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# Leaded-Gasoline ADDITIVES Still *Contaminate* Groundwater

**Ethylene dibromide and 1,2-dichloroethane persist at high levels despite a phaseout in the late 1980s, but they get little attention.**

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Much recent attention has focused on the gasoline additive methyl *tert*-butyl ether (MTBE), which is mobile and persistent in the environment. As demonstrated in several highly publicized cases, the additive has contaminated public water supplies. Hundreds of millions of dollars have been spent to address the MTBE problem, but two other gasoline additives that are far more toxic have been mostly overlooked.

The volatile organic chemicals 1,2-dibromoethane (ethylene dibromide; EDB) and 1,2-dichloroethane (DCA) were ubiquitous components of lead-based antiknock additive mixtures, which were used from the 1920s through the late 1980s to increase gasoline octane ratings. EDB and DCA are probable human carcinogens with federal maximum contaminant levels (MCLs) of 0.05 and 5 μg/L, respectively. Lead is no longer used in gasoline in the U.S., but EDB and DCA still linger in the environment.

Today, EDB and DCA are among the most commonly detected contaminants in U.S. public drinking-water systems that rely on groundwater (*1*). Typically, groundwater contamination by these chemicals is attributed to agricultural (EDB) or industrial (DCA) releases. Yet, in the 1970s, >80% of the EDB was consumed as a gasoline additive (*2*). DCA is a common industrial chemical feedstock that is also used as a solvent (*3*).

Compounding the problem are the >400,000 underground storage tank (UST) sites in the U.S. that have released gasoline (*4*). However, only a small percentage of these sites have been tested for EDB or DCA. Instead, site investigations at gasoline service stations have almost always focused on benzene, toluene, ethylbenzene, xylenes (BTEX), and, more recently, MTBE (*5–8*). Several analyses of hundreds of UST sites in the U.S. with leaks have concluded that most BTEX plumes are small and are stable or shrinking (*5–7*). MTBE plumes, on the other hand, can be much larger (*9*).

Recent research in South Carolina has revealed that about half of the state's UST sites with leaks have groundwater contaminated with EDB at concentrations above the MCL (*3*); a similar situation is expected for DCA. Very little information exists on the nature of dissolved EDB and DCA plumes in this context. Although both compounds are known to bio-

RONALD W. FALTA

degrade in certain settings, they can also be recalcitrant. EDB contamination has persisted for decades after known releases (*10–12*), but how typical that persistence is remains unknown. The lack of testing for EDB and DCA at UST sites and the uncertainty about their degradation mechanisms make it difficult to quantify the magnitude of this problem. What remains clear, however, is that thousands of potentially contaminated locations have not been tested.

**TABLE 1**

### Average EDB and DCA[a] concentrations in leaded automotive gasoline (g/L)[b]

| | 1976–1980 | 1981–1985 | 1986–1990 | 1991–1995 |
|---|---|---|---|---|
| Australia | | 0.38 | | 0.06 |
| Belgium | 0.20 | 0.18 | 0.07 | 0.03 |
| Canada | | | 0.07 | 0.00 |
| Egypt | | 0.36 | | 0.17 |
| Finland | | 0.16 | 0.06 | 0.02 |
| Greece | 0.36 | 0.14 | 0.07 | 0.05 |
| Italy | 0.27 | 0.18 | 0.14 | 0.05 |
| Mexico | | | 0.09 | 0.02 |
| New Zealand | 0.38 | 0.38 | 0.20 | 0.10 |
| Nigeria | | 0.30 | | 0.27 |
| Poland | | 0.19 | | 0.05 |
| South Africa | | 0.38 | 0.18 | 0.17 |
| Spain | | 0.27 | 0.18 | 0.06 |
| Sweden | 0.18 | 0.07 | | 0.00 |
| Switzerland | | 0.07 | 0.05 | 0.02 |
| U.K. | 0.19 | 0.17 | 0.06 | 0.03 |
| U.S. | 0.16 | 0.07 | 0.00 | 0.00 |
| Venezuela | | | 0.24 | 0.14 |

[a] EDB is ethylene dibromide and DCA is dichloroethane.
[b] Computed using lead concentrations reported in References 33–35.

