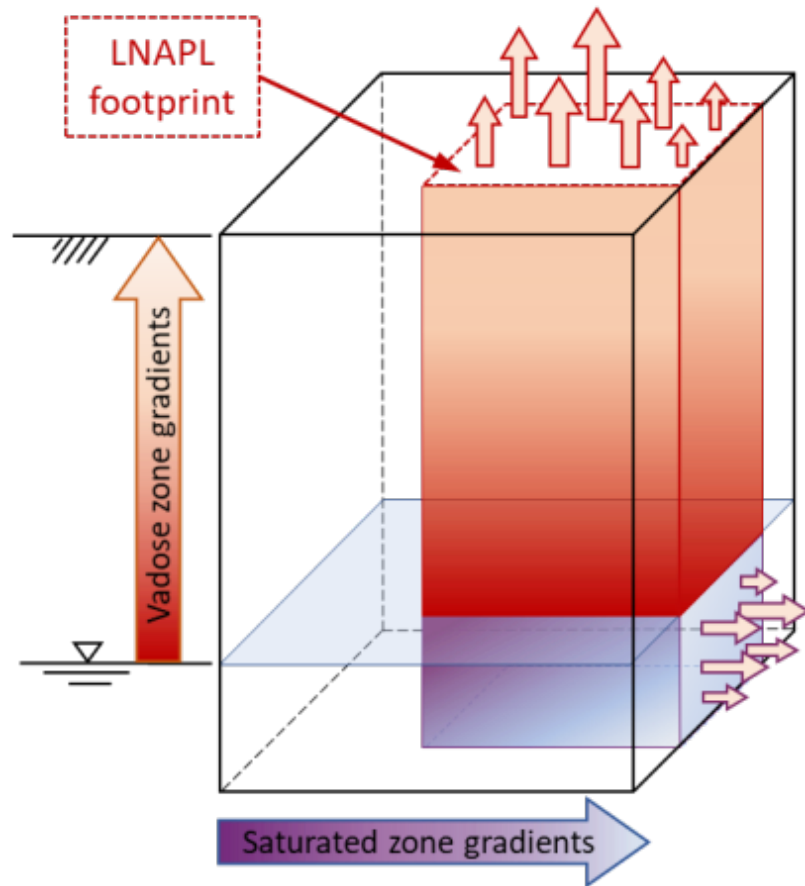


Soil Gas Gradient Method for Estimating Natural Attenuation Rates of NAPL and Specific Chemicals of Concern



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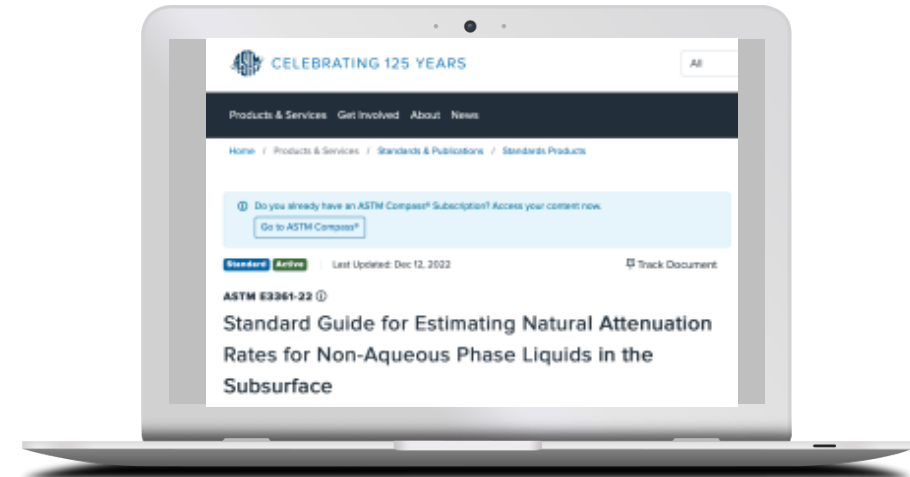
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Natural Attenuation Estimation Methods

1. CO₂ Efflux Method
2. Temperature Gradient Method
3. Soil Gas Gradient Method
4. Groundwater Monitoring Method
5. NAPL Composition Method

Multiple technologies & approaches for data collection & interpretation for each method...



<https://www.astm.org/e3361-22.html>



Summary of Methods

| Method | Type of Attenuation Measured ¹ | Location of Processes & Pathway |
|---------------------------|---|---------------------------------|
| 1. CO ₂ Efflux | Bulk NAPL | Vadose zone ² |
| 2. Temperature Gradient | Bulk NAPL | Vadose zone ² |
| 3. Soil Gas Gradient | Bulk NAPL & COCs | Vadose zone ² |
| 4. Groundwater Monitoring | Bulk NAPL & COCs | Saturated zone |
| 5. NAPL Composition | COCs | NAPL Source zone |

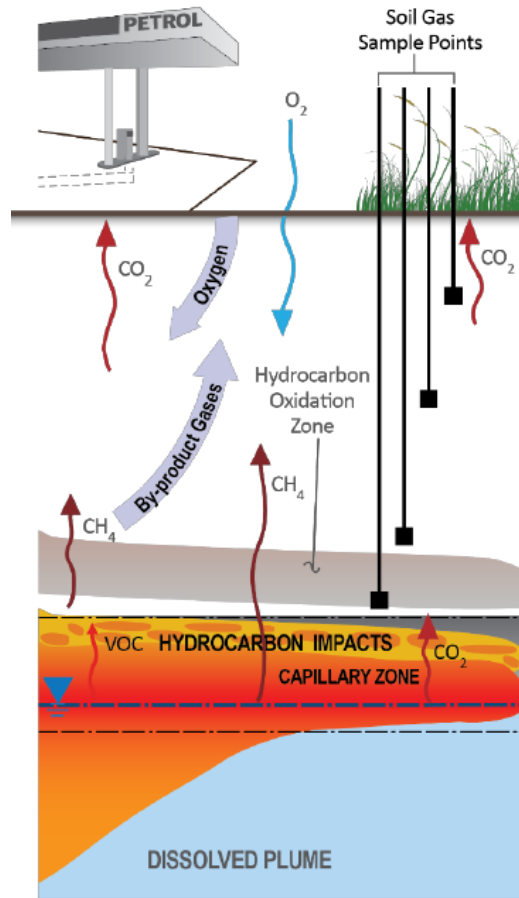
¹Depletion rate of bulk NAPL directly addresses saturation-based concern.

Estimates of **COC attenuation rates** have a more direct impact on composition-based concern.

Both bulk depletion of NAPL and COC attenuation impact the extent and longevity of the COCs in soil vapor and groundwater.

²Includes the transport of methane and other hydrocarbons produced from the biodegradation of NAPL in the saturated zone; and methane oxidation at the aerobic/anaerobic interface.

