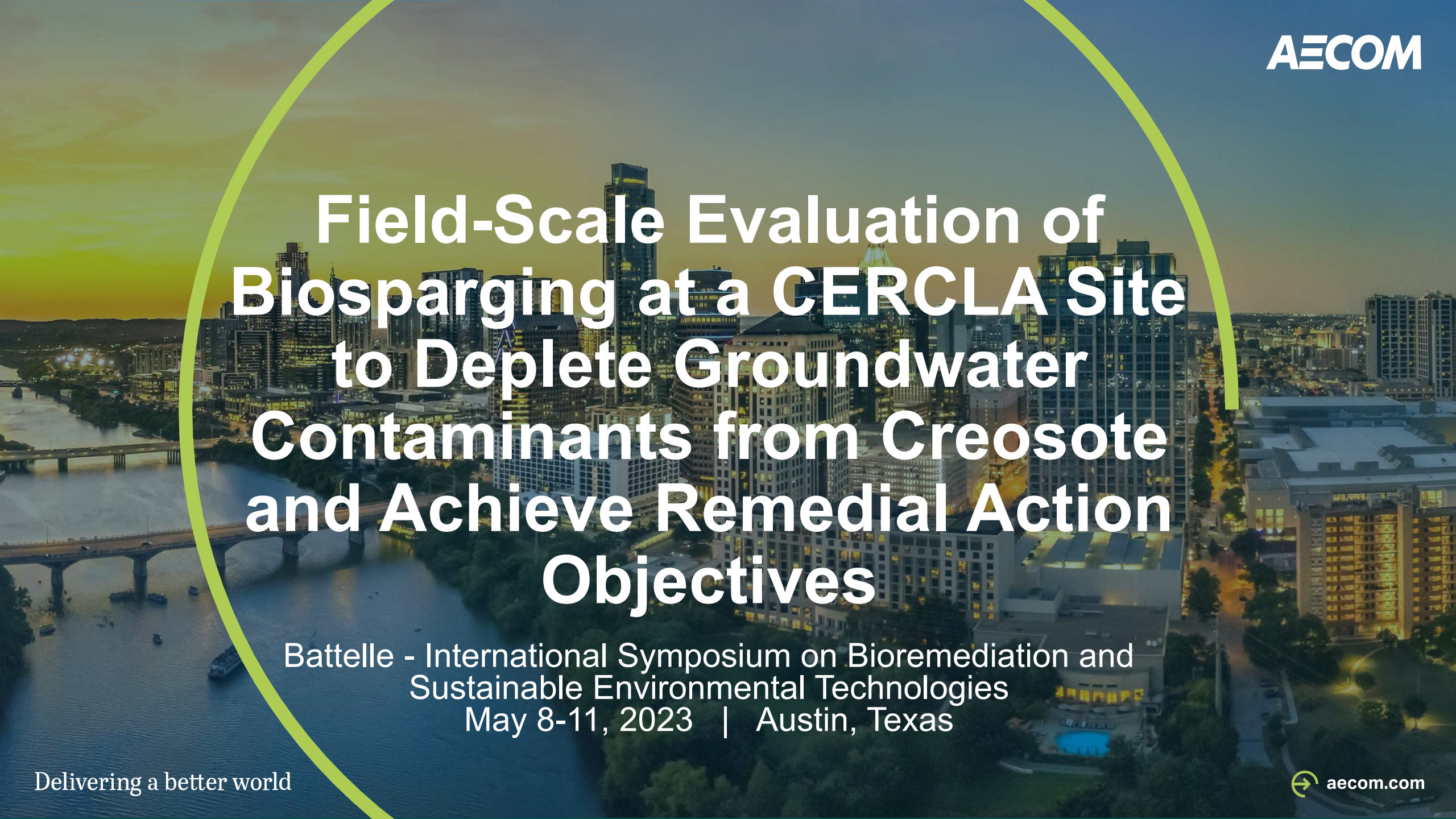

Field-Scale Evaluation of Biosparging at a CERCLA Site to Deplete Groundwater Contaminants from Creosote and Achieve Remedial Action Objectives

Battelle - International Symposium on Bioremediation and Sustainable Environmental Technologies
May 8-11, 2023 | Austin, Texas

