Engineering *In situ* Anaerobic Bio-Oxidation of Petroleum Hydrocarbons

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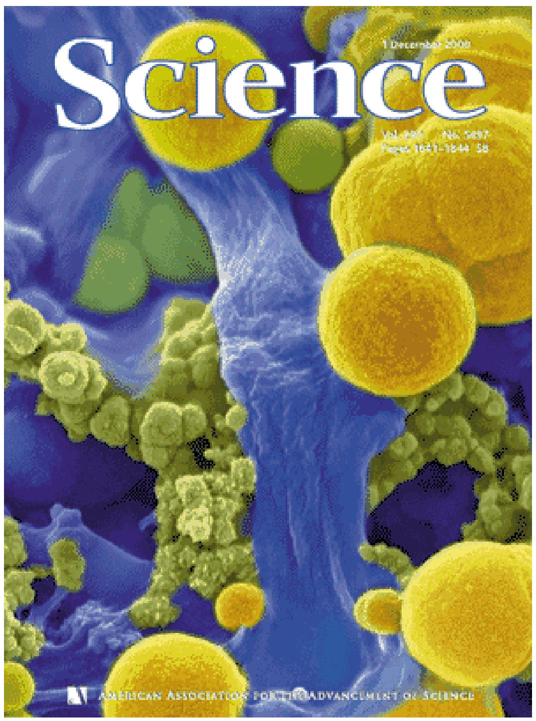
Outline

- Technology background
  - Definitions
  - Kinetic considerations
  - Why sulfate?
- Case Studies
  - Soluble sulfate injections
  - Intrinsic biogeochemical controls
  - Treatment performance
- Conclusions

What Is Enhanced ABOx?

- ABOx is the utilization of non-oxygen electron acceptors in metabolizing residual hydrocarbons
- Under appropriate biogeochemical conditions, sulfate reducing microorganisms proliferate



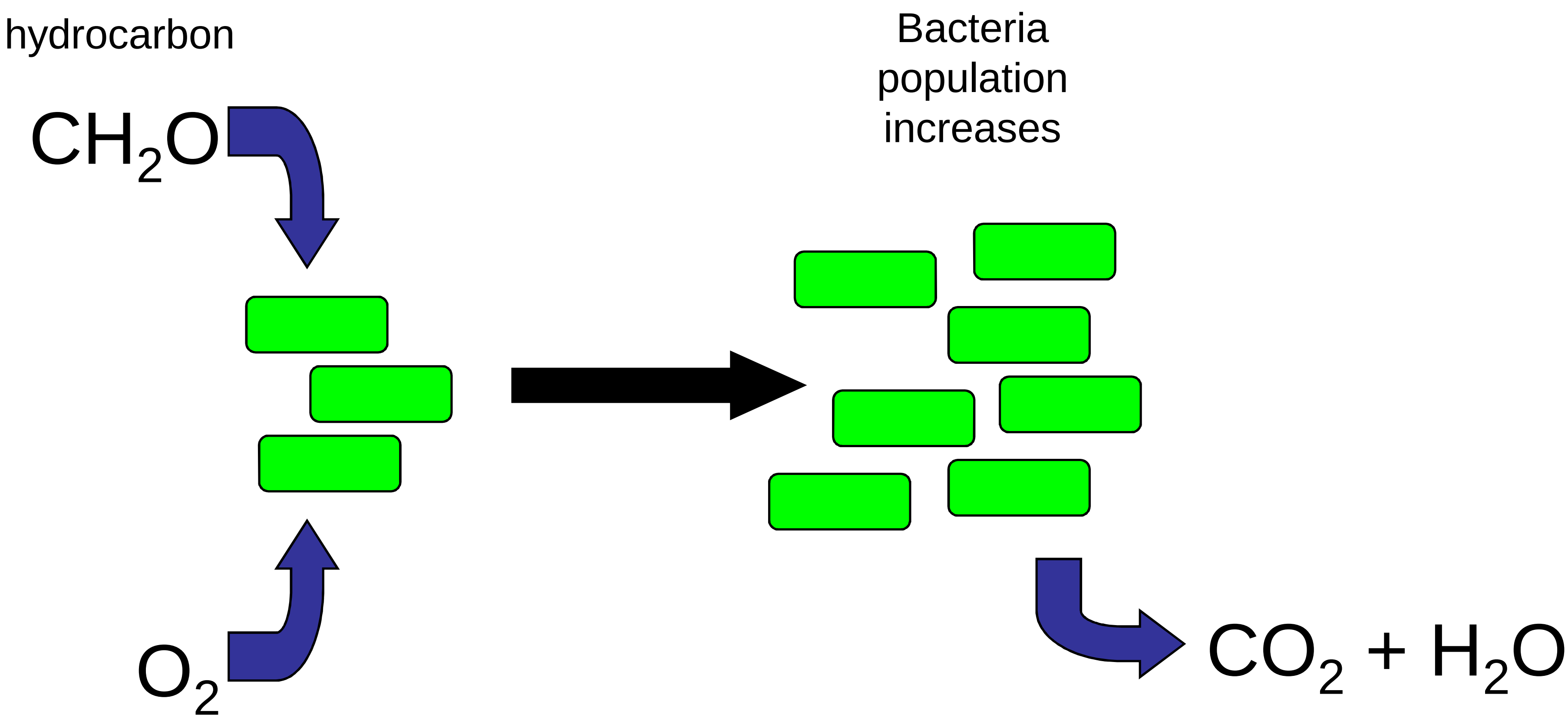
(Science, 2000)

