the laboratory studies. In general, the rate constants in the field are smaller than those extracted from the laboratory studies, corresponding to the lower end of the range of laboratory rates.

There is one important exception to the reasonable correspondence in rate constants. Falta (2004) extracted rates of attenuation of EDB and benzene from the distribution of their plumes of contamination that resulted from a release of aviation gasoline at the Massachusetts Military Reservation on Cape Cod, Massachusetts. The rate constant for EDB biodegradation was ten fold to one hundred fold slower than the rate constants seen at other sites (Table 2.3). The release was into an aquifer comprised of poorly sorted fine to coarse sands. The seepage velocity of ground water was in the range of 0.3 to 0.6 m per day. There may have been no opportunity to develop the strongly reducing conditions that would lead to BTEX fermentation to produce the H_2 that is needed by the organisms that biodegrade EDB.

The study of Henderson et al., (2008) is careful and comprehensive and is published in a respected peer reviewed journal. The study of Mayer (2006) uses conventional and generally accepted approaches to analyze data that was collected at the site for other purposes. These two studies are the only useful case studies in the literature on natural biodegradation of EDB and 1,2-DCA at gasoline release sites. It would be inappropriate to uncritically extrapolate the behavior of EDB and 1,2-DCA at these two sites to hundreds of thousands of sites across the United States. At present, the general contribution of biodegradation at sites across the United States is unknown.

The appropriate application of MNA, or risk management, requires a site-specific knowledge of the behavior of the contaminants of concern. It is important to remember that the data in Table 2.3 illustrate what might be possible at other sites. Data from Table 2.3 should not be used in the place of site specific data to conduct a risk evaluation at other gasoline release sites.

Table 2.3. Comparison of first order rate constants for biodegradation of EDB and 1,2-DCA in anaerobic aquifer sediment to rate constants for overall removal with ground water flow in anaerobic aquifers.

Material	First Order Rate Constant for Attenuation (per year)			Reference
	EDB	DCA	Benzene	
Microcosm studies in laboratory, all are conducted with methanogenic material.				
sediment from source zone of a spill of leaded gasoline, South Carolina	1.5±1.0	1.3±0.3	1.4±0.2	Henderson et al., 2008, SI
sediment from mid gradient zone of a spill of leaded gasoline, South Carolina	5.4±0.3	0.3±0.1	3.5±0.8	Henderson et al., 2008, SI
sediment impacted by leachate from a solid municipal waste landfill, Norman, Oklahoma	17		2.6	Wilson et al., 1986
sediment impacted by leachate from a solid municipal waste landfill, Norman, Oklahoma		1.7		Klećka et al., 1998
sediment from manufacturing site contaminated with DCA in Louisiana		4.4		Klećka et al., 1998
sediment from manufacturing site contaminated with DCA in Texas		1.2		Klećka et al., 1998
Field studies, flow path in aquifer				
spill of leaded gasoline, South Carolina	1.3	0.9	1.0	Henderson et al., 2008, Supporting Information
spill of leaded gasoline, North Carolina (1995 data)	0.63	0.71	0.9	Mayer, 2006
spill of leaded gasoline, North Carolina (2004 data)	0.22		0.26	Mayer, 2006
leachate from municipal solid waste landfill, Michigan		0.22±0.19	0.42±0.32	Ravi et al., 1998
fs-12 spill of aviation gasoline on Cape Cod, Massachusetts	0.03		0.14	Falta, 2004

2.3.3.2 Association of Geochemical Parameters with Removal of EDB and 1,2-DCA

Both EDB and 1,2-DCA are biodegradable under aerobic and anaerobic conditions. Based on the approach taken in the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (Wiedemeier et al., 1998), it may be possible to use geochemical parameters to identify environments where processes that destroy EDB are favored. This sub-section examines the association of concentrations of EDB with concentrations of the biogeochemical parameters nitrate-nitrogen, sulfate and sulfide, and methane. The association is evaluated to determine if there is information in these parameters that can be used to predict concentrations of EDB.

The sub-section is intended for staff of state regulatory agencies that determine which parameters are monitored in ground water contaminated by releases of leaded gasoline. The cost of sampling ground water and analyzing the samples for EDB could be reduced if it were possible to predict beforehand whether high concentrations of EDB should be expected at a particular gasoline release site.

To determine whether geochemical or hydrological parameters can be used to predict concentrations of EDB, certain sites from the EPA/ASTSWMO study that were sampled in 2006 were selected to be resampled in 2007 for concentrations of EDB and for concentrations of nitrate, sulfate, and methane. In the data set there was one site each from Colorado, Missouri, Montana, Tennessee, Utah,

and Vermont. Two sites each were selected from Oklahoma, New Hampshire, and South Carolina, and three sites were selected from Minnesota.

2.3.3.2.1 Dissolved Oxygen

Oxygen is particularly difficult to determine in monitoring wells. Collecting water samples with a bailer tends to introduce oxygen from the atmosphere into the sample so that the measured dissolved oxygen content of the sample is higher than that of the ambient ground water. This concern is illustrated in data that were collected by Kolhatkar et al., (2000) to investigate the role of various geochemical parameters in the natural biodegradation of MTBE in ground water. In 1999 and 2000, ground water samples were collected from wells at 74 sites in Pennsylvania (41 sites), New Jersey (8), New York (5), Florida (5), Indiana (7), Maryland (3), Washington DC (2), and Ohio (3). Analyses of dissolved oxygen, iron(III), and hydrogen sulfide were performed on site by staff of the contractors or consultants that normally sampled the monitoring wells using procedures for purging the wells that were prescribed by the appropriate state agencies. Because iron(II) is rapidly oxidized to iron(III) in the presence of molecular oxygen, detectable concentrations of iron(II) and dissolved oxygen should not occur together in ground water. Yet, in water produced from the monitoring wells (Figure 2.9), the sampling technicians reported high concentrations of oxygen in samples with high concentrations of iron(II). Because of the difficulty with measuring dissolved oxygen in water from monitoring wells, data on dissolved oxygen was not collected during the survey conducted by the EPA/ASTSWMO Lead Scavengers Team.

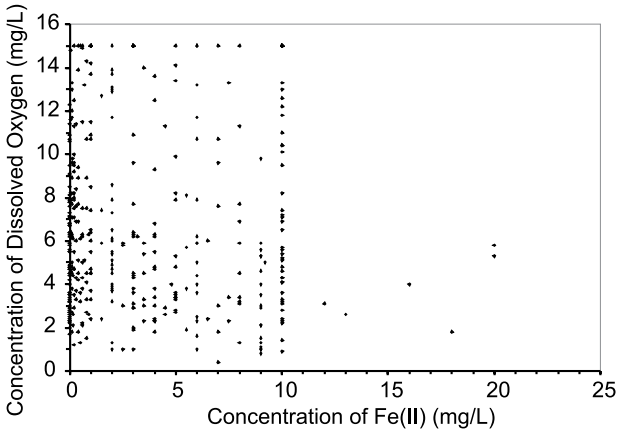

Figure 2.9. Co-occurrence of dissolved oxygen and reduced iron in water samples produced from monitoring wells at gasoline spill sites.

2.3.3.2.2 Nitrate

Concentrations of nitrate were used as a surrogate for the availability of dissolved oxygen in ground water. Higher concentrations of nitrate (and by inference of oxygen) would support aerobic biodegradation of EDB, and should be correlated with lower concentrations of EDB.

Figure 2.10 compares concentrations of nitrate to concentrations of EDB in the most contaminated well at each release site in the EPA/ASTSWMO study. Notice that the same data are plotted on an arithmetic and logarithmic scale for concentrations of nitrate nitrogen. The sites were selected to include both sites with high concentrations of EDB as well as sites with low concentrations of EDB. At five of the selected sites, the concentration of EDB was less than the reporting limit of 0.01 µg/L. These sites had low but detectable concentrations of EDB in 2006.

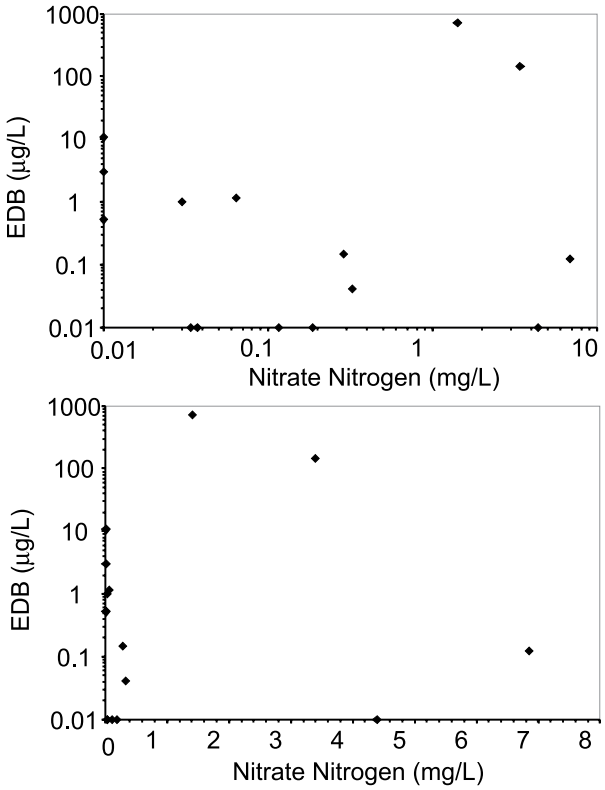

Figure 2.10. Association of concentrations of nitrate with concentrations of EDB in the most contaminated monitoring wells at sites.

There was no obvious relationship between concentrations of EDB and concentrations of nitrate nitrogen. The concentration of nitrate nitrogen in three of fifteen sites was less than the detection limit of 0.01 mg/L, and the concentration

in eleven of fifteen sites was less than 1.0 mg/L. At these sites, the concentration of EDB was 10 µg/L or less. Contrary to what was expected, in the two sites with the highest concentration of EDB (711 and 147 µg/L), the concentration of nitrate nitrogen was above 1 mg/L. There was no evidence that high nitrate concentrations (and by inference high oxygen concentrations) supported aerobic biodegradation of EDB.

The presence of detectable concentrations of nitrate nitrogen in the wells with high concentrations of EDB is problematic. Presumably the high concentrations of EDB were associated with wells screened near the source of residual gasoline. It is possible that the screens of the monitoring wells intercepted uncontaminated ground water over some depth interval, and contaminated water over another depth interval. This resulted in a sample of mixed water being collected and analyzed. When waters from different geochemical environments are mixed in a monitoring well, it will be difficult or impossible to use geochemical parameters to interpret both the geochemical nature of the ground water environment and the contaminant plume.

2.3.3.2.3 Sulfate and Sulfide

The consumption of sulfate during sulfate reduction can produce reactive HS- that can destroy EDB or react with iron(III) minerals to produce FeS which also reacts to degrade EDB. Lower concentrations of sulfate would indicate more extensive sulfate reduction and should be correlated with lower concentrations of EDB. Figure 2.11 compares the distribution of sulfate and EDB at the sites in the EPA/ASTSWAMO survey.

In general, the relationship seems to be as expected; the two highest concentrations of EDB were associated with concentrations of sulfate below 41 mg/L, and the very high concentrations of sulfate were associated with EDB concentrations below 0.1 µg/L. However, for the sites where the concentrations of both EDB and sulfate were above the detection limit, the correlation coefficient between the logarithm of EDB concentration and the logarithm of sulfate concentration is low (-0.15) and the sign of the correlation coefficient is in the wrong direction (concentrations of EDB go down as concentrations of sulfate go up). The concentration of sulfate in the wells that are contaminated with EDB can not be used to predict concentrations of EDB.

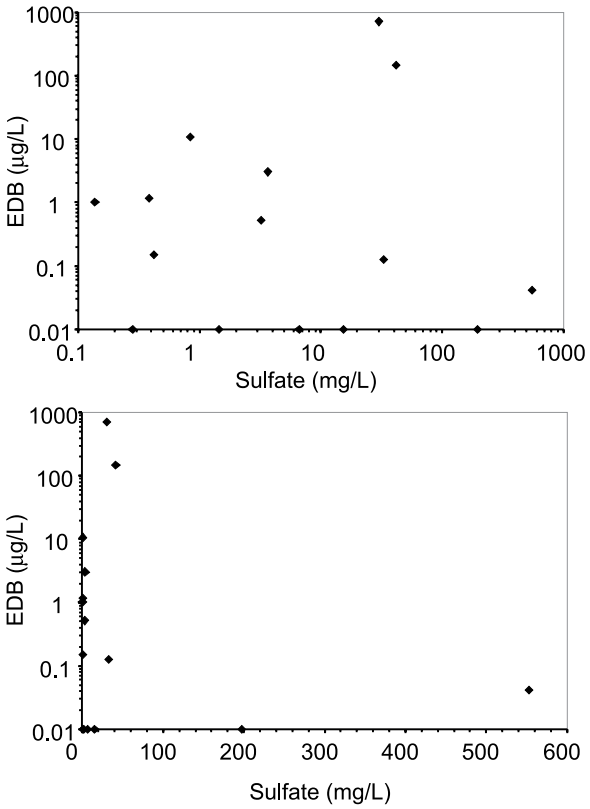

Figure 2.11. Association of concentrations of sulfate with concentrations of EDB in the most contaminated monitoring wells at sites.

In the survey conducted by EPA/ASTSWMO Lead Scavengers Team, the comparison was made between the concentrations of EDB and sulfate in the contaminated ground water. A better estimate of the extent of sulfate reduction might have been the reduction in concentration of sulfate between the contaminated ground water and ambient ground water up gradient or side gradient of the release of gasoline. To illustrate the extent of sulfate reduction that might be expected at gasoline spill sites, Figure 2.12 compares the distribution of sulfate and sulfide in the sites sampled by Kolhatkar et al. (2000). The maximum concentration of sulfate in any of the wells at a site was considered the background concentration. The median of the background concentrations was 107 mg/L, and 75% of sites had background concentrations above 57 mg/L. At most of the sites, at least one contaminated well had concentrations of sulfate that were below the detection limit of 1 mg/L. In every site, there was a substantial reduction in the concentration of sulfate between the contaminated wells and the background wells.

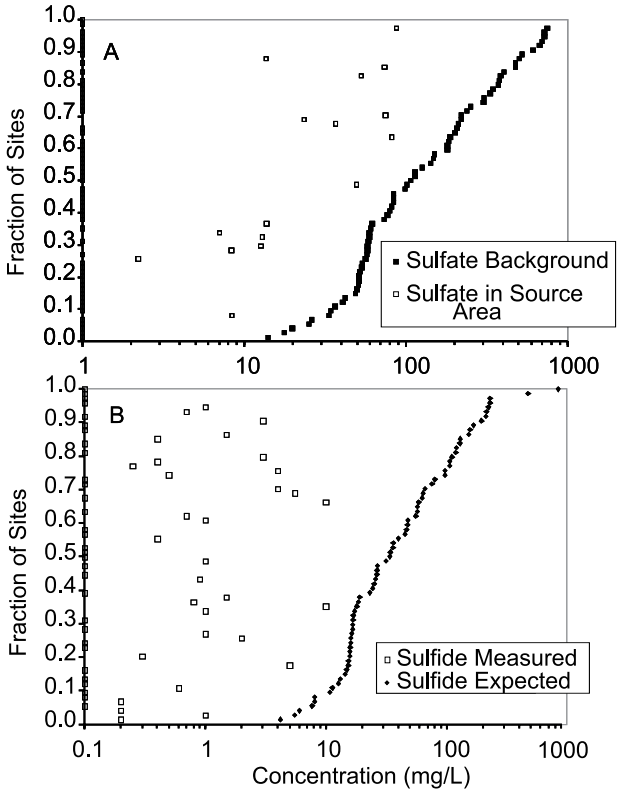

Figure 2.12. Panel A. Distribution of sulfate in the source area of the plume, and in background ground water, at gasoline spill sites in the Eastern United States. Panel B. Distribution of sulfide in the source area of the plumes, compared to the concentration of sulfide expected by the amount of sulfate remove. Data are from the survey of Kolhatkar et al., (2000).

The concentration of sulfide expected from sulfate reduction was calculated by subtracting the lowest concentration of sulfate in any well from the greatest concentration of sulfate in any well at the site, then multiplying by the ratio of the molecular weight of sulfide and sulfate. Sulfate was generally depleted in the contaminated wells in the sites (Figure 2.12, Panel A, and significant concentrations of sulfide were expected (Figure 2.12 Panel B).

The concentrations of sulfide actually measured were much lower than expected (Figure 2.12 Panel B). In half the wells, sulfide was not present above the detection limit of 0.1 mg/L. Only 10% of sites had a sulfide concentration above 3 mg/L and the maximum concentration of sulfide was 10 mg/L. The concentration of iron(II) was high in ground water at these sites (Figure 2.9). It is likely that the sulfide precipitated as iron(II) sulfides. If these minerals persist as Acid Volatile Sulfide (AVS), they may have a substantial contribution to natural attenuation of EDB and DCA at gasoline spill sites.

2.3.3.2.4 Methane

The source area of gasoline release sites usually contains high concentrations of methane that is produced by anaerobic metabolism of the BTEX compounds in gasoline. After the soluble electron acceptors such as oxygen, nitrate, and sulfate are depleted, the metabolism of the BTEX compounds shifts to a fermentation reaction that produces H_2 and fatty acids such as acetate. Methane producing bacteria require H_2 or acetate as substrates to produce methane. The H_2 and acetate produced during the fermentation of the BTEX compounds create a geochemical environment where EDB or 1,2-DCA can be metabolized by methane producing bacteria, or by *Dehalococcoides* strains, or by both. Higher concentrations of methane should be associated with lower concentrations of EDB.

