Investigation and Remediation

Which Compound Requires More Attorneys: MTBE or Benzene?

by Blayne Hartman

Editor's Note: This is the third in a series of articles reviewing some of the physical/chemical properties that are commonly used in environmental assessment and remediation. This article will focus on the property of solubility and how to apply it to a common environmental problem.

Okay, following the tradition of the prior two articles, see if you can answer this quiz:

Consider a site that has gasoline free product that is in contact with groundwater. In terms of corrective action at the site, which compound will ultimately involve more attorneys:

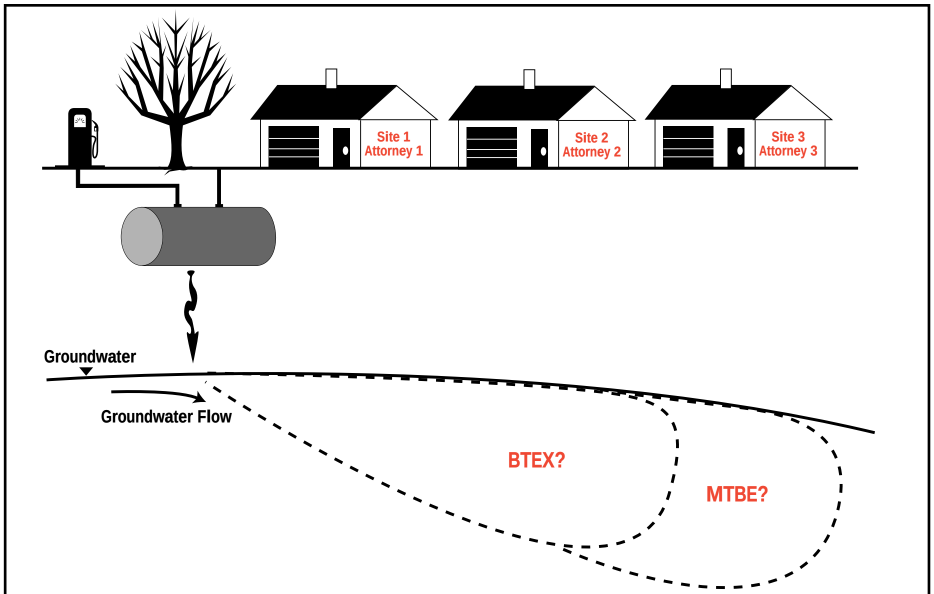
(a) MTBE

(b) Benzene

(c) Equal attorneys for both compounds.

(d) Is this another attorney joke?

Hint: It's not a joke. So we're down to three choices. Another hint: The answer has something to do with the length of the contaminant plumes and whether the groundwater concentrations that each compound will create exceed acceptable levels. To determine this, we need to make a comparison of the starting concentrations of these compounds at their source, relative to acceptable groundwater concentrations. We begin this task by looking at the concept of solubility.



Solubility

The solubility of a compound is defined as the equilibrium concentration of a compound dissolved in water when the water is in contact with the pure compound. The greater the solubility, the higher the concentration of a compound in the water.

Solubilities have been measured empirically (i.e., in the laboratory) for a wide variety of compounds and are tabulated in many reference books. They can be expressed in a variety of different units; most typically they are expressed in terms of mass of the compound per volume of water, such as milligrams per liter (mg/L) or micrograms per liter (µg/L).

Solubility is very compound-specific. If you reflect back to your days in high school or freshman chemistry (without too much pain, I hope), you might recall the old saying, "Like dissolves like." Water is a polar compound and hydrocarbons are primarily nonpolar, which means they are not alike. Consequently, hydrocarbons, by their nature, are generally not very soluble in water. However, where hydrocarbon compounds contain an oxygen molecule (e.g., ethers), solubilities increase dramatically. MTBE is such a compound, and as you've probably already figured out, this is why MTBE is much more soluble in water than benzene.

