



Laboratory Evaluations of ZVI and EVO in Combination with Sulfidation and Added Sulfur Containing Amendments

Michael Lee, Ph.D.

(mlee@terrasystems.net) Richard

Raymond, Jr. and Paul Dombrowski

2024 Chlorinated Conference – Denver, CO

June 6, 2024

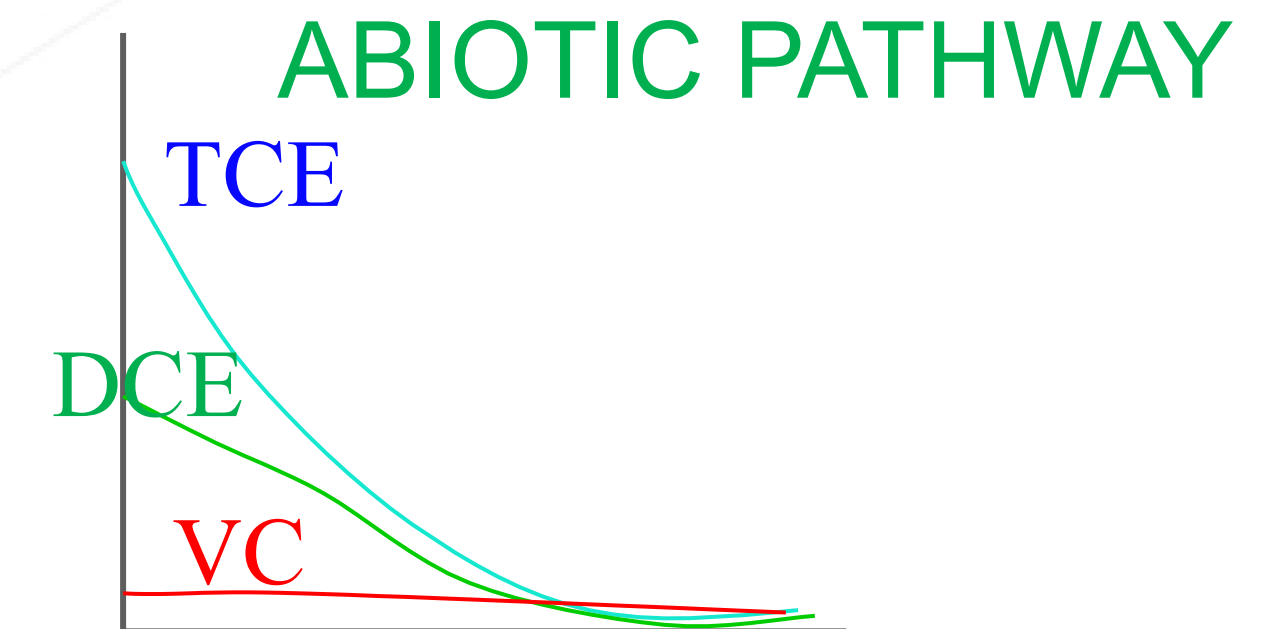
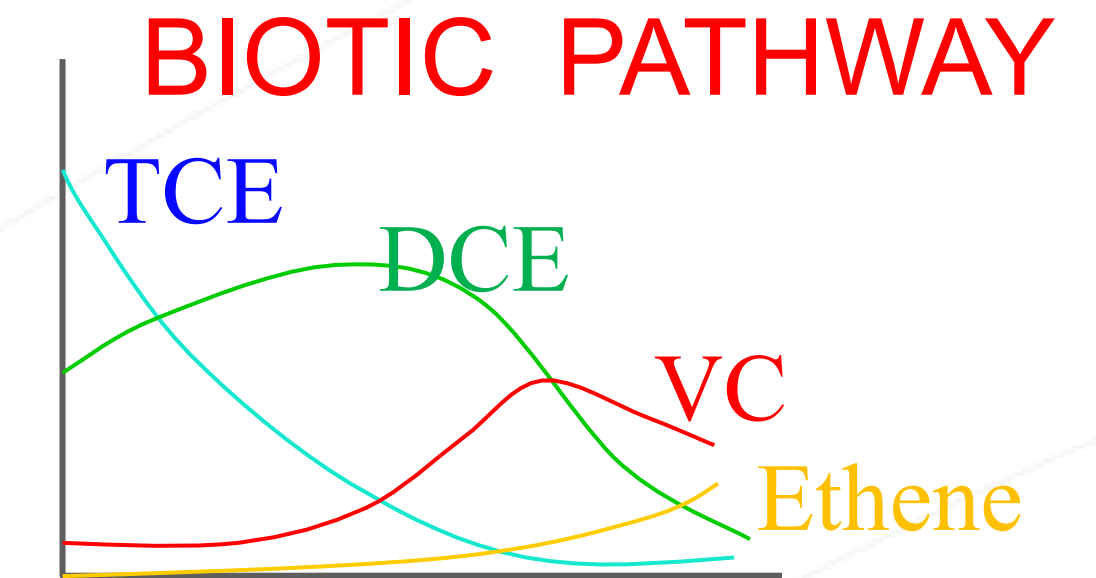
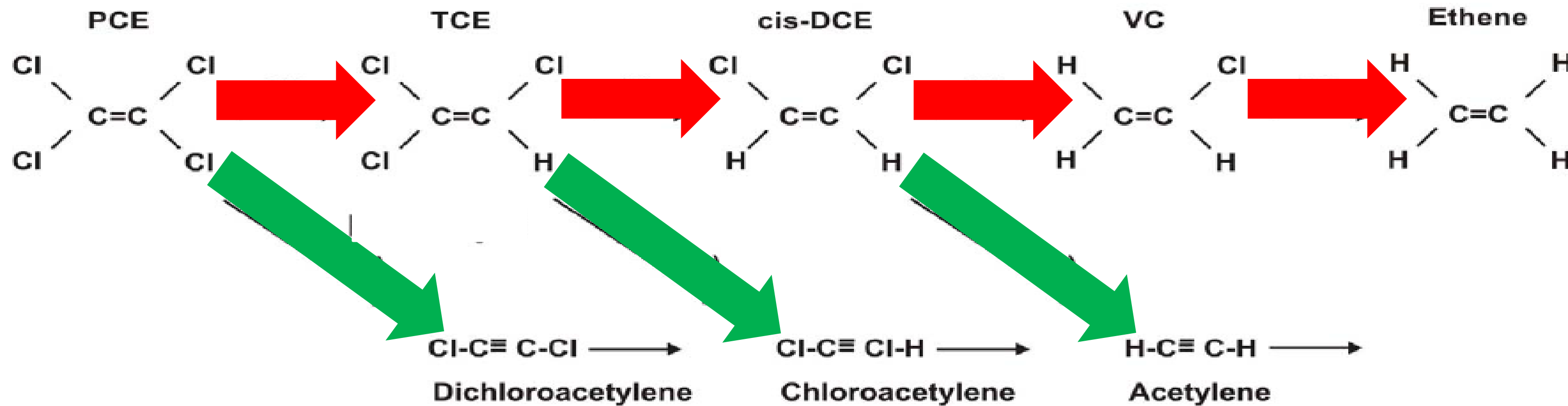


terrasystems

BIOTIC VERSUS ABIOTIC

Biotic Dechlorination in presence of e^- donor only

Biotic & Abiotic Dechlorination in presence of ZVI & e^- donor



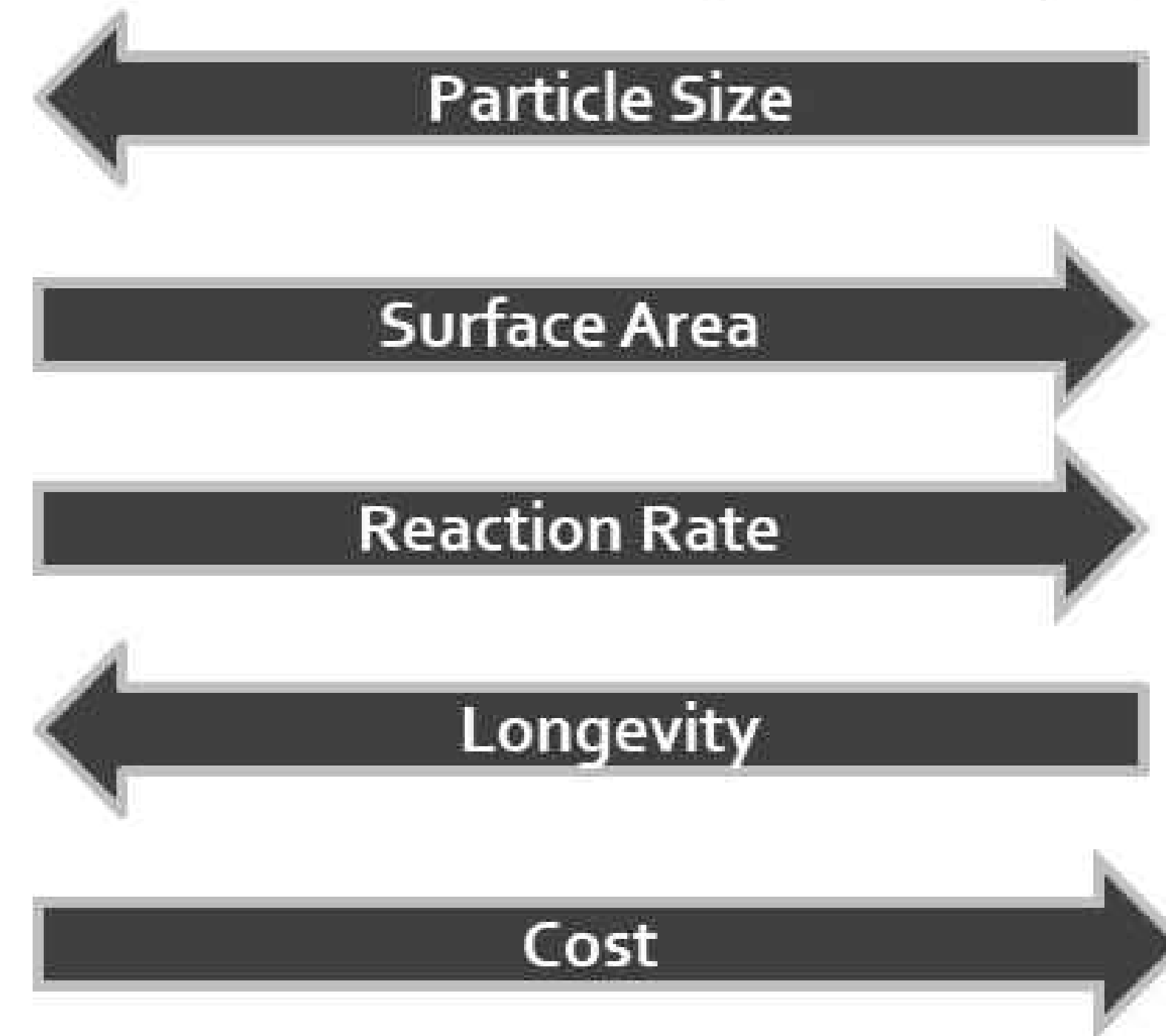
- Multiple reaction processes
- Reduce lesser chlorinated CVOCs
- Lower reducing conditions
- Extend reactivity
- Buffering

