Combinations of EVO with Sulfidated ZVI

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Outline

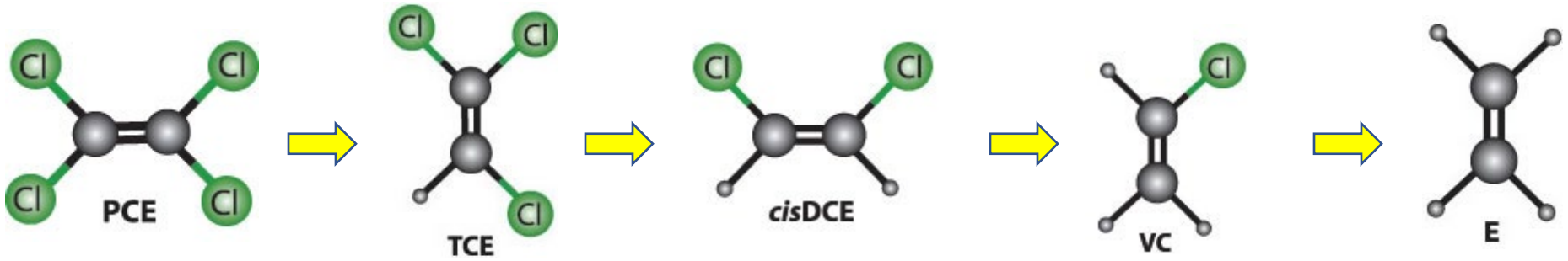
- Introduction
- Batch studies
- Column studies
- Case history
- Conclusions

Bioremediation allows natural processes to clean up harmful chlorinated solvents in the environment

Carbon substrates have been used as electron donors to enhance bioremediation for more than two decades

Many advantages

- food-grade materials
- low cost
- demonstrated effectiveness
- long persistence



Common Microbes

Dehalobacter Dehalospirillum
Desulfitobacterium Desulfuromonas
Dehalococcoides
Geobacter

Dehalococcoides or *Dehalogenimonas*

cisDCE and VC can stall if *Dehalococcoides* or *Dehalogenimonas* are not present

Zero Valent Iron

- 1972: earliest use of ZVI for environmental application (pesticides)
- 1990s: **publications** on ZVI for CVOC treatment
  - Abiotic reaction pathway

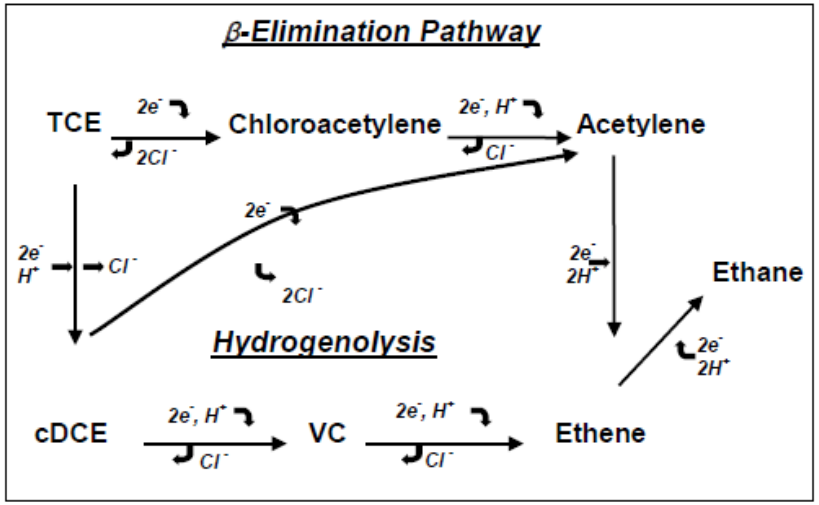
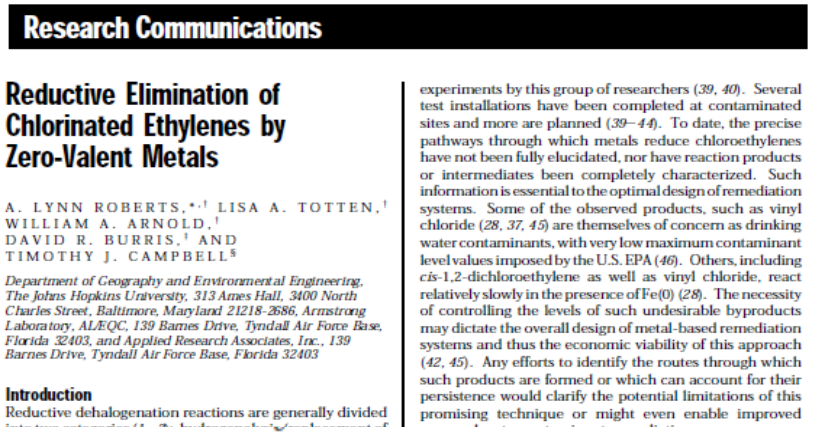


Figure 4-2. Iron degradation process for TCE. *Source:* Arnold and Roberts 2000.

(Permeable Reactive Barrier: Technology Update, ITRC, 2011)



Research Communications

Reductive Elimination of Chlorinated Ethylenes by Zero-Valent Metals

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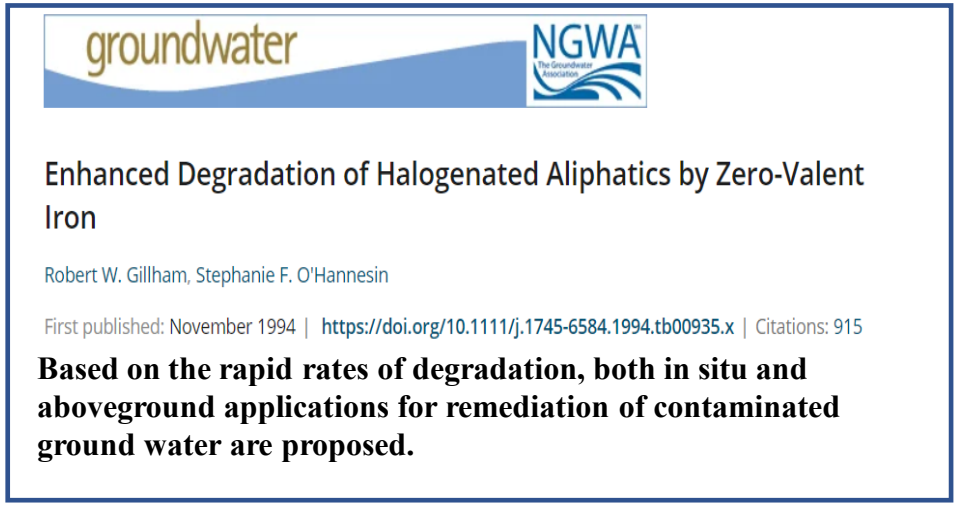
Introduction

Reductive dehalogenation reactions are generally divided

experiments by this group of researchers (*39*, *40*). Several test installations have been completed at contaminated sites and more are planned (*39*–*44*). To date, the precise pathways through which metals reduce chloroethylenes have not been fully elucidated, nor have reaction products or intermediates been completely characterized. Such information is essential to the optimal design of remediation systems. Some of the observed products, such as vinyl chloride (*28*, *37*, *45*) are themselves of concern as drinking water contaminants, with very low maximum contaminant level values imposed by the U.S. EPA (*46*). Others, including *cis*-1,2-dichloroethylene as well as vinyl chloride, react relatively slowly in the presence of Fe(0) (*28*). The necessity of controlling the levels of such undesirable byproducts may dictate the overall design of metal-based remediation systems and thus the economic viability of this approach (*42*, *45*). Any efforts to identify the routes through which such products are formed or which can account for their persistence would clarify the potential limitations of this promising technique or might even enable improved

The use of zero-valent metals to degrade contaminants represents an active research area (*28*–*38*). In large part,

ES&T, 1996. 30(8), p. 2654-2659



groundwater NGWA

Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron

Robert W. Gillham, Stephanie F. O'Hannesin

First published: November 1994 | https://doi.org/10.1111/j.1745-6584.1994.tb00935.x | Citations: 915

Based on the rapid rates of degradation, both in situ and aboveground applications for remediation of contaminated ground water are proposed.