Henderson et al. (2008) constructed microcosms from the source area of a release of leaded gasoline and from a mid gradient location. They noted the greatest removal of EDB in microcosms with the greatest production of methane. Anaerobic biodegradation of EDB in the microcosms of Henderson et al. (2008) produced significant fractions of 2-bromoethanol instead of ethylene. Bromoethanol was not identified as a product in the pure culture studies of methanogenic bacteria conducted by Belay and Daniels (1987), and has not been reported as a product in mixed culture studies of *Dehalococcoides* strains (Tandol et al., 1994). However, Bouwer and McCarty (1985) conducted ^{14}C label studies of the fate of EDB in a mixed methanogenic culture that was provided with acetate as the primary substrate. A significant fraction of label (59±6 %) was recovered in material that had the properties of bromoethanol. It is possible that the bromoethanol was produced by methane producing bacteria because certain aerobic organisms can metabolize EDB and produce bromoethanol as an intermediate, using an enzyme that does not require molecular oxygen (Poelarends et al., 1999; Scholtz et al., 1987). It is also possible that EDB was metabolized to bromoethanol by other anaerobic organisms that are yet to be characterized. In any case, the activity of methane producing bacteria and strains of *Dehalococcoides* can account for the observed anaerobic biodegradation of EDB and 1,2-DCA.

Figure 2.13 compares the association of methane and EDB in sites in the EPA/ASTSWMO study. Methane was present above its detection limit of 0.001 mg/l at fourteen of sixteen sites. Five sites met the criterion of greater than 0.5 mg/L of methane. In general there were lower concentrations of methane in the EPA/ASTSWMO study than was found in the study of Kolhatkar et al. (2000). This may reflect a depletion of the supply of BTEX compounds to produce the H_2 and acetate needed as substrates for methane production.

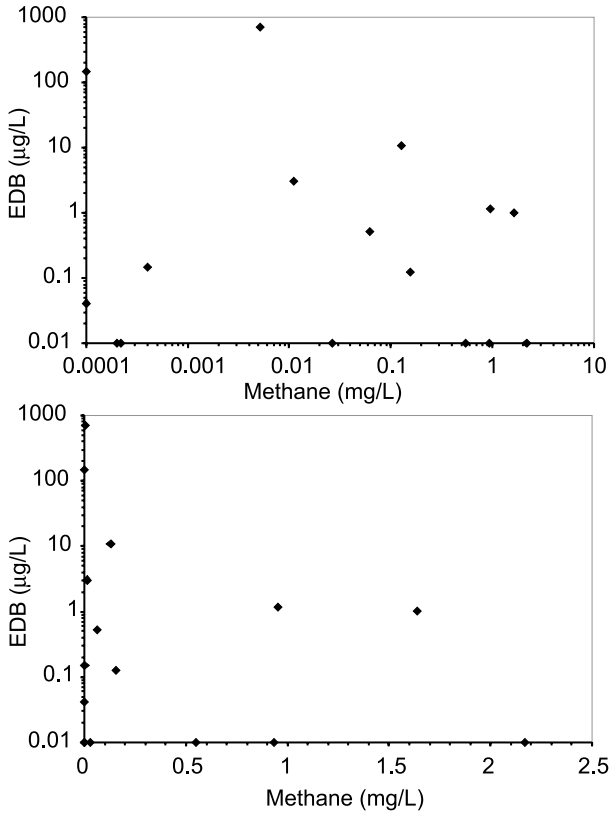

Figure 2.13. Association of concentrations of methane with concentrations of EDB in the most contaminated monitoring wells at sites.

On first examination, there appears to be a relationship between the concentrations of methane and the concentrations of EDB in the wells in the EPA/ASTSWMO study. The two sites with the highest concentrations of EDB (711 and 147 µg/L) had concentrations of methane less than 0.01 mg/L, and the five sites with concentrations of methane greater than 0.5 mg/L had EDB concentrations of 1 µg/L or less. However, there are only eight sites where the concentrations of both EDB and methane were above the detection limit. For these eight sites, the correlation coefficient between the logarithm of the EDB concentration and the logarithm of the methane concentration is -0.13. The sign of the correlation coefficient is in the right direction (concentrations of EDB go down as concentrations of methane go up) but the association is too weak to have any predictive value at other sites.

2.3.3.2.5 pH

The pH of ground water has a strong effect on the two processes that can destroy EDB and 1,2-DCA in ground water. The rate of abiotic transformation of TCE by iron(II) sulfide increases as the pH increases (Butler and Hayes, 2001). Transformation of EDB and 1,2-DCA by iron(II) sulfide should proceed by the same mechanism and pH should have the same effect on the rate of their transformation. The rates at pH of 5 or less should be one hundred fold lower than rates at pH 7. Similarly, the primary organism that is responsible for biological reductive dechlorination of EDB and 1,2-DCA is sensitive to acid conditions (Maymo´-Gatell et al., 1997). The EPA/ASTSWMO study compared concentrations of EDB to pH in the most contaminated well at eleven sites (Figure 2.14). The concentration of EDB was high at one site that was strongly acid (pH of 4), and the concentration of EDB was lower in wells with pH near 7. However, there were also several sites where the concentration of EDB was high and the pH was near 7; indicating that pH by itself cannot be used to predict the concentration of EDB in old leaded motor fuel release sites.

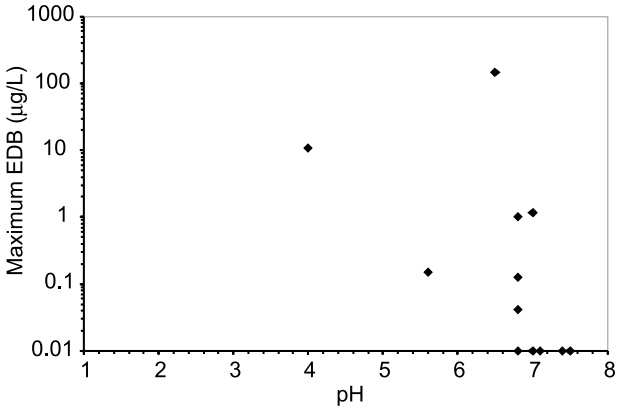

Figure 2.14. Association of pH with concentrations of EDB in the most contaminated monitoring wells at sites.

2.4 Applications of Compound Specific Isotope Analysis (CSIA) to Document Biodegradation and/or Abiotic Transformation of EDB and 1,2-DCA

This sub-section reviews the application of Compound Specific Isotope Analysis (CSIA) to evaluate the biodegradation and abiotic transformation of EDB and 1,2-DCA at motor fuel release sites. This sub-section is intended for technical staff that will interpret CSIA analyses to provide an estimate of the extent of biodegradation and/or abiotic transformation of EDB or 1,2-DCA in ground water at gasoline release sites.

Frequently, mathematical models of transport and fate are used to provide an exposure assessment as part of the risk management process. Because EDB and 1,2-DCA do not sorb strongly to aquifer sediments, the transport and fate models are very sensitive to the rate of biodegradation and the rate of abiotic transformation of the contaminants. It is difficult to extract unequivocal estimates of the rate of biodegradation or abiotic transformation from conventional field monitoring data, and as a consequence, there is a large amount of uncertainty in the calibration of the transport and fate models. In many circumstances, a determination of the isotopic ratio of carbon can unequivocally document the extent of biodegradation or abiotic transformation of EDB or 1,2-DCA that has occurred as the contaminant moves along a flow path in ground water. By providing an independent estimate of the extent of degradation or transformation, CSIA analysis can facilitate the calibration of transport and fate models by reducing the uncertainty in the estimates of exposure that are obtained from the models.

2.4.1 Theoretical Background for Using CSIA to Estimate the Extent of Biodegradation

There are two naturally occurring stable isotopes of carbon: (1) Carbon-12, which has a weight of twelve Daltons, and (2) Carbon-13, which has a weight of thirteen Daltons. Carbon-12 (^{12}C) is approximately one hundred times more abundant than Carbon-13 (^{13}C). During biodegradation or abiotic transformation, EDB or 1,2-DCA molecules with two ^{12}C atoms are degraded more rapidly than molecules with one ^{13}C atom and one ^{12}C atom, which leads to an increase in the ratio of ^{13}C to ^{12}C in the residual EDB or 1,2-DCA. The change in the ratio of ^{13}C to ^{12}C is described as enrichment of the carbon isotopes during biodegradation or abiotic transformation. In recent years, enrichment of stable carbon isotopes has been used to recognize and describe the natural biodegradation of MTBE in ground water (Hunkeler et al., 2001; Gray et al., 2002; Kolhatkar et al., 2002; Kuder et al., 2005a; Somsamak et al., 2006; Wilson et al., 2005; Zwank et al., 2005), and benzene in ground water (Mancini et al., 2003; Fischer et al., 2007).

The ratio of isotopes is determined with an isotope ratio mass spectrometer. The mass spectrometer does not measure the ratio of the stable carbon isotopes to each other. Rather, it measures the deviation of the ratio in the sample from the ratio of a standard used to calibrate the instrument. The conventional notation for the ratio of ^{13}C to ^{12}C in a sample ($\delta^{13}C$) reports the ratio in terms of its deviation from the ratio in the standard, as described in Equation 2.6 (Meckenstock et al., 2004; Schmidt et al., 2004).

$$\delta^{13}C = \left[\frac{\left(^{13}C/^{12}C\right)_{\text{sample}} - \left(^{13}C/^{12}C\right)_{\text{standard}}}{\left(^{13}C/^{12}C\right)_{\text{standard}}} \right] \times 1000 \qquad (2.6)$$

The units for $\delta^{13}C$ are parts per thousand, often represented as ‰, or per mil, or per mill. The usual pronunciation of $\delta^{13}C$ is "delta thirteen sea." The substance used as the international standard for stable carbon isotopes has a ratio of ^{13}C to ^{12}C of 0.0112372. During the course of biodegradation or abiotic transformation, the compound that is still remaining will have more of the heavy isotope ^{13}C, and the value of $\delta^{13}C$ will become more positive. The extent of isotopic enrichment is typically characterized by calculating a linear regression of the $\delta^{13}C$ in the compound being degraded versus the natural logarithm of the fraction of the compound remaining (C/Co) after biodegradation or transformation (Meckenstock et al., 2004; Schmidt et al., 2004). The slope of the regression line is termed the isotopic enrichment factor (ε). When $\delta^{13}C$ is expressed in units of ‰, the unit of ε is ‰.

When an appropriate value of ε is available, and when an estimate of the initial value of $\delta^{13}C$ in the compound as originally released in the gasoline is available, the fraction (F) of material remaining in ground water after biodegradation or abiotic transformation can be calculated from the value of $\delta^{13}C$ determined for the compound in ground water (Meckenstock et al., 2004; Schmidt et al., 2004; Wilson et al., 2005).

$$F = C/Co = e^{\left(\left(\delta^{13}C_{field} - \delta^{13}C_{i=0}\right)/\varepsilon\right)} \qquad (2.7)$$

The fraction of material degraded is simply one minus F.

The value of $\delta^{13}C$ in EDB or 1,2-DCA in ground water is measured directly in a water sample from monitoring wells at the release site ($\delta^{13}C_{field}$). Equation 2.7 also requires the isotopic enrichment factor (ε) and the initial value of $\delta^{13}C$ (i.e., at t = 0). The following material will review available literature on the isotopic enrichment factor for biodegradation and abiotic transformation of EDB and 1,2-DCA, followed by a discussion of the most plausible values for the initial $\delta^{13}C$ of EDB or 1,2-DCA originally released in leaded gasoline.

2.4.2 Isotopic Enrichment during Biodegradation of EDB and 1,2-DCA

At gasoline release sites, the oxygen demand associated with petroleum hydrocarbons generally consumes all the available dissolved oxygen in ground water. As a consequence, biological degradation of EDB or 1,2-DCA in close proximity to a spill of gasoline must occur through an anaerobic process. At this writing (spring 2008), there is only one value of ε for anaerobic biodegradation of EDB available in the literature (Henderson et al., 2008); the primary data are presented in Figure 2.15. The enrichment factor was extracted from microcosms that were constructed with sediment from a UST release site. The enrichment factor, as determined by the slope of the regression line, has a value of -5.7 ± 1‰.

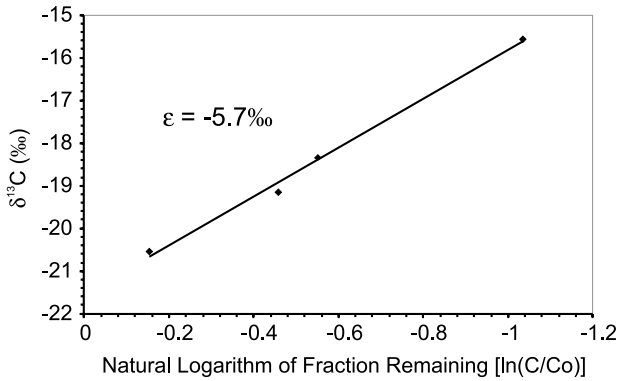

Figure 2.15. Enrichment of the heavy isotope of carbon in EDB during anaerobic biodegradation of EDB in a microcosm study. (Redrawn from Henderson et al. (2008).)

There are only two enrichment factors available in the literature for anaerobic biodegradation of 1,2-DCA. Hunkeler et al. (2002) reported a value of -32.1 ± 1.1‰ and Hirschorn et al. (2007) reported a value of -25.8 ± 3.5 ‰. These values of ε for biodegradation of 1,2-DCA are much more negative (show stronger enrichment) than is the case for EDB (ε = -5.7 ± 1‰).

There are several ways to account for the stronger enrichment of 1,2-DCA compared to EDB. Table 2.4 compares isotopic enrichment factors for biodegradation of a variety of halogenated compounds. In general, the value of ε becomes less negative as the molecular weight increases. The value of ε for anaerobic biodegradation of EDB is near the values for biological degradation of PCE and TCE, compounds that have a molecular weight similar to EDB.

This relationship between molecular weight and the enrichment factor has been explained by Nijenhuis et al. (2005) as the effect of a mass transport limitation of the compound across the cell wall of the bacteria that degrade the contaminant. They showed that the enrichment factor for degradation of PCE was most negative for the pure PCE reductive dehalogenase enzyme, was less negative for cell extracts, and was even less negative for the living bacteria. The compounds with lower molecular weight are more soluble in water, and enter the bacterial cells less readily.

Part of the difference in the value of the enrichment factor for anaerobic biodegradation of EDB compared to 1,2-DCA can be attributed to differences in the mechanisms of degradation. Figure 2.16 compares three pathways that are available for anaerobic biodegradation of EDB or 1,2-DCA. Biodegradation of EDB in the microcosm study of Henderson et al. (2008) was primarily through a mechanism of reductive dehalogenation, also called hydrogenolysis, with a minor amount of hydrolytic debromination. In contrast, in the study of Hunkeler et al. (2002) biodegradation of 1,2-DCA was through a process of dichloroelimination. Elsner et al. (2005) showed that a dichloroelimination reaction should produce more negative values for the enrichment factor than a hydrogenolysis reaction.

Table 2.4. Comparison of enrichment factors for EDB and DCA to the range of isotopic enrichment factors (ε) for carbon isotopes during reductive dehalogenation of halogenated organic compounds.

Halogenated hydrocarbon	Molecular Weight (Daltons)	Mechanism	$^{13}C/^{12}C$ ε ‰	Reference
EDB	187.9	mostly biological hydrogenolysis, some hydrolytic debromination	-5.7	Henderson et al., 2008
EDB	187.9		-20.2	This Report
PCE	165.8	biological hydrogenolysis	-5.2	Slater et al., 2001
PCE	165.8	biological hydrogenolysis	-2	Hunkeler et al., 1999
TCE	131.4	biological hydrogenolysis	-6.6 -2.5	Bloom et al., 2000
TCE	131.4	biological hydrogenolysis	-7.1	Sherwood Lollar et al., 1999
TCE	131.4	biological hydrogenolysis	-13.8	Slater et al., 2001
1,1,2-TCA	133.4	biological dichloroelimination	-2.0	Hunkeler et al., 2002
cis-DCE	96.9	biological hydrogenolysis	-14.1 -16.1	Bloom et al., 2000
cis-DCE	96.9	biological hydrogenolysis	-19.9	Hunkeler et al., 2002
cis-DCE	96.9	biological hydrogenolysis	-20.4	Slater et al., 2001
trans-DCE	96.9	biological hydrogenolysis	-30.3	Hunkeler et al., 2002
1,1-DCE	96.9	biological hydrogenolysis	-7.3	Hunkeler et al., 2002
1,2-DCA	98.9	biological dichloroelimination	-32.1	Hunkeler et al., 2002
1,2-DCA	98.9	biological hydrolytic dechlorination	-25.8	Hirschorn et al., 2007
VC	62.5	biological hydrogenolysis	-21.5 -26.6	Bloom et al., 2000
VC	62.5	biological hydrogenolysis	-22.4	Slater et al., 2001
VC	62.5	biological hydrogenolysis	-31.1	Hunkeler et al., 2002

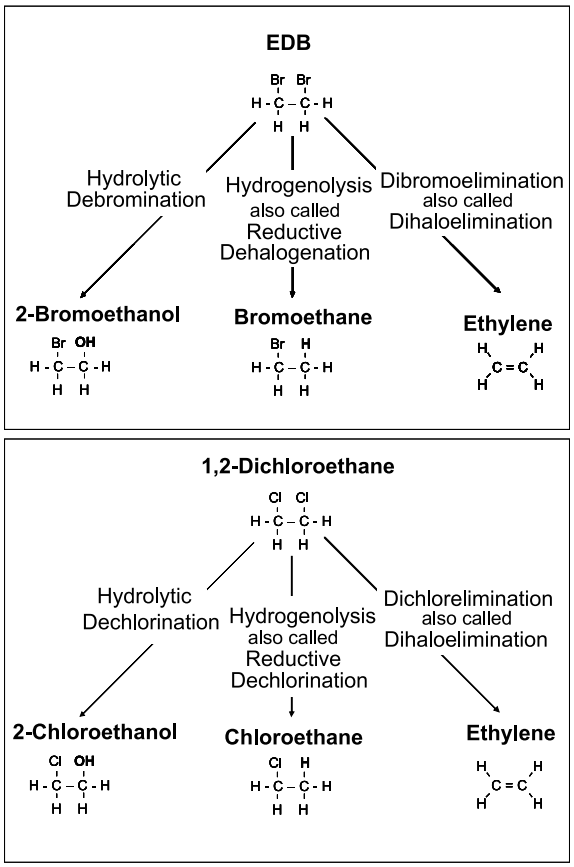

Figure 2.16. Biological or Abiotic Transformations of EDB and 1,2-DCA.

