

The Potential for Ground Water Contamination by the Gasoline Lead Scavengers Ethylene Dibromide and 1,2-Dichloroethane

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Abstract

Ethylene dibromide (EDB) is a synthetic organic chemical that was produced in large amounts for use as a leaded gasoline additive and pesticide. The chlorinated solvent 1,2-dichloroethane (1,2-DCA) is widely used in the chemical industry, and was also added to leaded gasoline. EDB and 1,2-DCA are classified as probable human carcinogens by the U.S. Environmental Protection Agency (U.S. EPA), and EDB's use as a pesticide was suspended in 1984. The current U.S. EPA maximum contaminant level (MCL) for EDB in drinking water is 0.05 µg/L, and the MCL for 1,2-DCA is 5 µg/L. EDB has proven to be both mobile and persistent in ground water, and contamination of ground water by EDB was documented in several states beginning in the early 1980s. The majority of this contamination is attributed to agricultural uses of EDB; however, ~90% of the EDB produced was used as a leaded gasoline additive and it was present in virtually all leaded gasoline sold in the United States. 1,2-DCA is commonly found as a ground water contaminant, and it is both mobile and persistent. Past investigations and remediation efforts at sites contaminated by leaded gasoline have rarely addressed the potential for EDB or 1,2-DCA contamination. For this reason, there is a substantial likelihood that undetected EDB and 1,2-DCA plumes above the MCL may exist at many sites where leaded gasoline leaked or spilled.

Introduction

Ground water contamination by gasoline and other hydrocarbon fuels is common throughout the industrialized world. In the United States, there have been 385,000 documented releases of gasoline from leaking underground storage tanks (Johnson et al. 2000). The principal contaminants of concern from these releases have been the relatively soluble aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes, known collectively as BTEX. These BTEX compounds make up a significant fraction of gasoline, typically ~15% or more. Benzene is by far the most hazardous of the BTEX compounds with a U.S. Environmental Protection Agency (U.S. EPA) maximum contaminant level (MCL) of 5 µg/L.

Extensive efforts were undertaken in the late 1980s and 1990s to characterize and remediate sites contaminated by BTEX. This work led to the observation that dissolved BTEX compounds may biodegrade both aerobically and anaerobically in natural ground water systems (Wiedemeier et al. 1999; Bedient et al. 1999; Fetter 1999; Kehew 2001). Analyses of BTEX plumes at hundreds of sites in California, Texas, and Florida by Rice et al. (1995), Mace et al. (1997),

and Groundwater Services Inc. (1997) showed that the benzene plumes were limited in most ground water systems, with average plume lengths from underground storage tank sites on the order of 100 m or less. These studies did not attempt to analyze possible plumes of ethylene dibromide (EDB) or 1,2-dichloroethane (1,2-DCA) from gasoline spills. The limited plume length of dissolved BTEX compounds in ground water is different than field experience with chlorinated organics, which tend to form longer plumes due to their resistance to biodegradation.

More recently, the gasoline oxygenate additive methyl tert-butyl ether (MTBE) has emerged as a widespread ground water contaminant. MTBE has been added to gasoline in various proportions since about 1979, and as many as 250,000 underground storage tank releases of gasoline containing this compound may have occurred (Johnson et al. 2000). Experience has shown that MTBE is much more persistent than the BTEX compounds, leading to more extensive ground water plumes at gasoline release sites. The U.S. EPA has not established a primary drinking water standard for MTBE, but a secondary taste and odor standard of 20 to 40 µg/L is currently in effect.

With some exceptions (Bruell and Hoag 1984; Hall and Mumford 1987; Pignatello and Cohen 1990; Ellis 2003),

little attention has been paid to the ground water contamination threat posed by lead scavenger additives. The compounds EDB and 1,2-DCA were added to leaded gasoline in significant quantities from the mid-1920s until the phase-down of lead in gasoline concluded in the late 1980s. EDB has an aqueous solubility of 4300 mg/L (Montgomery 1997), while 1,2-DCA has an aqueous solubility of 8700 mg/L (Bedient et al. 1999). Both EDB and 1,2-DCA were present in gasoline at sufficient concentrations to produce equilibrium ground water concentrations of thousands of $\mu\text{g/L}$. Moreover, there is strong field evidence that these compounds are mobile, and persistent in ground water.

The extent and magnitude of ground water contamination by EDB and 1,2-DCA due to leaks and spills of leaded gasoline are not currently known. There have been ~135,000 documented underground storage tank releases prior to 1979 (Johnson et al. 2000). These early documented releases (and many undocumented releases) would have involved leaded gasoline containing EDB and 1,2-DCA.

History of Leaded Gasoline Additives

The problem of premature ignition (knocking) in gasoline engines greatly restricted the development of more powerful and efficient engines in the period immediately following World War I. This led to an extensive search for gasoline additives that could act as engine knock suppressors. In 1921, Midgley and Boyd (1922) discovered that tetraethyllead was a particularly effective antiknock agent, requiring < 1 g/L of gasoline to suppress knock in their test engines. Later experiments, however, revealed that the use of tetraethyllead by itself caused severe engine fouling in the form of solid lead oxide deposits on engine valves and spark

plugs. This resulted in a second search for additives that could act as lead scavengers to remove the lead from the engine. It was soon discovered that organic compounds of bromine, or of bromine and chlorine, could perform this function by forming volatile lead halides during the combustion process (Boyd 1950).

Since the first commercial sale of leaded gasoline in 1923, leaded gasoline has contained brominated organic compounds (Stine 1929), with various amounts of chlorinated compounds (Hirschler et al. 1957; Jacobs 1980; Thomas et al. 1997). In the first few years of tetraethyllead additive production, bromine was added to gasoline in the form of triethylbromine, along with carbon tetrachloride and, later, trichloroethylene. In 1925, the triethylbromine was replaced with EDB, and EDB was the principal lead scavenger until the early 1940s, when 1,2-DCA was substituted for part of the EDB to reduce costs (Jacobs 1980; Thomas et al. 1997). 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 (Hirschler et al. 1957; Morriss et al. 1958; Working Group on Lead Contamination 1965; Pierrard 1969; Robbins and Snitz 1972; Otto and Montreuil 1976; Leinster et al. 1978; Jacobs 1980; Williamson et al. 1980; Lane 1980; Pignatello and Cohen 1990; Alexeeff et al. 1990; Thomas et al. 1997). Aviation gasoline does not contain 1,2-DCA and uses a Pb:Br molar ratio of 1:2, or twice the amount of bromine as the standard automotive motor mix (Jacobs 1980; Lane 1980; Pignatello and Cohen 1990; Thomas et al. 1997).

