Influence of Sulfate Reduction and Biogenic Reactive Minerals on Long-Term PRB Performance in a Sulfate Rich, High Flow Aquifer

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Our Portfolio of S&GW Remediation Technologies

In Situ Chemical Oxidation (ISCO)

- KLOZUR® SP *[$Na_2S_2O_8$]*
- KLOZUR® ONE *[$Na_2S_2O_8$ + Activators]*
- KLOZUR® KP *[$K_2S_2O_8$]*
- KLOZUR® CR *[$Na_2S_2O_8$ + CaO_2]*
- H_2O_2 *[35% dilution]*

In Situ Chemical Reduction (ISCR)

- DARAMEND® *[ZVI + Plant carbon]*
- EHC® *[ZVI + Plant carbon]*
- EHC® PLUS *[ZVI + Plant carbon + GAC]*
- EHC® LIQUID *[Organo-iron + $C_{35}H_{66}NO_7P$]*

Anaerobic Bioremediation (ERD)

- ELS® MICROEMULSION *[$C_{35}H_{66}NO_7P$; Lecithin]*

BioGeoChemical

- GEOFORM® *[Sulfate, Soluble & ZVI, Electron donors, Buffers, Nutrients]*

Aerobic Bioremediation

- TERRAMEND® *[Nutrients]*
- PERMEOX® *[CaO_2]*

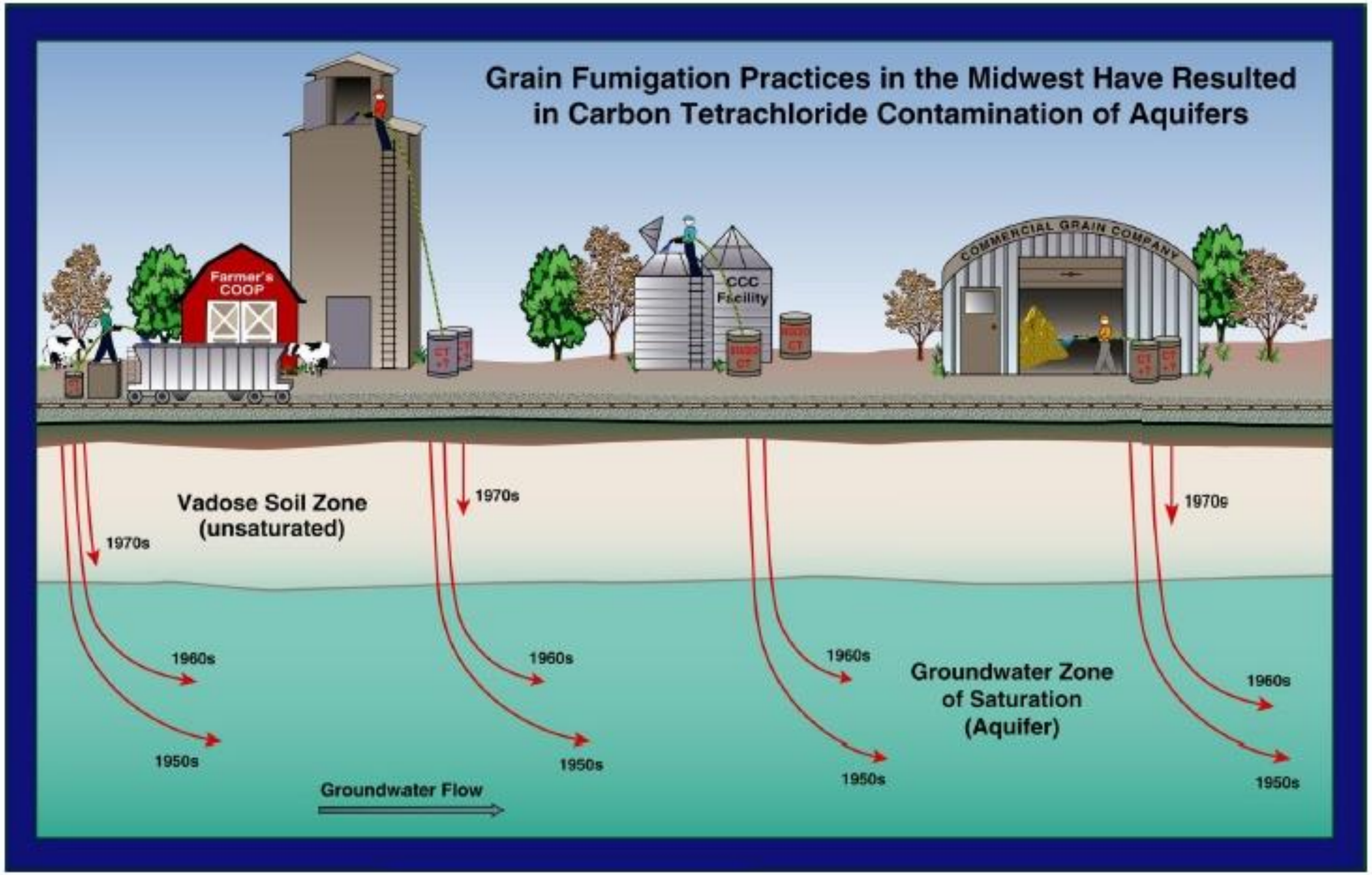
Metals Reduction / Precipitation / Adsorption

- METAFIX® *[Family of Reagents]*

NAPL Stabilisation / Mass Flux Reduction

- ISGS® *[MnO^{-}_4; modified permanganate]*

Primer



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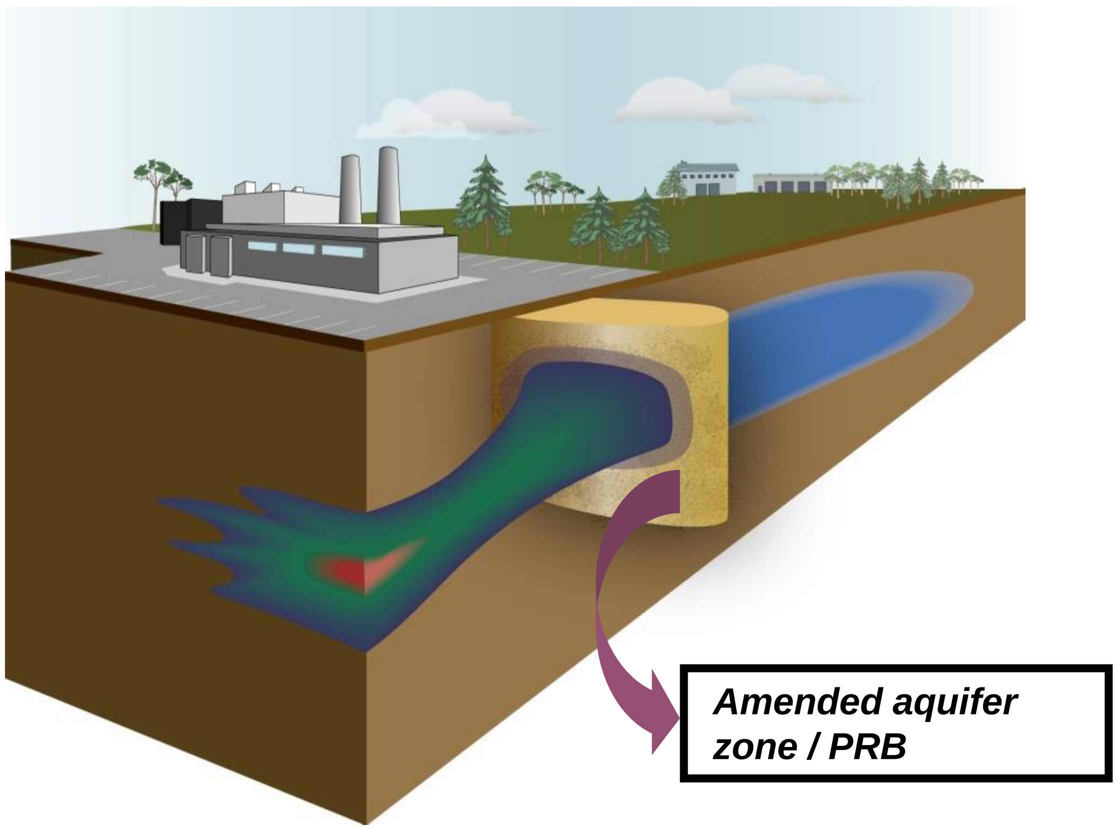
Site Introduction

