Heuristic Numerical Modeling Study of LNAPL Depletion under Natural Conditions

BATTELLE ELEVENTH INTERNATIONAL CONFERENCE ON THE REMEDIATION OF CHLORINATED AND RECALCITRANT COMPOUNDS

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Modeling Approaches

MODELING STUDIES AND APPLICATIONS TO BEMIDJI SITE

Process-based numerical models that incorporate biodegradation of LNAPL hydrocarbon components and transport in porous media

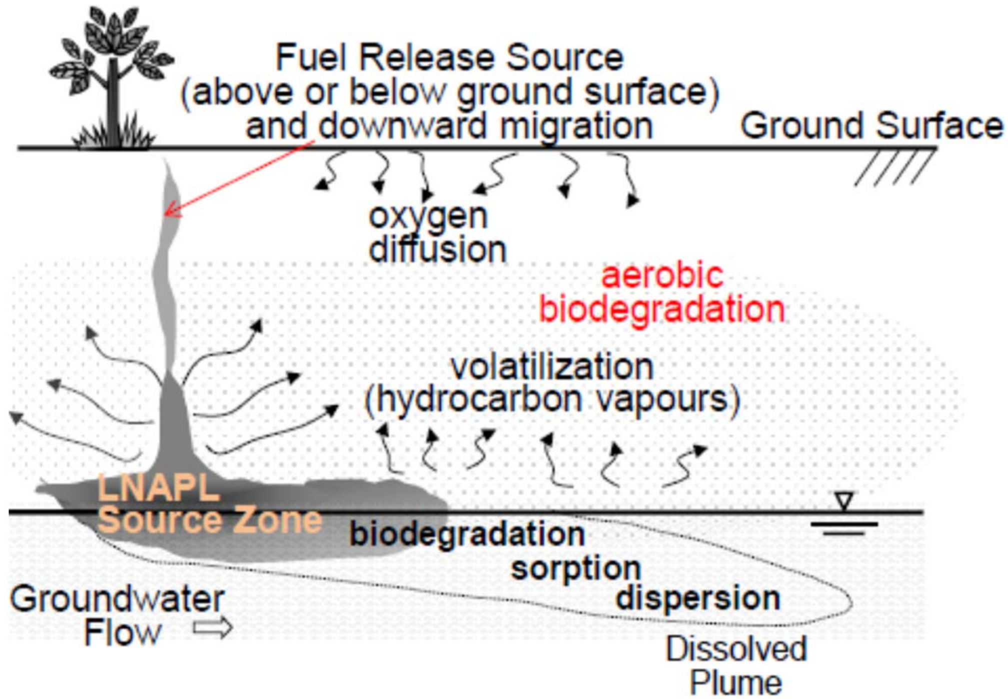
Number of applications of well established models to the Bemidji crude oil spill site that investigate:

- Gas generation and transport (Amos et al., 2005 and Amos and Mayer, 2006)
- Gas advection and dusty gas model (Molins et al., 2010)
- CO_2 efflux from NSZD processes and effect of natural soil respiration using ^{13}C and ^{14}C carbon isotopes in CO_2 and CH_4 (Sihota et al., 2012)
- LNAPL composition, biodegradation kinetics and outgassing (Ng et al., 2015)

Modeling of NSZD Processes

IDEAL FEATURES

- Processes
  - Biogeochemical reactions
  - Vapor phase transport
  - Aqueous phase transport
  - Multi-phase flow
  - Degassing and ebullition
  - Outgassing
- Porous medium
  - Saturated zone
  - Unsaturated zone
  - Multi-dimensional



- Multiple chemical components

Mass Depletion Processes

ITRC (2009)

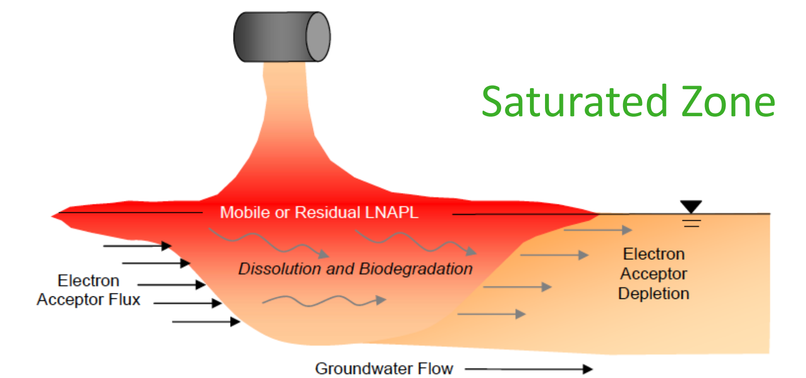


Figure 2-1. Groundwater transport–related NSZD processes.