## Historical use

The U.S. was one of the first countries to eliminate most uses of leaded gasoline in the early 1970s. Although many other countries reduced or eliminated leaded gasoline during the 1980s and 1990s, some uses persist, such as piston-engine airplanes and certain off-road vehicles such as racing autos. A few countries continue to use leaded gasoline.

Lead-based antiknock gasoline additives came into widespread use in the late 1920s (*13*). The principal antiknock component of these mixtures was either tetraethyl lead (TEL) or tetramethyl lead (TML). In the U.S., lead concentrations in gasoline averaged ~0.6 g/L, and this product was sold until it was phased out, starting in 1973 (*12*).

TEL and TML each form solid lead oxide deposits that foul engines. So, researchers soon teamed the lead with brominated or chlorinated organics, which act as lead scavengers and form volatile lead dihalides. EDB and, later, a mixture of EDB and DCA were the primary lead scavengers used from the beginning in these antiknock packages (*13*). Two formulations of the antiknock additive compositions were standardized in the early 1940s and are still used in some places to this day: Automotive gasoline contains 1 mole (mol) of DCA and 0.5 mol of EDB per mole of lead, whereas aviation gasoline contains just 1 mol of EDB per mole of lead (*12*, *13*). The automotive antiknock formulation can be used to estimate the average EDB and DCA concentrations in U.S. gasoline (*12*). Before the reductions of lead concentrations in gasoline in the mid-1970s, EDB and DCA concentrations were ~0.3 g/L each.

Table 1 gives estimates of the historical EDB and DCA concentrations in leaded gasoline in several countries during this lead reduction period. These EDB and DCA concentrations were calculated from historical average gasoline lead levels; the standard automotive antiknock additive formulation was assumed.

## Fate and transport

EDB and DCA have pure aqueous solubilities of 4300 mg/L (*14*) and 8500 mg/L (*15*), respectively. These high solubilities dictate low gasoline–water partition coefficients; therefore, EDB and DCA can rapidly dissolve out of free-phase gasoline. When typical EDB and DCA concentrations in leaded gasoline are used, the concentration of EDB in groundwater near an unweathered spill is estimated to be ~1900 µg/L (*12*). DCA can be expected to be twice this concentration.

Both EDB and DCA tend to be mobile in groundwater because of their low octanol–water partition coefficients of 58 and 30, respectively (*14*, *15*). They also have low dimensionless Henry's constants of 0.029 and 0.050, respectively (*14*, *15*). Although the two chemicals tend not to volatilize readily from water, each can evaporate from the free-phase gasoline.

Uncertainty about the mechanisms and rates of biotic and abiotic degradation is the major challenge to understanding the subsurface fate and transport of these chemicals. Many studies have addressed EDB degradation in agricultural settings (*10*, *16*). EDB has been found to degrade both aerobically and anaerobically, and in some cases, rates are rapid. However, several documented cases show that low levels of EDB (but higher than the MCL) have persisted in groundwater for decades after the initial release (*10–12*). Studies addressing DCA degradation have shown that this compound can degrade under both aerobic and anaerobic conditions but that decay rates may be low compared with those of benzene and other aromatic hydrocarbons (*15*, *17*). We are not aware of biodegradation studies of EDB or DCA at leaded-gasoline release sites.

**Both EDB and DCA tend to be mobile in groundwater because of their low octanol–water partition coefficients.**

The typical EDB and DCA plume geometry resulting from leaded-gasoline releases is unknown.

The Massachusetts Military Reservation (MMR) has several long (>1-km) plumes of EDB (*12, 18*). Each has been attributed to leaded-gasoline releases (mainly aviation gasoline), and the lengths of these plumes are comparable with those of chlorinated solvent plumes at the same site. Significantly, three of the four EDB plumes at MMR have completely separated from the source and from any dissolved BTEX (*11, 12*). It is not known whether this behavior is common or whether the hydrogeological and biogeochemical conditions there particularly favor EDB persistence relative to BTEX.

