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Answers to Frequently Asked Questions About Ethanol Impacts to Groundwater

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A SUMMARY OF RESEARCH RESULTS FROM API'S SOIL & GROUNDWATER TECHNICAL TASK FORCE

Answers to Frequently Asked Questions (FAQs) are intended to assist those who may need to manage releases to groundwater of denatured fuel ethanol or ethanol-blended gasoline. Three types of release scenarios are considered in these FAQs: (1) Denatured[1] Fuel Ethanol Release, (2) Ethanol-Blended Gasoline Release, and (3) Small Volume Release of Ethanol-Blended Gasoline. A number of studies that have contributed to these FAQs are described below.

- *In March 1999, a 19,000-gallon release of denatured fuel ethanol occurred from an above ground storage tank at the Northwest Terminal (Buscheck et al., 2001). This release occurred over a pre-existing hydrocarbon plume.*
- *There have been several modeling studies to predict the impact of ethanol-blended gasoline releases on benzene plume length. Ruiz-Aguilar et al. (2003) report on a field study that compared 217 Iowa sites with ethanol-free gasoline to 29 Kansas sites with ethanol-blended gasoline.*
- *In a study conducted for the CA State Water Resources Control Board (Young and Golding, 2002), Tracer Research Corporation used their TracerTight® method to evaluate the potential for releases from 182 underground storage tank (UST) systems (55 sites). The proprietary tracer was detected at 61% of the UST systems; only one of these detections was caused by a liquid release, the remainder was associated with a vapor phase release and the vast majority of those releases were smaller than 0.04 gallon/day (liquid equivalent). Lahvis (2003) conducted a modeling study for API to estimate the impact of small volume ethanol-blended gasoline releases, using the same 0.04 gallon/day release rate. In addition to these studies, the results of a field experiment (Dakhel et al., 2003) are also used to answer these FAQs.*

Denatured Fuel Ethanol Release

Will there be a dissolved ethanol plume?

The volume of the release, depth to groundwater, and soil type will determine whether there will be a dissolved ethanol plume. Depending on the ethanol to water ratio in the area beneath the release, ethanol concentrations can exceed 10,000 ppm (1% by volume).

Will there be an impact on the mobility of nonaqueous phase liquid (NAPL) hydrocarbons, if present before the release?

The potential exists to impact NAPL mobility. The magnitude of the impact will depend on the volume of the release and pre-existing site conditions. In the presence of ethanol there can be a reduction in interfacial tension, which enhances NAPL mobility (Powers and McDowell, 2001). This may result in the reappearance of NAPL in monitoring wells and collection sumps.

Will there be an impact on benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations?

Dissolved BTEX concentrations can increase because the solubility of BTEX is higher in ethanol:water mixtures than in plain water. This is known as "cosolvency." Ethanol concentrations need to exceed 10,000 ppm to have a significant effect. The source of the BTEX can be either residual hydrocarbons from pre-existing conditions or from the use of gasoline as the denaturant. Ethanol concentrations as high as 16,700 ppm were measured in a Northwest Terminal monitoring well within ten weeks of the release of denatured fuel ethanol (Buscheck et al., 2001).

[1] Neat ethanol is typically denatured with approximately 5% gasoline, making it undrinkable.

Benzene concentrations in a downgradient monitoring well increased by a factor of 15 within 5 months after the release and have since remained over eight times above the prerelease level.

Will there be an impact on BTEX plume length?

If the presence of ethanol increases BTEX solubilities, BTEX plume length is also likely to increase. The results of a modeling study suggest benzene plume length could increase by as much as 150% (Molson et al., 2002). Ethanol constitutes a significant demand on oxygen (and other electron acceptors); the presence of ethanol can deplete electron acceptors, retarding BTEX degradation.

Can methane be a problem?