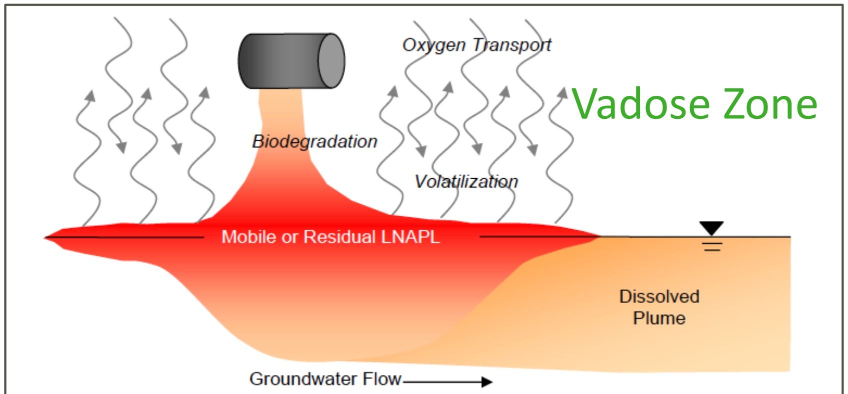


Figure 2-2. Vapor transport–related NSZD processes.

- Dissolution and flow
- Biodegradation

- Volatilization
- Biodegradation

Lundegaard and Johnson (2006): “Mass loss by dissolution and biodegradation in the saturated zone are currently approximately 2 orders of magnitude slower than mass loss associated with oxygen diffusion through the vadose zone”

Garg et al. (2017): typical saturated zone biodegradation capacity <~ 50 gal/acre/year.

Key Point: Saturated zone NSZD rates typically one to two orders of magnitude less.

The Challenge

1. Identifying a single model that incorporates all of the relevant processes in saturated and unsaturated zones.
2. Interconnected processes through
   - Infiltration (downward towards water table)
   - Soil gas transport (upwards towards ground surface)
3. LNAPL source zones typically straddle the water table

Numerical Models

EXAMPLE REACTIVE TRANSPORT MODELS

BIONAPL/3D

- 3D, multi-component NAPL dissolution and biodegradation (Molson and Frind, 2010)
- Does not include volatilization
- Example application: groundwater BTEX plume at an oil refinery site (Vaezihir *et al.*, 2012)
- This model is not commercially available

PHT3D

- 3D, multicomponent (Prommer et al., 2003)
- Saturated zone processes
- Commercially available
- Example 2D cross-sectional application to Bemidji crude oil spill site (Ng et al., 2015)
- Application includes direct outgassing from LNAPL and aqueous phase

MIN3P-DUSTY

- 3D, multicomponent (Molins and Mayer, 2007)
- Variably saturated porous media
- Application to Bemidji crude oil spill site (Molins et al., 2010)
- This model is not commercially available
- Option to include degassing

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MIN3P-Dusty Numerical Model

KEY FEATURES

- Saturated and unsaturated zones
- Flexible biogeochemical reaction network
- Coupled flow and reactive transport

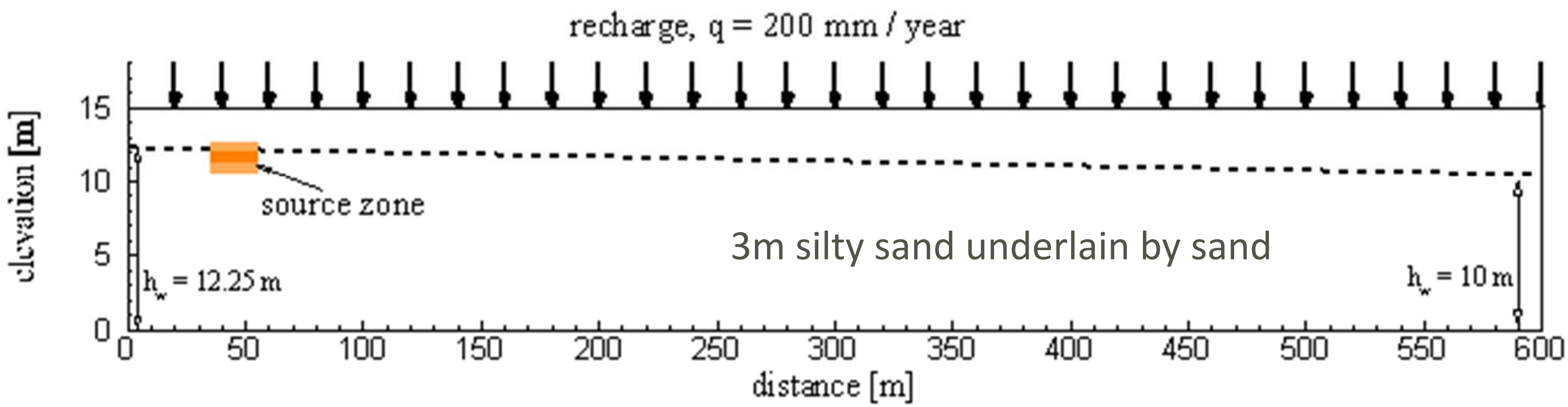
CURRENT LIMITATIONS

- Direct outgassing not included in model: microbes in direct contact with the oil such that biodegradation is not limited by the solubility of the hydrocarbons (e.g., Ng. et al., 2015)
- Degassing and ebullition to the unsaturated zone: current version of model includes degassing but work is needed to address the transport (ebullition) of dissolved gases to the unsaturated zone (Amos and Mayer, 2006)

Key Point: carefully assess the model results in context of the model limitations and uncertainties.