ZVI PARTICLES

- Remediation Objectives
- Hot Spot Treatment
 - Smaller ZVI – rapid reaction
- Permeable Reactive Barriers
 - Larger ZVI - persistence
- Combinations with reactive iron
 - Sulfidation
 - Substrate for biotic



(Photo Credit: Hepure)



LABORATORY BATCH AND COLUMN STUDIES

- **Compare different sulfidated zero valent irons (ZVI)**
- **Different loadings**
- **Incubation times**
- **Contaminants**
- **With and without bioaugmentation culture**

Chlorinated Ethenes (CE)	Chlorinated Methanes or CM	Chlorinated Ethanes (CA)	Brominated Methanes (BM)	Brominated Ethanes (BA)
Tetrachloroethene (PCE)	Carbon Tetrachloride (CT)	1,1,1-Trichloroethane (1,1,1-TCA)	Bromoform (BF)	Ethylene Dibromide (EDB)
Trichloroethene (TCE)	Chloroform (CF)	1,1,2-Trichloroethane (1,1,2-TCA)	Dibromomethane (DBM)	Bromoethane (BA)
Cis-1,2-Dichloroethene (cis-DCE)	Dichloromethane (DCM)	1,1-Dichloroethane (1,1-DCA)	Bromomethane (BM)	
Vinyl Chloride (VC)	Chloromethane (CM)	1,1-Dichloroethene (1,1-DCE)		
		Chloroethane (CA)		

- **EVO (SRS) Loading 0-15 g/L**
- **ZVI Particle Sizes 4 to <125 µm**
- **ZVI Loading 3 to 10 g/L**
- **Sulfidation Agent – Sodium dithionite (SD), sodium sulfide (Na₂S), sulfur (S), calcium polysulfide (CPS), and ferrous sulfide solution (FSS)**
- **Bioaugmentation with TSI-DC (DHC) and TSI-TCA (DHB)**

BATCH 1 WATER ONLY



			Control	SRS + TSI-DC	<125 µm ZVI	<125 µm ZVI Sulfide	<44 µm ZVI	<44 µm ZVI Sulfide	SRS <125 µm ZVI	SRS <125 µm ZVI Sulfide
ZVI Loading		g/L			10	9.7	10	9.7	10.1	10.1
EVO Loading		g/L		2.0					15.1	15.1
Sulfide		g/L				0.7 Na ₂ S		0.7 Na ₂ S		0.7 Na ₂ S
Bioaugmentation Culture		g/L (Day)		6 (12, 43)	2 (43)	2 (43)	2 (43)	2 (43)	2 (43)	2 (43)
Sampling	mg/L	1, 7, 22, 43, 70								
PCE	1.2	PCE % Rem	0.0	-8.3	72.5	95.5	76.7	97.9	73.3	80.8
		CE % Rem	0.0	-8.3	54.7	87.1	73.2	91.8	73.3	80.2
1,1,1-TCA	1.9	1TCA % Rem	21.1	31.6	>99.97	>99.97	99.8	>99.97	91.1	>99.7
		CA % Rem	16.5	29.5	70.4	87.9	71.3	91.3	86.4	91.6
1,2-DCA	4.4	2DCA % Rem	9.1	15.9	20.5	9.1	18.2	15.9	52.3	38.6
CT	1.8	CT % Rem	27.8	70.0	>99.97	>99.97	>99.97	>99.97	>99.7	>99.7
		CM % Rem	25.9	59.5	82.8	93.4	81.8	94.9	92.9	96.3
BF	5.6	BF % Rem	8.9	58.9	>99.99	>99.99	>99.98	>99.99	>99.9	>99.9
		BM % Rem	8.3	53.6	99.4	99.4	99.9	99.8	97.5	100.0
>90%		>80%	>70%							

BATCH 2 SOIL SLURRY

			Control	4 µm ZVI	4 µm ZVI Sulfur	4 µm ZVI SRS Z	4 µm ZVI SRS Z + Sulfur	4 µm ZVI SRS Z + Sulfur + TSI-DC
Day Sampled			0, 14, 42	14, 42	14, 42	14, 42	14, 42	14, 42
Soil		%	43	43	43	43	43	43
EVO		g/L				10.1	13	13
ZVI		g/L		6.4	3.1	6.7	4	4
Sulfur		g/L			0.2		0.2	0.2
TSI-DC	mg/L							1.7
1,1,1-TCA	3.3	Sum CA % Rem	38.1	83.3	97.9	87.7	95.6	97.0
TCE	4.0	Sum CE % Rem	62.5	89.3	99.2	79.6	87.9	93.9
CF	3.0	Sum CM % Rem	23.1	71.4	90.8	83.0	95.5	97.2
>90%		>80%	>70%					

BATCH TEST 3 WATER ONLY

Treatment			Control	4 µm ZVI	<125 µm ZVI	<44 µm ZVI	<44 µm ZVI Sulfide	SRS-Z <44 µm ZVI	SRS-Z <44 µm ZVI Sulfide
ZVI Loading		g/L		10	10	10	10	10	10
EVO Loading		g/L						15	15
Sodium Dithionite		g/L					3.1		3.1
Sampling	mg/L	Days	0, 7, 28	1, 7, 28	1, 7, 28	1, 7, 28	1, 7, 28	1, 7, 28	1, 7, 28
PCE	1.2	CE % Rem	16.7	75.0	54.2	57.9	43.2	33.3	64.2
1,1,1-TCA	1.5	CA % Rem	-13.3	74.2	53.8	52.4	70.2	36.9	25.5
1,2-DCA	3.7	2DCA % Rem	-21.6	-21.6	-29.7	-24.3	-21.6	2.7	-5.4
CT	0.84	CM % Rem	-5.9	78.6	72.0	71.3	63.8	73.8	72.0
BF	3.9	BM % Rem	2.4	98.4	97.6	96.7	90.6	79.6	55.6
EDB	4.2	BA % Rem	7.1	100.0	100.0	100.0	86.7	60.2	59.5
>90%		>80%	>70%						

BATCH TEST 4

Dry Cleaners Site in NJ

Groundwater Only

0.26 mg/L PCE, 0.13 mg/L TCE, 0.83 mg/L cis-DCE, 0.26 mg/L VC

Treatment		Control	SRS-Z	SRS-Z Bioaug	SRS	SRS + Bioaug
SRS	g/L		8	8	4	4
4 µm ZVI	g/L		2	2		
TSI-DC	g/L			3		3
Days Sampled	0, 1, 14, 35, 56, 84					
Sum CE % Removal		21.2	48.2	99.3	-6.4	40.7

FSS Alone (Water Only)						
Treatment g/L	Days	Sum CE	Sum CA	Sum CM		
1	27	38.5				
1.1	91	60.4	44.4	20.5		
5	48	74.6				
11	21	12.5	32.0	-6.7		
11	91	66.2	56.6	30.2		
14	56	30.1				
14	28	18.3	54.9	83.8		
20	91	60.4	52.2	16.8		
71 Ex S	28	99.95	98.8	98.5		
71	28	81.9	97.6	97.4		
143	56	60.1				
SRS + FSS (Water Only)						
SRS g/L	FSS g/L	Days	Sum CE	Sum CA	Sum CM	
1.1	11	21	37.3	36.7	-12.7	
11	5.3	91	79.1	74.8	100	
11	11	91	84.8	81.7	41.9	
10	5	48	85.8			
SRS + FSS + Bioaug (Water Only)						
SRS g/L	FSS g/L	Bioaug g/L	Days	Sum CE	Sum CA	Sum CM
11	5.3	2	91	>99.99	95.5	82.6
11	10	2	91	86.0	80.4	43.1
10	5	1	48	79.6		

BATCH TESTS CONCLUSIONS

- **ZVI or EVO + ZVI > EVO and bioaugmentation**
- **ZVI and sulfidation agent increased PCE and TCE degradation**
- **1,1,1-TCA, CT, CF, BF, and EDB degradation almost complete with ZVI alone**
- **1,2-DCA not treated as effectively**

BATCH TESTS CONCLUSIONS

- Sodium sulfide, sulfur, sodium dithionite, calcium polysulfide, and ferrous sulfide solution effective sulfidation agents
- Low S to Fe ratio required
- Sulfidation improvement with small (4 μm) to moderate (<125 μm) ZVI particles
- FSS solution alone or in combination with EVO and/or bioaugmentation
 - > Control or EVO alone but mostly not complete over up to 91 days

