# Use of MIN3P-Dusty Numerical Model to Simulate Rates of LNAPL Depletion for Natural and Bioventing Conditions

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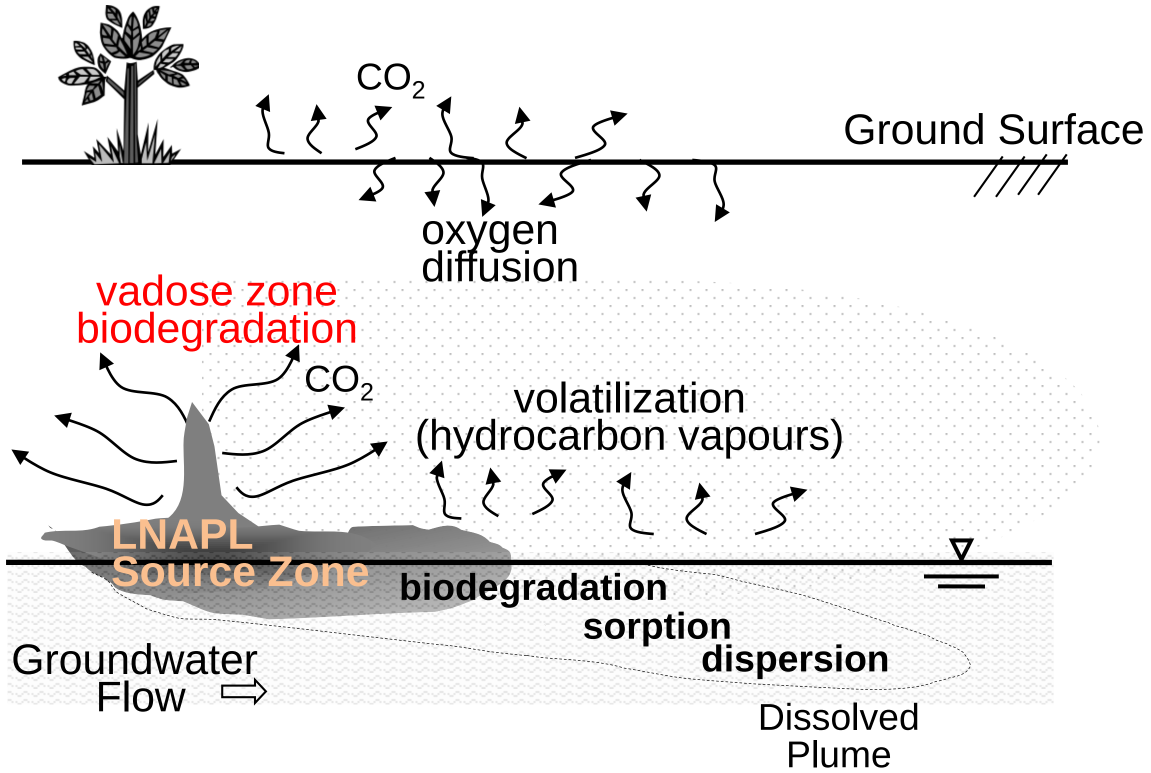
# Background & Objectives

- Natural source zone depletion (NSZD) is a significant process for LNAPL mass depletion and compositional change at many petroleum hydrocarbon impacted sites.

Key questions:

- How much does oxygen delivery from bioventing accelerate LNAPL mass depletion and compositional change during early stages of the remediation process?
- How can bioventing system design be optimized?
  (longer-term goal)




Key objective: to develop an improved mechanistic or process-based understanding of LNAPL depletion using the MIN3P-Dusty numerical model under natural and bioventing conditions



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# Reactive Transport Model – MIN3P-Dusty

- Finite-volume, multi-component, reaction & transport
- Variably saturated porous media
- MIN3P[1] developed by Dr. Ulrich Mayer (UBC)
- + multi-species gas diffusion and gas advection

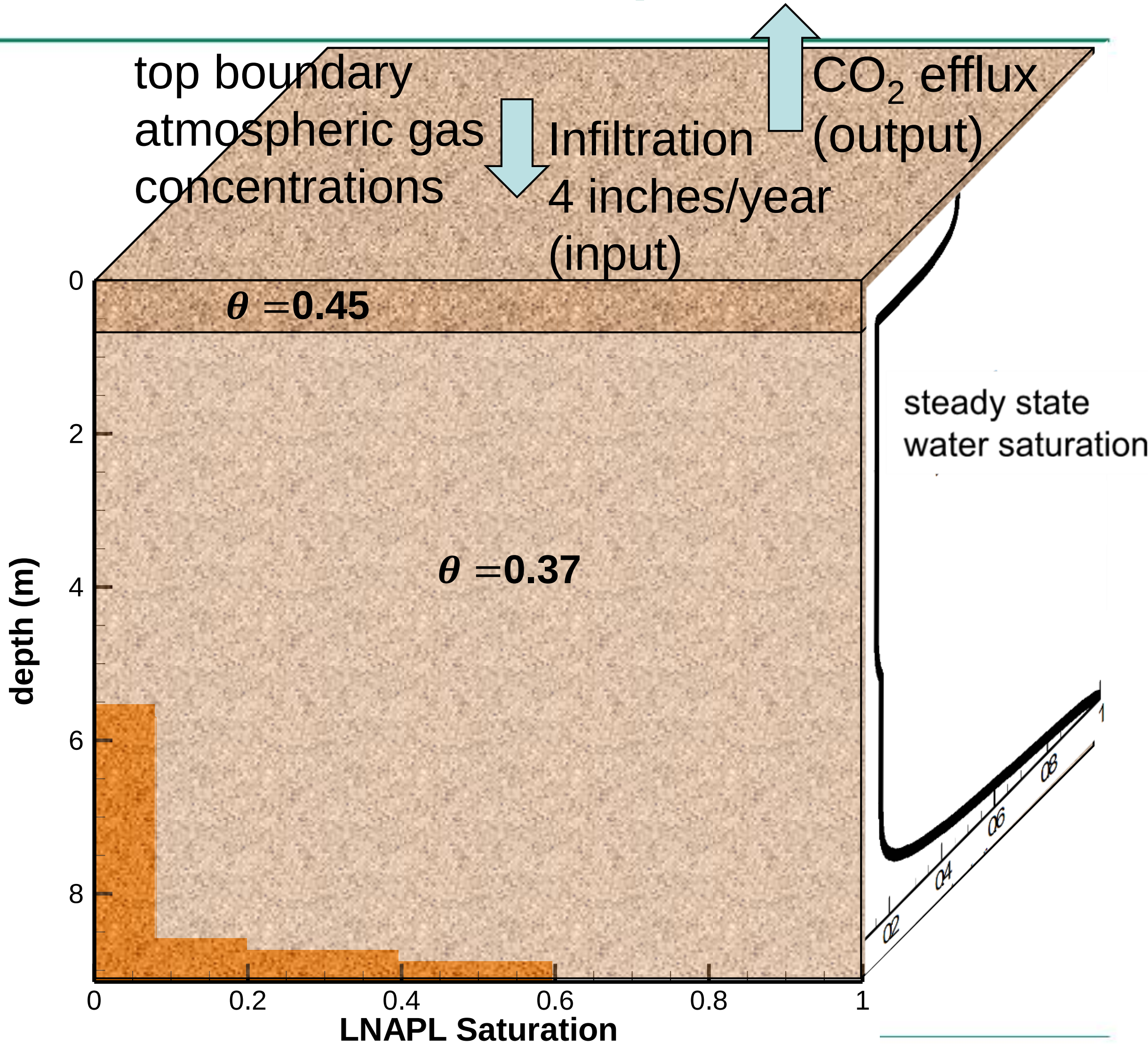
  = MIN3P-Dusty[2] by Dr. Sergi Molins

[1]Mayer, K. U., Frind, E. O. & Blowes, D. W. 2002. Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. Water Resources Research, 38.

