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

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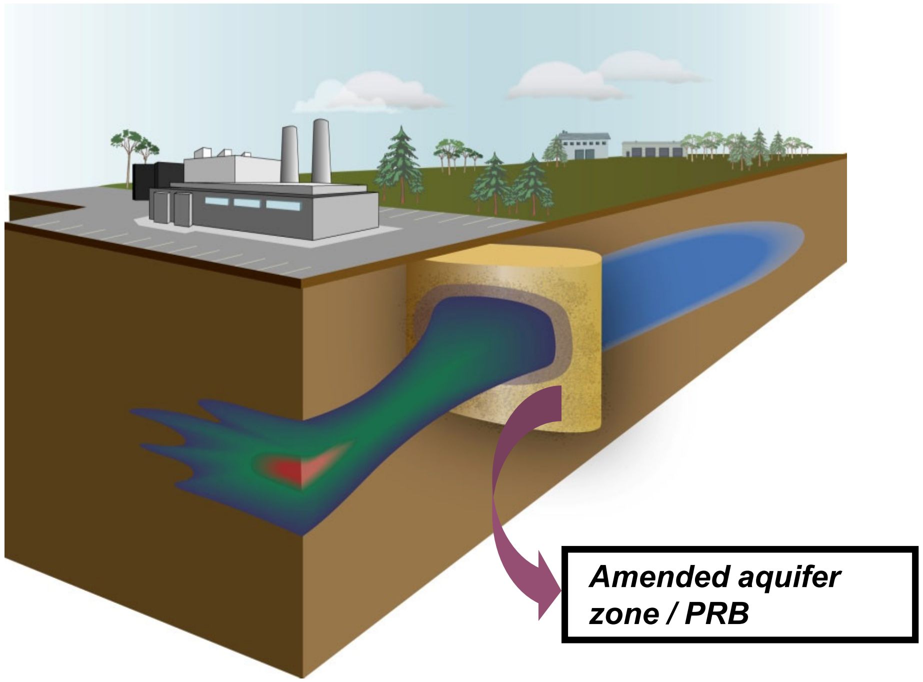
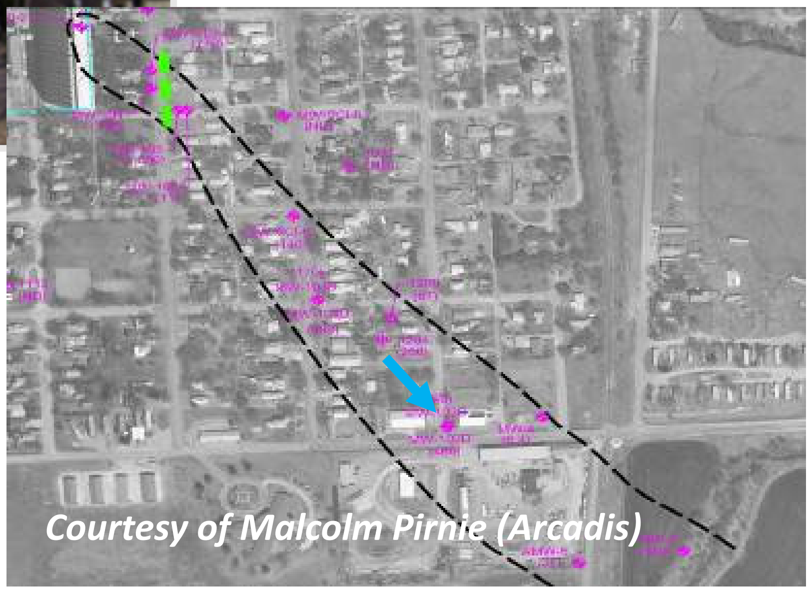
Fifth International Symposium on Bioremediation and Sustainable Environmental Technologies
(Baltimore, Maryland | April 18, 2019)

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
- The objective with this presentation is to assess long-term performance and changes to geochemical parameters since installation

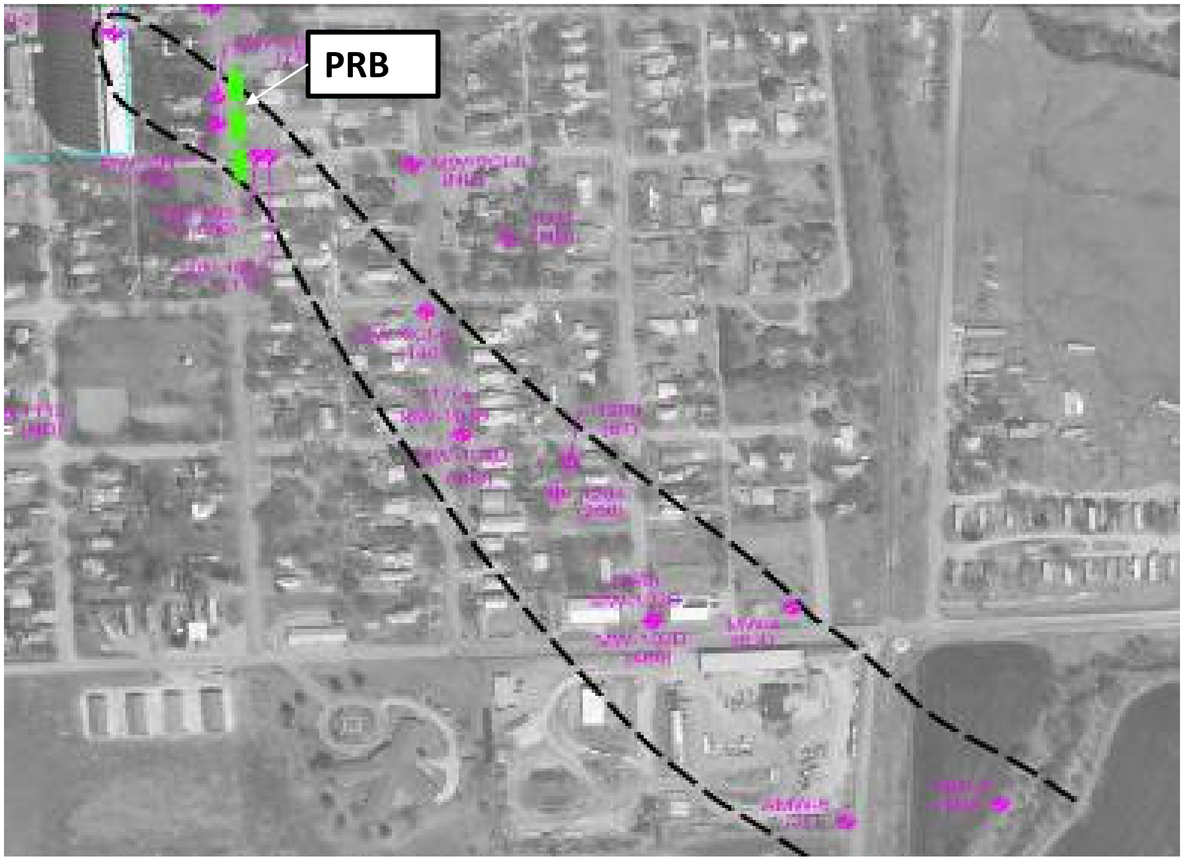


Site Background



- CT plume extends ~2,600 ft from grain elevators and discharges into small creek.
- The bedrock rises to an elevation of ca 9 ft above the present day water table at the presumed source area.
- The 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.