ZVI environmental applications in 1990s

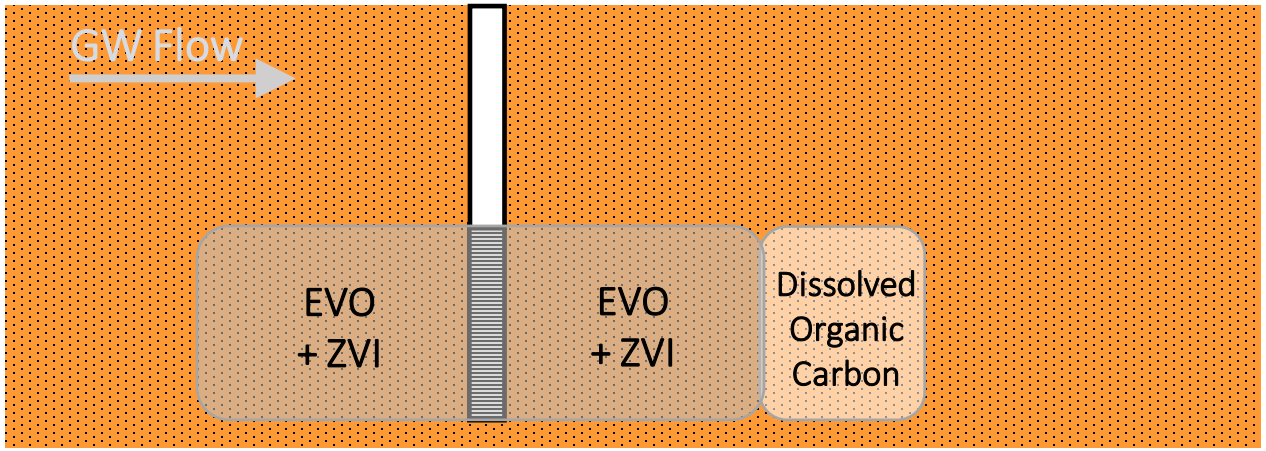
- Ex-situ soil treatment
- Soil tilling
- Permeable reactive barriers
  - Trench placement

(Photo Credit: Hepure)

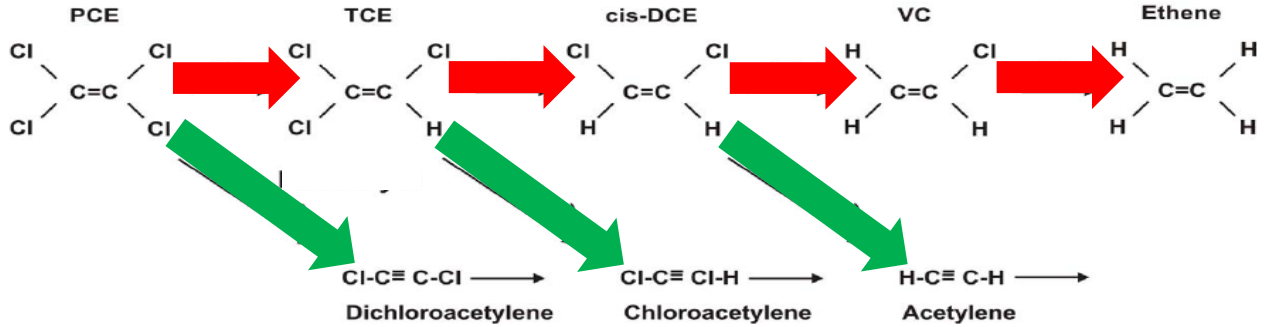
(Permeable Reactive Barrier: Technology Update, ITRC, 2011)

Combining EVO AND ZVI

Multiple Treatment Processes Occurring Simultaneously



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



CVOCs degraded by abiotic reactions with minerals formed in the subsurface

- **metal sulfide minerals (FeS)**
- **siderite ($FeCO_3$)**
- **sulfate green rusts**
- **magnetite (Fe_3O_4)**

Minerals are formed by anaerobic biological processes

Can this be engineered?

- **Biogeochemical Reductive Dechlorination (BiRD)**
- **US Patent Off. #6,884,352 B1**

Sulfate Reducing Conditions (Biotic)

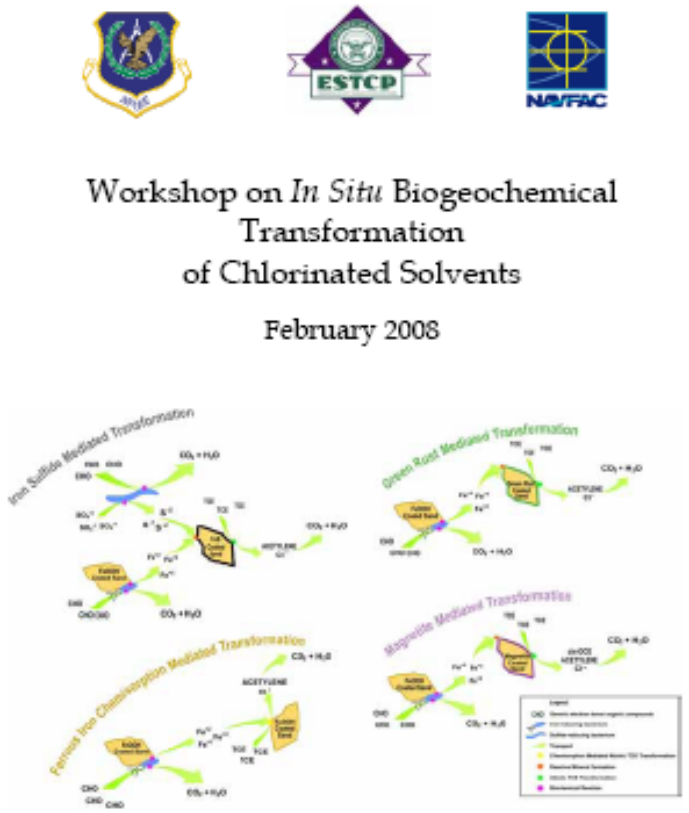
$SO_4^{2-} + 8H + S^{2-} + 4H_2O$

$FeCl_2 + S^{2-} \rightarrow FeS + 2Cl^-$

β-Elimination (Abiotic)