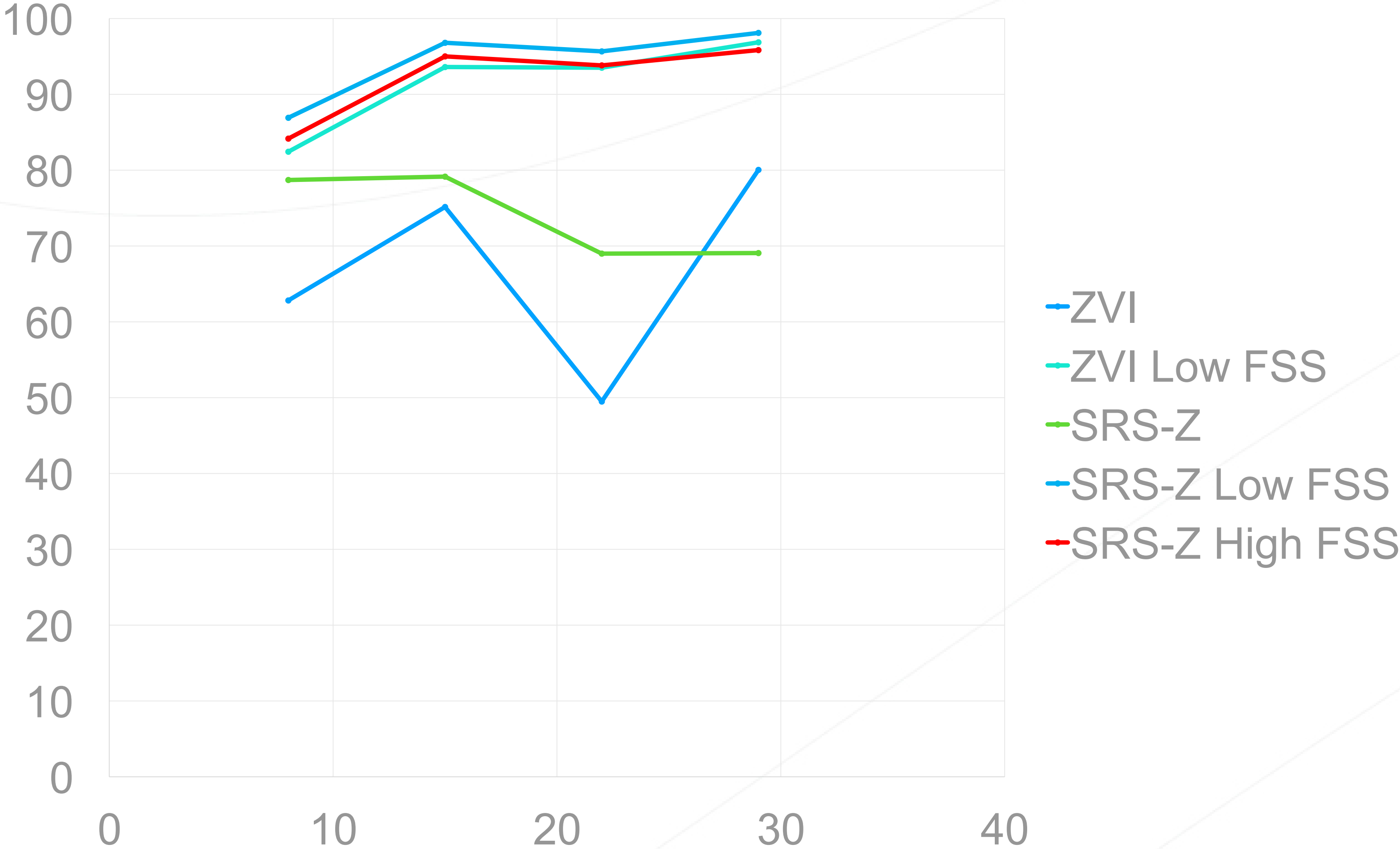
COLUMN TEST



- **Contaminants:** 1.3-3.1 mg/L TCE, 2.9-4.8 mg/L CF, 0.72-3.1 mg/L 1,1,1-TCA
- **Bioaugmentation with TSI-DC (DHC) and TSI-TCA (DHB) on Day 15**
- **Added 1.1 g/L FSS to influent on Day 17**
- **Average Retention time 1.6 to 2.8 days**

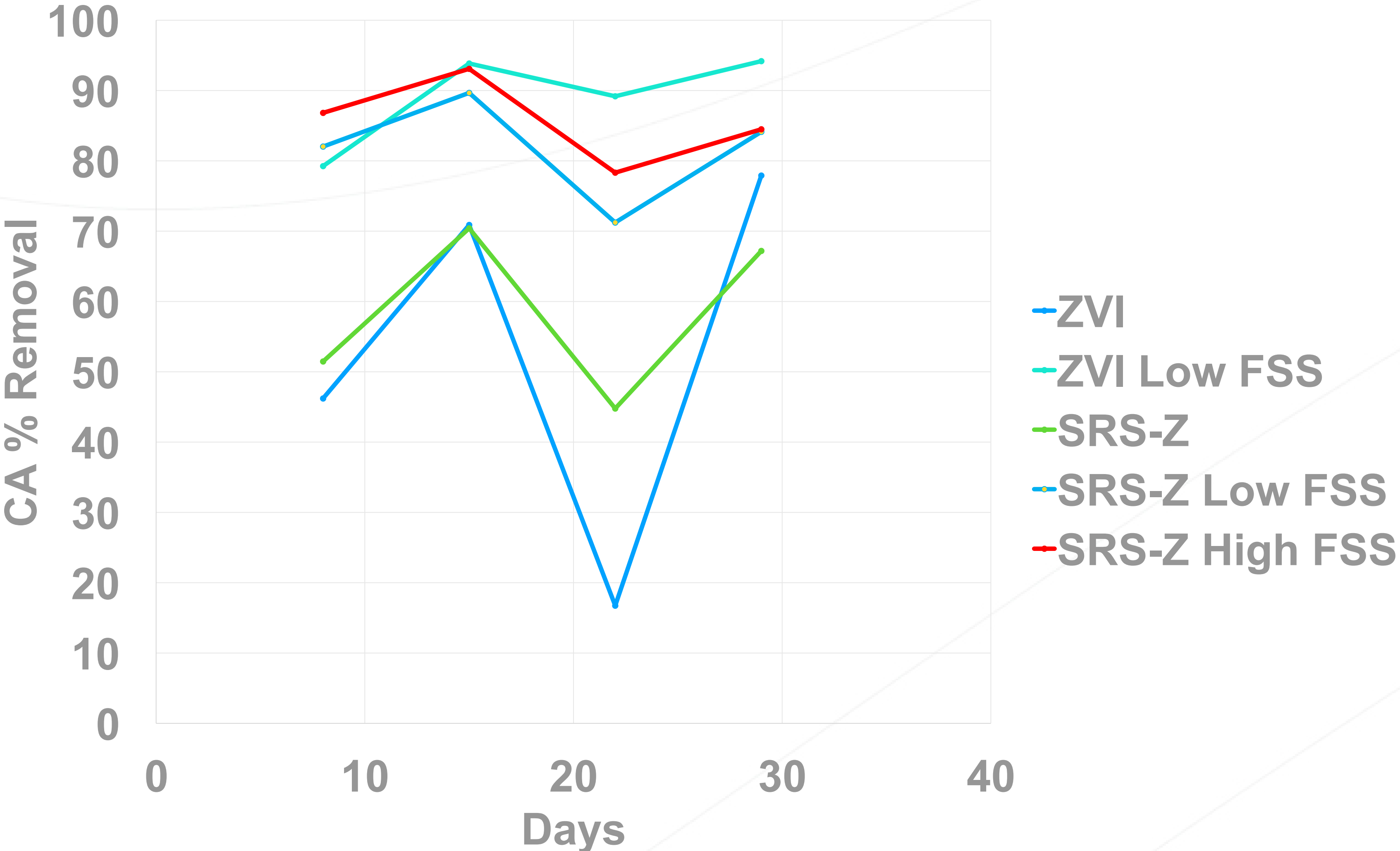
Treatment	EVO (g/kg)	4 µm ZVI (g/kg)	FSS (g/kg)
ZVI		10	
ZVI + Low FSS		10	1
SRS-Z	15	10	
SRS-Z Low FSS	15	10	1
SRS-Z High FSS	15	10	5

Chlorinated Ethenes w/o Gases % Reduction



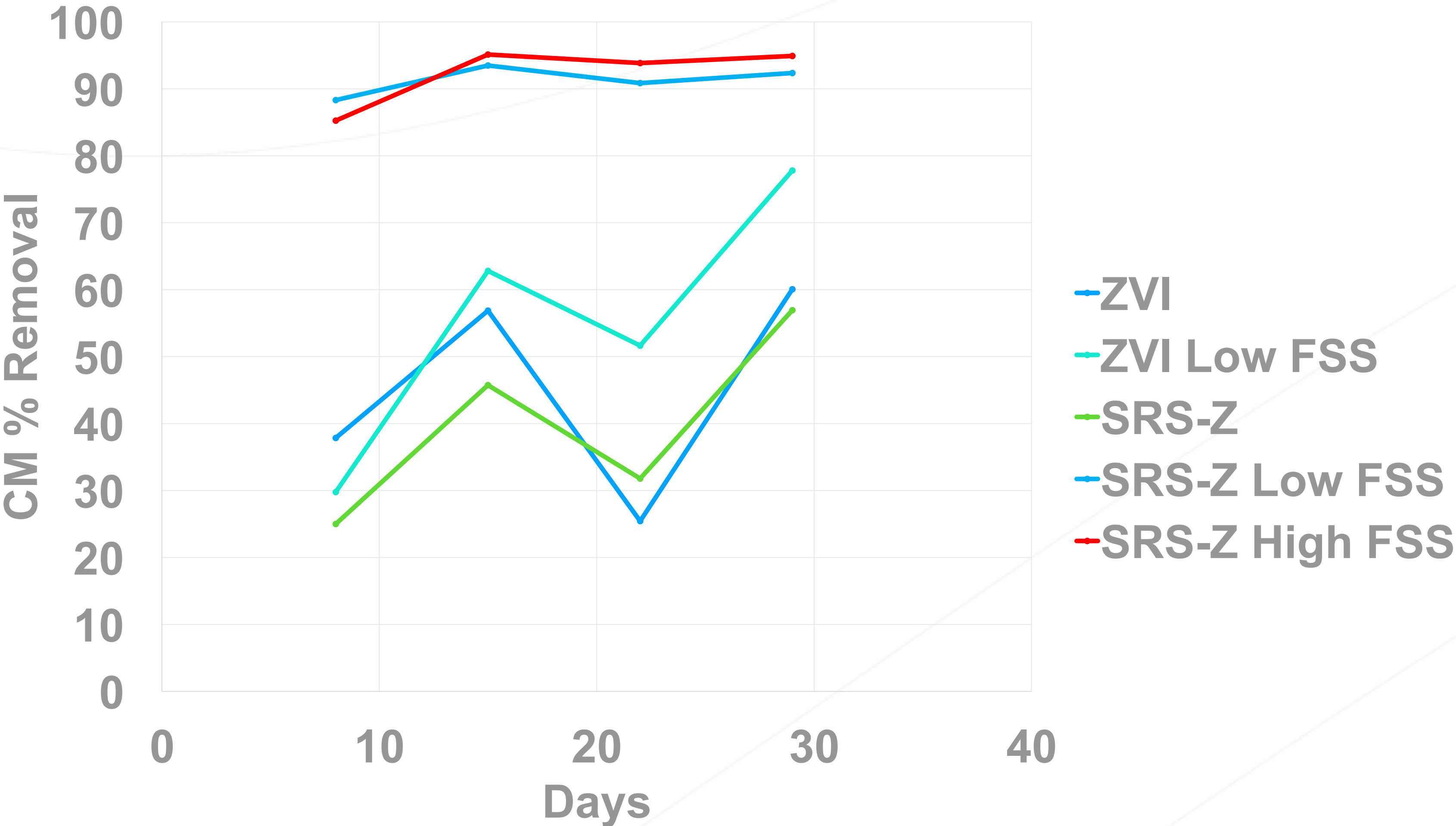
For Chlorinated Ethenes, SRS-Z with Low and High FSS and ZVI with FSS better than ZVI or SRS-Z

