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Field-Scale Evaluation of Aerobic Biooxidation to Deplete Groundwater Contaminants from Coal Tar and Creosote

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Risk-Based NAPL Management

Composition

soluble/volatile fractions

- Is there a dissolved-phase risk?
- Is there a vapor-phase risk?

Saturation

- Is NAPL Mobile?
- Is NAPL Migrating?

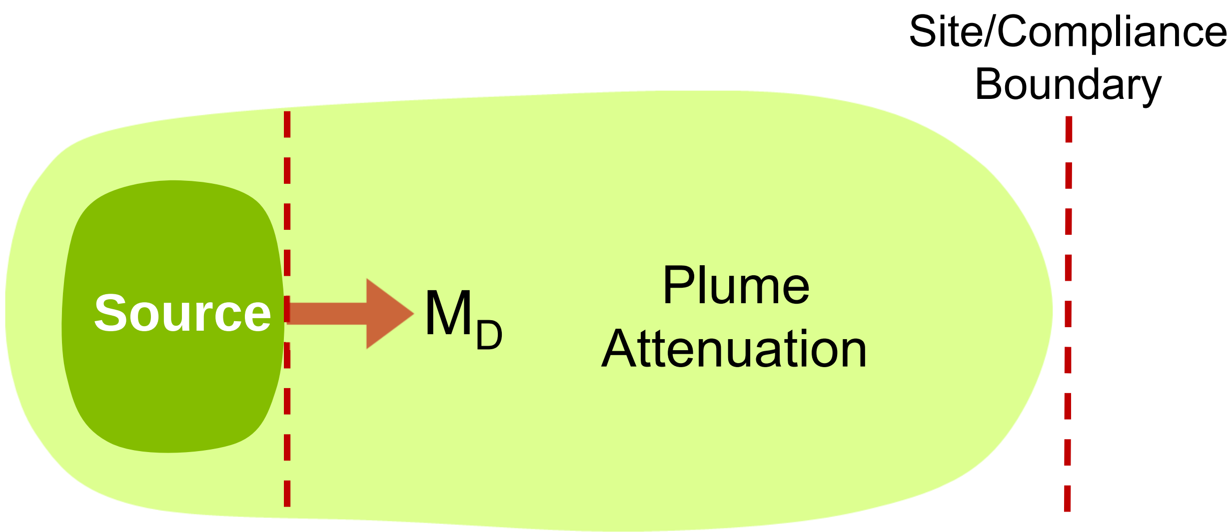
Management decisions based on a robust NAPL CSM →

Remedial actions that directly and efficiently mitigate risk

Risk-Based NAPL Management

Coal Tar and Creosote Sites

- NAPL is at residual saturations
- NAPL is highly weathered
- Primary risk is offsite migration of the dissolved-plume (BTEX and PAHs)



Decrease source mass → decrease mass discharge (M_D) → M_D < Plume Attenuation Rate

Remediation Strategies	• Saturation change • Containment • Composition change

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Risk-Based NAPL Management - Case Studies

Creosote

- Former wood treating facility and mill in Montana
  - Onsite creosote (DNAPL) source area with offsite dissolved plume
  - Primarily pentachlorophenol (PCP) and PAHs (naphthalene)
  - Aerobic biooxidation with biosparging evaluated for FS (Pilot Study in 2015-2016)

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Risk-Based NAPL Management - Case Studies

Coal Tar

- Former Manufactured Gas Plant (MGP) site in Florida
  - Onsite coal tar (DNAPL) source area with offsite dissolved plume
  - VOCs and PAHs
  - Aerobic biooxidation with biosparging at property boundary (testing in portion of source area)

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Risk-Based NAPL Management - Case Studies