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Agenda

01 Treatability Study Background

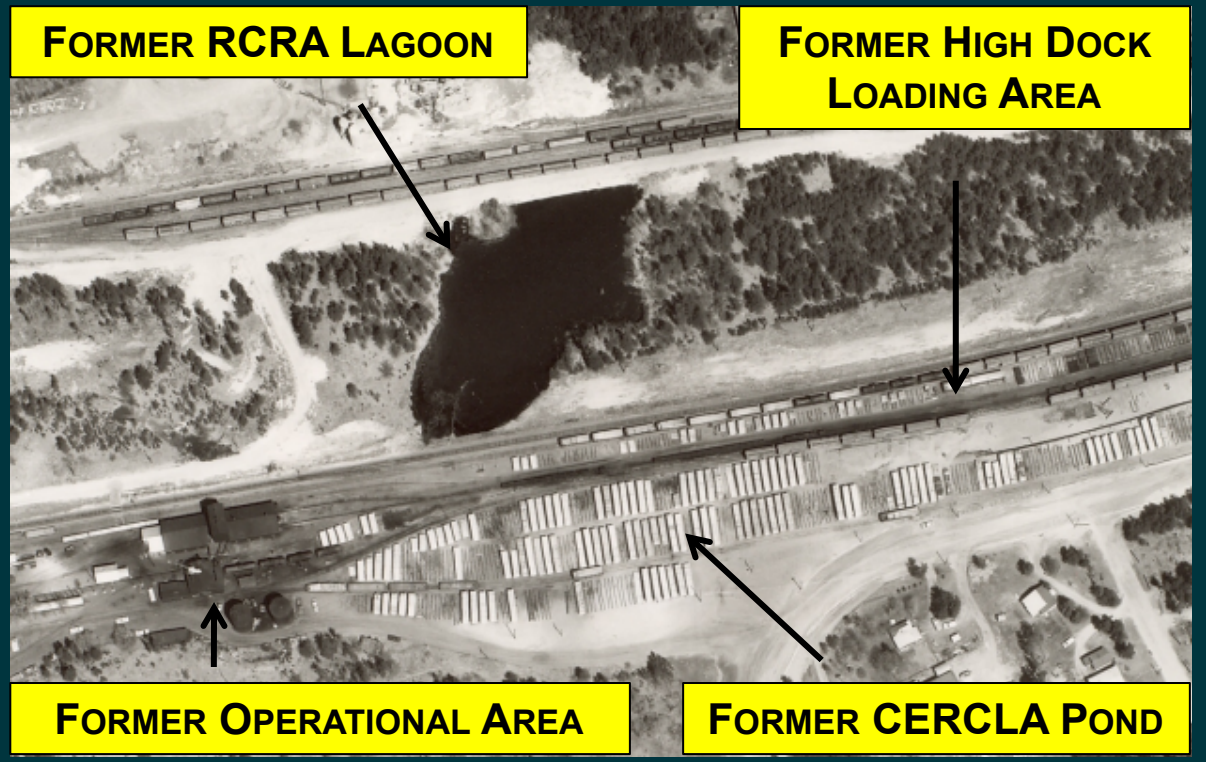
02 Phase 1 Results

03 NAPL Depletion Modelling

Treatability Study Background

Railroad Tie Treatment Plant

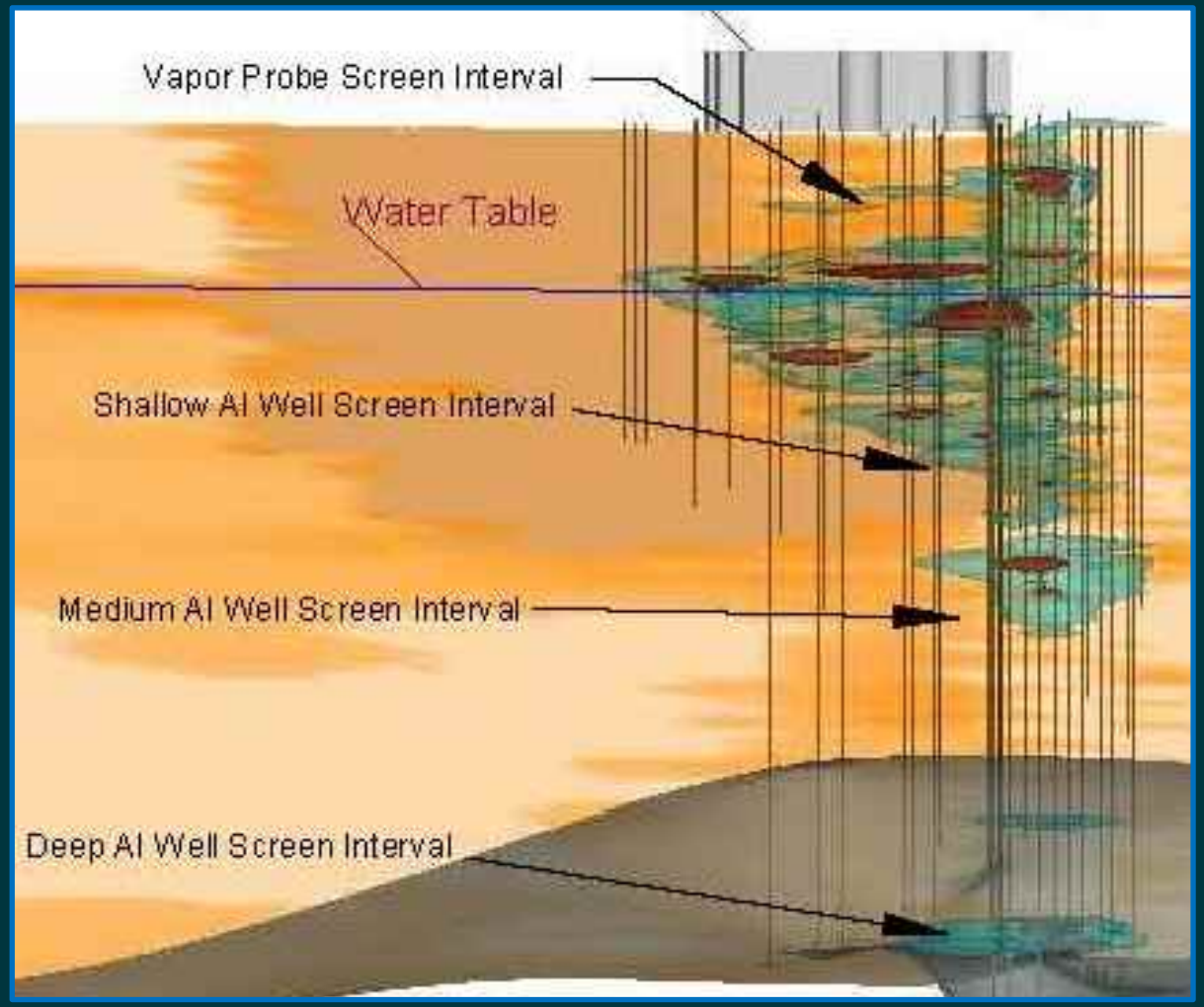
- 1907 – 1986, Plant operates until Consent Order
- 2012, New Settlement Agreement to prepare Supplemental RI/FS
- 2018, Supplemental Focused Feasibility Study
  - Evaluated 11 remedial alternatives
  - Recommended biosparging
  - Not accepted by EPA
- 2019, Agreement to perform Treatability Study
  - Meetings with EPA to advocate for recommended alternative
  - Presented experience from biosparging studies at other sites (creosote and MGP)
  - Developed/presented NAPL Depletion Model to show efficacy of biosparging



Treatability Study Background

Conceptual Site Model

- Creosote NAPL is source of COCs (PAHs and benzene) in groundwater plume
- Plume containment and treatment
  - 1986 – 2008, pump-n-treat
  - 2008 – present, downgradient biosparge treatment transects
  - Natural attenuation
- Natural source zone depletion of creosote
- No complete exposure pathways

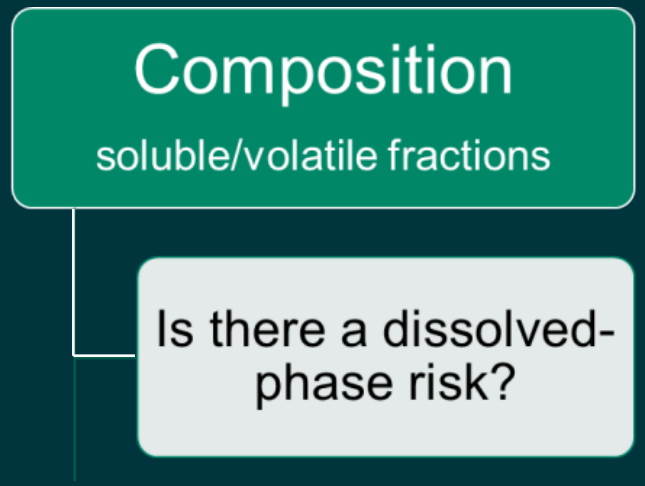


FFS Remedial Action Objective:
Where technically practical, restore groundwater to drinking water standards

Treatability Study Background

Risk-Based NAPL Management Strategy

- Effort is focused on managing risk from creosote



How does biosparging affect NAPL composition?