$C_2HCl_3 + FeS \rightarrow C_2H_2$

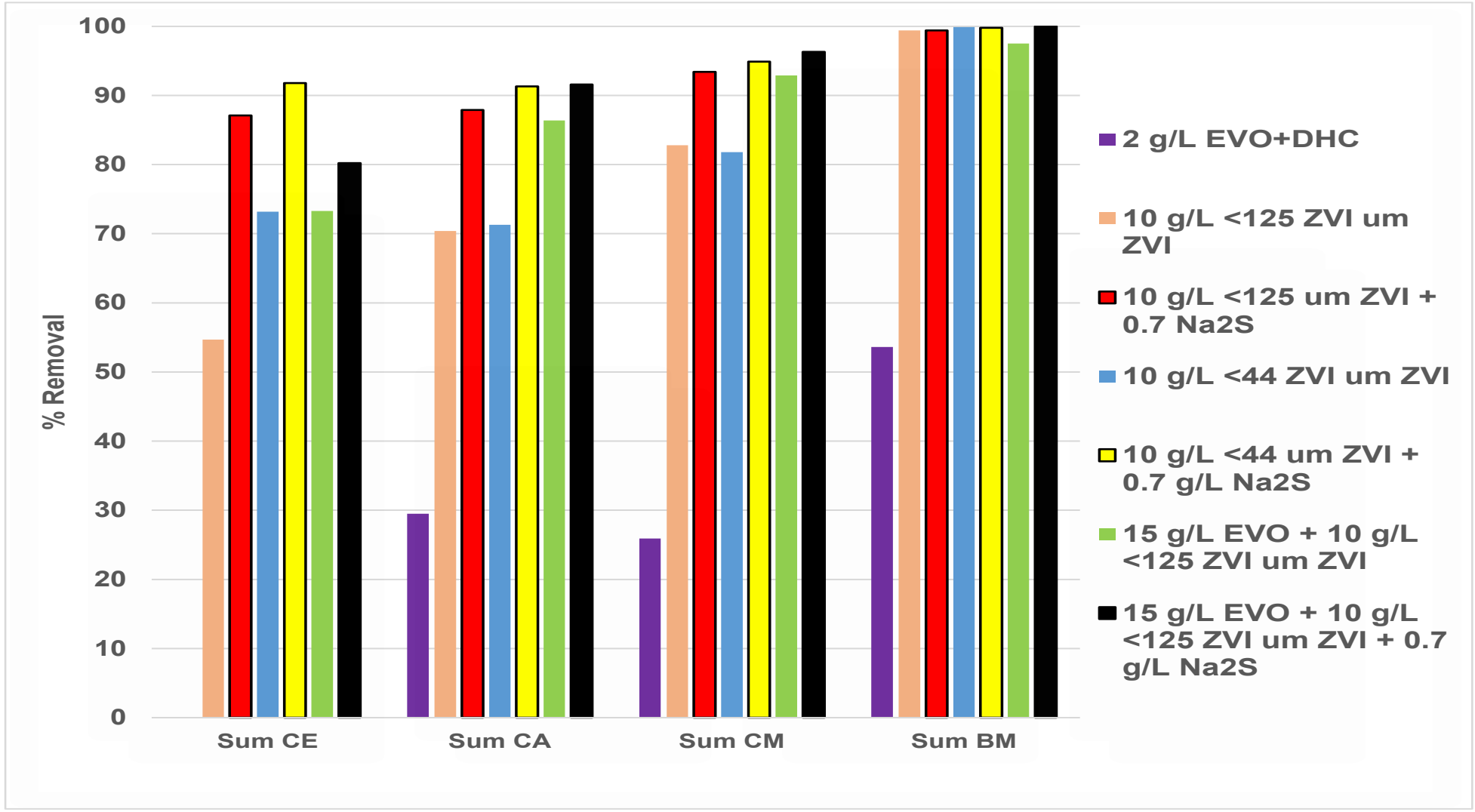
TCE — Acetylene



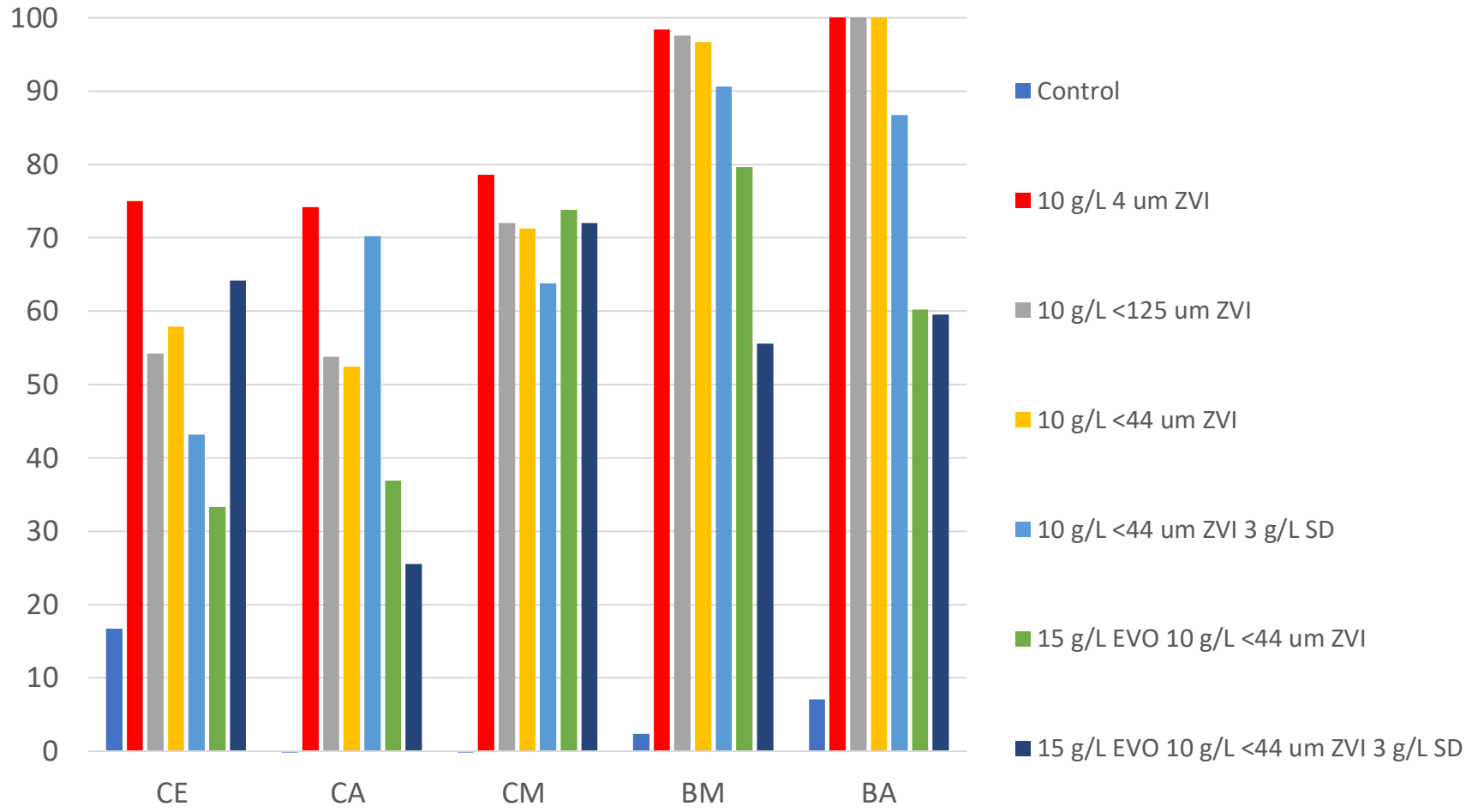
Batch Tests

- **Contaminants:**
- **Chlorinated Ethenes or CE - Tetrachloroethene (PCE), Trichloroethene (TCE), cis-1,2-Dichloroethene, Vinyl Chloride**
- **Chlorinated Methanes or CM - Carbon Tetrachloride (CT), Chloroform (CF), Dichloromethane, Chloromethane**
- **Chlorinated Ethanes or CA - 1,1,1-Trichloroethane (1,1,1-TCA), 1,1,2-TCA, 1,1-Dichloroethane, 1,1-Dichloroethene, Chloroethane**
- **1,2-Dichloroethane (1,2-DCA)**
- **Brominated Methanes or BM - Bromoform (BF), Dibromomethane, Bromomethane**
- **Brominated Ethanes or BA - Ethylene Dibromide (EDB), Bromoethane)**
- **EVO 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 (Na_2S), sulfur (S), calcium polysulfide (CPS), and ferrous sulfide solution (FeSS)**
- **Bioaugmentation with TSI-DC (DHC) and TSI-TCA (DHB)**

Batch 1 Sum Parent and Daughter Product Removals
Aqueous Only, DHC, 1.2-5.6 mg/L VOCs, 70 Days