Chlorinated Ethanes w/o Gases % Reduction



For Chlorinated Ethanes, SRS-Z with Low FSS or High FSS and ZVI with FSS better than ZVI or SRS-Z

Chlorinated Methanes w/o Gases % Reduction



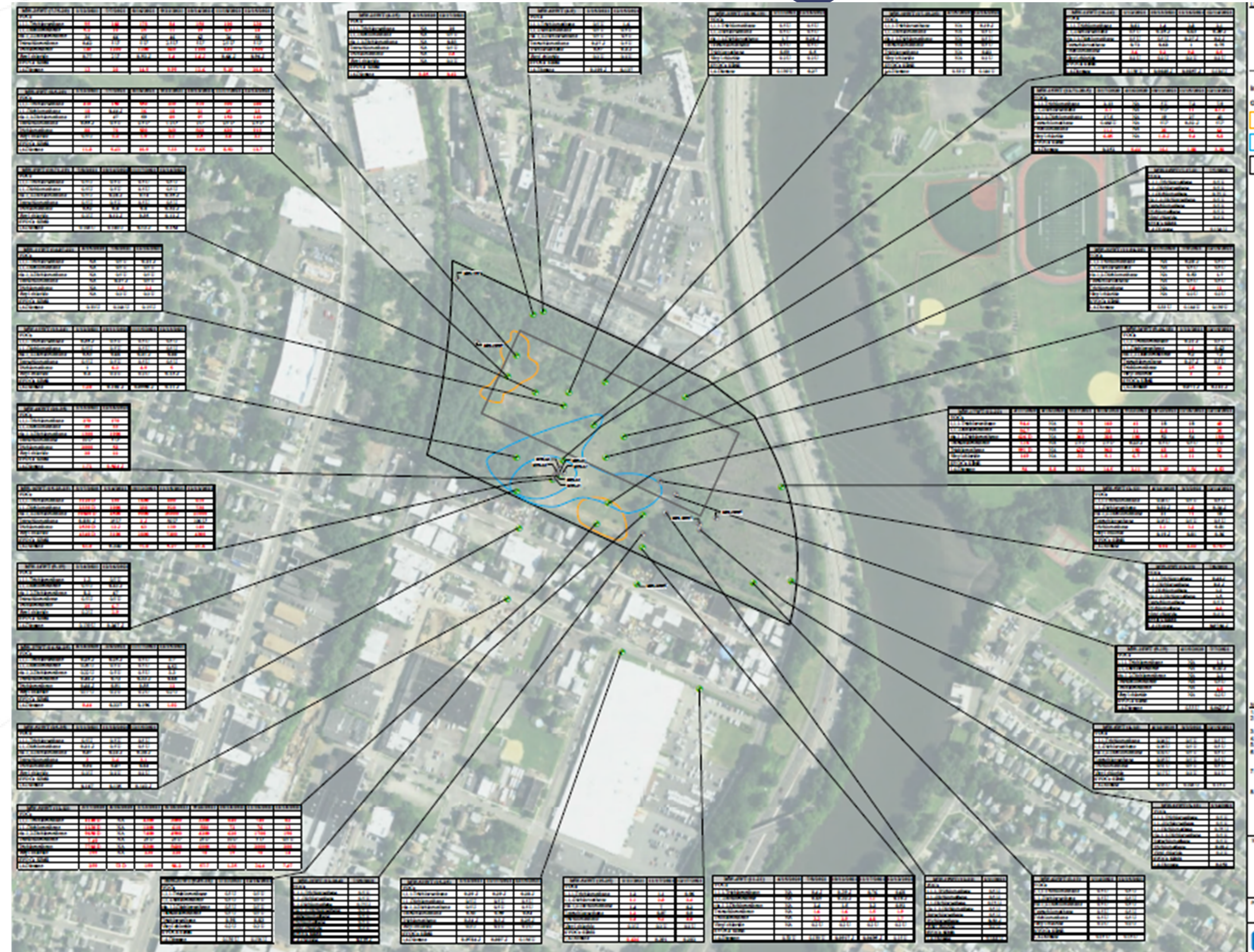
For Chlorinated Methanes, SRS-Z with Low and High FSS better than ZVI or SRS-Z or ZVI with FSS

COLUMN CONCLUSIONS

- **ZVI and SRS-Z treatments with FSS > without FSS.**
- **SRS-Z with low FSS highest treatment of TCE, 1TCA, and CF.**
- **Bioaugmentation and/or FSS influent increased dechlorination at Day 29.**
- **Less chlorinated intermediates with the FSS.**
- **Enhanced VOC dechlorination extent and degradation rates with sulfidated ZVI.**

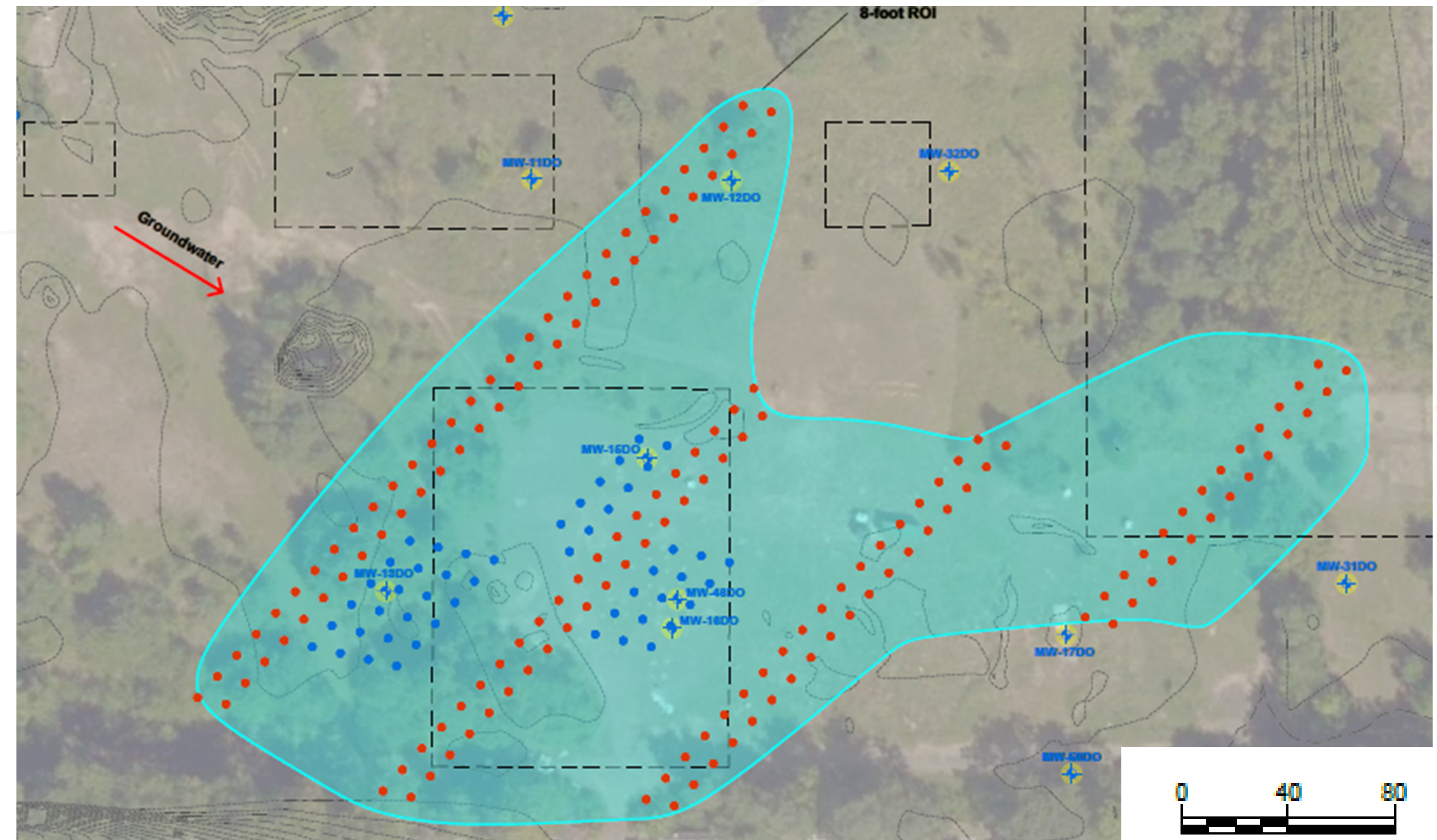
27 ACRE REDEVELOPMENT PROJECT

- New property owner wanted to initiate construction ASAP
- Overburden & bedrock impacted with chlorinated VOCs & 1,4-dioxane
 - Primary VOCs TCE & 1,1,1-TCA
 - Silt & fine sand
 - Sandstone bedrock