[2]Molins, S., and K.U. Mayer. 2007. Coupling between Geochemical Reactions and Multicomponent Gas and Solute Transport in Unsaturated Media: A Reactive Transport Modeling Study. Water Resources Research, 43.

# Process-Based Reactive Transport Model

- Transport
  - Water infiltration from precipitation
  - Soil gas diffusion (dusty gas model)
  - Soil gas advection
- Reactions
  - Biodegradation reactions
  - Acid/base equilibria
  - Sorption
- Variably Saturated Flow
  - Constant infiltration at ground surface
  - Constant head lower boundary



# Conceptual Model Setup

- Porosity
- Permeability
- Hydraulic function parameters
- Fraction organic carbon

Soil Properties (two layers)

LNAPL Constituents

- Benzene
- Heptane
- 2-methylnaphthalene
- Tetradecane
- Pristane

LNAPL Saturation Profile

- Dissolution and volatilization
- Raoult's law

Biodegradation Reactions

- Baseline soil respiration
- Aerobic biodegradation reactions
- Anaerobic/methanogenic biodegradation reactions

# Hydrocarbon Source Composition

| LNAPL Fraction | Component | Molecular Weight (g) | Mole Fraction* |
|---|---|---|---|
| **Aromatics** | benzene ($C_6H_6$) | 78.11 | 0.100 |
| **Light alkanes** | heptane ($C_7H_{16}$) | 100.21 | 0.157 |
| **PAHs** | 2-methylnaphthalene ($C_{11}H_{10}$) | 142.20 | 0.209 |
| **Heavy alkanes** | tetradecane ($C_{14}H_{30}$) | 198.40 | 0.175 |
| **Isoprenoids** | pristane ($C_{19}H_{40}$) | 268.53 | 0.311 |
| | | **Total** | 0.952 |

* Based on the average of relative peak areas of GC/FID data of eight representative LNAPL (weathered) samples

# 1D Simulation – Background $CO_2$ Efflux

- Chemical Components: natural organic carbon, $CO_2$, $O_2$, $N_2$, Ar
- Kinetic reaction: aerobic degradation of organic carbon
- Assuming natural soil respiration limited to the top 2 m
- Background respiration rate, $R$, due to natural organic carbon content of the soil assumed proportional to fraction organic carbon, $F_{oc}$:

$$R = k_{oc} F_{oc}$$

where, $k_{oc}$ is the rate constant ($mol/L_{(aq)}/s$)

- Biodegradation reaction assuming a 1:1 molar ratio for oxygen consumption and $CO_2$ production

| Degradation Rate Constant, $k_{oc}$ (mol/L/s) | Background $CO_2$ Efflux |
|---|---|
| 3.35E-5 | 5 µmol/m²/s |

$k_{oc}$ calibrated to match background $CO_2$ efflux



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# Aerobic Biodegradation Reactions

- Overall aerobic biodegradation reaction for hydrocarbon component with chemical formula $C_aH_b$:

$$C_aH_b + (a + b/4)O_2 + (a - b/2)H_2O \rightarrow aCO_3^{2-} + 2aH^+$$

- Kinetic rate formulation that consists of dual Monod terms with respect to substrate and oxygen:

$$R_{aerobic} = v_{max} \frac{C_{HC}}{C_{HC} + K_{HC}} \frac{C_{O2}}{C_{O2} + K_{O2}}$$

- In addition, pristane degradation is assumed to be inhibited by alkanes through non-competitive inhibition terms:

$$R_{aerobic}(pristane) = v_{max} \frac{C_{HC}}{C_{HC} + K_{HC}} \frac{C_{O2}}{C_{O2} + K_{O2}} \frac{K_{i\_1}}{C_{HC} + K_{i\_1}} \frac{K_{i\_2}}{C_{HC} + K_{i\_2}}$$

- Half-saturation constant of each hydrocarbon component $K_{HC}$ is related to the respective initial effective solubility ($S_e$) divided by a factor ψ

Key objective: relating the half-saturation constant to the effective solubility of a constituent to represent first-order rates in the vadose zone away from the source, and zero-order rates close to the source zone.

# Aerobic Biodegradation Reactions - Parameters

| Component | First-Order Rate Constants (per hour) | Source / Rationale |
|---|---|---|
| **benzene** | 0.3 | ITRC PVI Guidance (2014) |
| **heptane** | 36 | Geometric mean values of hexane and octane from ITRC PVI Guidance (2014) |
| **2-methylnaphthalene** | 0.25 | Two-thirds of the value for naphthalene from ITRC PVI Guidance (2014) based on the relative difference of BioHCwin half-life values |
| **tetradecane** | 12 | One-third of the rate constant for heptane based on the relative difference of BioHCwin half-life values |
| **pristane** | 0.03 | One-tenth of the rate constant for benzene based on the relative difference of BioHCwin half-life values |

- Maximum rates estimated from first-order rate constants and half-saturation constants.
- $O_2$ half-saturation constant 0.25% in gas phase for all hydrocarbon biodegradation reactions.



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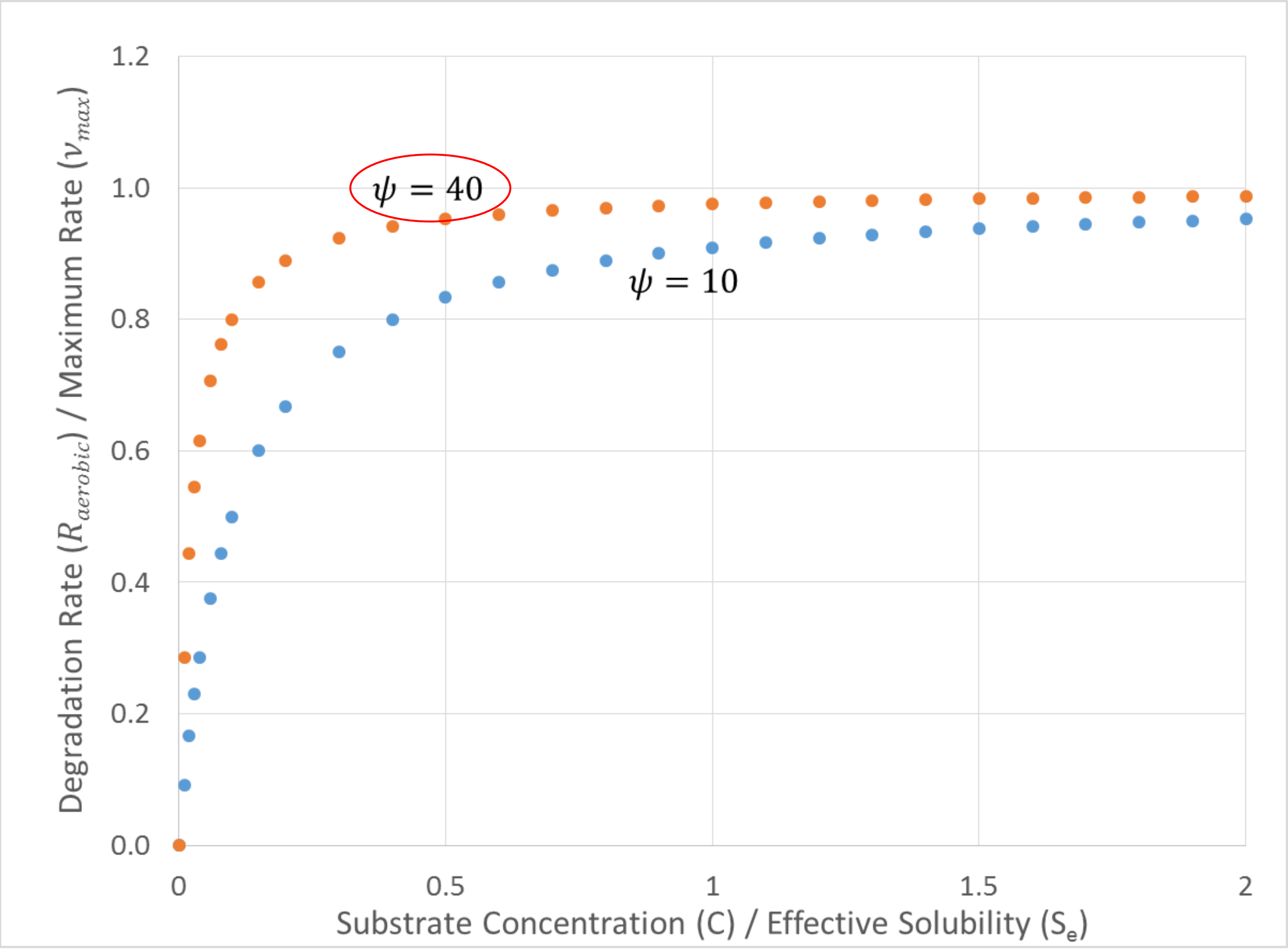
# Effective Solubilities & Half-Saturation Constants – Data from Past Studies

