Biodegradation of Petroleum Hydrocarbon Vapors in the Vadose Zone

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Use concentrations in ground water to estimate vapor concentrations in soil gas

Conventional approach using J&E model.

Sampling a diving plume may over-estimate vapor concentrations in soil gas

Sampling ground water below LNAPL may under-estimate or over-estimate vapor concentrations in soil gas

How can you get a robust estimate of ground water concentrations if there is free product in the well?

Current state of practice to estimate the contribution of biodegradation of vapors in soil gas in risk evaluations for vapor intrusion.

Assign a factor to correct for removal through biodegradation.

This is a OSFAFF.

Needed is a site specific approach using data from available field measurements to account for the contribution of biodegradation.
Biodegradation of Hydrocarbon Vapors in the Unsaturated Zone

Avgas spill into sandy glacial outwash at the U.S. Coast Guard Air Station at Traverse City, Michigan.

Approach:
1) Collect core samples at various depths.
2) Extract the cores and determine concentrations of TPH and Benzene in the sediment (mg/kg).
3) Determine weight loss of core sediment on drying.
4) Calculate concentration of benzene in pore water.
5) Multiply the concentration of benzene in pore water by the Henry’s Law Constant to calculate the concentration of Benzene in soil gas.
6) Compare the calculated concentration to the concentration expected from vapor diffusion (the transport mechanism in the J&E model).
The “expected” benzene concentration in soil pore water is calculated as:

\[ C_w = \frac{C_o,\text{NAPL}}{K_{\text{NAPL}}} + \frac{\theta_{\text{NAPL}}}{\theta_{\text{w}}} \]

Where:
- \( C_w \) is the concentration in the ground water
- \( C_o,\text{NAPL} \) is the concentration in the gasoline that was spilled
- \( \theta_{\text{NAPL}} \) is the porosity filled with gasoline
- \( \theta_{\text{w}} \) is the water-filled porosity
- \( K_{\text{NAPL}} \) is the distribution coefficient between gasoline and water

\( \theta_{\text{w}} \) (the water-filled porosity) is estimated from the dry weight of the sample and the weight lost on drying.

Assume that the weight loss on drying is the water content of the sediment.

\( \theta_{\text{w}} = \text{bulk density of sediment (gm/ml) multiplied by the water content of the sample (ml = gm) divided by the dry weight of the sediment (gm).} \)

If direct measurements are not available, assume the bulk density of the sediment is 2 g/ml.

\( C_o,\text{NAPL} \) (the concentration of benzene in the gasoline that was spilled) is estimated from the concentrations of Benzene and TPH in the core extracts:

\[ C_o,\text{NAPL} = \frac{\text{Benzene mg/kg}}{\text{TPH mg/kg}} \]

\( \theta_{\text{NAPL}} \) (the porosity filled with gasoline) is calculated from the concentration of TPH (mg/kg), the density of gasoline (mg/L), and an estimate of the bulk density of the sediment (kg/L).

\[ \theta_{\text{NAPL}} = \frac{\text{Concentration TPH divided by density of product spilled, then multiplied by bulk density.}}{\text{If direct measurement of bulk density not available, assume 2.0 kg/L.}} \]

Assume density of gasoline is 800,000 mg/L.

\( K_{\text{NAPL}} \) (the distribution coefficient between gasoline and water) is taken from Cline et al. Environmental Science & Technology 25 (5): 914-920 (1991). \( K_{\text{NAPL}} \) for benzene is 350.
C_{sg}\text{ (Concentration in soil gas)}

C_{sg} (mg/m^3) = \text{Conc. Water (µg/L)} \times H

where H is the dimensionless Henry’s Law Constant.

At HaI’s site in Utah, H expected to be 0.126

Google EPA Henry’s Law Constant Calculator
Benzene measured in soil gas and Benzene estimated from analysis of core samples is much lower than Benzene concentrations predicted by diffusion from contaminated ground water.

Removal due to biodegradation at 2.5 and 4 feet. In presence of ≥100 mg/kg TPH, lower in profile, no evidence of biodegradation of benzene vapors.
Suggestion:
As an alternative to calibrating a J&E model with ground water data from wells, estimate a concentration of the contaminant in pore water in the unsaturated zone using data from core samples, and calibrate J&E with the estimated concentration and appropriate depth of the core sample.

Advantages of Core Samples
Know where the sample came from. No concern of short circuiting or leaks.
Often collect core samples at sites, may already have data to make calculation in a file.
Less subject to temporal variation.
No concern with free product in well water sample.

Disadvantages of Core Samples
Need good field technique to assure sample integrity.
Sensitivity depends on the concentration of TPH. Often not quite as sensitive as soil gas measurements.

The shallow region of the smear zone more weathered than the deeper region.
Substantial removal of Benzene above the smear zone at depths less than 12 feet.