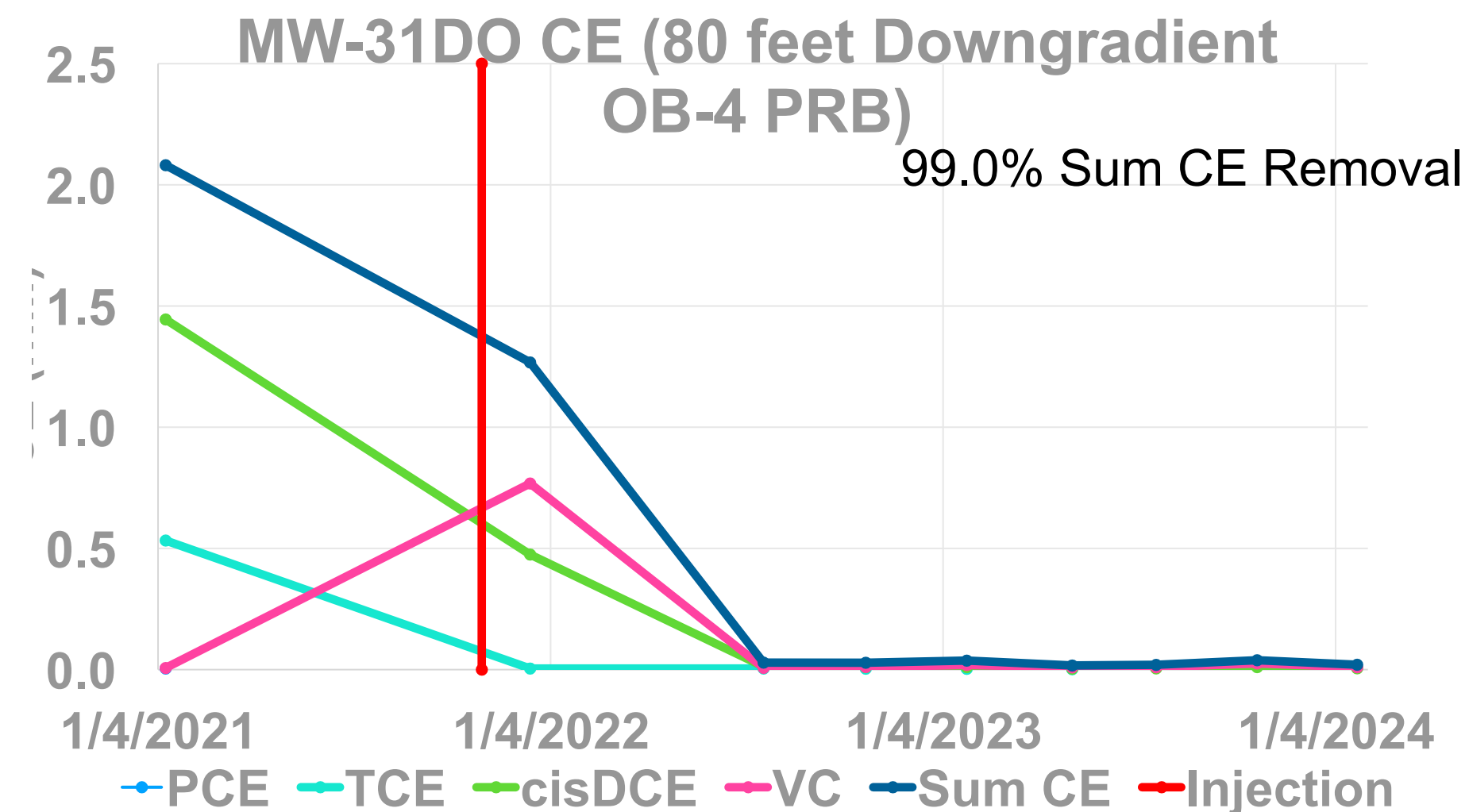
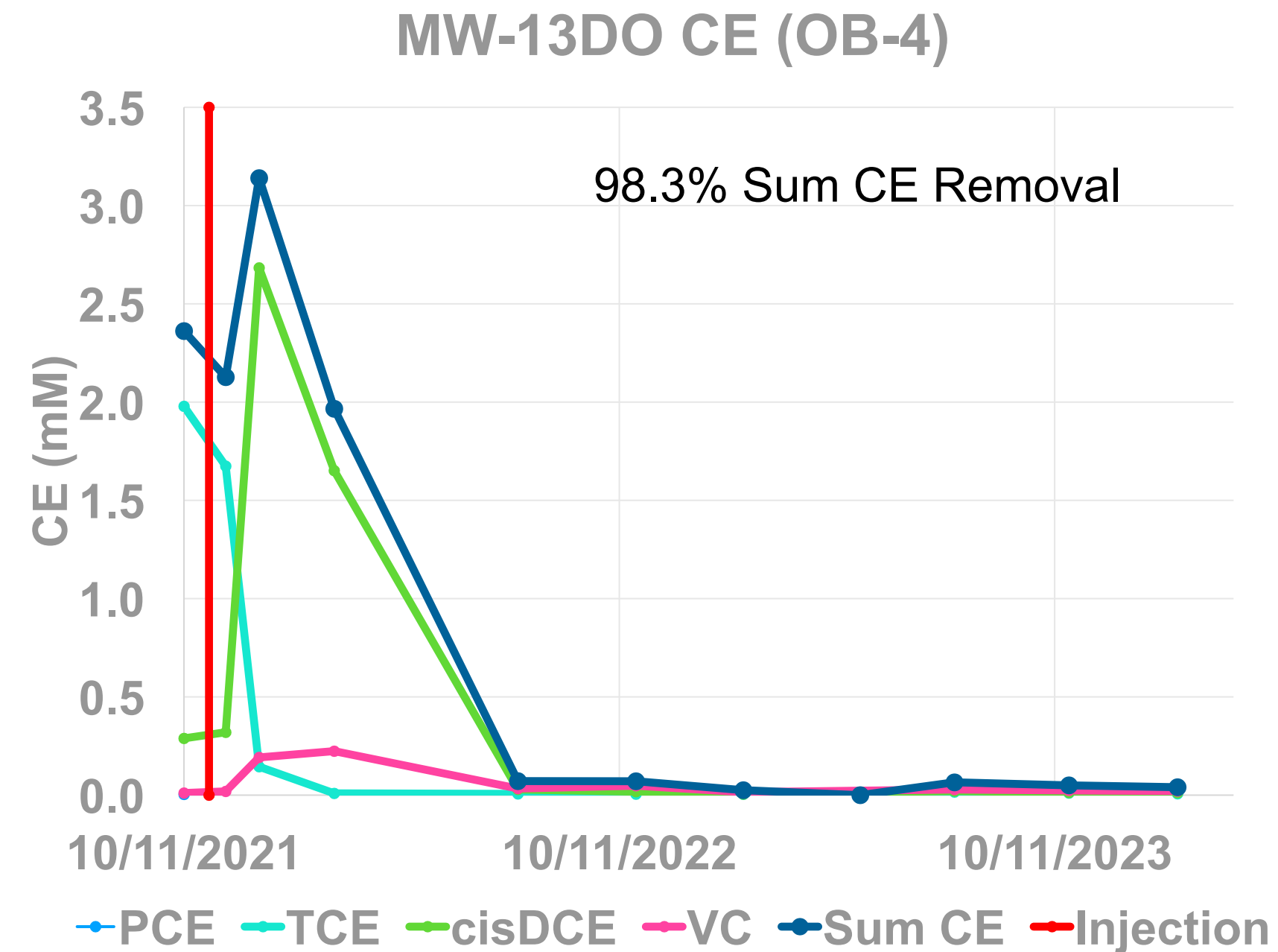
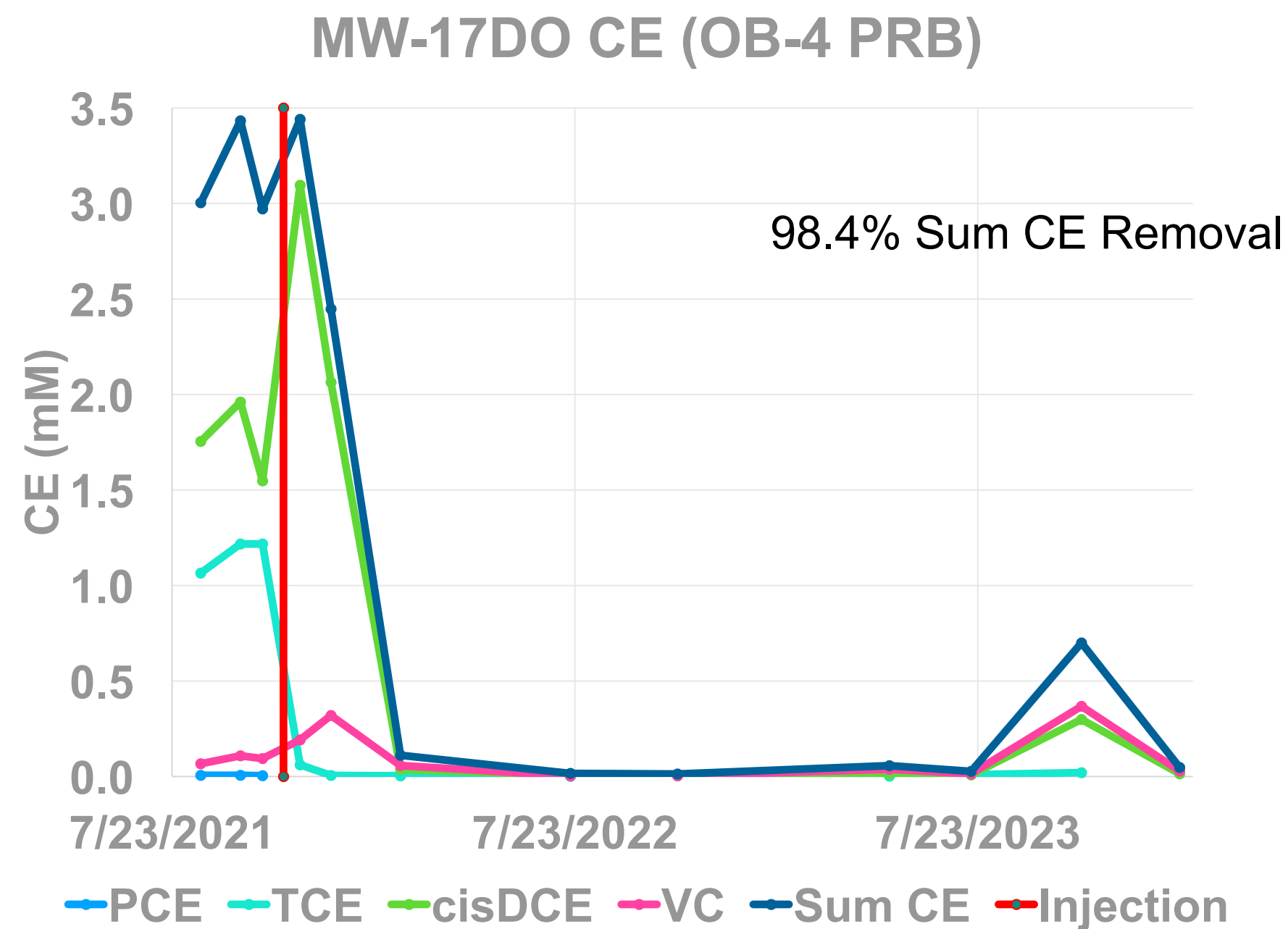
ENHANCED IN-SITU DECHLORINATION - OVERBURDEN

- 2 overburden areas of concern
- Multiple components
 - Small droplet EVO (SRS®-SD)
 - Sulfidated ZVI (SRS®-Z) – 4 micron
 - Bioaugmentation (DHC+DHB)
 - Nutrient blend (N, P) + sulfate
- Injection points
 - Hot spot grids
 - Permeable reactive barriers (>1,100 LF)