$$\text{(benzene) } C_6H_6 + 3.75\ SO_4^{2-} + 3H_2O \rightarrow$$

$$1.875\ H_2S + 1.875\ HS^{-} + 6\ HCO_3^{-} + 0.375\ H^{+}$$

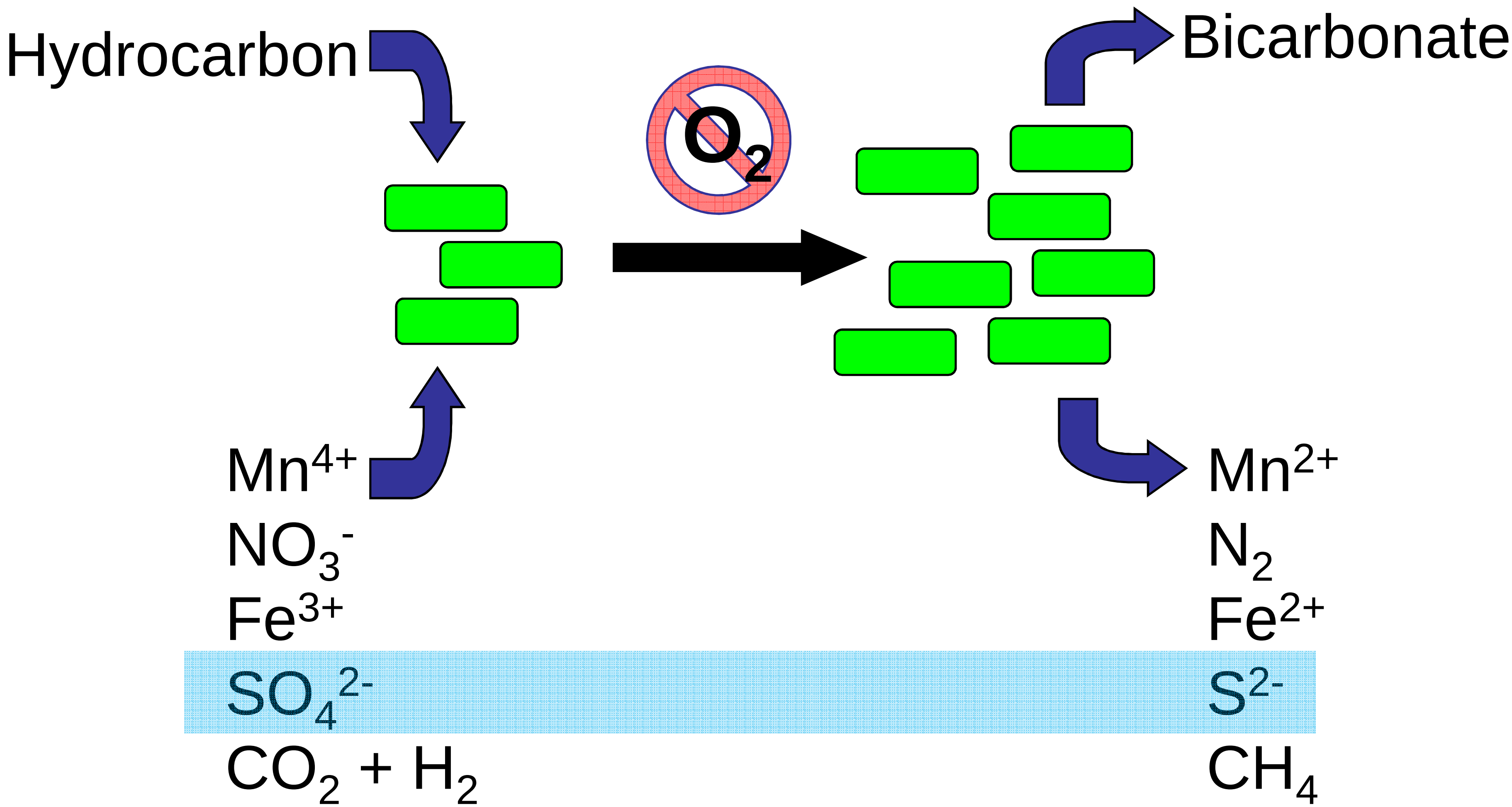
- Anaerobic oxidative processes are effective on broad classes of petroleum hydrocarbons (electron donors)
- ABOx is the engineered application of non-oxygen electron acceptors
  - Potential to be passive and effective

Definition: Aerobic Bio-Oxidation



Redrawn from ITRC BioDNAPL training materials

Definition: Anaerobic Bio-Oxidation



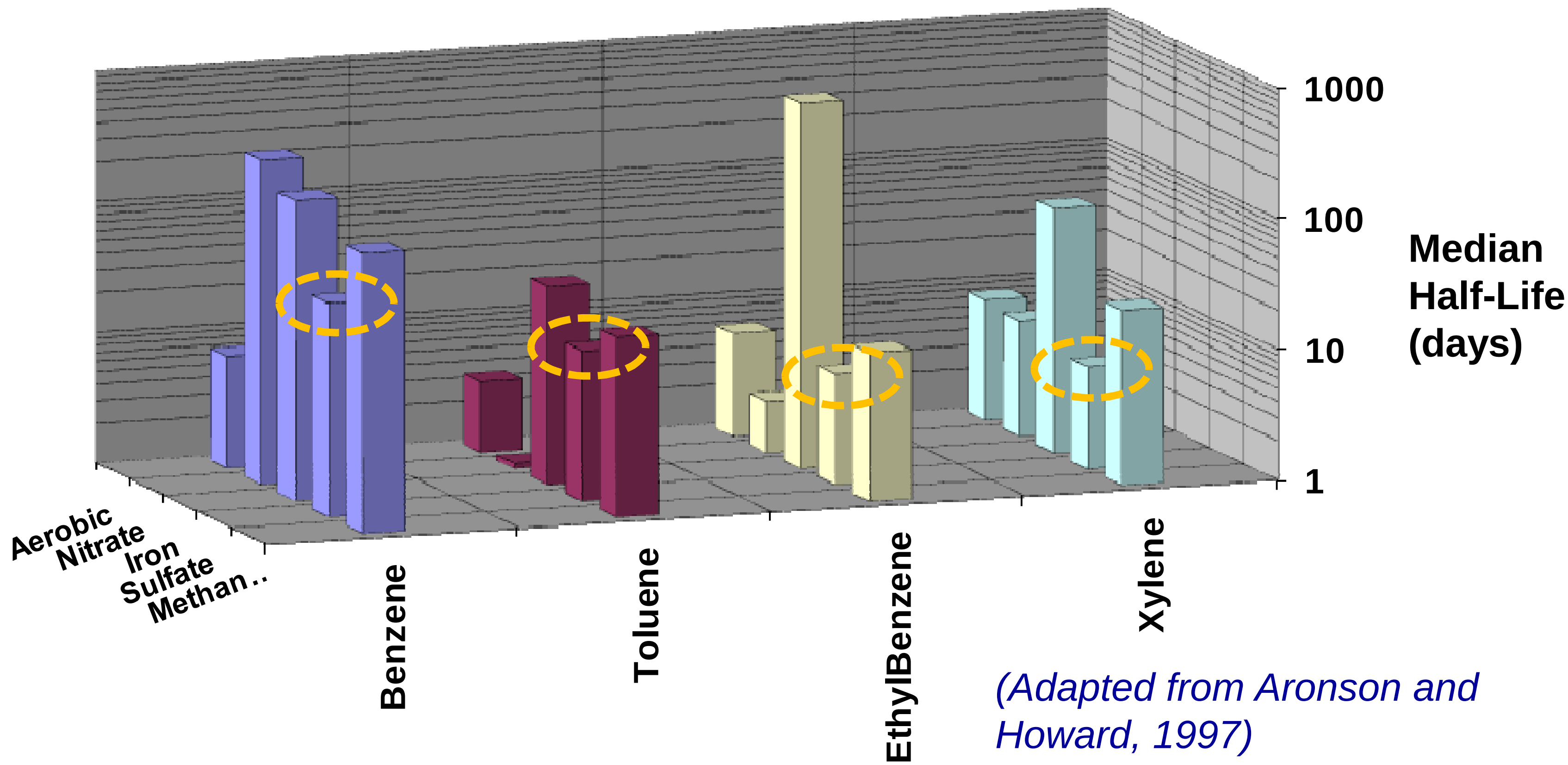
Redrawn from ITRC BioDNAPL training materials

Comparative Electron Acceptor Potential to Degrade Benzene

Electron Acceptor (EA)	Effective Max Concentration in Water (mg/L)	Reaction Yield: benzene mass degraded per unit mass of EA	Potential Max Benzene Degraded (mg/L)	Potential Complications
Oxygen (ambient air sources)	9 – 10	0.33	3.0 – 3.3	•Limited solubility •Numerous non-target scavengers •Potential for aquifer clogging through biofouling and iron precipitation
Oxygen (pure)	60 – 70	0.33	19.8 – 23.1	
Nitrate	670,000 ($NaNO_3$) 1.1x105 ($Mg(NO_3)_2$)	0.21	140,000 220,000	•Primary MCL – 10 mg/L NO_3-N (45 mg/L NO_3)
Iron (III)	0 - 1	0.024	0 – 0.024	• Not practical to inject – very low solubility at neutral aquifer pH
Sulfate	70,000 (Na_2SO_4) 250,000 ($MgSO_4$)	0.20	9,000 25,000	•*Secondary MCL for sulfate – 250 mg/L •Hydrogen sulfide; rarely documented as an issue in the field

(Adapted from Cunningham et al., 2001)