MIN3P-Dusty Numerical Model

EXAMPLE APPLICATION



Transport

- Water infiltration from precipitation
- Soil gas diffusion (dusty gas model)
- Soil gas advection

Reactions

- Biodegradation reactions
- Acid/base equilibria
- Complexation
- Sorption

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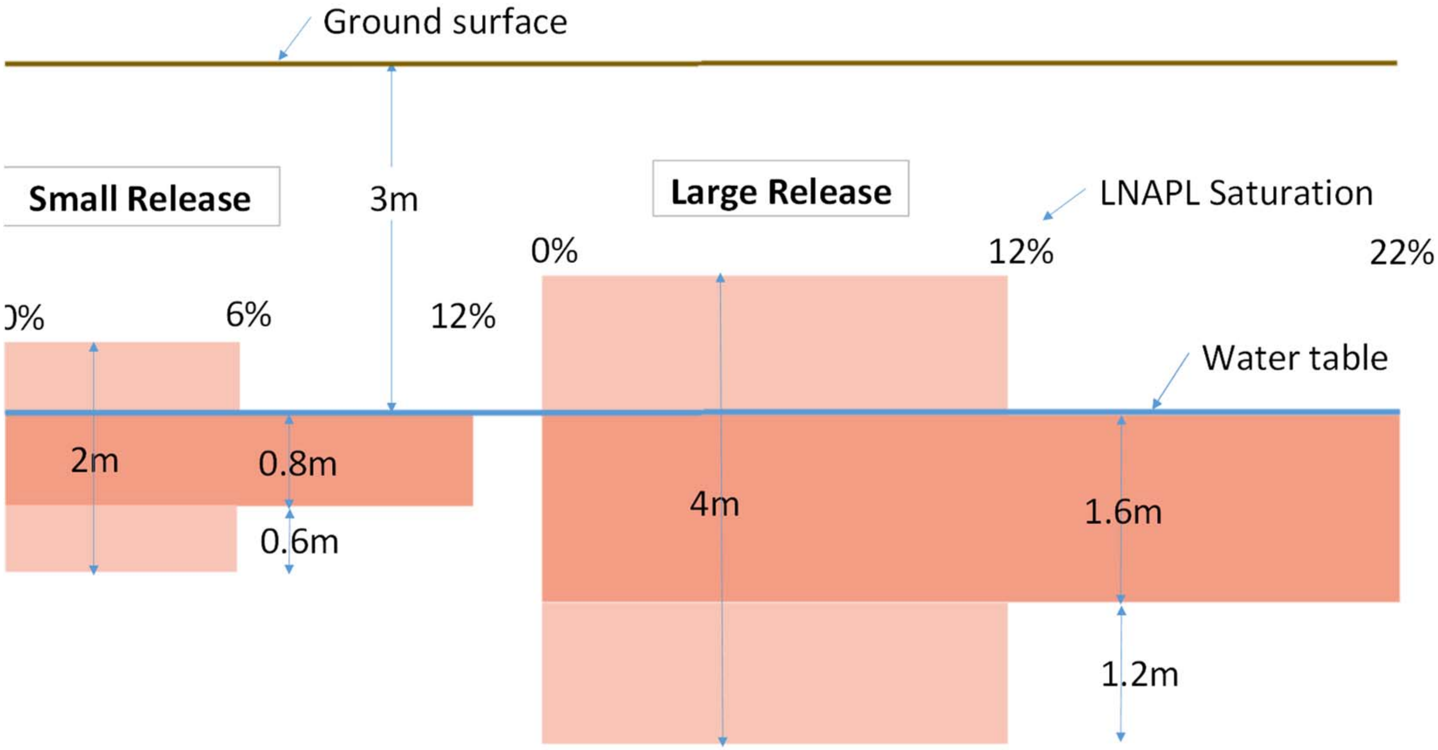
Modeling Objectives

1. Use of a process-based reaction transport model to quantify rates of NSZD for hypothetical scenarios representative of small gasoline releases (gas station) and large releases of fuel mixtures (refinery)
2. Comparison of natural depletion rates between scenarios and processes considered
3. Estimate the change in depletion rates (individual components and total mass) over time
4. Quantify the effects of soil moisture conditions in the vadose zone and location of source zone with respect to the water table on the predicted CO_2 efflux at ground surface
5. Investigate the potential for degassing through evaluation of pressure build-up below water table

Model Scenarios

SATURATION PROFILES



- Small gasoline releases (gas station)
- Two hydrocarbon components to represent LNAPL

- Large releases of fuel mixtures (refinery)
- Five hydrocarbon components to represent LNAPL

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Model Scenarios

BASELINE AND VARIATIONS – INITIAL PLAN

Baseline defined for each of the small and large release scenarios

What if variations to the baseline:

- Wetter conditions (double the infiltration or recharge at ground surface)
- Drier conditions (no infiltration)
- Source zone entirely above the water table
- Source zone entirely submerged below the water table
- Above four variations for each of the small and large release scenarios for a total of 10 simulations