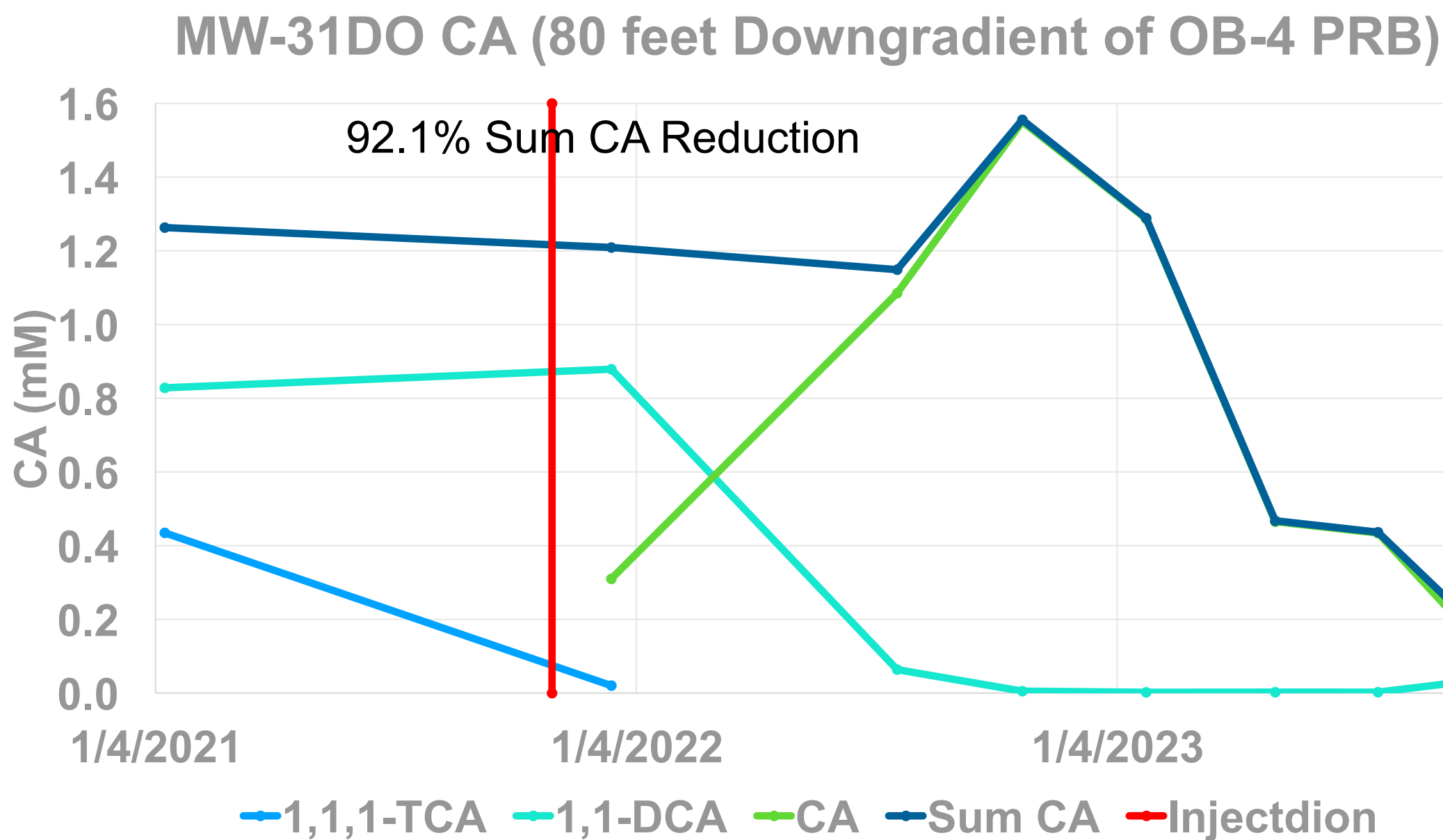
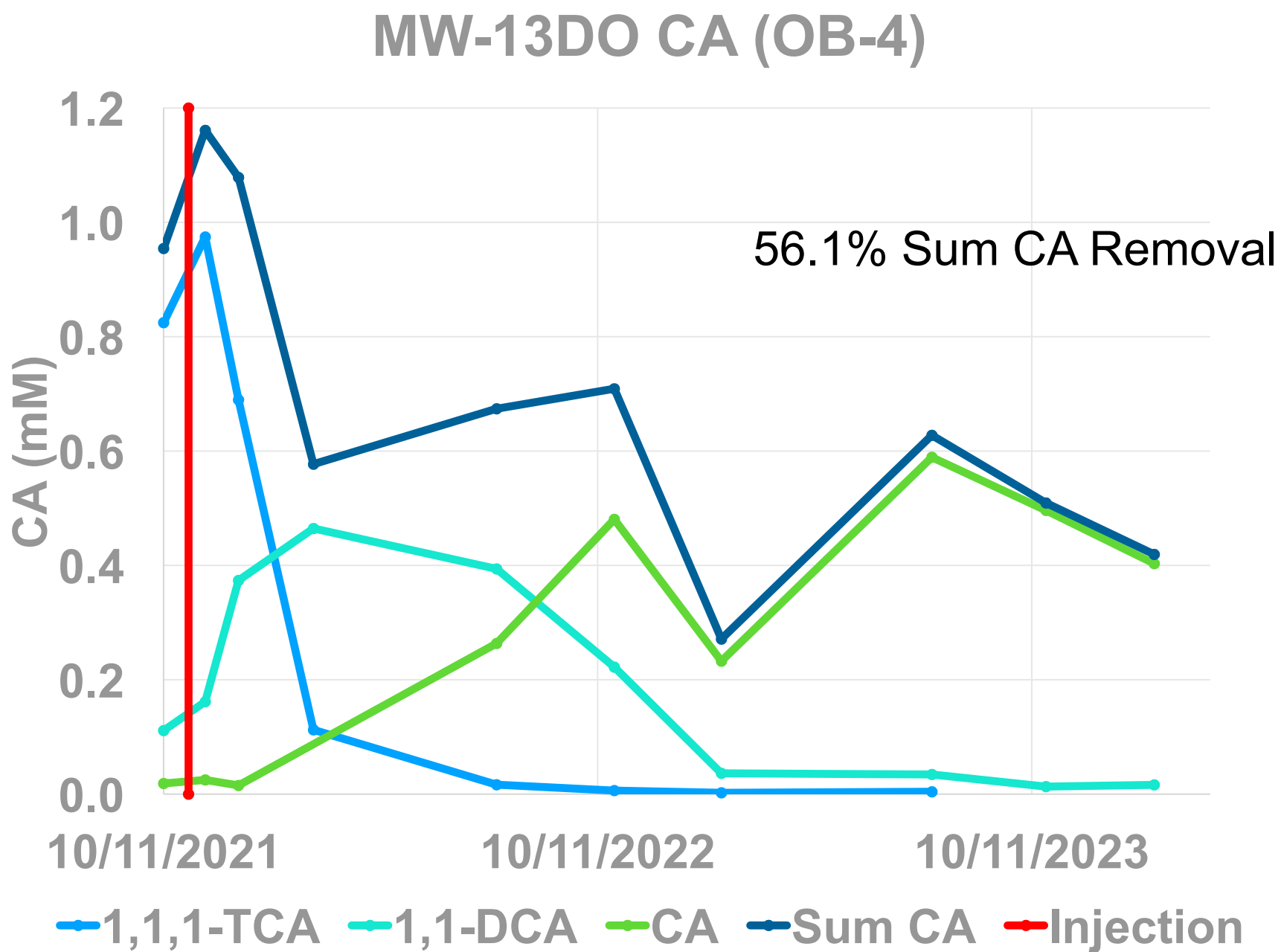
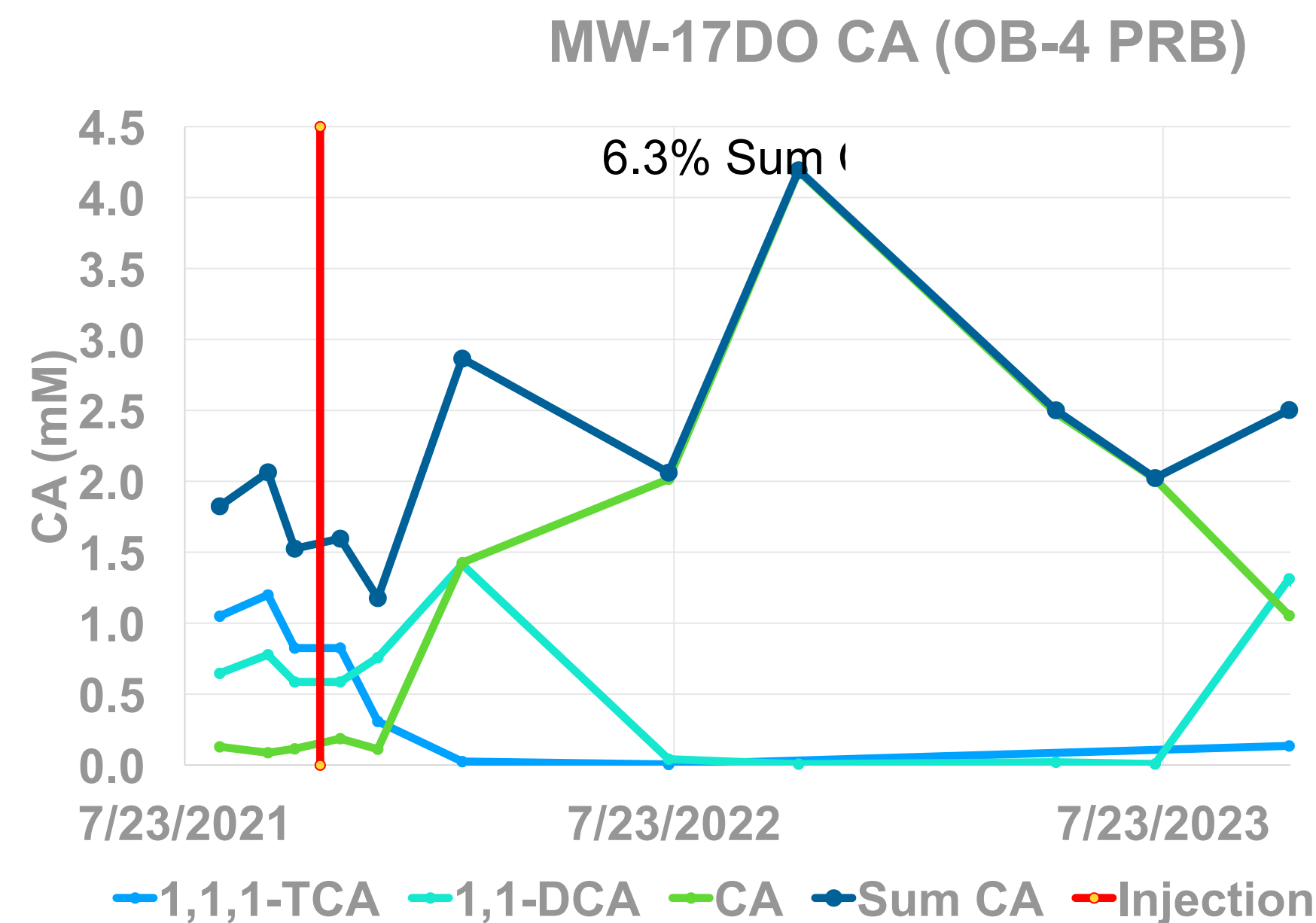
RESULTS – EISD OVERBURDEN