Considering the atomic weight of lead (207.19 g/mol), bromine (79.91 g/mol), and chlorine (35.45 g/mol), and the molecular weights of EDB (187.88 g/mol) and 1,2-DCA (98.96 g/mol), it is possible to calculate the concentrations of

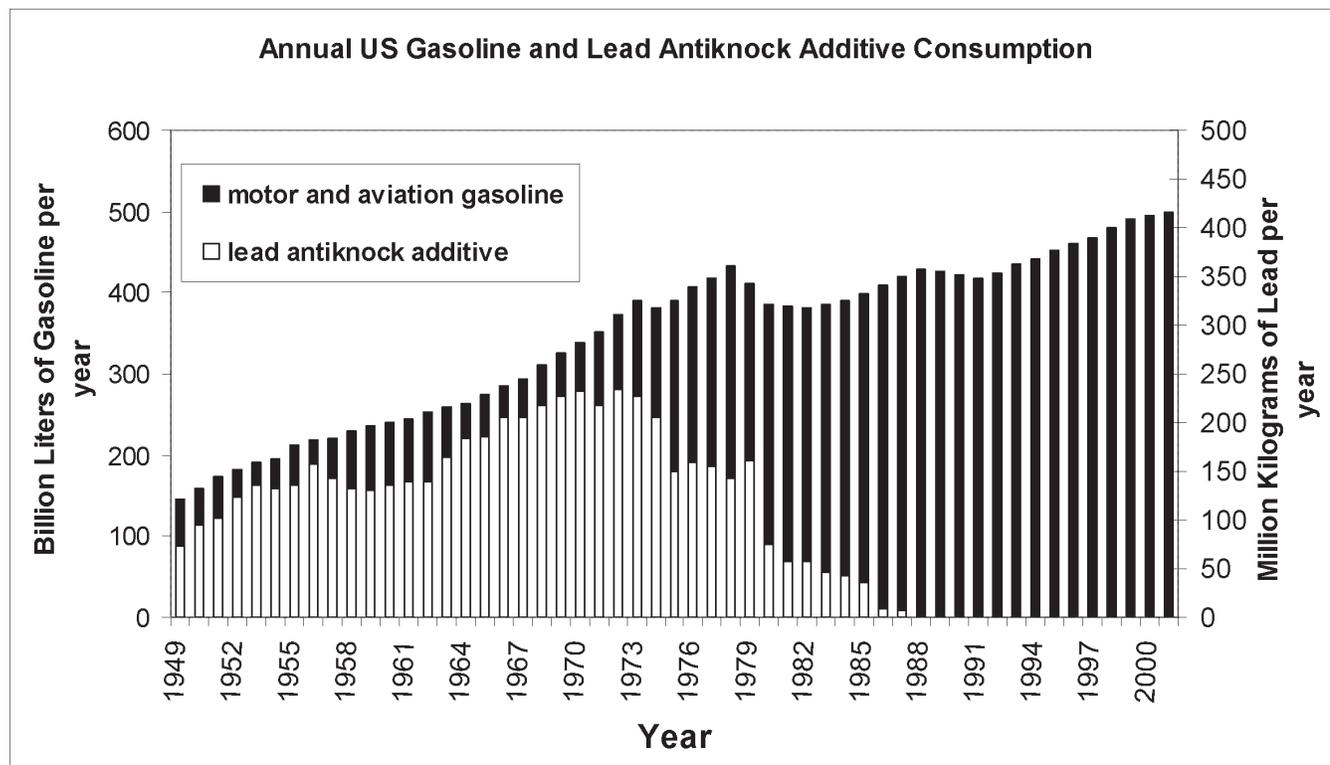


Figure 1. Annual U.S. gasoline and lead antiknock additive consumption (data from DOE [2001] and Thomas et al. [1997]).

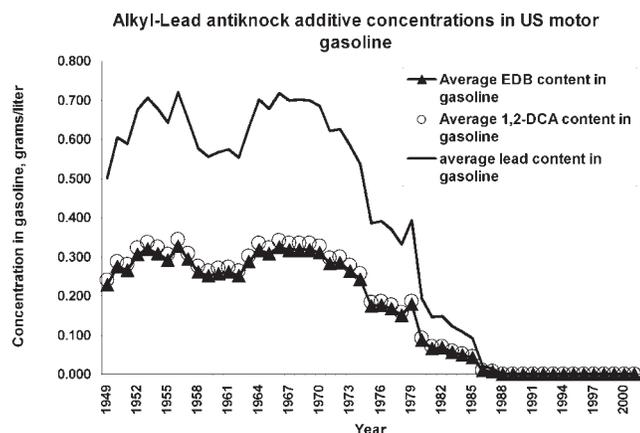


Figure 2. Estimated annual U.S. average lead, EDB, and 1,2-DCA concentrations in automotive gasoline, computed from data in Figure 1, using the standard motor mix tetraalkyl-lead/1,2-DCA/EDB ratios from industry.

EDB and 1,2-DCA in automotive and aviation gasoline as a function of the lead content. Historical lead scavenger concentrations in gasoline are not readily available in the literature, but the lead levels in gasoline are fairly well known. In automotive gasoline, the molar ratio of Pb:1,2-DCA:EDB is 1:1:0.5, so the mass ratio is 1:0.48:0.45. In aviation gasoline, the mass ratio of Pb:EDB is 1:0.91.

During the period of 1949–1973, the lead consumption from gasoline use (Figure 1) approximately tracked the gasoline consumption, peaking at more than 200,000 t Pb/yr in the late 1960s and early 1970s (U.S. EPA 1973). Beginning in 1975, the U.S. EPA-mandated phasedown of lead in gasoline resulted in a substantial drop in the amount of lead consumed, and this dropped further in 1980, with a nearly complete elimination of lead in U.S. gasoline by 1988. Currently, only aviation gasoline contains lead, and at a reduced concentration compared to the early 1970s.

The U.S. average concentration of lead in all gasoline can be estimated by dividing the lead consumption (lead used in gasoline) by the gasoline consumption. Then using the standard lead additive motor mix package formulation, the average U.S. concentration of EDB and 1,2-DCA in automotive gasoline can be estimated (Figure 2). The annual consumption of EDB as a gasoline additive was nearly 100,000 t/yr in the late 1960s and early 1970s (Jacobs 1980; Alexeeff et al. 1990; Thomas et al. 1997). In 1981, the use of EDB as a lead scavenger accounted for > 80% of all EDB consumed. EDB production accounted for 77% of all bromine produced in 1963 (Alexeeff et al. 1990; Alaei et al. 2003) and 69% of all bromine produced in 1976 (Alexeeff et al. 1990).

The average lead concentration in gasoline was relatively constant until the U.S. EPA reduction in 1974, with typical concentrations of 0.5 g/L to 0.7 g/L. The average lead concentration dropped sharply in 1974 and 1975 to a level of ~0.4 g/L. By 1982, lead levels averaged only ~0.15 g/L (considering all grades). Lead was removed from U.S. automotive gasoline almost entirely by 1988.