| Reference* / Location | Maximum Porewater Total Hydrocarbon Concentration, $S_e$ (mg/L) | Model Calibrated Parameters | | $\psi = k^1 \frac{S_e}{v_{max}}$ |
|---|---|---|---|---|
| | | $v_{max}$ in Aqueous Phase (mg/L/hour) | $k^1 = \frac{v_{max}}{K_{HC}}$ (1/hour) | |
| Moyer et al. (1996) / 50CL | 4.84 | 2.61E-02 | 4.00E-01 | 74 |
| Ostendorf and Kampbell (1991) / PT4 | 4.62 | 7.55E-03 | 4.47E-02 | 27 |
| Ostendorf and Kampbell (1991) / DG109 | 4.62 | 7.81E-03 | 3.72E-02 | 22 |
| Ostendorf and Kampbell (1991) / DG280 | 8.57 | 9.84E-03 | 4.76E-02 | 41 |
| Ostendorf and Kampbell (1991) / M30 | 8.18 | 4.84E-03 | 3.60E-02 | 61 |

*All studies conducted at a weathered aviation gasoline release site

# Effective Solubilities & Half-Saturation Constants



# Methane Oxidation – Kinetic Rate Formulation

$$CH_4 + 2O_2 \rightarrow CO_3^{2-} + 2H^+ + H_2O$$

Dual Monod Formulation

$$R_m = V_{max} \frac{[CH_4]}{[CH_4] + K_{m\_CH4}} \frac{[O_2]}{[O_2] + K_{m\_O2}}$$

$V_{max}$ = maximum methane oxidation rate (8 x $10^{-8}$ mol ($CH_4$)/$L_{(aq)}$/s)
$K_{m\_CH4}$ = methane half saturation constant (1 x $10^{-5}$ mol/$L_{(aq)}$)
$K_{m\_O2}$ = oxygen half saturation constant (1 x $10^{-5}$ mol/$L_{(aq)}$)

Represent the geometric means of the Monod parameters from five studies (details in Jourabchi et al., Battelle 2013)

# Anaerobic Biodegradation Reactions

- Under methanogenic conditions, where oxygen concentrations are depleted
- Overall degradation pathways:

$$C_aH_b + \frac{3(4a-b)}{8}H_2O \rightarrow \frac{(4a-b)}{8}CO_3^{2-} + \frac{2(4a-b)}{8}H^+ + \frac{(4a+b)}{8})CH_4,$$

- Rate formulation is assumed to follow a Monod expression with respect to the substrate (except for 2-methylnaphthalene) and a non-competitive $O_2$ inhibition term as follows:

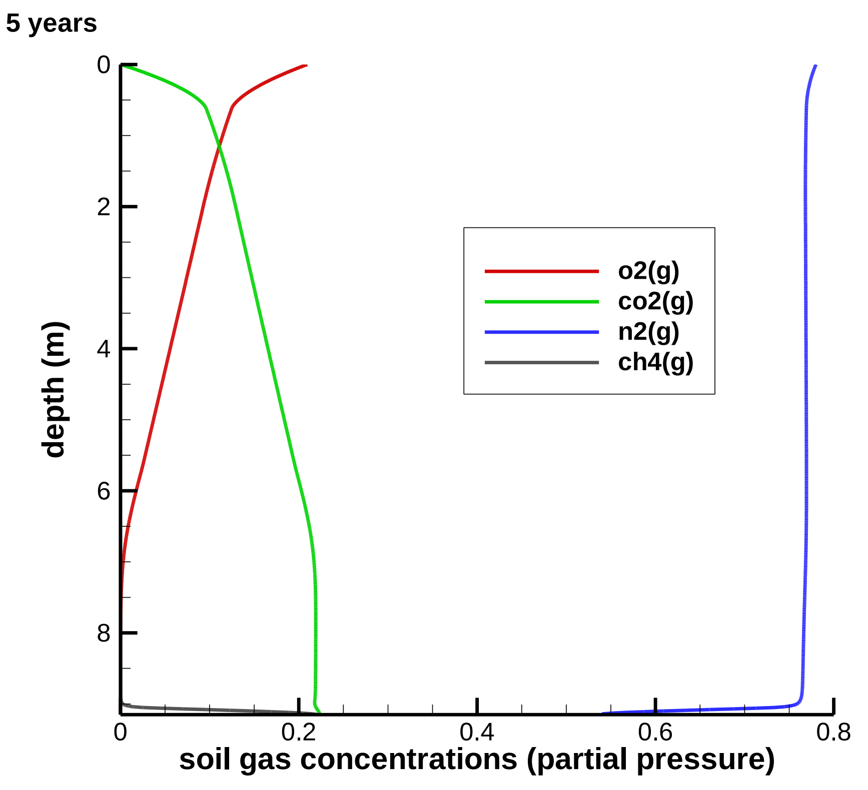
$$R_{anaerobic} = k_{max}\frac{C}{C+K_{an}}\frac{K_{i\_o2}}{[O_2]+K_{i\_o2}}$$