Remediation Objectives

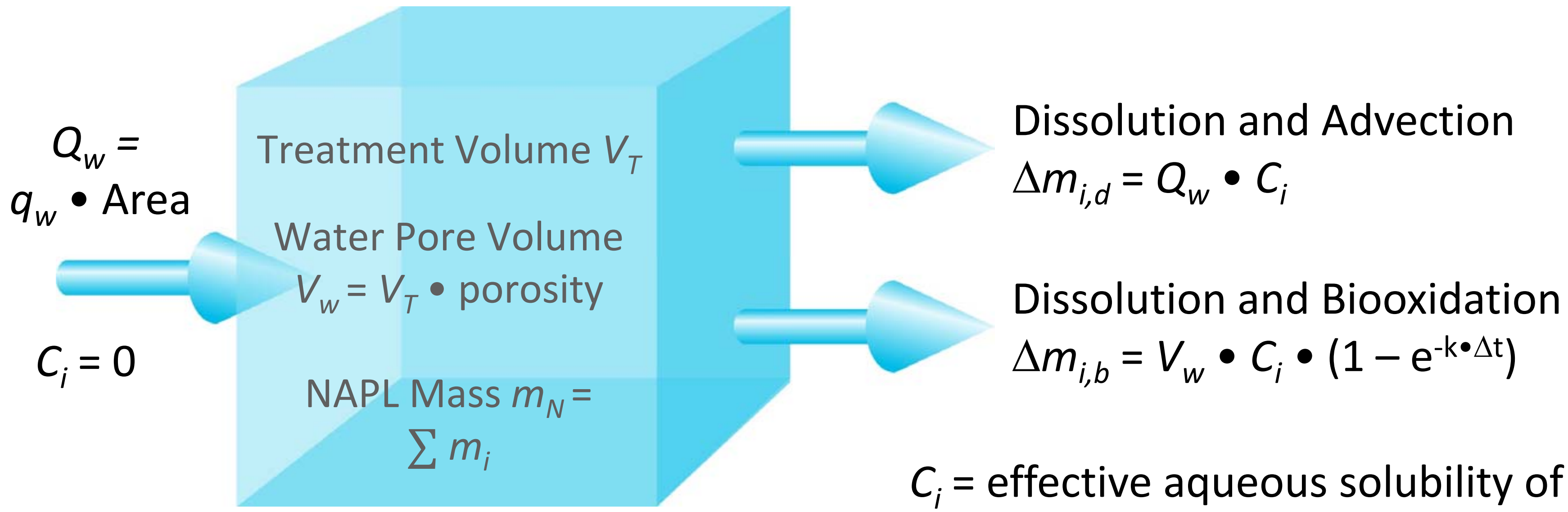
- Change composition of the NAPL by enhancing removal of groundwater contaminants
- Decrease mass discharge to less than the attenuation capacity of the groundwater system
- Contain dissolved plume onsite via natural attenuation

How does biosparging affect NAPL composition?

Can biosparging achieve remediation objectives?

NAPL Depletion Evaluation Approach

Developed a NAPL depletion model with two key elements:
Lab-based Raoult’s Law Method and Biooxidation



C_i = effective aqueous solubility of compound *i* from the NAPL

NAPL Depletion Evaluation Approach – Solubility Modeling

Raoult's Law

The effective aqueous solubility of compound *i* from the NAPL is

$$C_i \quad = C_S^i \frac{\chi_i}{FR_i}$$

C_S^i = pure phase aqueous solubility of compound *i*

χ_i = mole fraction of compound *i* in NAPL

FR_i = solid-liquid fugacity ratio of compound *i*

Mole Fraction

$$\chi_i = C_N^i \frac{\boldsymbol{MW_N}}{MW_i}$$

C_N^i = mass fraction of compound *i in NAPL*

MW_i = molecular weight of compound *i*

MW_N = average molecular weight of the NAPL

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NAPL Depletion Evaluation Approach – Solubility Modeling

Raoult's Law-Based Method for Determination of Coal Tar Average Molecular Weight

Brown et al. 2005. *Environmental Toxicology and Chemistry*, Vol. 24, No. 8, pp. 1886-1892

Laboratory Method

- Mass fraction of target compounds in the NAPL
- NAPL-water equilibrium studies to quantify effective aqueous solubility of target compounds

Key Concept: Linear slope of effective solubility for target compounds versus rearrangement of Raoult's Law is the average molecular weight of the NAPL