Because the proportion of lead scavengers to lead has been nearly constant during this period, the average EDB and 1,2-DCA concentrations closely track the lead concentration, at a proportion of ~45% and 48% of the lead concentration,

respectively. The average EDB and 1,2-DCA concentrations in U.S. automotive gasoline were likely between ~0.250 and 0.320 g/L prior to the lead phasedown in 1974. Average EDB and 1,2-DCA concentrations in gasoline (considering all grades) were ~0.180 g/L in the late 1970s, and they dropped to ~0.060 g/L by the early 1980s. These estimated EDB concentrations are consistent with the leaded gasoline value of 0.190 g/L reported by Cline et al. (1991) and the range of 0.051 to 0.271 g/L reported by Bruell and Hoag (1984).

Aviation gasoline concentrations of EDB were ~0.600 g/L prior to the reduction of lead concentrations (assuming a similar lead content to automotive gasoline). It should be noted, however, that aviation gasoline has accounted for only a small fraction of total gasoline used in the United States, reaching a maximum of ~6% of total gasoline consumption in 1958, and declining to ~0.22% by 2001. Jet fuel, which is consumed in much larger amounts, does not contain lead or lead scavengers. It should be recognized, too, that the actual amount of lead and lead scavengers in any given sample of gasoline during the leaded gasoline era would have been variable depending on the gasoline supplier, the gasoline grade, the date, and the location.

EDB and 1,2-DCA Carcinogenicity

EDB and 1,2-DCA are suspected human carcinogens. The U.S. EPA has set an extremely low drinking water MCL for EDB of 0.05 µg/L, and the MCL for 1,2-DCA is 5 µg/L. The U.S. EPA has calculated drinking water concentrations that correspond to specific cancer risk levels for chemicals suspected of causing cancer in humans. These levels are defined as the concentration of a known or probable carcinogen in drinking water that leads to a 10^{-4} , 10^{-5} , or 10^{-6} probability for excess risk of cancer during a lifetime exposure. Table 1 lists the drinking water concentrations for these cancer risk levels for benzene (U.S. EPA 2003a), 1,2-DCA (U.S. EPA 1991), and EDB (U.S. EPA 1997). According to the U.S. EPA, the excess cancer risk associated with drinking water containing benzene at the MCL of 5 µg/L is about 10^{-6} , the risk for 1,2-DCA at the MCL of 5 µg/L is $> 10^{-5}$, and the risk for EDB at the MCL of 0.05 µg/L is $> 10^{-4}$. Put another way, drinking water containing EDB at a concentration of 0.04 µg/L poses the same cancer risk (10^{-4}) as water containing benzene at 100 to 1000 µg/L. In order to achieve a 10^{-6} cancer risk, EDB drinking water concentrations would need to be reduced to 0.0004 µg/L or 0.4 ppt, a level that is ~50 times lower than current analytical detection limits. This relatively high probability for causing cancer has prompted the states of Florida and Massachusetts to reduce their drinking water MCLs for EDB to 0.02 µg/L, while the state of California has set its MCL for 1,2-DCA at 0.5 µg/L. Reviews of EDB toxicology may be found in Alexeeff et al. (1990) and California Environmental Protection Agency (2002).

Occurrence of EDB and 1,2-DCA in Drinking Water

Several large studies have documented EDB and 1,2-DCA contamination in public drinking water systems. The U.S. EPA (2003b) analyzed drinking water data from more

than 20,000 public drinking water systems in a 16-state national cross section. These public water systems serve more than 110 million people. EDB was detected above the MCL in 0.72% of the systems, ranking it fourth among the regulated drinking water contaminants in this study. The occurrence of EDB above the MCL in these public drinking water systems was similar to that of tetrachloroethylene (0.78%) and trichloroethylene (0.65%), and somewhat larger than that of 1,2-DCA (0.13%) and benzene (0.19%).

The halogenated organic chemicals appear to disproportionately affect the larger public drinking water systems. EDB was found above the MCL in systems serving 12.3% of the population, ranking it third among the regulated contaminants. The first and second ranked contaminants, tetrachloroethylene and trichloroethylene, were found above the MCL in systems serving 13.5% and 13.3% of the population, respectively, while 1,2-DCA was found above the MCL in systems serving 8.4% of the population (U.S. EPA 2003b). Benzene, on the other hand, was only found above the MCL in systems serving 0.52% of the population.

Grady and Casey (2001) conducted a study of 2110 randomly selected community water systems in 12 northeastern and mid-Atlantic states. The selected water systems serve 9.6 million people, and they represent 20% of the community water systems in the 12-state region. The detection frequencies of EDB, 1,2-DCA, and benzene in finished drinking water in this study were 1.7%, 1.9%, and 1.4% of the community water systems, respectively. EDB and 1,2-DCA were among the 16 chemicals found above the MCL or drinking water advisory in some community water systems.

As in the U.S. EPA (2003b) study, EDB was found to disproportionately affect larger water systems. EDB was detected above the MCL in community water systems that served a total population of 539,000 (Grady and Casey 2001). Only total trihalomethanes (likely from disinfection processes) and tetrachloroethylene affected the drinking water of a larger population in this study. For comparison, MTBE exceeded the drinking water advisory level of 20 to 40 $\mu\text{g/L}$ in community water systems serving a total population of only 49,900, and benzene exceeded the MCL in community water systems serving a total population of only 400.

Drinking water contamination by EDB has primarily been attributed to its use as a soil fumigant, and the relative contribution of leaded gasoline sources of EDB have not been quantified. Similarly, 1,2-DCA contamination of ground water is generally attributed to the use of chlorinated solvents, and the relative contribution from leaded gasoline has not been studied. Grady and Casey (2001) have provided co-occurrence data for the different chemicals that can be analyzed to estimate the impact of leaded gasoline sources of EDB and 1,2-DCA on drinking water supplies. These data show the percentage of samples containing a specified compound that contains another specified compound. For example, 73% of the water samples that contained ethylbenzene in this study also contained xylenes, indicating likely contamination by gasoline.

EDB occurrence in drinking water samples was strongly correlated with dibromochloropropane (1,2-dibromo-3-chloropropane, or DBCP) occurrence. In samples containing EDB, DBCP also occurred 76% of the time. DBCP, like

EDB, was widely used as a soil fumigant in agriculture. DBCP was not likely to have been used as a lead scavenger in gasoline or as a cleaning solvent. The co-occurrence of EDB with DBCP suggests that a large fraction of the EDB contamination detected in these community water systems was due to the agricultural use of EDB.

However, EDB occurrence was also correlated with 1,2-DCA, and 27% of the samples containing EDB also contained 1,2-DCA (Grady and Casey 2001). There was no co-occurrence of 1,2-DCA with DBCP. Therefore, it can be inferred that there are two sources of EDB that contaminated these drinking water supplies: one from agricultural uses and the other from leaded gasoline contamination. It appears that ~75% of the EDB detections in the community water systems in this study can be attributed to agricultural uses of EDB, while the remaining 25% of the EDB detections could be due to leaded gasoline leaks and spills. Further research is needed to confirm these estimates.