Hirschorn et al. (2007) compared the enrichment factor for biodegradation under aerobic conditions to the enrichment factor under nitrate reducing conditions. The enrichment factor under aerobic conditions was strongly negative (-25.8 ± 0.4‰). The values of the enrichment factor under aerobic and nitrate reducing conditions were essentially identical. Hirschorn et al. (2007) used the correspondence in enrichment factors to argue that anaerobic biodegradation of 1,2-DCA under nitrate reducing conditions proceeded through the same hydrolytic dechlorination reaction that was used under aerobic conditions.

A third possible explanation for the difference in the enrichment factors during anaerobic biodegradation of EDB and 1,2-DCA would relate to the differences between the C-Cl and C-Br bond. Miller et al. (2001) compared the enrichment factors produced by aerobic biodegradation of methyl chloride, methyl bromide, and methyl iodide. The enrichment factors were essentially the same; the nature of the halogen in the compound does not seem to matter.

2.4.3 Isotopic Enrichment During Abiotic Transformation of EDB and 1,2-DCA

As of this writing (spring 2008) there is no literature available on the isotopic enrichment of EDB during abiotic transformation. As described in Section 2.3.2, a laboratory study was conducted on the transformation of EDB in the presence of biogenic FeS. The biogenic FeS was formed in a laboratory column that simulated a passive reactive barrier constructed with plant mulch and sand. The plant mulch supported sulfate reduction to produce sulfide, and the sulfide reacted with hematite and other iron minerals in the column to produce FeS in the column. To determine the kinetics of EDB transformation by the biogenic FeS and carbon isotope enrichment during transformation, the column was sampled and FeS and sand were separated from the plant mulch under an oxygen free atmosphere and then incubated with a dose solution that contained approximately 50 mg/L EDB. Incubations were conducted in five separate preparations taken from two locations in the original column. The $\delta^{13}C$ of EDB in the porewater was determined after 1 hour of incubation and after 7, 15, 22, and 29 days of incubation.

The relationship between the extent of removal of EDB and the $\delta^{13}C$ of EDB is presented in Figure 2.17. The isotopic enrichment factor, as determined by a linear regression of $\delta^{13}C$ of EDB on the natural logarithm of the fraction of EDB remaining (where the data from all five incubations were pooled) was -20.2 ± 2.23‰ at 95% confidence.

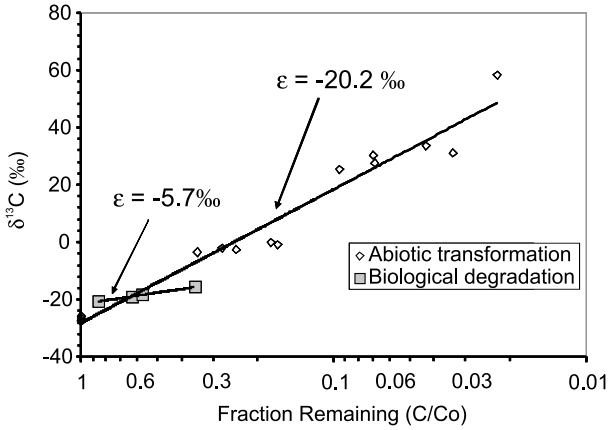

Figure 2.17. A comparison of the enrichment of the heavy carbon isotope in EDB during anaerobic biodegradation of EDB in a microcosm study (Henderson et al., 2008) against enrichment during abiotic transformation of EDB by FeS.

The enrichment of carbon isotopes during abiotic degradation of EDB during reaction with FeS (-20.2 ‰) is significantly greater than the enrichment during biodegradation (-5.7‰). This relationship has been observed for other halogenated organic compounds. Liang et al., (2007) compared the enrichment of stable carbon isotopes during biological and nonbiological degradation of PCE and TCE. Enrichment of PCE and TCE during transformation by FeS at pH 7 was -30.2 ± 4.3‰ and -33.4 ± 1.5‰ respectively. Enrichment during biodegradation varied with the culture, ranging from -1.39‰ to -7.12‰ for PCE and from -4.07‰ to -15.27‰ for TCE. In each case, the enrichment during abiotic transformation was substantially greater than the enrichment during biodegradation.

The contrast in behavior of stable carbon isotopes in EDB during biodegradation and abiotic transformation parallels the behavior of PCE and TCE. If the reaction EDB with FeS followed the dihaloelimination pathway (Figure 2.16) the enrichment factor should be close to the enrichment factor observed by Liang et al. (2007) for reaction of TCE and PCE with FeS. According to Equation 2.7, as the value $\delta^{13}C$ of EDB in ground water becomes less negative, the predicted value of the fraction remaining (C/Co) is smaller, and the predicted extent of biodegradation is greater. For a given change in the value of $\delta^{13}C$, the predicted extent of biodegradation becomes greater as the value of the enrichment factor (ε) becomes less negative. Liang et al. (2007) warn that the approach used in Equation 2.7 will over predict the extent of biodegradation of PCE or TCE if a value of ε that is appropriate for biodegradation is used to interpret enrichment in ground water samples where abiotic processes are primarily responsible for the destruction of PCE or TCE.

The same warning applies to EDB. If a range of values of ε are available for the same process, or if several processes can operate simultaneously and they vary widely in the value of ε, a more conservative estimate of the extent of EDB destruction is provided by choosing the most negative value of the isotopic enrichment factor.

2.4.4 The Initial Value of $\delta^{13}C$ of EDB or 1,2-DCA Originally Released in Leaded Motor Fuel

To use equation 2.7 to estimate the extent of degradation of EDB from the $\delta^{13}C$ of EDB in ground water, it is necessary to have an initial value for $\delta^{13}C$ of EDB in the leaded motor fuel that was spilled. The analytical techniques for CSIA were developed in the late 1990s, while EDB and 1,2-DCA were banned in conventional motor gasoline after 1980. As a result, there is no direct information available on the $\delta^{13}C$ of EDB or 1,2-DCA originally released in leaded motor fuel. Five samples of modern leaded motor fuels were analyzed for $\delta^{13}C$ of EDB. Four samples of aviation gasoline (Avgas LL 100 octane) returned values of -29.6‰, -30.1‰, -30.2‰, and -30.7‰. One sample of 110 octane automobile racing fuel returned a value of -30.2‰. In the absence of additional information, a value of -30‰ is recommended as the best estimate currently available of the original value of $\delta^{13}C$ in EDB in leaded motor fuels.

Similar processes are used to manufacture both EDB and 1,2-DCA and PCE, TCE, and 1,1,1-TCA, and they often were produced at the same manufacturing plants. Table 2.5 summarizes published values for $\delta^{13}C$ of PCE, TCE, and 1,1,1-TCA produced by a number of manufactures in the past. The most negative value reported was -37.2‰, the least negative value reported was -23.2‰.

If the assumed initial value of $\delta^{13}C$ in EDB is more negative than the true value, the extent of degradation predicted by Equation 2.7 will overestimate the true extent of degradation. To provide a conservative lower boundary on the fraction of EDB remaining after degradation, and a conservative upper boundary on the fraction degraded, it is most appropriate to use the least negative value within the plausible range of values of $\delta^{13}C$ that would be expected in leaded motor fuel. In the absence of other direct information, a value of -23.2‰ will be taken as conservative upper boundary on the value of $\delta^{13}C$ in EDB or 1,2-DCA in leaded gasoline.

2.4.5 Measured Concentrations of EDB and $\delta^{13}C$ of EDB in Ground Water

If measured concentrations of EDB in ground water are related to the destruction of EDB in ground water, there should be a relationship between the concentration of EDB and the $\delta^{13}C$ of EDB. To search for a relationship, water samples from the most contaminated wells at selected sites in the EPA/ASTSWMO study were analyzed for concentrations of EDB and for $\delta^{13}C$ of EDB. The population of candidate sites was limited by two factors: (1) access to the sites so that they could be resampled, and (2) the relatively high concentration of EDB required for determination of $\delta^{13}C$ in EDB in the sample. A concentration of at least 4 µg/L of EDB is required to attain the quality objective

Table 2.5. Range of $\delta^{13}C$ in samples of commercial chlorinated solvents.

Compound	Source	$\delta^{13}C$ (‰/PDB)	Reference
PCE	Manufacturer A	-27.12±0.03	Jendrzejewski et al. (2001)
PCE	Manufacturer B	-35.27±0.12	Jendrzejewski et al. (2001)
PCE	Manufacturer C	-24.06±0.08	Jendrzejewski et al. (2001)
PCE	Dow	-23.19±0.10	van Warmerdam et al. (1995)
PCE	ICI	-37.20±0.03	van Warmerdam et al. (1995)
PCE	PPG	-33.84±0.03	van Warmerdam et al. (1995)
PCE	Vulcan	-24.1±0.04	van Warmerdam et al. (1995)
PCE	Range	-23.19 to -37.20	
TCE	Manufacturer A	-31.53±0.01	Jendrzejewski et al. (2001)
TCE	Manufacturer B	-27.90±0.08	Jendrzejewski et al. (2001)
TCE	Manufacturer C	-29.93±0.18	Jendrzejewski et al. (2001)
TCE	Aldrich	-33.49±0.08	Jendrzejewski et al. (2001)
TCE	Dow	-31.90±0.05	van Warmerdam et al. (1995)
TCE	ICI	-31.32±0.03	van Warmerdam et al. (1995)
TCE	PPG	-27.80±0.01	van Warmerdam et al. (1995)
TCE	Range	-27.80 to -33.49	
1,1,1-TCA	Manufacturer A	-31.64±0.09	Jendrzejewski et al. (2001)
1,1,1-TCA	Dow	-29.42±0.06	van Warmerdam et al. (1995)
1,1,1-TCA	ICI	-26.64±0.09	van Warmerdam et al. (1995)
1,1,1-TCA	PPG	-25.80±0.46	van Warmerdam et al. (1995)
1,1,1-TCA	Vulcan	-28.42±0.07	van Warmerdam et al. (1995)
	Range	-25.80 to -31.64	

Summarized from Wilson (2008).

of a sample standard deviation of 0.5‰ or less. Five sites met both criteria, one each in Montana, Minnesota, Virginia, and two sites in New Hampshire. As was expected, the two sites with lower concentrations of EDB had higher values for $\delta^{13}C$ of EDB (Figure 2.18 and Table 2.6).

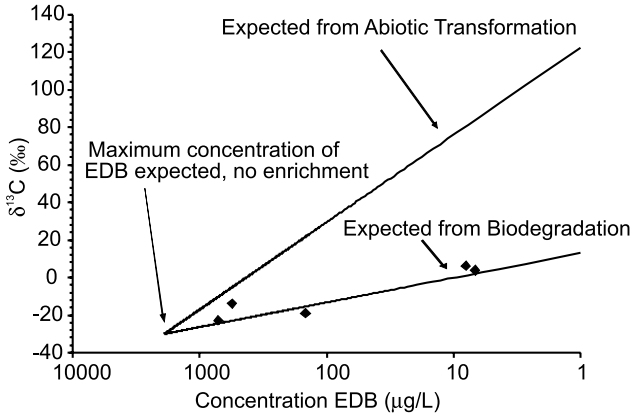

Figure 2.18. Relationship between the concentrations of EDB in the most contaminated wells at each of five sites and the $\delta^{13}C$ of EDB. (Note that the concentration on x-axis decreases from left to right).

Falta (2004) used the expected concentration of EDB in leaded gasoline, and Raoult's Law to estimate the concentration of EDB in ground water that would be in equilibrium with typical leaded gasoline. The predicted concentration is 1,900 µg/L. Equation 2.7 was rearranged to produce Equation 2.8, and Equation 2.8 was in turn used to calculate the value of $\delta^{13}C$ of EDB that would correspond to various concentrations of EDB (Table 2.6).

$$\delta^{13}C_{field} = \left(\delta^{13}C_{t=0}\right) - \varepsilon * \ln\left(Con._{field} / 1900\right) \quad (2.8)$$

Where $\delta^{13}C_{field}$ is the expected value of $\delta^{13}C$ of EDB in ground water in units of ‰, $Conc._{field}$ is the expected concentration of EDB in ground water in units of µg/L, $\delta^{13}C_{t=0}$ is the initial value of $\delta^{13}C$ of EDB in the gasoline (assumed to be -30‰) and ε is the appropriate value for the isotopic enrichment factors in units of ‰. Equation 2.8 assumes that destruction of EDB is the only process that attenuates the concentration of EDB. There is no allowance for attenuation due to dilution in the monitoring wells. If there were dilution of the plume in the monitoring well, the expected concentration of EDB would shift to a lower value.

In Figure 2.18, a value of -5.7‰ was used for ε to predict the relationship dominated by biodegradation and a value of -20.2‰ was used to predict the relationship dominated by abiotic transformation. The data best fit the projections of fractionation that would be expected from biodegradation of EDB.

In general, the few data in Figure 2.18 are consistent with the assumption that reductions in concentration of EDB are caused by processes that

Table 2.6. Relationship between the concentrations of EDB in the most contaminated wells at five motor fuel release sites, enrichment of stable carbon isotopes in EDB, and a conservative estimate of the fraction of EDB destroyed.

Location	Concentration EDB	$\delta^{13}C$	Fraction Remaining*	Fraction Destroyed
	µg/L	‰		
Station A, New Hampshire	711	-22.8	0.70	0.30
Virginia	557	-13.9	0.45	0.55
Station B, New Hampshire	147	-18.9	0.58	0.42
Montana	8.0	6.1	0.17	0.83
Minnesota	6.8	3.9	0.19	0.81

* Fraction remaining calculated from Equation 2.7 assuming $\delta^{13}C_{t=0}$ = -30.‰ and ε = -20.2‰

destroy EDB, and can be recognized by analysis of $\delta^{13}C$ in EDB. This suggests that CSIA will be a useful tool to recognize biodegradation or abiotic transformation of EDB in residual gasoline in the source area of plumes.

2.4.6 Predictions of the Extent of Degradation or Transformation

At present there is no straightforward approach to attribute one portion of EDB destruction to biodegradation and the remaining portion to abiotic transformations. As a consequence, the most conservative approach is to attribute all of the destruction of EDB to abiotic transformation.

Figure 2.19 presents a prediction of the extent of destruction of EDB based on various measured values of $\delta^{13}C$ in EDB in ground water, and the assumption that abiotic processes are entirely responsible for destruction of EDB. Figure 2.9 presents predictions of the fraction of EDB remaining that correspond to the best estimate of the initial value of $\delta^{13}C$ in EDB in the leaded motor fuel that was originally spilled (-30‰) and to the most conservative estimate of the initial value of $\delta^{13}C$ in EDB in the leaded motor fuel that was originally spilled (-23.2‰). As an example, at the best estimate of the initial value of $\delta^{13}C$ in EDB in gasoline, a measured value of $\delta^{13}C$ in EDB in ground water of +24‰ would predict that 7% of the original quantity of EDB remained. The most conservative estimate of the initial $\delta^{13}C$ in EDB in ground water predicts that 10% of the original quantity of EDB remains.

Figure 2.19 was used to provide a conservative boundary on the extent of destruction of EDB at the five release sites listed in Table 2.6. Even with a small data set, CSIA could distinguish sites with minor amounts of EDB destruction from sites where a major fraction of EDB had been destroyed.

If the data are available, a better approach to evaluate EDB destruction at a particular site would use the most negative value of $\delta^{13}C$ in EDB in any monitoring well at a site as the local best estimate of $\delta^{13}C$ in EDB in gasoline, then use Equation 2.6 to predict the extent of degradation in the other wells. This approach is particularly recommended if data are available from wells along a flow path in the aquifer that are down gradient of the area with known residual gasoline. Figure 2.19 is offered to provide a quick and conservative boundary on the extent of EDB destruction when the available data are few, or when the hydraulic relationships of wells are not readily apparent.