- Site wide significant reduction in Chlorinated Ethenes
- Maintained for over 24 months
- Biotic and Abiotic Dechlorination
- Limited VC generation



RESULTS – EISD OVERBURDEN

- Site wide reduction in Chlorinated Ethanes
- Significant CA Generation but Decreasing



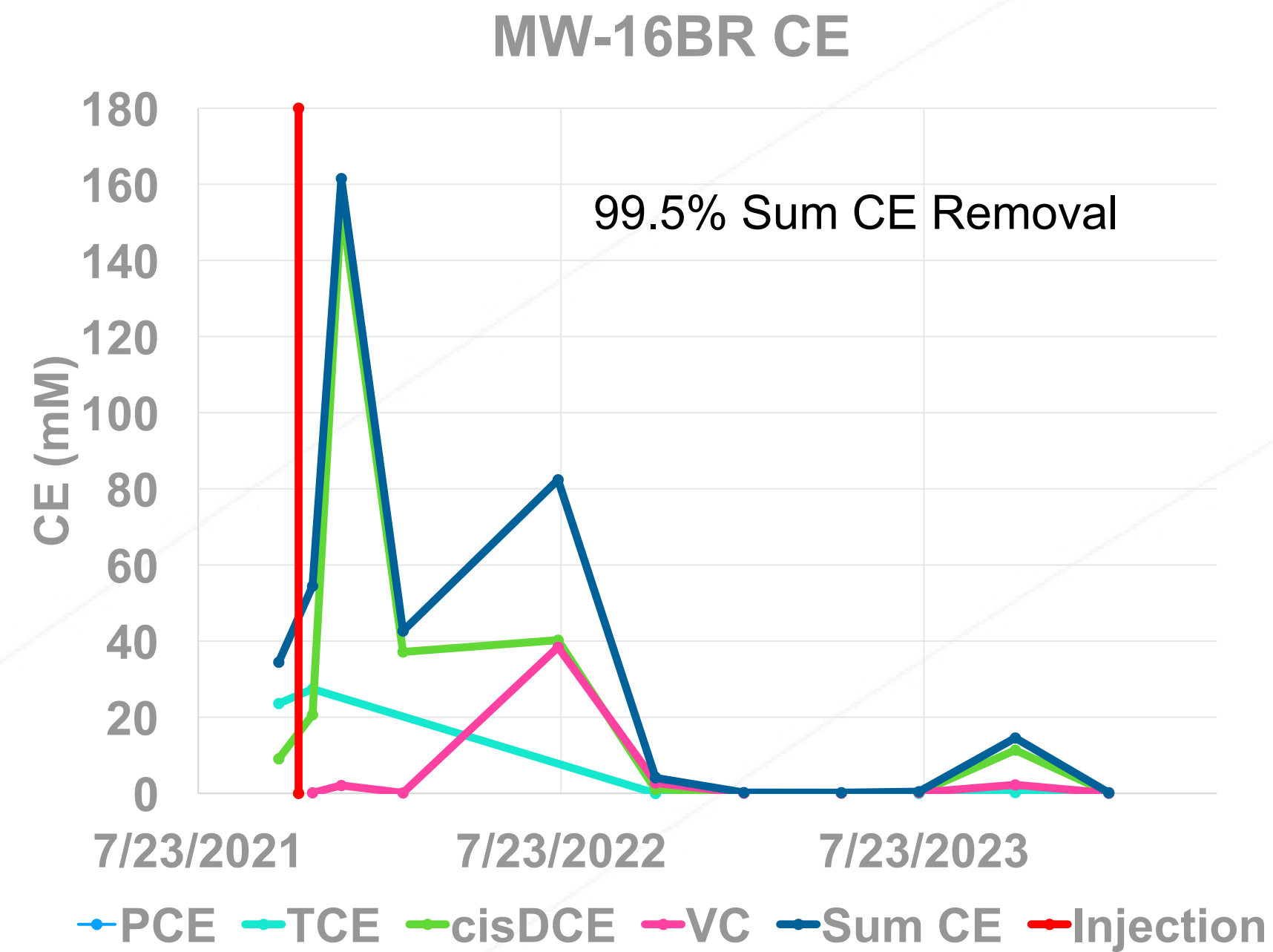
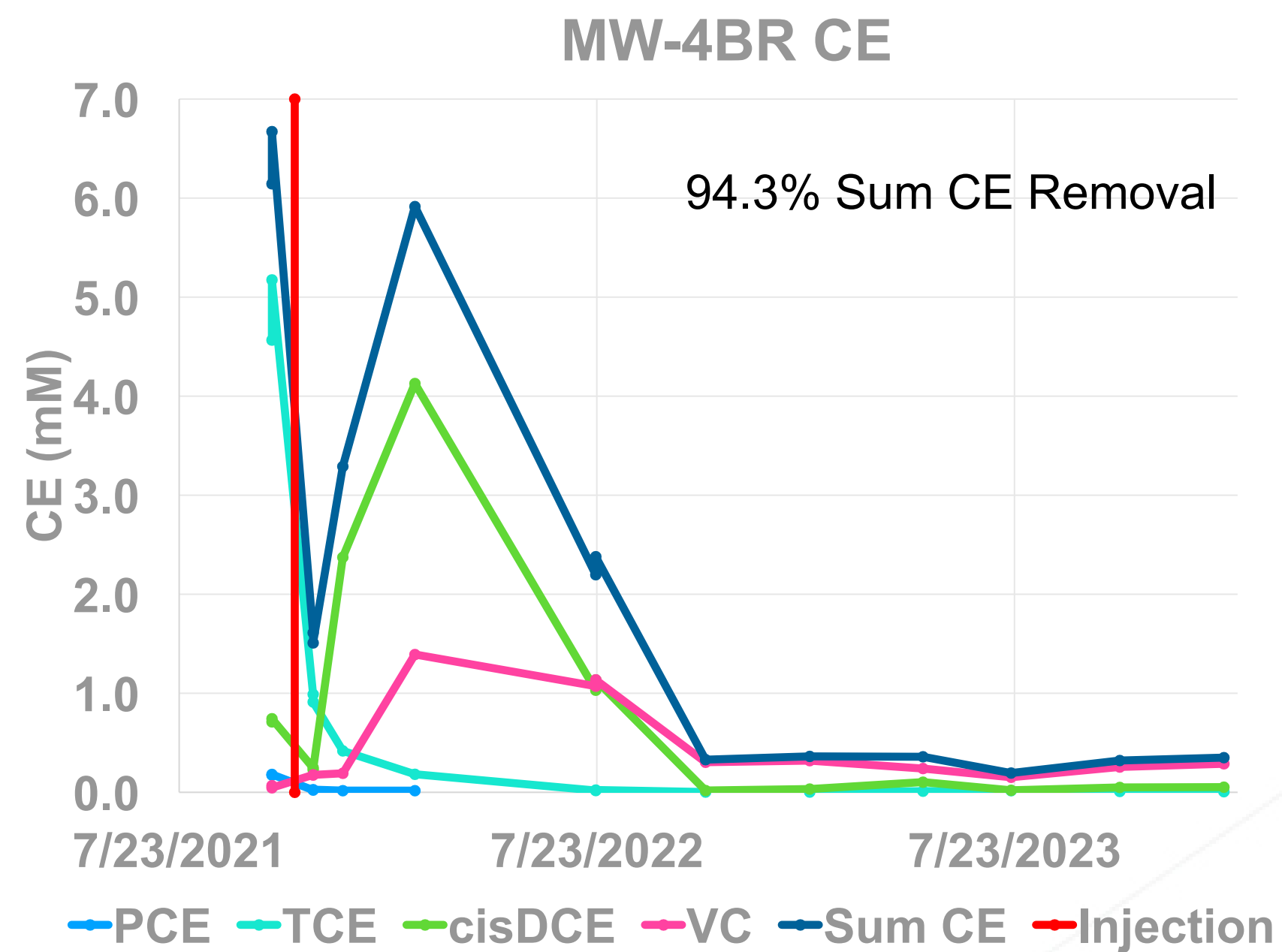
ENHANCED IN-SITU DECHLORINATION - BEDROCK

- **EISD focused for treating fractures**
 - **Large Droplet EVO**
 - **Sulfidated ZVI (SRS®-Z)**
 - ~11% 4 micron
 - ~89% 44 micron
 - **Bioaugmentation (DHC+DHB)**
 - **Nutrient blend (N, P) + sulfate**
- **Open-Hole Bedrock Injection Wells**
 - **Straddle packers to target identified fractures**