Now Back to Our Calculation

If we had a pure compound, the resulting maximum water concentration would simply be equal to the solubility. However, for a mixture of compounds (e.g., gasoline), the concentration of each compound in the water is equal to its mole fraction in the mixture multiplied by its individual solubility:

$$C_w = S * MF$$

Where:

- C_w is the concentration of a compound in the water,
- S is the solubility of the pure compound, and
- MF is the mole fraction of that compound in the mixture.

Using this expression, the equilibrium groundwater concentration of any compound in gasoline can be calculated easily. Values for MTBE and benzene are summarized in Table 1. Note that the starting concentration of MTBE in the groundwater is 120 times greater than the starting concentration of benzene (!), due to a solubility that is more than 20 times higher than that of benzene and a mole fraction in gasoline that is 5 times higher than that of benzene.

Based on the concentrations noted in Table 1, you might immediately conclude that MTBE is defi-

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nitely more of a problem than benzene. But wait—it all depends on what groundwater concentrations we eventually have to reach to meet acceptable, or nonthreatening, levels. Even though MTBE might start out 120 times higher than benzene, it doesn't matter if the acceptable levels for MTBE in groundwater are 120 times greater than those for benzene (all else being equal).

The crux of the matter is this: By how much, or by what factor, must the starting concentrations be reduced to reach acceptable levels? Let's define a reduction factor as the amount that we need to reduce the starting concentration to reach acceptable concentrations (starting concentration divided by the acceptable concentration). Table 2 summarizes reduction factors for MTBE and benzene for two different acceptable groundwater concentrations.

Depending on the acceptable levels chosen, the numbers in Table 2 show that MTBE starting concentrations need to be reduced anywhere from 24 to 40 times more than benzene. This in itself is a formidable task, but the situation is exacerbated when one considers that many of the natural processes that reduce groundwater concentrations are thought to be not nearly as effective for MTBE as they are for benzene (e.g., biodegradation or sorption onto soils).

Table 1. *Summary of relevant physical properties and calculated equilibrium groundwater concentrations of MTBE and benzene from gasoline. Mole fractions of the various compounds were selected to represent an "average gasoline" composition.*

	S (mg/L)	MF	C_w (mg/L)
Benzene	1,750	0.025	44
MTBE	42,000	0.125	5,250

Table 2. *Reduction factors (RF) for benzene and MTBE from their equilibrium water concentrations (C_w) to two acceptable levels (C_{a1}) and (C_{a2}).*

	C_w (mg/L)	C_{a1} (mg/L)	RF	C_{a2} (mg/L)	RF
Benzene	44	0.005	8,800	0.001	44,000
MTBE	5,250	0.015	350,000	0.005	1,050,000
Ratio			40		24

Table 3. *Expected plume lengths for benzene and MTBE starting at equilibrium water concentrations (C_w) and reaching an acceptable level (C_a). Values assume a constant source and the daily attenuation rate of benzene taken to be 10 to 100 times greater than that of MTBE.*

	C_w (mg/L)	C_a (mg/L)	0.1 ft/day	1 ft/day
Benzene	44	0.005	70 to 300	300 to 900
MTBE	5,250	0.020	750 to 10,000	3,000 to 10,000

Table 4. *Expected plume lengths for benzene and MTBE starting at water concentrations more commonly observed in groundwater (C_w) and reaching an acceptable level (C_a). Values assume a constant source and the daily attenuation rate of benzene taken to be 10 to 100 times greater than that of MTBE.*

	C_w (mg/L)	C_a (mg/L)	0.1 ft/day	1 ft/day
Benzene	10	0.005	60 to 230	230 to 560
MTBE	75	0.020	260 to 1,060	760 to 1,090

Factoring in Distance

Let's try to put some hypothetical distances to this concept. Using a very simple groundwater flow model (Domenico), we can calculate the expected lengths of the contaminant plumes in groundwater based on starting concentrations and acceptable ending concentrations for various groundwater flow rates (Table 3). As you can see in Table 3, expected lengths of benzene plumes above acceptable concentrations are in the range of hundreds of feet, while expected lengths of MTBE plumes are in the range of thousands of feet. In fact, these calculations indicate MTBE plumes on the order of two miles in length!