$$C_i = \boldsymbol{MW_N} G_i$$

$$G_i = \frac{C_S^i}{FR_i}\frac{C_N^i}{MW_i}$$

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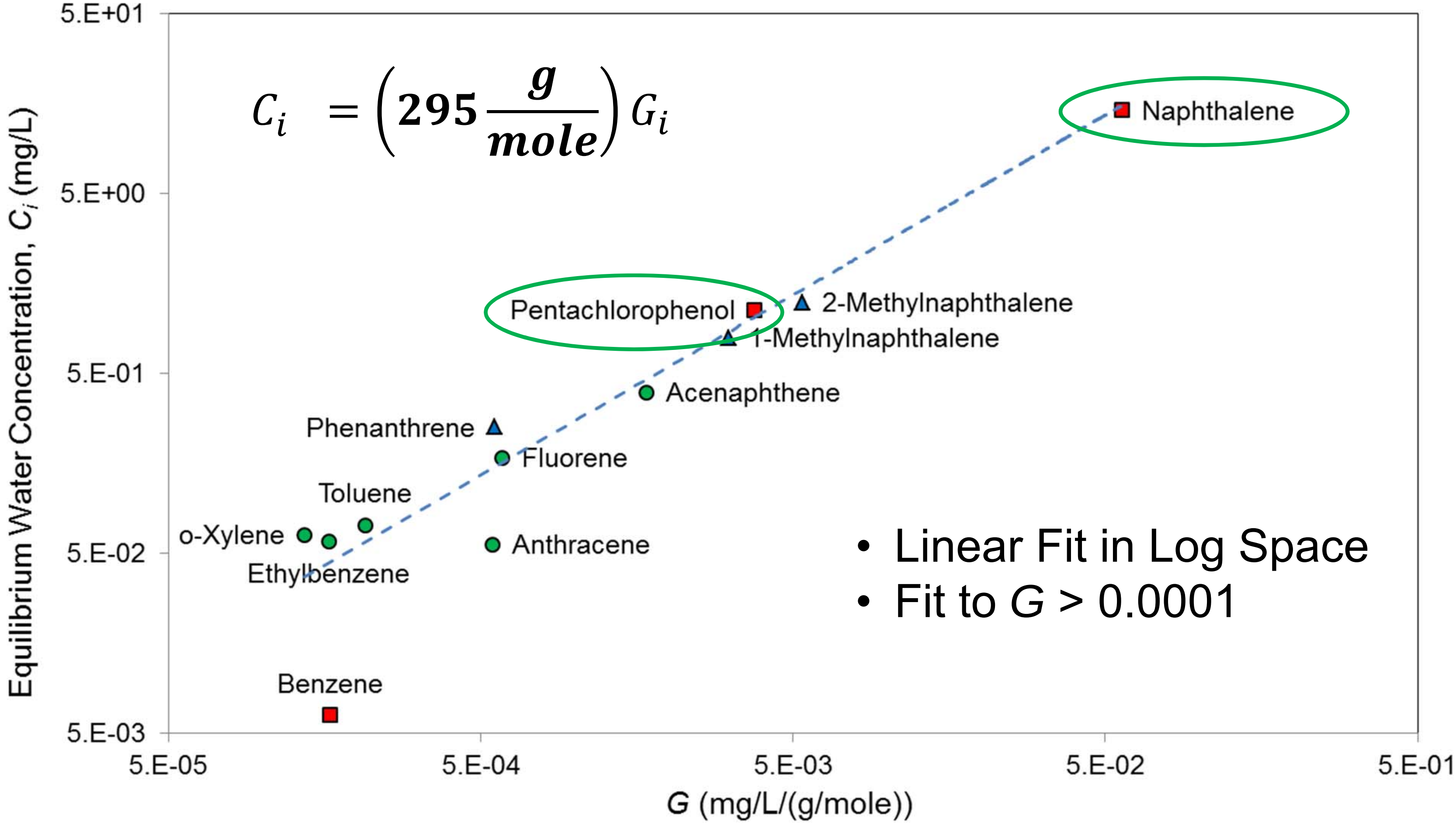
Solubility Modeling – Creosote Case Study



- Linear Fit in Log Space
- Fit to *G* > 0.0001

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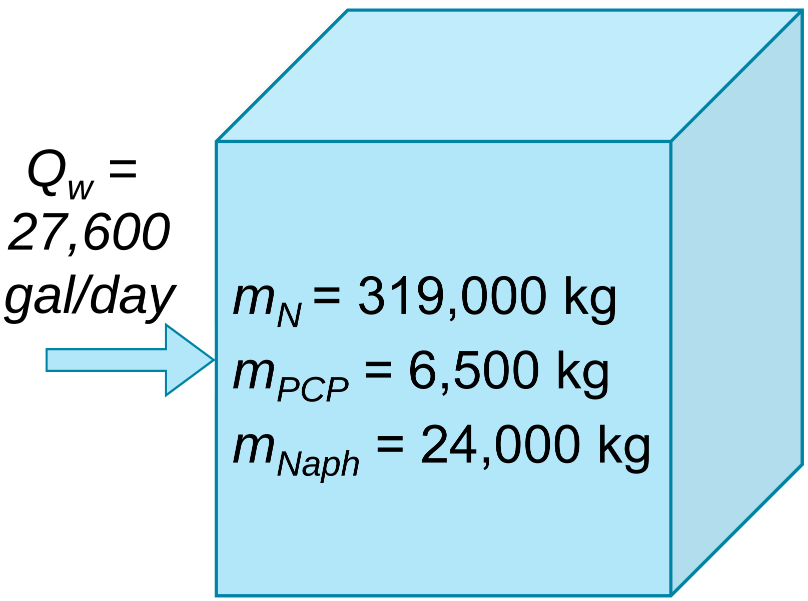
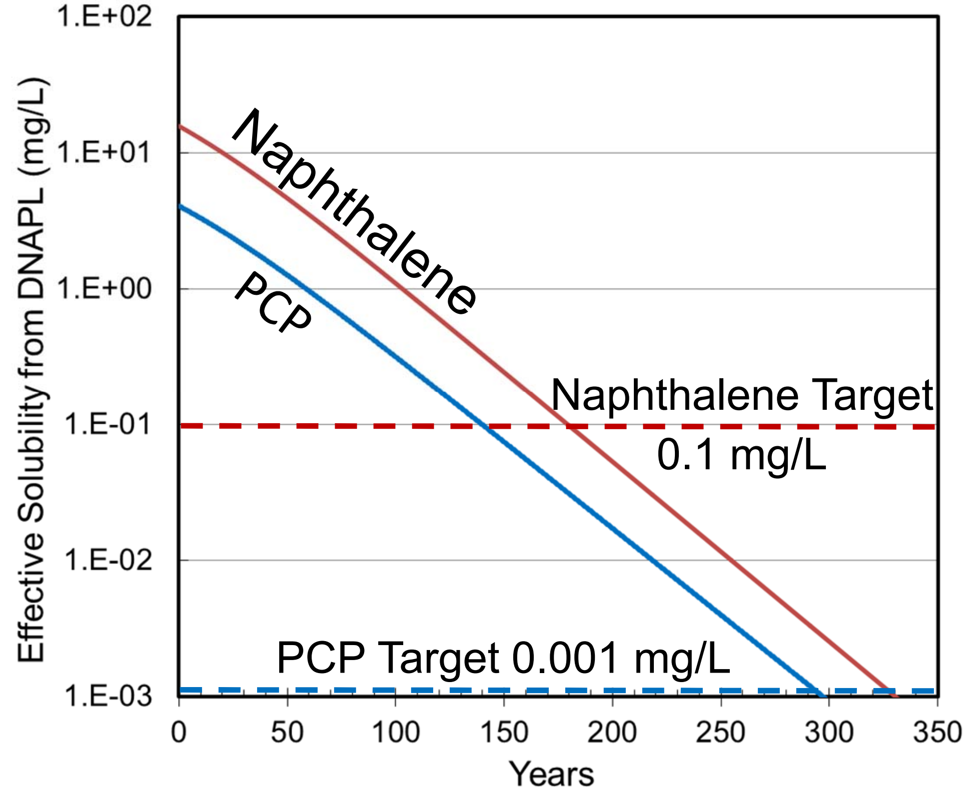
NAPL Depletion Evaluation – Creosote Case Study