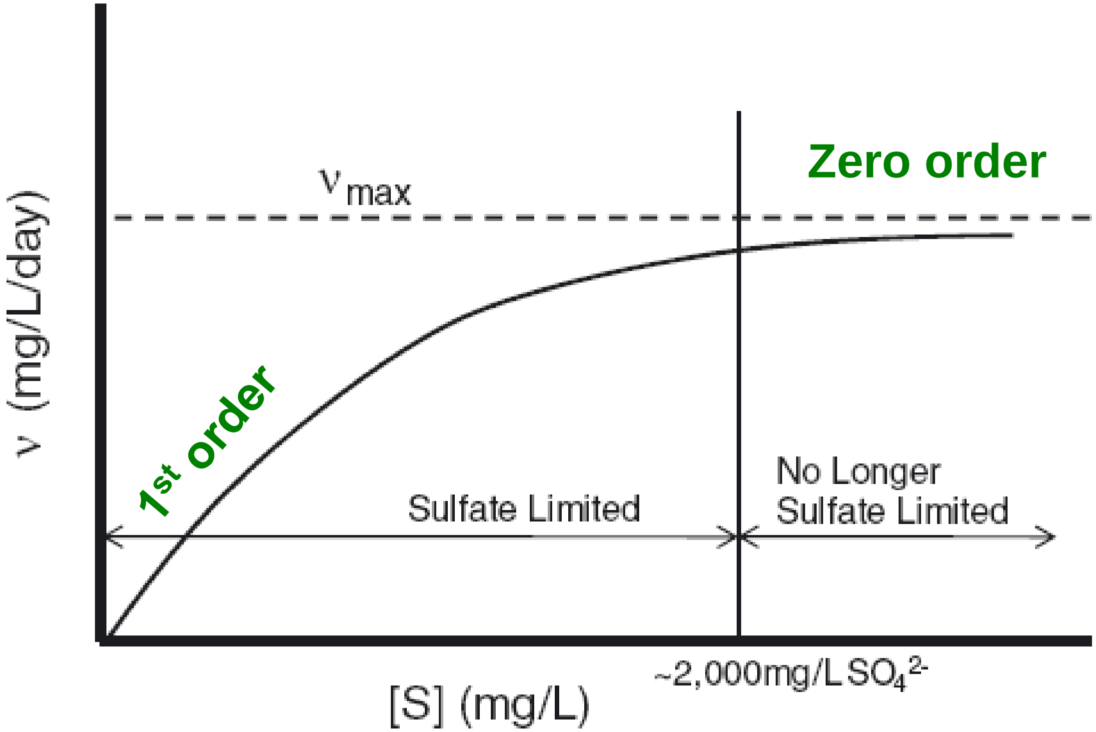
Petroleum Hydrocarbons Oxidation



(Adapted from Aronson and Howard, 1997)

Anaerobic biodegradation of petroleum hydrocarbons is well-founded in the literature

Microbial-Mediated Kinetic Rates

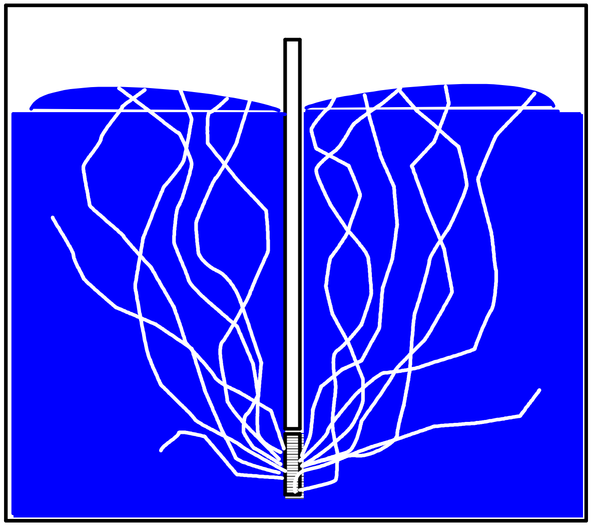


Based on sulfate reduction kinetic data provided by Roychoudhury and McCormick (2006)

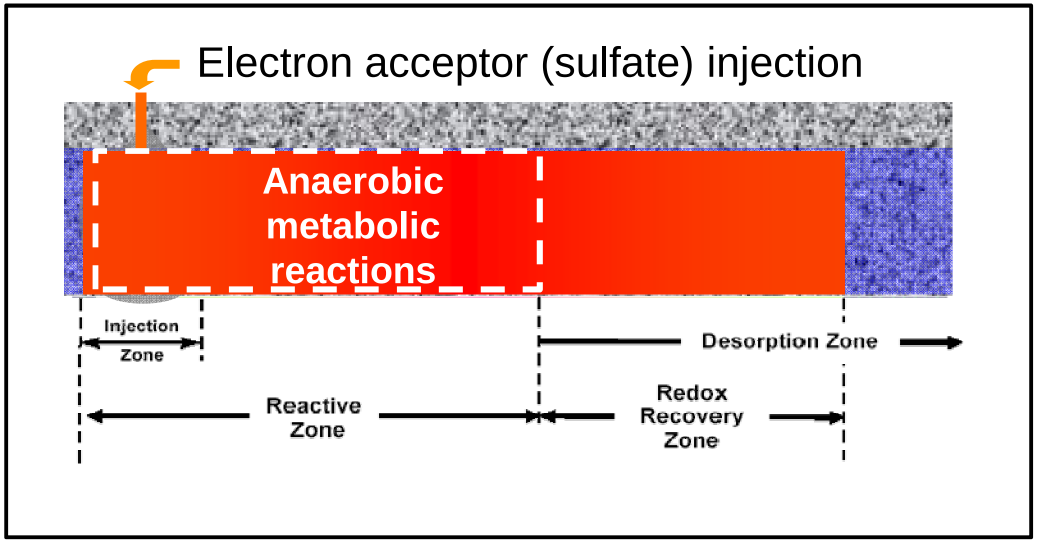
- Most petroleum hydrocarbon sites are sulfate-limited
- Increased sulfate-based oxidation rates with increased sulfate concentrations
  - Intrinsic
    10s to 100s mg/L
  - Engineered
    1,000s mg/L

ABOx of Petroleum Hydrocarbons Using Alternate Electron Acceptors

Air sparge/aerobic bio



Liquid injection/anaerobic bio



Why use sulfate?

- Much higher solubility than oxygen – greater than 1,000 fold increase
- Higher efficiency of delivery – mass injected versus mass that facilitates treatment
- Lower matrix demand losses, less fouling
- Anaerobic bioremediation – expedited hydrocarbon dissolution, faster cleanup

