The Distribution of EDB, Benzene, and 1,2-DCA at Gasoline Spill Sites

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Introduction

Leaded gasoline amended with Ethylene Dibromide (EDB) and 1,2-Dichloroethane (1,2-DCA) was used from the mid 1920's until the government-ordered phase out of leaded gasoline concluded in 1986. The U.S. EPA Office of Underground Storage Tanks was created in 1985. Since leaded gasoline had been banned and was no longer present in motor gasoline, there was a common conception that lead scavengers were no longer a problem and there was no need to monitor for EDB and 1,2-DCA in ground water at gasoline spill sites. However, a recent paper by Ronald W. Falta and his co-workers at Clemson University revealed that many sites in South Carolina had significant concentrations of EDB. Figure 1 depicts the EDB concentrations from 537 sites in South Carolina. These findings raised concerns in the Office of Underground Storage Tanks about the distribution of EDB contamination across the nation. The purpose of this work is to determine the distribution of EDB at gasoline spill sites throughout the United States and to compare the distribution to the distribution of benzene and DCA.

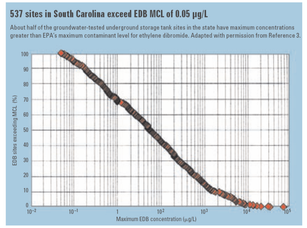

Figure 1. *EDB data for South Carolina from Ron Falta's paper*

Response

A Lead Scavengers Team was formed by the Office of Underground Storage Tanks with assistance from The Association of State and Territorial Solid Waste Management Officials (ASTSWMO) (see *http://www.epa.gov/oust/pbscavms.pdf)*. The ASTSWMO and EPA solicited state agencies to participate in the survey. EPA agreed to provide sample containers, shipping containers, and cover shipping costs. Wells were sampled for EDB during the regular scheduled monitoring event for each site. Samples were preserved with HCl to pH < 2 and refrigerated. Samples were shipped to the Robert S. Kerr Environmental Research Center in Ada, Oklahoma for EDB analysis using EPA method 8011. Figure 2 shows the states that participated in the survey.

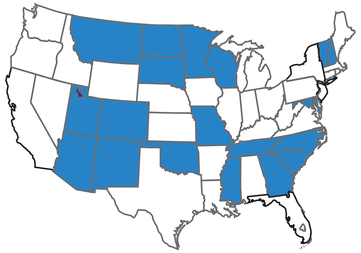

Figure 2. *States participating in the lead scavengers survey*

Results

Nineteen states submitted 802 samples from 102 sites for EDB analysis. The occurrences of EDB, benzene, and DCA are listed in Table 1.

Table 1. Participation in the Survey Conducted by the Lead Scavengers Team

	States	Sites	Samples
Total Number of EDB analyses	**19**	**102**	**802**
EDB detected (>0.01 ppb)	19 (100%)	54 (53%)	151 (19%)
EDB above MCL (0.05 ppb)	17 (89%)	43 (42%)	103 (13%)
Total Number of Analyses for EDB, Benzene, & 1,2-DCA	**12**	**39**	**293**
Benzene detected (>0.5 ppb)	12 (100%)	39 (100%)	118 (40%)
Benzene above MCL (5 ppb)	12 (100%)	39 (100%)	105 (36%)
1,2-DCA detected (>0. 5 ppb)	6 (50%)	9 (23%)	18 (6%)
1,2-DCA above MCL (5 ppb)	5 (42%)	6 (15%)	8 (3%)

Figure 3 compares the distribution of EDB in the survey conducted by the Lead Scavengers Team to the distribution of EDB at gasoline spill sites in South Carolina (as published in Falta et al. 2005). The distribution of EDB in the sites included in the OUST State Survey was similar to the distribution in South Carolina.

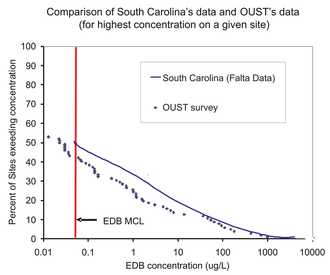

Figure 3. *EDB comparison data*

What is the chance for EDB contamination in your state?

In Figure 4:

- EDB Density is the estimated amount of EDB ever sold in motor gasoline in a state, divided by the surface area of the state.
- The number of Shallow Ground Water Drinkers is from the 1990 census.