Can biosparging achieve remediation objectives?

NAPL Depletion Model – New tool to quantify changes in creosote composition and risk to groundwater as a result of biosparging was critical for acceptance

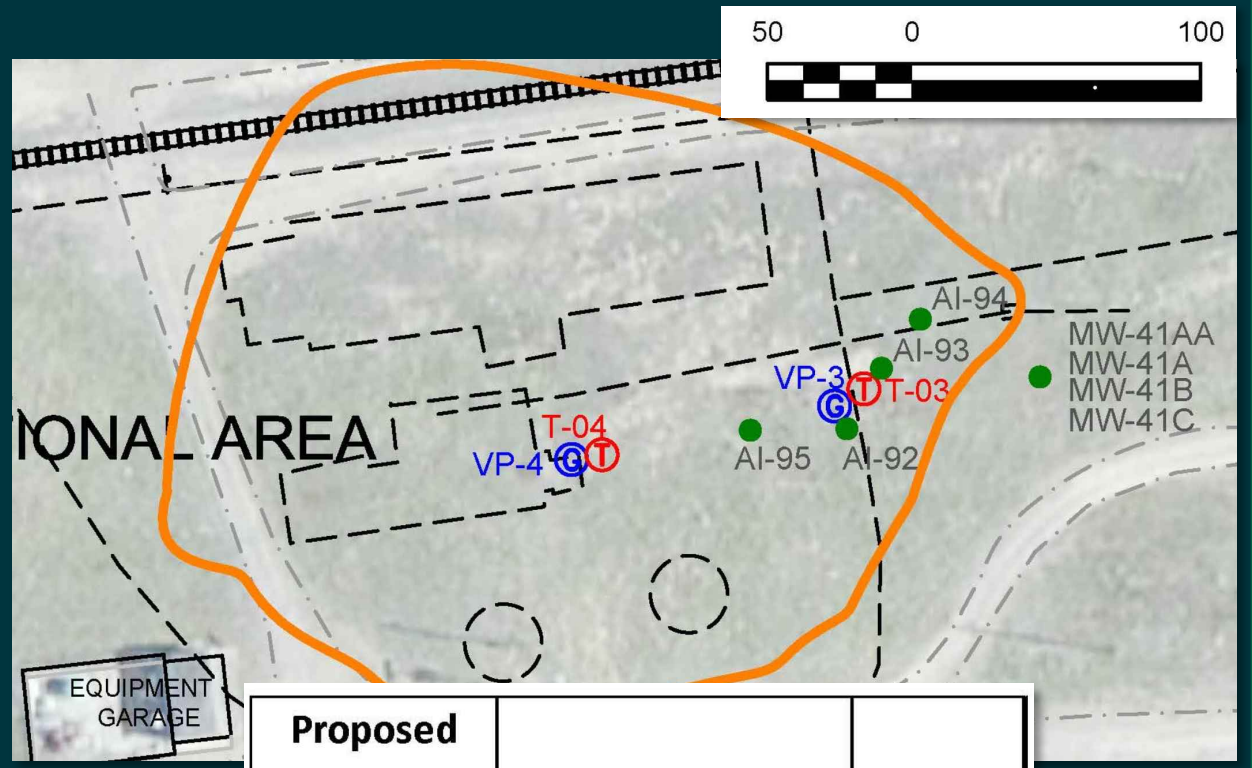
Libby, MT CERCLA Site

- Biosparging treatability studies 2015-2016
- 2018 FFS recommended biosparging
- Quantified and simulated long-term risks to groundwater from NAPL
- Biosparging selected by EPA
- Currently being constructed

Treatability Study Background

Railroad Tie Treatment Plant

- Phase 1 (Sept 2020 – April 2021)
  - Short duration study to support the design and implementation of the long-term Phase 2 study
  - ROIs, flow rates, cycle timing
  - Baseline data (NAPL composition, COCs in groundwater, soil vapor, microbial consortia)
- Phase 2 (startup June 2023)
  - Long-term study (~5 years)
  - Collect performance data and prove feasibility of biosparging achieving RAOs