Soil Gas Gradient method: bulk NSZD rate of the NAPL



Source: CRC care (2018)

Traditional soil gas gradient method (Johnson et al. 2006)

Based on the gradients in O₂ (or CO₂) concentrations in soil gas it is possible to estimate the O₂ (or CO₂) fluxes that are stoichiometrically converted in a **bulk NSZD rate of the NAPL**.

O₂ flux (Fick's law):

$$J = -D^{eff} \cdot \frac{dC}{dz}$$

$$\frac{dC}{dz} = \frac{C_2 - C_1}{z_2 - z_1}$$

Concentration gradient is estimated assuming a linear concentration profile

Traditional soil gas gradient method

The flux of O₂ can be stoichiometrically converted into **bulk NSZD rate of the NAPL** considering a reference hydrocarbon compound (e.g. C₈H₁₈):

$$NSZD \approx 0.29 \cdot J_{O_2}$$

Soil Gas Gradient method: COC-specific NSZD rates

Since mid-late 80s Lahvis et al. proposed the use of soil gas data and numerical models to estimate the attenuation rate of specific chemicals of concern (COCs). The application of this approach requires specific skills and some computational efforts.

Aim of this work: use of simplified approach for the screening of COC-specific NSZD rates based on the soil gas gradient method

Long-Term Evolution of Biodegradation and Volatilization Rates in a Crude Oil-Contaminated Aquifer

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WATER RESOURCES RESEARCH, VOL. 35, NO. 3, PAGES 753-765, MARCH 1999

Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions

Matthew A. Lahvis, Arthur L. Baehr, and Ronald J. Baker
Water Resources Division, U.S. Geological Survey, West Trenton, New Jersey

Abstract. Aerobic biodegradation and volatilization coupled pathway that contributes significantly to the attenuation of hydrocarbons at gasoline spill sites. Rates of hydrocarbon biodegradation and volatilization were quantified by analyzing vapor transport in the unsaturated zone near the water table. Aerobic biodegradation rates for benzene, toluene, ethylbenzene, and xylene, ranging from 0.20 to 1.5 g m⁻³ d⁻¹ for benzene, 0.09 to 0.24 g m⁻³ d⁻¹ for ethylbenzene, and from 0.02 to 0.08 g m⁻³ d⁻¹ for xylene, were estimated. Volatilization rates were estimated to be 0.07 to 0.31 d⁻¹ for benzene and 0.07 to 0.31 d⁻¹ for ethylbenzene. The coupled aerobic biodegradation and volatilization rates were determined by extrapolating gas transport rates from groundwater were highest for toluene.

WATER RESOURCES RESEARCH, VOL. 32, NO. 7, PAGES 2231-2249, JULY 1996

Estimation of rates of aerobic hydrocarbon biodegradation by simulation of gas transport in the unsaturated zone

Matthew A. Lahvis and Arthur L. Baehr
U.S. Geological Survey, West Trenton, New Jersey

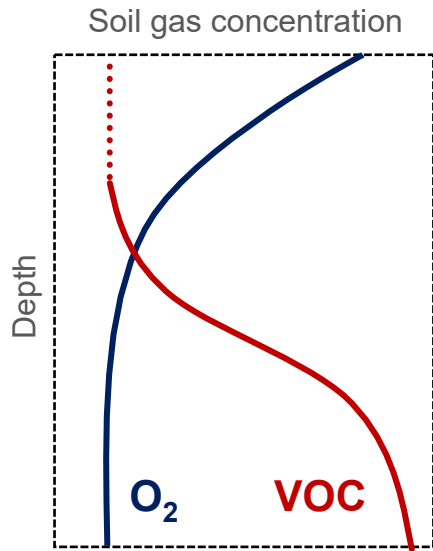
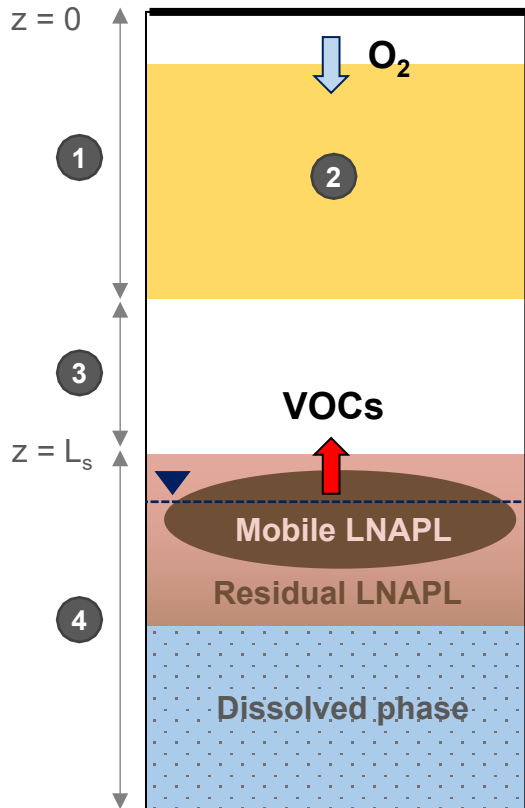
Abstract. The distribution of oxygen and carbon dioxide gases in the unsaturated zone provides a geochemical signature of aerobic hydrocarbon degradation at petroleum product spill sites. The fluxes of these gases are proportional to the rate of aerobic biodegradation and are quantified by calibrating a mathematical transport model to the oxygen and carbon dioxide gas concentration data. Reaction stoichiometry is assumed to convert the gas fluxes to a corresponding rate of hydrocarbon degradation. The method is applied at a gasoline spill site in Galloway Township, New Jersey, to determine the rate of aerobic degradation of hydrocarbons associated with passive and bioventing remediation field experiments. At the site, microbial degradation of hydrocarbons near the water table limits the migration of hydrocarbon solutes in groundwater and prevents hydrocarbon volatilization into the unsaturated zone. In the passive remediation experiment a site-wide model calibration to carbon dioxide gas concentration data collected in December 1989, yielded a biodegradation rate estimate of 34,400 g yr⁻¹ (11.7 gal. yr⁻¹) of hydrocarbon was obtained by (1.45 × 10⁻³ and 1.51 × 10⁻³ gal. ft. yr⁻¹) of hydrocarbon were obtained by model calibration to oxygen and carbon dioxide gas concentration data, respectively. Method application was successful in quantifying the significance of a naturally occurring process that can effectively contribute to plume stabilization.