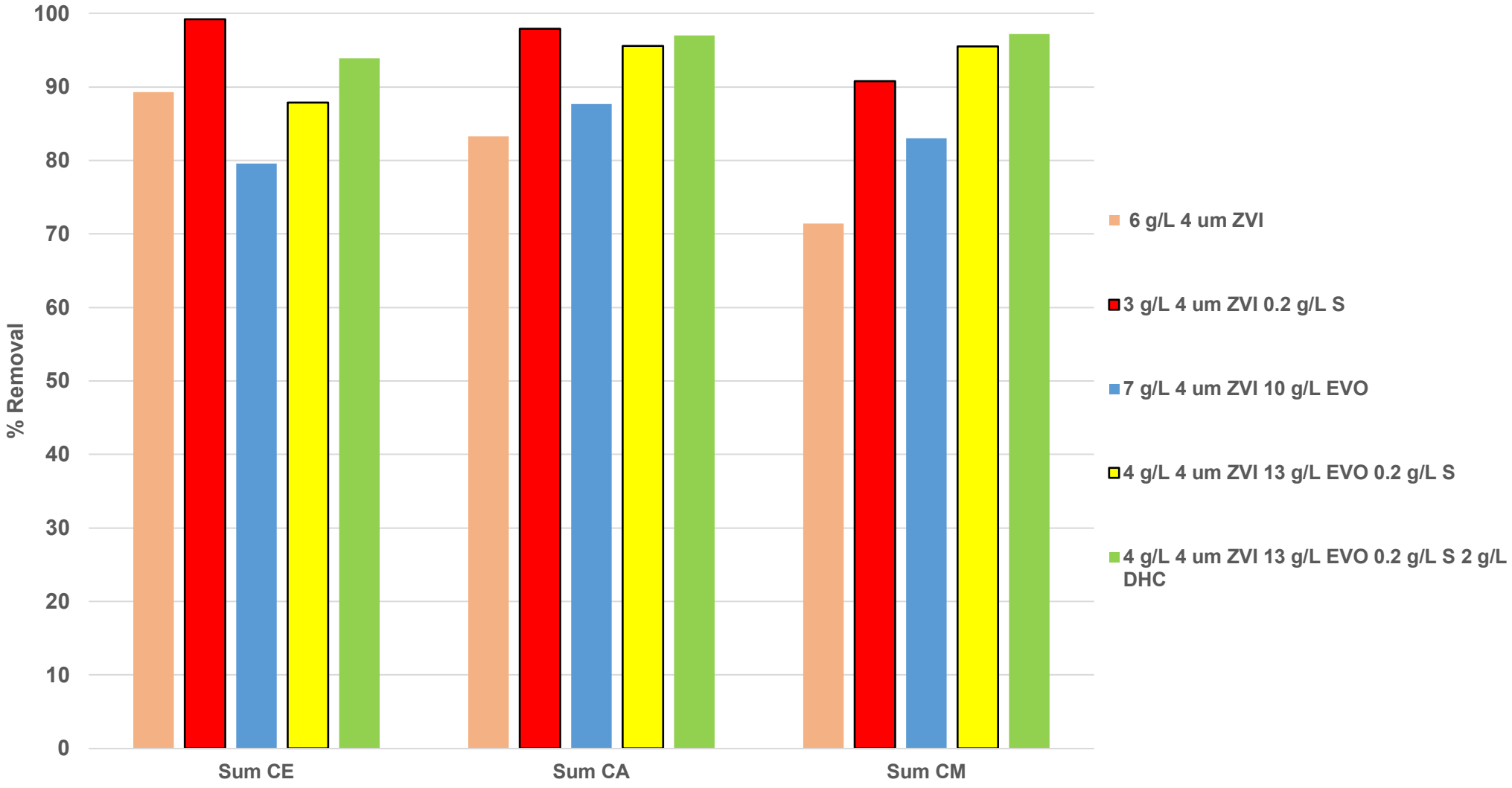


Batch Test 2
Aqueous Only, 0.8 to 4.2 mg/L VOCs, 28 Days



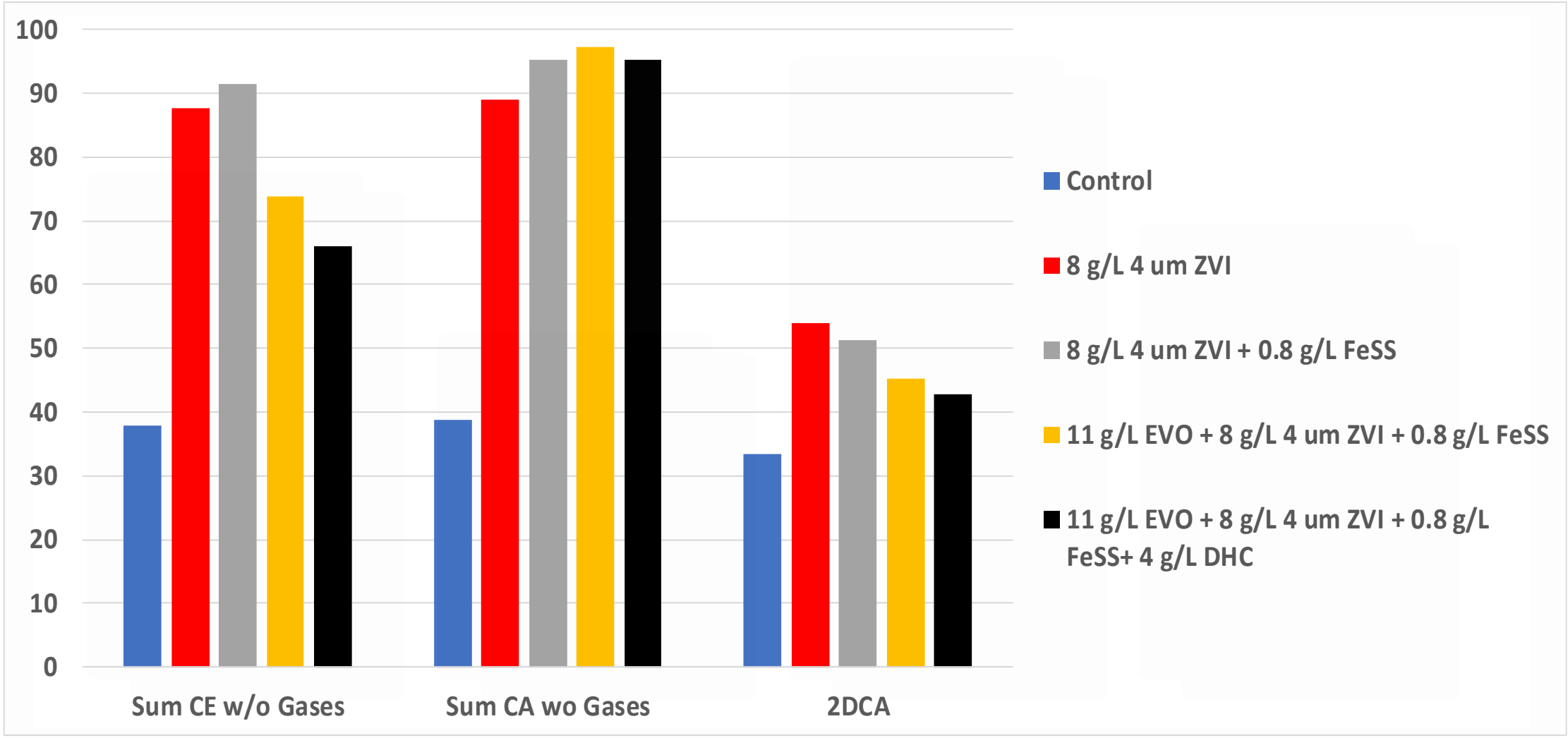
Batch Test 3 Sum CE, CA, CM

67% Soil, 3.0-4.0 mg/L VOCs, 43 Days



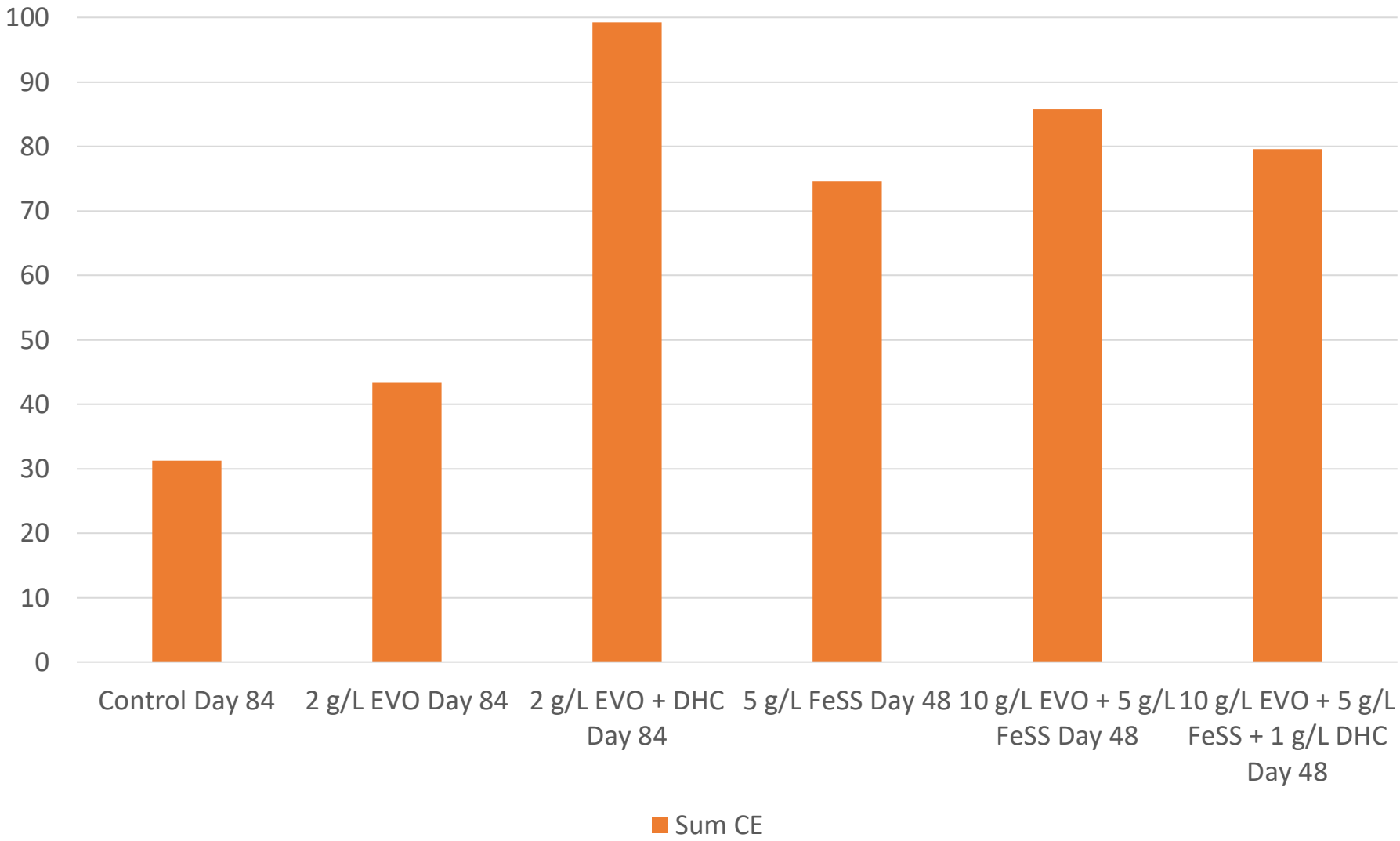
Batch Test 4 % Removal Sum CE, CM, 2DCA

50% Soil, 0.3-16 mg/L Contaminants, 27 Days



Batch Test 5

67% Soil, 0.3 mg/L PCE & 0.3 mg/L TCE, 48 to 84 Days



Batch Conclusions

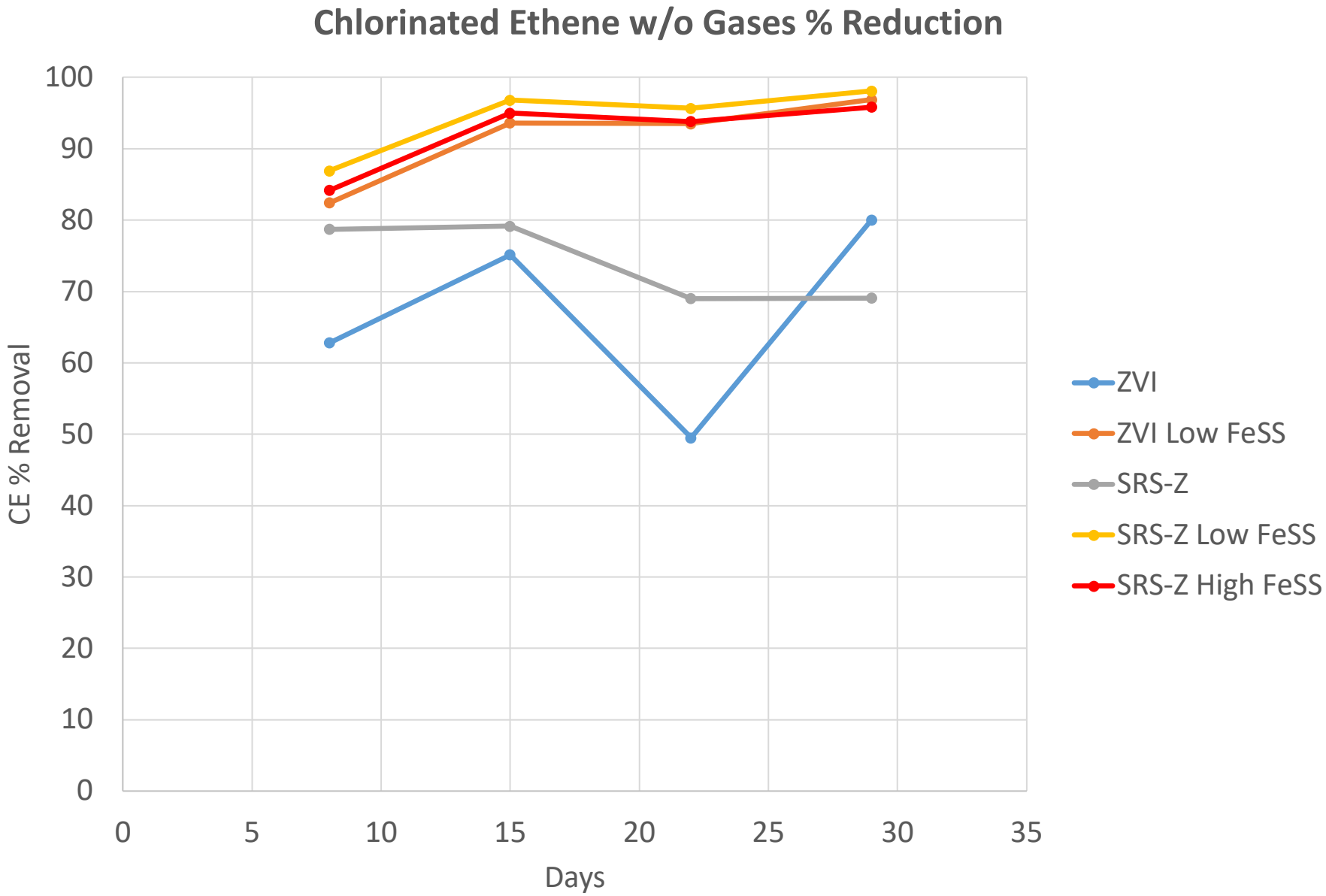
- Generally higher extent of degradation with ZVI or EVO + ZVI than EVO and bioaugmentation.
- Improvement of degradation extent and rate with ZVI and sulfidation agent for PCE and TCE
- 1TCA, 2TCA, CT, CF, BF, and EDB all went almost to completion with just ZVI
- 2DCA not treated as effectively as other compounds. 2DCA is aerobically and anaerobically biodegradable.
- Sulfidation agent from sodium sulfide, sulfur, sodium dithionite, ferrous sulfide solution, and calcium polysulfide worked
- Low S to Fe ratio required
- Improvement with sulfidation for small (4 μm) to moderate (<125 μm) ZVI particles
- Incorporation of substrate with ZVI reduced CE treatment in some cases, but expect more biodegradation in situ with longer treatment time than in batch studies
- Complete degradation with EVO and bioaugmentation culture possible but slower than ZVI + S + EVO
- FeSS solution alone or in combination with EVO and/or bioaugmentation culture showed some improvement over Control or EVO alone but not complete over 48 days