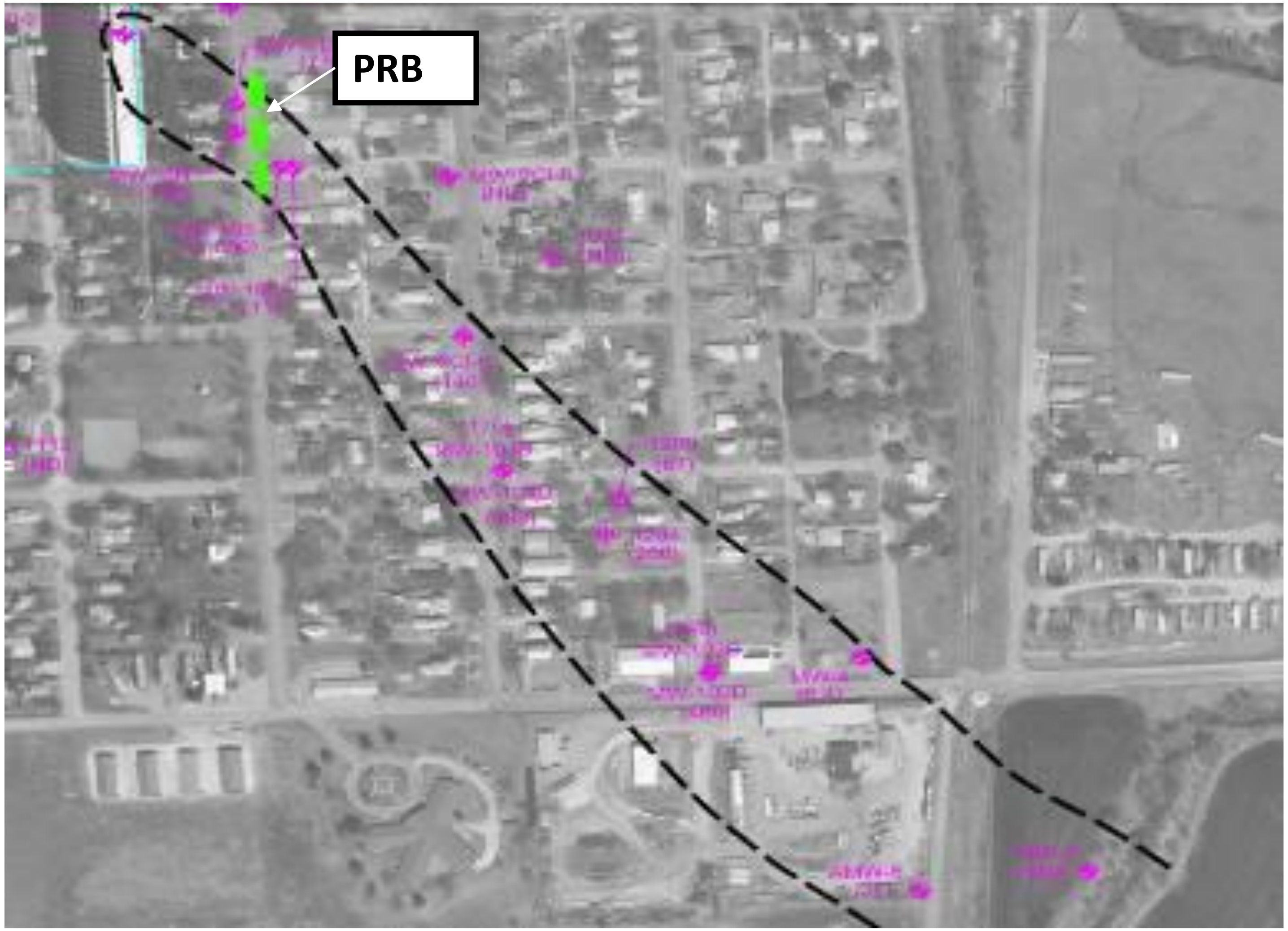
- EHC® PRB installed in 2005 for treatment of carbon tetrachloride (CT)
- One of the first full-scale applications of ISCR reagents into an injection PRB
- Presentation objective is to assess long-term performance, and changes to geochemical parameters, since installation



Site Background

- CT plume extends ~823 m from grain elevators and discharges into small creek.
- Bedrock rises to an elevation of ca. 2,7 m above present day water table at the presumed source area.
- CT is believed to have transported along the topography of the bedrock surface to the downgradient aquifer.
- Access restrictions due to residential properties further complicates source area clean-up.

Remedial Approach



- **Remedial approach developed by Malcolm Pirnie (Arcadis)**
- In April 2005, a PRB was installed across the width of the plume downgradient from the source to limit further plume migration.
- It was installed along the first available roadway by injecting EHC ISCR reagents into a line of direct push injection points.

Reagent Selection

- EHC selected over "ZVI alone" following bench scale testing, due to its ability to more effectively treat CT break-down products
- Rapid abiotic CT degradation possible with ZVI alone, but a portion of the CT is converted to CF, and a portion of the CF is converted to DCM
- EHC ISCR reagent composed of:
  - 40% micro-scale ZVI (50 - 150 µm)
  - 60% fine-grained processed plant fiber particles
- EHC promotes both abiotic and biotic degradation mechanisms

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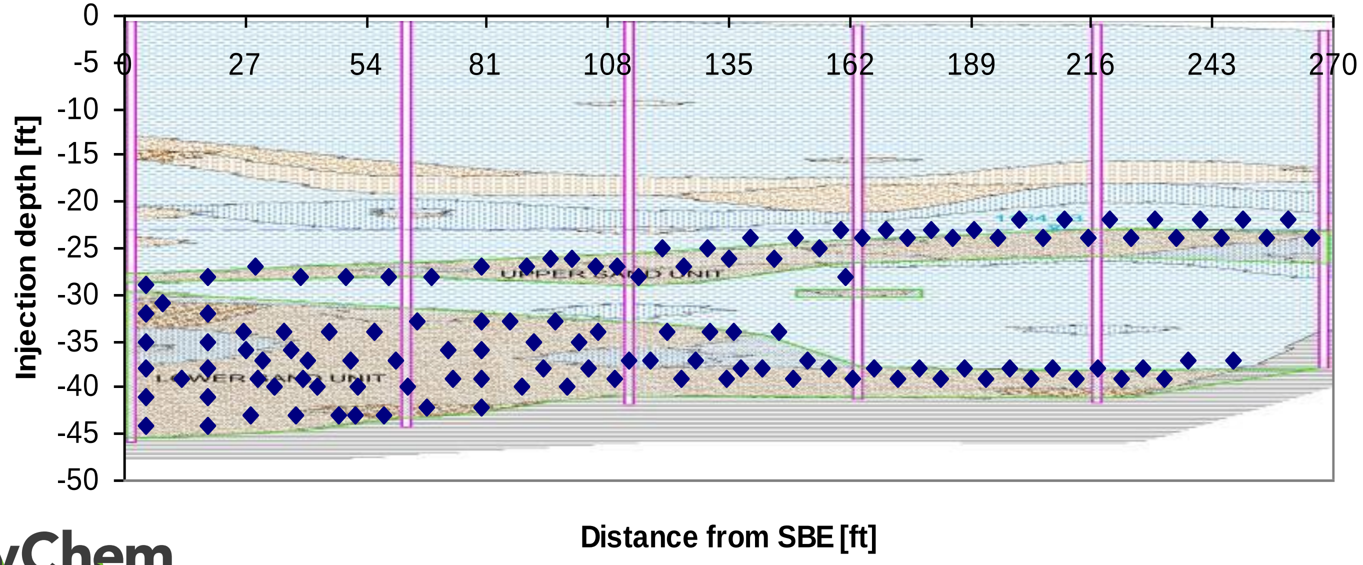
PRB installation via DPT injection