Solubility Model:

$$C_i = C_N^i \frac{C_s^i}{FR_i} \frac{295 \frac{\text{g}}{\text{mole}}}{MW_i}$$



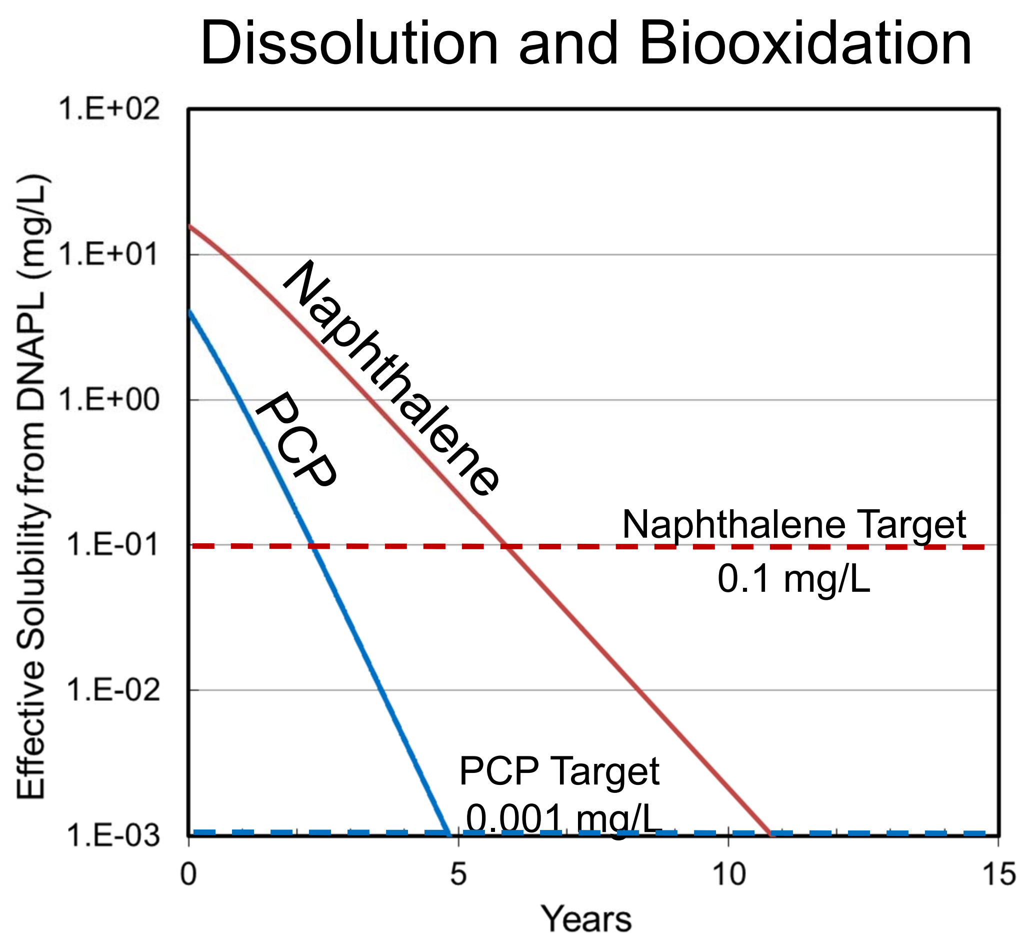
Dissolution and Advection $\Delta m_{i,d} = Q_w \cdot C_i$
(No biooxidation)