FIELD DEMONSTRATION STUDY

FUEL DISTRIBUTION CENTER

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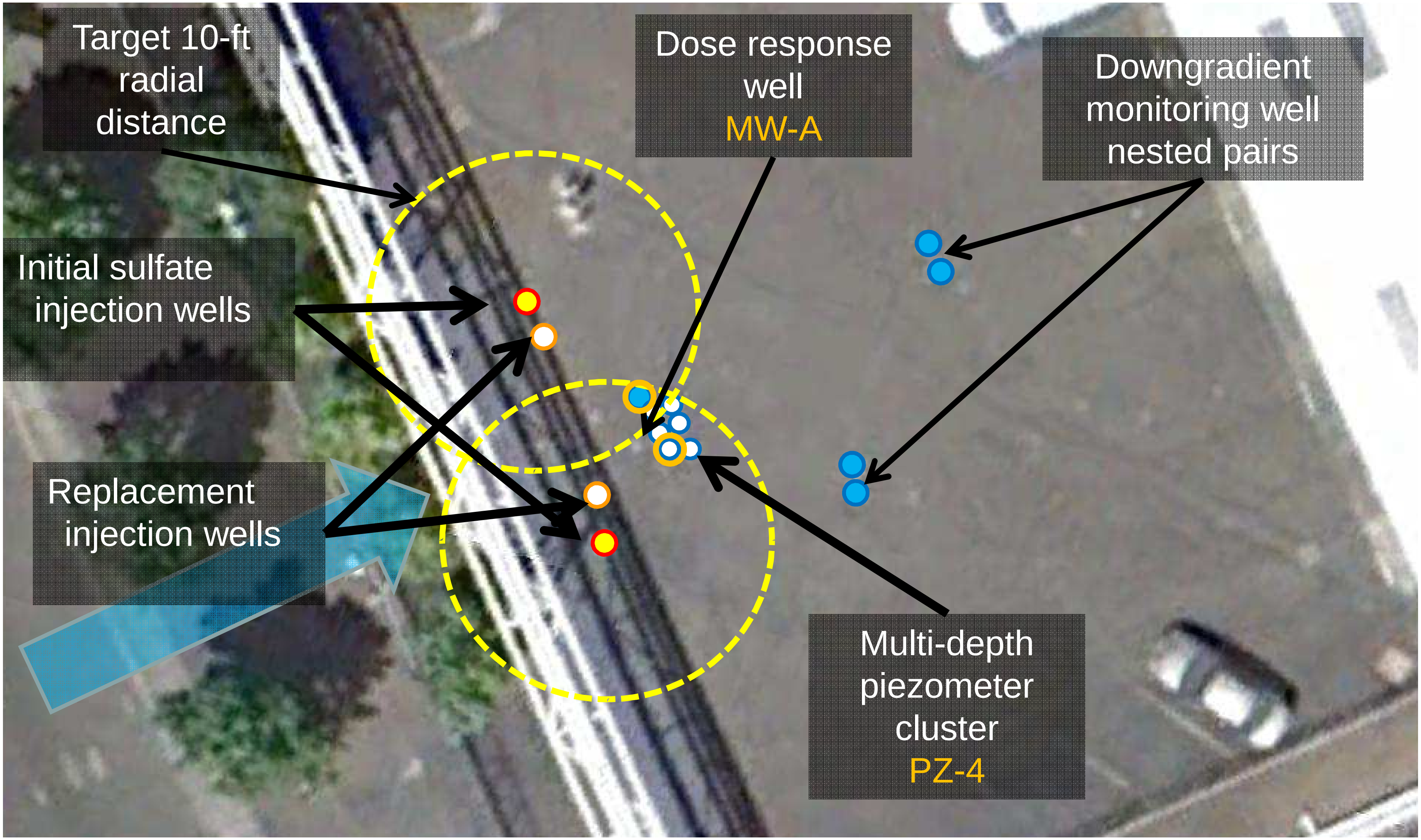
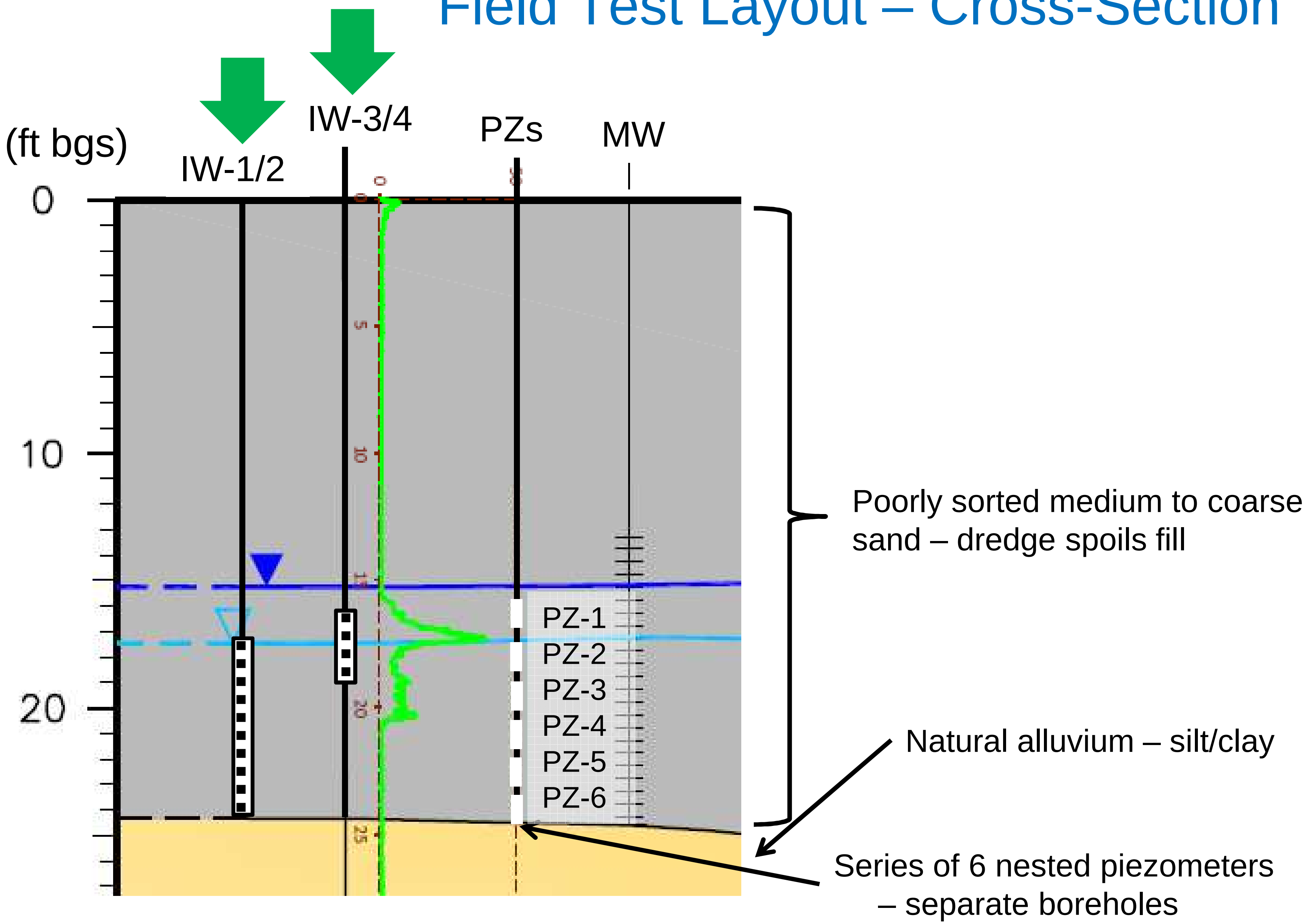
Field Test Layout – Plan