- EHC PRB installed as a line of DPT injection points across the plume width
- Upper and lower sand units targeted for injection
- PRB Dimensions: 83 m long x 4,6 m wide x 3,0 m deep, on average
- Total of 21.818 kgs of EHC injected
- EHC Application Rate = ca. 1% to soil mass



Evaluation of EHC Placement

Soil cores obtained at beginning of the installation to verify radius of influence (ROI) and determine injection spacing:

→ EHC slurry was found to distribute in discrete seams, and detected 1,6 m away from the injection location

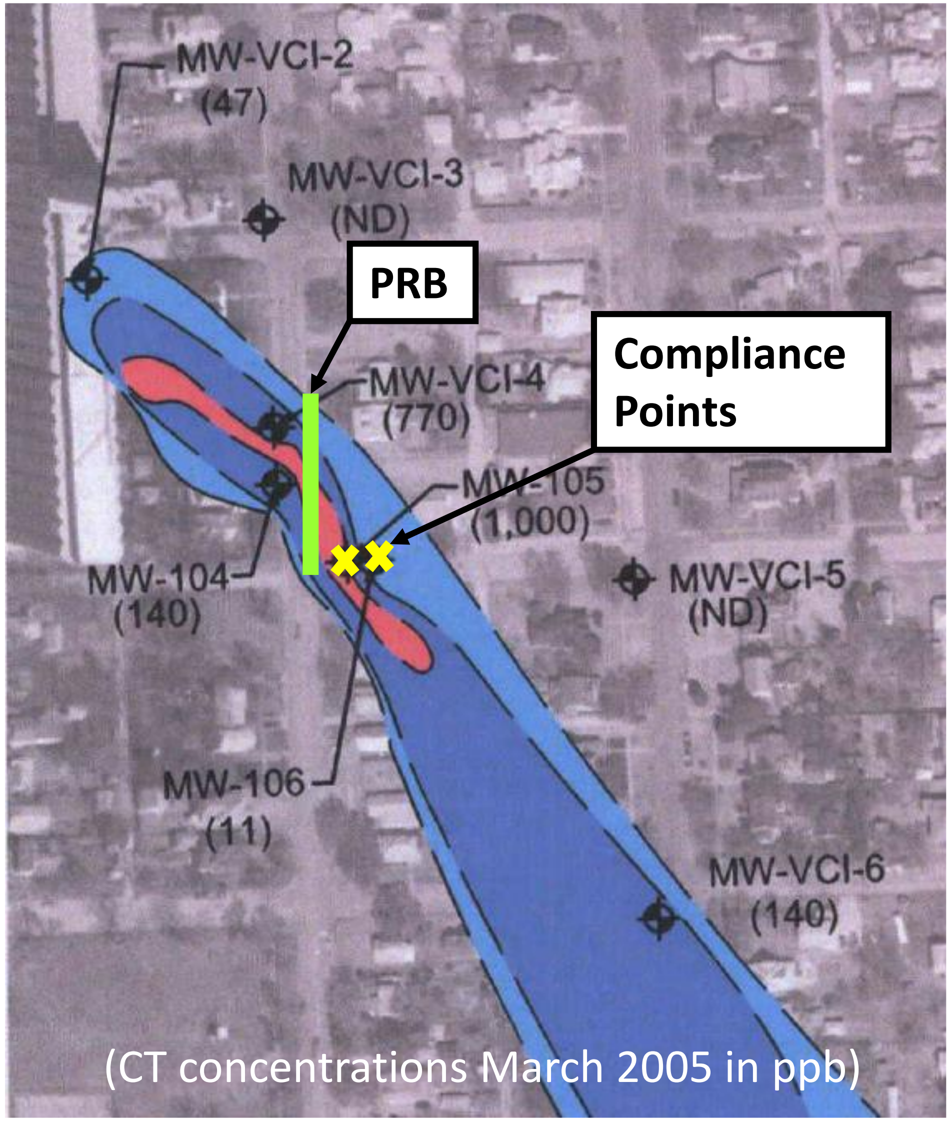
→ Injection points spaced 3,0 m apart

Horizontal fracture

Vertically dipping fracture

PRB Performance Evaluation

- **Remedial goal:** Maintain removal efficiency of at least **95% reduction** in CT -- compared to baseline concentrations at compliance points located 21 and 43 meters downgradient from the PRB.



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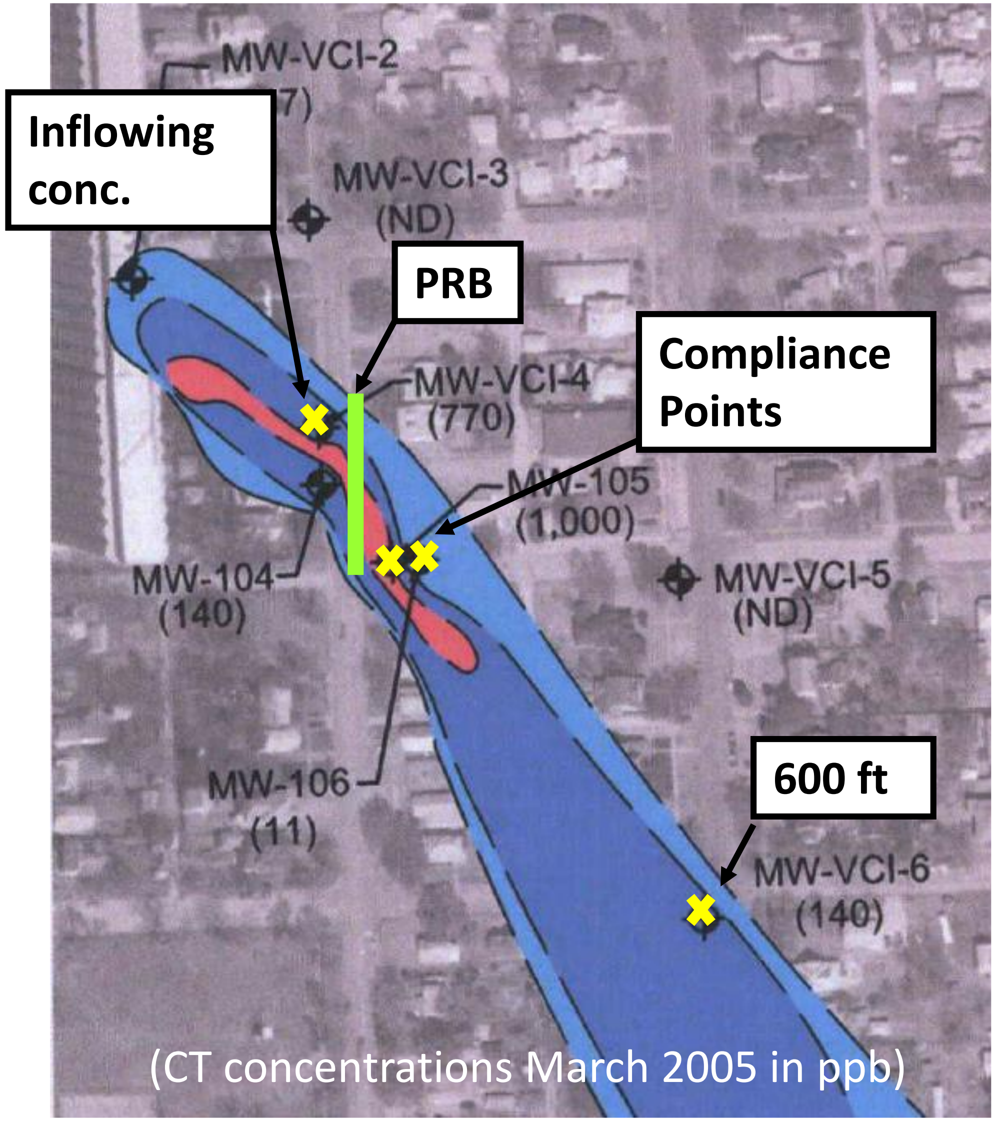
PRB Performance Evaluation

