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EDB and 1,2-DCA from leaded gasoline may dominate health risk at underground storage tank sites

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Abstract Ethylene dibromide (EDB) and 1,2-dichloroethane (1,2-DCA) were integral parts of the tetra-alkyllead-based anti-knock gasoline additive packages used in the USA and other countries from the mid 1920s through to the late 1980s. EDB and 1,2-DCA are suspected carcinogens, and in animal studies, EDB was found to be one of the most potent carcinogens ever tested by the US National Cancer Institute. On this basis, the maximum contaminant level (MCL) for EDB has been set by the US EPA at 0.05 μg/L, or 50 parts per trillion. The MCL for 1,2-DCA is 5 μg/L. Prior to the phase-out of leaded gasoline, these chemicals were added to gasoline at an average concentration of about 0.3 g/L. Because of their high aqueous solubilities, this would be expected to produce equilibrium groundwater concentrations of thousands of μg/L. Despite the universal use of EDB and 1,2-DCA in leaded gasoline, and their toxicity, few states or countries require testing for these compounds at leaking underground storage tank (UST) sites. Furthermore, little research exists to document EDB and 1,2-DCA attenuation or plume behaviour at UST sites. Field data from some sites have demonstrated that EDB from leaded gasoline can form detached plumes of more that one mile (1.6 km) in length, but this behaviour is probably not typical. The State of South Carolina in the USA has recently tested more than 1000 petroleum release sites for EDB (out of about 7000 sites). EDB has been detected in groundwater above the MCL at about half of these sites. The median maximum EDB concentration at these is 5 μg/L, but EDB exceeds 50 μg/L at more than 100 sites, and it exceeds 200 μg/L at more than 50 sites in the state. A nation-wide sampling programme by the US EPA has confirmed these rates. Overall, it appears that dissolved EDB in groundwater from leaded gasoline releases will pose human health risks that are greater than the benzene risk at about 15% of all underground storage tank sites in the USA. Approximately 1–2% of all UST sites are likely to have very high (>1000 μg/L) concentrations of EDB in the groundwater.

Key words gasoline; gasoline additives; leaded gasoline; LNAPL; ethylene dibromide; dichloroethane

INTRODUCTION

Current environmental concern at gasoline service stations and other underground storage tank (UST) sites focuses on contamination and risks posed by benzene and methyl *tert*-butyl ether (MTBE). While benzene is a natural component of crude oils, MTBE is a synthetic compound that has been widely used as a gasoline additive to increase anti-knock performance of the gasoline, and to increase the oxygen content of gasoline to comply with clean air regulations. While benzene is a known carcinogen,

dissolved plumes of benzene tend to biodegrade, and thus are usually limited in extent (Rice *et al.*, 1995; Mace *et al.*, 1997). MTBE, on the other hand, is not very toxic, and there is some controversy as to whether it may be a weak carcinogen. However, MTBE has proven to be recalcitrant to biodegradation, and extremely mobile in groundwater at many sites.

There are two additional gasoline additives that have been largely ignored at UST sites. These additives, ethylene dibromide (1,2-dibromoethane or EDB) and 1,2-dichloroethane (1,2-DCA) were critical components of tetra-alkyllead anti-knock packages used in gasolines worldwide from the 1920s. The purpose of these halogenated organic additives is to form volatile lead halides in the engine in order to prevent solid lead oxide deposit formation (Boyd, 1950; Lane, 1980). Because their purpose is to remove the lead additive from the engine, EDB and 1,2-DCA are commonly called lead scavengers. In fact, tetra-alkyllead cannot be used as a gasoline additive without these scavengers because the engine would quickly be fouled.

The lead scavengers are blended with the tetra-alkyllead in molar proportions that ensure a complete or nearly-complete reaction inside the engine. Table 1 shows the typical composition of these lead-based anti-knock packages in the USA. EDB is a more effective (and less corrosive) lead scavenger compared to 1,2-DCA, and aviation gasoline used in piston-engine airplanes use only EDB as a lead scavenger. Current aviation gasolines contain both lead and EDB. Automotive gasolines have historically used a cheaper blend of EDB and 1,2-DCA (motor mix). The motor mix molar ratio of 0.5 moles of EDB and 1 mole of 1,2-DCA per mole of lead has remained unchanged since the 1940s. In parts of the world where leaded gasoline is still in use, these compositions are also still used.

Table 1 Molar composition of lead-based gasoline anti-knock packages in the USA (from Jacobs, 1980).