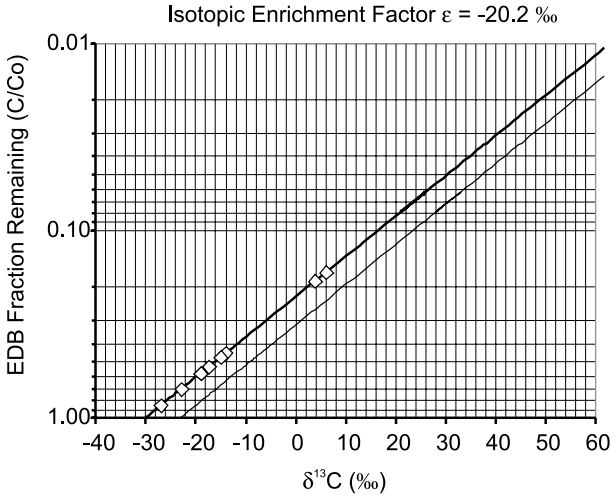

Figure 2.19. A conservative estimate of the relationship between the measured value of $\delta^{13}C$ of EDB in ground water at a Leaded Motor Fuel Release Site, and the extent of destruction of EDB by abiotic and biological processes. The heavy solid line projects destruction based on the best available estimate of the initial value of $\delta^{13}C$ of EDB in leaded gasoline. The light solid line projects destruction based on the most conservative estimate for the initial value of $\delta^{13}C$ of EDB in leaded gasoline. The diamonds represent estimates of the fraction of EDB remaining in monitoring wells in the spill sites described in Table 2.6. See text for further discussion.

3.0
Distribution of EDB and 1,2-DCA at Motor Fuel Release Sites, and the Associated Chance of Contaminating Ground Water

This section describes the existing concentrations of EDB, benzene, and 1,2-DCA in monitoring wells at gasoline service stations. It is intended for decision makers and other staff of regulatory agencies that must apportion resources for monitoring and risk management of the hazard associated with EDB, benzene, and 1,2-DCA in ground water used for drinking water. It is also useful to case workers in regulatory agencies as a basis for comparison of the distribution of EDB and 1,2-DCA at their sites to concentrations that were determined at other sites.

3.1 Existing Distribution of EDB, 1,2-DCA, and Benzene in Ground Water at Selected Motor Fuel Release Sites

Figure 3.1 provides a map showing the states that participated in the study. Participation in the EPA/ASTSWMO study was entirely voluntary on the part of the state agencies. The coverage of the USA was reasonably representative; however, the states on the Pacific Coast chose not to participate. The number of stations that were sampled in each state was variable. Two of the states provided samples from only one station each, and two of the states provided samples from ten stations each (Table 1.1).

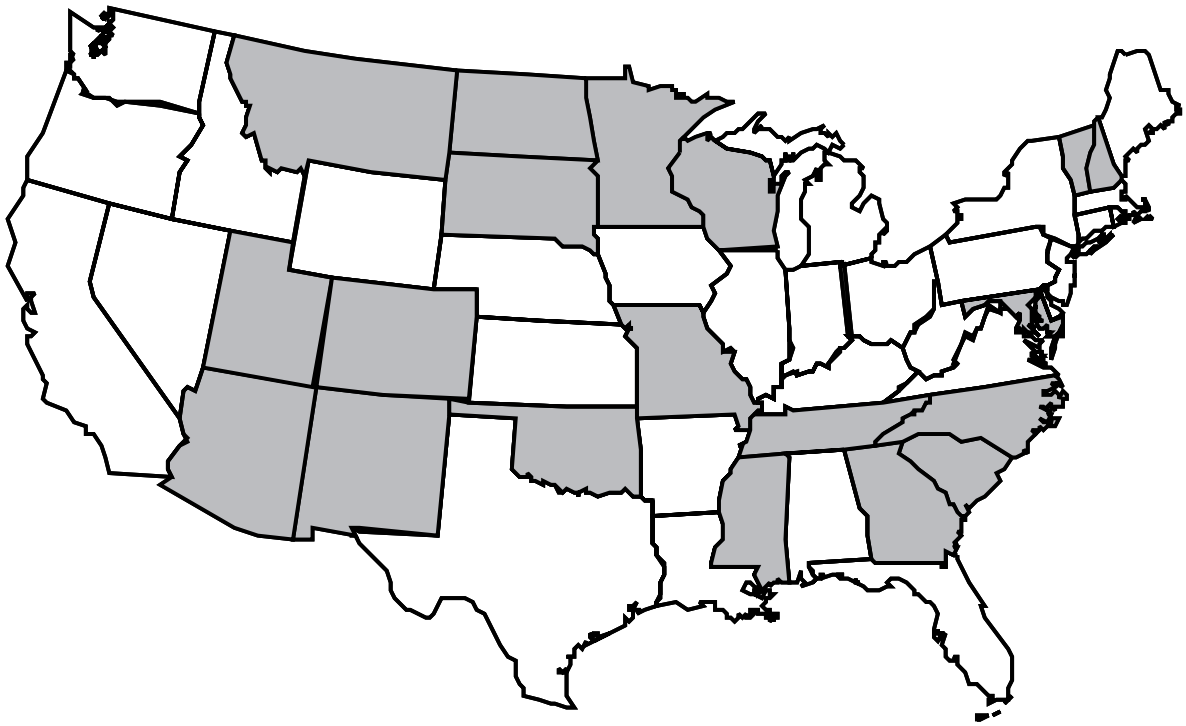

Figure 3.1. Distribution of states participating in the EPA/ASTSWMO Study.

Because the sampling locations were not selected randomly, the samples can not be taken to represent the population of gasoline service station sites in the USA. At best, the samples represent a population of service station sites in the USA where the relevant case worker in the state agency was interested in the possibility that EDB was present in ground water at the site. Nevertheless, there is a close correspondence between the distribution of EDB concentrations in South Carolina, and in the sites that were sampled in the EPA/ASTSWMO study (Figure 1.2). The total fraction of sites that exceeded the MCL was very similar, and the distribution of sites with concentrations above 20 µg/L was almost identical. Table 3.1 summarizes the data in Figure 1.2.

As discussed earlier, not all the EDB used in the US was used in motor fuel. Approximately 10% was used in agriculture. Background wells were not sampled at all of the sites that participated in the EPA/ASTSWMO study. As a consequence, it is not possible to exclude the possibility that a portion of the EDB detected in wells at the gasoline service stations resulted from agricultural application.

3.2 Relative Distribution of EDB, 1,2-DCA, and Benzene at Selected Motor Fuel Release Sites

There were 39 sites in the EPA/ASTSWMO study with detectable concentrations of both EDB and benzene. In the 39 sites, there were seven sites from Colorado, two sites from Maryland, one site from Montana, three sites from North Carolina, four sites from North Dakota, two sites from New Hampshire, two sites from Oklahoma, five sites from South Carolina, one site from South Dakota, three sites from Tennessee, two sites from Utah, and seven sites from Wisconsin.

Data are summarized in Table 3.2. As was expected, benzene was detected above the MCL at every site that was sampled. In contrast, EDB was detected in 53% of sites, but detected above the MCL at only 42% of sites, and 1,2-DCA was detected at 23% of sites, but detected above the MCL at only 15% of sites. Both EDB and 1,2-DCA were present at concentrations above the MCL at a significant number of sites.

Table 3.1. The distribution of EDB in the sites included in the EPA/ASTSWMO State Study compared to distribution in South Carolina.

Maximum Concentration at Site	South Carolina (Falta data)	EPA/ASTSWMO State Study
	Percent of Sites	
Above 100 µg/L	7%	6%
Above 50 µg/L	11%	10%
Above 1 µg/L	35%	25%

Table 3.2. Occurrence of EDB, benzene, and DCA in sites sampled during the EPA/ASTSWMO State Study.

	States	Sites	Samples
Method 8011 for EDB	19	102	802
EDB detected	19 (100%)	54 (53%)	151 (19%)
EDB above MCL	17 (89%)	43 (42%)	103 (13%)
Method 8260 for Benzene	12	39	335
Benzene detected	12 (100%)	39 (100%)	118 (40%)
Benzene above MCL	12 (100%)	39 (100%)	105 (36%)
Method 8260 for DCA	12	39	293
DCA detected	6 (50%)	10 (26%)	18 (6%)
DCA above MCL	5 (42%)	6 (15%)	8 (3%)

Figure 3.2 plots the frequency distribution of the concentrations of benzene, 1,2-DCA, and EDB independent of each other at a particular site. For comparison, the figure also plots the concentration that would be predicted for benzene, 1,2-DCA, and EDB in ground water that was in equilibrium with un-weathered leaded gasoline. The predicted values for concentrations were taken from Table 2 of Falta (2004). He calculated the predicted values based on the average concentrations of benzene, 1,2-DCA, and EDB in leaded gasoline, and on the gasoline to water partition coefficient in the case of EDB and benzene, or based on Raoult's Law for 1,2-DCA.

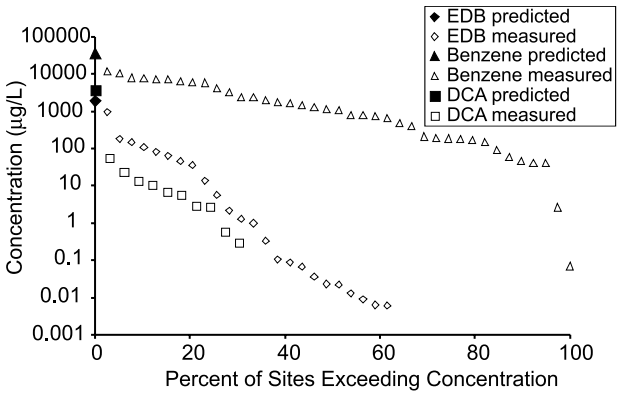

Figure 3.2. Distribution of the maximum concentrations of EDB, 1,2-DCA, and benzene in ground water from monitoring wells at motor fuel release sites in the EPA/ASTSWMO study, compared to the concentrations predicted for ground water in contact with unweathered leaded gasoline.

The predicted concentration of benzene in ground water that is equilibrated with leaded gasoline is ten fold higher than the predicted concentration of 1,2-DCA, and the predicted concentration of 1,2-DCA is two fold higher than the predicted concentration of EDB. The actual concentrations of benzene, 1,2-DCA, and EDB are less than predicted. There are a number of possible explanations. Weathering of the residual gasoline over time may have reduced the concentrations of benzene, 1,2-DCA, and EDB in the residual gasoline. Ground water that was exposed to the residual gasoline in the aquifer and contaminated with benzene, 1,2-DCA, and EDB may have been diluted with uncontaminated ground water in the monitoring well. There may have been mass transfer limitations on dissolution of benzene, 1,2-DCA, and EDB from the residual gasoline into flowing ground water. In any case, the ground water samples that were most contaminated with EDB or benzene were within a factor of two of the predicted concentration. The highest measured concentration of 1,2-DCA was more than 60 fold lower than the predicted concentration.

With the exception of two lowest concentrations of benzene in the data set, the concentrations of benzene, EDB, and 1,2-DCA all follow a log-linear frequency distribution. There were ten sites that reported concentrations of 1,2-DCA above the method detection limit. As a basis of comparison, the geometric mean concentration was calculated for the ten sites with the highest concentrations of benzene, of EDB, and of 1,2-DCA. On average the concentration of benzene was much higher than EDB or 1,2-DCA. The geometric mean concentrations for benzene, EDB, and 1,2-DCA were 7,300 µg/L, 68 µg/L, and 5.0 µg/L respectively.

The MCL for EDB (0.05 µg/L) is one hundred fold lower than the MCL for benzene and 1,2-DCA (5 µg/L). As a result, it can be confusing and misleading to evaluate the chance for ground water contamination by comparing the concentrations in ground water. A better comparison that is relevant to beneficial use of an aquifer as a ground water supply is the chance that a source of EDB or benzene will contaminate a water supply well at any concentration above the MCL, making it useless for drinking water unless the water is treated.

It is possible to estimate a relative chance that a water supply well will be impacted at concentrations above the MCL if the following three assumptions are accepted. First, the chance that a plume of contamination will impact a water well is proportional to the surface area of the plume. Second, the surface area of a plume is proportional to the square of its length. Third, the length of the plume is proportional to the logarithm of the maximum concentration of the contaminant. Studies of the distribution of contaminants in ground water indicate that concentrations attenuate with distance following a pseudo first order rate law. As a consequence, the length of the plume is proportional to the logarithm of the ratio of the maximum concentration to the MCL. If the MCL is 0.05 µg/L and the maximum concentration is 0.5 µg/L, the length would be some distance X. If the maximum concentration is 5 µg/L, the length would be 2X, if the maximum concentration is 50 µg/L, the length would be 3X, if the maximum

concentration is 500 µg/L, the length would be 4X and so on.

Ignoring the particular hydrogeological context and cultural context of a release, the relative chance that a ground water supply well will be contaminated at concentrations above the MCL is described by Equation 3.1.

$$\text{Relative Chance} = (\text{Ln}[\text{MaximumConc.}/\text{MCL}])^2 \quad (3.1)$$

Figure 3.3 plots the frequency distribution of the relative chance that EDB, benzene, and 1,2-DCA from fuel spill sites in the EPA/ASTSWMO Study will contaminate a water supply well. The data are ranked independently of each other at a particular site. For comparison, the figure also plots the relative chance that would be predicted for EDB, benzene, and 1,2-DCA in ground water that was in equilibrium with un-weathered leaded gasoline. The predicted chance that EDB in ground water that is equilibrated with leaded gasoline will exceed the MCL is greater than the predicted chance for benzene, which in turn is greater than the predicted chance for 1,2-DCA. The greatest chance to exceed the MCL for a particular site and particular contaminant was associated with EDB.

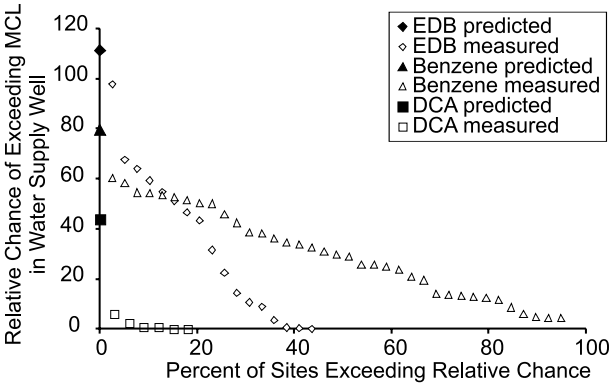

Figure 3.3. Distribution of the relative chance that EDB, 1,2-DCA, and benzene in ground water at motor fuel release sites in the EPA/ASTSWMO Study will impact a water supply well at concentrations above the MCL, compared to the relative chance predicted for ground water in contact with unweathered leaded gasoline. The relative chance is proportional to the surface area of the plume of EDB or benzene, or 1,2-DCA with concentrations above the MCL. See text for details.

Notice from Figure 3.3 that for approximately 20% of the sites in the EPA/ASTSWMO study, the relative chance that EDB would impact a water supply well was roughly equivalent to the chance that benzene would impact a water supply well. However, for the remaining 80% of sites, the chance of EDB impacting a water supply well was much less than the chance that benzene would impact a well. Also notice that in the worst case, the chance that 1,2-DCA would impact a water supply well was roughly 10% of the worst case chance for EDB or benzene, and that the relative chance for 1,2-DCA fell off rapidly as a percent of the sites in the survey.

Although the relative chance that EDB or benzene would impact a water supply well is roughly the same in 20% of the sites in the EPA/ASTSWMO study, the 20% of sites are not the same sites for EDB and for benzene. Figure 3.4 compares the chance associated with the highest reported concentration of benzene in any well at a particular site to the chance associated with the highest reported concentration of EDB in any well at the same site. At 10 of 39 sites, the chance associated with EDB was greater, and the chance associated with benzene was greater at the remaining 29 sites. EDB was the risk driver for impact to water supply wells at approximately one fourth of the sites.

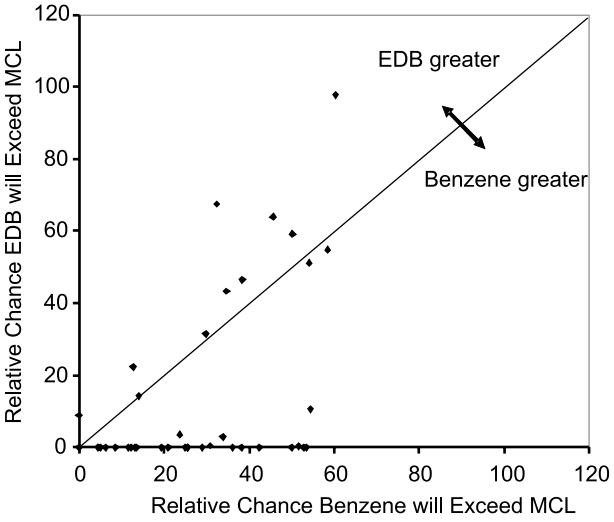

Figure 3.4. Comparison of the relative chance that EDB will exceed the MCL in a water supply well to the relative chance that benzene will exceed the MCL in a water supply well for ground water from motor fuel release sites in the EPA/ASTSWMO Study.