## Health effects

On the basis of animal testing, the U.S. EPA considers EDB and DCA probable human carcinogens. EDB is a particularly powerful animal carcinogen. In 1978, the National Cancer Institute reported that EDB was the most potent carcinogen found in its animal test program (*19*). This study (*20*) has been the primary basis for the current EPA assessment of EDB cancer risk (*21, 22*).

The lifetime risk of cancer from consuming EDB- and DCA-contaminated drinking water is estimated with a cancer risk slope factor, $\rho_f$, in an exponential model that approaches 100% risk at high doses. This factor has units of risk that are expressed as the proportion of the exposed population with tumors per milligram of contaminant per kilogram of body mass per day (*23*).

This exponential model gives the following linear relationship between risk and dose at low-to-moderate doses:

$$\text{Risk} = \rho_f * C_w * q_w \,/ m$$

in which $C_w$ is the carcinogen's concentration in water (mg/L), $q_w$ is the daily water intake (L/d), and $m$ is the body mass (kg).

The known carcinogen benzene is the primary risk driver in risk assessments for almost all UST sites. The value of $\rho_f$ for benzene is $(1.5–5.5) \times 10^{-2}$ $[\text{mg}/(\text{kg}\cdot\text{d})]^{-1}$ (*24*). For example, if typical values for body mass and water consumption are used, a lifetime cancer risk of $10^{-4}$ due to benzene exposure occurs at a concentration of ~100 µg/L.

The slope factor for DCA is somewhat higher, $9.1 \times 10^{-2}$ $[\text{mg}/(\text{kg}\cdot\text{d})]^{-1}$ (*25*), and a cancer risk of $10^{-4}$ occurs at a drinking-water concentration of 40 µg/L. EDB has a much higher slope factor of 2.0 $[\text{mg}/(\text{kg}\cdot\text{d})]^{-1}$, which was recently reduced from 85 $[\text{mg}/(\text{kg}\cdot\text{d})]^{-1}$ (*21, 22*). A cancer risk of $10^{-4}$ therefore occurs at a concentration of only ~2 µg/L for EDB. Given that EDB and DCA can be present in groundwater at concentrations of thousands of µg/L, it is clear that these chemicals should be considered in human health risk assessments at UST sites.

## Few states require testing

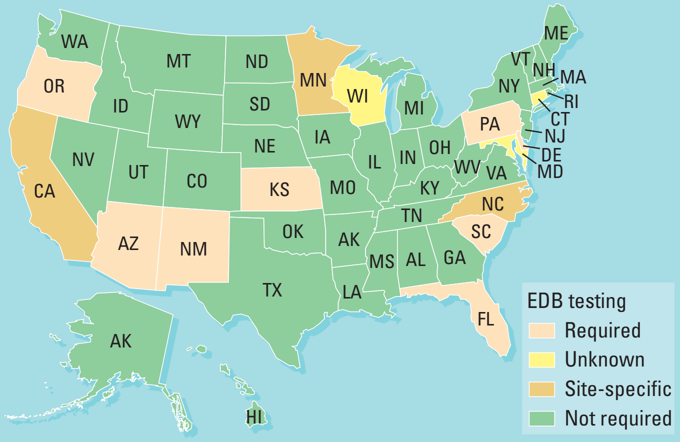
Regulations that control activities at contaminated UST sites vary state-by-state. Despite the existence of federal MCL values for drinking water, states are generally allowed to develop their own procedures and regulations for UST site investigation and remediation, provided that the EPA standards are met. Because every state is unique in its approach to UST site investigations, determining the degree to which EDB and DCA testing has occurred nationwide is difficult. Frequently updated regulations further complicate the testing.