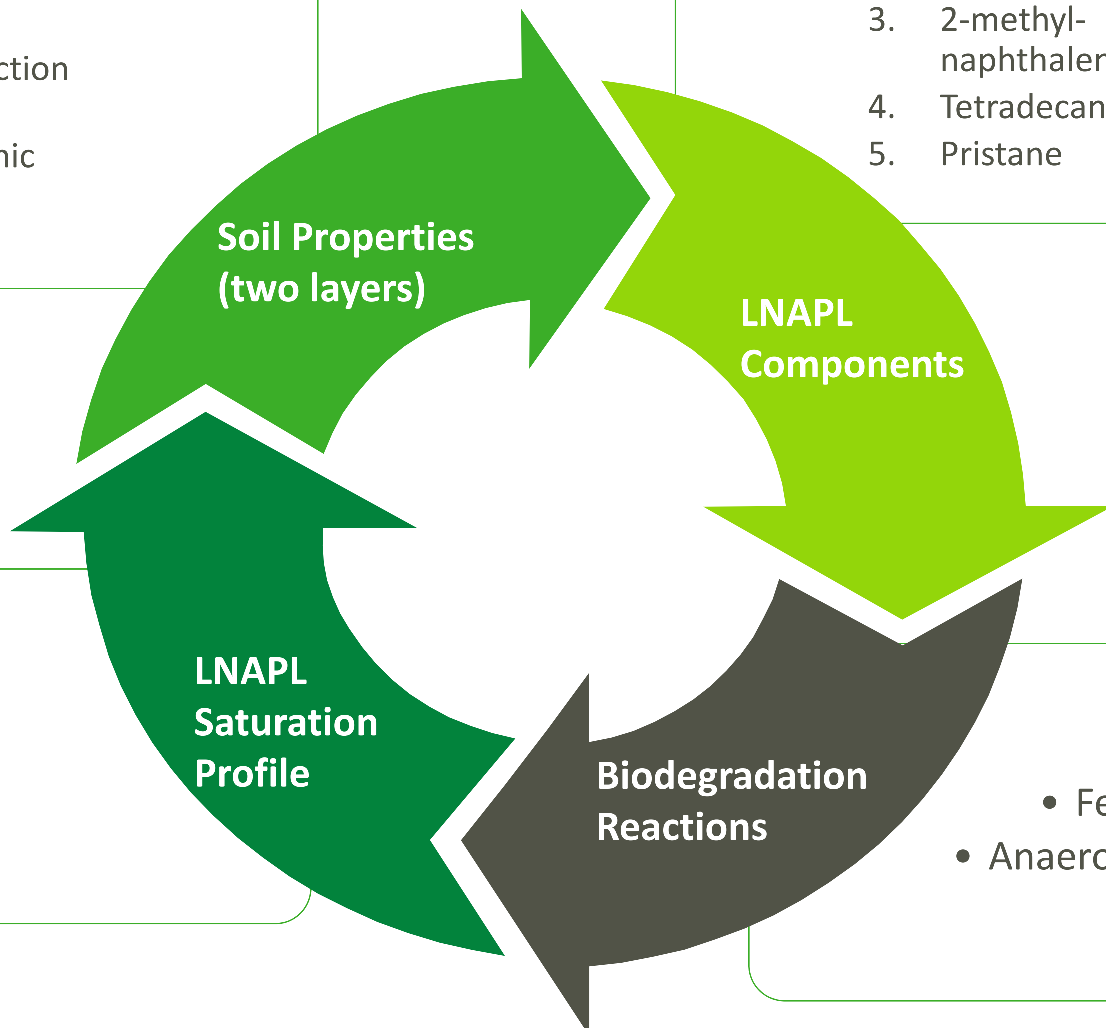
Results of baseline scenarios to be assessed in context of the model limitations related to potential for degassing prior to implementing the variations.

Conceptual Model Setup

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

Small Release
1. benzene
2. heptane
3. 2-methyl-naphthalene
4. Tetradecane
5. Pristane

Large Release
1. benzene
2. isooctane



- Dissolution and volatilization

- Aerobic
- Ferric iron reduction
- Anaerobic/methanogenic

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Biodegradation Reactions

PRIMARY REDOX REACTIONS

Primary Redox Reaction	Reaction Formula (Hydrocarbon C_aH_b)
Aerobic biodegradation of hydrocarbon	$C_aH_b + (a + b/4)O_2 + (a - b/2)H_2O \rightarrow aCO_3^{2-} + 2aH^+$
Reductive dissolution of iron mineral goethite	$\frac{1}{4a+b}C_aH_b + FeO(OH) + \frac{6a+2b}{4a+b}H^+ \rightarrow Fe^{2+} + \frac{a}{4a+b}CO_3^{2-} + \frac{5a+2b}{4a+b}H_2O$
Reductive dissolution of iron mineral ferrihydrite	$\frac{1}{4a+b}C_aH_b + Fe(OH)_3 + \frac{6a+2b}{4a+b}H^+ \rightarrow Fe^{2+} + \frac{a}{4a+b}CO_3^{2-} + \frac{9a+3b}{4a+b}H_2O$
Fermentation and Methanogenesis	$C_aH_b + \frac{3(4a-b)}{8}H_2O \rightarrow \frac{(4a-b)}{8}CO_3^{2-} + \frac{2(4a-b)}{8}H^+ + \frac{(4a+b)}{8})CH_4$