The total chance that EDB, 1,2-DCA, or benzene at the 39 sites in the EPA/ASTSWMO study might

contaminate a water supply well above the MCL can be estimated by summing the individual relative chances for each site. The sum over the 39 sites for EDB is 1100, for benzene is 580 and for 1,2-DCA is 10. In aggregate, in the sites sampled in the EPA/ASTSWMO study, the chances of contaminating a water supply well with EDB or benzene at concentrations above the MCL are roughly equivalent, and the chance for 1,2-DCA is orders of magnitude lower. These estimates can be compared to data released by the U.S. Geological Survey from their comprehensive survey of the occurrence of volatile organic compounds in ground water and drinking-water supply wells in the USA (Zogorski et al., 2006, see Appendix 7). They sampled ground water supplying domestic and public wells; EDB was not detected in 462 samples of ground water supplying public water supply wells. However, EDB was detected in 3 of 2,085 samples of ground water supplying domestic water supply wells. All three detections were above the MCL for EDB of 0.05 µg/L. In comparison, benzene was detected in five of 1,095 samples of ground water supplying public water supply wells, and in five of 2,401 samples of ground water supplying domestic water supply wells, but in each case the concentration was less than the MCL of 5 µg/L. In a sampling effort that was approximately equivalent, three samples were contaminated with EDB above the MCL and no sample was contaminated with benzene above the MCL.

In summary, there were significant concentrations of EDB and 1,2-DCA at the sites that were sampled during the EPA/ASTSWMO study. As a consequence, EDB was the risk driver at approximately one quarter of the sites in the study.

3.3 The Chance that Conventional Monitoring Using EPA Method 8260 will fail to detect EDB

Method 8260B prepares a water sample for analysis by purge-and-trap, separates the volatile organic compounds by gas chromatography, and determines the chemical identity and the concentration of volatile organic compounds by mass spectrometry. It is widely applied for analysis of the petroleum components of gasoline in ground water. Method 8260B can also determine EDB or 1,2-DCA, however the effective method detection limit for EDB and 1,2-DCA is near 3 µg/L. This detection limit is problematic for interpretation of concentrations of EDB because it is almost one hundred fold higher than the MCL. The detection limit is not a problem for determination of 1,2-DCA, which has an MCL of 5 µg/L.

Method 8011 prepares the water sample by micro-extraction, separates volatile organic compounds by gas chromatography, and determines the concentration of the volatile organic compounds by the response of an electron capture detector. This detector is exquisitely sensitive to halogenated compounds, but responds hardly at all to conventional hydrocarbons. The detection limit for EDB is 0.01 µg/L, which is a reasonable margin lower than the MCL of 0.05 µg/L.

Analysis of EDB can be included in the routine analysis of BTEX compounds by Method 8260B at minimal extra cost. In contrast, monitoring for EDB by 8011 and monitoring for the BTEX compounds by Method 8260B can essentially double the total cost of analysis. The selection of one method over the other depends on the goals and priority in risk management.

Figure 3.5 presents the practical consequence of the difference in detection limits using Method 8260B or Method 8011. It compares the distribution of EDB that was determined in the EPA/ASTSWMO survey to the distribution that would have been discovered if the survey had been conducted using Method 8260B. Method 8260B would have discovered only 40% of the sites with concentrations of EDB above the MCL.

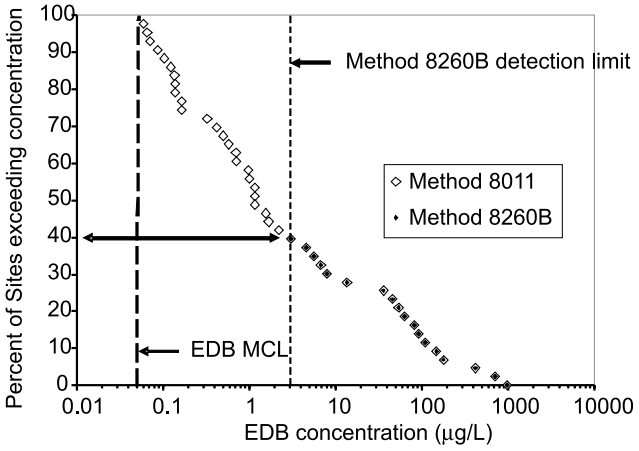

Figure 3.5. Distribution of concentrations of EDB at the leaded gasoline spill sites in the EPA/ASTSWMO Study where the concentrations were above the MCL. Note that the concentrations of EDB in only 40% of the sites were above the method detection limit for EPA Method 8260B.

3.4 Co-Distribution of EDB with 1,2-DCA, Benzene, Xylenes, and Ethylbenzene at Selected Motor Fuel Release Sites

At many gasoline release sites no ground water samples have been analyzed for EDB or 1,2-DCA, but analyses for BTEX compounds are common. Is there an association between concentrations of any of the BTEX compounds and EDB and 1,2-DCA that could be used to predict whether EDB and 1,2-DCA might be present and at what concentrations? Using the idea that a co-occurring compound of gasoline might serve as a conservative tracer, Wiedemeier et al., (1996) compared the concentrations of benzene in a release of JP-4 jet fuel to concentrations of the xylenes. The xylenes and ethylbenzene are a major fraction of gasoline, they tend to partition from gasoline slowly, and they are resistant to biodegradation under anaerobic conditions. In a similar manner Falta (2004) used the average composition of gasoline and partitioning theory to estimate the concentration of EDB, 1,2-DCA, benzene, ethylbenzene, and total xylenes that would be expected in ground water in contact with un-weathered leaded gasoline. The predicted concentrations for EDB, 1,2-DCA, benzene, ethylbenzene, and xylenes were 1,900 mg/L, 3,700 mg/L, 37,100 mg/L, 3,000 mg/L, and 13,100 mg/L respectively.

Figure 3.6 compares the predicted concentrations in contact with un-weathered gasoline, and the concentrations that would be predicted from dilution, to the measured concentrations of EDB, ethylbenzene, and total xylenes in wells sampled during the EPA/ASTSWMO study. The method detection limit for EDB, ethylbenzene, and individual xylenes was 0.005, 0.05, and 0.15 µg/L respectively, and values less than the method detection limit are plotted at the method detection limit.

The dotted line in the panels of Figure 3.6 are the predicted concentrations of EDB and ethylbenzene (Panel A) or EDB and total xylenes (Panel B) that would be expected in water based on the assumptions and calculations of Falta (2004). If a datum falls above the line, there is more EDB in the ground water than would be predicted from the concentration of total xylenes or ethylbenzene.

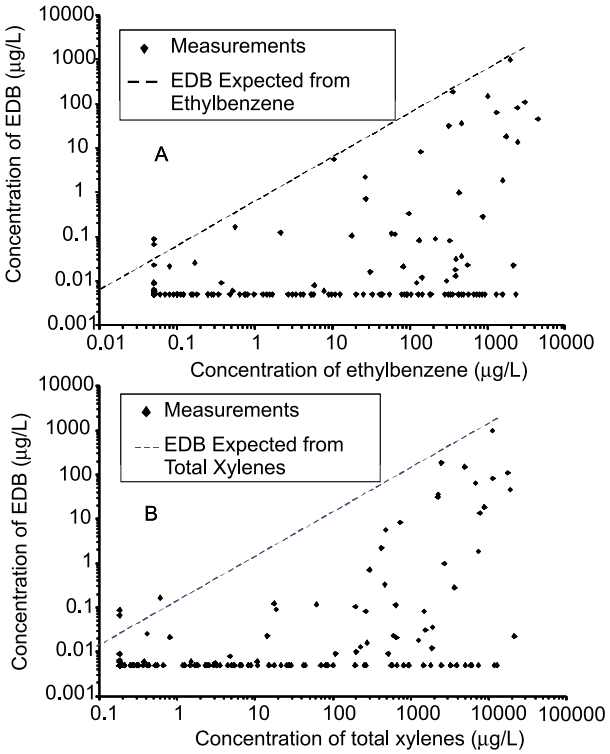

Figure 3.6. Association of concentrations of EDB with concentrations of ethylbenzene (Panel A) or total xylenes (Panel B).

The maximum concentrations of ethylbenzene and total xylenes were close to the concentrations that should be in contact in leaded gasoline. For any particular concentration of total xylenes or ethylbenzene, the highest measured concentrations of EDB were in good agreement with the concentrations that would be predicted from the calculations of Falta (2004). The only exceptions were for concentrations of ethylbenzene and total xylenes below 1 µg/L. The very low concentrations of ethylbenzene and total xylenes may have been influenced by biodegradation or by retardation due to differential sorption of ethylbenzene or total xylenes compared to EDB.

Most of the measured concentrations of EDB were many fold lower than the concentrations that would be predicted from measured concentrations of total xylenes or ethylbenzene. For a release of leaded gasoline, at concentrations in the range of 1 µg/L or higher of ethylbenzene and 0.1 µg/L of total xylenes, the dotted lines in Figure 3.6 and the measured concentration of ethylbenzene or total xylenes can be used to estimate a conservative upper boundary on the concentration of EDB. These estimates could be used to conduct a

preliminary RBCA assessment for EDB if data on the concentrations of EDB are not available.

Figure 3.7 compares concentrations of EDB to concentrations of 1,2-DCA and benzene wells sampled under the EPA/ASTSWMO study. The method detection limit for EDB, 1,2-DCA, and benzene was 0.005, 0.13, and 0.07 µg/L respectively, and values less than the method detection limit are plotted at the method detection limit.

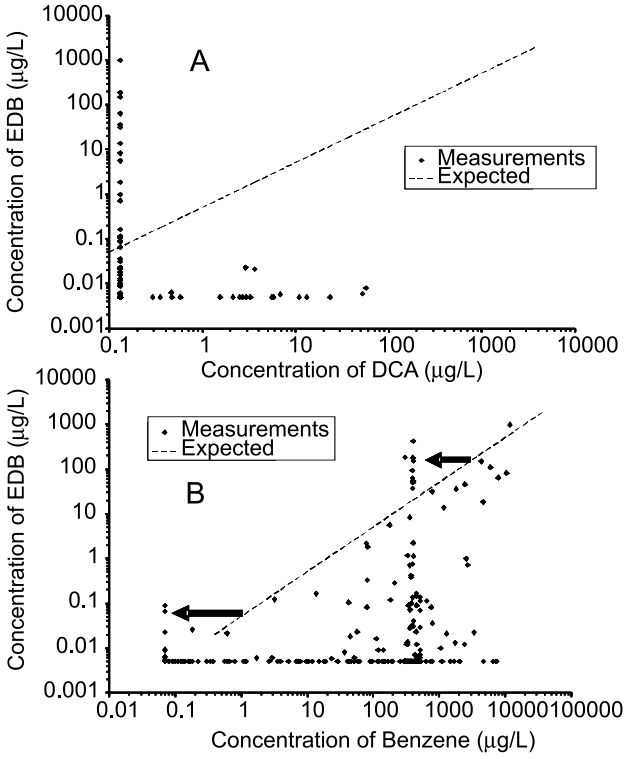

Figure 3.7. Association of concentrations of EDB with concentrations of 1,2-DCA (Panel A) and benzene (Panel B).

When EDB was measured in the ground water, the concentration of 1,2-DCA was low or below the detection limit. When 1,2-DCA was measured in the ground water, the concentration of EDB was low or below the detection limit. We have no explanation for the strong negative association of concentrations of EDB and 1,2-DCA. The maximum concentration of EDB was near the maximum that would be predicted for ground water in contact with residual leaded gasoline (based on calculations of Falta, 2004). The maximum concentration of 1,2-DCA was almost two orders of magnitude lower than would be predicted, suggesting extensive degradation of 1,2-DCA compared to degradation of EDB. In any case, concentrations of 1,2-DCA cannot be used to predict concentrations of EDB.

The maximum concentrations of benzene were near the concentrations that would be predicted for ground water in contact with leaded gasoline. There were several samples clustered at a benzene concentration near 400 µg/L where the EDB concentration was up to an order of magnitude higher than would be predicted from the concentration of benzene. This probably reflects preferential degradation of benzene compared to EDB. There was a second cluster of samples at benzene concentrations less than 1 µg/L that indicated a preferential degradation of benzene compared to EDB. As a consequence, benzene concentrations can not be used to calculate a conservative upper boundary on predicted concentrations of EDB.

3.5 Local Vulnerability of Exposure to EDB based on Past Usage of Leaded Motor Fuel

This section estimates the chance that drinking water will be contaminated with EDB from gasoline that was released from a leaking underground storage tank. In particular, it estimates on a state wide basis the relative chance that a resident of one of the forty eight contiguous states will be affected. This section presents maps relating the regions with high densities of residents that drink water from shallow wells to regions with high historical use of leaded gasoline. This section is intended for decision makers and other staff of regulator agencies that must apportion resources for monitoring and risk management of the hazard associated with EDB in ground water used for drinking water.

In 2006, the U.S. Geological Survey released a comprehensive study of the occurrence of volatile organic compounds in ground water and drinking-water supply wells in the USA (Zogorski et al., 2006). They sampled 462 public water supply wells for EDB and EDB was not detected in any of them; however, EDB was detected in three of 2,085 domestic water supply wells that were sampled. All three detections were above the MCL for EDB of 0.05 µg/L. In comparison, benzene was detected nine times in 997 public water supply wells, but in each case the concentration was less than the MCL of 5 µg/L. Based on the findings of Zogorski et al., (2006), the most likely scenario for contamination of drinking water by EDB from leaded motor fuel is contamination of private domestic water wells in a suburban residential landscape.

The chance that an individual will consume drinking water that is contaminated with EDB from a leaking underground storage tank is influenced by a number of site-specific factors including the source of drinking water, the proximity of underground storage tanks, and the amount of leaded gasoline that was stored in the tanks and might have leaked to contaminate ground water. It is impossible to calculate a precise estimate of the chances for exposure from data that are readily available. The following approach was taken to provide a broad estimate of the local vulnerability of exposure to EDB based on past usage of leaded gasoline in the state.

The first task was to access data on the content of lead in leaded gasoline. Beginning in the 1930s, the National Institute for Petroleum and Energy Research (NIPER) has collected data on the composition of gasoline. The successor to NIPER (Northup-Grumman) continues to analyze approximately 1,000 gasoline samples taken twice per year. Data are available from 174 areas around the USA; however, the record is often incomplete. About 35 locations have been sampled on a continuous basis. This data base is the most extensive historical record (that is publically available) of the composition of conventional and reformulated gasoline in the USA. The data base provided concentrations of lead in gasoline from 1976 through 1995 (approximately 27,800 samples), collected at locations within 101 cities representing 42 states. The weighted average lead concentrations (gram per liter) of all octane levels were calculated for five-year categories as follows: 1976-1980, 1981-1985, 1986-1990, and 1991-1995. The weighted averages for these categories are 0.43 g/L, 0.15 g/L, 0.038 g/L, and 0.015 g/L respectively. These averages are in good agreement with estimates provided in Figure 2 of Falta et al., (2005). Estimates provided in Figure 2 of Falta (2004) were applied as the estimate average lead concentrations for the 5-year categories 1951-1955, 1956-1960, 1961-1965, 1966-1970, and 1971-1975.

The second task was to estimate the amount of leaded gasoline sold in the USA. The U.S. Department of Transportation (2008) has published data on the volume of gasoline sold in each state in each year between 1949 and 1995. To estimate the amount of lead in gasoline sold in each state in each year category, the volume of gasoline sold in each state for all the individual years within each year category was summed, and the resulting sums were multiplied by the average lead concentration for each respective year category.

The third task was to convert the amount of lead to the amount of EDB. In the interval 1951 to 1995, the molar ratio of lead and EDB in gasoline has been one to one (Falta, 2004). From stoichiometry, there was 0.435 gram of EDB for each gram of lead in leaded motor fuel sold in the USA in the period of interest. To estimate the amount of EDB in gasoline sold in each state in each year category, the amount of lead was multiplied by 0.453. Figure 3.8 compares the total amount of EDB in gasoline sold in five states with small populations, and Figure 3.9 compares EDB in gasoline sold in states with large populations. Notice the difference in the scale of the axis showing EDB sold in gasoline between the figures. In general, sales of EDB in gasoline increased more than two fold between 1951-1960 and 1976-1980, and then declined substantially by 1991-1995.

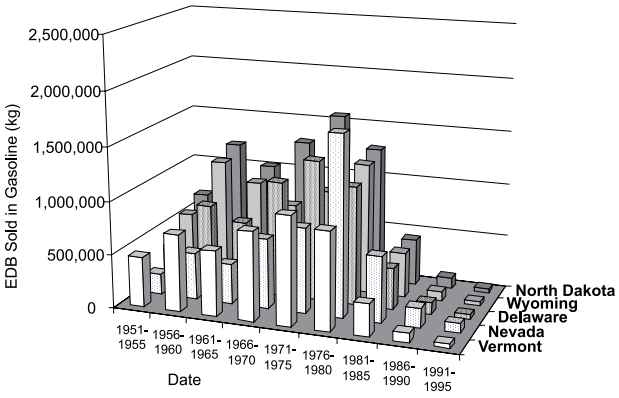

Figure 3.8. Consumption of EDB in leaded motor fuel in five small states in the USA in the forty-five years before lead was banned in automotive motor fuel.