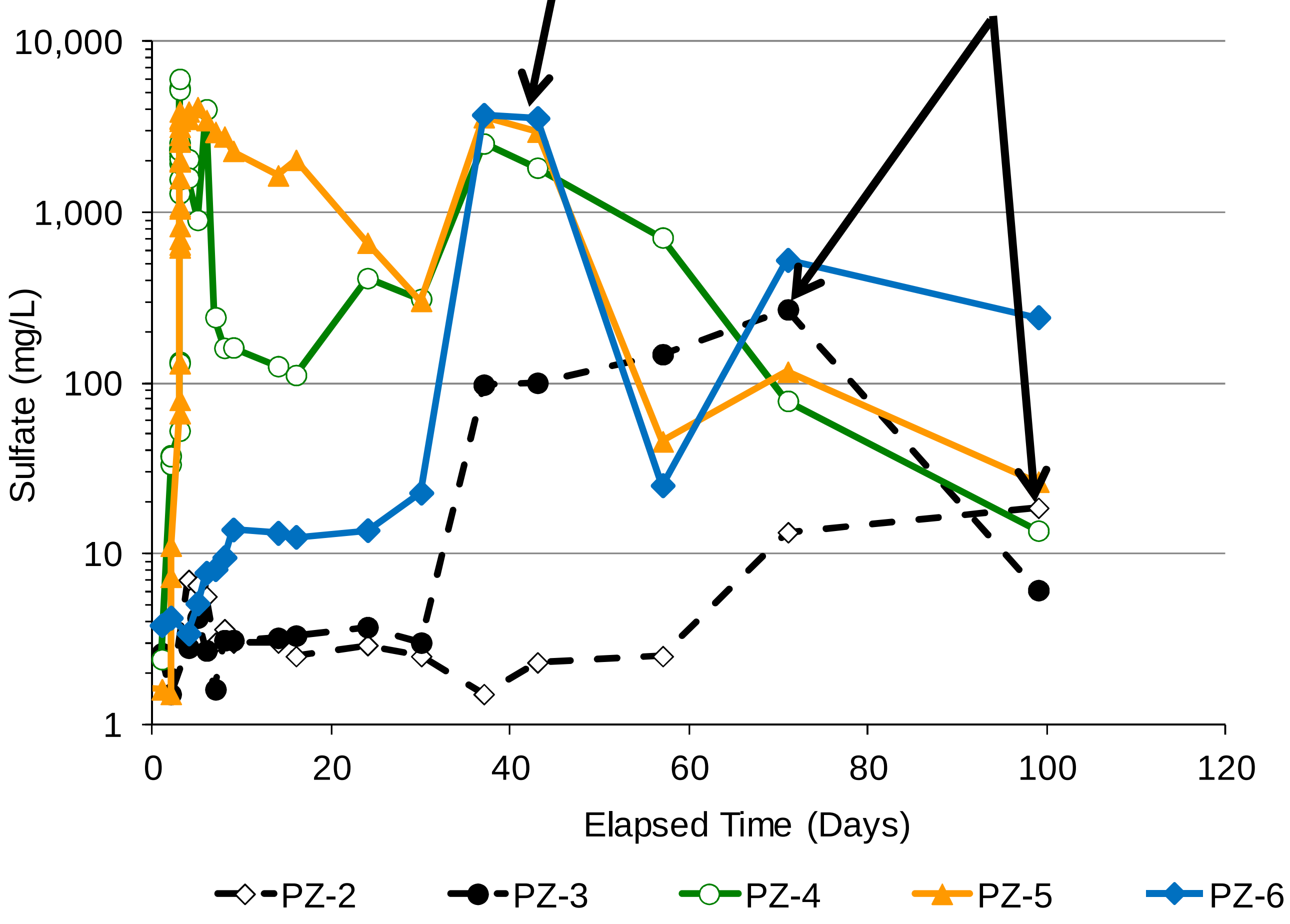
Field Test Layout – Cross-Section



Vertical Dose Response - Sulfate

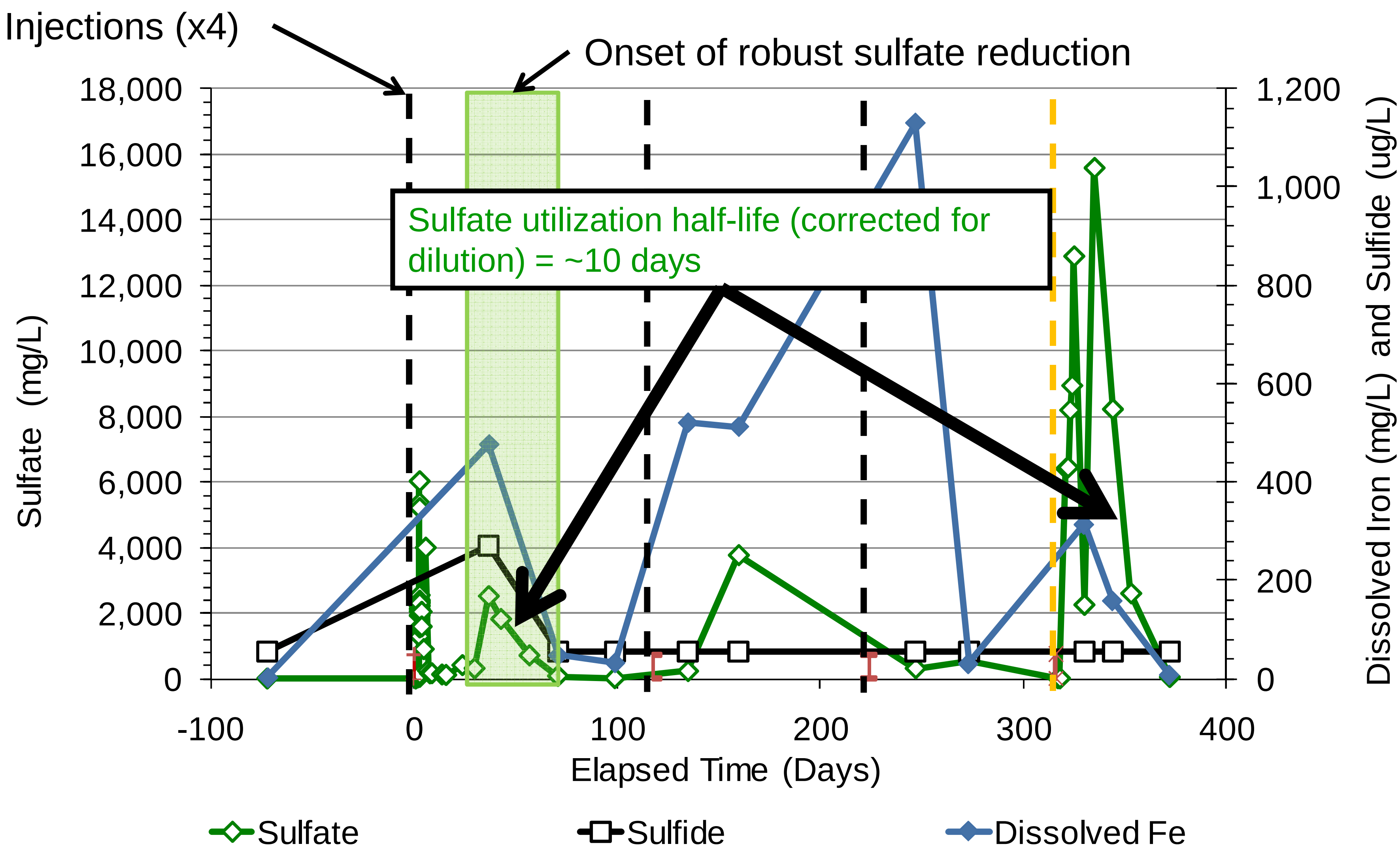
Peak concentration at PZ-4, PZ-5, PZ-6

Peak concentrations at PZ-2 and PZ-3 arrive later



- Sulfate arrival following first injection is slower and muted in the smear zone (PZ-2 and PZ-3)