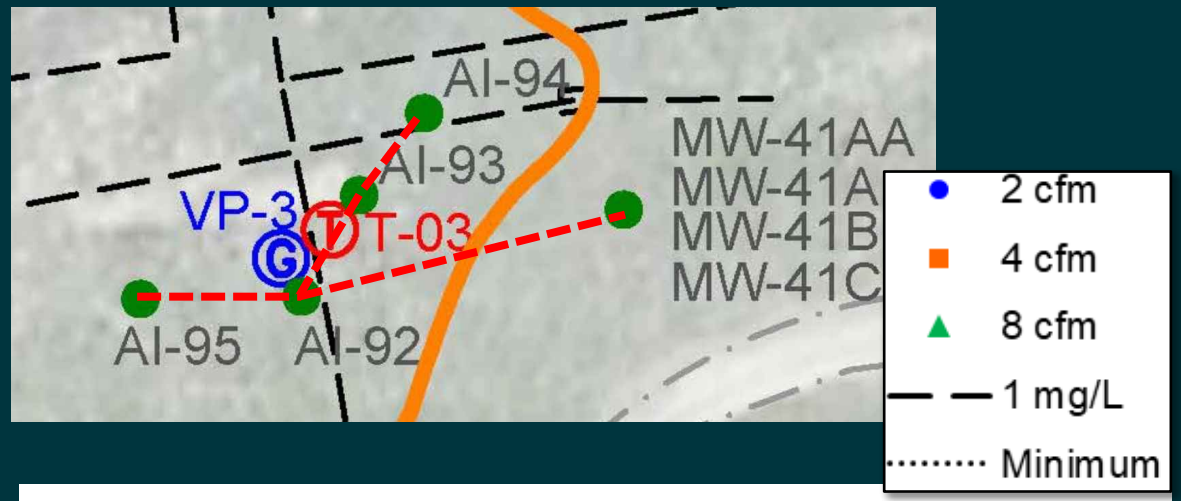


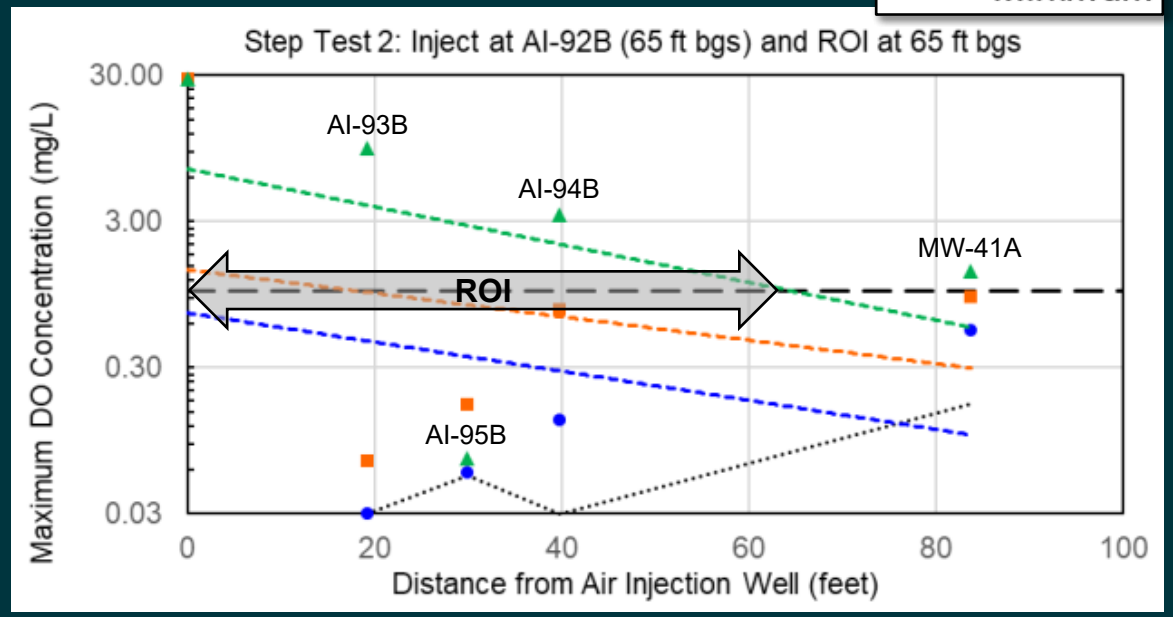
Proposed Phase 1 Well Nest ID	Anticipated Screen Bottom Depth	Screen Length
AI-92	45', 65', 103'	2'
AI-93	45', 65', 103'	2'
AI-94	45', 65', 103'	2'
AI-95	45', 65'	2'
MW-41	30', 45', 65', 100'	5'

Treatability Study – Phase 1 Results

Estimated ROI

- ROI varied based on air flow rate, direction, and depth
  - Shallow (45 ft bgs) – 40 to 60 ft
  - Middle (65 ft bgs) – 20 to 50 ft
  - Deep (103 ft bgs) – 20 ft
- Air injection at middle or deep wells provided sufficient DO laterally and vertically to treat the entire saturated zone
- Provided design basis for Phase 2
  - Entire Operational Area
  - 6 Deep biosparge wells
  - 12 Shallow biosparge wells



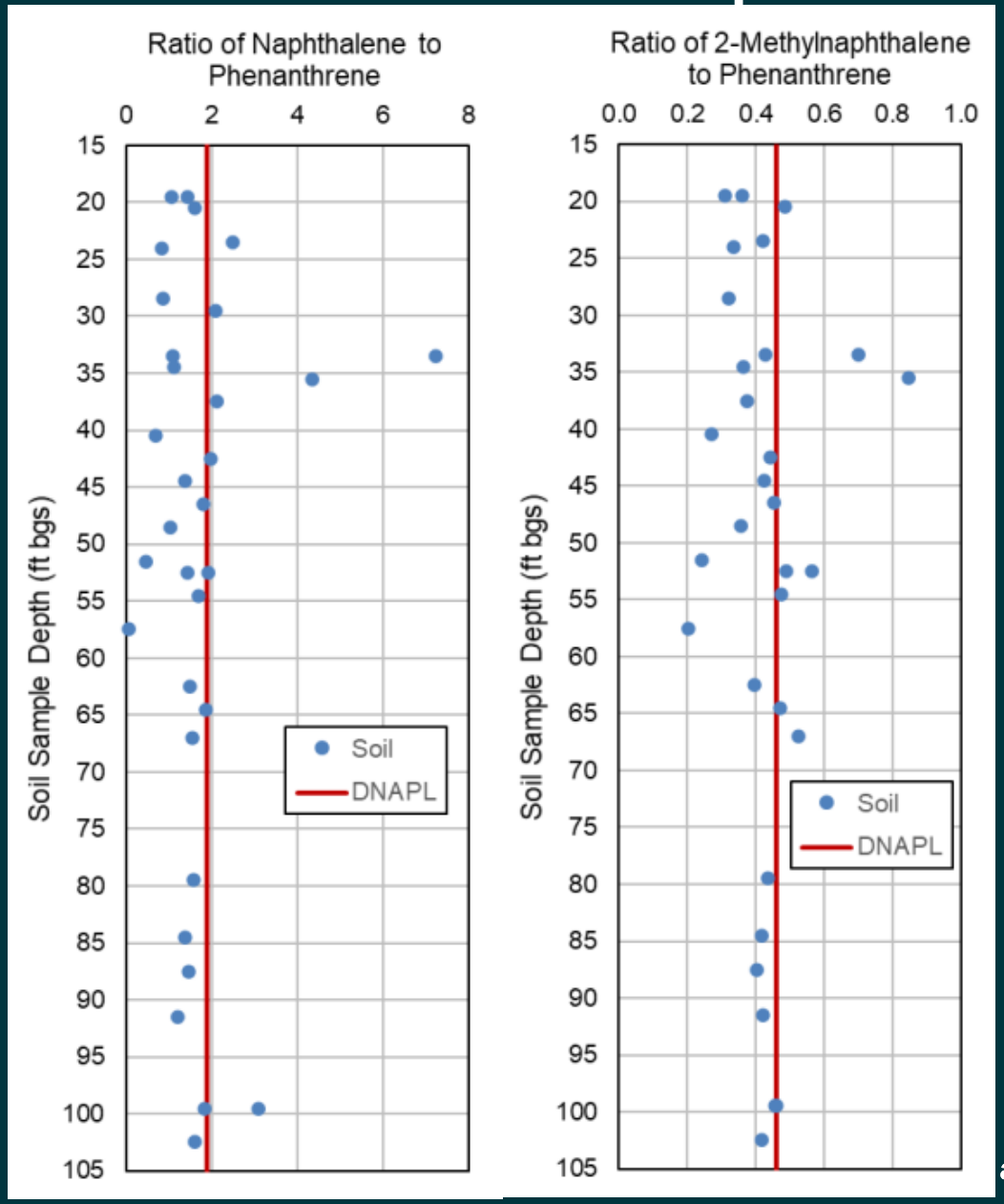


Treatability Study – Phase 1 Results

Performance Evaluation

- Established aerobic conditions and microbial communities
- Significantly reduced concentrations of COCs in groundwater
- Provided baseline estimate of creosote composition
- During 6-month study, decreased the mass and mass fraction of COCs in the creosote
  - BTEX: 31% mass and 23% mass fraction reduction
  - Naphthalene: 14% mass and 4% mass fractions reduction