- **MW-105 –** 21 m downgradient at center of plume / ~39 days ground water travel time*
- **MW-106** – 43 m downgradient at edge of plume / ~78 days ground water travel time*
- **MW-VCI-6 –** 183 m downgradient / ~333 days ground water travel time*
- Inflowing concentrations monitored at **MW-VCI-4**

*based on an estimated ground water **flow velocity of 0.55 m/day**



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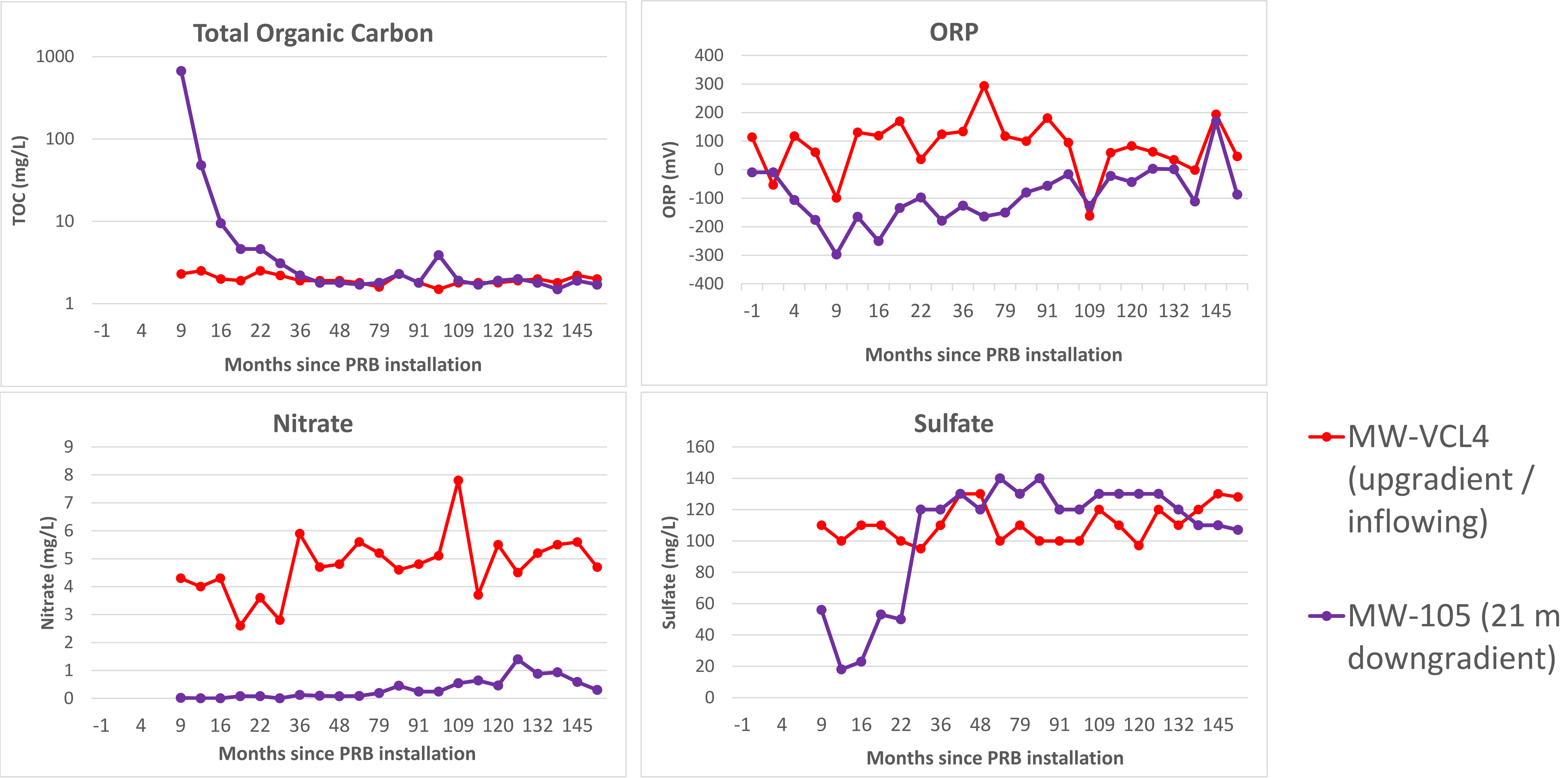
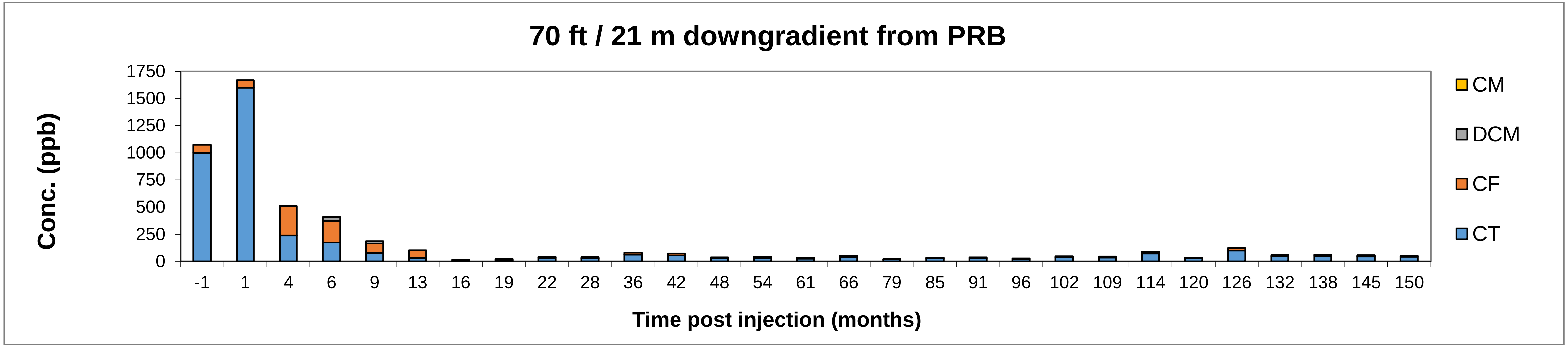
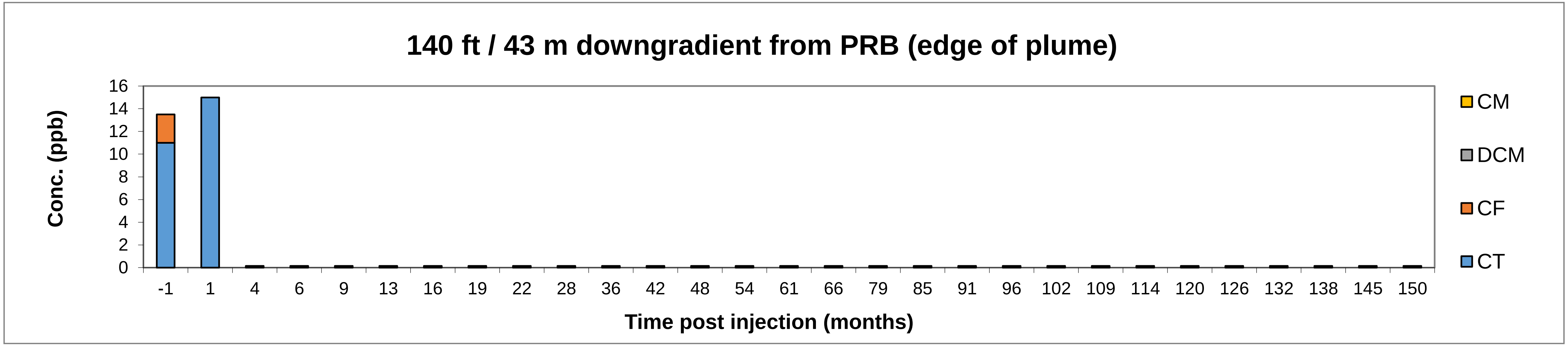
Geochemical Response – 12.5 years