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Reagent Selection

- EHC selected over straight ZVI following bench scale testing due to its ability to more effectively treat CT break down products.

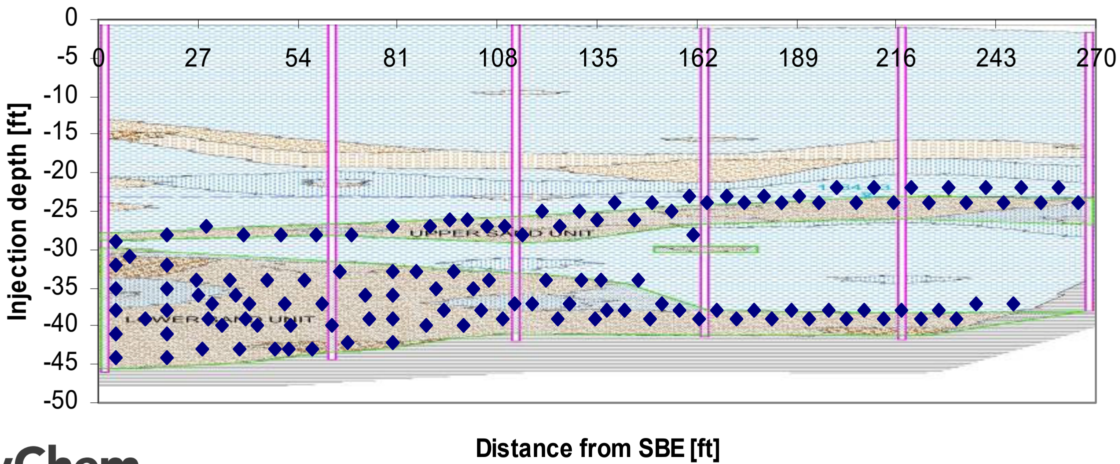
- Rapid abiotic CT degradation with ZVI alone, but a portion of the CT is converted to CF and a portion of the CF is converted to DCM

- 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

PRB installation via DPT injection

- EHC PRB installed as a line of DPT injection points across the width of the plume
- Upper and lower sand unit targeted for injection
- PRB Dimensions: 270 ft long x 15 ft wide x 10 ft deep on average
- A total of 24 tons of EHC injected
- EHC Application Rate = ca 1% to soil mass



Evaluation of EHC Placement

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

→ EHC slurry was found to distribute in discrete seams and detected 5 ft away from the injection location

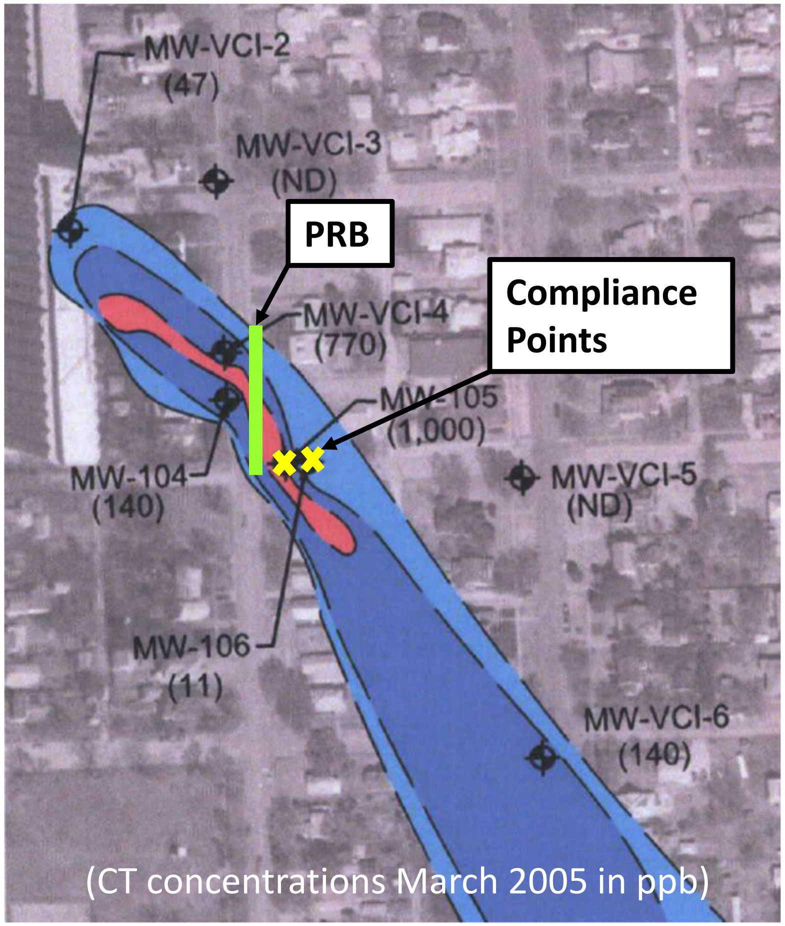
→ Injection points spaced 10 ft apart

Horizontal fracture

Vertically dipping fracture

PRB Performance Evaluation

- **Remedial goal:** Maintain a removal efficiency of at least **95% reduction** in CT compared to baseline concentrations at compliance points located 70 and 140 ft downgradient from the PRB.



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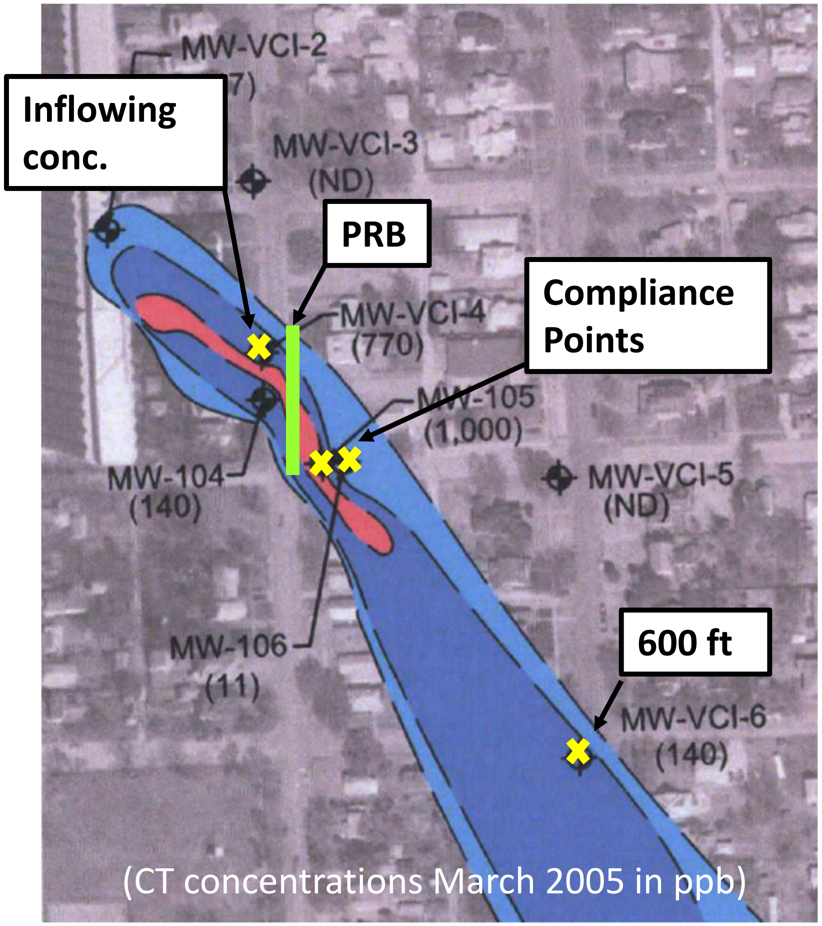
PRB Performance Evaluation