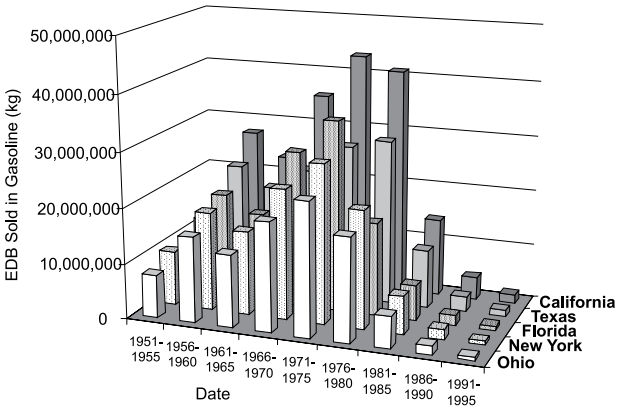

Figure 3.9. Consumption of EDB in leaded gasoline in five large states in the USA in the forty-five years before lead was banned in motor gasoline.

The estimated total amount of EDB in leaded gasoline sold in each state in the period 1951-1995 is presented in Table 3.3. Almost all of the leaded gasoline was stored in underground storage tanks prior to sale. The amount of EDB in leaded gasoline sold in a state will be taken as a predictor of the amount of EDB released from releases of leaded gasoline from underground storage tanks.

The next task is to estimate the probability of encountering a release of leaded gasoline in an aquifer, expressed as the amount of leaded gasoline released per unit surface area. One obvious approach would be to normalize the amount of EDB sold by the surface area of each state. Table 3.3 lists, by state, the total amount of EDB sold in gasoline in that state divided by the surface area of the state. This is intended as an estimate of the chance that ground water under a suburban residential landscape has been contaminated by EDB from a release of leaded gasoline. The relative exposure of an individual in a particular state consuming ground water with EDB from leaded gasoline is estimated by dividing the total amount of EDB in gasoline sold in the state by the surface area of the state, and then by multiplying by the fraction of people in the state that drink ground water from shallow wells, as tabulated in the 2000 census. The estimate is termed the Relative Exposure Index.

In Table 3.3, the states are ranked by the value of the Relative Exposure Index. The older industrialized states on the Atlantic Coast and the Great Lakes area rank particularly high. The states in the mid-continent and in the arid western USA rank particularly low. Figure 3.10 compares the amount of EDB sold in gasoline divided by the surface area of the state to regions where shallow ground water is used for drinking water. Figure 3.11 provides a closer view of the New England and Mid-Atlantic states where the Relative Exposure Index is particularly high.

Table 3.3. Exposure to Drinking Ground Water Contaminated with EDB from Leaded Motor Fuel.

State	Total EDB Sold in Motor Fuel	EDB Sold in Motor Fuel	Population Drinking Water from Shallow Wells	Relative Exposure Index*
	(kg per State)	(kg per hectare)	Percent of Total Population	
Connecticut	27,528,745	21.35	8.4	179
New Jersey	66,527,161	34.21	3.8	130
Rhode Island	8,009,494	29.59	4.2	124
Delaware	5,856,848	11.00	8.7	96
Maryland	37,661,911	14.93	6.0	90
Massachusetts	50,397,289	9.06	3.2	77
Pennsylvania	106,478,053	23.80	8.5	76
Michigan	93,618,641	6.24	11.2	70
Ohio	107,154,665	10.04	6.7	67
Indiana	57,014,485	6.05	9.4	57
North Carolina	59,481,984	4.68	11.8	55
New Hampshire	7,865,305	3.28	15.9	52
New York	125,731,461	9.99	4.7	47
Vermont	5,011,479	2.01	21.9	44
Florida	125,947,001	8.71	5.0	44
Virginia	52,072,141	5.05	8.3	42
Wisconsin	45,375,403	3.12	12.6	39
West Virginia	18,960,163	3.02	12.0	36
South Carolina	31,454,595	3.93	8.1	32
Maine	11,364,807	1.36	21.3	29

State	Total EDB Sold in Motor Fuel	EDB Sold in Motor Fuel	Population Drinking Water from Shallow Wells	Relative Exposure Index*
	(kg per State)	(kg per hectare)	Percent of Total Population	
Illinois	104,486,891	7.16	3.5	25
Kentucky	37,360,830	3.58	6.9	25
Tennessee	48,344,985	4.43	5.0	22
Georgia	57,010,862	3.75	5.9	22
Missouri	55,806,135	3.08	6.3	19
Minnesota	41,275,045	1.89	10.0	19
Iowa	33,112,275	2.27	7.3	17
Alabama	41,607,861	3.11	4.9	15
Louisiana	40,237,026	3.39	4.2	14
Arkansas	24,123,265	1.76	6.9	12
Oklahoma	34,808,511	1.92	5.3	10
Washington	35,527,773	2.04	4.8	10
Mississippi	25,868,121	2.10	4.5	9.4
California	201,242,695	4.92	1.5	7.4
Oregon	24,419,926	0.97	6.3	6.1
Texas	149,485,144	2.18	2.8	6.1
Nebraska	17,431,282	0.87	6.4	5.6
Kansas	27,511,908	1.29	4.1	5.3
Idaho	9,045,453	0.42	9.3	3.9
North Dakota	7,622,837	0.42	9.0	3.7
Montana	9,297,566	0.24	13.6	3.3
South Dakota	8,589,734	0.43	7.2	3.1
Colorado	25,159,205	0.93	3.1	2.9
New Mexico	14,068,219	0.45	5.8	2.6
Wyoming	6,108,986	0.24	9.0	2.2
Arizona	18,415,405	0.63	1.7	1.1
Utah	11,781,586	0.54	1.1	0.59
Nevada	5,045,588	0.18	1.9	0.33
Alaska	5,265,059			
District of Columbia	6,909,170		0	
Hawaii	2,387,037			

* The Relative Exposure Index is calculated as the product of total EDB sold in gasoline in the state (kg), divided by the surface area of the state (hectares), and then multiplied by the fraction of the people in the state that drink ground water from shallow wells.

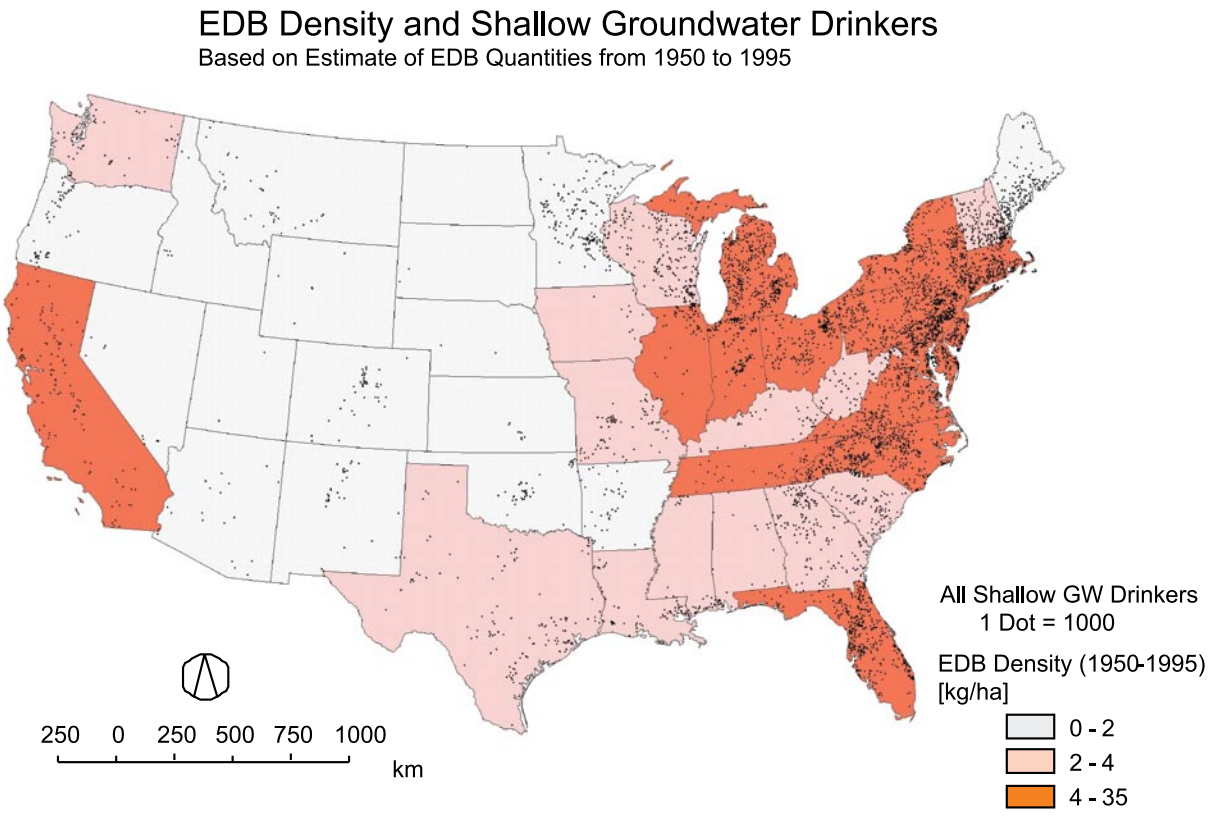

Figure 3.10. Relationship between heavy use of leaded motor fuel and the use of shallow ground water for public water supplies in the contiguous USA.

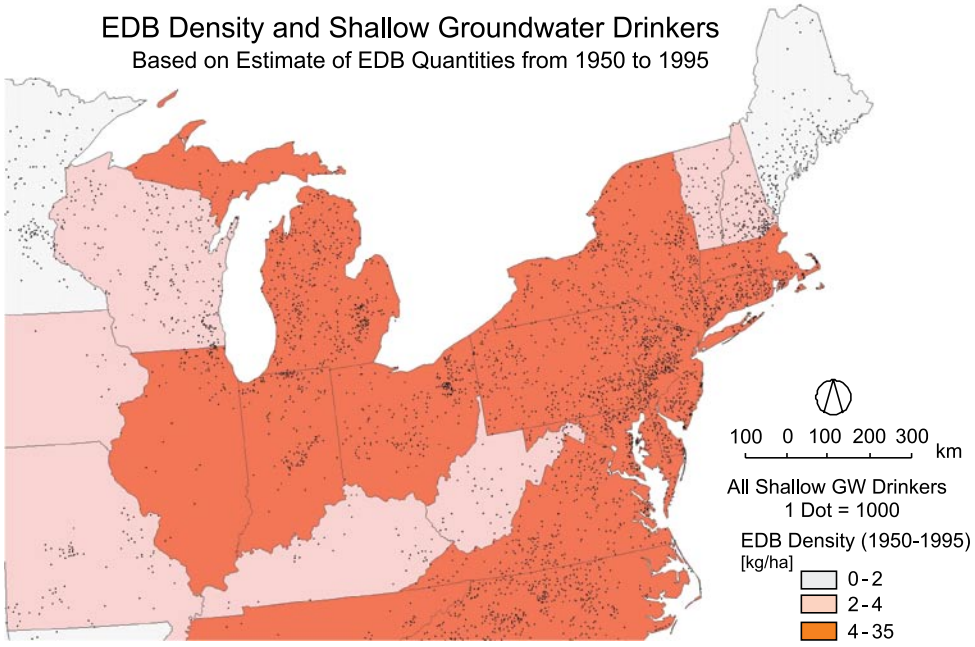

Figure 3.11. Relationship between heavy use of leaded motor fuel and the use of shallow ground water for public water supplies in New England, the Mid-Atlantic States, and the Great Lakes region of the USA.

The Relative Exposure Index takes no account of the fact that the states in the USA vary widely in the use and extent of development of the landscape. Within a state, some areas are urbanized, some areas are largely suburban residential land, some areas are farmland or pasture, and some areas are military reservations or parkland. As an alternative to normalizing the total amount of EDB sold in gasoline by the surface area of the state, the calculation presented in Table 3.4 normalizes the total amount sold to the population of the state in the 2000 census.

The total amount of EDB sold in gasoline in a state divided by the population of the state in the 2000 census is intended as an estimate of the chance that ground water under a suburban residential landscape has been contaminated by EDB from a release of leaded gasoline. The relative vulnerability of an individual in a particular state consuming ground water with EDB from leaded gasoline is estimated by dividing the total amount of EDB in gasoline sold in the state by the population, and then by multiplying by the fraction of people in the state that drink ground water from shallow wells, as tabulated in the 2000 census. The estimate is termed the Relative Vulnerability Index in Table 3.4.

There is a reasonably close correlation between the population of a state and the volume of gasoline sold. Figure 3.12 compares the liters of gasoline sold in states (in 1995, the latest data available) to the population (in 2000, the latest data available). The ratio varies by less than a factor of two between the extremes. Gasoline service stations are clustered near major highways, shopping areas, and suburban residential areas, which is also where drinking water sources are located. The current population of a state should serve as a proxy for the surface area of the state that contains both gasoline service stations and suburban residential areas where the inhabitants might have shallow private wells.

The Vulnerability Index varies by a factor of 30 across all the states in the USA. It is most sensitive to the fraction of the population that drinks ground water from shallow wells. The rankings change for some of the states between the Relative Exposure Index and the Relative Vulnerability Index. However, the general trends are the same. The older industrialized states on the Atlantic Coast and the Great Lakes area rank particularly high. The states in the mid-continent rank lower and the states in the arid western USA rank particularly low.

Table 3.4. Vulnerability to Drinking Ground Water Contaminated with EDB from Leaded Motor Fuel.

State	Total EDB Sold in Motor Fuel	EDB Sold in Motor Fuel	Population Drinking Water from Shallow Wells	Relative Vulnerability Index*
	(kg per State)	(kg per resident)	Percent of Total Population	
Vermont	5,011,479	8.23	21.9	181
Maine	11,364,807	8.95	21.3	191
New Hampshire	7,865,305	6.34	15.9	101
Montana	9,297,566	10.31	13.6	140
Wisconsin	45,375,403	8.47	12.6	107
West Virginia	18,960,163	10.48	12.0	126
North Carolina	59,481,984	7.39	11.8	87
Michigan	93,618,641	9.42	11.2	105
Minnesota	41,275,045	8.39	10.0	84
Indiana	57,014,485	9.38	9.4	88
Idaho	9,045,453	7.01	9.3	65
North Dakota	7,622,837	11.87	9.0	107
Wyoming	6,108,986	12.37	9.0	112
Delaware	5,856,848	7.47	8.7	65
Pennsylvania	106,478,053	8.66	8.5	73
Connecticut	27,528,745	8.07	8.4	68

State	Total EDB Sold in Motor Fuel	EDB Sold in Motor Fuel	Population Drinking Water from Shallow Wells	Relative Vulnerability Index*
	(kg per State)	(kg per resident)	Percent of Total Population	
Virginia	52,072,141	7.35	8.3	61
South Carolina	31,454,595	7.84	8.1	64
Iowa	33,112,275	11.30	7.3	82
South Dakota	8,589,734	11.38	7.2	82
Kentucky	37,360,830	9.25	6.9	63
Arkansas	24,123,265	9.03	6.9	62
Ohio	107,154,665	9.40	6.7	63
Nebraska	17,431,282	10.19	6.4	65
Missouri	55,806,135	9.97	6.3	63
Oregon	24,419,926	7.14	6.3	45
Maryland	37,661,911	7.11	6.0	43
Georgia	57,010,862	6.96	5.9	41
New Mexico	14,068,219	7.73	5.8	45
Oklahoma	34,808,511	10.09	5.3	54
Tennessee	48,344,985	8.50	5.0	43
Florida	125,947,001	7.87	5.0	40
Alabama	41,607,861	9.35	4.9	46
Washington	35,527,773	6.03	4.8	29
New York	125,731,461	6.62	4.7	31
Mississippi	25,868,121	9.11	4.5	41
Louisiana	40,237,026	9.00	4.2	38
Rhode Island	8,009,494	7.63	4.2	32
Kansas	27,511,908	10.23	4.1	42
New Jersey	66,527,161	7.91	3.8	30
Illinois	104,486,891	8.43	3.5	30
Massachusetts	50,397,289	7.94	3.2	26
Colorado	25,159,205	5.85	3.1	18
Texas	149,485,144	7.15	2.8	20
Nevada	5,045,588	2.52	1.9	5
Arizona	18,415,405	3.59	1.7	6
California	201,242,695	5.94	1.5	9
Utah	11,781,586	5.28	1.1	6
Alaska	5,265,059	8.40		
District of Columbia	6,909,170	12.08	0	
Hawaii	2,387,037	1.97		

*The Relative Vulnerability Index is calculated as the product of total EDB sold in gasoline in the state (kg) in the period 1951 through 1965, divided by the population of the state (2000 census data), and then multiplied by the fraction of the people in the state that drink ground water from shallow wells (1990 census data).

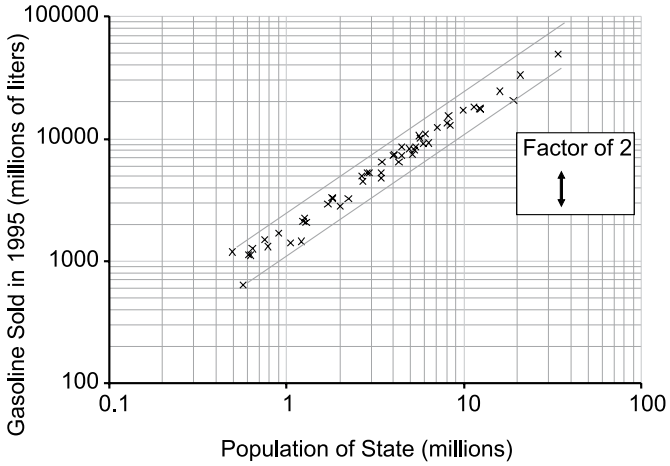

Figure 3.12. Relationship between the population of a state in the USA (2000 census) and the sales of gasoline (1995 data).