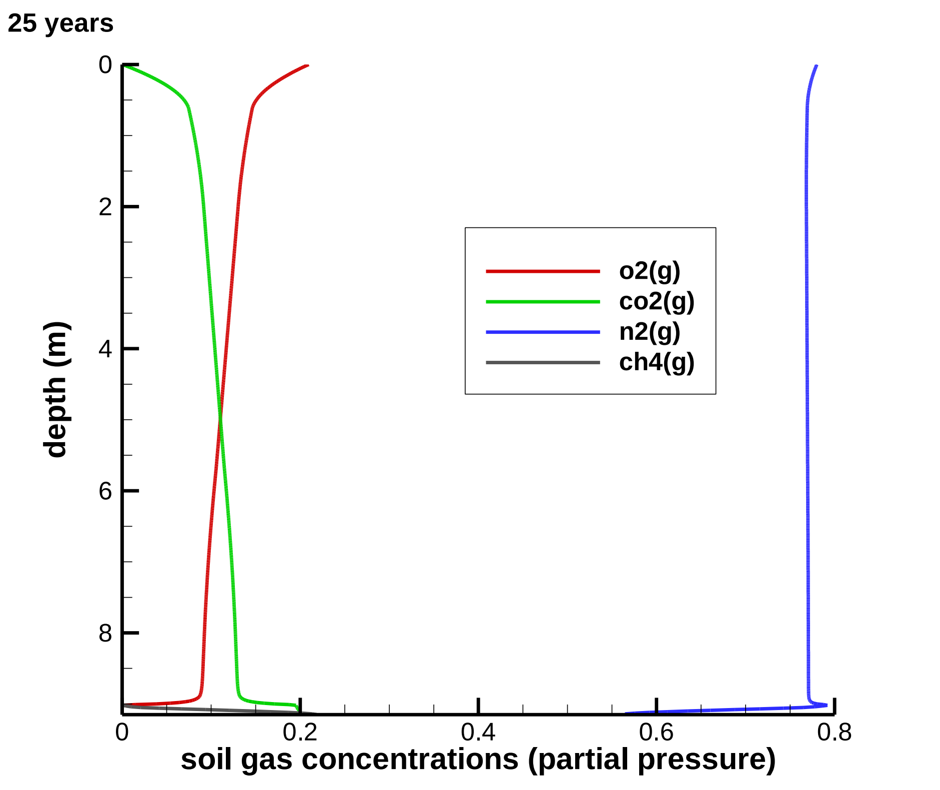
- $O_2$ inhibition constant $K_{i\_o2}$ is assumed to be 31 µmol/L for all components (Mayer et al., 2002) for the anaerobic biodegradation reactions.

# Anaerobic Biodegradation Reactions - Parameters

| Component | Rate Formulation | Half Saturation Constant (mol/L) | Zeroth Order or Maximum Rate (mol/L-s) | First-Order Rate Constant* | Source |
|---|---|---|---|---|---|
| **benzene** | Monod + $O_2$ inhibition | 1.0E-04 | 2.5E-12 | 2.5E-08 | Mayer et al. (2002) for toluene |
| **heptane** | Monod + $O_2$ inhibition | 2.5E-03 | 7.8E-10 | 3.1E-07 | Siddique et al. 2008; C7 alkane as surrogate |