Biogeochemical Indicator Data – PZ-4



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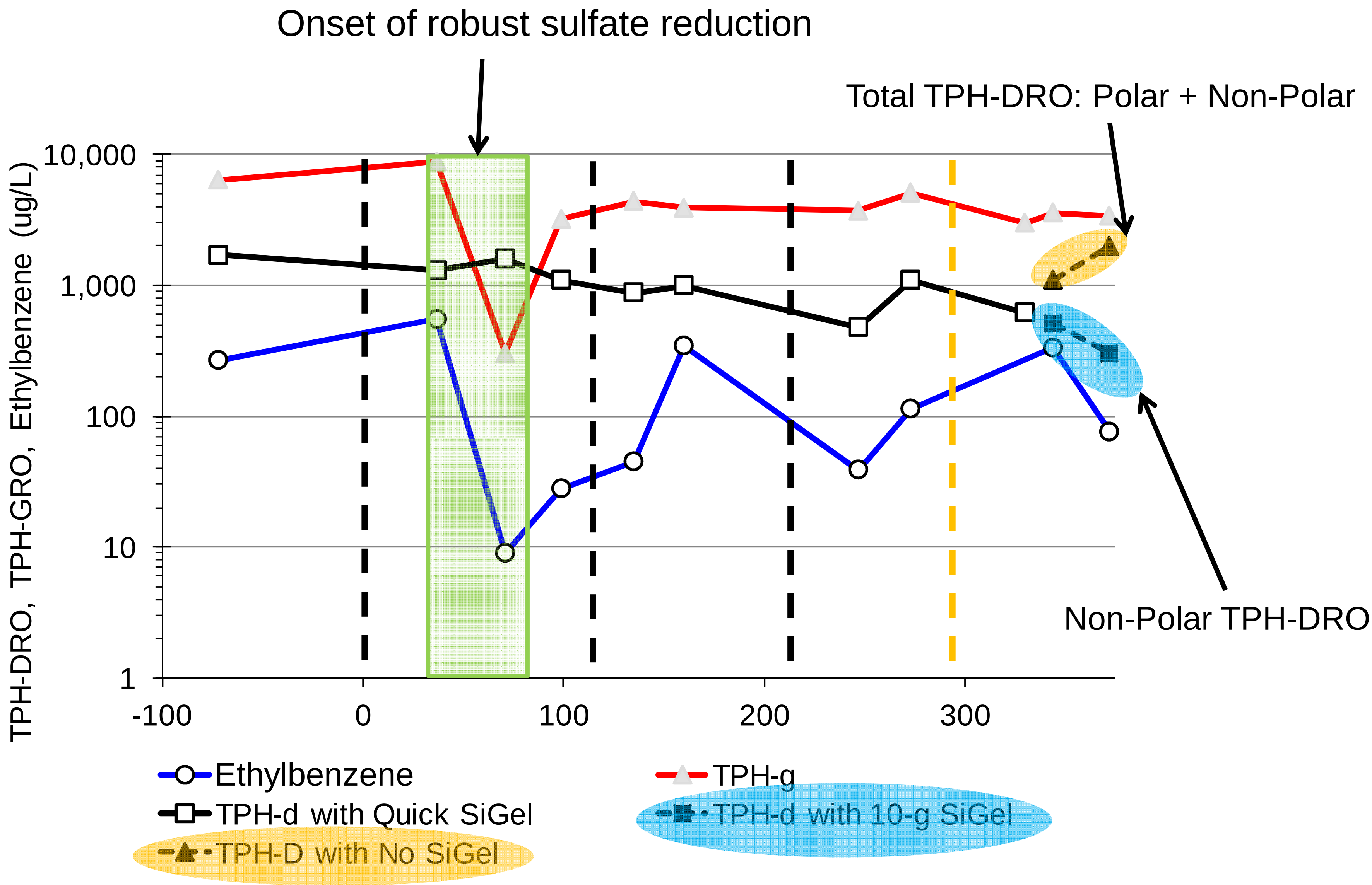
Hydrocarbon Treatment Data – PZ-4