Biodegradation Reactions

SECONDARY REDOX REACTIONS

Primary Redox Reaction	Reaction Formula (Hydrocarbon C_aH_b)
Aerobic oxidation of methane	$CH_4 + 2O_2 \rightarrow CO_3^{2-} + 2H^+ + H_2O$
Aerobic oxidation of dissolved ferrous iron	$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$
Oxidation of methane coupled to reductive dissolution of goethite	$\frac{1}{8}CH_4 + FeO(OH) + \frac{7}{4}H^+ \rightarrow Fe^{2+} + \frac{1}{8}CO_3^{2-} + \frac{13}{8}H_2O$
Oxidation of methane coupled to reductive dissolution of ferrihydrite	$\frac{1}{8}CH_4 + Fe(OH)_3 + \frac{7}{4}H^+ \rightarrow Fe^{2+} + \frac{1}{8}CO_3^{2-} + \frac{21}{8}H_2O$

Baseline Scenarios

POTENTIAL FOR DEGASSING?

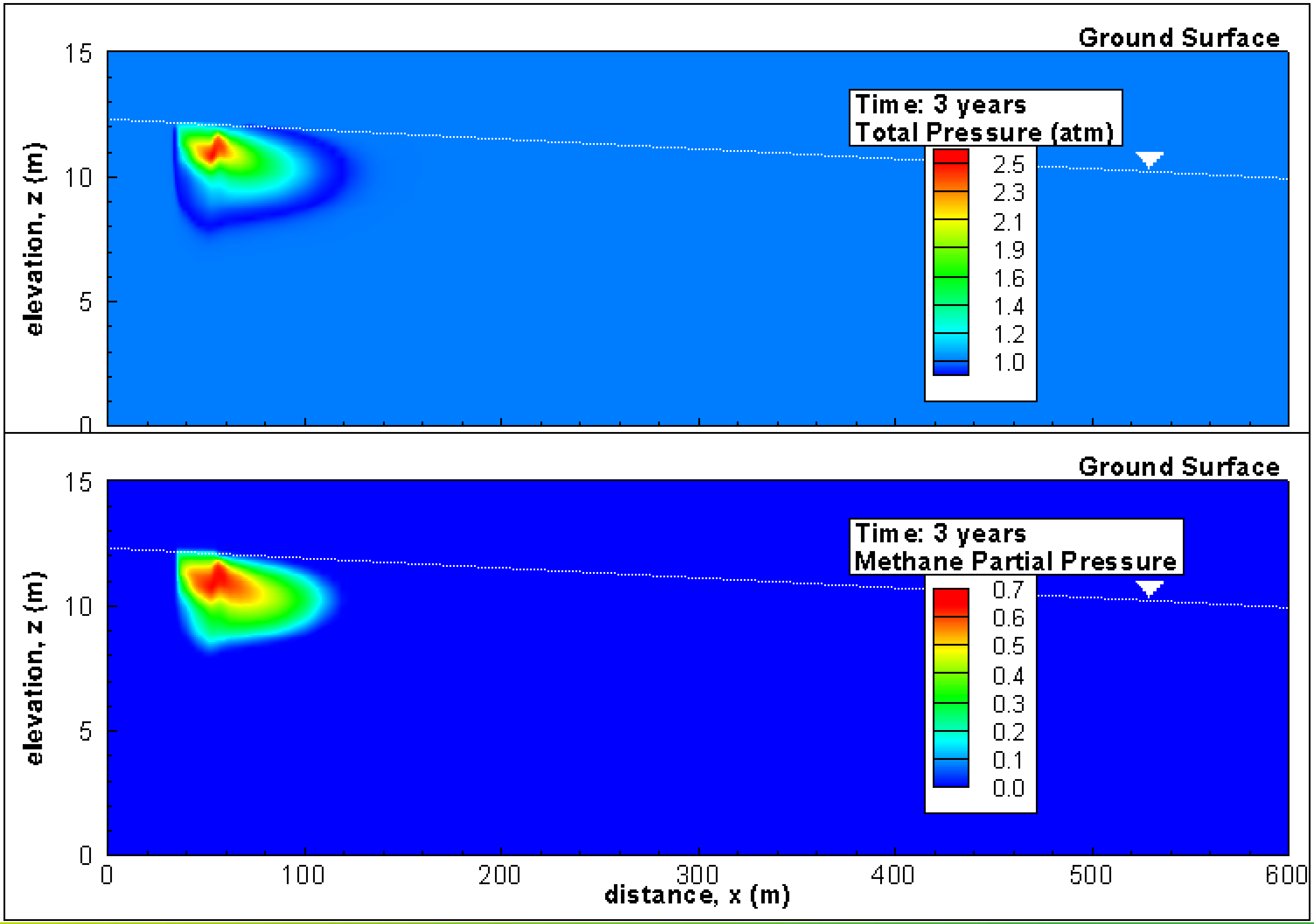
One objective was to test suitability of model without option for degassing and ebullition.

Results of baseline scenarios for both the small and large release simulations indicate significant build-up and methane and pressure.

Model with degassing option needed to best represent the selected baseline scenarios.