Baseline Creosote Composition



Treatability Study – Phase 1 Results

Initial Creosote Properties (103 ft bgs)

- Density (50 °C) = 1.059 g/mL
- Viscosity (50 °C) = 49 cP
- Composition
  - BTEX = 0.16%
  - Naphthalene = 11.2%
  - 2-Methylnaphthalene = 2.7%
  - C8-C35 Aliphatics & Aromatics = 57%

Preliminary Performance Modeling

- NAPL composition and equilibrium studies
- NAPL Depletion Model
  - Raoult's Law Solubility Model
  - 1st-Order Biooxidiation

Creosote Composition Change	BTEX	Naphthalene	2-Methylnaphthalene
Mass Fraction (6 mos)	-23%	-4%	+15%
Mass Fraction (1.5 yr)	-34%	-2%	+14%
Mass (6 mos)	-31%	-14%	No change
Mass (1.5 yr)	-56%	-18%	-4%

Treatability Study – Preliminary Performance Modeling

NAPL Depletion Model

- Pore-scale model that simulates enhanced dissolution of creosote constituents caused by biooxidation in groundwater
- Equilibrium Solubility Model – Raoult's Law

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

MW_N = average molecular weight of the NAPL

Laboratory Method to Estimate MW_N

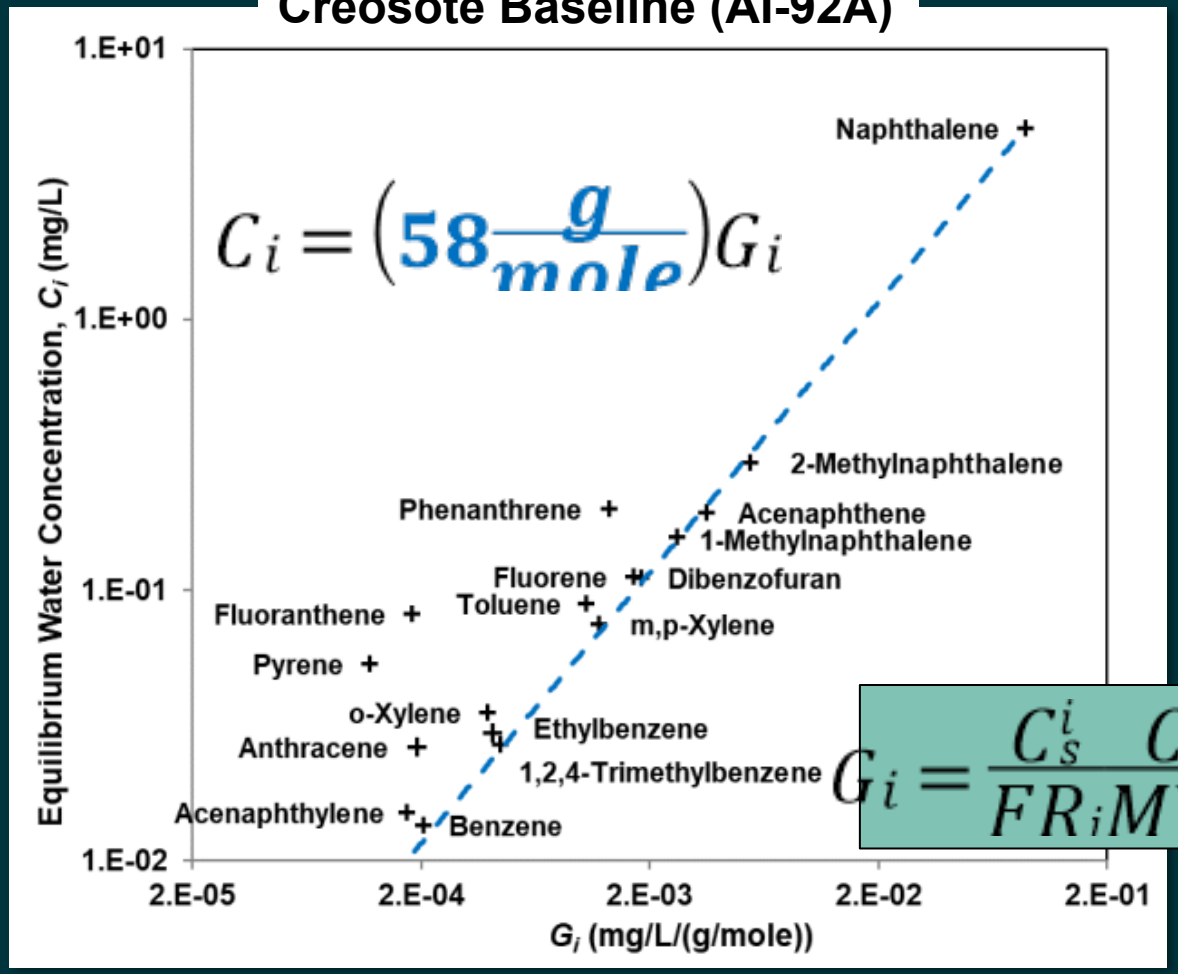
- Mass fraction of target compounds in the NAPL
- NAPL-water equilibrium studies to quantify equilibrium aqueous solubility of target compounds

For More Information on Model

- Brown et al. 2005. Environmental Toxicology and Chemistry, Vol. 24, No. 8, pp. 1886-1892
- Modeling Depletion of Mixed NAPLs to Evaluate Risk to Groundwater and Remediation Timeframe, Battelle Chlorinated Conference, May 2022, Palm Springs, CA