The most readily accessible and comprehensive source of information on state regulations related to petroleum-contaminated sites is a periodic survey conducted by the Association for Environmental Health and Sciences (AEHS; *26*). Approximately every two years, regulators are asked to report their state requirements for soil and groundwater cleanup standards at sites contaminated by petroleum products. The typical response consists of tables of chemicals of concern, such as BTEX and MTBE; analytical methods and their detection limits; and cleanup levels. An analysis of the responses for the 1998 and 2003 surveys indicated that most states do not list EDB and DCA in their regulations for petroleum-contaminated sites (*12*, Figure 1). We have verified these regulations individually for several states, and have found that, in general, the survey accurately reflects state policies. Our experience to date indicates that if a state does not require testing (or cleanup) of EDB and DCA at UST sites, then groundwater samples are typically not analyzed for these chemicals.

**FIGURE 1**

### Eleven states test groundwater

As of 2003, only 11 states require testing for ethylene dibromide in groundwater at sites contaminated by gasoline. Data have not been verified on a state-by-state basis. Adapted with permission from Reference 3.



All states require BTEX analysis of groundwater at UST sites and typically specify chemical analysis by EPA methods 8021B or 8260B (*27, 28*). Both methods are capable of detecting EDB and DCA on the order of 5 µg/L. However, unless EDB and DCA specifically appear on the target analyte list, they are not quantified or reported. Some analytical laboratories may retain the chromatograms from previous BTEX analyses at UST sites, in which case it might be possible to estimate the EDB and DCA concentrations from these samples.

Another important consideration is that groundwater samples analyzed by these methods often must be diluted because of high levels of BTEX. The dilution process results in a corresponding increase in the method's detection limits, often to levels of 100 μg/L or more, which are far higher than the EDB and DCA MCLs.

**Unless EDB and DCA specifically appear on the target analyte list, they are not quantified or reported.**

With an MCL of 0.05 μg/L, EDB poses a special analytical challenge. EPA method 8011, which is specific to EDB, must be used to achieve such a low detection limit (*29*). This method involves liquid–liquid extraction into hexane followed by gas chromatographic analysis with an electron capture detector. Again, this method is not in general use at UST sites unless specifically required by state regulation.

## South Carolina sites

Beginning in the early 1990s, the South Carolina Department of Health and Environmental Control (SCDHEC) tested some UST sites for EDB. Most of these earlier analyses were done using methods 8021B or 8260B, which have detection limits of ~5 μg/L for undiluted samples. Beginning in 2001, method 8011, which has a detection limit of 0.02 μg/L, was specified for all UST sites in South Carolina that had been in operation when leaded gasoline was used. SCDHEC maintains an electronic database of the ~7200 petroleum release sites in the state.

Since 2003, we have been working with SCDHEC to analyze this database and perform various quality-control checks with the individual site files (*3*, *30*, *31*). The most recent analysis of this database, conducted in December 2004, indicated that 537 UST sites in the state had EDB concentrations exceeding the MCL (Figure 2). The median maximum EDB concentration at these sites is 5 μg/L, and ~10% of the sites have maximum EDB concentrations >200 μg/L.