4.0
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Appendix A.
Partitioning of EDB and 1,2-DCA between Gasoline and Water

When leaded gasoline is spilled into ground water, the EDB and 1,2-DCA in the residual gasoline diffuses out of the gasoline into the adjacent ground water until the concentrations of EDB and 1,2-DCA come to equilibrium. As EDB and 1,2-DCA are transferred from gasoline to water, the concentrations remaining in gasoline decline. As a result, the final concentration of EDB or 1,2-DCA in ground water depends on the ratio of gasoline to ground water in the aquifer, as described in Equation A.1.

$$C_{water} = \frac{C_{original,gasoline}}{K_{gasoline,water} + \frac{\theta_{water}}{\theta_{gasoline}}} \qquad (A.1)$$

Where C_{water} is the final concentration in ground water, $C_{original,\ gasoline}$ was the original concentration in the gasoline that was released, $\theta_{gasoline}$ is the porosity filled with residual gasoline (expressed as the volume of gasoline divided by the total volume of aquifer), θ_{water} is the water-filled porosity (expressed as the volume of water divided by the total volume of aquifer), and $K_{gasoline,water}$ is the distribution coefficient between gasoline and water (expressed as the concentration in gasoline divided by the concentration in water).

Equation A.1 was provided by personal communication from Dr. William Rixey at the University of Houston, see also Rixey and Joshi (2000).

Falta (2004) provided estimates of $K_{gasoline,water}$ for EDB and 1,2-DCA of 152 and 84 respectively. Typical original concentrations of EDB and 1,2-DCA in leaded gasoline were near 290 mg/L and 310 mg/L (Falta, 2004). At these estimated values, Equation 2.9 predicts maximum possible concentrations of EDB and 1,2-DCA of 1,900 µg/L and 3,700 µg/L respectively.

Figure A.1 extrapolates the predictions of Equation A.1 for a range of concentrations of un-weathered residual leaded gasoline. Calculations assume a total porosity of 0.3. The value of $\theta_{gasoline}$ was calculated from the value of Total Petroleum Hydrocarbons (mg/kg) by multiplying by the bulk density of aquifer sediment at a porosity of 0.3 (1.855 g/cm^3) and dividing by the density of gasoline (0.78 g/cm^3). The value of θ_{water} was calculated by subtracting $\theta_{gasoline}$ from 0.3.

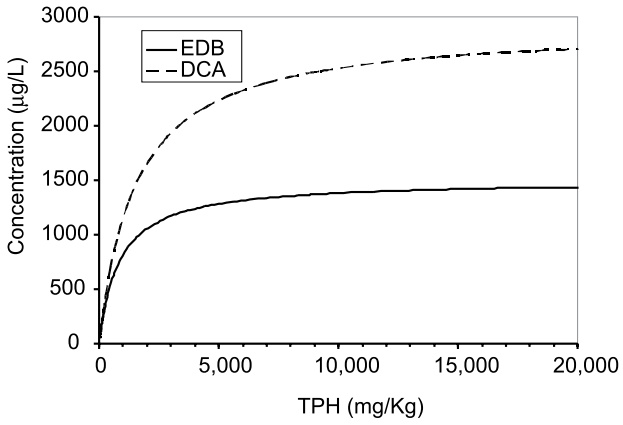

Figure A.1. Predicted maximum groundwater concentrations of EDB and DCA for a range of possible concentrations of un-weathered residual gasoline in aquifer sediment.

Typical values for the concentration of residual gasoline in unconsolidated sediments vary from 2,000 to 10,000 mg/kg. The corresponding predicted concentrations of EDB under typical conditions vary from 1,100 µg/L to 1,400 µg/L and corresponding concentrations of 1, 2-DCA vary from 1,700 µg/L to 2,500 µg/L.

As EDB and 1,2-DCA partition from residual gasoline to ground water, and as the moving ground water carries EDB and 1,2-DCA away from the

residual gasoline, the concentrations of EDB and 1,2-DCA in ground water will decline over time. The rate of this weathering process is controlled by the distribution of EDB and 1,2-DCA between residual gasoline and ground water, and by the seepage velocity of the ground water.

Figure A.2 estimates the fraction of EDB and 1,2-DCA that is dissolved in ground water, and can be flushed away from the residual gasoline by the flow of ground water, as a function of the concentration of residual gasoline. For a given value of TPH (mg/kg), values of $\theta_{gasoline}$ and θ_{water} were calculated as described above, and C_{water} was calculated using Equation A.1. An estimate of the concentration of the contaminant in the residual gasoline ($C_{gasoline}$) was calculated by multiplying C_{water} by $K_{gasoline,water}$. Then Equation A.2 was used to calculate the fraction of contaminant in ground water.

$$Fraction, water = \frac{C_{water} * \theta_{water}}{\left(C_{water} * \theta_{water} + C_{gasoline} * \theta_{gasoline}\right)} \quad (A.2)$$

At typical values of TPH between 2,000 and 10,000 mg/kg, the fraction of EDB in ground water would vary between 30% and 7%, and the fraction of 1,2-DCA in ground water would vary from 40% and 12%. With each exchange of the pore water in contact with residual gasoline, roughly 12% of EDB and 20% of 1,2-DCA would be flushed away from the source area. Because a relatively small proportion of the EDB or 1,2-DCA is in the ground water, these contaminants would be expected to weather slowly from residual gasoline.

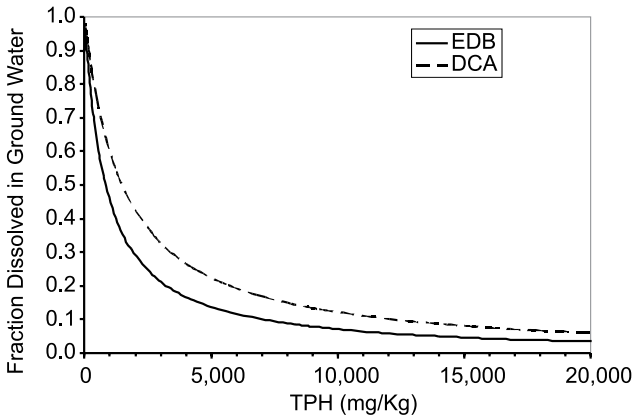

Figure A.2. Expected relationship between the fraction of EDB or DCA that is dissolved in ground water, and can be flushed away by ground water flow, and the concentration of residual leaded motor fuel.

Appendix B
Materials and Methods for Laboratory Studies of Abiotic Degradation of EDB and 1,2-DCA

Batch experiments were conducted with material collected from the column described in Shen and Wilson (2007) as the Column with Mulch and Hematite (column B3). After 875 days of operation, Column B3 was put into a freezer for one week. The column was frozen solid, and the glass container broke apart. The glass was removed from the column of frozen pore water, shredded plant mulch, river sand, and hematite and then the frozen column was cut into nine sections with a cross cut saw. The original column was 45 cm long and 15 cm in diameter, each section was 5 cm long and 15 cm in diameter. The sections were numbered 1 through 9, with 1 being adjacent to the column influent and 9 adjacent to the column effluent. The sections were returned to the freezer before they could thaw.

Each section was thawed in an anaerobic glovebox (N_2:H_2=92.5%:7.5%), homogenized and separated into 4 equal subsections, transferred to a plastic bag with a zip seal, sealed without headspace, and refrozen until used for chemical analysis or preparation of batch microcosms.

For analysis of Fe and S partitioning, samples were thawed in the anaerobic glovebox in sealed plastic bags without headspace. Wet sediments were used directly for analysis. Analytical results were corrected for the water content; the water content was determined gravimetrically. The analysis of total iron and HCl extractable iron was modified after Kosta and Luther (1994). The analysis of acid volatile Sulfide (AVS) and Chromium Reducible Sulfide (CRS) followed procedures used by Wilkin and Bischoff (2006). Results are presented in Table B.1. Data are from He et al., (2008).

Acid Volatile Sulfide includes and is expected to be dominated by FeS, and CRS includes and is expected to be dominated by FeS_2. Batch microcosms were constructed with column material from section 2 and section 6. The concentration of iron associated with AVS and CRS in section 2 is 4706 mg/kg, and the concentration of iron that was associated with AVS and CRS in section 6 is 3856 mg/kg. This represents 92% and 84% of the total iron remaining in the columns. Allowing for uncertainty in the determinations, the iron(III)

Table B.1: Distribution of iron, AVS, and CRS along the Column with Mulch and Hematite as described in Shen and Wilson (2007).

Section	Distance from inlet	H_2O	Fe fractionation		S fractionation	
			HCl*	total Fe**	AVS	CRS
	cm	Volume %	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
s1	0-5	41.36	2216±183	3710±0	1020±100	2774±625
s2	5-10	40.12	4926±291	5095±1110	2642±371	104±219
s3	10-15	30.63	4303±936	5610±268	2087±101	530±254
s4	15-20	36.40	4612±1181	5110±282	2158±187	2120±370
s5	20-25	32.45	3645±925	6475±855	1630±74	987±275
s6	25-30	33.25	2967±123	4610±311	1449±153	1517±64
s7	30-35	30.79	2897±297	6755±7	1295±229	1793±463
s8	35-40	31.55	3181±510	5080±0	1190±231	955±336
s9	40-45	33.85	1702±125	5400±0	577±76	1583±395

Data from He et al., (2008).
*extracted for one hour in 0.5M HCl at pH <2.0, extracts amorphous Fe oxides, AVS
**extracted for 0.5 hr, microwave digestion in HNO^3

minerals originally present in the river sand and the hematite added to the column were almost entirely converted to FeS and FeS_2.

Material from section 2 and section 6 was selected to prepare batch microcosms.

To remove the confounding effects of sorption to the plant mulch on concentrations of contaminants, the sections were sieved to remove the plant mulch. The frozen section (contained in a plastic bag without headspace) was allowed to thaw in a glovebag filled with oxygen free nitrogen, but no hydrogen. This was done to minimize enrichment of anaerobic bacteria in the microcosms. The atmosphere of the glovebag was exchanged three times before the bags were opened.

Microcosms were prepared with material from section 2 and labeled as 2-10, 2-11, and 2-12. Material from section 6 was used to prepare microcosms labeled 6-15, 6-16, 6-17, and 6-19. The microcosms were prepared as follows. To separate the fine sand and iron sulfide precipitates from the plant mulch, each of the thawed sections was sonicated in a Branson 1510 sonicator for two cycles of ten minutes each. Then the sediment and pore water was sieved to remove the shredded plant mulch. The wet sediment that passed the sieve was blended thoroughly and then distributed to 20 ml serum vials. Each vial received 19 ml of wet sediment, and 1.0 ml of a solution that contained 14 gm per liter of Na_2SO_4. The serum vials were then sealed with a Teflon-faced butyl rubber septum and an aluminum crimp cap.

An additional microcosm was prepared using material from section 6 and labeled as 6-s4. The microcosm was prepared as follows. The mulch from section 6 was placed in boiled reverse osmosis water and sonicated again for 10 minutes (500 gm wet mulch, 150 ml water). Then the mulch was removed from the water and sediment by sieving. The material that passed the sieve was allowed to stand to separate the sediment from the water. The sediment was collected, while the water was added back to the mulch and sonicated again for 10 minutes. After the water and sediment were removed from the mulch be sieving, the water and sediment were combined with the previous sediment, and the mixture was allowed to settle overnight. The water was decanted, the settled sediment was mixed well, and then 19 ml of wet sediment was added to a 20 ml serum vial. The vial received 1.0 ml of a solution that contained 14 gm per liter of Na_2SO_4. Then the serum vial was sealed with a Teflon-faced butyl rubber septum and an aluminum crimp cap.

The water content of the microcosms and the concentrations of AVS and CRS are presented in Table B.2.

Dose solutions of EDB and 1,2-DCA were prepared as follows. A 165-ml serum bottle was filled with 3.42 grams of Na_2SO_4, a magnetic spin bar, and boiled reverse osmosis water to make a positive meniscus. Then 53 microliters of EDB or 92 microliters of 1,2-DCA were added with a syringe, and the bottle was sealed with a Teflon faced septum and an aluminum crimp cap. The dose solution was stirred overnight to dissolve the EDB or 1,2-DCA.

The dose solution contained Na_2SO_4 to ensure that adequate sulfate was available to sustain sulfate reducing conditions over the course of the incubations. Figure B.1 presents data for the microcosms dosed with EDB. Sulfate concentrations above 100 mg/L were sustained on any date where EDB was detected.

Table B.2: Distribution of pore water, AVS, and CRS in microcosms.

Microcosm	Water content	CRS	AVS	AVS
	% volume basis	mg/kg	mg/kg	mM/L*
2-10	43.5	2222	1907	198
2-11	43.1	2417	2577	272
2-12	43.8	3349	2700	278
6-15	46.0	6319	4054	381
6-s4	40.2	3454	1983	236
6-16	48.7	3309	2537	279
6-17	57.4	2309	1488	121

*millimole in contact with a liter of pore water.

The microcosms and the dose solutions were taken into a glovebag with an atmosphere of oxygen free nitrogen. The microcosms were opened; 1.0 ml of standing pore water was removed and replaced with 1.0 ml of the appropriate dose solution. The microcosms were sealed with new septa and crimp caps.

The dosed microcosms were removed from the glove bag and incubated at room temperature in the dark on a roller that slowly stirred the contents of the microcosms. The microcosms were sampled after one hour and then after one, two, three, and four weeks of incubation. At each sampling period, the microcosms were removed from the roller and allowed to settle. The microcosms were placed inside the anaerobic glove bag and the septa were removed. For each microcosm, 0.5 ml of standing water was collected and transferred to a 1.5 ml micro centrifuge tube for analysis of sulfate. An additional 0.5 ml aliquot of standing water was collected and transferred to a 20 ml serum vial containing 14.5 ml of reverse osmosis water for analysis of EDB or 1,2-DCA. Three drops of 1:1 HCl were added to the 20 ml serum vials to adjust the pH to less than 2. The vials were then sealed with a septum and crimp cap and stored at 4 °C until analyzed.

Concentrations of EDB and 1,2-DCA were determined as described earlier by head space gas chromatography/mass spectrometry (GC/MS).

Concentrations of sulfate were determined with a Waters Quanta 4000 Capillary Ion Analyzer, using a modification of EPA Method 6500, "Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis," January 1998. The method detection limit for sulfate was 0.172 mg/L. The lowest calibration standard was 1.0 mg/L.

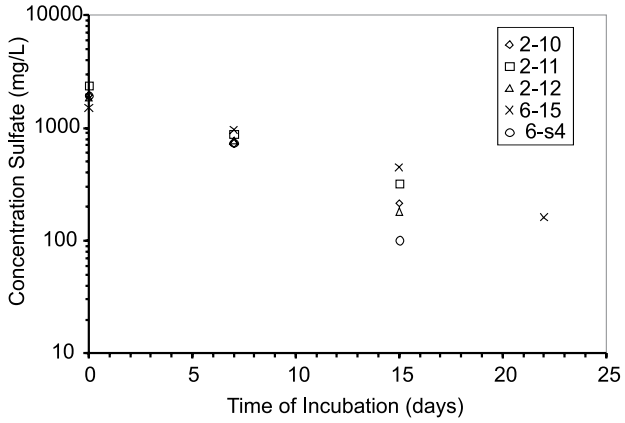

Figure B.1. Consumption of sulfate during incubation of microcosms.

Appendix C
Method for Compound Specific Isotope Analysis to Determine the Ratio of Stable Carbon Isotopes in EDB and 1,2-DCA

This method applies compound specific isotope ratio mass spectrometry to determine the ratio of the stable isotopes of carbon in 1,2-dibromethane (EDB) and in 1,2-dichloroethane (1,2-DCA) dissolved in ground water that is contaminated with gasoline.

Because there was no available protocol for analysis of EDB and 1,2-DCA in ground water, U.S. EPA contracted with the University of Oklahoma (Dr. Paul Philp, *pphilp@ou.edu*) to develop a protocol. Because the method for analysis of stable isotopes requires baseline separation of peaks in the gas chromatogram, it was necessary to separate EDB from the other fuel components by two-dimensional gas chromatography. To our knowledge, at this writing the University of Oklahoma is the only commercially available source for analysis of stable isotopes of carbon in EDB in ground water contaminated with gasoline. It is possible that other vendors will choose to provide this service in the future. U.S. EPA makes no endorsement of the services provided by the University of Oklahoma.

The analytes were extracted by a purge and trap (P&T model OI 4660) interfaced to a GC-IRMS instrument (Finnigan MAT 252 IRMS). Due to the chromatographic complexity of the samples, satisfactory resolution of EDB and 1,2-DCA required a 2-dimensional chromatographic approach (separation on polar GC phase followed by separation on non-polar GC phase). The cryogenic focuser at the P&T-GCIRMS interface described in Kuder et al., (2005b) was programmed for collecting 2 minute heart-cuts from the retention window of EDB or DCA of the sample eluting from the polar pre-column. The heart-cuts were directed onto a non-polar phase GC column for final separation followed by on-line combustion and analysis of the isotope composition. The analyses were otherwise performed as described in Kuder et al., (2005a) and Kuder et al., (2005b).