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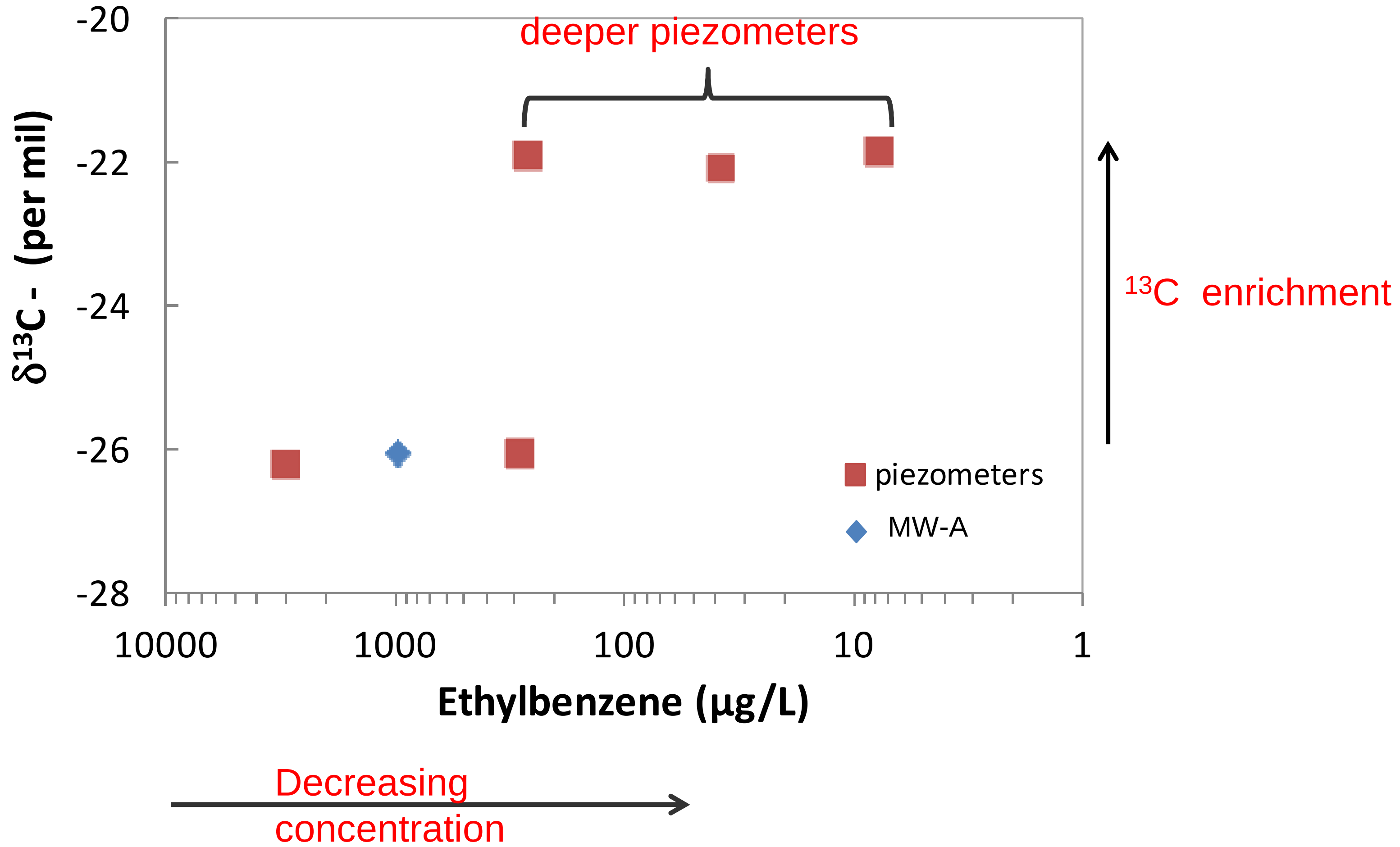
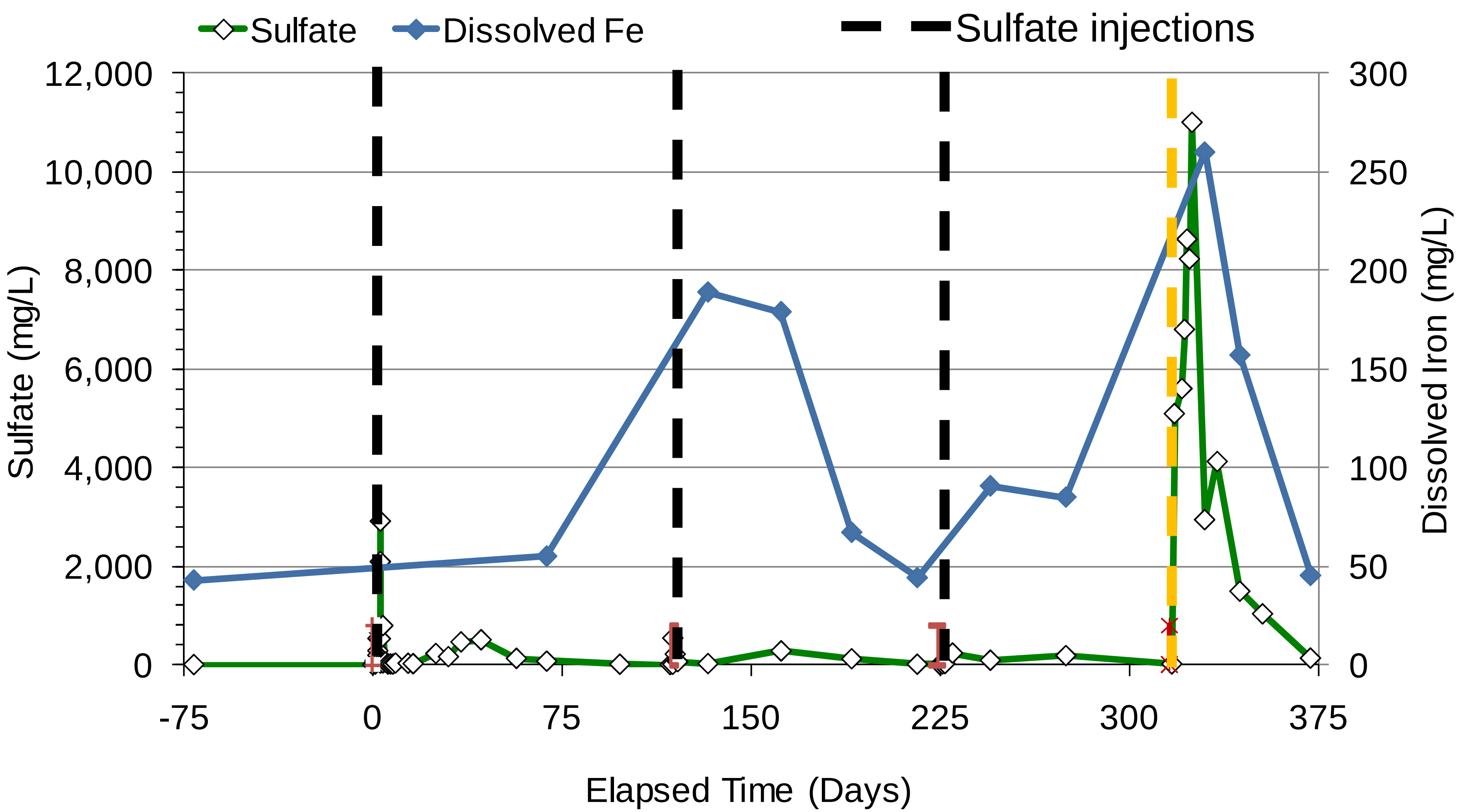
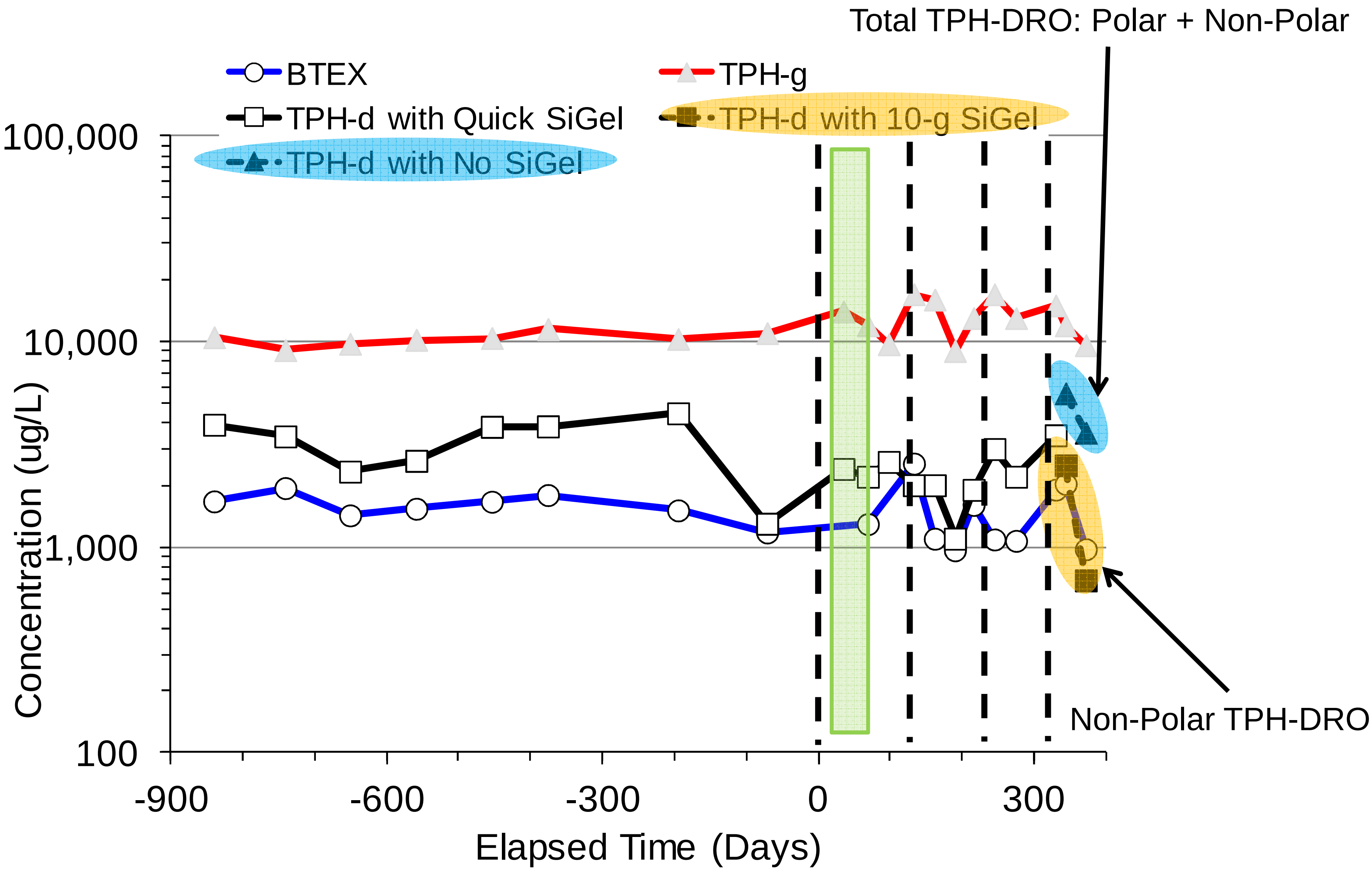
Ethylbenzene Carbon CSIA Indicates Biodegradation