A similar analysis of the Grady and Casey (2001) data could be performed to assess the fraction of 1,2-DCA contamination of drinking water due to its use as a lead scavenger. This calculation is complicated somewhat by the fact that more than twice as many analyses were made for 1,2-DCA as for EDB, so less than half of the samples that were analyzed for 1,2-DCA were also analyzed for EDB.

Very little correlation was found in the Grady and Casey (2001) study between the occurrence of the lead scavengers and BTEX compounds in drinking water samples. This was also the case for drinking water samples contaminated with MTBE, suggesting that these gasoline additives may tend to form ground water plumes that separate from the BTEX plumes.

The frequency of EDB and 1,2-DCA contamination of private drinking water wells is largely unknown. A study of 1926 rural private drinking water wells by Moran et al. (2002) and Moran and Hamilton (2003) found EDB and 1,2-DCA contamination in 0.19% and 0.32% of the wells. Among the 54 volatile organic compounds (VOCs) analyzed in this study, EDB and 1,2-DCA were among the top 25 most frequently detected contaminants, and their frequency of detection was similar to that of benzene (0.21%). Only six of the 54 VOCs exceeded the drinking water standard, health criterion, or drinking water advisory for taste and odor in this study. EDB was the second most frequently encountered chemical to exceed the MCL in this study (approximately tied with trichloroethylene and tetrachloroethylene), and the EDB concentrations exceeded the MCL by a larger amount than any other compound (Moran and Hamilton 2003).

Considering that there are ~15 million individual household private wells serving 40 million people in the United States (Job 2002), these results should be viewed with some caution. The sample size of 1926 wells in this study represents only about 0.013% of the private drinking water wells in the United States.

State Regulations and Analytical Methods

It appears that few states have required chemical analyses for EDB or 1,2-DCA in ground water at sites contaminated by leaded gasoline. The Association for Environmental

Health and Sciences (AEHS) has, for several years, conducted surveys of soil and ground water cleanup standards for sites contaminated by petroleum hydrocarbons. In each survey, regulators from each of the 50 states provided their most recent standards for soil and ground water cleanup (AEHS 2004). Reviewing the data from the 1998 AEHS survey, only five states had requirements to test for EDB and 1,2-DCA in ground water at sites contaminated by gasoline. Thirty-seven states did not require analyses for these compounds, and eight states did not provide information to the survey sufficient to determine the degree to which EDB and 1,2-DCA are tested. In the most recent survey (AEHS 2004), conducted in September 2003, eight states required testing for EDB, and seven required testing for 1,2-DCA; 34 states did not require testing for either. It would be useful to conduct a more thorough review of state regulations to confirm these survey results.

Current analytical methods used to quantify concentrations of BTEX in ground water—U.S. EPA method 8021B and U.S. EPA method 8260B—are also capable of detecting EDB and 1,2-DCA (Ellis 2003; U.S. EPA 1996a; U.S. EPA 1996b). Method 8021B is a gas chromatography (GC) method that uses a photoionization or electrolytic conductivity detector. Using this method, with the electrolytic conductivity detector, the estimated quantitation limits for these chemicals in ground water are 8 µg/L for EDB and 0.3 µg/L for 1,2-DCA (U.S. EPA 1996a). Method 8260B is a GC mass spectrometry method commonly used for VOCs. The estimated quantitation limits using this method are 3 µg/L for EDB and 1 µg/L for 1,2-DCA in ground water (U.S. EPA 1996b). These estimated quantitation limits could be difficult to achieve in highly contaminated samples because of strong matrix effects. Analytical laboratory dilution of ground water samples due to the presence of high concentrations of VOCs also results in a corresponding decrease in the sensitivity of these methods.

It is doubtful that standard operating procedures for BTEX analyses using these methods would include calibration for EDB or 1,2-DCA unless it was specifically requested. Furthermore, it is not known to what extent these compounds would be included in target analyte lists in cases where only BTEX concentrations were required for compliance. If EDB or 1,2-DCA were present at detectable concen-

trations in these samples, the peaks would be registered in the chromatograms, but would probably be ignored.

The few states that do require specific analyses for EDB at gasoline sites usually specify U.S. EPA method 8011 or U.S. EPA method 504.1. Method 8011 is specific to EDB and DBCP. It is a microextraction technique using hexane, with GC analysis using an electron capture detector. This technique has a method detection limit of 0.01 µg/L, and it has been demonstrated to be useful over the concentration range of 0.03 to 200 µg/L (U.S. EPA 1992). States that require analysis for 1,2-DCA at gasoline sites typically specify either method 8021B or method 8260B for this compound.

Dissolution from Gasoline into Ground Water

Gasoline is a complex mixture, composed of hundreds of hydrocarbons; of these compounds, the low molecular weight aromatic hydrocarbons, BTEX, are the most soluble and have proven to be hazardous to human health. The composition of gasoline is variable depending on the date, refinery, grade, season, and location. Table 2 gives representative values for the average mass concentrations of BTEX (API 2002) and EDB and 1,2-DCA in leaded gasoline. These chemical concentrations in the gasoline phase are used to calculate equilibrium aqueous phase concentrations in ground water.

The partitioning of a gasoline component, *i*, between the gasoline phase and the aqueous phase (ground water) is described by an experimentally measured gasoline-water partition coefficient, K_p^i . This coefficient is defined as the ratio of the equilibrium gasoline phase mass concentration of component *i*, C_o^i (g/L) to the equilibrium aqueous phase mass concentration of component *i*, C_w^i (g/L):

$$K_p^i = \frac{C_o^i}{C_w^i} \quad (1)$$

Gasoline-water partition coefficients for BTEX components in gasoline were measured by Cline et al. (1991), and are listed in Table 2. Pignatello and Cohen (1990) report a partition coefficient value of 152 for EDB in leaded gasoline. The equilibrium partition coefficient can be estimated in the absence of experimental data by assuming an activity coefficient of 1 in the gasoline phase. This assumption is known as

Table 1
Drinking Water Concentrations (µg/L) at Specified Cancer Risk Levels for a Lifetime Exposure

Chemical	10 ⁻⁴ (1 in 10,000)	10 ⁻⁵ (1 in 100,000)	10 ⁻⁶ (1 in 1,000,000)
Benzene ^a	100–1000 µg/L	10–100 µg/L	1–10 µg/L (MCL = 5 µg/L)
1,2-dichloroethane ^b	40 µg/L	4 µg/L (MCL = 5 µg/L)	0.4 µg/L
Ethylene dibromide ^c	0.04 µg/L (MCL = 0.05 µg/L)	0.004 µg/L	0.0004 µg/L

^aU.S. EPA (2003a)
^bU.S. EPA (1991)
^cU.S. EPA (1997)