- **MW-105 -** 70 ft downgradient at center of plume / ~39 days gw travel time*
- **MW-106** - 140 ft downgradient at edge of plume / ~78 days gw travel time*
- **MW-VCI-6** - 600 ft downgradient / ~333 days gw travel time*
- Inflowing concentrations monitored at **MW-VCI-4**

*based on an estimated **gw flow velocity of 1.8 ft/day**



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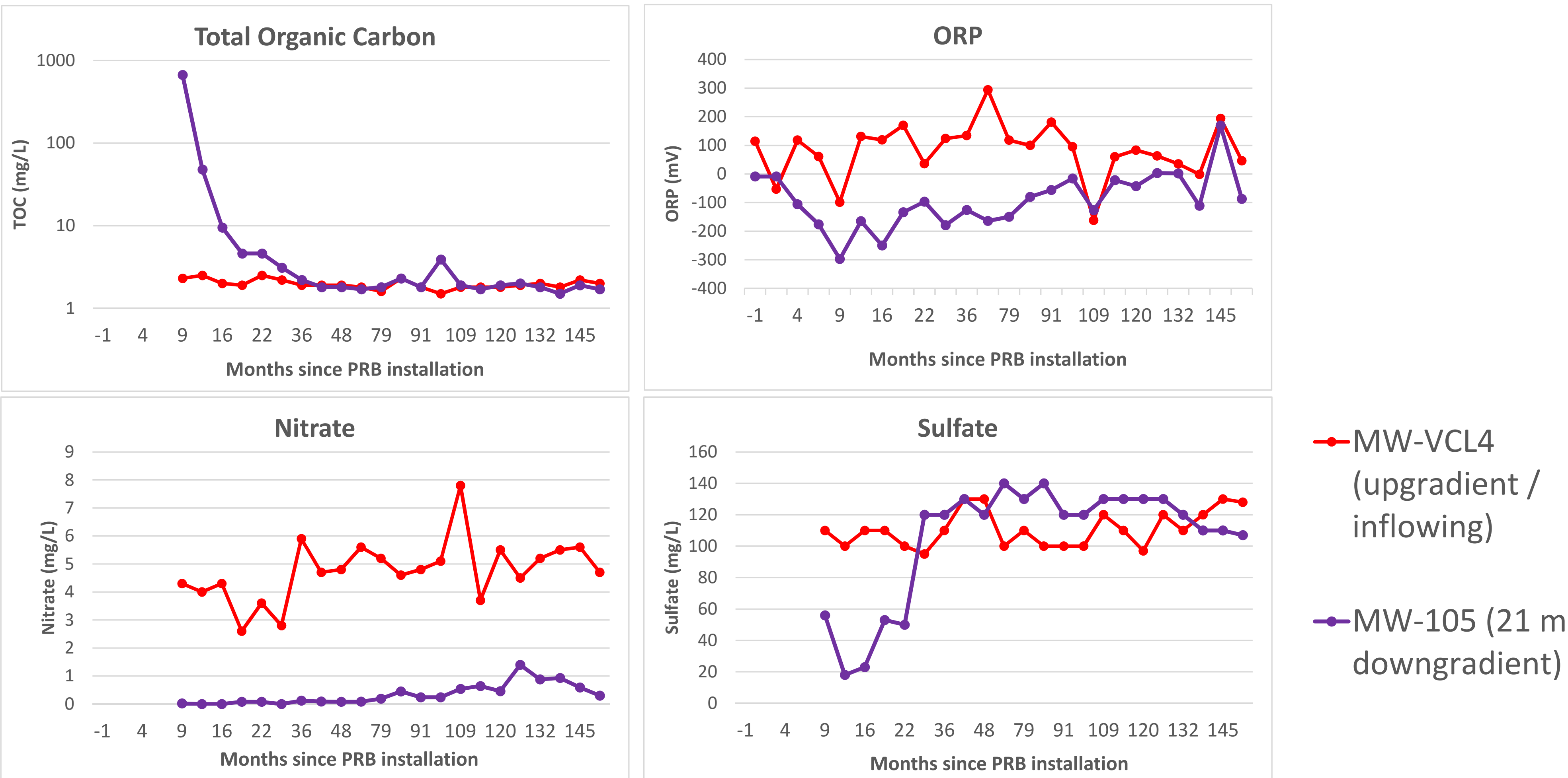
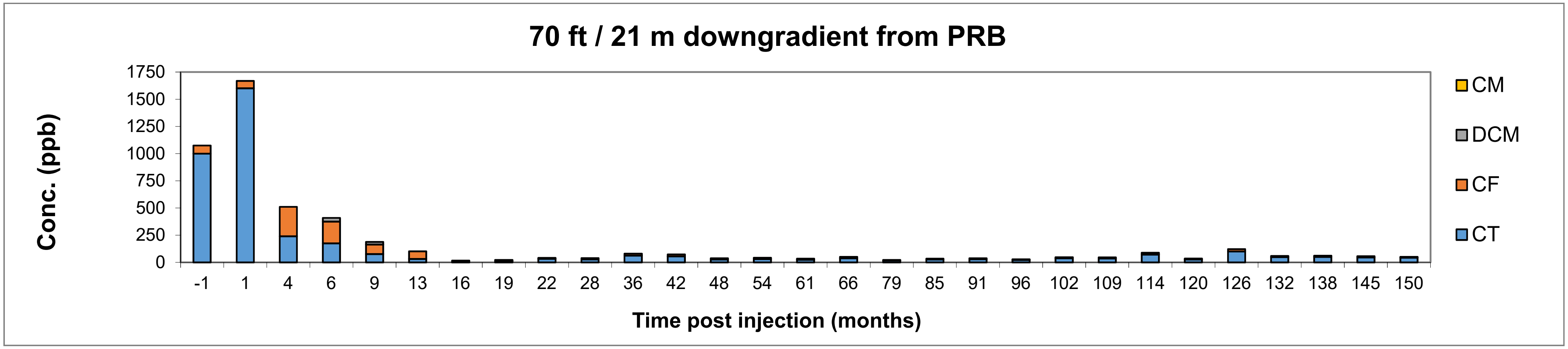
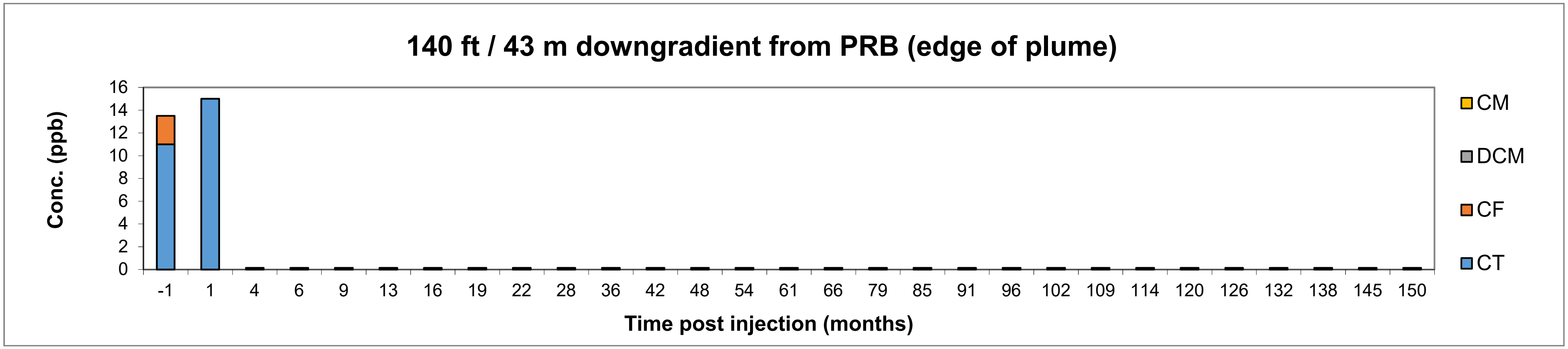
Geochemical Response – 12.5 years