For determination of the $\delta^{13}C$ values for EDB and 1,2-DCA, the analytes were purged from a 25 ml water sample on to a Vocarb 3000 trap for 12 minutes. The sample temperature was 50 °C. The sample was desorbed over a 3 minute period. The trap temperature was 25 °C at purge, 240 °C at desorption, and the trap was baked for 15 minutes at 260 °C before the next cycle. The initial GC separation was achieved on a DB-Wax column, 30 m, 250 µm i.d., film thickness 0.5 µm with Helium as the carrier gas at an initial flow of 6 ml/min (constant flow). The GC temperature program was isothermal at 40 °C during 5 minutes, then 4 °C/min up to the time of elution of 1,2-DCA or EDB. The second stage of separation was achieved on a DB-MTBE column, 60 m, 320 µm i.d, film thickness 1.8 µm, with Helium as the carrier gas at an initial flow of 1.5 ml/min (constant flow). The GC temperature program was isothermal at 40 °C during 5 minutes, then 2.5 °C/min up to 120 °C and 25 °C/min up to 220 °C (hold time 15 min.). The combustion reactor for combustion of the components to CO_2 and water was maintained at 980 °C.

The isotopic composition of the samples was measured relative to a CO_2 standard directly introduced as a reference into the ion source. A standard solution of EDB and 1,2-DCA was run randomly between the tests to check the reproducibility of the PT-GC-IRMS method.

To eliminate problems with method linearity (relationship between signal strength and the obtained $\delta^{13}C$), the concentrations of diluted samples and standards were kept within a narrow range of concentrations, approximately 12 µg/L of EDB. For samples that were lower in concentration, standards were run at a corresponding concentration. It was observed that a portion of EDB was degraded on active surfaces of the P&T and/or the GC-IRMS interface. This resulted in isotope fractionation, and as a result, the overall method bias for EDB was larger than the typical

range for volatile organic compounds. The samples discussed in this report were analyzed in several batches, with varying degrees of analytical bias (from +1 to +4 ‰). The bias affected the samples and standards in the same extent. The bias remained steady over the duration of analytical work (over several days) and could be corrected based on the EDB standards.

To evaluate the method, standards of EDB and 1,2-DCA were purchased, and standard solutions were prepared in water at concentrations of 4.2 µg/L, 8.4 µg/L, and 12 µg/L. The reproducibility was good, the sample standard deviation of duplicate analyses of $\delta^{13}C$ in EDB standards averaged 0.5‰. There were several outliers with standard deviations of 1‰.

To determine whether the presence of gasoline hydrocarbons would bias the samples, a "standard" of contaminated ground water was prepared by dissolving gasoline (4 µl) into methanol (43 ml) and then by spiking 15 µl of this diluted gasoline into 25 ml of distilled water. The standards of EDB and DCA were spiked into the "standard" contaminated ground water, and measured values were compared to each other. Results are in Table C.1. Concentrations of EDB and 1,2-DCA varied from 3.6 to 48 µg/L. Concentrations at 4.2 µg/L, 8.4 µg/L, and 36 µg/L were determined in replicate. The values of $\delta^{13}C$ in EDB in 19 replicate samples varied from -27.0‰ to -28.5‰, and values for 1,2-DCA varied form -27.8‰ to -28.9‰. The sample standard deviation for $\delta^{13}C$ in EDB and 1,2-DCA was the highest at the lowest concentration (4.2 µg/L). A sample standard deviation of 0.5‰ was be taken as the data quality objective for determination of $\delta^{13}C$ in EDB and 1,2-DCA, as a consequence, 4 µg/L is the lowest concentration of EDB and 1,2-DCA that could be analyzed for $\delta^{13}C$ with acceptable precision.

Table C.1. Reproducibility of $\delta^{13}C$ values for EDB and 1,2-DCA prepared by a purge and trap sampler from ground water containing aqueous solutions of EDB and 1,2-DCA and gasoline.

Run #	Conc	EDB			DCA		
	µg/L	$\delta^{13}C$			$\delta^{13}C$		
			Mean	Stan dev n=2		Mean	Stan dev n=2
1975	3.6	-27.7			-28.4		
1976	4.2	-27.9	-27.475	0.5	-28.4	-28.05	0.4
1979	4.2	-27.5			-27.8		
1981	4.2	-27.2			-27.9		
1982	4.2	-27.3			-28.1		
1973	4.8	-27.8			-28.6		
1984	8.4	-27.3	-27.26	0.4	-28.2	-28.46	0.4
1986	8.4	-27.6			-28.6		
1988	8.4	-27.3			-28.3		
1990	8.4	-27.1			-28.8		
1991	8.4	-27			-28.4		
1971	12	-27.6			-28.5		
1972	21.6	-28.2			-28.4		
1974	36	-28.3	-28.42	0. 1	-28.7	-28.76	0.1
1978	36	-28.3			-28.8		
1980	36	-28.5			-28.7		
1985	36	-28.5			-28.9		
1989	36	-28.5			-28.7		
1977	48	-28.0			-28.5		

Appendix D.
Analytical Methods and Quality Assurance

Six compounds were considered critical parameters in the Quality Assurance Project Plan; EDB, 1,2-DCA, benzene, nitrate, sulfate, and methane.

Appendix D.1

1,2-Dibromoethane (EDB) in Water Samples from Field Sites

When EDB was determined in samples of ground water from field sites, EDB was determined by EPA Method 8011. In some analyses, the method detection limit was 0.010 µg/L, and the lowest calibration standard was 0.03 µg/L. In other analyses the method detection limit was 0.005 and the limit of quantitation was 0.020 µg/L.

The acceptance value for the method blank was a value less than the method detection limit for the particular report for that sample set. A total of 507 method blanks were analyzed in sample sets analyzed on 137 different dates, and all 507 method blanks were below the method detection limit reported with the sample set.

A total of 414 continuing calibration checks were performed for EDB in sample sets analyzed on 130 different dates. The acceptance value was 60% to 140% of the nominal value of the calibration check standard. The range of reported values was 62.6% to 255% of the nominal values. Two continuing calibration checks were out of the acceptable range, a value of 206% and a value of 255% in samples reported 05-07-2007.

A total of 112 performance standards (secondary source standards) were evaluated for EDB in sample sets analyzed on 84 different dates. The acceptable range of recoveries was 60% to 140% of the nominal value of the secondary source standard. None of the secondary source standards were out of the acceptable range.

A total of 74 matrix spikes were performed for EDB on samples analyzed on 58 different dates. The acceptable range of recoveries was 60% to 140% of the spiked concentration. The actual range of recoveries was 48% to 309%; five samples were out of the acceptable range.

A total of 11 laboratory control spikes were analyzed for EDB on samples analyzed on nine different dates. The acceptable range of recoveries was 60% to 140% of the spiked concentration. The actual range of recoveries was 72.4% to 134%. No samples were out of the acceptable range.

Appendix D.2

1,2-Dibromoethane (EDB) in Water Samples from Microcosm Studies

In samples from laboratory microcosms, EDB was determined by head space gas chromatography/ mass spectrometry (GC/MS) using a modification of EPA Method 5021A, "Volatile Organic Compounds in Various Sample Matrices using Equilibrium Headspace Analysis," June 2003. Samples were collected for analysis with an automated static head space sampler. Analytes were determined by gas chromatography/mass spectrometry using an Ion Trap Detector. The lowest calibration standard was 0.5 µg/L; the method detection limit was 0.1 µg/L.

The acceptance value for EDB in the method blank was less than the method detection limit. A total of 29 method blanks were analyzed in sample sets analyzed on five different dates, and all 29 method blanks were below the method detection limit.

A total of 52 continuing calibration checks were performed for EDB in sample sets analyzed on five different dates. The acceptance value was 60% to 140% of the nominal value of the calibration check standard. The range of reported values was 88% to 112% of the nominal values. No continuing calibration check samples were out of the acceptable range.

A total of 15 matrix spikes were performed for EDB on samples analyzed on five different dates. The acceptable range of recoveries was 60% to 140% of the spiked concentration. The actual range of recoveries was 96% to 107%. No spike samples were out of the acceptable range. A total of 46 secondary source standards were analyzed for EDB on samples analyzed on five different dates. The acceptable range of recoveries was 60% to 140% of the spiked concentration. The actual range of recoveries was 90% to 113%. No samples were out of the acceptable range. A total of seven laboratory duplicates were analyzed on five different dates. The acceptable range of agreement was for the laboratory duplicates to agree with each other with a relative percent difference of ± 25%. Two of the seven laboratory duplicates had detectable

concentrations of EDB; the relative percent difference was 5% and 11%.

Appendix D.3

1,2-Dichloroethane (DCA) in Water Samples from Field Sites

Concentrations of 1,2-DCA were determined by head space gas chromatography/mass spectrometry (GC/MS) using a modification of EPA Method 5021A, "Volatile Organic Compounds in Various Sample Matrices using Equilibrium Headspace Analysis," June 2003. Samples were collected for analysis with an automated static head space sampler. Analytes were determined by gas chromatography/mass spectrometry using an Ion Trap Detector. The lowest calibration standard was 0.5 µg/L; the method detection limit was 0.13 µg/L.

A total of 79 method blanks were analyzed for 1,2-DCA in sample sets analyzed on 44 different dates. All method blanks were less than the method detection limit.

A total of 86 continuing calibration checks were analyzed in sample sets on 50 different dates. The range of acceptable values was 80% to 120% of the nominal value of the check samples. The values of the continuing calibration check samples ranged from 81% to 120% of the nominal value. All samples were within the acceptable range.

A total of 39 performance evaluation standards, or secondary source standards, were analyzed on 29 different dates. The range of acceptable values was 80% to 120% of the nominal value of the check samples. The values of the secondary source standards varied from 90% to 117% of the nominal value. All samples were within the acceptable range.

A total of 25 matrix spikes were performed in water samples analyzed on 19 separate dates. The acceptable range of recoveries was 70% to 130% of the spiked concentration. The actual range was 83% to 119% of the spiked concentration. All samples were within the acceptable range.

Appendix D.4

1,2-Dichloroethane (DCA) in Water Samples from Microcosm Studies

Samples from microcosms were analyzed using the same method as described above for samples from field sites. A total of 29 method blanks were analyzed for 1,2-DCA in sample sets analyzed on five different dates. All method blanks were less than the method detection limit.

A total of 52 continuing calibration checks were analyzed in sample sets on five different dates. The range of acceptable values was 80% to 120% of the nominal value of the check samples. The values of the continuing calibration check samples ranged from 91% to 112% of the nominal value. All samples were within the acceptable range.

A total of 46 performance evaluation standards, or secondary source standards, were analyzed on five different dates. The range of acceptable values was 80% to 120% of the nominal value of the check samples. The values of the secondary source standards varied from 91% to 120% of the nominal value. All samples were within the acceptable range.

A total of 15 matrix spikes were performed in water samples analyzed on five separate dates. The acceptable range of recoveries was 70% to 130% of the spiked concentration. The actual range was 91% to 115% of the spiked concentration. All samples were within the acceptable range.

A total of seven laboratory duplicates were analyzed on five different dates. The acceptable range of agreement was for the laboratory duplicates to agree with each other with a relative percent difference of ± 25%. Five of the seven laboratory duplicates had detectable concentrations of 1,2-DCA; the relative percent differences were 6%, 0.8%, 6%, 0.6% and 4.4%.

Appendix D.5

Benzene in Water Samples from Field Sites

Concentrations of benzene were determined by headspace gas chromatography/mass spectrometry (GC/MS) using a modification of EPA Method 5021A, "Volatile Organic Compounds in Various Sample Matrices using Equilibrium Headspace Analysis," June 2003. Samples were collected for analysis with an automated static head space sampler. Analytes were determined by gas chromatography/mass spectrometry using an Ion Trap Detector. The lowest calibration standard was 0.5 µg/L; the method detection limit was 0.07 µg/L.

A total of 78 method blanks were analyzed for benzene in sample sets analyzed on 45 different dates. All method blanks were less than the method detection limit.

A total of 88 continuing calibration checks were analyzed in sample sets on 50 different dates. The range of acceptable values was 80% to 120% of the nominal value of the check samples. The values of the continuing calibration check samples ranged

from 89% to 115% of the nominal value. All samples were within the acceptable range.

A total of 38 performance evaluation standards, or secondary source standards, were analyzed on 29 different dates. The range of acceptable values was 80% to 120% of the nominal value of the check samples. The values of the secondary source standards varied from 87% to 107% of the nominal value. All samples were within the acceptable range.

A total of 25 matrix spikes were performed in water samples analyzed on 19 separate dates. The acceptable range of recoveries was 70% to 130% of the spiked concentration. The actual range was 89% to 109% of the spiked concentration. All samples were within the acceptable range.

Appendix D.6

Nitrate

Samples were analyzed for nitrate plus nitrite nitrogen using an automated hydrazine reduction method based on EPA Method 353.2. The method detection limit was 0.01 mg/L and the lowest calibration standard was 1.0 mg/L

A total of 14 method blanks were analyzed for nitrate plus nitrite nitrogen in sample sets analyzed on 6 different dates. There were four method blanks below the method detection limit, and concentrations in the remainder of the samples were below 0.047 mg/L. All data were considered of adequate quality for the purpose of this report.

A total of 19 continuing calibration checks were analyzed in sample sets on six different dates. The range of acceptable values was 90% to 110% of the nominal value of the check samples. The values of the continuing calibration check samples ranged from 94% to 105% of the nominal value. All samples were within the acceptable range.

A total of seven performance evaluation standards, or secondary source standards, were analyzed on six different dates. The values of the secondary source standards varied from 93% to 101% of the nominal value. No data were flagged as being out of the acceptable range.

A total of 10 matrix spikes were performed in water samples analyzed on six separate dates. The acceptable range of recoveries was 80% to 120% of the spiked concentration. The actual range was 88% to 115% of the spiked concentration. All matrix spikes were less than the method detection limit.

A total of 13 laboratory duplicates were performed on six separate days. The acceptable range was a percent relative difference of ± 10%. The relative percent difference ranged from 0.05% to 1.05%.

Appendix D.7

Sulfate

Concentrations of sulfate were determined by two separate methods. In some samples, concentrations of sulfate were determined with a Waters Quanta 4000 Capillary Ion Analyzer, using a modification of EPA Method 6500, "Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis," January 1998. The method detection limit for sulfate was 0.172 mg/L. The lowest calibration standard was 1.0 mg/L.

A total of 14 method blanks were analyzed for sulfate in sample sets analyzed on seven different dates. All method blanks were less than the method detection limit. Two field blanks were analyzed on one day. Both were less than the method detection limit.

A total of 14 continuing calibration checks were analyzed in sample sets on seven different dates. The range of acceptable values was 90% to 110% of the nominal value of the check samples. The values of the continuing calibration check samples ranged from 94% to 102% of the nominal value. All samples were within the acceptable range.

A total of seven performance evaluation standards, or secondary source standards, were analyzed on six different dates. The values of the secondary source standards varied from 86% to 97% of the nominal value. No data were flagged as being out of the acceptable range.

A total of six matrix spikes were performed in water samples analyzed on six separate dates. The acceptable range of recoveries was 80% to 120% of the spiked concentration. The actual range was 89% to 97% of the spiked concentration. One matrix spike was out of range by 1%. Despite this one excursion out of the acceptable range in the SOP, all data were considered of adequate quality for the purpose of this report.

A total of six laboratory duplicates were performed on five separate days. The acceptable range was a percent relative difference of ± 10%. The relative percent difference ranged from 0% to 2.74%.

Water samples that had been preserved with HCl were analyzed by an automated turbidimetric method based on EPA Method 375.4. The method detection limit was 1.14 mg/L and the lowest calibration standard was 2.0 mg/L.

A total of eight method blanks were analyzed for sulfate in sample sets analyzed on three different dates. All method blanks were less than the method detection limit.

A total of 13 continuing calibration checks were analyzed in sample sets on three different dates. The range of acceptable values was 90% to 110% of the nominal value of the check samples. The values of the continuing calibration check samples ranged from 93% to 104% of the nominal value. All samples were within the acceptable range.

A total of four performance evaluation standards, or secondary source standards, were analyzed on three different dates. The values of the secondary source standards varied from 86% to 97% of the nominal value. No data were flagged as being out of the acceptable range.

A total of four matrix spikes were performed in water samples analyzed on two separate dates. The acceptable range of recoveries was 80% to 120% of the spiked concentration. The actual range was 85% to 114% of the spiked concentration. All matrix spikes were less than the method detection limit.

A total of four laboratory duplicates were performed on four separate days. The acceptable range was a percent relative difference of ± 10%. The relative percent difference ranged from 0.70% to 7.75%.

Appendix D.8

Methane

Concentrations of methane were analyzed using a headspace equilibration technique based on Kampbell and Vandegrift (1998). The method detection limit was 0.0001 mg/L and the lowest calibration standard was 0.0010 mg/L.

A total of 18 method blanks were analyzed for methane in sample sets analyzed on five different dates. All method blanks were below the method detection limit.

A total of 27 continuing calibration checks were analyzed in sample sets on seven different dates. The range of acceptable values was 85% to 115% of the nominal value of the check samples. The values of the continuing calibration check samples ranged from 93% to 105% of the nominal value. All samples were within the acceptable range.

A total of six performance evaluation standards, or secondary source standards, were analyzed on five different dates. The expected values of the secondary source standards varied from 85% to 115% of the nominal value. The measured values of the secondary source standards varied from 99% to 101% of the nominal value.

A total of eight laboratory duplicates were performed on six separate days. The acceptable range was a percent relative difference of ± 20%. The relative percent difference ranged from 0.95% to 3.17%. Two field duplicates were analyzed; however, they both were below the detection limit.

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