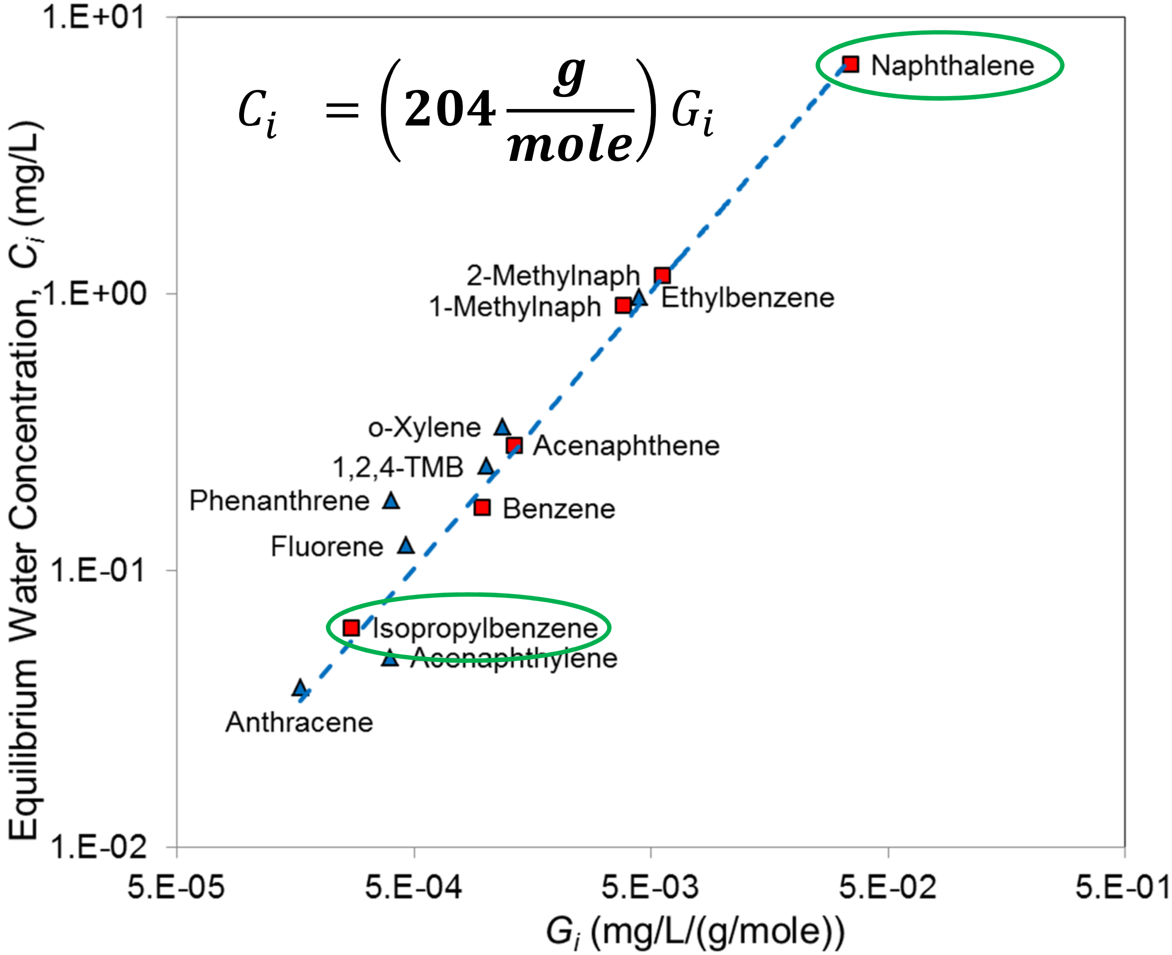
NAPL Depletion Evaluation – Creosote Case Study

Field-Scale Biosparging Study

- Fit rates (k) to mass fraction reduction from soil data (baseline vs. 270-day)
- Naphthalene
  - 39% decrease
  - Half-life = 1.8 to 2.8 days
- PCP
  - 66% decrease
  - Half-life = 0.8 to 1.4 days
  - Onsite aerobic bioreactor, half-life = 0.1 day