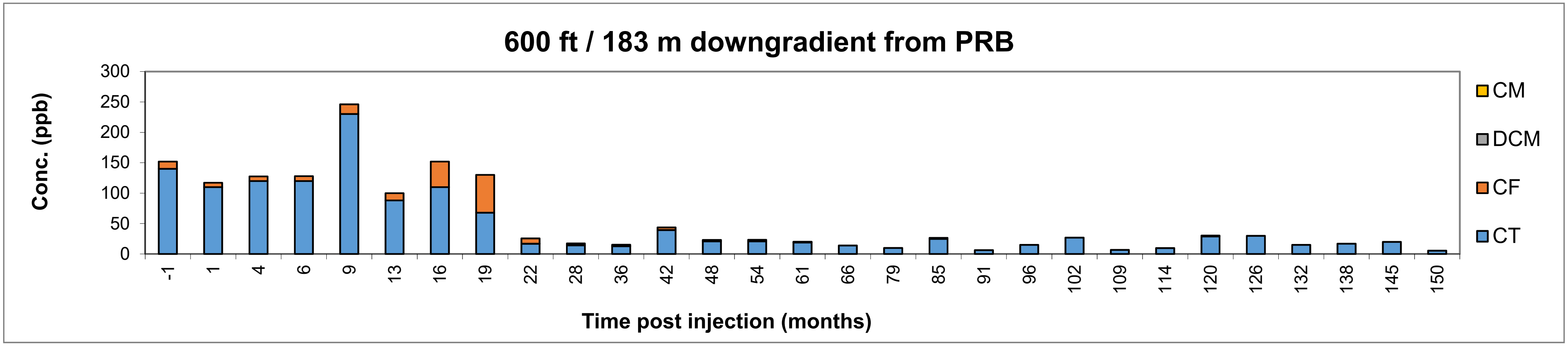


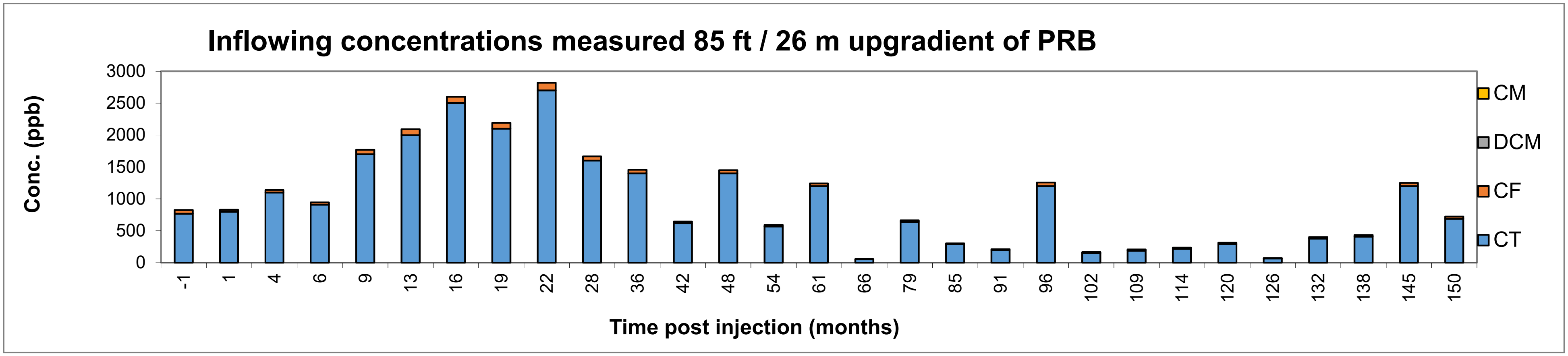
Performance Data





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):

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

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Theoretical Calculation of ZVI Longevity

PRB interface for gw flow (m2)	PRB width (m)	ZVI Dose Rate (mass)	ZVI Mass (kg)	GW velocity (m/day)	Effective porosity	Volume gw passing thru PRB (L/yr)
251	4.6	0.4%	8709	0.55	15%	7,534,688

Estimation assuming 100% of inflowing sulfate being reduced:

	Influent (mg/L)	Mass flux (kg/yr)	Mass flux (kmol/yr)	ZVI used (kmol/yr)	ZVI used (kg/yr)	% ZVI used per year
Water corrosion	---	---	---	---	142	1.6%
DO	0.4	3	94	126	7	0.1%
CT	1	8	49	98	5	0.1%
CF	0.01	0.8	6	6	0.4	0.004%
NO3	4	30	486	1,944	108	1.2%
SO4	**120**	904	9,418	37,673	2,102	**24.1%**
					Total	**27.2%**
					Estimated ZVI Longevity (yrs)	**3.7**