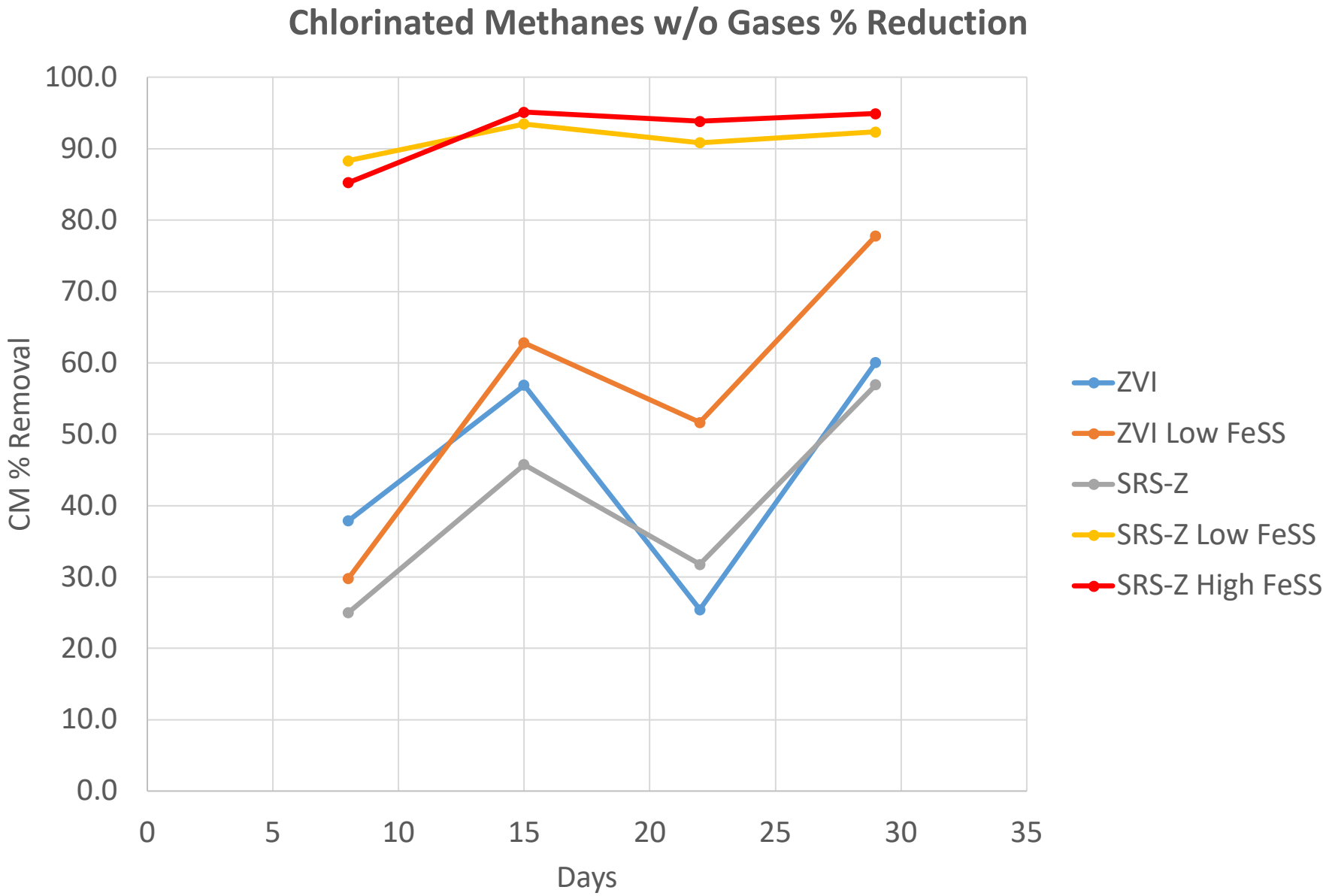
Column Test

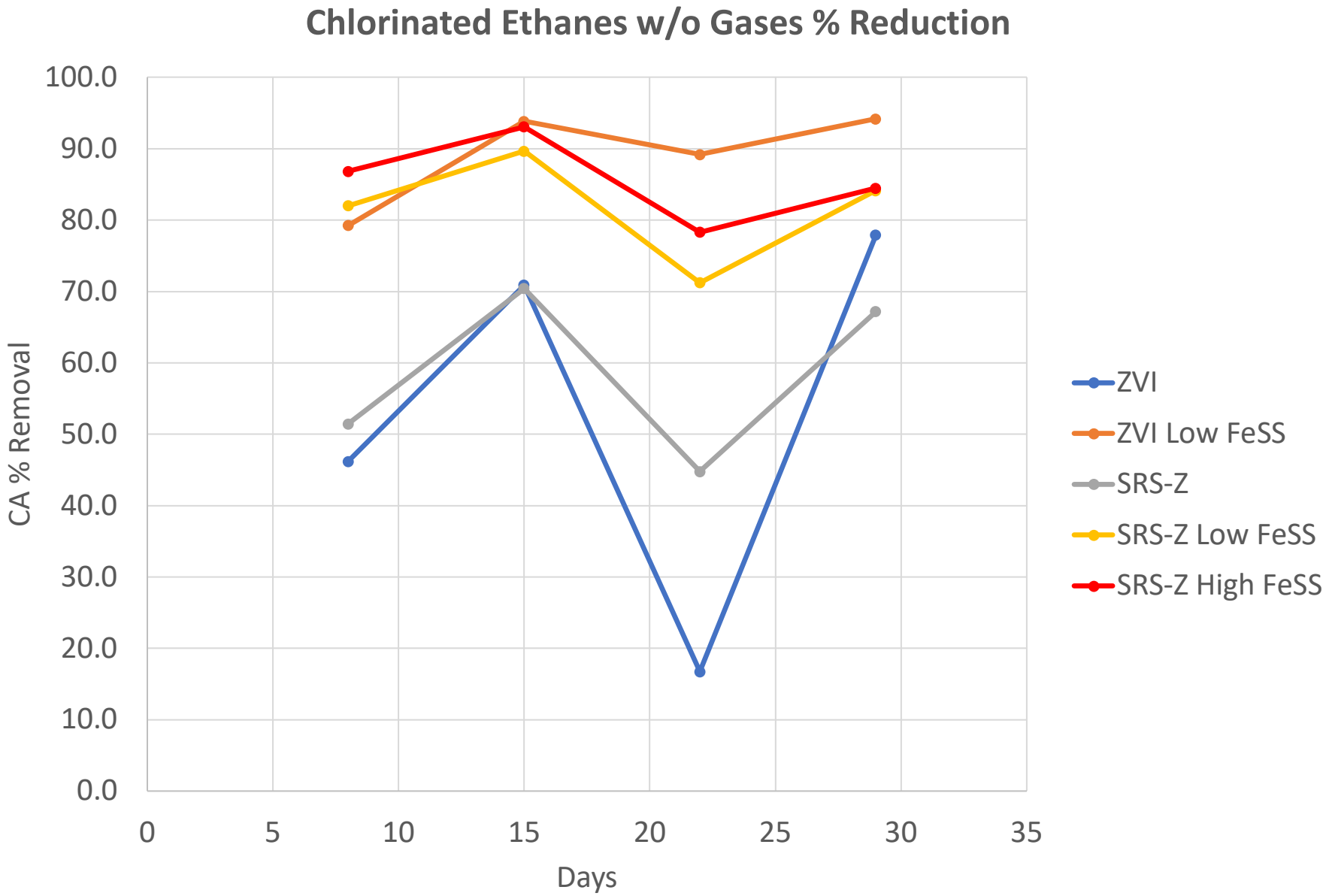
- Contaminants: 1.3-3.1 mg/L TCE, 2.9-4.8 mg/L CF, 0.72-3.1 mg/L 1,1,1-TCA
- Sand columns 5.1 cm diameter x 30.5 cm long. Average retention times 2.0 to 2.9 days.
- EVO Loading 0 or 15 g/kg
- 4 µm ZVI Loading 10 g/kg
- Sulfidation Agent – 1 and 5 g/kg ferrous sulfide solution (FeSS)
- Bioaugmentation with TSI-DC (DHC) and TSI-TCA (DHB) on Day 15
- Added 1.1 g/L FeSS to influent on Day 17

Treatment	EVO (g/kg)	4 um ZVI (g/kg)	FeSS (g/kg)
ZVI		10	
ZVI + Low FeSS		10	1
EVO-Z	15	10	
EVO-Z Low FeSS	15	10	1
EVO-Z High FeSS	15	10	5