RESULTS –EISD BEDROCK FOR CHLORINATED ETHENES

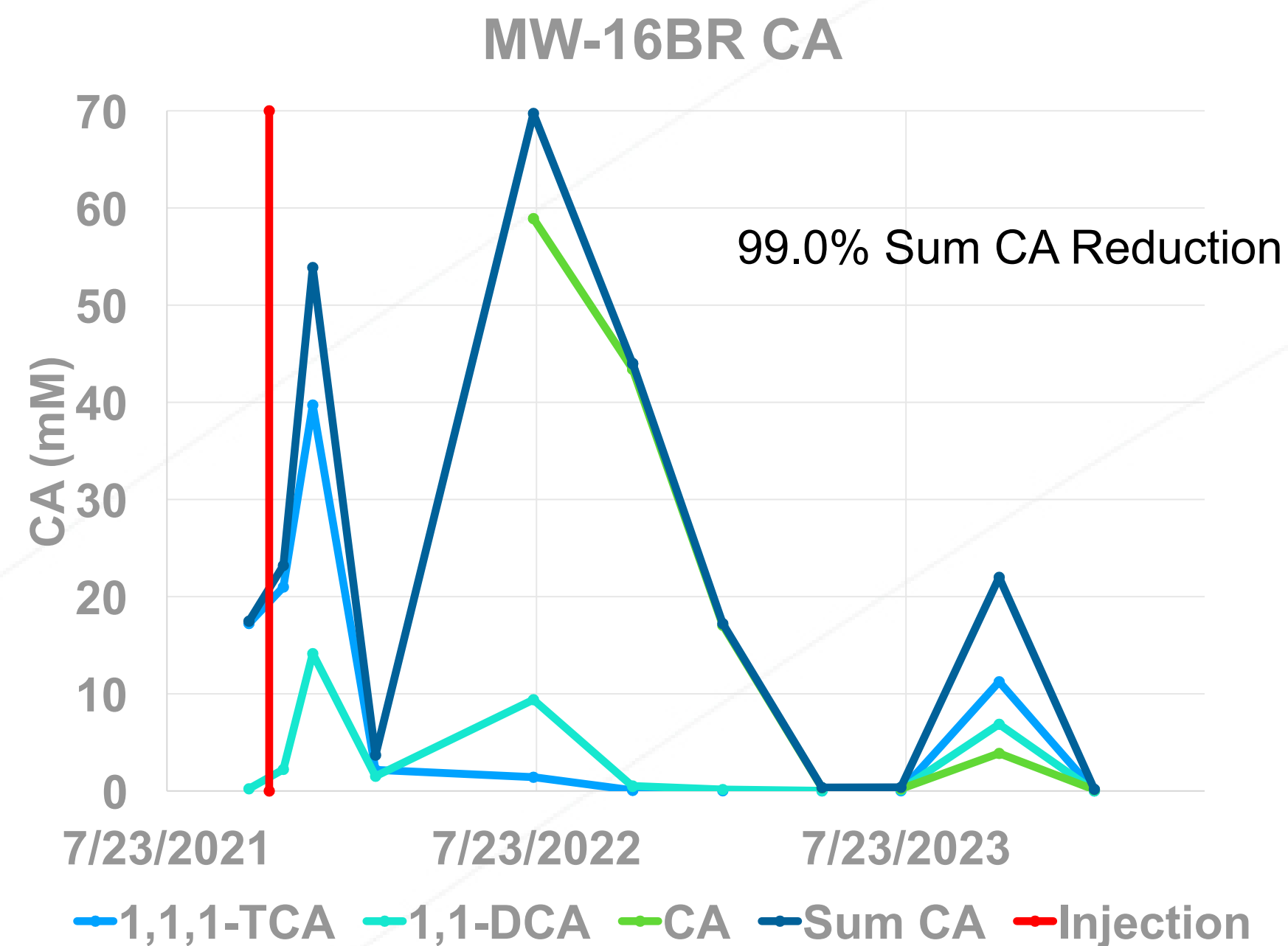
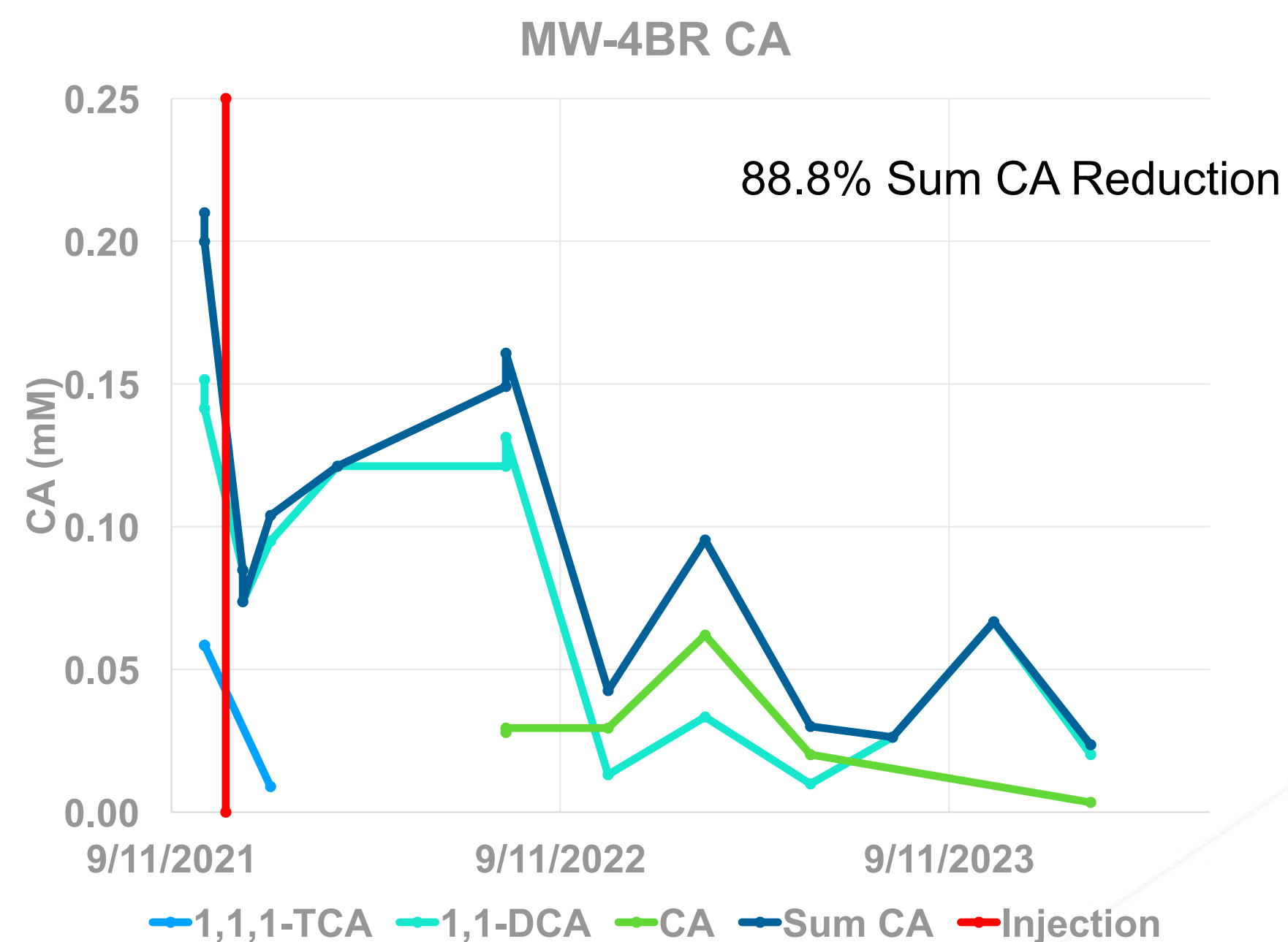
- **2 months post-injection**
 - 4/4 monitoring wells – TOC > 20 mg/L & TCE reduced by >90%
- **24 months post-injection**
 - 4/4 monitoring wells –92% - 99% reduction in Sum Chlorinated Ethenes



RESULTS –EISD BEDROCK FOR CHLORINATED ETHANES



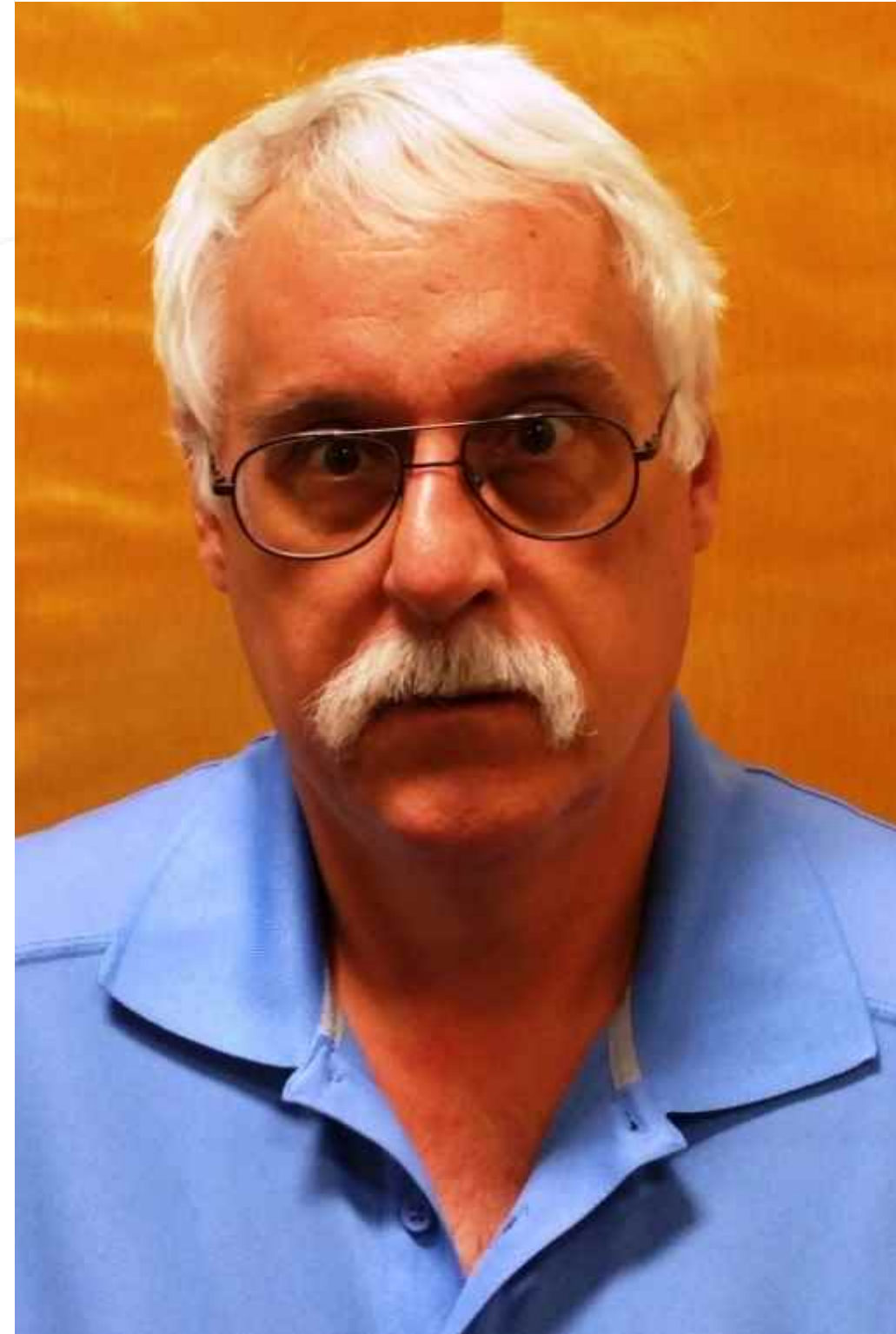
- 24 months post-injection
 - 4/4 monitoring wells increase 14% to 99% reduction in total Chlorinated Ethanes



CONCLUSIONS

- **Sulfidation increases reactivity of ZVI**
- **Works with various ZVI particle sizes**
- **Several forms of sulfur effective**
- **Can be used with EVO and bioaugmentation**
- **Case history shows effectiveness**

QUESTIONS



Michael Lee, PhD
Vice-President R&D
Terra Systems
(office) 302-798-9553 (cell) 302-753-8149
Email: mlee@terrasystems.net
www.terrasystems.net