Table 2
Approximate Composition of BTEX and Lead Scavengers in Leaded Gasoline

Compound	Concentration- in Gasoline (g/L)	Gasoline Water Partition Coefficient	Equilibrium Aqueous Concentration to (µg/L)	U.S. EPA MCL in Drinking Water (µg/L)	Ratio of Eq. Aqueous Concentration to the MCL
Aromatic hydrocarbons					
Benzene	13.0 g/L ^a	350 ^b	37,100	5	7420
Toluene	57.7 g/L ^a	1250 ^b	46,200	1000	46
Ethylbenzene	13.3 g/L ^a	4500 ^b	3000	700	4.3
Xylenes (total average)	54.2 g/L ^a	4150 ^{b,c}	13,100	10,000	1.3
Lead scavengers					
Ethylene dibromide	0.290 ^d g/L	152 ^e	1900	0.05	38,000
1,2-dichloroethane	0.310 ^d g/L	84 ^f	3700	5	740

^aAPI (2002)
^bCline et al. (1991)
^cAverage of o, m, p-xylene
^dAverage values from 1950 through 1974
^ePignatello and Cohen (1990)
^fEstimated using Raoult's law

Raoult's law, and equilibrium aqueous phase mass concentration is calculated as the product of the component mole fraction in the gasoline with its pure aqueous solubility. Following Cline et al. (1991), Raoult's law can be used to derive an expression for estimating the gasoline-water partition coefficient:

$$K_p^i = \frac{\rho_o M_{wt}^i}{\bar{C}_w^i M_{wt}^{ave}} \quad (2)$$

where ρ_o is the density of the gasoline phase (g/L), M_{wt}^i is the molecular weight of the gasoline component (g/mol), M_{wt}^{ave} is the average molecular weight of gasoline phase (g/mol), and \bar{C}_w^i is the component's pure solubility in water (g/L). Raoult's law is often a good approximation for mixtures of chemicals that are structurally similar, and the partition coefficient values listed in Table 2 for the BTEX compounds are close to Raoult's law values (Cline et al. 1991). The measured partition coefficient for EDB, however, is ~0.5 of the Raoult's law value, resulting in an aqueous concentration twice as high as the Raoult's law value. This difference is likely due to the different molecular structure of EDB compared to gasoline hydrocarbons. The gasoline-water partition coefficient for 1,2-DCA in Table 2 was estimated using Raoult's law, so this value should be considered approximate.

Calculated aqueous concentrations of BTEX, EDB, and 1,2-DCA in equilibrium with leaded gasoline are shown in Table 2. These are the maximum dissolved chemical concentrations that could be expected in ground water near a leaded gasoline spill. All of these compounds can dissolve from leaded gasoline into ground water at concentrations of thousands of µg/L. Comparing these dissolved concentrations to the U.S. EPA drinking water MCLs, it is clear that

EDB and 1,2-DCA from leaded gasoline could pose a substantial contamination threat to ground water supplies. The ratio of EDB equilibrium aqueous concentration to its MCL is ~5 times greater than the benzene ratio and nearly 30,000 times greater than the xylenes ratio. Similarly, the ratio of 1,2-DCA equilibrium aqueous concentration to its MCL is ~15 times greater than the toluene ratio, and >500 times greater than the xylenes ratio. On the basis of equilibrium ground water concentrations and MCLs, the ranking of ground water contamination potential for the leaded gasoline compounds in Table 2 would be EDB, benzene, 1,2-DCA, toluene, ethylbenzene, and xylenes. These contamination potential estimates only apply to source locations at times immediately following a spill of leaded gasoline. The environmental risk posed by dissolved plumes must account for the fate and transport of these chemicals in ground water.

Mobility in Ground Water

The chemical properties of EDB and 1,2-DCA favor transport in the aqueous phase. Due to their moderate vapor pressures (1.47 kPa for EDB and 8.10 kPa for 1,2-DCA) and high solubilities, these compounds have low dimensionless Henry's constants of 0.029 for EDB (Montgomery 1997) and 0.050 for 1,2-DCA (Bedient et al. 1999). These Henry's constants are 5 to 10 times lower than that of benzene. In the vadose zone, EDB and 1,2-DCA vapors leaving the gasoline would partition very strongly into the pore water and could subsequently move downward to the water table with infiltrating water. Volatilization losses of EDB and 1,2-DCA from pore water and ground water would be minimal due to the low Henry's constants. Detection of EDB and 1,2-DCA in soil gas surveys could also be complicated by the strong partitioning of these compounds from the gas phase into the aqueous phase.

Once EDB and 1,2-DCA reach ground water, they are highly mobile. They have low octanol-water partition

coefficients (K_{ow}) of 58 (Montgomery 1997) and 30 (Bedient et al. 1999), respectively, so they would not be expected to adsorb significantly to soil or aquifer organic matter. Pignatello and Cohen (1990) list organic carbon partition coefficients (K_{oc}) measured for EDB in five experimental studies. These EDB K_{oc} values range from 12 to 134 L/kg, with an average value of 66 L/kg. Charbeneau (2000) reports a K_{oc} value for EDB of 44 L/kg, and a K_{oc} value for 1,2-DCA of 14 L/kg. Considering typical aquifer organic carbon contents, EDB and 1,2-DCA would be expected to have retardation coefficients < 2 , and they are both more mobile than benzene. 1,2-DCA has a mobility similar to MTBE.

Degradation in the Subsurface

EDB was used as a soil fumigant in the United States from 1948 to 1983. The fairly widespread agricultural use of this chemical, combined with concerns about its toxicity, led to numerous studies of its behavior in shallow soil and aquifer systems. The principal abiotic processes affecting EDB are hydrolysis and reactions with sulfur nucleophiles. Environmental hydrolysis first-order half-lives for EDB reported by Pignatello and Cohen (1990) range from 1.5 to 15 yrs. They report that reactions with H_2S species were substantially faster than hydrolysis reactions. Howard et al. (1991) report a hydrolysis half-life of 2.2 yrs for EDB.

Experiments summarized by Pignatello and Cohen (1990) show that EDB can be microbially degraded by aerobic cometabolism and anaerobic reductive dehalogenation processes. In many cases, the reported experimental reaction rates are rapid with half-lives on the order of days to weeks. Howard et al. (1991) give a ground water half-life value for EDB ranging from a low of 19.6 days to a high of 120 days. They also list the soil first-order half-life for EDB as ranging from 4 weeks to 6 months.

These experimental data would seem to indicate that EDB should degrade rapidly in ground water systems, but field data suggest that this is not the case. Pignatello and Cohen (1990) note that in contrast to microcosm studies showing rapid degradation of EDB, EDB is not readily biodegraded to extinction in real aquifers. Some of this resistance to biodegradation may be due to nonequilibrium sorption processes such as intraparticle diffusion and trapping in micropores (Steinberg et al. 1987). An alternative explanation could be that the biodegradation of EDB ceases at some lower concentration limit (Freedman 2003). The Agency for Toxic Substances and Disease Registry characterizes EDB breakdown in ground water as "hardly at all" (ASTDR 1995).