Year	EDB to lead ratio	DCA to lead ratio
1926–1928	1.5	0.1
1928–1929	1.15	0.1
1929–present	1.0	0 (aviation gas)
1930–1933	0.85	0.3
1933–1934	0.75	0.4
1934–1942	0.70	0.45
1942–present	0.50	1.0 (motor mix)

Based on the lead content of gasolines, the average amounts of EDB and 1,2-DCA in leaded gasolines over time can be estimated (Falta, 2004). In the USA, gasoline lead concentrations peaked at about 0.6 to 0.7 g/L in the 1950s to 1970s. Converting the motor mix automotive scavenger molar ratios to mass units, and using annual consumption data, Falta (2004) estimated that EDB and 1,2-DCA concentrations in USA gasoline averaged about 0.3 g/L from the 1950s to the 1970s. Lead levels in USA gasoline declined after 1973, and EDB and 1,2-DCA concentrations dropped accordingly. Similar lead, EDB and 1,2-DCA concentrations have been used around the world (Falta *et al.*, 2005), and leaded gasoline was used through the 1990s in many countries.

EDB and 1,2-DCA have chemical properties that make them mobile in groundwater. They are characterized by high aqueous solubilities, low octanol-water partition coefficients, and low Henry's constants. Because of their high solubilities, they readily partition out of the gasoline LNAPL phase, and into groundwater. Falta (2004) estimated equilibrium aqueous concentrations of EDB and 1,2-DCA from typical leaded gasolines at 1900 and 3700 μg/L, respectively. To put this into perspective, USA drinking water standards for EDB and 1,2-DCA are 0.05 and 5 μg/L, respectively.

OCCURRENCE OF EDB AND 1,2-DCA AT UST SITES

A review of the literature, as well as USA state regulations show that relatively few UST sites in the US have been tested for the presence of EDB or 1,2-DCA in groundwater (Falta, 2004; Falta *et al.*, 2005). This situation is likely similar in other countries, where these compounds have been essentially overlooked. The US State of South Carolina is an exception to this pattern; since about the early 1990s, the South Carolina Department of Health and Environmental Control (SCDHEC) has tested selected sites for EDB. Early testing was done using a detection limit of about 5 μg/L, but testing since 2001 has used an analytical method with a detection limit of 0.02 μg/L. As of late 2004, SCDHEC has tested about 1100 UST sites in South Carolina with known petroleum contamination. Of these, 537 sites had groundwater EDB concentrations above the drinking water standard of 0.05 μg/L. Groundwater concentrations of EDB at these sites ranged from the detection limit, up to several thousand μg/L (Fig. 1). SCDHEC only recently started testing groundwater at these sites for 1,2-DCA, and these data are not available yet.

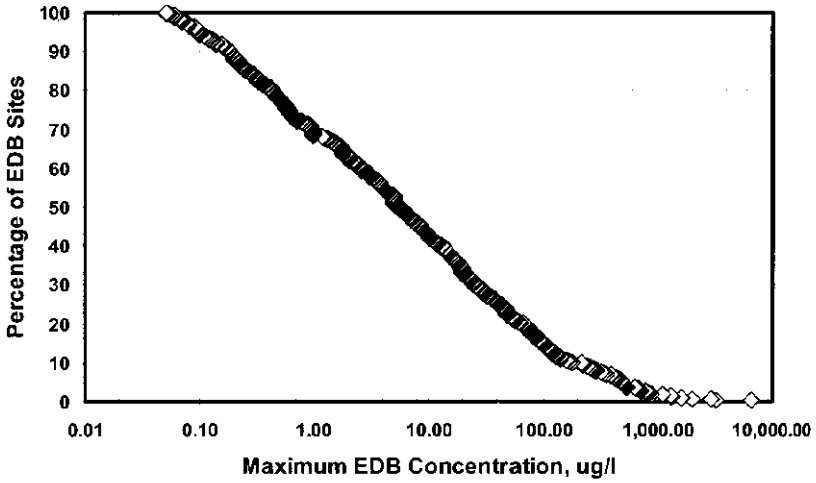

Fig. 1 Distribution of maximum EDB concentrations in groundwater at 537 UST sites in South Carolina where EDB was detected at concentrations above USA drinking water standards. A total of about 1100 sites were tested, and EDB was not present above USA drinking water standards at about half of these sites (from Falta *et al.*, 2005).

The US Environmental Protection Agency (USEPA), is currently conducting a national survey of EDB occurrence in groundwater at UST sites. Their results to date confirm the South Carolina results; EDB is present above the drinking water standard at about half of the sites, and dissolved concentrations of hundreds or a thousand µg/L are seen at some sites (Wilson *et al.*, 2007).

Both the SCDHEC and USEPA studies show that approximately 7–8% of all UST sites have maximum EDB groundwater concentrations above 100 µg/L, and about 1% of all sites have maximum EDB concentrations above 1000 µg/L. At these sites, the potential human health risk posed by the EDB is likely to dominate the risk posed by all of the other gasoline compounds (benzene, toluene, ethylbenzene, xylenes, MTBE, and 1,2-DCA).