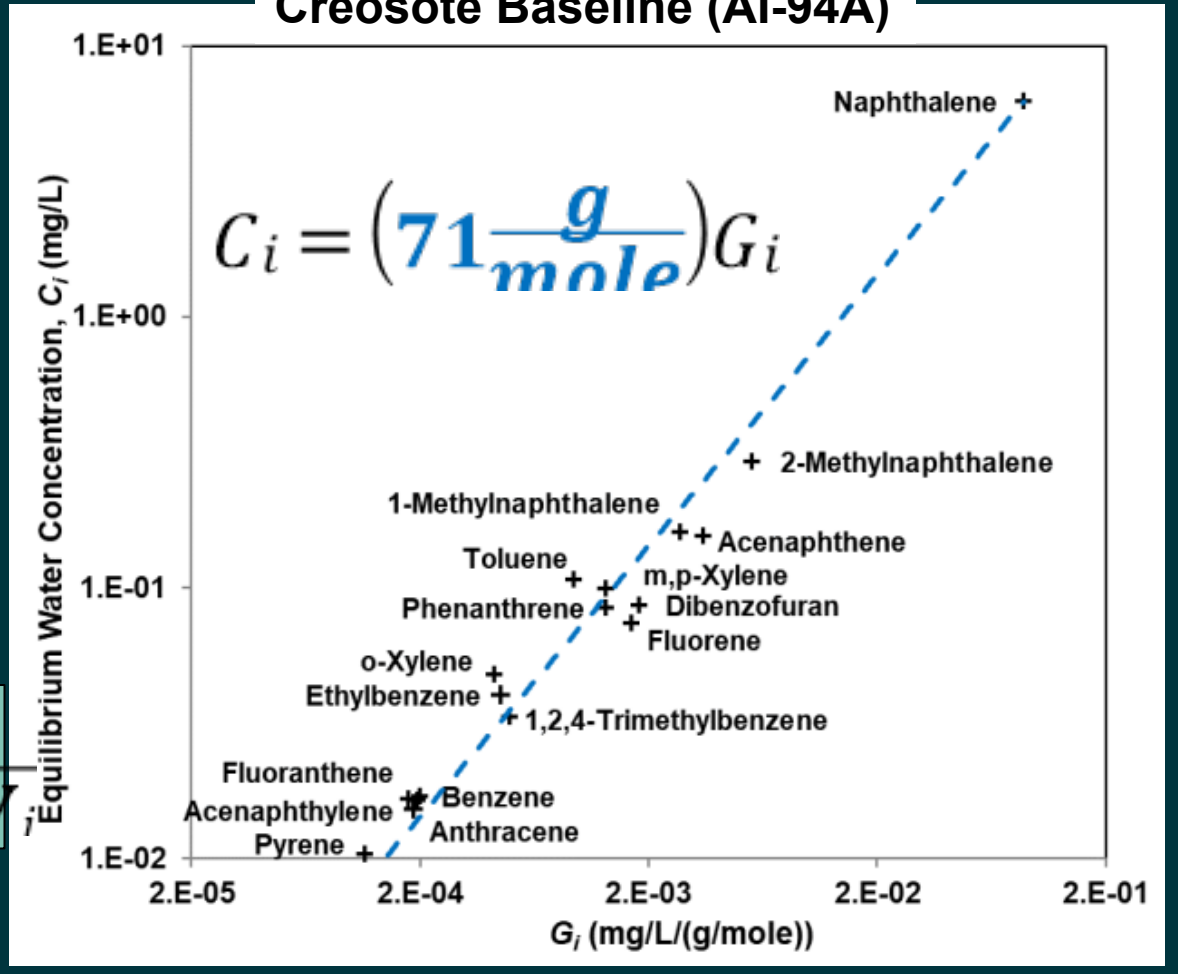
Treatability Study – Preliminary Performance Modeling

Creosote Baseline (AI-92A)



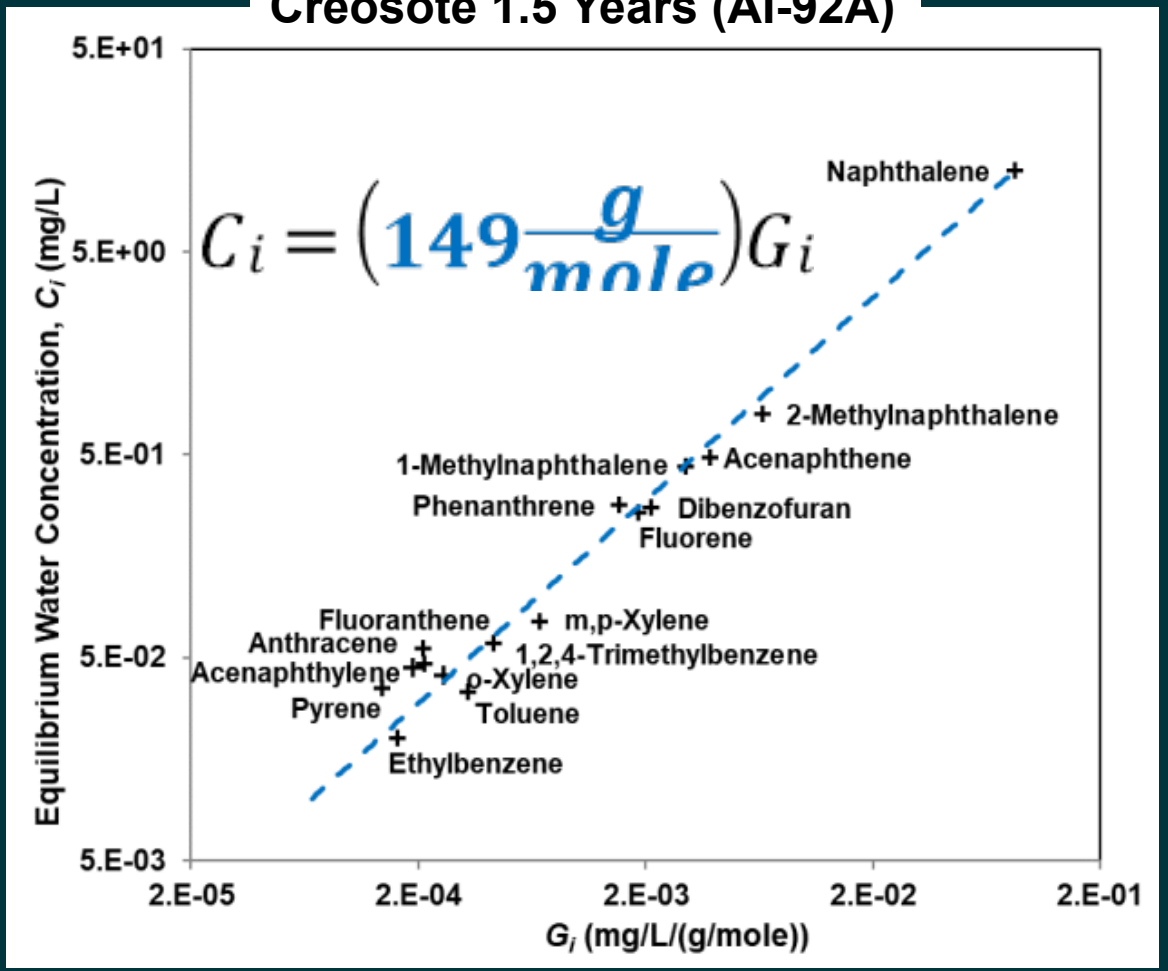
$$G_i = \frac{C_s^i \quad C_N^i}{FR_i MW_i}$$