Introduction

Petroleum product spills from underground storage tanks and pipelines are a common cause of groundwater contamination throughout the industrialized world. Typically, significant volumes of the contaminant remain immobilized by capillary forces after the primary response of physical product removal by excavation or collection has ceased. Aerobic biodegradation has been achieved. This phenomenon also is evident at a gasoline spill site in Galloway Township, New Jersey, where microbial degradation limits the lateral spreading of dissolved hydrocarbons and prevents vertical diffusion of hydrocarbons into the overlying unsaturated zone [Baehr and Fischer, 1996]. The environmental regulatory community has recently acknowledged the limitations of engineered remediation solu-

Simplified Soil Gas Gradient method for COC-specific NSZD rates

VOC and O₂ soil gas profiles



- 1 Aerobic zone ($O_2 > 2\%$)
- 2 Oxidation zone
- 3 Anaerobic zone ($O_2 < 2\%$)
- 4 Source zone

Diffusion and 1st order biodegradation (not limited by O_2)

$$C(z) = C_{source} \cdot \exp\left(-\frac{L_s - z}{LR}\right)$$

hydrocarbon soil gas concentration profile

At the source zone depth ($z = L_s$) the flux is equal to:

$$J(z = L_s) = -D^{eff} \cdot \frac{dC}{dz} = D^{eff} \cdot \left(\frac{C_{source}}{LR}\right)$$

The COC-specific NSZD rate due to volatilization is:

$$NSZD = D^{eff} \cdot \left(\frac{C_{max}}{LR}\right)$$

C_{max} = maximum soil gas concentration
 D^{eff} = effective diffusion coefficient
 LR = diffusive reaction length

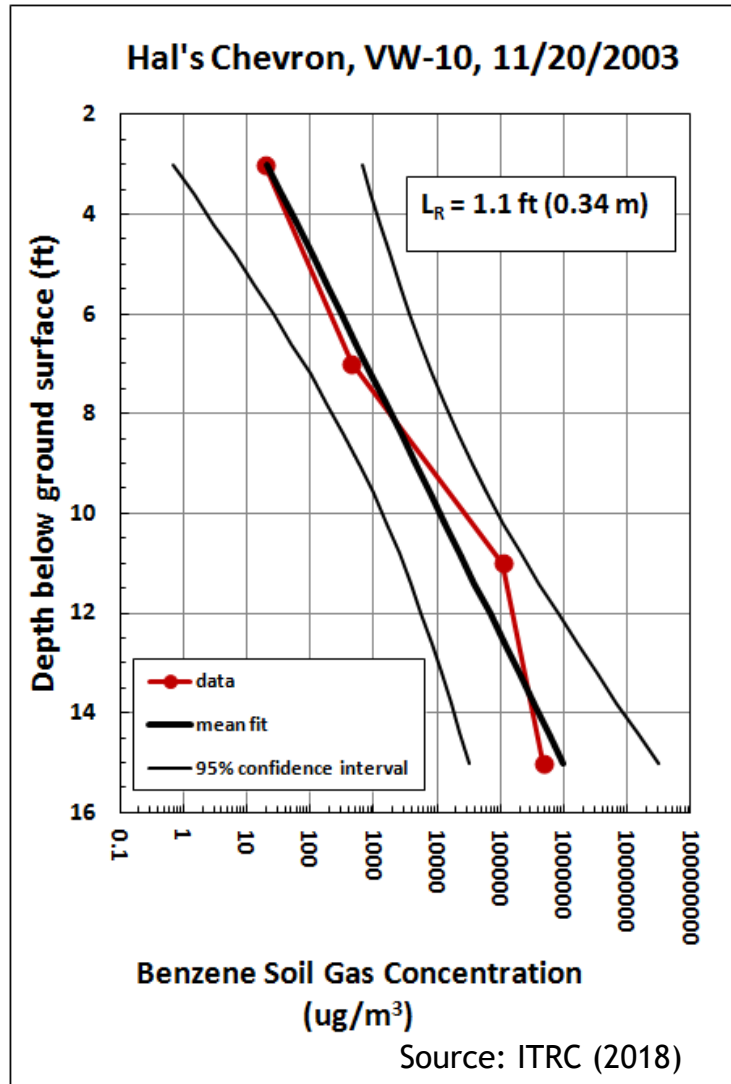
The diffusive reaction length can be empirically estimated from the change in VOC concentration over a specified depth:

$$LR = \frac{\Delta z}{\ln[C(z + \Delta z)] - \ln[C(z)]}$$

Approximate 1-D model

COC-specific NSZD rates

Estimation of the reaction length from measured soil gas profiles



As shown in the ITRC (2018) PVI guidance the diffusion-reaction length (LR) can be directly estimated from measured soil gas profiles.

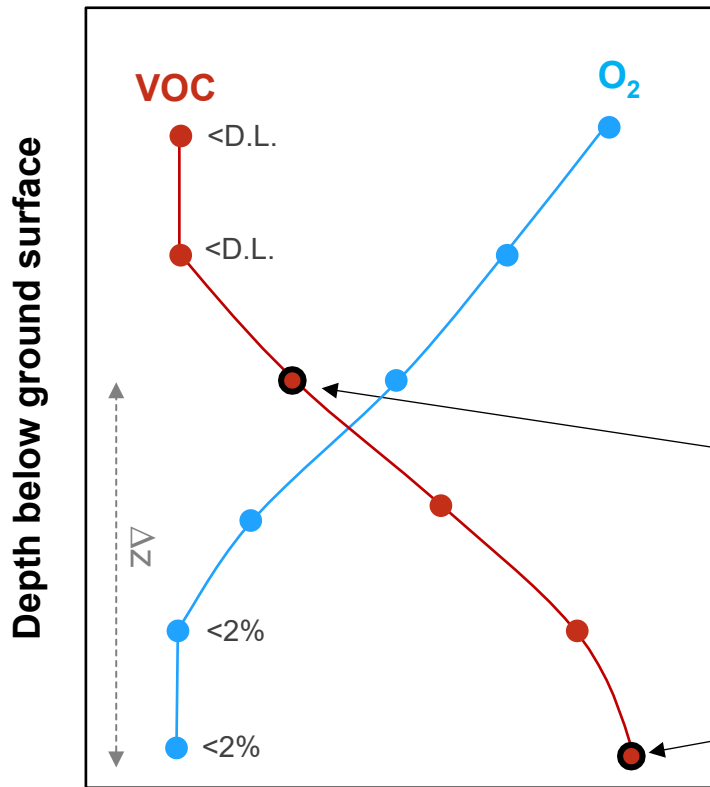
$$LR = \frac{\Delta z}{\ln [C(z + \Delta z)] - \ln [C(z)]}$$

where $C(z)$ and $C(z+\Delta z)$ are the soil gas concentrations measured at depths z and $z + \Delta z$ and Δz is the vertical distance between the sample points.

Note that the concentration data in the figure decrease over four orders of magnitude in 12 feet

Control points for the application of the simplified approach

VOC and O₂ soil gas profiles



VOC and O₂ soil gas concentrations

The diffusive reaction length (LR) can be empirically estimated from the change in VOC concentration over a specified depth:

$$LR = \frac{\Delta z}{\ln(C_2) - \ln(C_1)}$$

C₁: concentration of VOC in upper control point

C₂: concentration of VOC in lower control point

Δz: vertical distance between the two control points

C₁: Lower concentration in the aerobic zone above the detection limit (D.L.)