RELATIVE HEALTH RISKS FROM GASOLINE COMPONENTS

The gasoline components benzene, EDB, and 1,2-DCA are considered by the USEPA to be either known or probable human carcinogens. The USEPA does not classify MTBE as a carcinogen, but some studies have suggested a weak cancer link, and some states classify MTBE as a possible carcinogen (OEHHA, 2007). The relative potency of a carcinogen is reflected by its cancer risk slope factor, which has units of lifetime cancer risk per mg of contaminant, per kg of body mass, per day. Given the carcinogens oral slope factor, the lifetime risk is calculated by multiplying the average lifetime dose (average concentration times daily water consumption divided by body mass) by the slope factor. Table 2 lists values of the oral (ingestion) slope factors used in California for benzene, MTBE, EDB, and 1,2-DCA. It should be noted that these may be somewhat different from USEPA values (for example, USEPA does not give a slope factor for MTBE).

EDB is by far the most carcinogenic of these gasoline compounds; it has a cancer potency that is 36 times greater than that of benzene, and 2000 times greater than that of MTBE. 1,2-DCA has a cancer potency similar to benzene, and it is about 26 times greater than that of MTBE (if MTBE is considered a carcinogen).

Table 2 Cancer risk slope factors (from OEHHA, 2007).

Compound	Oral slope factor (risk per (mg/kg) per day)	Compound	Oral slope factor (risk per (mg/kg) per day)
Benzene	0.1	EDB	3.6
MTBE	0.0018	1,2-DCA	0.047

The calculated lifetime cancer risk for these compounds is plotted as a function of drinking water concentration in Fig. 2. From Fig. 1 (and the USEPA study by Wilson *et al.*, 2007) it was apparent that about 20% of all UST sites are likely to have EDB concentrations in groundwater that are greater than 10 µg/L. From Fig. 2, the cancer risk from drinking groundwater containing 10 µg/L of EDB is about one in one-thousand, which is well above what is generally considered to be an acceptable risk.

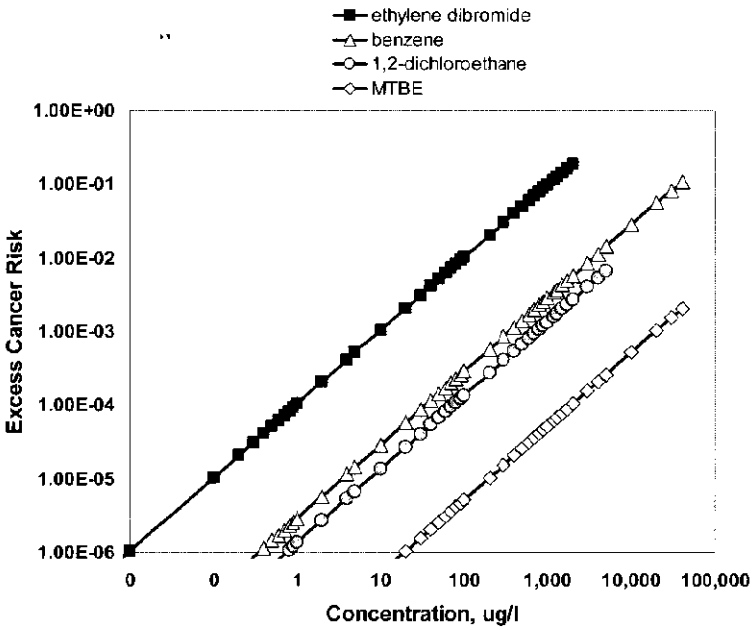

Fig. 2 Lifetime excess ingestion cancer risk calculated using the State of California cancer risk slope factors (OEHHA, 2007).

To get the same risk from benzene ingestion, the drinking water concentration would need to be 360 μg/L, while the MTBE concentration would need to be 20 000 μg/L.

SUMMARY

The leaded gasoline additives EDB and 1,2-DCA commonly occur in groundwater at UST sites, but they are rarely tested for. State and national surveys in the USA are still preliminary, but they suggest that EDB is present in groundwater at concentrations above USA drinking water standards at about one-half of all UST sites. EDB concentrations are very high (>1000 μg/L) at about 1–2 percent of all UST sites. Due to the lack of testing, most of these sites with potentially high EDB risk remain unidentified. In the USA, where about 460 000 petroleum releases have been identified, the EDB occurrence data suggest that there may be 5000 to 10 000 sites where health risks from EDB may be much larger than risks from benzene or other compounds.

A key variable in the potential for EDB and 1,2-DCA exposure is their rate of degradation in groundwater. Past studies of EDB use in agriculture (as a pesticide) suggested that rapid degradation in groundwater was possible, but some studies have found EDB to be persistent (Falta, 2004). Recent work by Henderson *et al.* (2008) shows that EDB can biodegrade under anaerobic conditions and the rate of degradation can be enhanced by the addition of an electron donor such as lactate. This same work,

however, finds 1,2-DCA to be resistant to degradation under similar conditions, and 1,2-DCA appears to be more persistent at some field sites. Rates of aerobic degradation of EDB and 1,2-DCA are not well known, but there is some evidence that it is slow (Falta, 2004). Further investigation on the biodegradation of these compounds under conditions that are relevant to UST sites is needed to design effective measures for remediation and risk reduction.

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