Creosote Baseline (AI-94A)

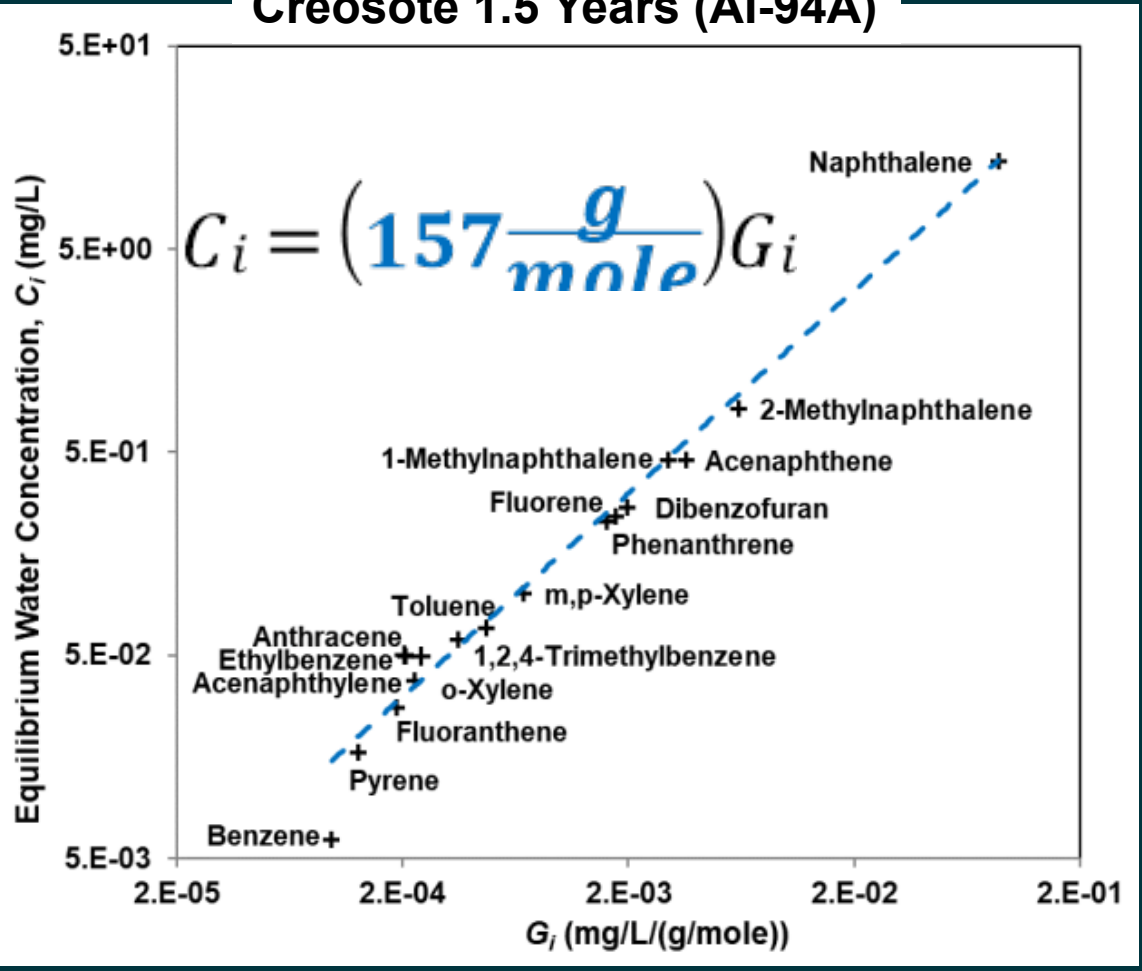


Treatability Study – Preliminary Performance Modeling

Creosote 1.5 Years (AI-92A)



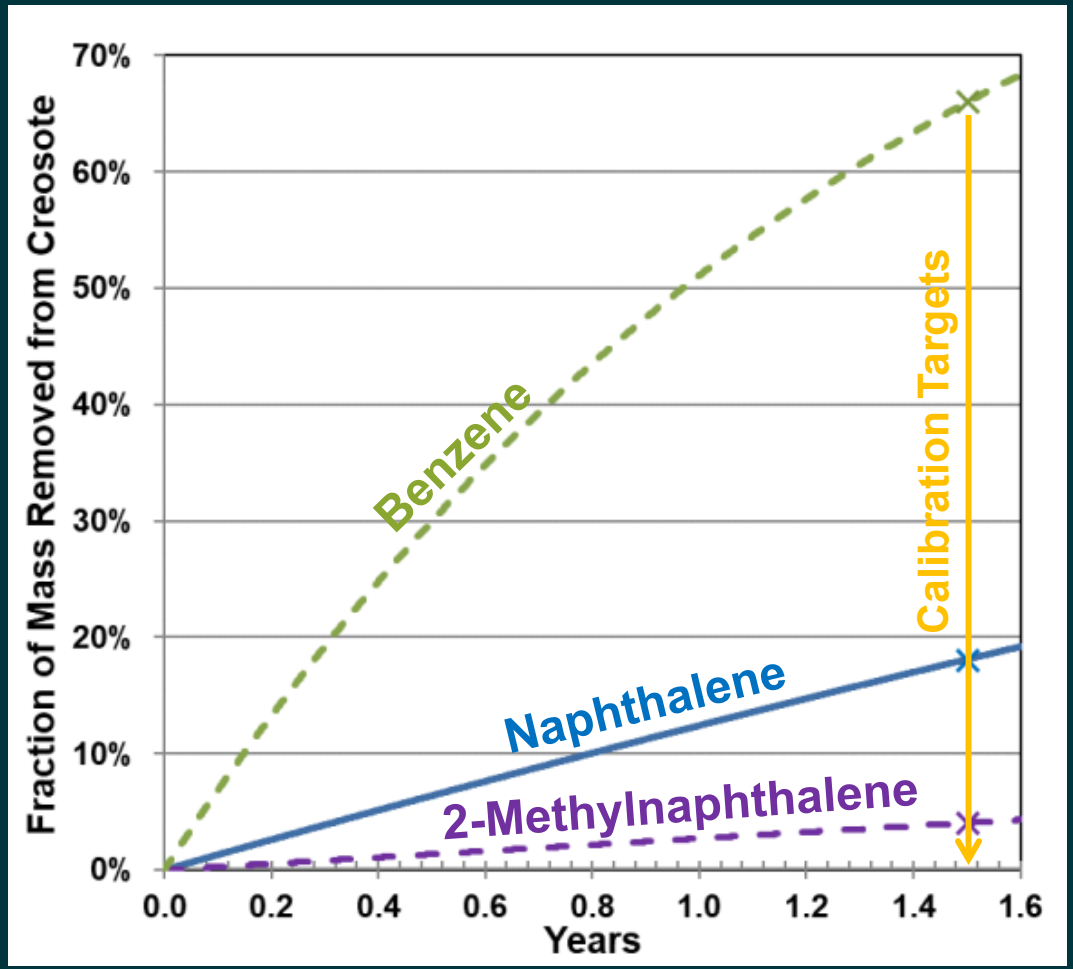
Creosote 1.5 Years (AI-94A)