C₂: Maximum concentration at the greatest depth

Notes: for an accurate estimate, the lower control point should be selected at the bottom of the reaction zone in the aerobic zone. As typically the discrete sampling does not allow to have information of the concentration in this location, we propose to use the maximum concentration at the greatest depth. This leads to a conservative estimate of the NSZD rates: the higher the Δz, the higher the LR and thus the lower the estimated NSZD = $D^{\text{eff}} \times C_{\text{max}} / LR$

Simplified approach vs. Numerical model (Lahvis et al., 1999)

| Constituent | C _{max} (g/m ³) ^a | Reaction length, LR (m) ^b | D ^{eff} (m ² /day) ^c | NSZD rate (g/m ² /day) | |
|--------------|---|--------------------------------------|---|-----------------------------------|----------------------|
| | | | | Simplified approach ^d | Lahvis et al. (1999) |
| Benzene | 0.145 | 0.15 | 1.35E-02 | 0.013 | 0.0139-0.0433 |
| Toluene | 5.41 | 0.19 | 1.33E-02 | 0.379 | 0.361-0.839 |
| Ethylbenzene | 0.592 | 0.11 | 1.14E-02 | 0.059 | 0.0457-0.117 |
| Xylenes | 3.12 | 0.10 | 1.33E-02 | 0.415 | 0.280-0.691 |

^a Gaseous phase concentrations detected @ 12 cm distance from water table (ref. Table 1 of Lahvis et al. 1999)

^b Calculated as $LR = \Delta z / [\ln[C(z+ \Delta z)] - \ln[C(z)]]$ using the gaseous phase concentrations detected @ 12 cm and 73 cm distance from water table (ref. Table 1 of Lahvis et al. 1999)

^c Calculated with the Millington & Quirk (1961) equation assuming an average porosity of 0.36 and air-filled porosity of 0.17 (geometric mean of the values between 12 and 104 cm above water table. Ref. Table 2 of Lahvis et al. 1999)

^d Calculated as $NSZD = D^{eff} \times C_{max} / LR$

The NSZD rates by the simplified approach consistent with NSZD by numerical modeling.

Source: Lahvis, M. A., Baehr, A. L., Baker, R. J. (1999). Quantification of aerobic biodegradation and volatilization rates of gasoline hydrocarbons near the water table under natural attenuation conditions. *Water Resources Research*, 35(3), 753-765.

Empirical Soil-Gas database

Extrapolation* from 2 soil-gas databases (<https://www.epa.gov/ust/petroleum-vapor-intrusion-database>):

- U.S.EPA PVI Database: Robin Davis, (Utah DEQ); Ian Hers (Golder Assoc. Ltd.)
- Australian PVI Database Jackie Wright (Australia – Environ. Risk Sci. Pty Ltd)

Criteria:

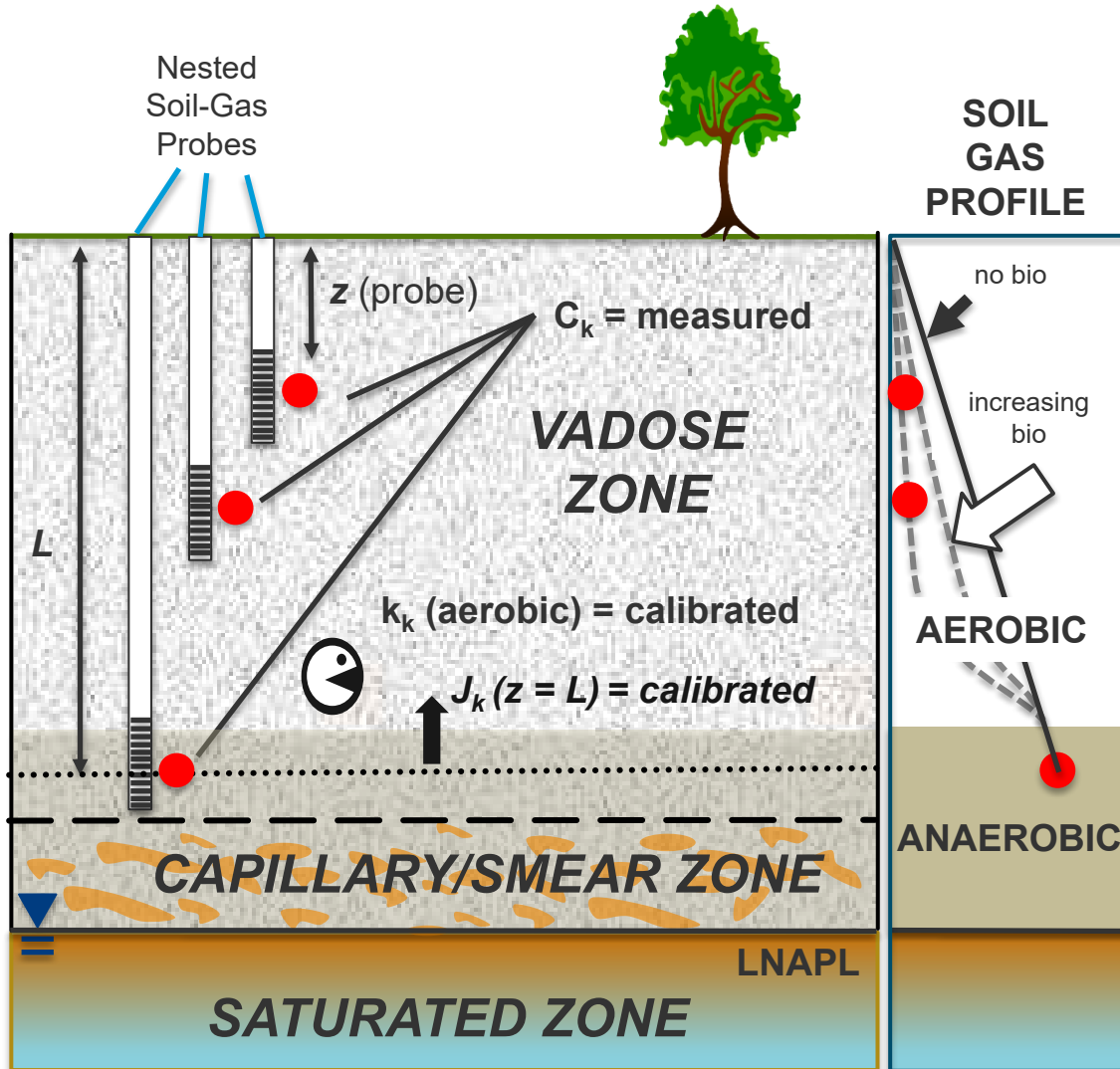
- minimum 2 soil-gas measurements from same location (soil-gas profile)
- primarily gasoline releases from UST sites
- 7 petroleum industrial sites (e.g., terminals, refineries)
- soil type (no fractured rock)
- TPH** and benzene soil-gas data

**TPH concentrations inferred if not available (8 sites, 11 probe locations): BioVapor Users Manual

- **Measurements: 82 samples; 35 sites; 55 probe locations**
- **Soils: 28% sands; 51% loams/silts; 21% clays**
- **Surface cover: 56% pavement; 29% open ground; 15% buildings**

*Source: Lahvis (2018). NSZD Rate Estimates From Soil-Gas Data. Battelle Chlorinated Conference.