Performance Data





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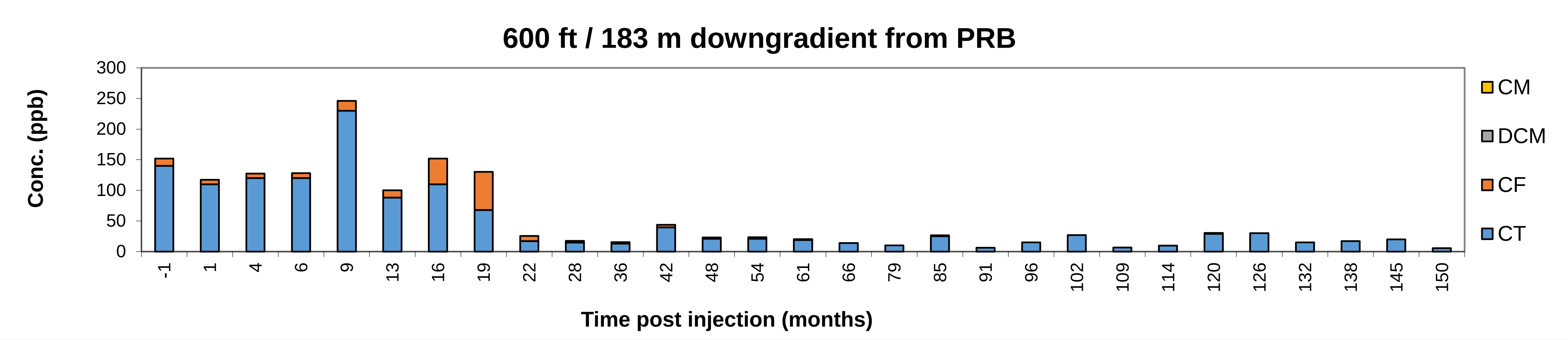
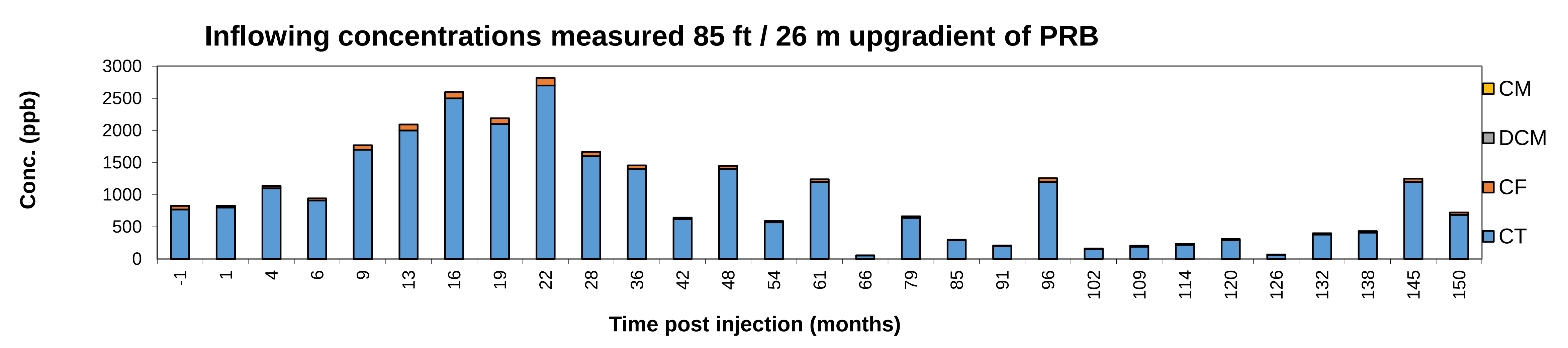
Performance Data





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Micro-Scale ZVI Longevity

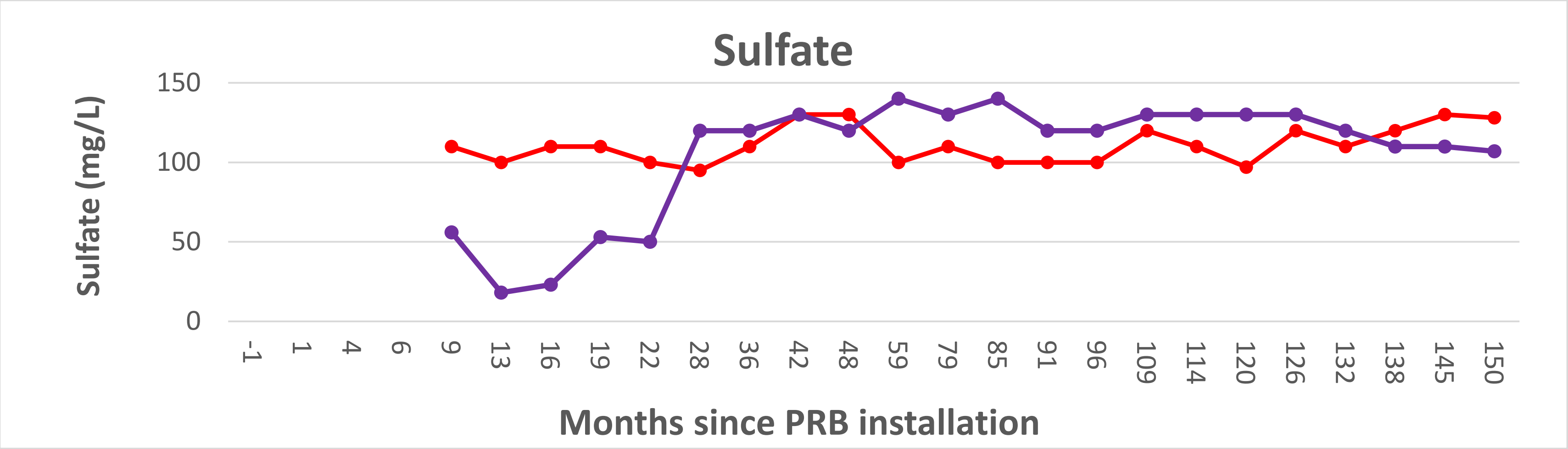
Theoretical estimation of micro-scale ZVI longevity:

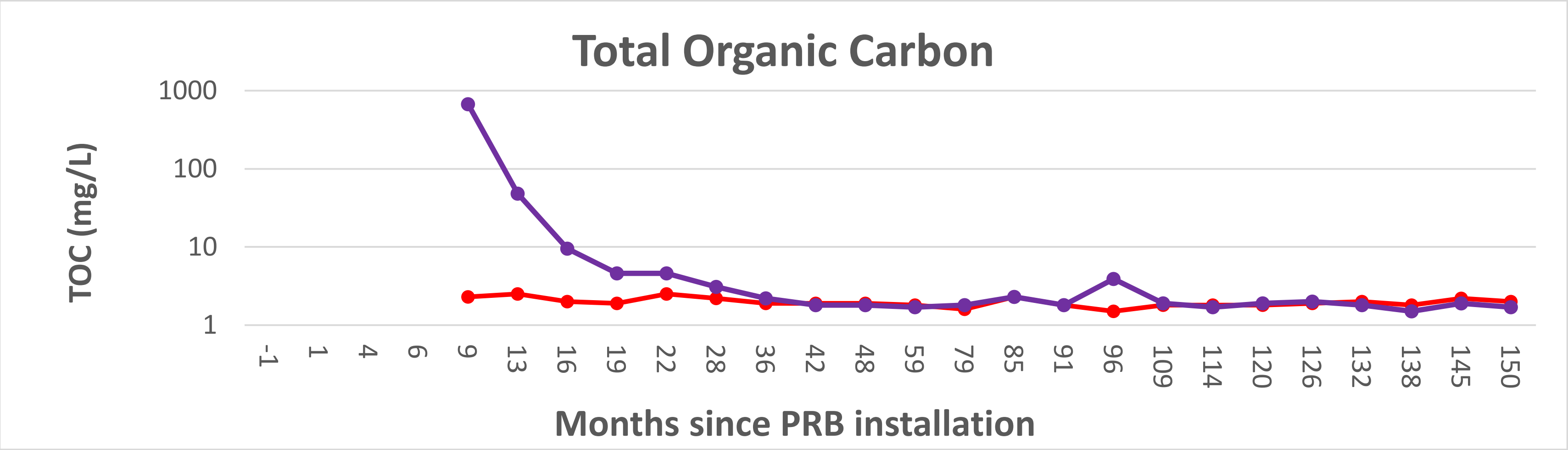
- **ZVI oxidation** due to reduction of terminal electron acceptors; calculated based on Stoichiometric demand from:
  - Naturally occurring terminal electron acceptors such as dissolved oxygen (DO), nitrate and sulfate;
  - Chlorinated contaminant reduction.