Column Test


Chlorinated Ethene w/o Gases % Reduction
CE % Removal
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
Days
ZVI
ZVI Low FeSS
SRS-Z
SRS-Z Low FeSS
SRS-Z High FeSS


Chlorinated Methanes w/o Gases % Reduction
CM % Removal
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0
5
10
15
20
25
30
35
Days
ZVI
ZVI Low FeSS
SRS-Z
SRS-Z Low FeSS
SRS-Z High FeSS

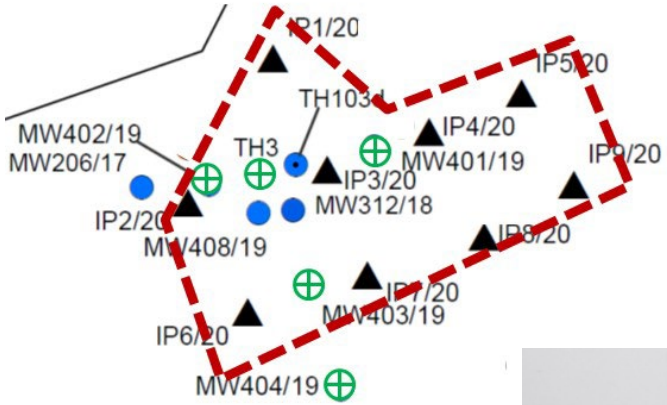

Chlorinated Ethanes w/o Gases % Reduction
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
CA % Removal
0
5
10
15
20
25
30
35
Days
ZVI
ZVI Low FeSS
SRS-Z
SRS-Z Low FeSS
SRS-Z High FeSS