| **2-methyl-naphthalene** | First-order + $O_2$ inhibition | - | - | 2.3E-07 | Chang et al. (2002) |
| **tetradecane** | Monod + $O_2$ inhibition | 1.9E-03 | 6.8E-10 | 3.6E-07 | Siddique et al. 2008; C10 alkane as surrogate |
| **pristane** | No degradion under methanogenic conditions | - | - | - | Townsend et al. 2003 |

# Predicted Soil Gas Concentration Profiles



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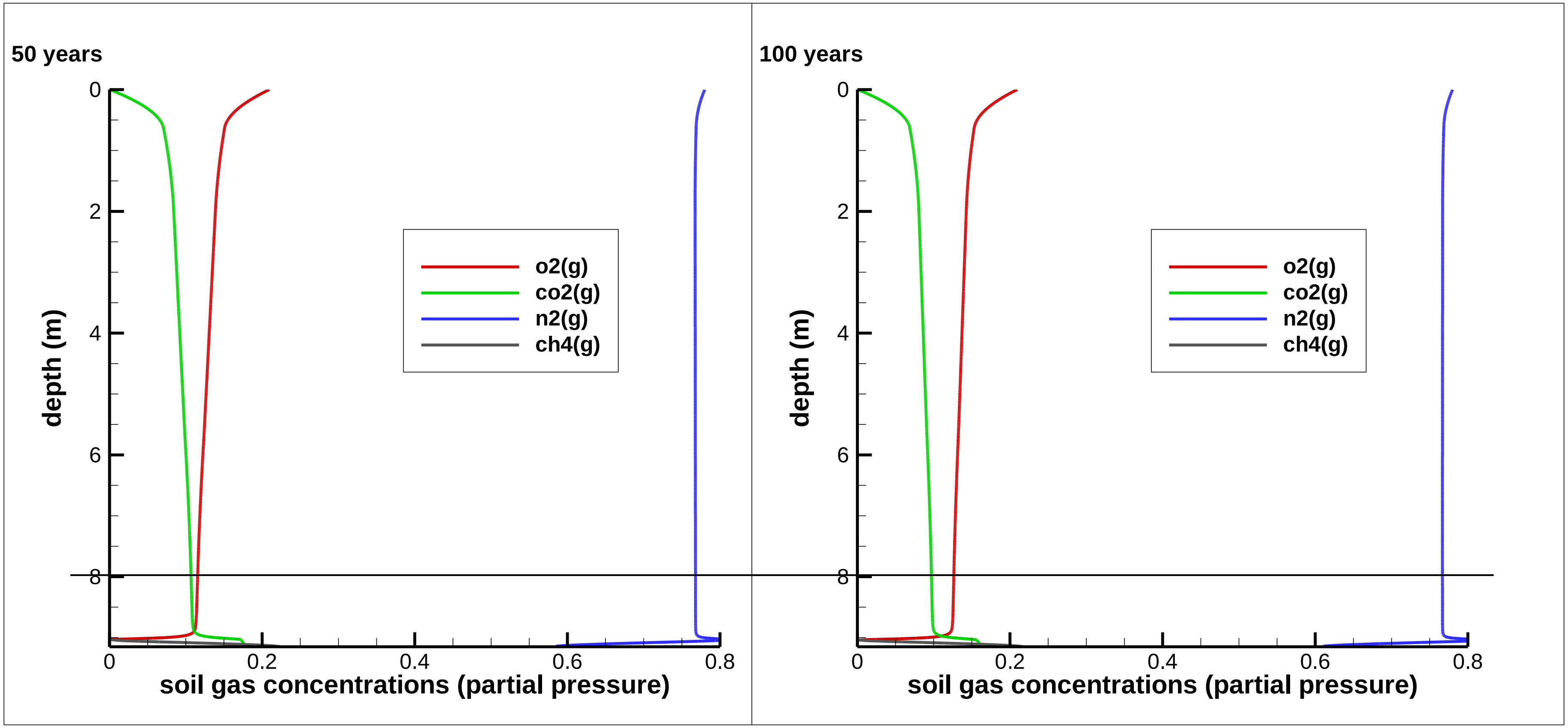
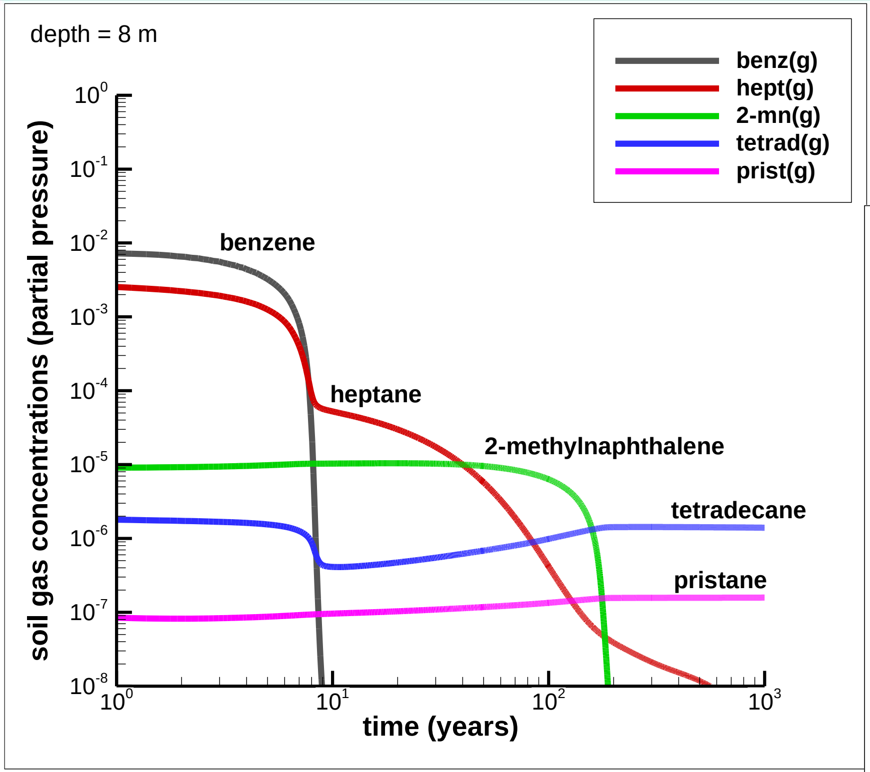
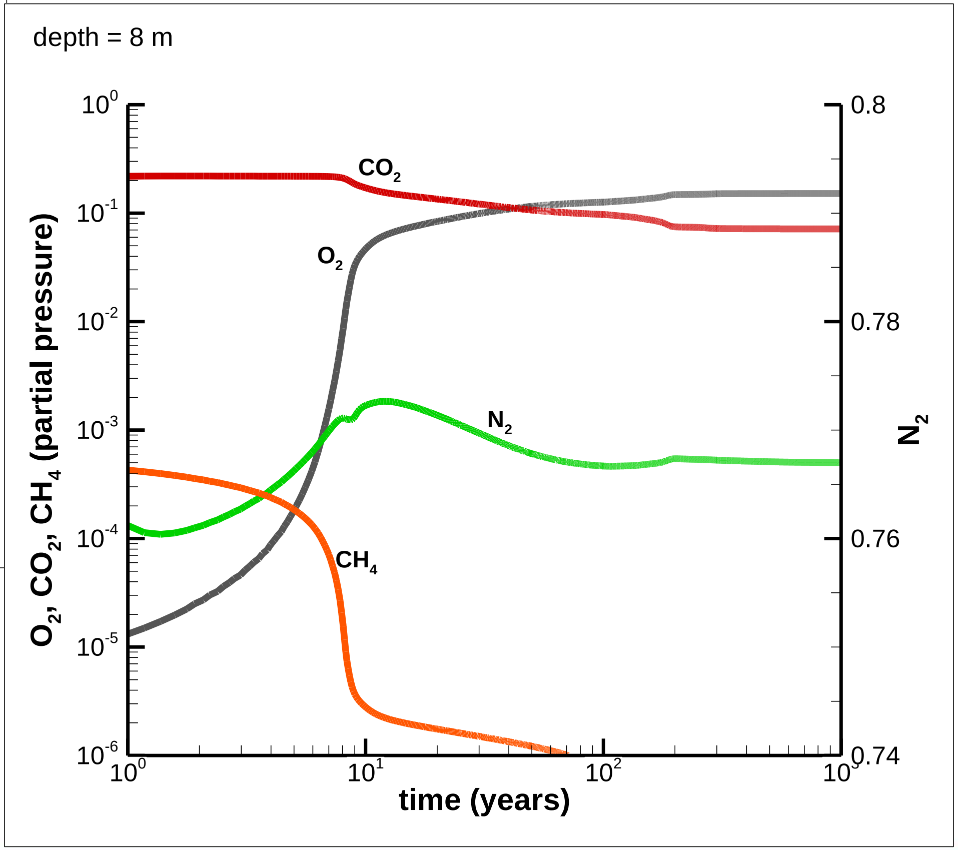
# Predicted Soil Gas Concentration Profiles