- **Corrosion** is an important ZVI consumption process and rates are expected to be more constant over time (estimated at 0.8 mmol/kg/day for micro-scale ZVI):

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_{2(aq)} + 2OH^-$$

Sulfate Reduction vs. TOC





MW-VCL4 (upgradient / inflowing)

MW-105 (21 m downgradient)

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Likely Contribution from Biogenic Minerals

- Biogeochemical transformation refers to processes where contaminants are degraded by abiotic reactions with naturally occurring and biogenically-formed minerals in the subsurface.
- Reactive minerals include iron sulfides (e.g. pyrite, mackinawite, greigite) and oxides (e.g. magnetite)
- **Inflowing sulfate = ~120 mg/L → iron sulfides are likely precipitation products downgradient from PRB → biogeochemical transformation may be an important mechanism to explain extended reactive life**

Mechanisms for Generating Reactive Iron Sulfide Minerals

Sulfate
+
Fe(II)
+
Electron donor

REACTIONS PROMOTED

Reduced RedOx Conditions

Sulfate reduction by SRBs:

$2CH_2O_{(s)} + SO_4^{2-} + 2H^+_{(aq)} \rightarrow H_2S + 2CO_{2(aq)} + H_2O$

Precipitation of Ferrous Iron with Sulfide:

$Fe^{2+}_{(aq)} + H_2S_{(aq)} \rightarrow FeS_{(s)} + 2H^+_{(aq)}$

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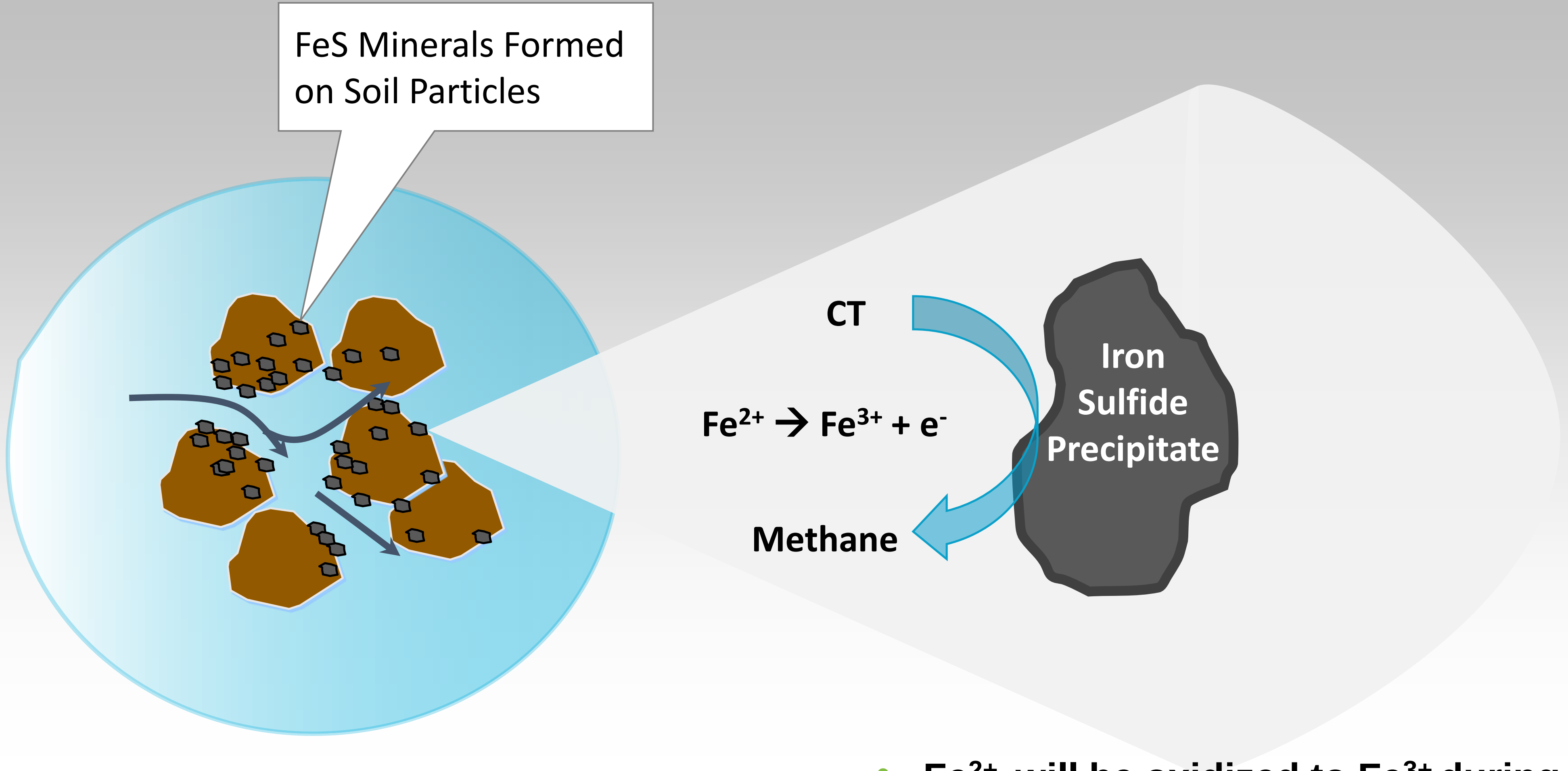
Iron Sulfide Minerals May Serve as a Reservoir of Electrons



- Fe^{2+} will be oxidized to Fe^{3+} during reaction with chlorinated contaminants