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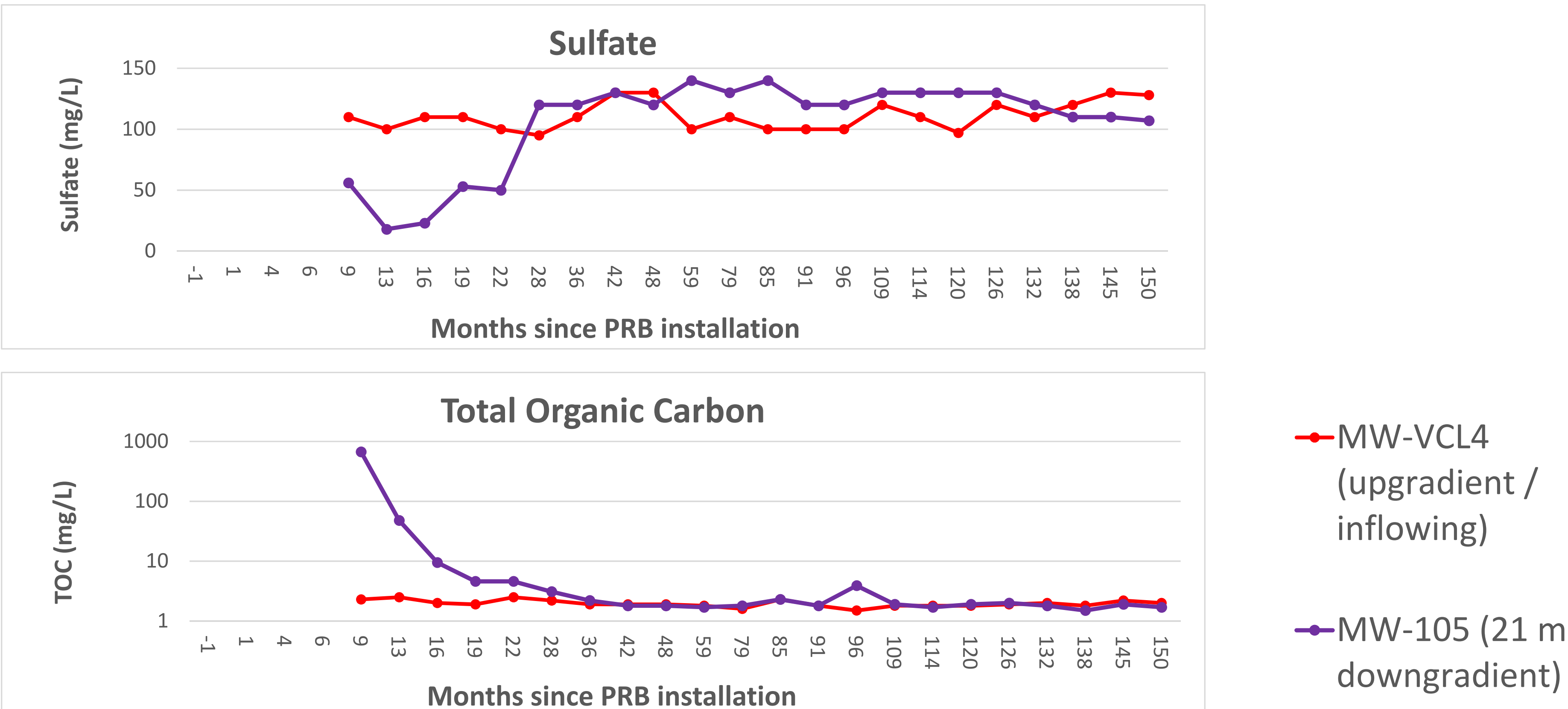
Sulfate Reduction vs. TOC



Theoretical Calculation of ZVI Longevity

PRB interface for gw flow (m2)	PRB width (m)	ZVI Dose Rate (mass)	ZVI Mass (kg)	GW velocity (m/day)	Effective porosity	Volume gw passing thru PRB (L/yr)
251	4.6	0.4%	8709	0.55	15%	7,534,688

Estimation assuming no sulfate reduction from ZVI:

	Influent (mg/L)	Mass flux (kg/yr)	Mass flux (kmol/yr)	ZVI used (kmol/yr)	ZVI used (kg/yr)	% ZVI used per year
Water corrosion	---	---	---	---	142	1.6%
DO	0.4	3	94	126	7	0.1%
CT	1	8	49	98	5	0.1%
CF	0.01	0.8	6	6	0.4	0.004%
NO3	4	30	486	1,944	108	1.2%
SO4	-	-	-	-	-	-
					Total	**3.0%**
					Estimated ZVI Longevity (yrs)	**33.1**

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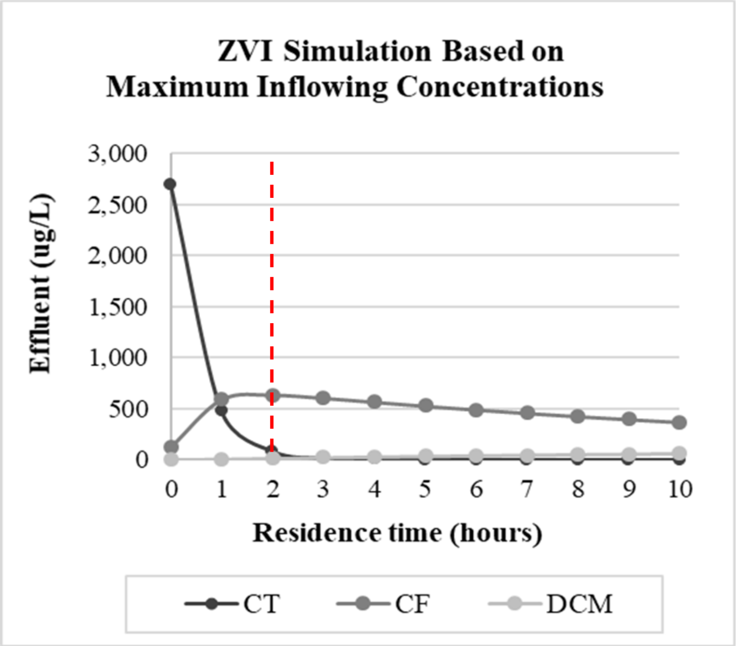
Simulated Effluent Concentrations

- Simulations performed based on ZVI only (assuming organic carbon mostly depleted)

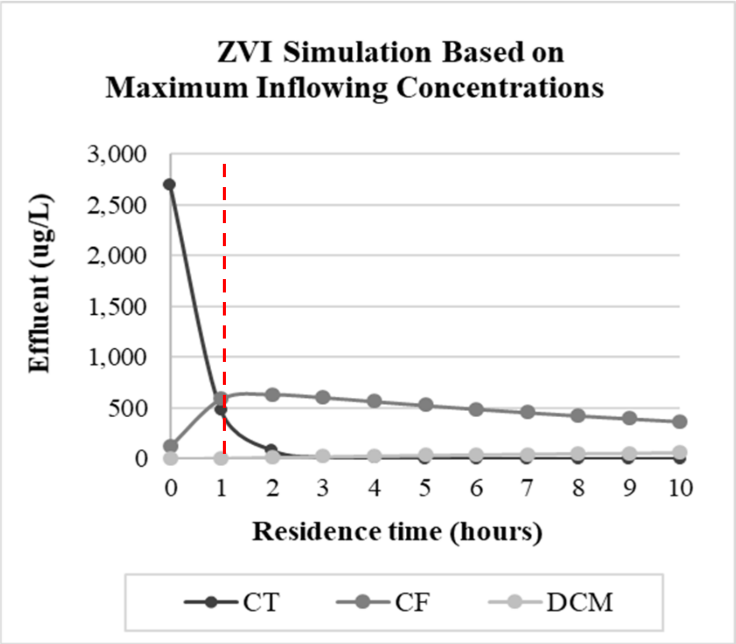
- Effluent concentrations simulated using lab determined half life data (100% ZVI):
  - $CT_{1/2}$ = 0.4 hours ; $CF_{1/2}$ = 9.6 hours
  - Molar conversion: CT to CF: 29%; CF to DCM: 22%