# Soil Gas Concentrations – Transient Results



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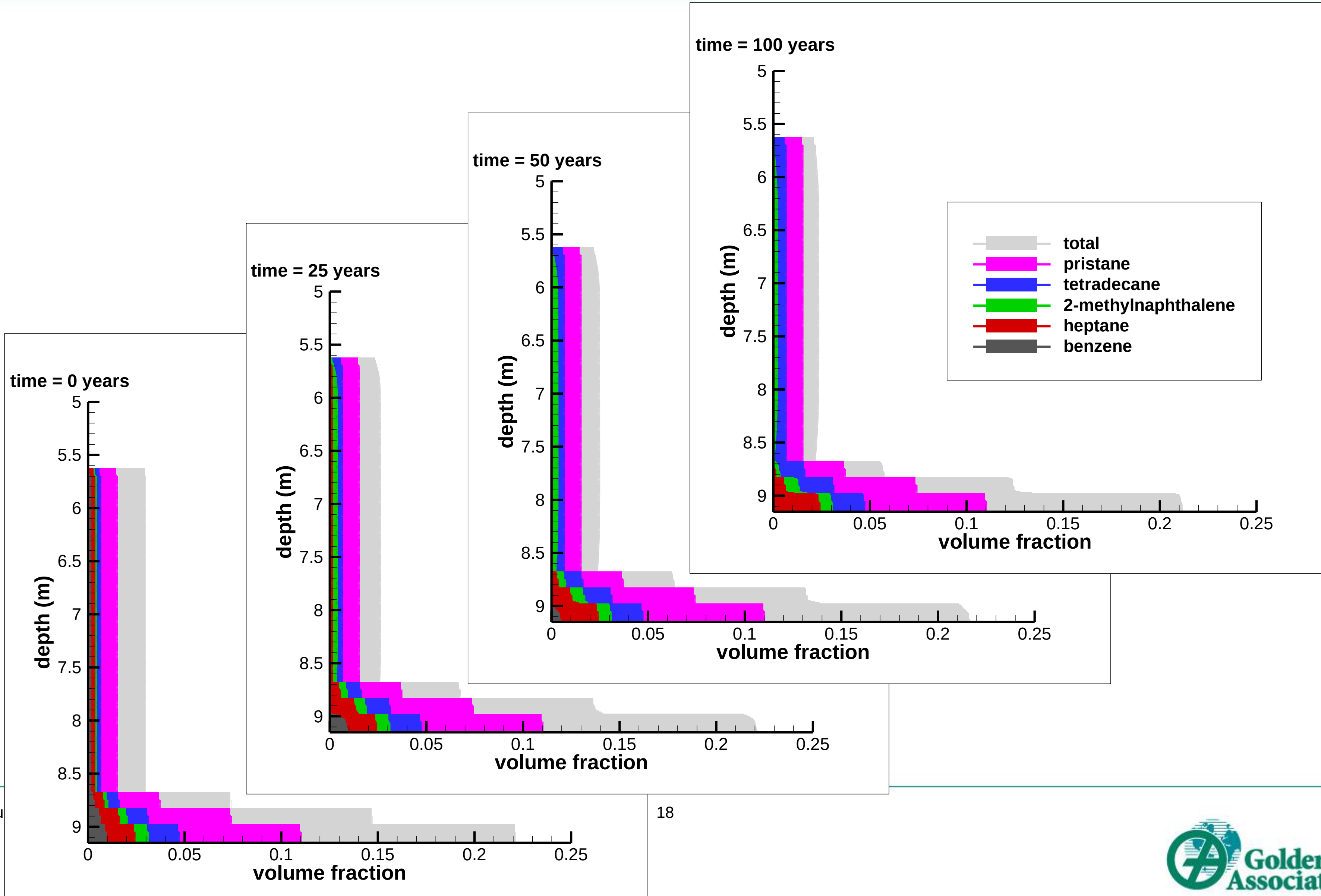
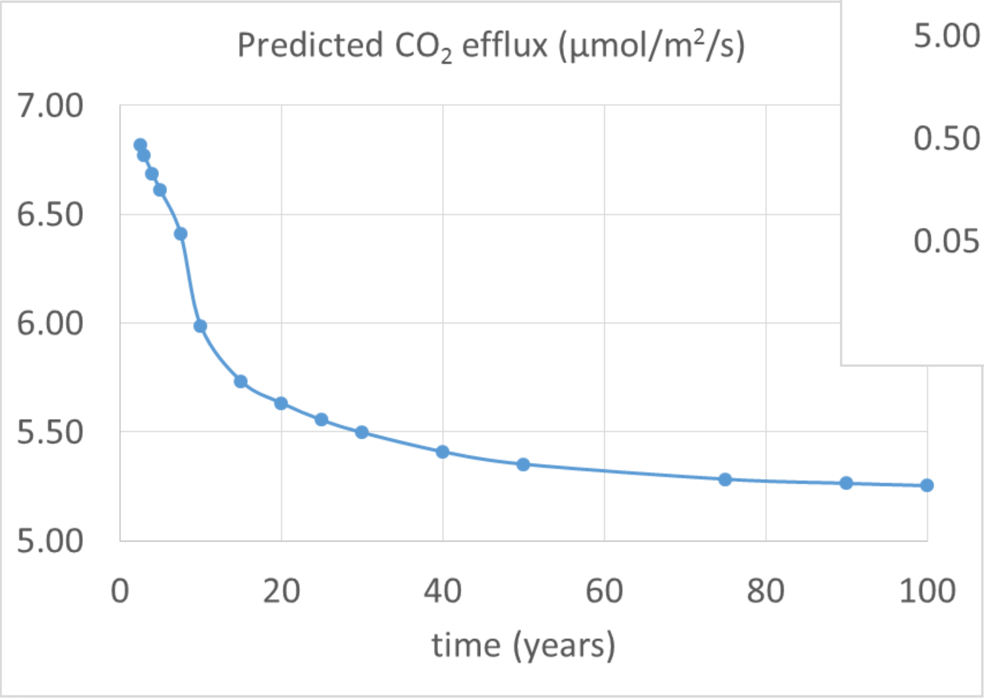
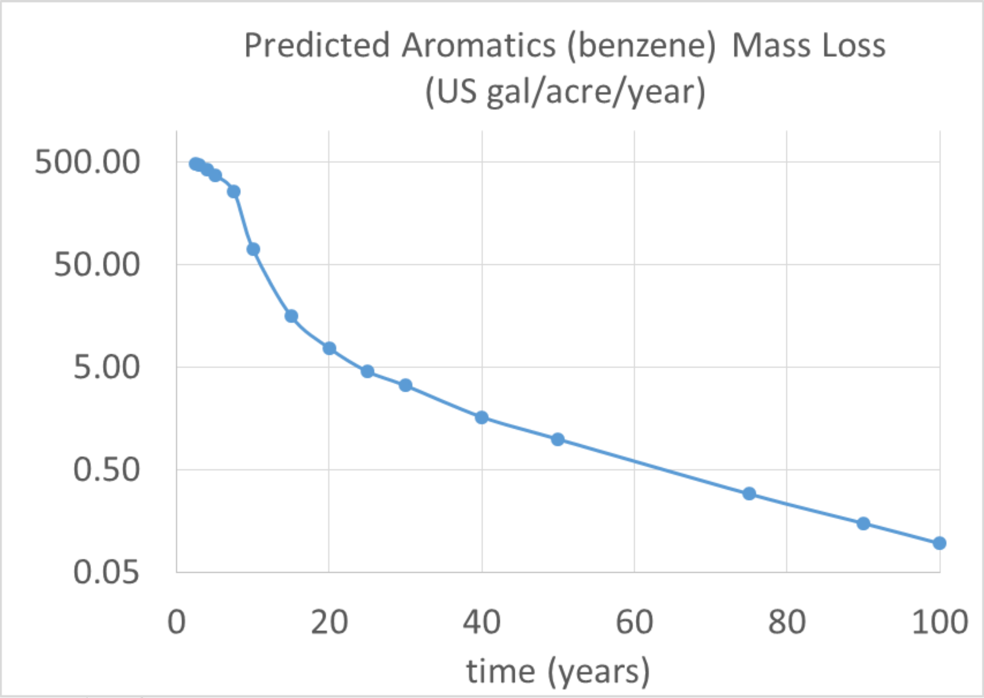
# Natural Depletion – LNAPL Evolution