Solubility Modeling – Coal Tar Case Study

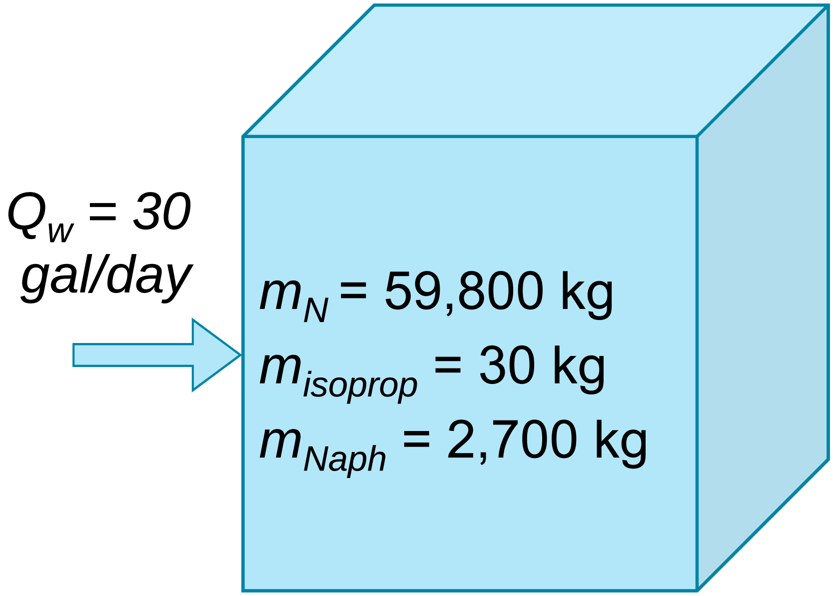


- DNAPL outside of biosparge treatment area
- Mass Fractions
  - 4.4% Naphthalene
  - 0.05% Isopropylbenzene
  - 66% TPH (C8-C40)

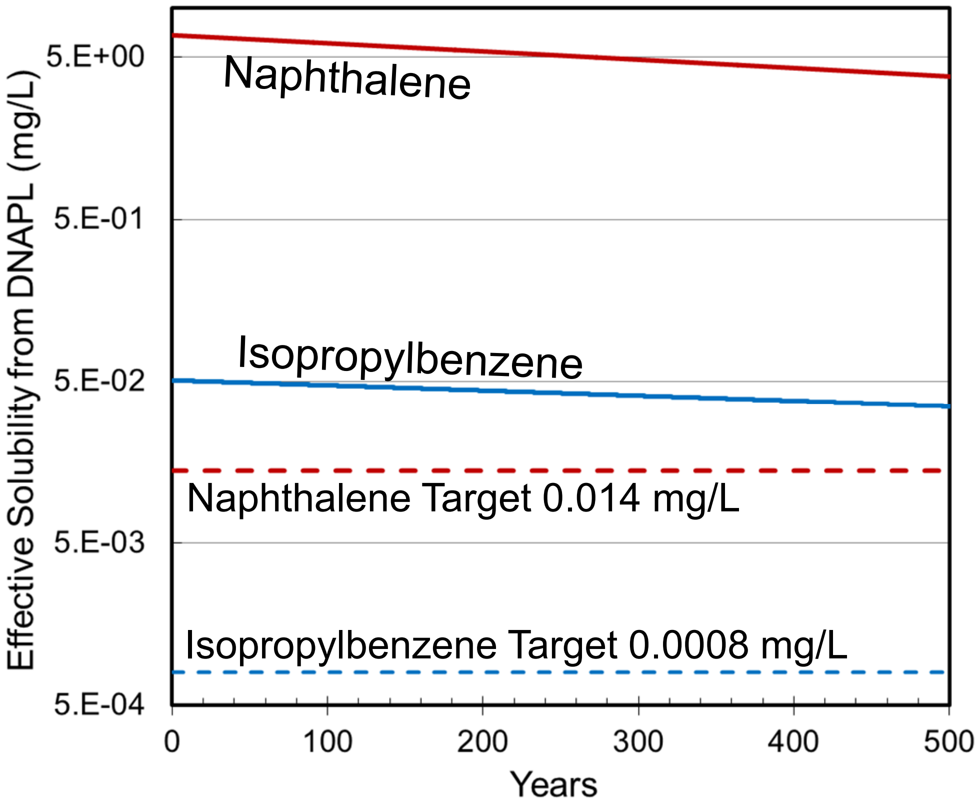
NAPL Depletion Evaluation – Coal Tar Case Study

Solubility Model:

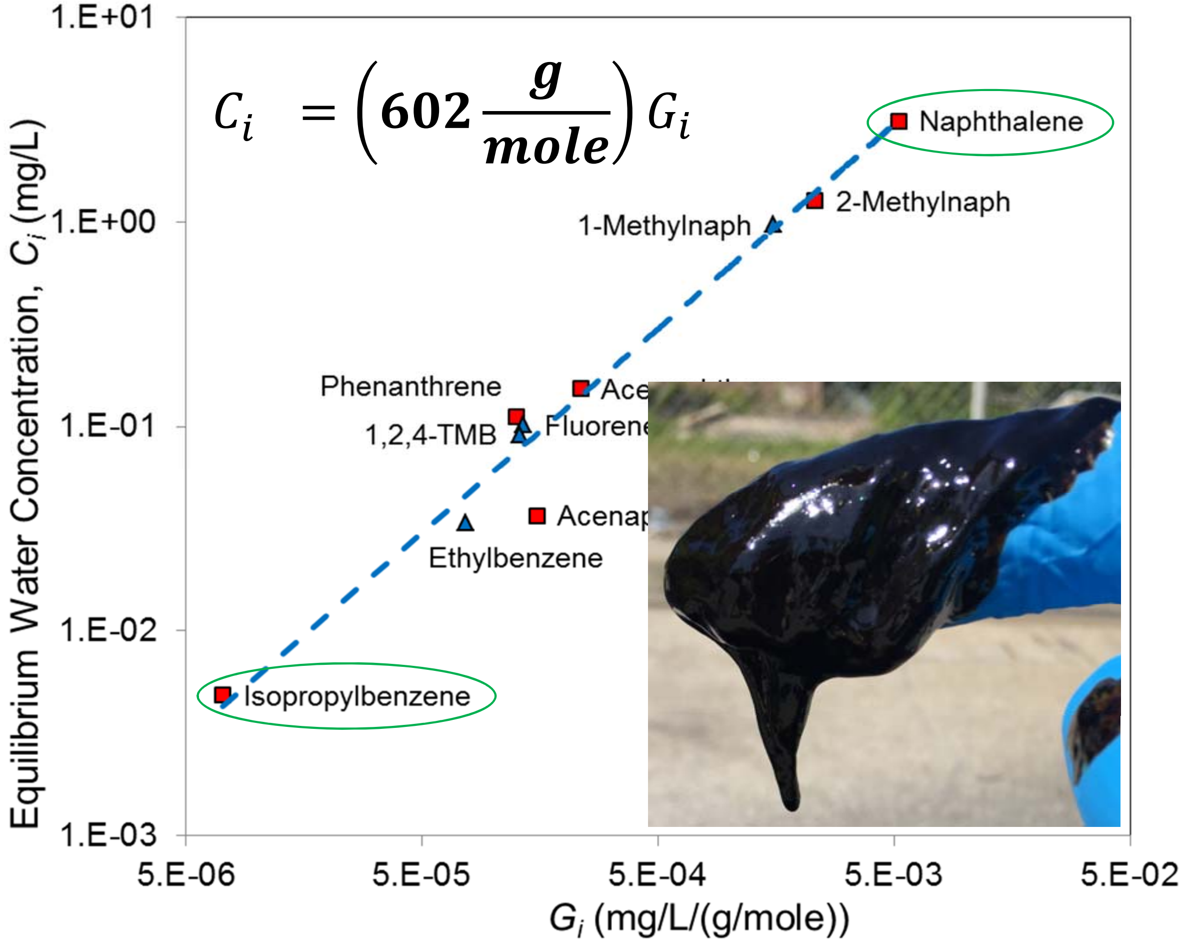
$$C_i = C_N^i \frac{C_s^i}{FR_i} \frac{204 \frac{\text{g}}{\text{mole}}}{MW_i}$$



Dissolution and Advection $\Delta m_{i,d} = Q_w \bullet C_i$ (No biooxidation)



Solubility Modeling – Coal Tar Case Study



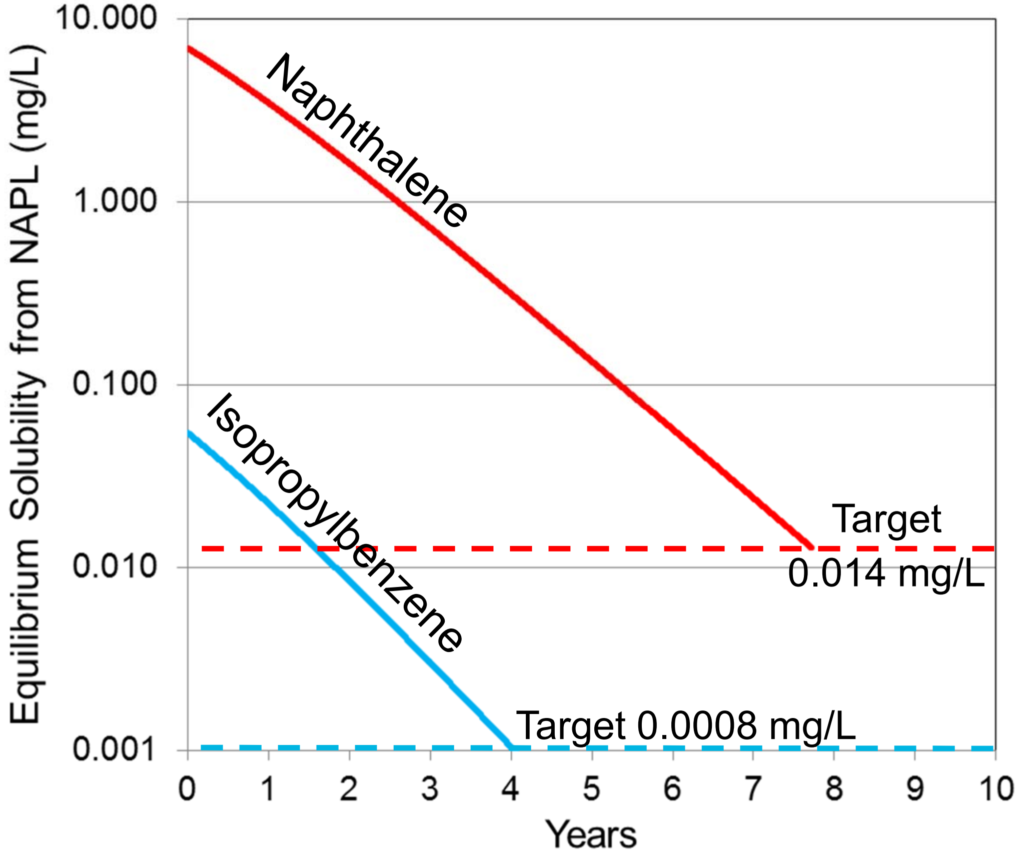
- DNAPL within biosparge treatment area for 1 year
- Mass fractions
  - 0.7% Naphthalene
  - 0.001% Isopropylbenzene
  - 22% TPH (C8-C40)
- Decrease in mass fraction
  - 85% Naphthalene
  - 97% Isopropylbenzene
  - 67% TPH (C8-C40)

