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Anticipating Environmental Impacts of Future Fuels

by Jim Weaver

Automotive fuels are composed of hundreds of compounds and the formulations aren't uniform; they vary geographically and seasonally and sometimes specifically in response to regulatory requirements. As a result, very few state underground storage tank (UST) regulators know what is in the fuel stream at a service station or bulk plant in their state. Consequently, difficulties abound in anticipating which compounds to sample, choosing analytical methods and eventually selecting technologies for effective remediation in the case of a release. We face the new challenge of determining the correct approach to protecting human health and the environment that includes prioritization of chemicals based on toxicity, fate, and transport in the subsurface. This article touches on some basic new fuel-related concerns in leaking underground storage tank (LUST) site assessment and remediation, particularly those associated with ethanol in gasoline.

Multicomponent Compounds

For the most part, our liquid fuels are multicomponent mixtures that can include hundreds of compounds. Some are natural components of crude oil, some are produced from the crude during refining, and some are introduced as additives. On the petroleum supply side, there are numerous benefits from this situation—the availability of variable sources of crude oil, the ability to make adjustments with respect to engine performance under varying operating conditions, the flexibility to boost octane ratings to match modern engine requirements, to name a few.

On the regulatory side, we are concerned with how the components of these fuels enter the environment and behave when there is a release from the fuel-storage system. Once released into the environment, fuel constituents partition into the different environmental compartments—air, water, and soil. We can predict some behavior of a multicomponent fuel, based on its chemical properties and our knowledge of how much of each is present. We have learned a lot about how fuels interact with the environment over the last 30 years, but this knowledge has limits. In addition to the examples mentioned above, ethanol has shown some characteristics that were predicted and others that were not.

What Determines Fuel Behavior in the Subsurface?

The major properties that influence fuel-component behavior are solubility, volatility, sorptivity, and biodegradability. Along with the amount of each chemical present in the fuel, these properties determine how the chemical interacts with the environment, including its persistence. As such, the properties can act as a screen for behavior.

For example, if the solubility of a compound is low, so that it is immiscible (i.e., cannot be mixed or blended) with water, there is a major distinction in its behavior. The chemical forms a separate phase from water that persists in the environment. This phase forms our familiar light nonaqueous-phase liquid (LNAPL), a characteristic of petroleum contamination from leaking UST systems.

Recent recognition of lead scavengers such as Ethylene Dibromide (EDB) as persistent pollutants illustrates this point. EDB is immiscible with water and has physical-chemical properties that are roughly similar to benzene. Thus it partitions from gasoline much like benzene, another water-immiscible chemical. EDB differs from benzene because of its biotransformation pathway. In essence, the bromium in the compound causes it to degrade under reductive conditions, as opposed to the oxidative conditions required for benzene. Much of this can be predicted in a general way. Specific field and laboratory studies are needed, however, to determine the rates of transformation and the potential for widespread plume persistence.

Likewise, our historic interest in BTEX contamination arises because benzene is a carcinogen. BTEX has a relatively high water solubility and volatility and is present in a significant amount in gasoline. Biodegradation, in many cases, reduces its extent, but the combination of these factors: water immisciblity, solubility, presence in fuel, and toxicity make it a candidate for our concern.

In these examples the compounds are all immiscible with water and, therefore, contribute in a similar way to the separate phase NAPL (gasoline). In contrast compounds such as ethanol, that are miscible (i.e., can mix) with water, interrupt this paradigm and force us to consider phase separation and its impact on releases.

So, What About Those Alcohols?

Based on our knowledge, it was anticipated that the approximately 10 percent ethanol in E10 gasoline could cause BTEX plumes to extend farther out as microorganisms preferentially chowed down on the ethanol and ignored the BTEX. In essence we have one component interfering with our expected behavior of another. Our previous focus on individual components of fuel did not, however, provide all the information needed to assess the impacts from the newly added ethanol. Ultimately our understanding of this behavior required modeling, laboratory and field studies.

At high concentration, ethanol, in particular, causes a qualitative change in the behavior of a fuel. Field studies are beginning to show that the aqueous/ethanol phase associated with an E95 spill hangs around in the vadose zone. Groundwater impacts, when they appear, are happening months or years after the release. Some of this behavior may be predictable from knowledge of the composition and the chemical properties. But would this entire scenario have been anticipated? Likely not.

So how would these scenarios change if we switched from ethanol to propanol or butanol? There are published phase-separation data for gasoline containing propanol and butanol, So far so good. Those data show that the alcohol tends to remain held in the phase-separated organic phase rather than the water, as does ethanol. From available information, can we predict the impact on vadose-zone transport, materials compatibility, vapor releases, effectiveness of remedial technologies, and biotransformation pathways and rates?

Our 30 years of experience in dealing with these problems gives us some ability to predict some of the behavior of new fuels, but there are properties that aren't predictable, such as the biodegradation rates in groundwater. This means that as a regulatory and scientific community we need to take a proactive look at the coming composition of fuels and their potential impacts. This work is partially underway in various places. Some states are looking more closely at their gasoline supply as is the

USEPA. (See USEPA's ongoing gasoline composition study at: http://www.epa.gov/athens/research/regsupport/gasoline.html). Transport and transformation studies are being supported by USEPA, the American Petroleum Institute (API) and some states and conducted by USEPA ORD and universities. Take home message? As fuel compositions continue to change in the coming years, we need to be moving quickly to supply the needed and unpredicted scientific information.

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