Biogeochemical Indicator Data – MW-A



Hydrocarbon Treatment Data – MW-A

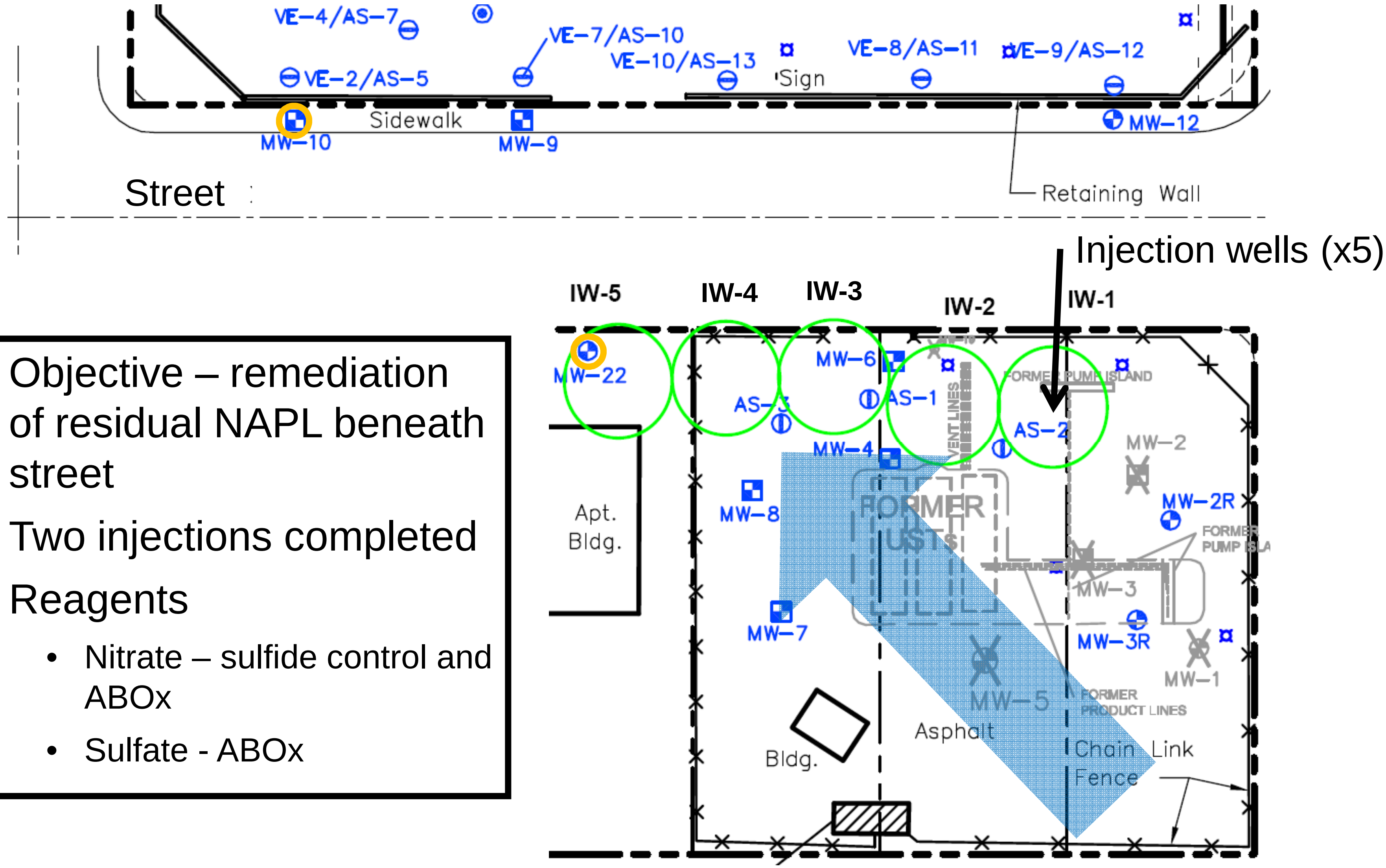


FIELD DEMONSTRATION STUDY

FORMER RETAIL STATION

Alaska

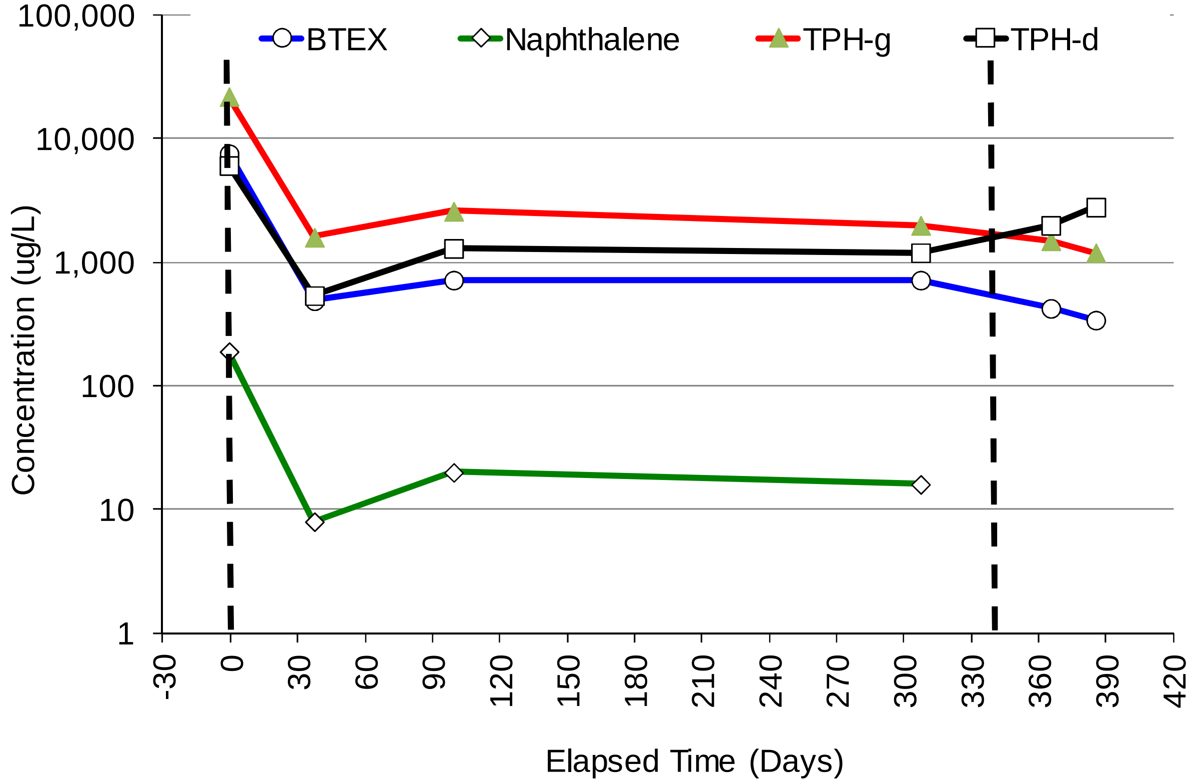
Site Plan



- Objective – remediation of residual NAPL beneath street
- Two injections completed
- Reagents
  - Nitrate – sulfide control and ABOx
  - Sulfate - ABOx

Downgradient Observations

- Monitoring well across the street, ~110 ft from injection well transect
- Sulfate persists >200 mg/L at 300 days following injection
  - 70 day half-life
- Nitrate is non-detect
- Sulfide is stable at baseline levels
- Reductions in petroleum hydrocarbon concentrations observed



Conclusions

- Sulfate-based anaerobic bio-oxidation is a viable technology for *polishing* petroleum hydrocarbon treatment
    - Consider source strength and viable sulfate payload
- Microbial lag phase for sulfate reduction
    - Expectation – 30 to 60 days based on acid mine drainage (AMD) experience
    - Reality – less than 45 days
- Sulfate effective half-lives
    - Expectation – 40 days based on reported hydrocarbon MNA rates and stoichiometry
    - Reality – 10 to 20 days, based on observed sulfate decay
- Enhanced dissolution – observed
- Sulfate and sulfide control – confirmed

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THANK YOU.