# Predicted Depletion Rates

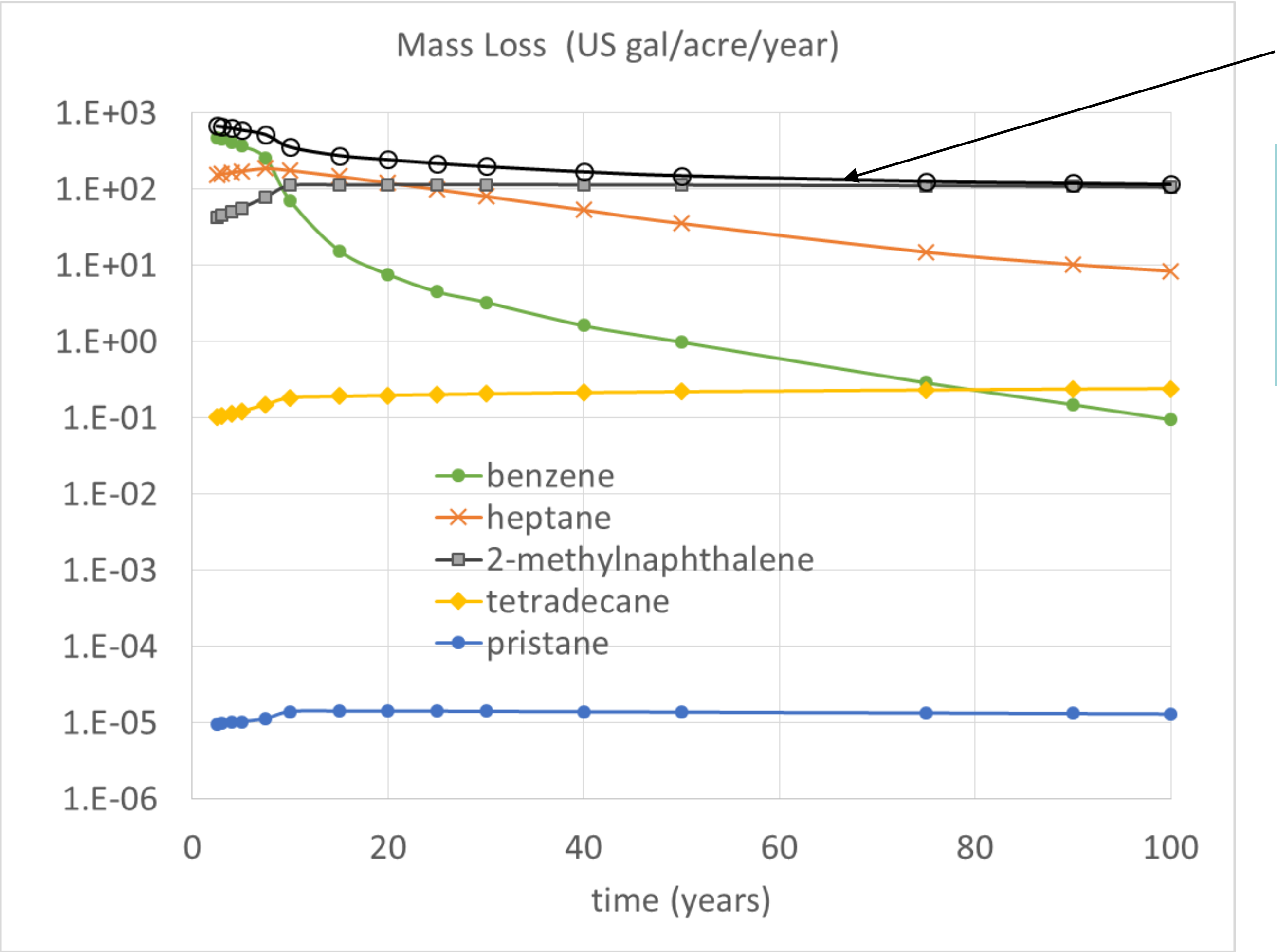
$CO_2$




benzene

# TPH Depletion Rate

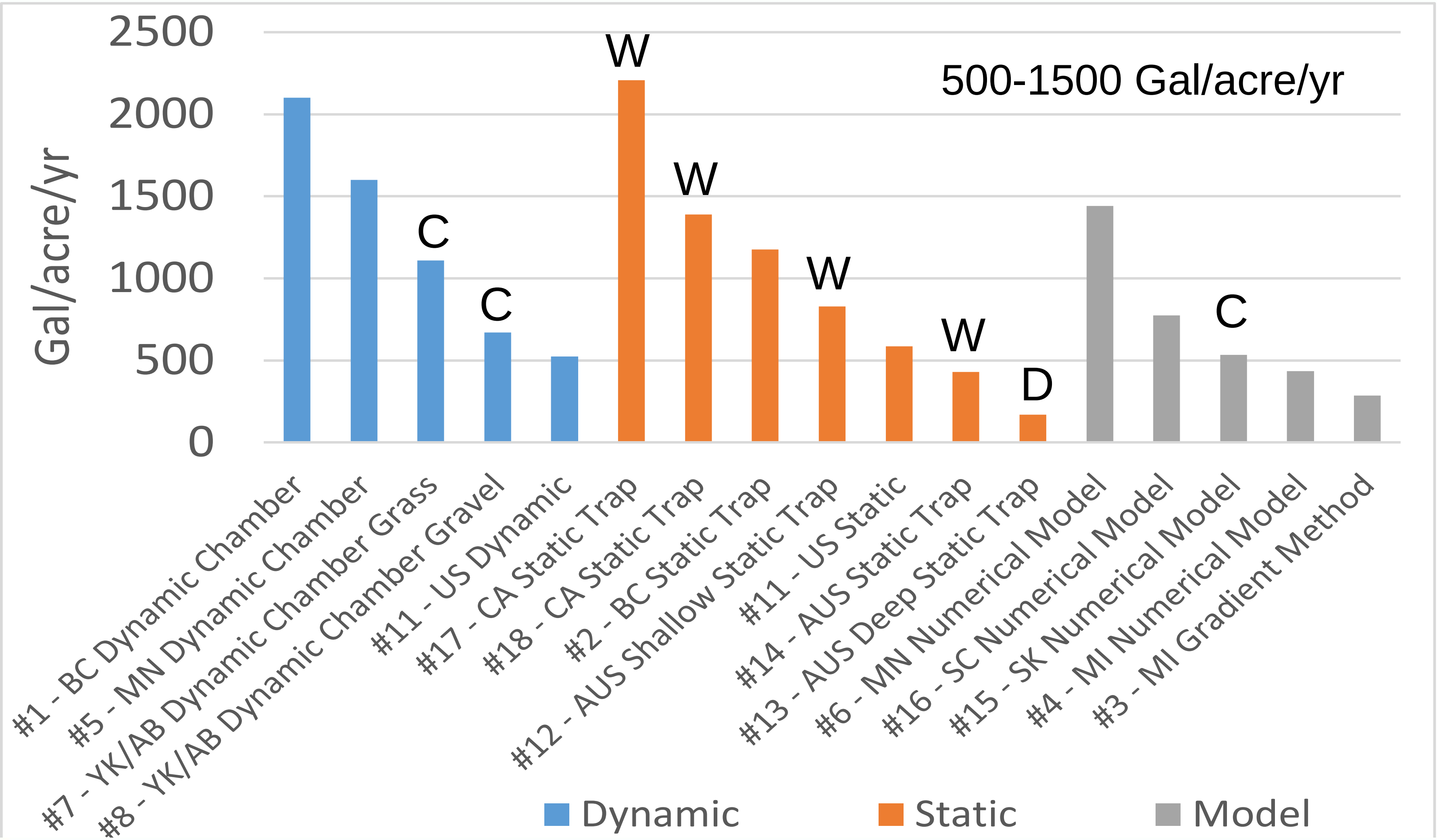



Rate decreasing from 700 to 120 gal/acre/year

Are rates for pristane & tetradecane underestimated?

- Direct outgassing (Ng et al., 2015)
- Biosurfactant effects (Hua and Wang, 2014)