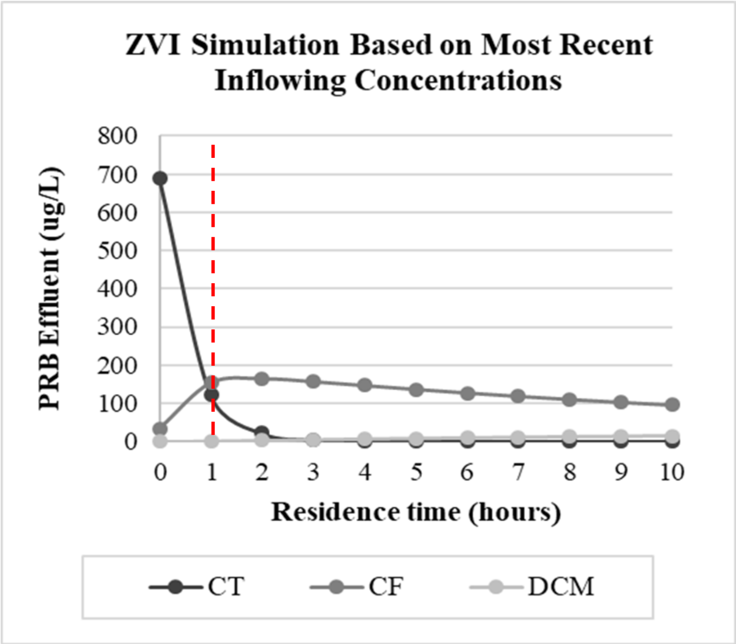
- A residence time of ~2 hours required to achieve the goal of reducing CT by 95%:
  - Flow-through thickness of 0.15 ft (4.6 cm) of 100% ZVI required



Simulated Effluent Concentrations

- The EHC PRB contained an equivalent of 1.8 cm of 100% ZVI:
  - 0.4% ZVI distributed over a 15 ft PRB width
  - Equates to a residence time of <1 hour





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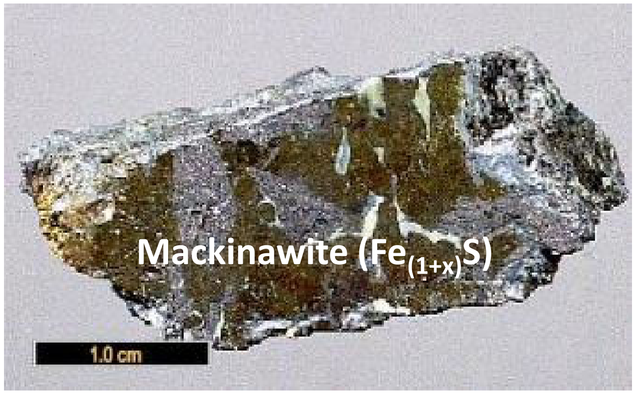
Simulated vs. Actual Effluent
1 hour residence time

	Feb 2007 (Max Inflowing Conc.)	Oct 2017 (Most Recent Data)
Influent concentrations:		
CT (ppb)	2,700	689
CF (ppb)	120	34
DCM (ppb)	ND (<5)	ND (<5)
Simulated effluent concentrations:		
CT (ppb)	477	122
CF (ppb)	589	154
DCM (ppb)	5	1
Actual effluent concentrations:		
CT (ppb)	33	44
CF (ppb)	8	8
DCM (ppb)	ND (<5)	ND (<5)

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**



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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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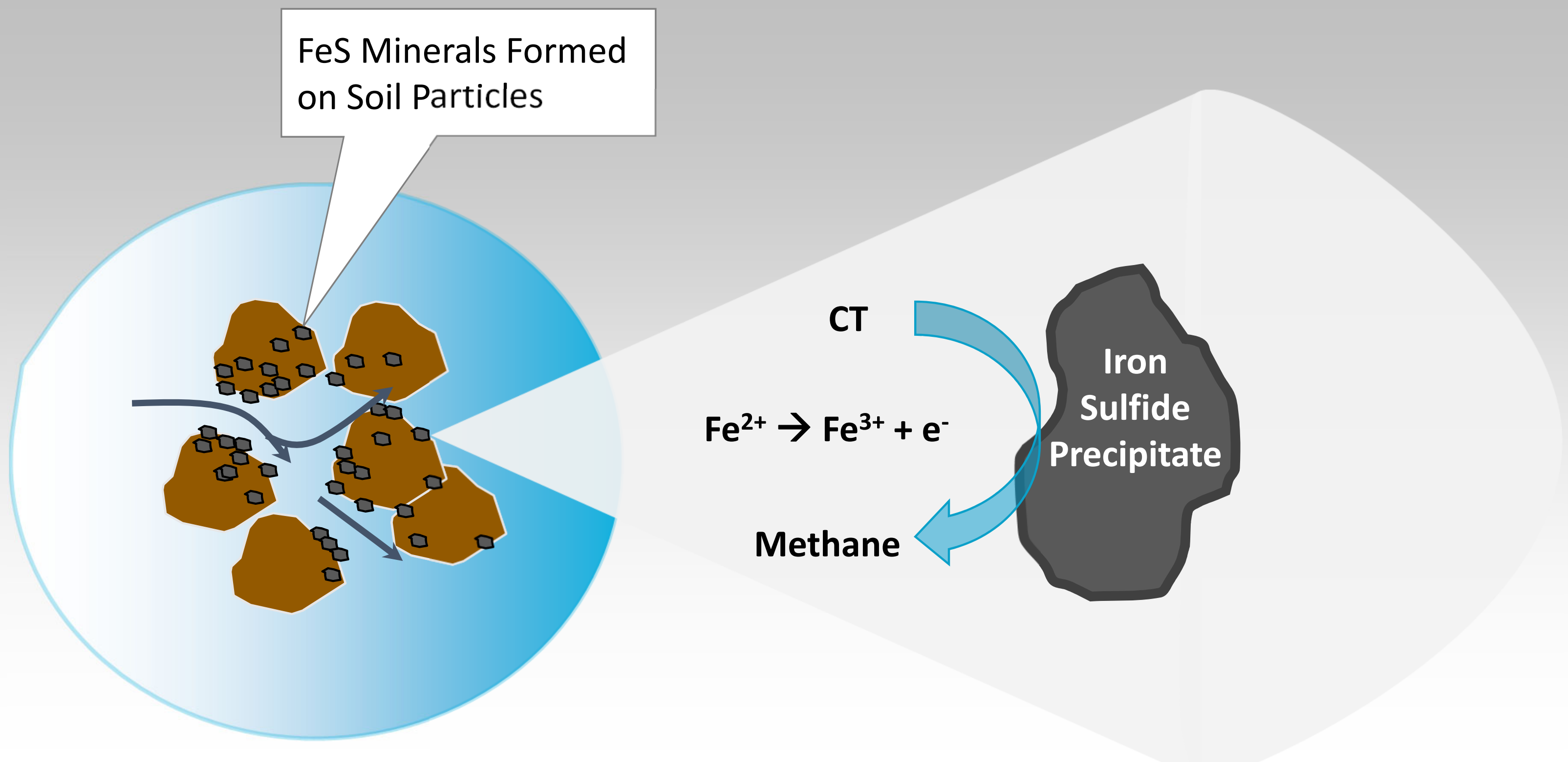
Iron Sulfide Minerals May Serve as a Reservoir of Electrons