Fortunately, in the real world, equilibrium concentrations are rarely observed at the contaminant source. Starting concentrations for both MTBE and benzene are significantly lower than the equilibrium values, and the resulting plume lengths, primarily for MTBE, are significantly shorter.

Table 4 summarizes the calculated plume lengths using starting concentrations for benzene and MTBE equal to the 95 percentile from Orange County, California, well data. Note that while the calculated lengths of the benzene plumes are nearly the same as in Table 3, the lengths of the MTBE plumes are significantly shorter. While we can all breathe a sigh of relief that contaminant plumes of one or two miles in length are not common, these calculations still suggest that MTBE plumes will be longer than benzene plumes by two to five times.

The Answer to the Quiz

Longer plumes tend to cross more properties. The more properties involved, the more property owners involved—all with their own attorneys. So, based on the values shown in Tables 3 and 4, the correct answer is (a): MTBE. The high solubility of MTBE, along with its relative high percentage in gasoline, creates the potential for higher starting concentrations in groundwater. Meanwhile, the low acceptable groundwater concentrations for MTBE, coupled with its poor natural attenuation potential, yields plume lengths that are significantly longer than benzene.

Before you start congratulating yourself for choosing the right answer, you need to be aware of recent studies by the Lawrence Livermore National Laboratory (June 1998) and the University of Texas (1998) that compare *measured* plume lengths (not calculated) of BTEX and

MTBE. In a comparison of data from 63 leaking underground fuel tank (LUFT) sites in California, the Livermore study concludes that the plume lengths for MTBE and BTEX are either the same or shorter than benzene! This would suggest that choice (b) is the correct answer.

How can the plume lengths be the same, you wonder? Well, so did the Lawrence Livermore group. Its answer? The MTBE plumes are "young" (i.e., relatively recent releases that haven't reached steady state) and are still expanding. In other words, the researchers expect that the MTBE plumes will increase in length over the years, much like we'd expect from our modeling results. So, choice (a) it is.

But wait. There may be another explanation. Could it be that, just as with BTEX plumes, bioactivity is responsible for controlling the size of the MTBE plumes? Is it possible that when the BTEX is no longer available, the MTBE becomes the preferred food source (electron donor)? This conclusion goes against conventional dogma that MTBE is not readily degraded by microorganisms (MTBE—also known as **M**any **T**hings **B**ioremediate **E**asier).

The University of Texas paper suggests that natural attenuation of MTBE is occurring at rates much faster than expected. If this is the case, it may be possible that the reason that the plume lengths for BTEX and MTBE in the Livermore study are nearly the same is because MTBE, like BTEX, is being controlled by biological activity, not necessarily the age of the input. Translated: The MTBE plumes may already be at maximum length!

So, now what's the answer to the quiz? Well, if you're a modeler, the answer is (a). If you look at the plume length data from the recent Livermore study, the answer is (b). If you believe the explanation offered by the Livermore group (plumes will be growing), the answer is (a). If you believe that natural attenuation of MTBE could be occurring faster than we think, the answer is (c).

In Truth...

We don't know the right answer. At present, not enough actual field data have been collected on MTBE to really know how it behaves. We still have much to learn. It may, indeed, turn out that risk-based decision making is very appropriate for MTBE, just as it has been for BTEX in the past five years. For this reason, it is crucial that regulatory agencies be careful before attempting to apply basin-wide action levels and equally important that reasonable groundwater concentrations be set, or the cleanup costs for MTBE contamination could "break the bank." Fortunately, it may be that the microorganisms are already working on the problem. *Stay tuned.* ■

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