NAPL Depletion Evaluation – Coal Tar Case Study

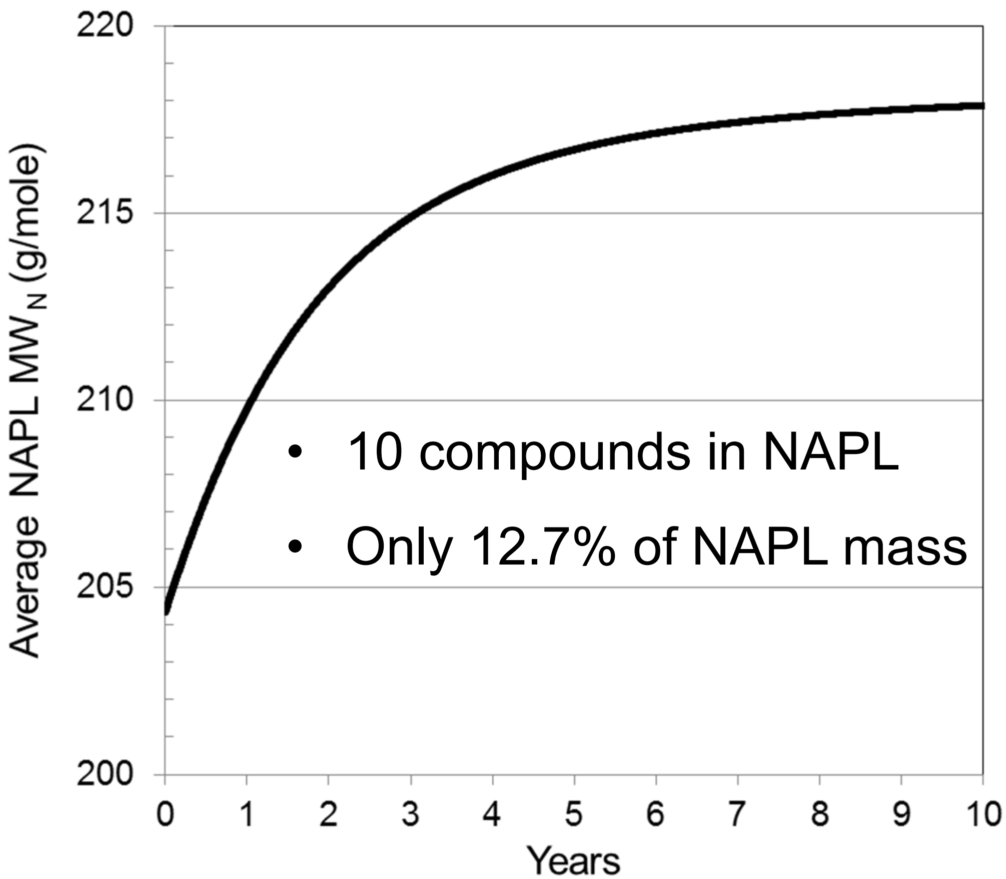
Field-Scale Biosparging Study

- Fit rates (k) to mass fraction reduction in NAPL samples (1 year)
- Naphthalene
    - 85% decrease
    - Half-life = 0.9 days, k = 0.8/d
- Isopropylbenzene
    - 97% decrease
    - Half-life = 0.3 days, k = 2.2/d
- Partitioning to air ignored

Dissolution and Biooxidation



NAPL Depletion Evaluation – Coal Tar Case Study



- 10 compounds in NAPL
- Only 12.7% of NAPL mass

≠ 602 g/mole

Not simulating depletion of TPH (C8-C40)

- 66% to 22%

Effect on solubility model:

$$C_i = \boldsymbol{MW_N} \frac{C_S^i}{FR_i} \frac{C_N^i}{MW_i}$$

As MW_N ⇧ → C_i ⇧ → C_N^i ⇩

- Deplete compound *i* faster
- Time to achieve targets ?

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Summary

- A laboratory-based Raoult's Law solubility model provides a basis for modeling long-term NAPL dissolution
- Biooxidation processes enhance NAPL dissolution and weathering
- Simple mass-balance models are viable tools to evaluate remedial alternatives in the context of a feasibility study

Take Home: Dissolved-phase remediation strategies (including chemical and biological oxidation) are viable alternatives to enhance NAPL composition change and mitigating long-term dissolution from NAPL

- Cost effectively
- Reasonable time

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Thank You!

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