Total Pressure and Methane Concentrations

SMALL RELEASE SCENARIO – PARTIALLY SUBMERGED



Model Scenarios

PLAN FORWARD

Initial plan modified in context of preliminary results of baseline simulation

Degassing potentially significant at predicted pressures

Scenarios defined for:

- Source entirely above the water table
- Source entirely below the water table + degassing option

Initial Results – Source Below Water Table

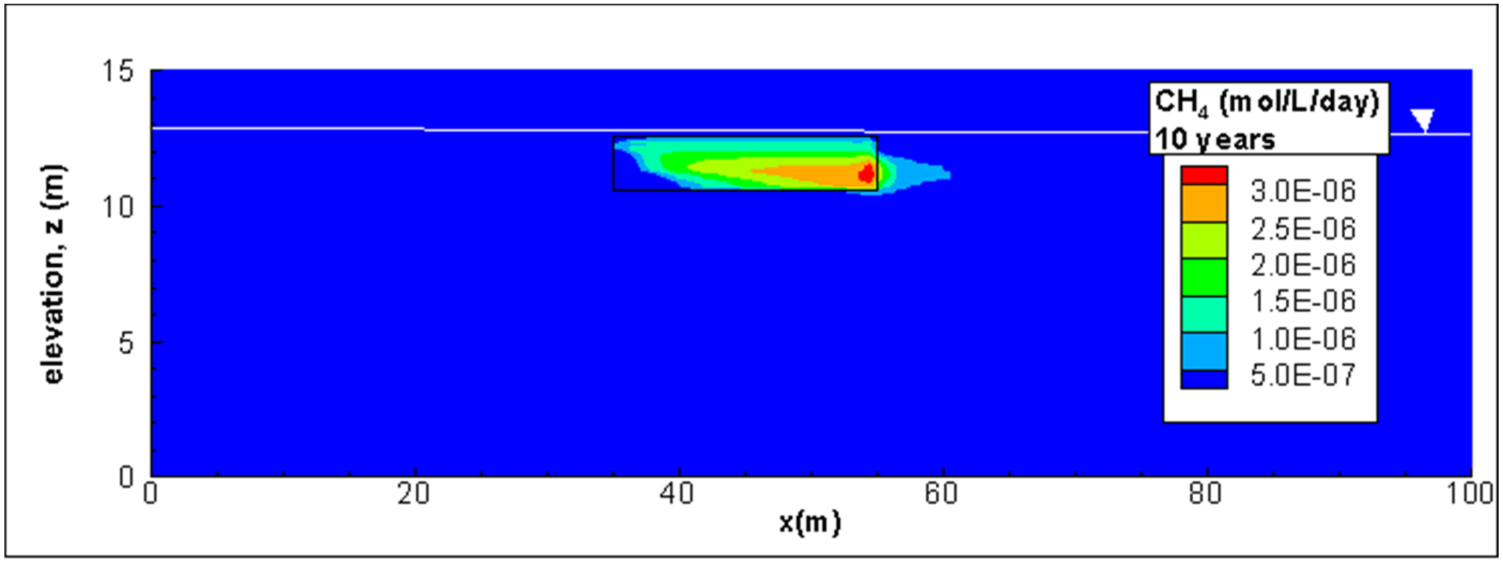
SMALL GASOLINE RELEASES (GAS STATION)

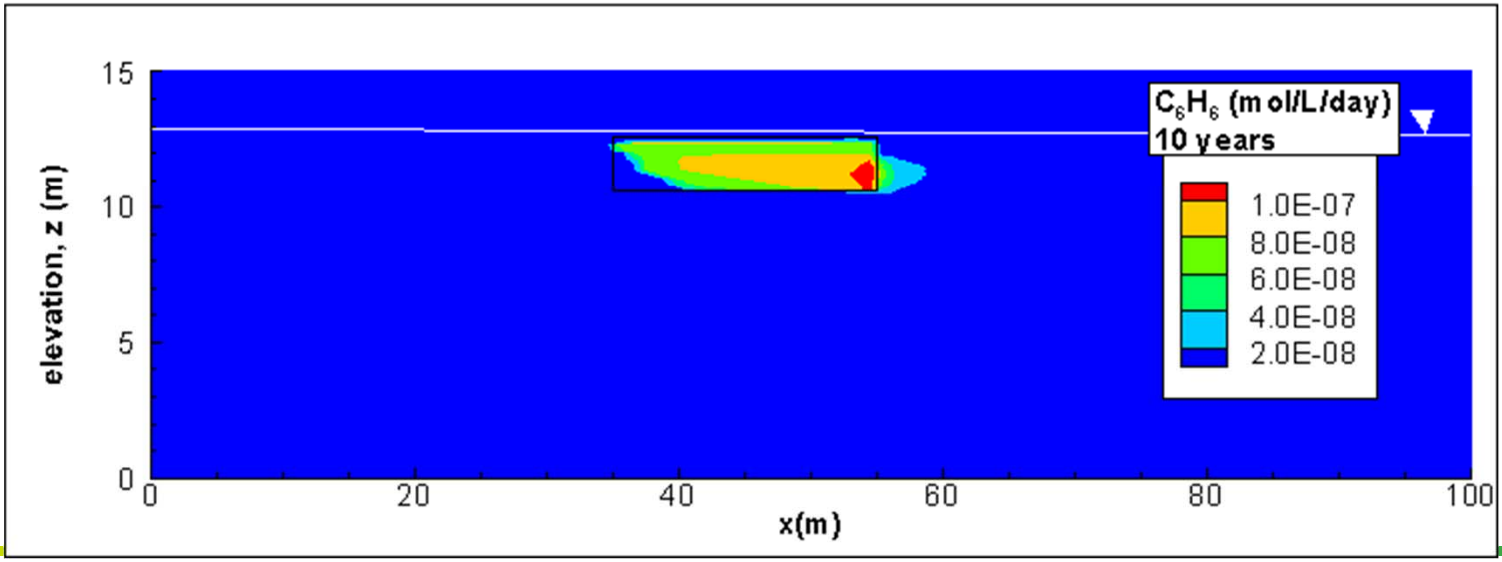
Degassing rates

LNAPL depletion rates:

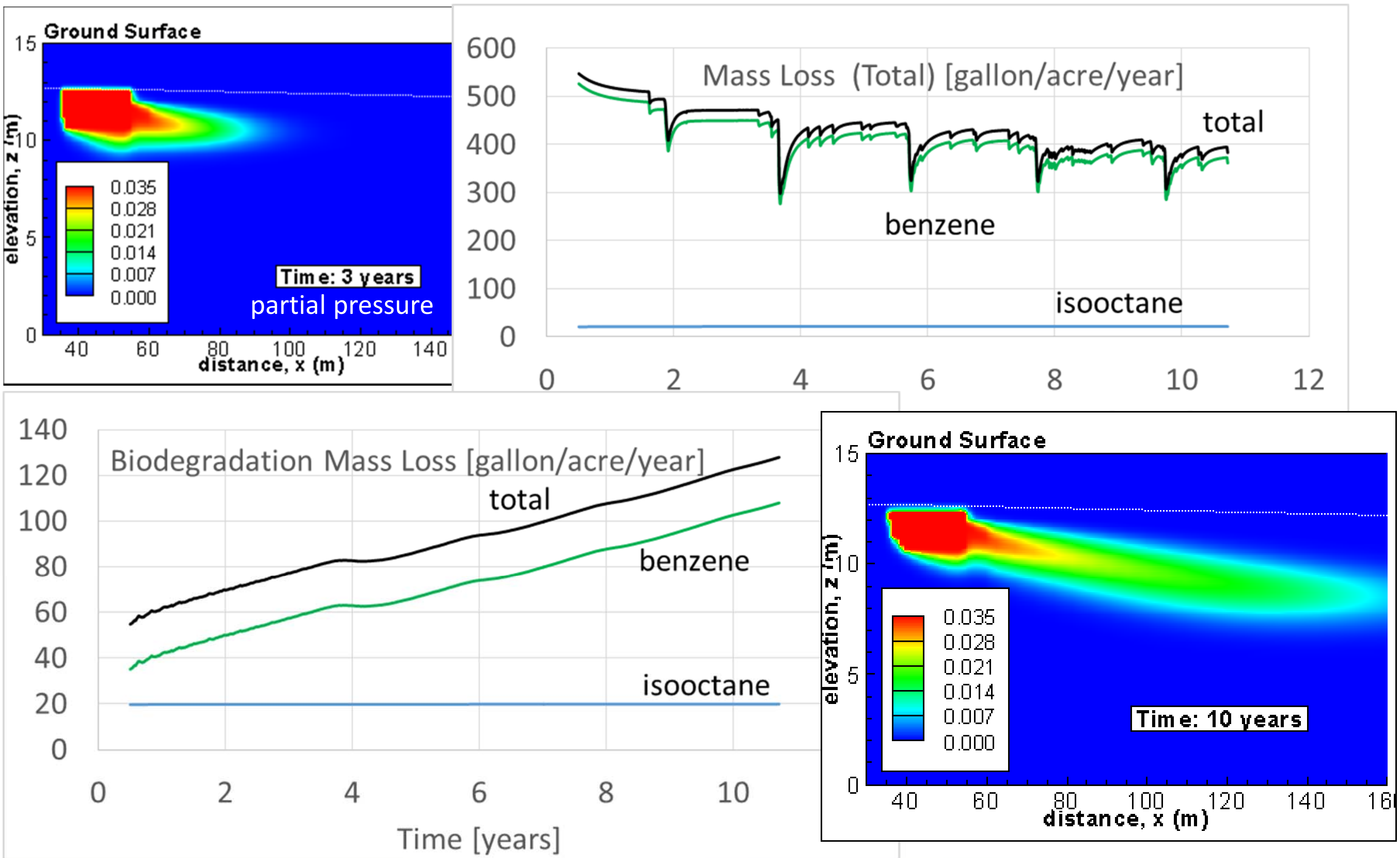
- Total and individual LNAPL components
- Mass loss in saturated versus unsaturated zone

Degassing Rates (10 years)