Soil-Gas Methods applied



The NSZD rates from the PVI database were estimated using two methods:

- **BioVapor tool*** (www.api.org)
- **Simplified approach** (this work)

Assumptions

Effective diffusion coefficient (estimated – site soil type)

- vadose zone - homogeneous/isotropic
- default moisture & total porosity values (USEPA, 2004)
- gas-phase tortuosity (Millington-Quirk, 1961)

ND soil-gas concentrations = DL

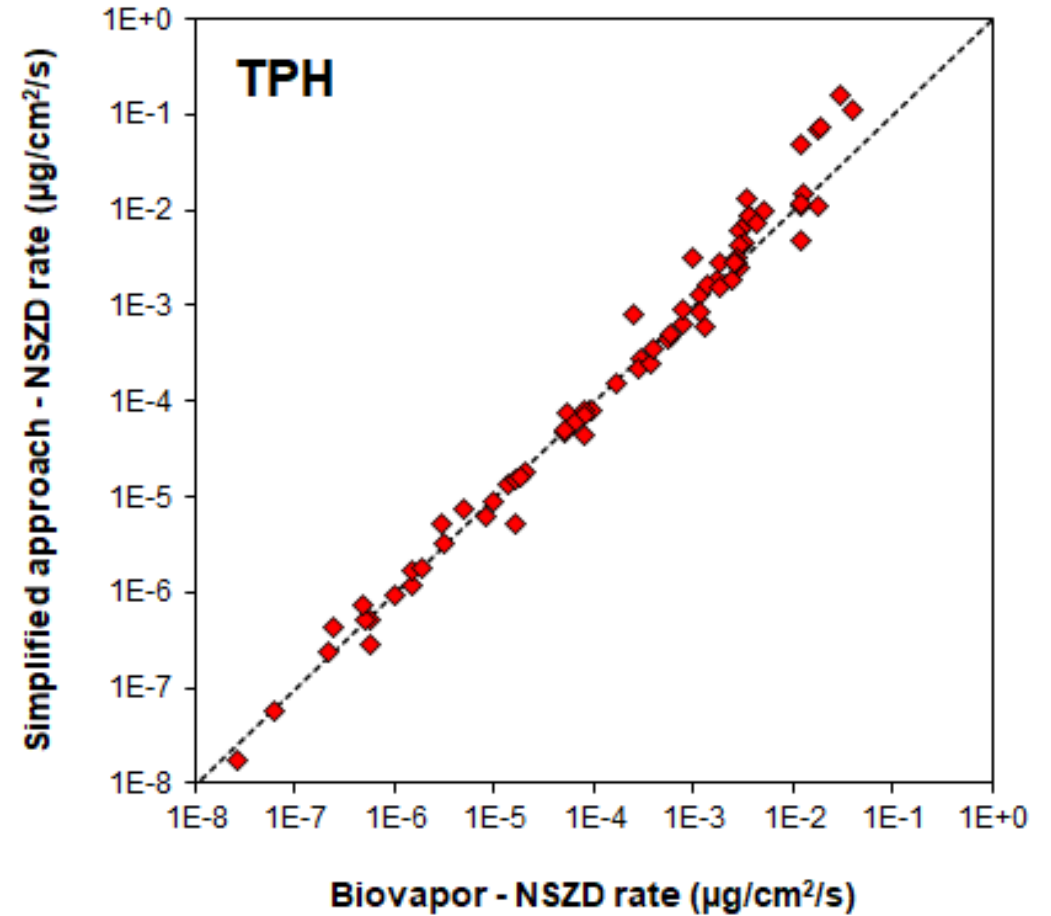
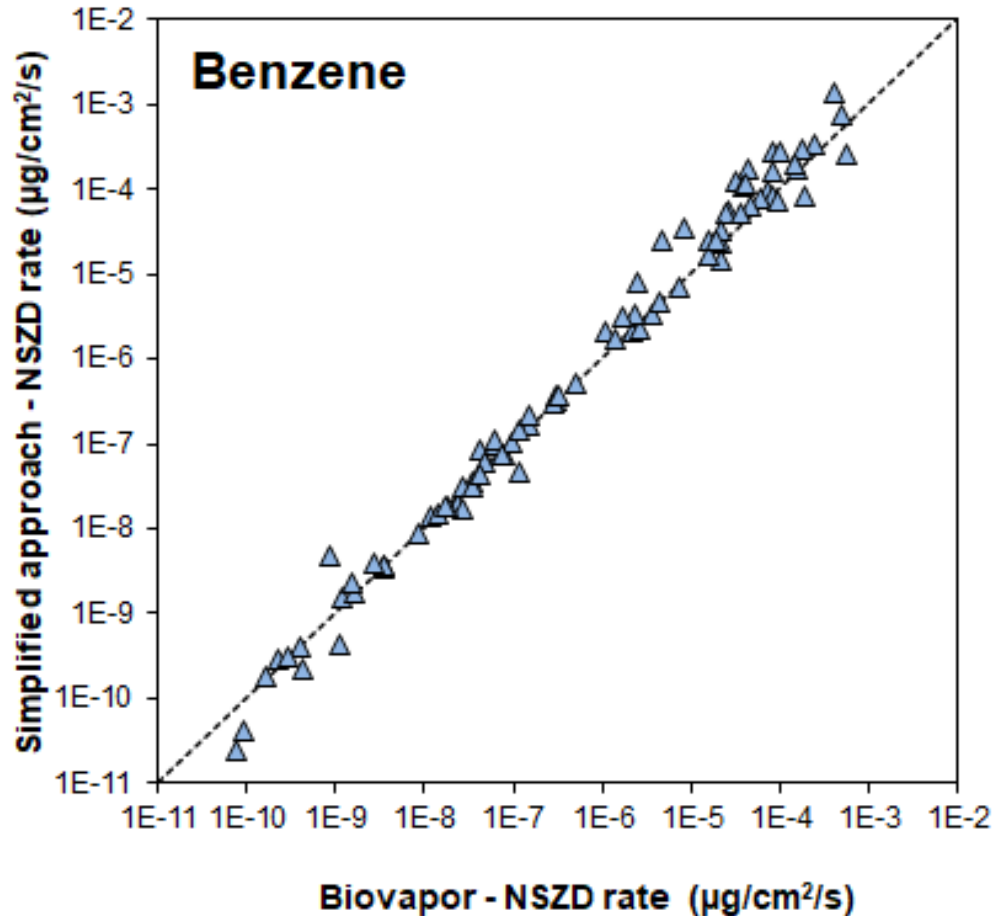
Simplified approach: reactive diffusive length was estimated using as control points the concentrations at the greatest depth and the lower concentrations above the detection limit.