Treatment	4 um ZVI	FeSS	SRS	RT	% TCE Red	% Sum CE Red	TCE Half-Life	Time To TCE MCL	% 1TCA Red	% Sum CA Red	1TCA Half-Life	Time To 1TCA MCL	% CF Red	% Sum CM Red
	g/kg	g/kg	g/kg	Days	from Infl	from Infl	Days	Days	from Infl	from Infl	Days	Days	from Infl	from Infl
					TCE (mg/L)				1TCA (mg/L)				CF (mg/L)	
Influent					1.3-3.1				0.72-3.1				2.9-4.8	
ZVI	10			2.0	67.3±13.8	66.8±13.6	1.4±0.8	11.8	85.2±10.5	52.9±27.7	0.8±0.5	2.5	61.4±16.5	45.1±16.4
ZVI + Low FeSS	10	1		2.2	92.4±6.4	91.6±6.3	0.6±0.4	5.5	93.1±7.4	89.2±7.0	0.6±0.5	2.0	57.8±21.2	55.5±20.2
SRS-Z	10		15	2.9	74.4±5.4	74.0±5.7	1.5±0.7	14.1	75.3±13.8	58.5±12.3	1.5±0.8	4.9	45.0±17.1	40.0±14.3
SRS-Z Low FeSS	10	1	15	2.3	97.8±3.2	94.4±5.1	0.3±0.1	2.8	99.8±0.2	81.8±7.7	0.2±0.1	0.8	98.8±2.0	91.3±2.3
SRS-Z High FeSS	10	5	15	2.4	96.0±4.9	92.2±5.4	0.5±0.2	4.1	99.5±0.5	85.7±6.1	0.3±0.1	1.0	97.5±4.1	92.3±4.7
>90%	>80%	>70%												

Column Conclusions

- ZVI and EVO-Z treatments amended with FeSS outperformed the columns without FeSS.
- EVO-Z with low FeSS provided the most complete degradation of TCE, 1TCA, and CF.
- Addition of the bioaugmentation culture on Day 15 and/or FeSS on Day 17 to the influent increased the extent of dechlorination at Day 29 compared to Day 22 for all treatments.
- More final chlorinated ethene degradation products (ethene, ethane, and acetylene) were generated with FeSS than without FeSS.
- Less dichloromethane and chloromethane from chloroform and 1,1-dichloroethane, 1,1-dichloroethene, and chloroethane from 1TCA were produced with the FeSS.
- Enhanced VOC dechlorination extent and degradation rates with the sulfidated ZVI.
- Laboratory studies not conducted for long enough to show increased longevity of the sulfidated ZVI that has been reported by others.

Field Pilot Study Case Study



- 900 square foot area
- 9 direct push points (11’ spacing)

- EISD Reagents
  - SRS®-SD small droplet EVO
  - SRS®-Z_{VI} (2 µm ZVI)
  - Sodium Bicarbonate
  - Bioaugmentation culture

- 2,300 gallons solution
- 500 gallons deoxygenated water

- High sulfate in groundwater provided FeS

2 & 4 months post injection

Rapid reduction of TCE in injection area

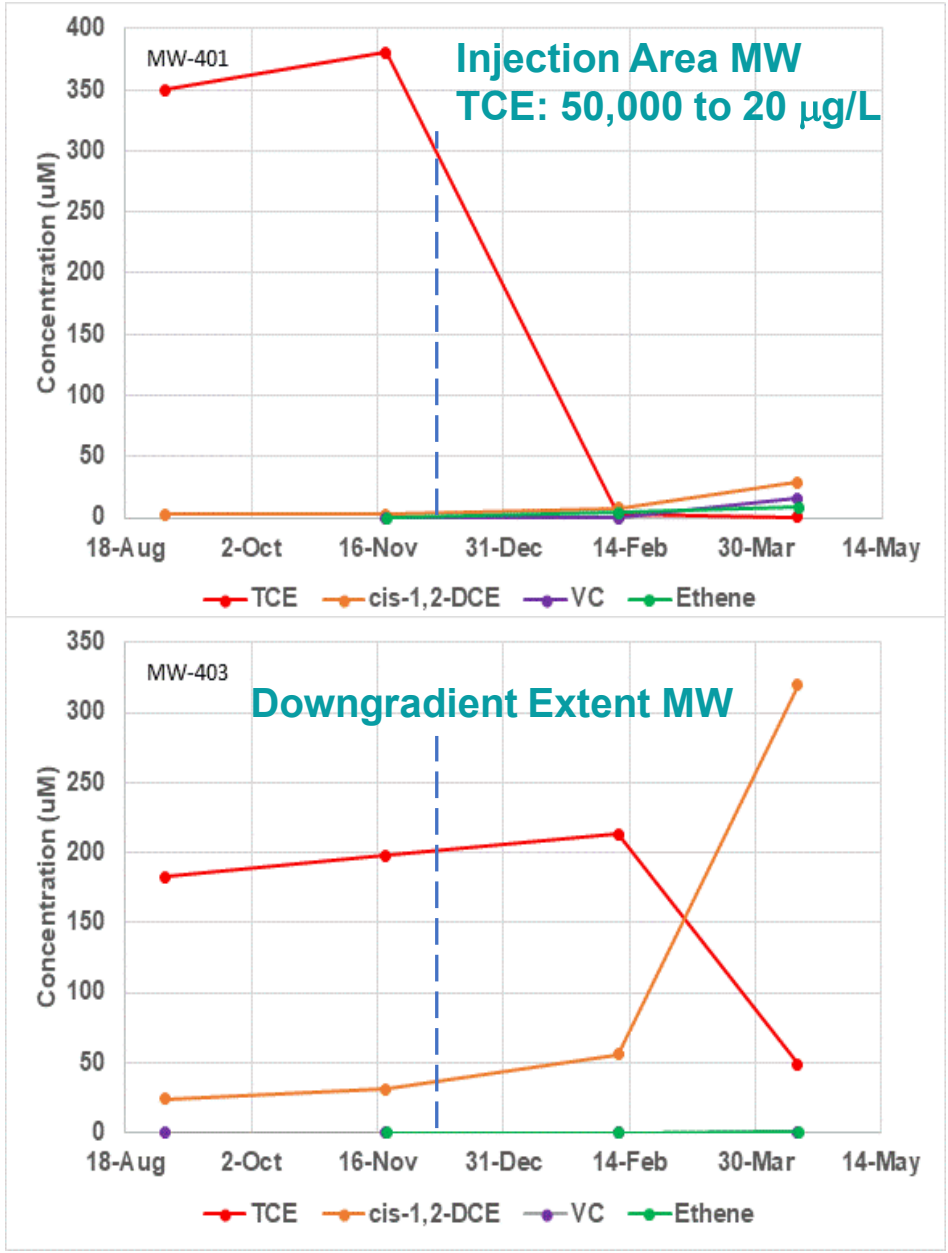
- Limited biotic dechlorination starting in 4-month samples

TOC and dechlorination migrating downgradient

- Biotic dechlorination

Evidence of FeS formation

- Baseline sulfate 200-2,700 mg/L



Conclusions

- Sulfidation increases reactivity and extent of many chlorinated and brominated compounds degradation by ZVI
- Variety of sulfur compounds at low concentrations effective with ZVI including sulfate in groundwater or added to groundwater
- Combinations of emulsified vegetable oil, ZVI, sulfidation, and bioaugmentation were effective in promoting degradation although longer reaction times may be required than with ZVI