The U.S. use of EDB as an agricultural soil fumigant ended in 1983, yet EDB consistently is detected at low levels in wells in agricultural areas. At a former tobacco farm in Connecticut, where EDB was applied until 1966 or 1967, EDB was found in ground water nearly 20 yrs later, and during a 2 yr study period, EDB concentrations in the wells were stable (Pignatello and Cohen 1990). EDB concentrations in 23 wells in Fresno and Clovis, California, were analyzed by Kloos (1996). In this study, mean EDB concentrations in six contaminated wells for which data were available dropped by 40% from 1989 to 1993. This drop would suggest a ground water half-life on the order of several years. In con-

trast, a field study in an agricultural area of Florida has suggested a more rapid decay of EDB with an estimated half-life of 0.65 yr (Katz 1993).

The degradation of 1,2-DCA in ground water appears to occur at a variety of rates, depending on site conditions. Howard et al. (1991) give ground water half-life values for 1,2-DCA ranging from 100 days to 1 yr, but these are estimated values. Bedient et al. (1999) summarize first-order decay rates for DCA isomers (combined) in ground water, and their median DCA (all isomers) half-life for all studies is 2.7 yrs. They show cometabolism and reductive dechlorination as being the primary biodegradation pathways. Ravi et al. (1998) analyzed the behavior of a 1,2-DCA plume in Michigan and estimated the first-order decay half-life at 3.8 yrs. Cox et al. (1998) and Cox and Major (2000) describe sites in California and Louisiana where 1,2-DCA appears to be degrading under both anaerobic and aerobic conditions. Similarly, Kelly et al. (1998) describe effective anaerobic reductive dechlorination of 1,2-DCA at a site in Nevada.

Much information is available on the degradation of EDB and 1,2-DCA, but the data are often contradictory, and there is a great uncertainty in the rates of degradation of these compounds under field conditions. Studies have not focused on the fate and transport of EDB and 1,2-DCA from gasoline spills. It is likely that the complex geochemistry that arises from the aerobic and anaerobic degradation of the BTEX compounds could have significant effects on EDB and 1,2-DCA biodegradation, but these effects have not been quantified. In particular, it remains unclear how EDB can be effectively degraded under some conditions, while it persists under other conditions.

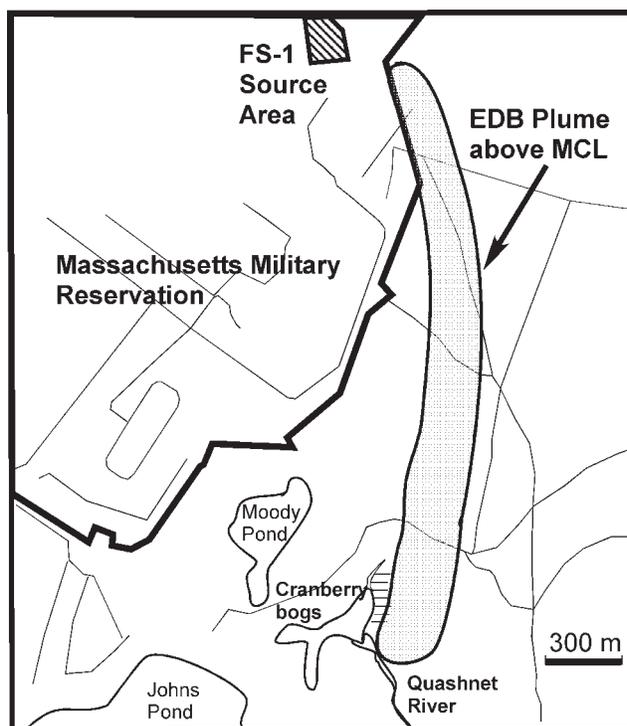


Figure 3. 1998 ethylene dibromide plume from FS-1 source area (adapted from MMR [1999]). The Massachusetts MCL for EDB is 0.02 $\mu\text{g/L}$.

Field Evidence for EDB Persistence and Mobility

One location where EDB plumes in ground water have been associated with leaded gasoline is the Massachusetts Military Reservation (MMR), located on western Cape Cod, ~100 km south of Boston. The site has been used for military operations since 1911. Most operations at the site occurred after 1935, and through 1946 these operations mainly consisted of mechanized Army training and military aircraft operations. Large-scale aircraft operations took place at the site between 1955 and 1970, and the most likely period for contaminant releases was between 1940 and 1970 (U.S. EPA 2000a).

The site was listed as a Superfund site in 1989 following the discovery of multiple contaminant source areas and ground water plumes of VOCs, polychlorinated biphenyls, and other compounds. In the 1990s, EDB was detected in ground water and surface water outside of the MMR boundaries. Subsequent investigations have delineated four large ground water plumes of EDB that have moved off-site (MMR 2003a). Each of these plumes is > 1 km in length. These EDB plumes are all associated with fuel spills, and are known as the fuel spill-1 (FS-1), fuel spill-12 (FS-12), fuel spill-28 (FS-28), and fuel spill-29 (FS-29) plumes. EDB use at the base was only as a component of leaded gasoline, including aviation gasoline (MMR 2001).

The geology at the site consists of glacial deposits with poorly sorted fine to coarse sands. The aquifer system is unconfined and the site is considered a recharge area. Ground water flow velocities are on the order of 0.3 to 0.6 m/day, and there are extensive surface water features nearby (U.S. EPA 2000a).

One of the EDB plumes (Figure 3), FS-1, resulted from spills of aviation gasoline during testing of fuel dump valves on EC-121 Super Constellation aircraft between 1955 and 1970 (U.S. EPA 2000a). The amount of aviation gasoline released into the subsurface is not known. An initial investigation of the source area in 1985 did not identify any contamination, but a subsequent 1989 study detected fuel-related chemicals in ground water above MCLs. In 1990, a remedial investigation was performed and seven wells were installed in the source area to supplement the existing four wells. Twelve downgradient wells were installed in two transects. The source area wells were found to contain toluene and lead above the MCLs, but the downgradient wells did not contain any contaminants above MCLs.

In 1993, seven of the source area wells were tested for EDB, but none was detected. In 1995, a Geoprobe® was used to attempt to track a possible downgradient path of fuel contamination from the source zone. No contamination was found in 20 multilevel samples, nor in three new wells.