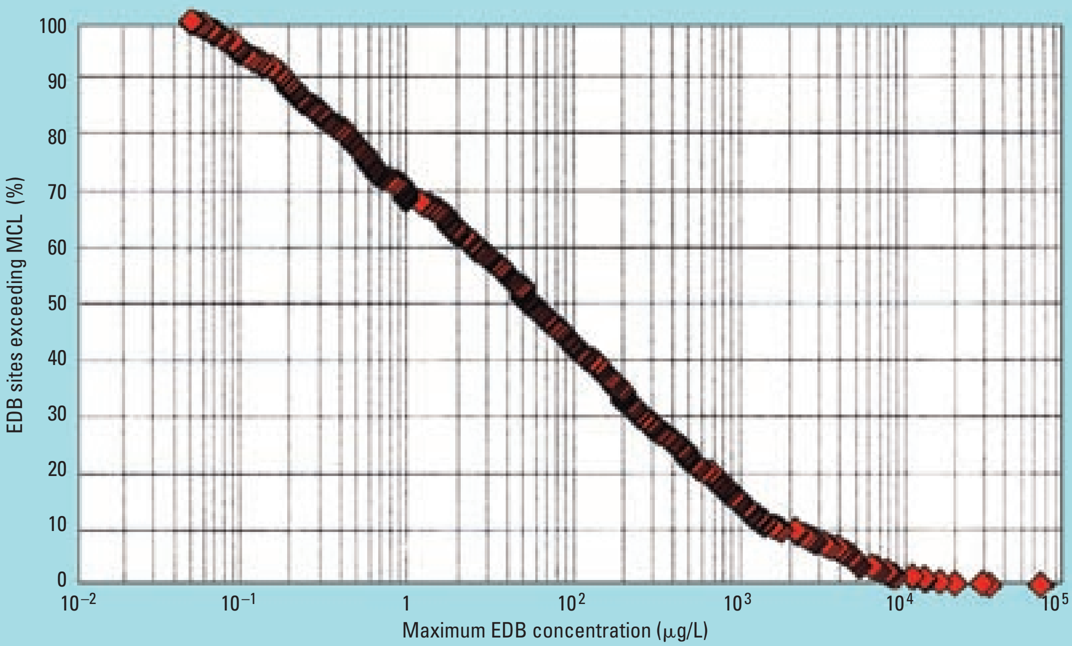
Analysis of the database has been complicated somewhat by the presence of "0.00" entries for the maximum EDB concentration at >800 sites. After reviewing ~100 of these case files, we concluded that many of these were simply default entries for sites that had not yet been tested for EDB. Correcting for these entries, we estimated that EDB is higher than the MCL at about half of the UST sites tested in South Carolina (*3*). This conclusion is consistent with the results of a separate SCDHEC study of 149 UST sites in 6 counties in South Carolina.

The history of gasoline releases at sites where EDB has been detected is generally uncertain because of the lack of UST regulations before the mid-1980s. More than half of all of the petroleum releases contained in the SCDHEC database were reported

**FIGURE 2**

### 537 sites in South Carolina exceed EDB MCL of 0.05 μg/L

About half of the groundwater-tested underground storage tank sites in the state have maximum concentrations greater than EPA's maximum contaminant level for ethylene dibromide. Adapted with permission from Reference 3.



between 1989 and 1993 (*30*), a result of the implementation of the 1988 South Carolina State Underground Petroleum Environmental Response Bank (SUPERB) Act (*32*). Under this statute, taxes on gasoline were used to establish a state fund that would pay for remediation at sites with petroleum releases. All owners reporting releases on or before June 30, 1993, were granted amnesty under the SUPERB program and had no obligation to pay a deductible. Companies reporting releases after June 30, 1993, received no amnesty protection and were required to pay a $25,000 deductible per site. Moreover, after June 30, 1994, the gasoline tax funds could only be used at UST sites where the owner or operator was in compliance with current regulations for release detection and prevention. Many of the gasoline stations reporting releases had been in operation for decades before the official reported release date, and they probably have experienced multiple undocumented gasoline releases.

SCDHEC started testing UST sites for DCA in the past year; results are not yet available. Field data from several sites in North Carolina, however, show that DCA is present at these UST sites, often in much higher concentrations than EDB and further away from the source.

EDB concentrations are not necessarily declining with time, according to an analysis of time trends in more than 50 individual wells at petroleum release sites in South Carolina (*30*). In fact, in ~40% of the wells, the EDB concentration continues to increase with time even though EDB is no longer used in gasoline. An excellent statistical correlation exists between the time trends for EDB concentrations and those for benzene in the same wells. This is clear evidence that these two chemicals have a common source at these sites. One possible explanation for the increasing EDB and benzene concentrations in wells is that in 2003, after a four-year drought, regional water levels began rising. This rise may have facilitated better groundwater contact with the free-phase gasoline at some sites.

**EDB concentrations are not necessarily declining with time.**

Responsible management of sites contaminated by leaded gasoline will require a better knowledge of the occurrence, transport, degradation, and remediation of EDB and DCA than currently exists.

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RONALD W. FALTA

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