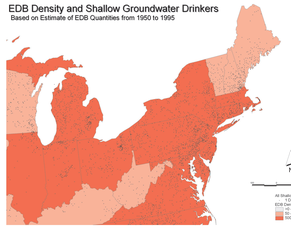

Figure 4.

Risk Evaluation

At 12 states and 39 sites, samples were analyzed for EDB and Benzene. The relative risk associated with EDB and Benzene at theses sites was evaluated and compared. The maximum measured concentration of EDB or Benzene in any well at each site was divided by the Maximum Contaminant Level (MCL) to produce a normalized concentration. This normalized concentration was taken to be a measure of the relative risk associated with EDB or Benzene at each site. The normalized Benzene concentration was divided by the normalized EDB concentration and plotted against the percent of sites sampled. The ratio of risk associated with Benzene to the risk associated with EDB is depicted in Figure 5. For approximately 75% of the sites, Benzene is the risk driver.

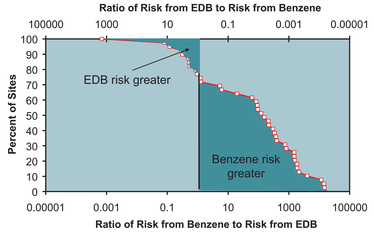

Figure 5. *Risk Ratio Data*

In Figure 6, the normalized concentrations of Benzene and EDB and DCA were ranked, and then plotted against the percent of sites sampled. As a point of reference, the normalized concentrations corresponding to the maximum concentrations of EDB and DCA and Benzene that might be expected in ground water are also plotted. These maximum concentrations are the expected concentrations of EDB or DCA or Benzene in ground water in equilibrium with un-weathered gasoline as predicted from Raoult's Law. The few sites with the highest concentrations of EDB pose more of a risk than the risk associated with Benzene at any site, or the maximum expected risk associated with Benzene. The risk from DCA was minimal compared to the risk from Benzene.

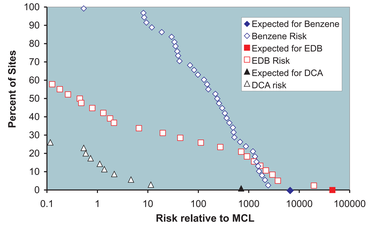

Figure 6. *EDB, Benzene and 1,2-DCA risk comparison data*

Figure 7 plots the highest concentrations of EDB and Benzene at the sites ranked by concentration. The EDB concentrations decline more rapidly than the Benzene concentrations. To determine a possible explanation for this occurrence, Table 2 compares the rate of decline in concentrations to the partition coefficients between water and gasoline for Benzene and EDB. The rate of decline in concentration from one site to the next was determined as the slope of an exponential regression of the concentration on the rank of the site (straight lines in Figure 7). The rates of decline in concentrations of Benzene and EDB and DCA are roughly proportional to the water-to-gasoline partition coefficients for each compound. Since DCA and EDB partition more readily from gasoline to ground water, they would be expected to weather more rapidly from residual gasoline. The EDB and DCA concentrations in an LNAPL source area would be expected to decline more rapidly than the Benzene concentrations.

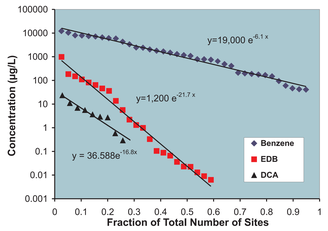

Figure 7. *EDB and Benzene concentration data*

Table 2. Relationship between water to gasoline partition coefficients and the apparent relative rate of physical weathering of EDB and Benzene from the source areas of the plumes.

	Water to Gasoline Partition Coefficient	Instantaneous Rate of Decline in Concentration With Rank in Concentration from one Site to next
Benzene	2.9 E-03	-6.1
EDB	6.6 E-03	-21.7
DCA	12 E-03	-16.8

Conclusion

Important concentrations of EDB remain at old gasoline spill sites, almost thirty years after leaded gasoline containing EDB was banned from motor gasoline in the United States.

Milestones

- June 30, 2007 - all remaining samples submitted to lab
- July 31, 2007 - all remaining analyses completed and results available
- September 30, 2007 - draft memorandum submitted to OUST
- October 31, 2007 - final memorandum submitted to OUST, briefing for OUST Office Director

Reference

Falta et al. 2005. Leaded-Gasoline Additives Still Contaminate Groundwater. *Environmental Science and Technology* September 15, 2005, pages 379-384A.

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