In August 1997, EDB was detected in surface water at the Quashnet River cranberry bogs at concentrations up to 1.4 µg/L (Figure 3), prompting a new investigation. Thirty-two new wells were installed in 1997–1998 along a path that had not been investigated before, and a plume of EDB discharging into the Quashnet River was identified (U.S. EPA 2000a). The maximum ground water concentration detected in this plume is 10 µg/L (MMR 1999). The EDB plume is completely detached from the source zone and fuel constituents are believed to have degraded naturally. As of 1999,

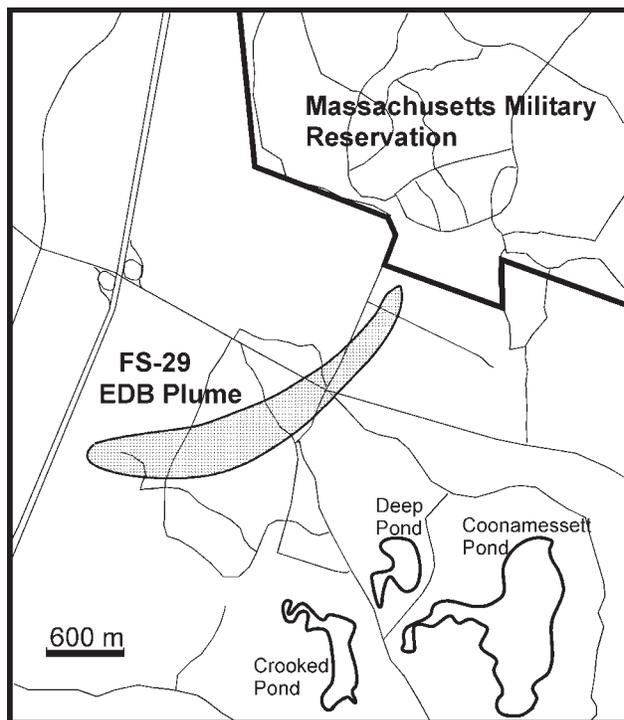


Figure 4. FS-29 ethylene dibromide plume above Massachusetts MCL (0.02 µg/L) in 2000 (adapted from MMR [2000]). The total EDB mass in this plume is only ~160 g (U.S. EPA, 2000b).

the plume extended 2400 m, was up to 360 m wide, and averaged 30 m in thickness, beginning 30 m below ground surface (MMR 1999). The experience at FS-1 illustrates the potential mobility and longevity of EDB released from a gasoline spill. It also highlights the difficulties that may be associated with EDB plume detection.

Another long EDB plume, FS-29, was discovered in 1998. This detached EDB plume (Figure 4) is not associated with any known contamination source at the site (U.S. EPA 2000b). This plume is remarkable in that it is completely detached from any source; it extends for more than 2700 m with a maximum width of 400 m, yet the maximum EDB concentration ever detected in the plume is only 0.071 µg/L. Since the plume boundaries are defined by the Massachusetts MCL of 0.02 µg/L, there appears to be very little change in EDB concentration throughout the plume. The total EDB mass in this plume is estimated to be 160 g, which is approximately the amount of EDB in 600 L of leaded automotive gasoline from the early 1970s. This small mass of EDB has contaminated 1.2 billion gallons of ground water at an average concentration of 0.035 µg/L (U.S. EPA 2000b).

A fuel pipeline leak in 1972 released an estimated 265,000 L of aviation gasoline to the soil at what is now known as the FS-12 source area (MMR 2003b). This spill resulted in a 1400 m long, 600 m wide, plume of dissolved benzene and EDB. The EDB plume was larger than the benzene plume, and maximum contaminant concentrations were 1600 µg/L benzene and 600 µg/L EDB (Kavanaugh et al. 1999). A soil vapor extraction and air sparging system was installed in the source zone in 1995, and it removed ~20,000 kg of gasoline components by 1999 (MMR 1998).

In 1997, an extensive ground water pump-and-treat system was installed to capture and remove the ground water plume. This system consists of 25 ground water extraction wells, a treatment plant, and 23 injection wells (MMR 1998). The construction costs for this system were \$14,830,000, and the projected life cycle cost of the system is \$34,300,000 in 1998 dollars (Kavanaugh et al. 1999). As of June 2003, the plume treatment system has removed 127 kg of benzene and 61 kg of EDB from the ground water. This is more than 98% of the cleanup goal, based on estimates of benzene and EDB in the plume (MMR 2003c). The ground water treatment system is scheduled to operate until 2012.

Given the volume of the FS-12 aviation gasoline spill and the EDB mass recovered by the ground water treatment system, it is possible to construct a rough mass balance on EDB. Assuming an average EDB concentration of ~0.6 g/L in aviation gasoline (twice the automotive level), the 265,000 L spill would have released ~159 kg of EDB to the subsurface. Some of this EDB could have evaporated during the spill and some of it was likely removed by the soil vapor extraction-air sparging system. Since 1997, the ground water extraction system has removed 61 kg of EDB, or ~38% of the original amount. Put another way, at least 38% of the original EDB in the gasoline spill persisted in the environment for at least 25 yrs (1972-1997). Assuming first-order kinetics, the decay of EDB in the subsurface can be described by

$$\frac{M}{M_0} = e^{-kt} \quad (3)$$

where M_0 is the initial mass of EDB released to the environment (159 kg), M is the mass of EDB remaining in the environment after some time t , and k is the first-order rate constant. If it is assumed that the EDB not recovered by the ground water treatment system degraded in the environment, Equation 3 can be used to estimate the apparent first-order decay constant for using a time (t) of 25 yrs and a remaining EDB mass (M) of 61 kg. The environmental EDB half-life can then be estimated from

$$t_{1/2} = \frac{\ln(2)}{k} \quad (4)$$

Following this logic, the computed half-life for the EDB mass in the spill is ~18 yrs. This half-life is approximate because the EDB residence time in the gasoline (where it would not degrade) is not known, nor are the EDB losses to evaporation. Nonetheless, it gives some idea about the longevity of EDB at this site, and this value is much longer than the reported half-lives from most laboratory experiments.

A similar calculation can be performed for the benzene in the plume. Assuming an initial benzene concentration of 13 g/L in aviation gasoline (Table 2), the initial benzene mass in the spill can be estimated at 3400 kg. Since 1997, the ground water treatment system has removed 127 kg, or 3.7%, of the original amount, so at least 3.7% of the benzene has persisted in the environment for at least 25 yrs. Using these same assumptions, the apparent benzene half-life from this source is ~5 yrs. Therefore, it can be estimated that the EDB half-life is between 3 and 4 times longer than the benzene half-life at this site. This conclusion is significant, because it suggests that EDB from leaded gasoline spills is likely to form ground water plumes that are larger than the benzene plumes at some sites.

Case Study of a Retail Gasoline Service Station

A gasoline service station at a major intersection in Orangeburg, South Carolina, opened in 1953 and operated continuously until it closed in 1987. The original underground storage tanks installed in 1953 were abandoned in place in 1971 and replaced with new tanks. The 1971 tanks were removed in 1987, but the 1953 tanks were not removed until 2003. This site is located on Atlantic Coastal Plain sediments that mainly consist of sandy clays and silts with a low fraction of organic carbon. The water table depth is ~4.5 to 6 m, and ground water velocities are estimated to be ~1.5 to 6 m/yr.

There were no documented large spills or leaks of gasoline during the operation of the station. However, a ground water investigation at the site in 1989 identified dissolved BTEX components in ground water. Subsequent ground water sampling at the site has identified BTEX contamination at levels that would be expected for ground water in contact with gasoline (Figure 5). Separate phase gasoline has been found in several of the on-site wells on occasion. As is typical of many past gasoline underground storage tank investigations, the soil and ground water analyses at this site focused on BTEX components. However, a round of monitoring well samples in 1998 was analyzed for EDB along with BTEX, and EDB was detected in an on-site well at a concentration of 106 µg/L, which is ~2100 times above the MCL. Due to laboratory sample dilution, most of the EDB detection limits during these analyses were from 50 to 100 µg/L. The maximum benzene concentration detected during this round of ground water sampling was 6280 µg/L, or ~1250 times above the MCL.