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

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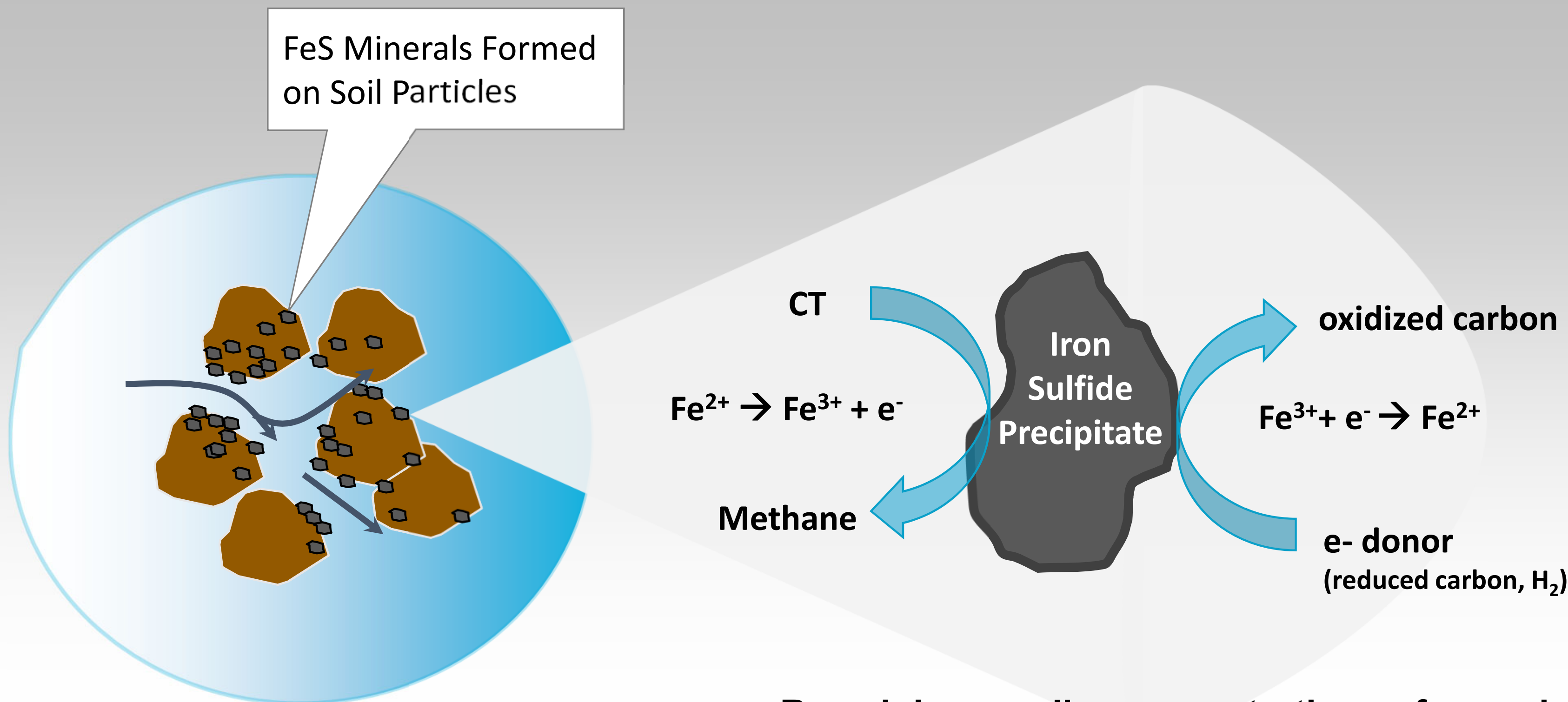
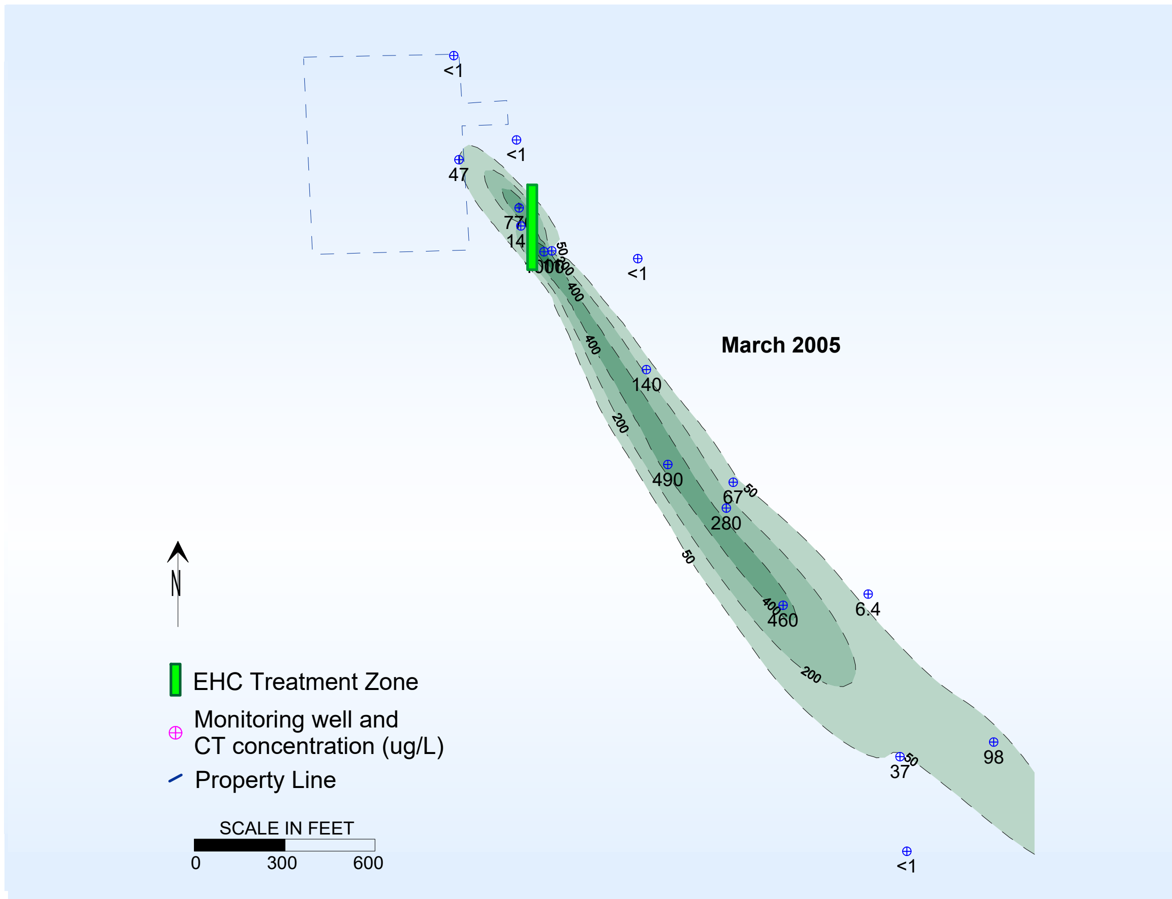
Regeneration of Reactive Minerals – Iron Redox Cycle