Biovapor: 1st-order aerobic degradation rate constant (k_k) and

- source-vapor flux (J_k^L) (calibrated):
- no biodegradation anaerobic zone
- soil $f_{oc} = 0.002$ (default – EPA, 1996)

*Source: Lahvis (2018). NSZD Rate Estimates From Soil-Gas Data. Battelle Chlorinated Conference.

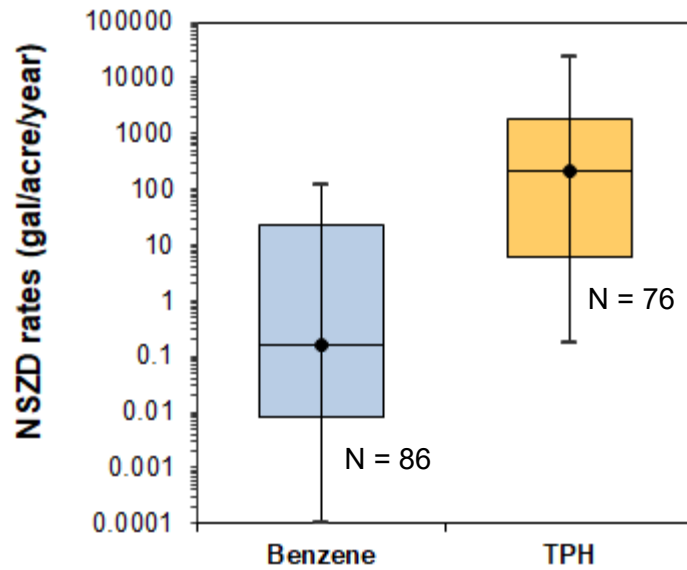
NSZD rates obtained by the two methods



NSZD rates obtained by the simplified approach consistent with BioVapor results

NSZD rates obtained by the two methods

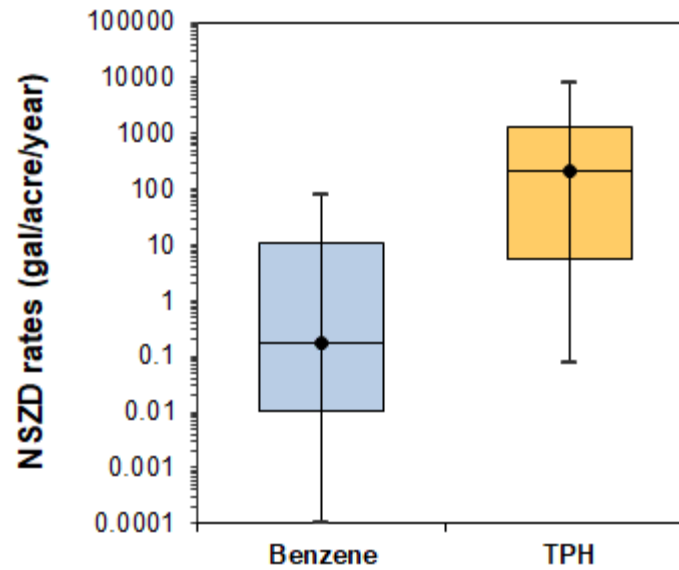
Simplified approach (this work)



Median rates:

- B: 0.2 gal/acre/yr
- TPH: 212 gal/acre/yr

BioVapor



Median rates:

- B: 0.2 gal/acre/yr
- TPH: 207 gal/acre/yr

Note that BioVapor Model equations, 'far' from the foundation and within the homogeneous aerobic soil layer simplifies to:

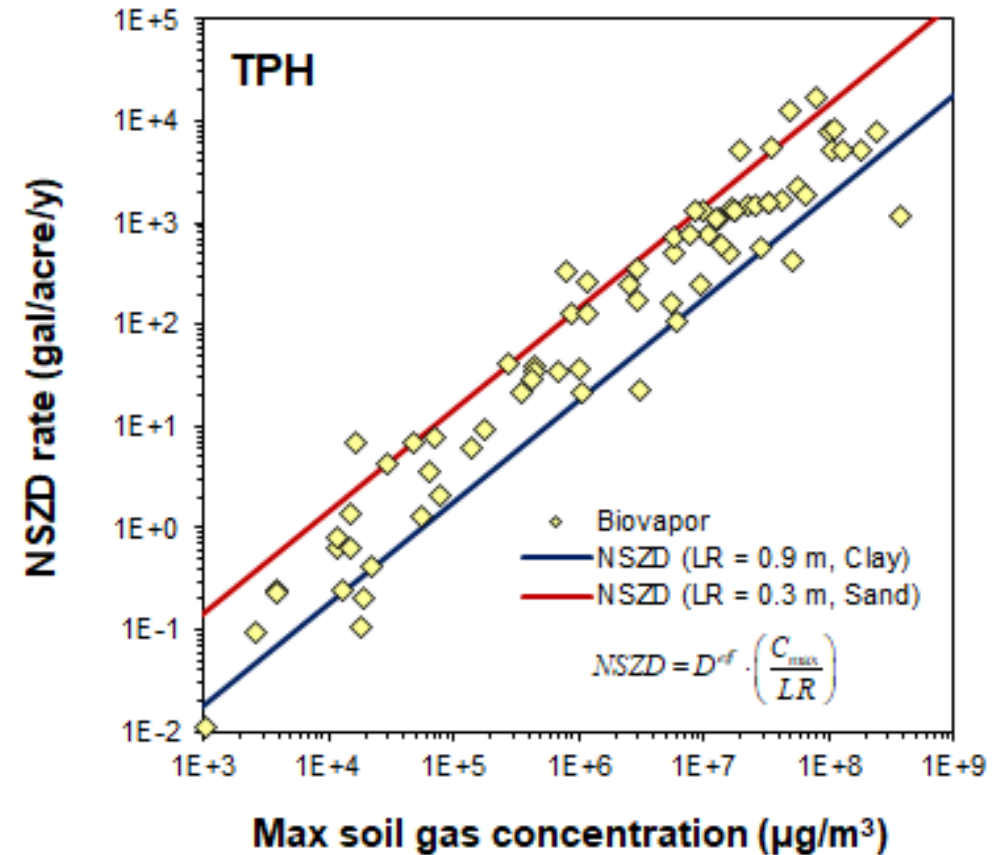
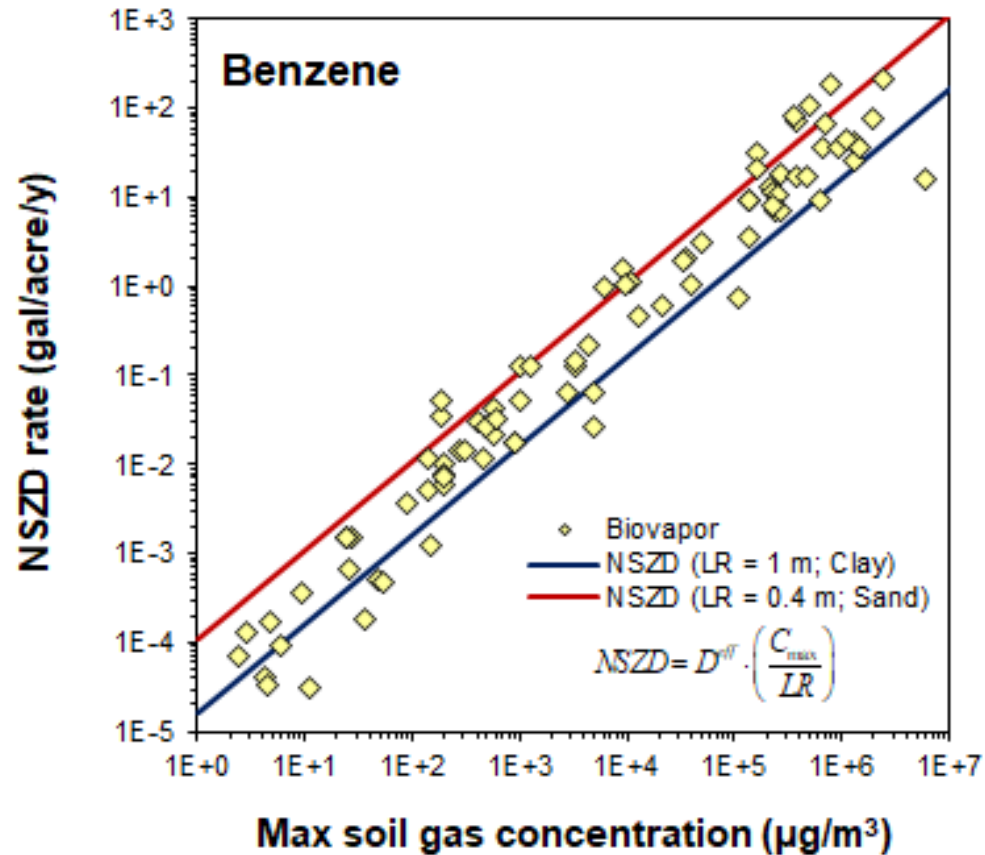
$$\frac{C(z_E)}{C(z_E = 0)} = \exp\left(-\frac{z_E}{LR}\right)$$