Ethanol biodegradation can produce elevated methane concentrations in groundwater and vapor phases that may persist for long periods. At the Northwest Terminal the highest methane concentrations were measured in groundwater more than 2 years after the release. A soil gas survey was conducted at the same time, 4 feet below grade. In the unsaturated zone above the groundwater with the highest methane concentrations, methane vapor concentrations exceeded the upper explosive level, which is 19% by volume (Buscheck et al., 2001). Thus, methane should be considered in groundwater sampling programs for monitoring wells in the vicinity of a denatured fuel ethanol release.

Ethanol-Blended Gasoline Release

Will there be a dissolved ethanol plume?

The volume of the release and depth to groundwater determine whether there will be a dissolved ethanol plume. Depending on the ethanol-to-water ratio in the area beneath the release, ethanol concentrations can exceed 10,000 ppm (1% by volume).

Will there be an impact on benzene, toluene, ethylbenzene, and xylene (BTEX) concentrations?

If the ethanol concentration exceeds 10,000 ppm, there can be an increase in BTEX concentrations.

Will there be an impact on BTEX plume length?

The field study by Ruiz-Aguilar et al. (2003) compared benzene and toluene plume lengths for 217 Iowa sites impacted with ethanol-free gasoline to 29 Kansas sites impacted with ethanol-blended gasoline. This study generated the following results:

- The presence of ethanol resulted in mean benzene plume lengths that were 36% longer (70 feet); this difference was statistically significant.
- The mean toluene plume length was only slightly longer in the presence of ethanol (17% longer or 26 feet); this difference was not statistically significant.

This study suggests the presence of ethanol could inhibit benzene biodegradation to a greater extent than toluene. While the mean benzene plume length was somewhat longer at the ethanol-blended gasoline sites, it is still within the expected range of stable benzene plume lengths and should not hinder the application of natural attenuation as a remediation strategy. The impact on ethylbenzene and xylene should be similar to that observed on toluene.

Small Volume Release of Ethanol-Blended Gasoline

Small volume releases of ethanol-blended gasoline may be vapor or NAPL. In the case of a NAPL release, the volume is assumed not sufficient to contact groundwater.

Will ethanol impact groundwater?

- The field experiment (Dakhel et al., 2003) simulating a finite source showed no impacts to groundwater for a release more than one meter above the water table. If considerable infiltration (> 0.5 cm/day) is applied, ethanol was detected in groundwater.
- Modeling results for a steady state release (0.04 gal/day) and constant infiltration rates (0 to 20 cm/year) indicate biodegradation is likely to limit groundwater impacts. Actual infiltration rates associated with individual precipitation events could affect ethanol transport more than was demonstrated in this modeling study (Lahvis, 2003).

Will the presence of ethanol allow benzene vapor/leachate to impact groundwater?

- The field experiment (Dakhel et al., 2003) suggests any benzene impacts to groundwater would be localized and short-lived.

- Modeling results for a steady state release (0.04 gal/day) indicate that even in the presence of ethanol, biodegradation can significantly limit benzene transport to groundwater. The potential for benzene impacts to groundwater increases in fine-grained soils, because of limitations on oxygen availability (Lahvis, 2003).

Is soil vapor monitoring needed?

No, the small volume releases detected in the Young and Golding (2002) study may go undetected by conventional soil vapor monitoring methods. However, there may be reasons to conduct conventional soil vapor monitoring for a large volume release of ethanol-blended gasoline.

Most importantly, the results of the field and modeling studies corroborate each other; ethanol and benzene impacts to groundwater associated with these small volume releases are not expected to be significant.

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About The API Soil and Groundwater Technical Task Force

The API Soil and Groundwater Technical Task force provides an expert, multidisciplinary focal point within API to address soil and groundwater issues. The Task Force identifies and defines emerging technical issues develops research programs to address these issues. API-sponsored research yields practical tools and basic science for risk-based, cost-effective solutions to the oil and natural gas industries' soil and groundwater protection problems. The Task Force disseminates information and research results through publications, presentations and interaction with industry clients and regulatory agencies.

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