A subsequent round of monitoring well samples collected in 1999 were analyzed for a full suite of VOCs by U.S. EPA method 8260B with detection limits on the order of 5

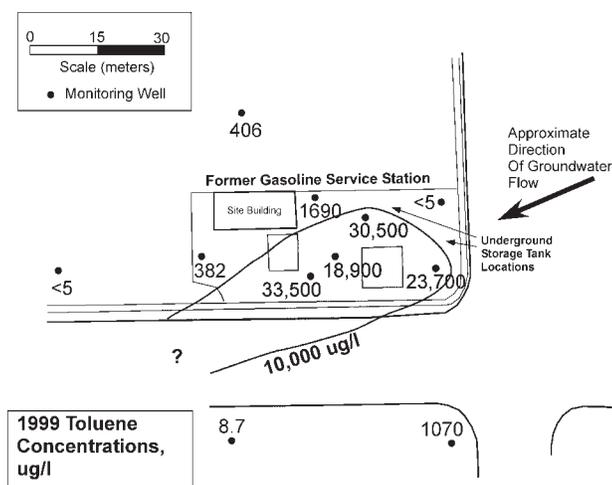


Figure 5. Dissolved toluene concentrations in ground water at a former South Carolina gasoline service station (data from ARM [1999]).

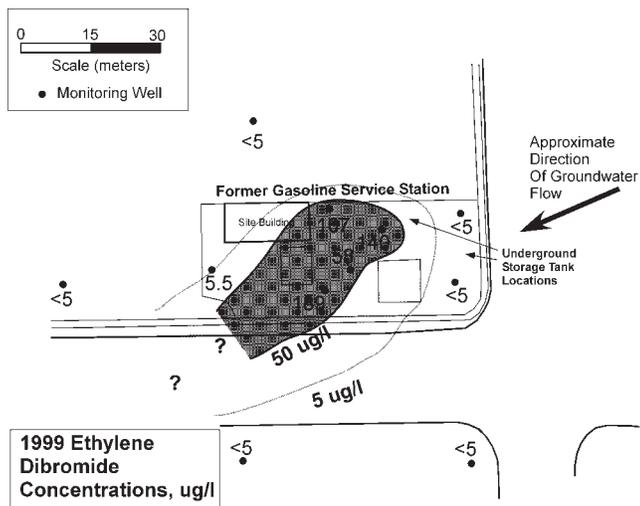


Figure 6. Dissolved ethylene dibromide concentrations in ground water at a former South Carolina gasoline service station (data from ARM [1999]).

$\mu\text{g/L}$. EDB was detected in five of the on-site wells (Figure 6) at concentrations up to $189\ \mu\text{g/L}$, and 1,2-DCA was detected in seven wells (Figure 7) at concentrations up to $111\ \mu\text{g/L}$ (ARM 1999). The dissolved plumes of EDB and 1,2-DCA approximately coincide with the toluene plume shown in Figure 5 (as well as with the other BTEX compounds that are not shown). It is believed that the BTEX plume at this site has a limited extent, but downgradient sampling has not been reported beyond the wells shown in these figures. The full extent of the EDB and 1,2-DCA ground water plumes are not known, and it is worth noting that the EDB detection limit of $5\ \mu\text{g/L}$ used in these analyses is 100 times above the U.S. EPA MCL.

The maximum on-site benzene concentration measured during this round of sampling was $6250\ \mu\text{g/L}$, which is 1250 times above the MCL. For comparison, the maximum EDB concentration of $189\ \mu\text{g/L}$ was 3780 times above the MCL. It could be concluded from these data that the risk associated with EDB at this site is at least as great as that associated with benzene. A similar analysis shows that the risk from

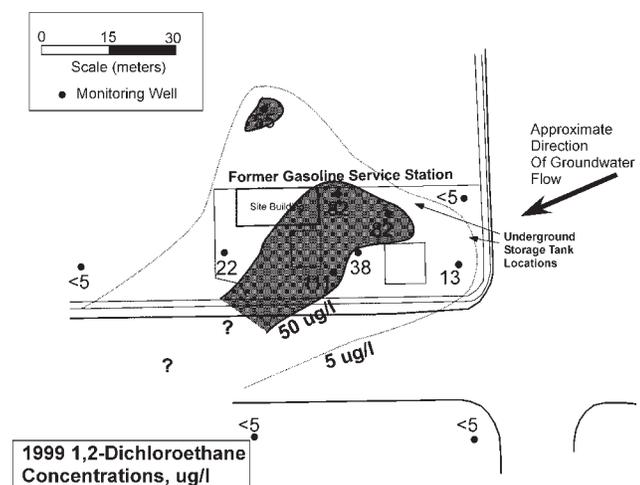


Figure 7. Dissolved 1,2-dichloroethane concentrations in ground water at a former South Carolina gasoline service station (data from ARM [1999]).

1,2-DCA at the site is comparable to that posed by toluene, and is greater than that posed by ethylbenzene or total xylenes.

There is no reason to believe that operations or conditions at this site are unusual or particularly favorable for ground water contamination by EDB or 1,2-DCA. Considering the fact that there are tens of thousands of similar old gasoline service station sites in the United States, the potential for ground water contamination by EDB and 1,2-DCA is apparent.

Summary

In view of the widespread use of EDB and 1,2-DCA in leaded gasoline, it is surprising that these chemicals are not considered to be major environmental risk factors at sites contaminated by leaded gasoline. There are several possible reasons for this.

First, it is possible that EDB and 1,2-DCA have degraded below the MCLs at many leaded gasoline sites. There may be fortuitous reductive dehalogenation and aerobic cometabolic reactions that degrade EDB and 1,2-DCA in the presence of dissolved BTEX compounds. These reactions, and the hydrogeologic conditions under which they occur, should be quantified.

Second, it is possible that the environmental focus on BTEX and MTBE have allowed some EDB and 1,2-DCA contamination to be overlooked. Common analytical methods used for BTEX and MTBE are not likely to detect EDB and 1,2-DCA unless these compounds are specifically included in the target analyte list.

Finally, the low MCL for EDB means that a specialized analytical technique (U.S. EPA method 8011) must be used to detect it at or near the MCL, and it is doubtful that this analysis is routinely performed unless required for compliance.

It would seem prudent to initiate a research program to establish the magnitude and extent of ground water contamination by these lead scavengers. In addition to data analysis and site investigations, such a program should address the considerable uncertainty in the subsurface fate of EDB and 1,2-DCA from leaded gasoline spills. This future research should also analyze current underground storage tank site characterization, remediation, and management practices to ensure they control human and environmental risks from exposure to these compounds.

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Editor's Note: The use of brand names in peer-reviewed papers is for identification purposes only and does not constitute endorsement by the author, his employer, or the National Ground Water Association.

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