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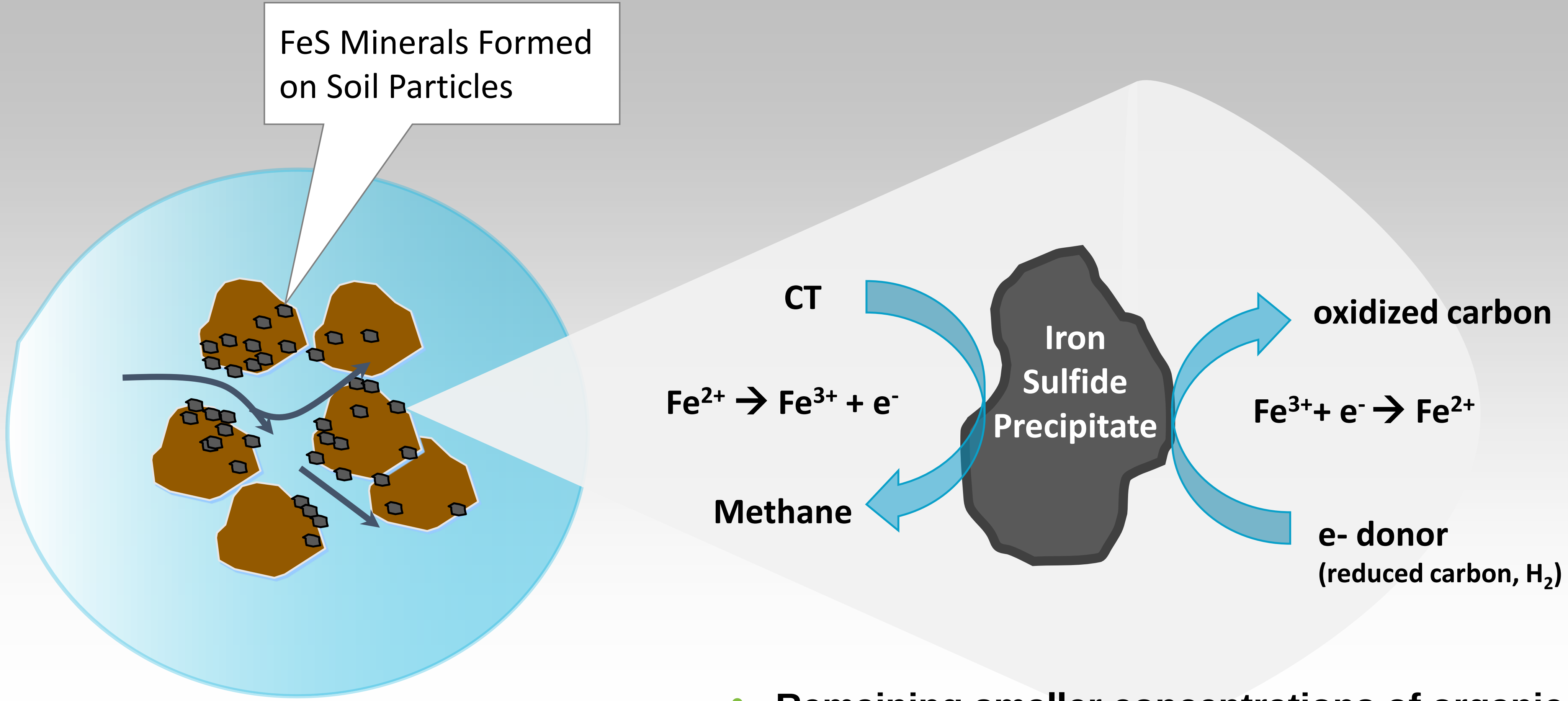
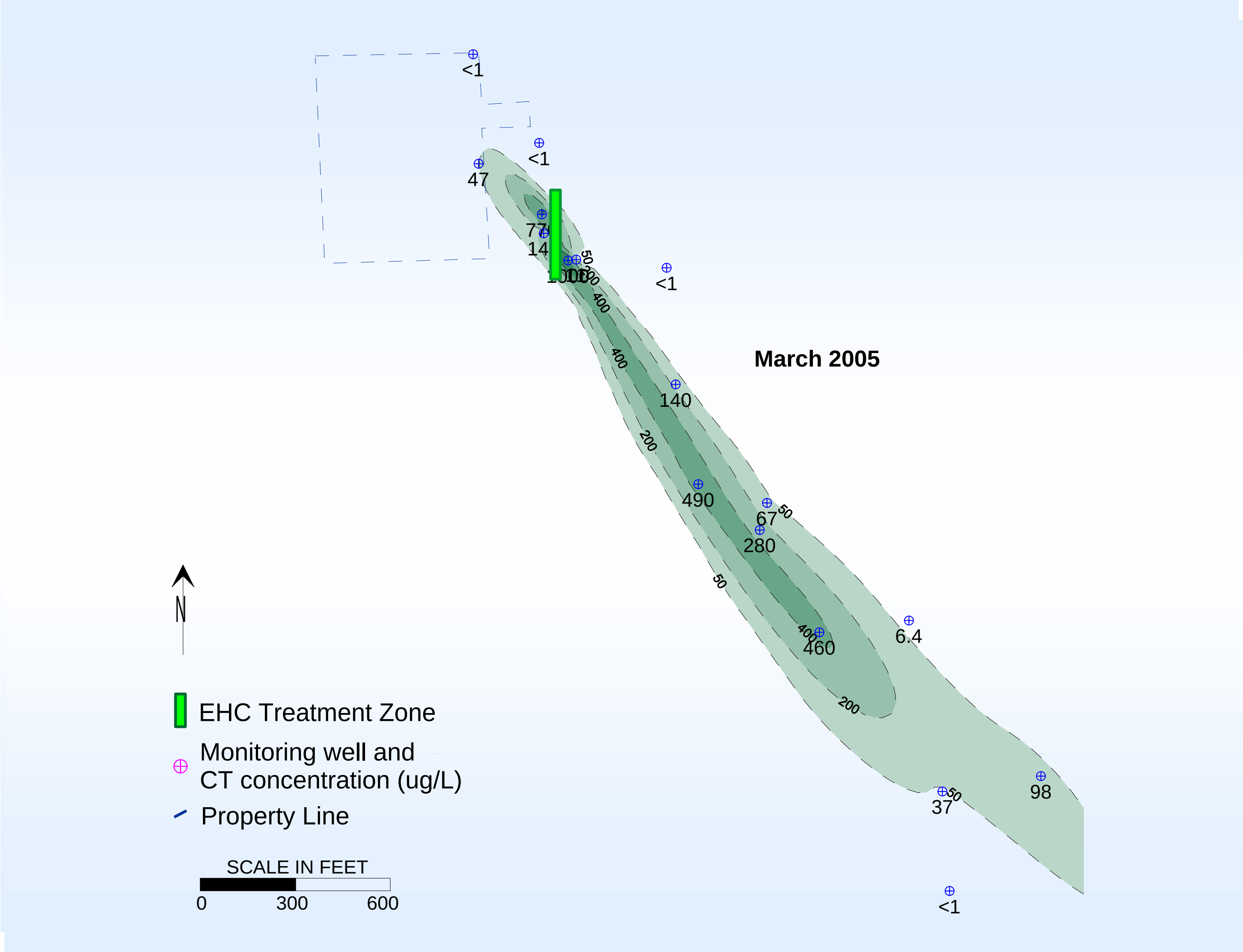
Regeneration of Reactive Minerals – Iron Redox Cycle



- **Remaining smaller concentrations of organic carbon and/or natural background TOC (~2 mg/L) may be sufficient to continuously restore Fe^{3+} to Fe^{2+}**