with $LR = \sqrt{\frac{D^{eff} \cdot H}{\theta_w \cdot k_w}}$

z_E = elevation from the source

- Range of TPH NSZD rates consistent with literature (e.g. Garg et al. 2017: 300 - 7,700 gal/acre-yr)
- Benzene NSZD rates are 2-3 OoM < TPH NSZD rates: consistent with typical mass fraction

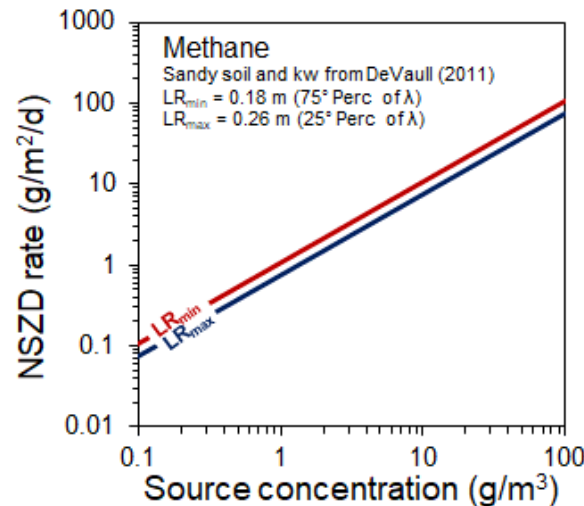
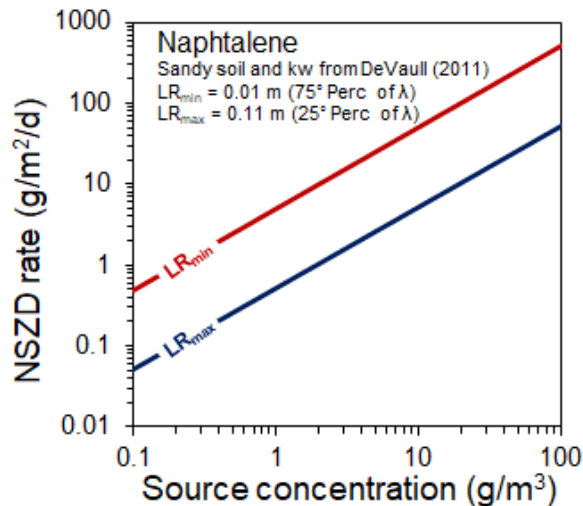
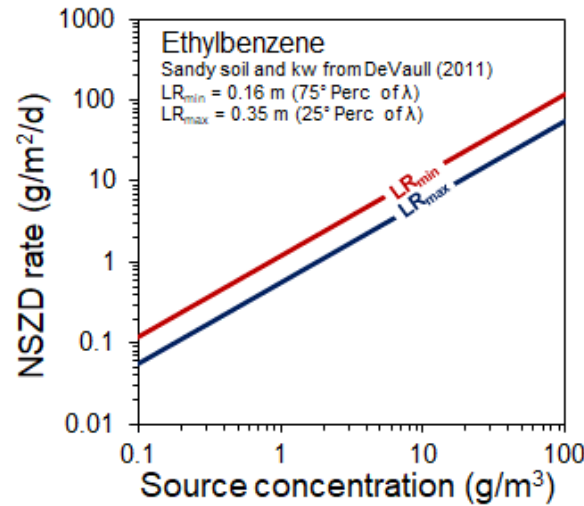
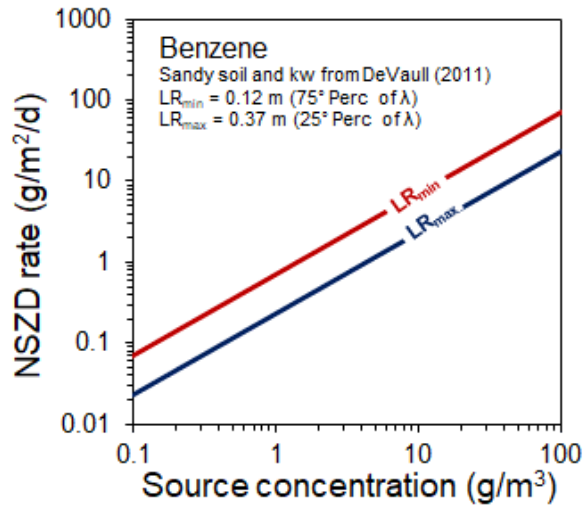
Rates as a function of the maximum soil gas concentration



The LR values indicated in the figures represent the 25° and 75° Percentile calculated from PVI database for Benzene and TPH

Source vapor concentration measurements may be sufficient for a screening of NSZD rates