Treatability Study – Preliminary Performance Modeling

Model Calibration (1.5 years)

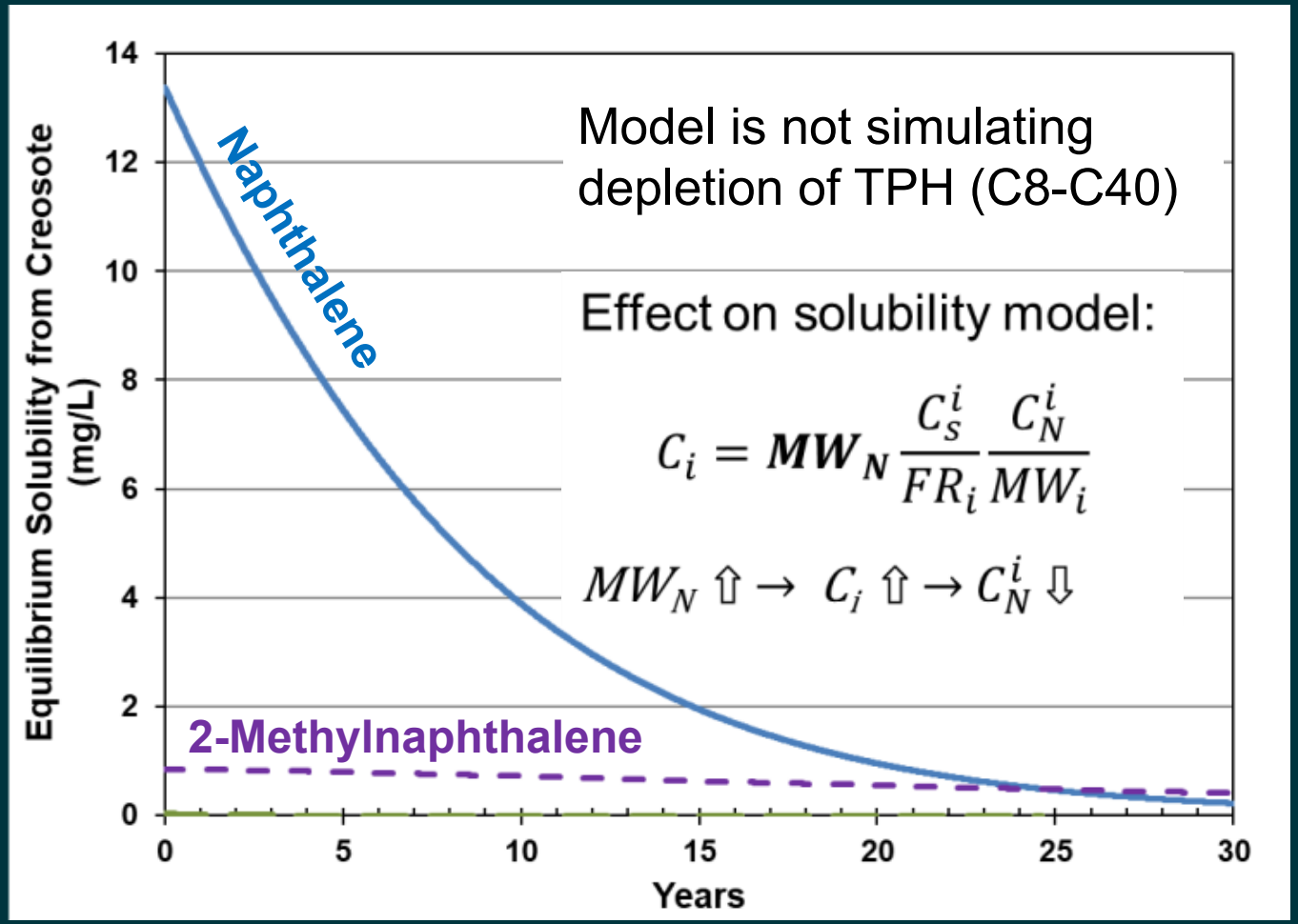
- Assumed S_N=10%
- Fit rates (k) to mass reduction from NAPL data
- Naphthalene
  - 18% decrease
  - $t_{1/2}$ = 2.2 days
- 2-Methylnaphthalene
  - 4% decrease
  - $t_{1/2}$ = 2.8 days
- Benzene
  - 66% decrease
  - $t_{1/2}$ > 10 days (not likely)



Treatability Study – Preliminary Performance Modeling

Preliminary Model

- Indicates benzene will be depleted after ~5 years
  - More uncertainty in solubility model because of very low initial mass fraction
- Indicates remediation timeframes for PAHs are much longer than observed at other sites (creosote and MGP/tar)
- Average creosote MWs are significantly less than observed at other sites
- Current model unable to simulate observed increase in creosote MW



Treatability Study – Performance Modeling

Observations

- Evaluation of creosote composition during the Phase 1 study shows biosparging is decreasing the mass of groundwater contaminants in the creosote and decreasing risk to groundwater
- Increasing creosote average MW shows depletion of lighter-end hydrocarbons
- The preliminary NAPL depletion model estimates PAH depletion is longer than observed at other sites because of current model limitations

Recommendations

- Update model calibration as creosote composition data is collected during the Phase 2 study (at least annually)
- Revise NAPL depletion model to include observed changes in creosote average MW
  - Based on estimates of MW from laboratory solubility studies
  - Include more creosote constituents in the model
  - Fit curve to trends in average MW to override calculation of changes to MW as constituents are depleted

Thank You!

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