- **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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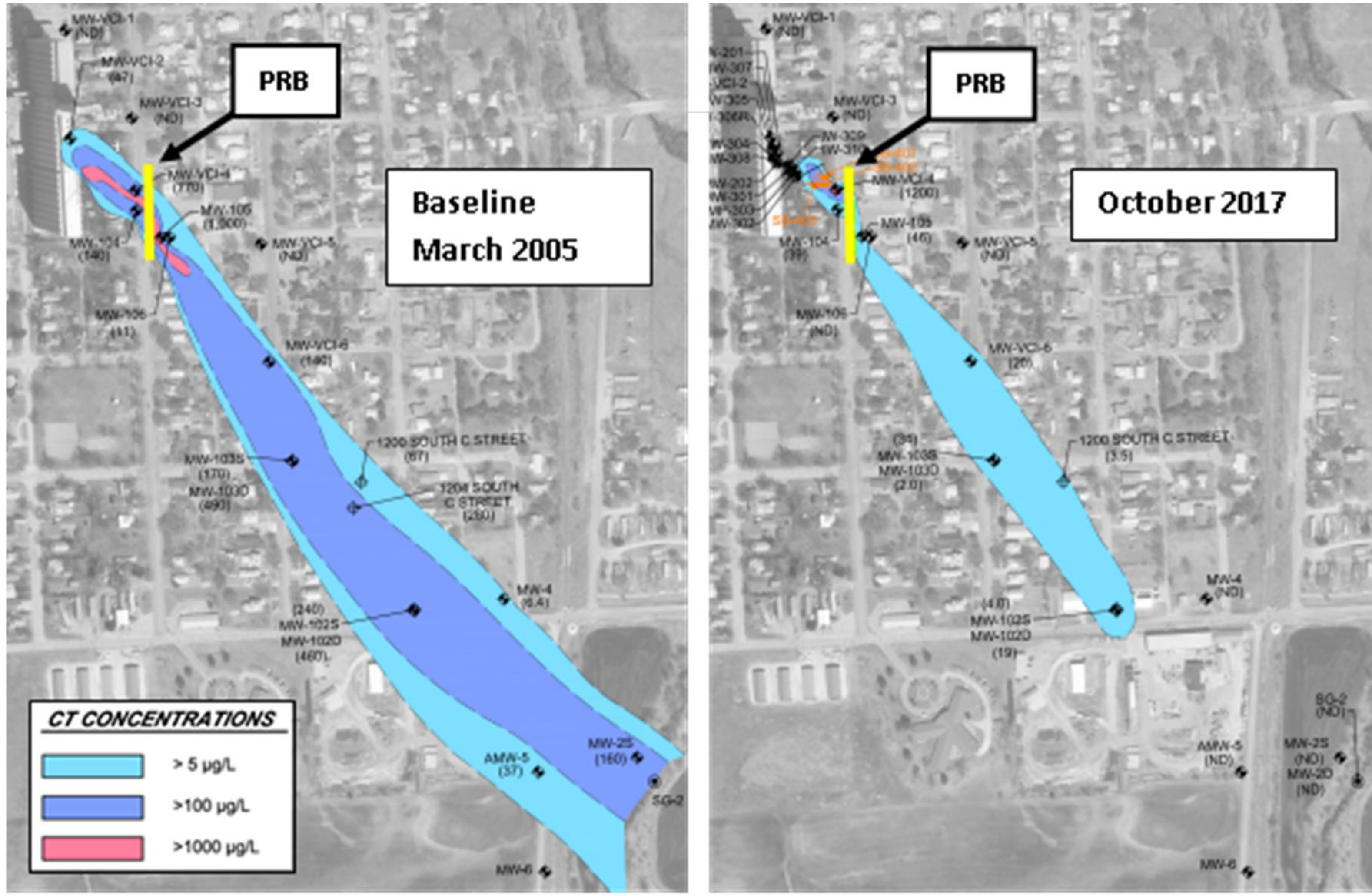
PRB
Baseline
March 2005
CT CONCENTRATIONS
> 5 µg/L
>100 µg/L
>1000 µg/L
MW-VCI-1 (ND)
MW-VCI-2 (67)
MW-VCI-3 (ND)
MW-VCI-4 (770)
MW-105 (1,900)
MW-104 (140)
MW-VCI-5 (ND)
MW-106 (11)
MW-VCI-6 (190)
1200 SOUTH C STREET (67)
MW-103S (170)
MW-103D (490)
1204 SOUTH C STREET (280)
MW-4 (6.4)
(240) MW-102S MW-102D (460)
AMW-5 (37)
MW-2S (160)
SG-2
MW-6
PRB
October 2017
MW-VCI-1 (ND)
MW-VCI-3 (ND)
MW-VCI-4 (1200)
MW-105 (46)
MW-104 (39)
MW-VCI-5 (ND)
MW-106 (ND)
MW-VCI-6 (26)
1200 SOUTH C STREET (3.5)
(36) MW-103S MW-103D (2.0)
MW-4 (ND)
(4.8) MW-102S MW-102D (19)
AMW-5 (ND)
SG-2 (ND)
MW-2S (ND) MW-2D (ND)
MW-6

PRB Economics

Installation costs:

Amendment:	24 tonnes of EHC used in PRB Product cost = ~$100,000
Injection:	2 weeks of Geoprobe Injection Cost = ~$50,000
Total Fixed Cost:	$150,000
Operating Cost:	None

Longevity:

A single application of EHC has remained active for a period of ~12 years before indications of breakthrough started to be observed, continuously supporting >95% removal of CT without the accumulation of catabolites.

PRB treated an estimated ~175,000 m^3 GW over its reactive life

Product Cost = ~$0.57 /$m^3$

This is significantly lower than the pump and treat alternative where just the annual O&M Costs can range from $ 50K to $ 300K

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Thank you,
questions are welcome!

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