# Vadose Zone Biodegradation Loss Rates



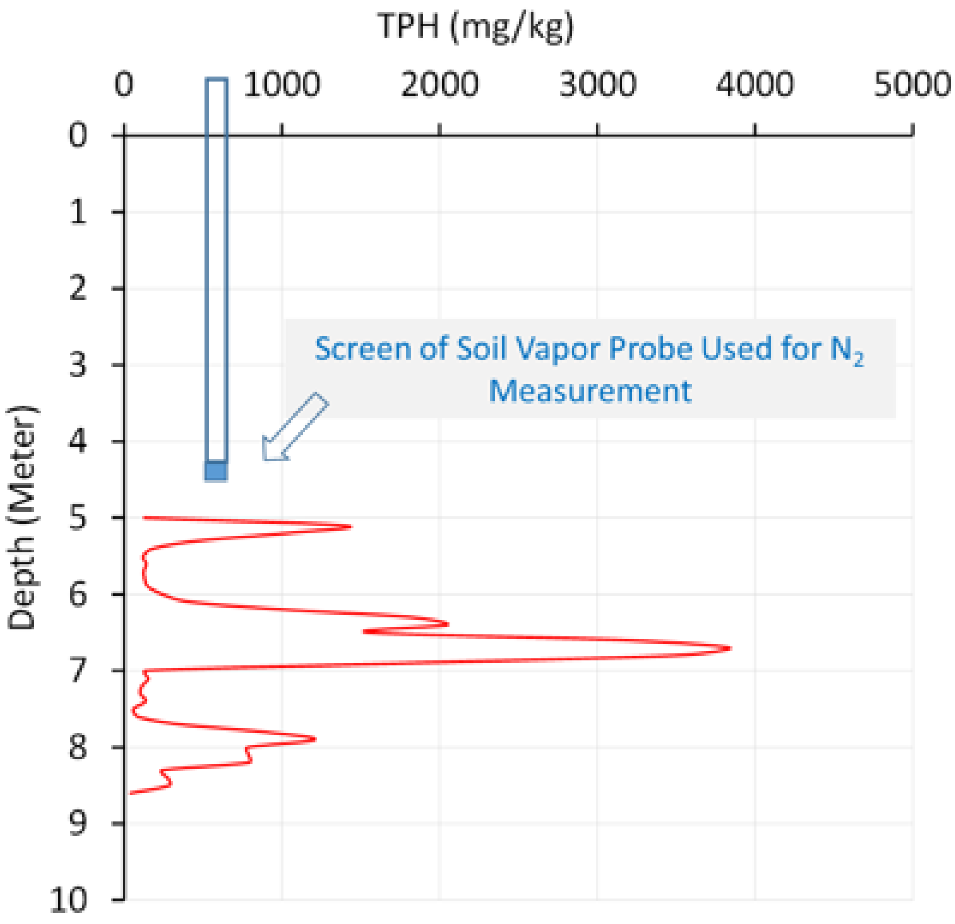

C = cold climate, W = warm climate, D = deep source (confined)
Hers et al. (Battelle 2016)

# Comparison to Screening Model

- Vadose Zone Biodegradation Loss (VZBL) Model
- Predict mass loss rates and depletion times based on readily available data: TPH concentration profile in soil, water table, and soil properties
- Simplified method for aerobic and anaerobic degradation rate estimates
- Model features:
  - Variable water table
  - Multi-layered soil
  - Optional baseline $O_2$ respiration

(Wilson et al., Battelle 2016)

# VZBL Calculations & Assumptions




**Calculation Procedure for Anaerobic Biodegradation**

The anaerobic biodegradation rate is calculated from the methane flux in soil gas, which in turn is estimated from the concentration of $N_2$ in soil gas at any convenient depth interval that is above and close to the TPH. The rate of anaerobic biodegradation is assumed to be uniform and constant across the depth interval contaminated with TPH.

**Calculation Procedure for Aerobic Biodegradation**

The flux of oxygen available for biodegradation is calculated from the depth to the most shallow interval in the profile with TPH. The oxygen demand of the flux of methane is subtracted from the flux of oxygen. If any oxygen remains, then a corresponding amount of TPH is removed from the most shallow layer with TPH.

# MIN3P-Dusty & VZBL

- Equivalent Input Parameters
  - Porosity and moisture content
  - Total petroleum hydrocarbon concentrations in soil
  - Baseline soil respiration
  - $N_2$ concentrations in soil gas
  - LNAPL properties & stoichiometric molar ratio of $O_2$:HC; $CH_4$:HC
- Predicted hydrocarbon mass loss rates
  - VZBL mass loss rates approximately greater by a factor of two
  - Ranges from 1,400 gal/acre/year (initial) to 790 gal/acre/year (100 years)
  - Mass is predicted to remain beyond 100 years



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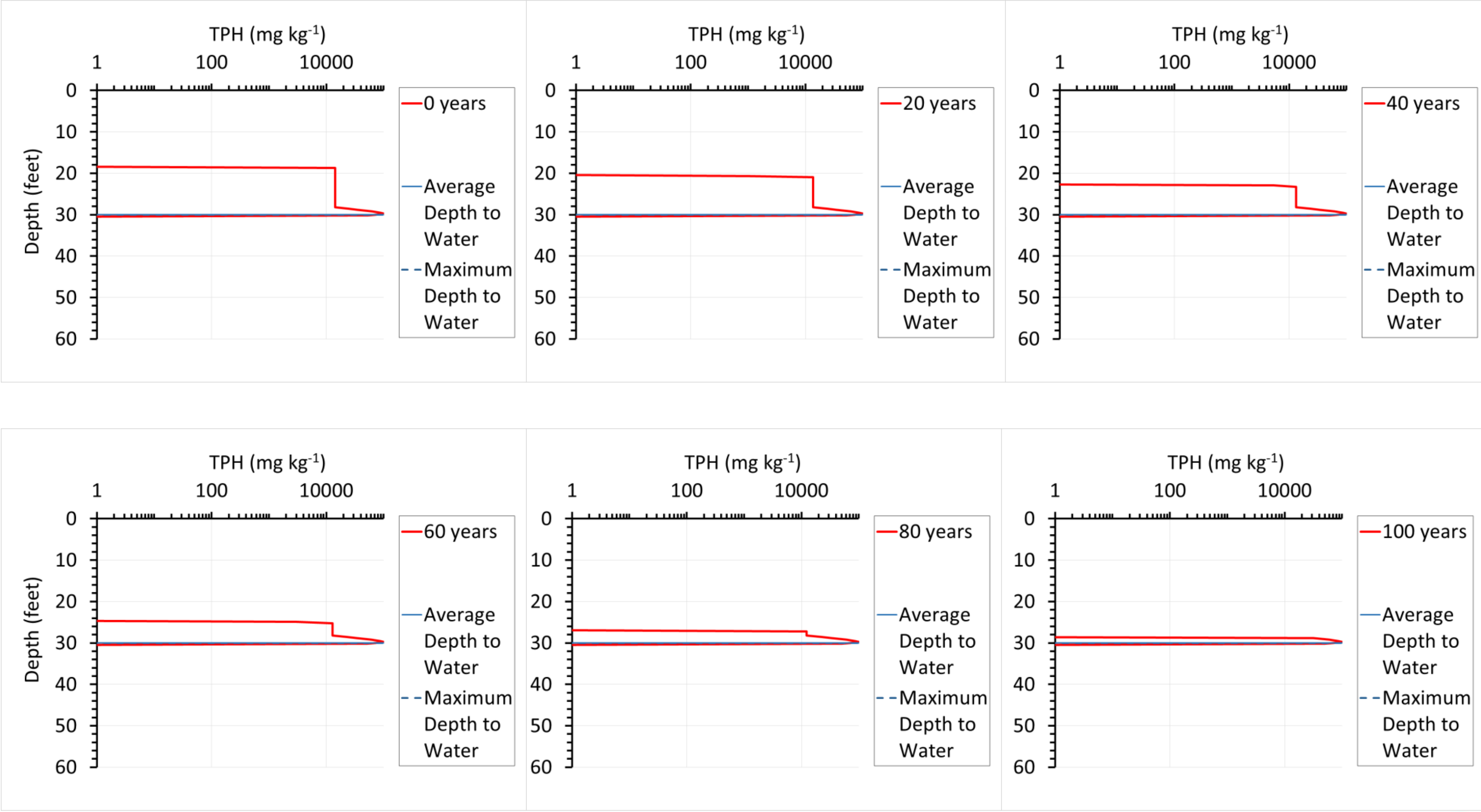
# VZBL Predicted TPH Profiles in Soil



# Summary & Work in Progress

- Process-based and mechanistic model (MIN3P-Dusty) used for improved understanding of NSZD processes
- NSZD rates for hydrocarbon components initially at 700 gal/acre/year and depletion times greater than 10 years, depending on component and depth
- Predicted rates within range of vadose zone NSZD rates determined from other modelling studies and $CO_2$ efflux measurements
- Data gap remains: evaluation of biodegradation process for the heavier and less soluble hydrocarbon components
- VZBL screening model based on simplified processes yet estimated depletion rates within approximately a factor of two
- Three-dimensional bioventing simulations that incorporate addition of air at specified rate and depth interval – in-progress!