CT Concentrations - 5 Years



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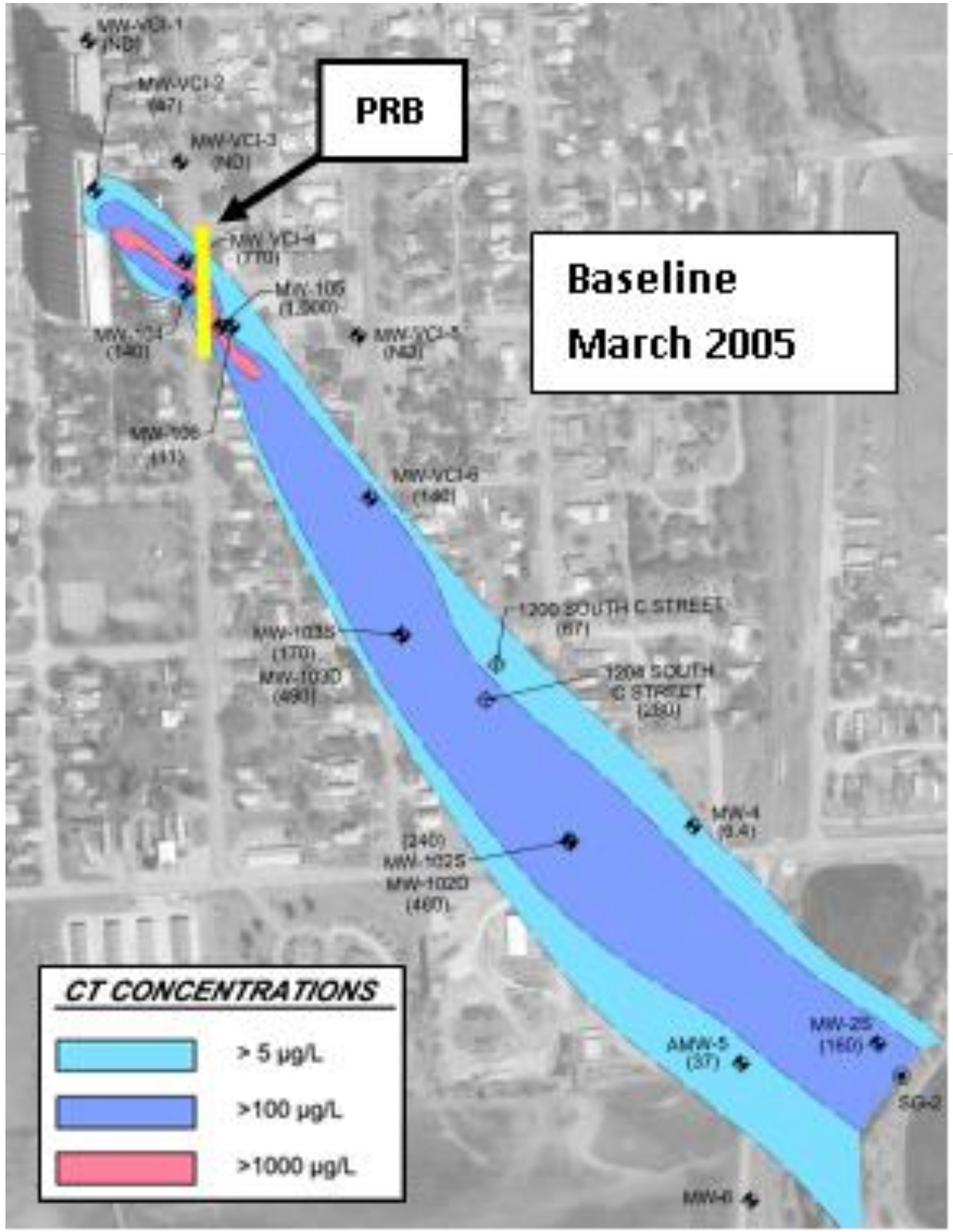
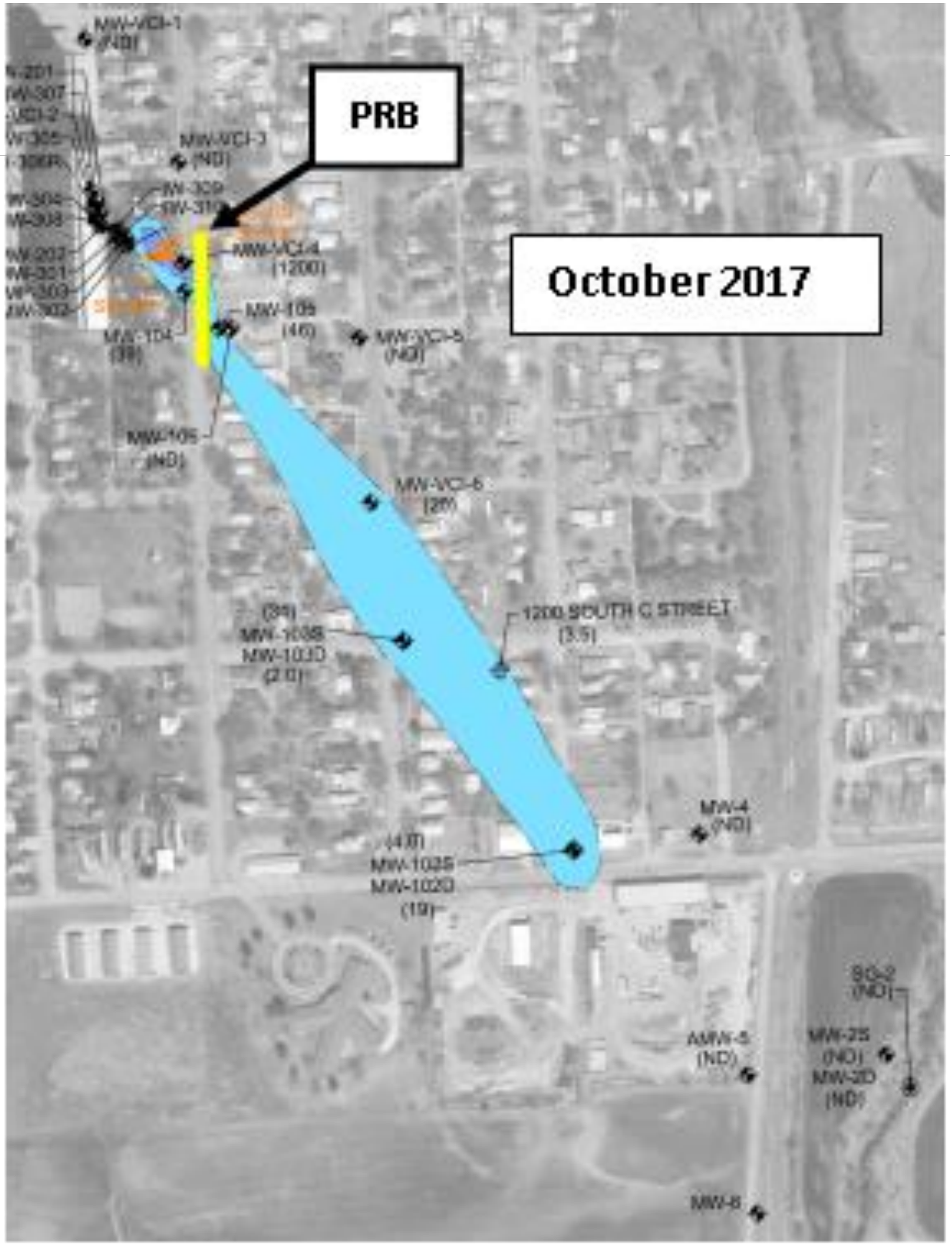


MW-VCI-1 (ND)
MW-VCI-2 (87)
MW-VCI-3 (ND)
PRB
MW-VCI-4 (770)
MW-105 (1,300)
MW-104 (140)
MW-VCI-5 (ND)
Baseline
March 2005
MW-106 (41)
MW-VCI-6 (140)
1200 SOUTH C STREET (67)
MW-103S (170)
MW-103D (490)
1204 SOUTH C STREET (280)
MW-4 (8.4)
(240) MW-102S
MW-102D (460)
AMW-5 (37)
MW-2S (160)
SG-2
MW-6
CT CONCENTRATIONS
> 5 µg/L
>100 µg/L
>1000 µg/L



MW-VCI-1 (ND)
MW-VCI-3 (ND)
PRB
MW-VCI-4 (1200)
MW-105 (46)
MW-104
MW-VCI-5 (ND)
October 2017
MW-106 (ND)
MW-VCI-6 (28)
1200 SOUTH C STREET (5.5)
MW-103S
MW-103D
MW-4 (ND)
MW-102S
MW-102D (19)
SG-2 (ND)
AMW-5 (ND)
MW-2S (ND)
MW-2D (ND)
MW-6

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PRB Economics

Installation costs:

Amendment: 24 tonnes of EHC used in PRB
Product cost = ~ €75.000

Injection: 2 weeks of GeoProbe
Injection Cost = ~ €40.000

Total Fixed Cost: €115.000

Operating Cost: None (a green solution with no ongoing energy requirements)

Longevity:

Single EHC application remained active for ~12 years, before indications of breakthrough started to be observed.

Continuously supported >95% removal of CT without catabolite accumulation.

PRB treated an estimated ~90.000 m^3 of GW since installation

Summary Product Cost = ~ €1,20/m^3

<u>Significantly lower than a Pump & Treat alternative</u>

<u>where just the annual O&M Costs can range from €50K to € 200K</u>

Thank you for your attention!

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RESEARCH ARTICLE

WILEY

Long-term evaluation of an EHC injection permeable reactive barrier in a sulfate-rich, high-flow aquifer

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