Screening of NSZD rates in the headspace of monitoring wells



For a screening of the COCs-specific NSZD rates it can be used the soil gas concentrations measured in monitoring wells that had a portion of their screen in the vadose zone with literature values for the reaction length

$$NSZD = D^{eff} \cdot \left(\frac{C_{vap}}{LR} \right)$$

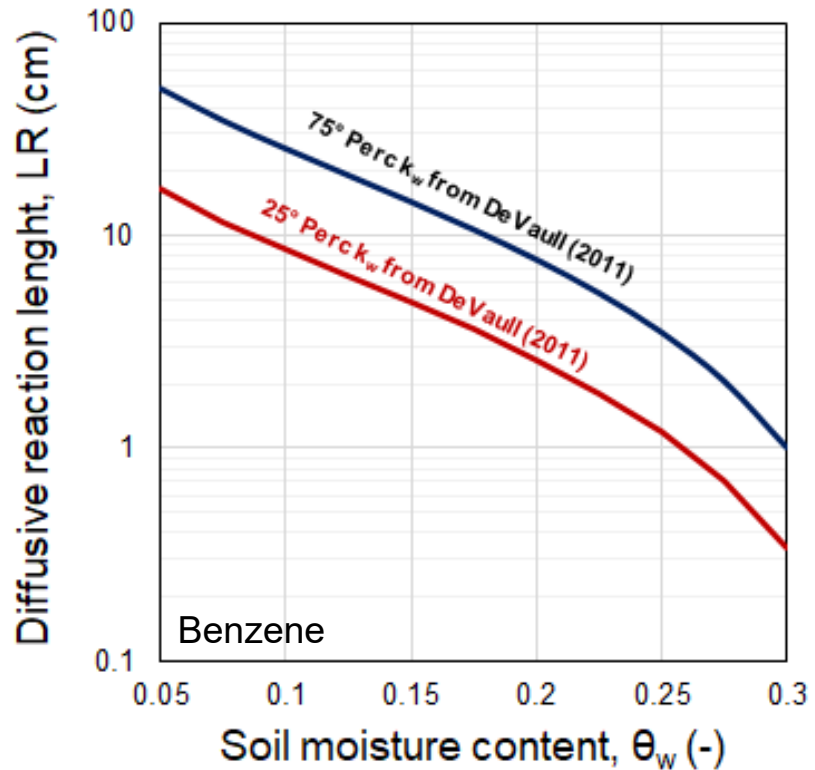
C_{vap} = concentration in the well
D^{eff} = effective diffusion coefficient
LR = diffusive reaction length

Reaction length estimated on the basis of literature values of biodegradation constant(kw) and soil type

$$LR = \sqrt{\frac{D^{eff} \cdot H}{\theta_w \cdot k_w}}$$

θ_w = soil moisture content
k_w = first-order biodegradation constant
H = dimensionless Henry's constant

Sensitivity analysis of the diffusive reaction length (LR)



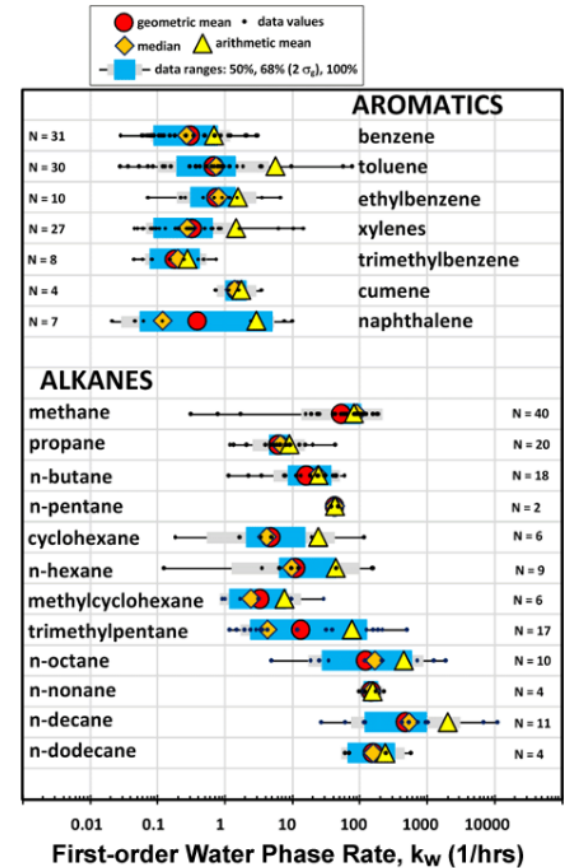
Diffusive reaction length

$$LR = \sqrt{\frac{D^{eff} \cdot H}{\theta_w \cdot k_w}}$$

θ_w = soil moisture content (variable: 0.05-0.3)
 k_w = first-order biodegradation constant (Devaull, 2011)
 H = dimensionless Henry's constant (0.228, Benzene)
 D^{eff} = effective diffusion coefficient:

$$D^{eff} = D_{air} \cdot \frac{\theta_a^{10/3}}{\theta_e^2}$$

D_{air} = diffusion coefficient in air (0.0318 m²/h, Benzene)
 θ_a = air-filled porosity (variable: 0.05-0.3)
 θ_e = soil porosity (variable: 0.35)



Depending on the moisture content of the soil and on the first-order water phase rate (k_w), the diffusive reaction length (LR) can vary over one order of magnitude

Source: DeVaul (2011) from ITRC PVI (2018) guidance

Practical Considerations

Soil gas concentrations in samples collected from soil gas probes or headspace of monitoring wells (field or laboratory measurements):

Evidence of Source Zone Biodegradation

- Lower oxygen concentrations relative to atmospheric
- Elevated carbon dioxide and methane concentrations

Potential for advective soil gas transport

- Laboratory measurement of N₂ and Ar that are depleted or enriched relative to atmospheric (related to methane generation and pressure-driven flow)

(ASTM E2993; Amos et al. 2005; and Molins et al. 2010)

- Barometric pumping effect significant at sites with deep vadose zone and highly gas permeable soils (Forde et al. 2019)

- Indicators and layers of NAPL contamination in soil (additional sources) – soil gas profiles can still be collected above the NAPL contaminated soil for the simplified approach.
- Evidence of heat signature of biodegradation
- Soil gas permeability factors:
 - High moisture content
 - Ground surface cover
 - High clay content
 - Submerged NAPL source
- Estimated diffusion coefficient: heterogeneity; moisture content
- Vertical placement of soil gas probes?
- Depth to NAPL source does not limit applicability of the approach

Conclusions

- Soil-gas gradient method is simple to apply and can provide estimates of both bulk and constituent specific NSZD rates
- The simplified approach presented in this work can be used for a simple and fast screening of **COC-specific NSZD rates**
- NSZD rates (TPH) estimated from PVI USEPA and Australian database are consistent with literature values
- Source vapor concentration measurements may be sufficient for a screening of NSZD rates
- The simplified approach also provides a practical tool to evaluate the **temporal variability** in the natural attenuation rates, since they have been shown to vary both seasonally and over years and decades