Predicted LNAPL Depletion Rates



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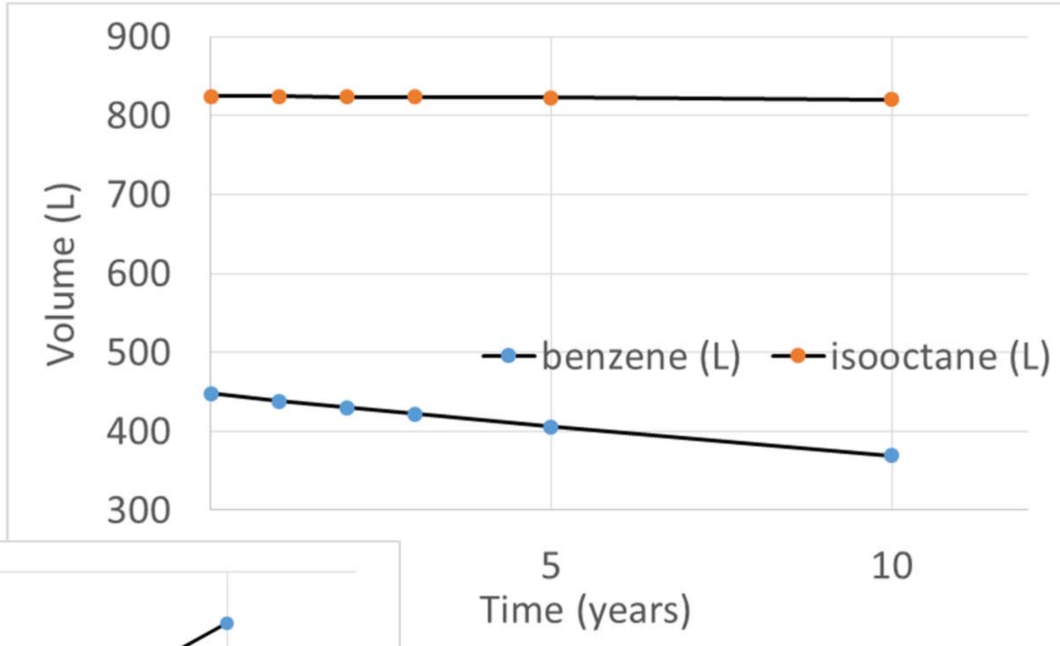
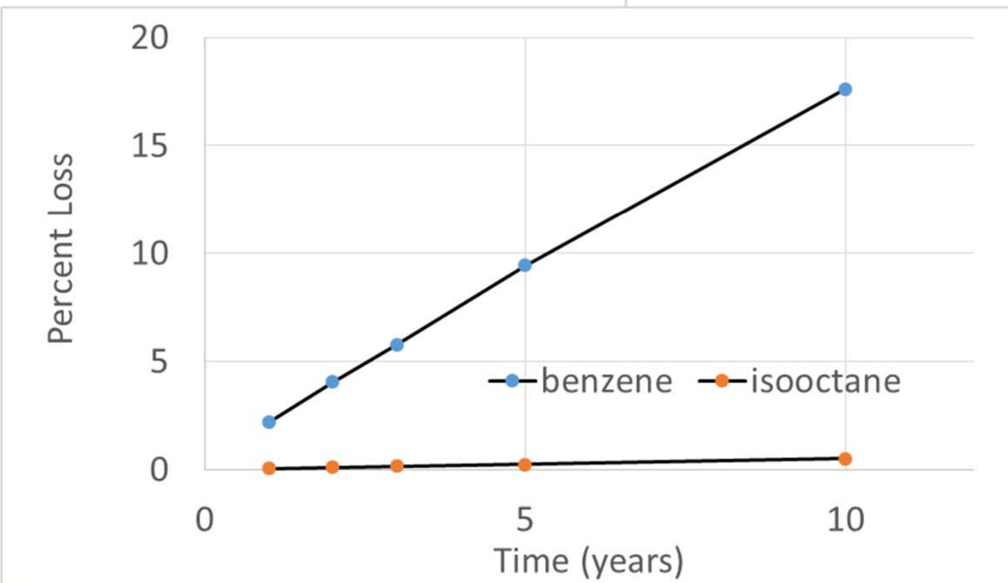
Predicted Mass Loss





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Predicted Biodegradation Rates (g/day)

AT 10 YEARS SIMULATION TIME

Hydrocarbon	aerobic	methanogenic	iron reduction	
			goethite	ferrihydrite
Benzene	5.3E-1	4.1E0	2.2E-2	4.3E-3
Isooctane	5.1E-3	6.9E-1	2.8E0-3	4.6E-7
Methane	1.9E-1	-	2.4E-2	3.2E-2

integrated rates over saturated and unsaturated zones

Comparison to degassing rate (g/day):

- benzene: 1.2E-1
- Isooctane: 6.3E-2
- Methane: 1.0E0

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Fraction of Rates from Saturated Zone

AT 10 YEARS SIMULATION TIME

Hydrocarbon	aerobic	methanogenic	iron reduction	
			goethite	ferrihydrite
Benzene	0.5	1	1	1
Isooctane	1.0	1	1	1
Methane	0.9	-	1	1

Only aerobic benzene degradation significant in the vadose zone, noting LNAPL source entirely submerged in this scenario

Work in progress…

1. Scenario with source entirely above the water table (no degassing)
2. Large release of fuel mixtures (refinery)
3. Model scenarios with degassing only in the saturated zone (requires code modification)
4. Use of model to evaluate effect of source size, saturation, soil properties on predicted NSZD rates, NAPL composition and CO_2 efflux at ground surface

Key point: Improved understanding of the saturated-unsaturated zone gas transport needed to better capture NSZD processes

Thank You!

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