In Situ Chemical Reduction with ZVI and ZVI-Sulfide

Battelle In Situ Bioremediation and Sustainable Remediation Symposium

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Outline

- Background
- Batch microcosm studies
- Column studies
- Conclusions

Background

- **Zero Valent Iron (ZVI) used to treat many solvents including tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), carbon tetrachloride (CT), chloroform (CF), and Bromoform (BF).**
- **1,2-Dichloroethane (1,2-DCA) is more recalcitrant to ZVI.**
- **Combination of ZVI and sulfide can reduce corrosion of iron with water and extend reactivity of ZVI.**

Background

- **Sulfide can be added to ZVI with sodium sulfide, sodium dithionite, calcium polysulfide, sodium thiosulfate, or other methods.**
- **Han and Yan (2016)[1] found above a S:Fe ratio of 0.025, the TCE transformation rates were similar.**

[1]Han, Y. and W. Yan. 2016. Reductive Dechlorination of Trichloroethene by Zero-valent Iron Nanoparticles: Reactivity Enhancement through Sulfidation Treatment. Environmental Science and Technology 50:12992-13001

Microcosm Study

- Batch microcosm study with
- Two ZVI products
  - Hepure Ferox Flow (<37 to 149 microns)
  - Hepure Ferox Target (<37 microns)
- With and without sodium sulfide (0.1 S:Fe ratio)
- Combined Flow with Emulsified Vegetable Oil (SRS)
- HEPES buffered tap water with 500 mg/L sulfate spiked with PCE, 1,1,1-TCA, CT, 1,2-DCA, and BF
- Bioaugmented Day 43
- Sampled for VOCs and gases (methane, ethene, ethane, and acetylene) after 1, 7, 21, 43, and 70 days

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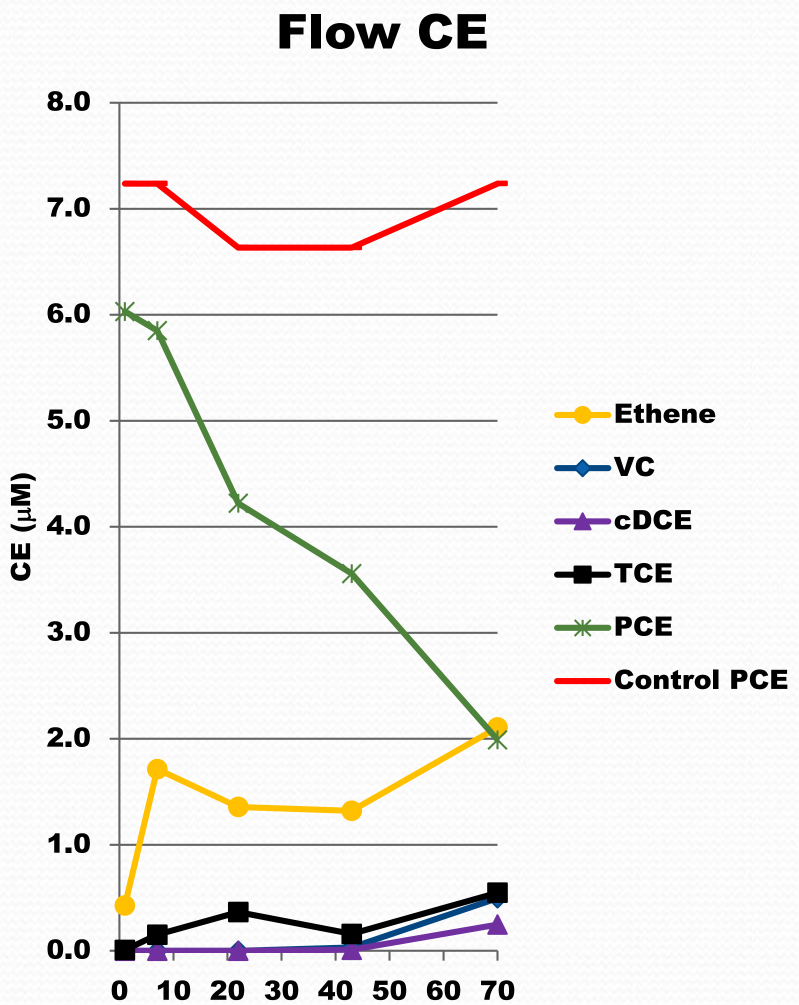
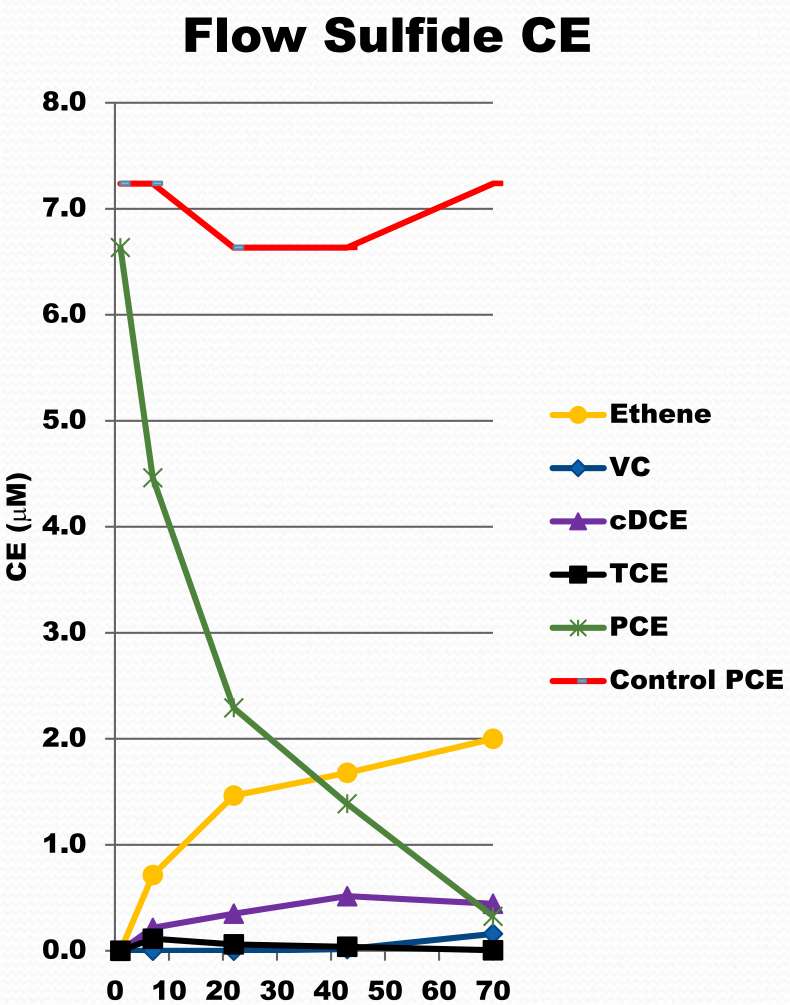
Microcosm Treatments

Treatment	ZVI Particle Size	Spiked Water	ZVI	Sodium Sulfide Nonahydrate	SRS	Culture Added on Day
	µm	g	g	g	g	
Control		532				
Ferox Flow	<37-149	530	5.3			43
Ferox Flow Sulfide	<37-149	531	5.3	2.3		43
Ferox Target	<37	532	5.3			43
Ferox Target Sulfide	<37	531	5.3	2.3		43
SRS Flow	<37-149	523	5.3		8.8	43
SRS Flow Sulfide	<37-149	525	5.3	2.3	8.8	43

Chlorinated Ethenes





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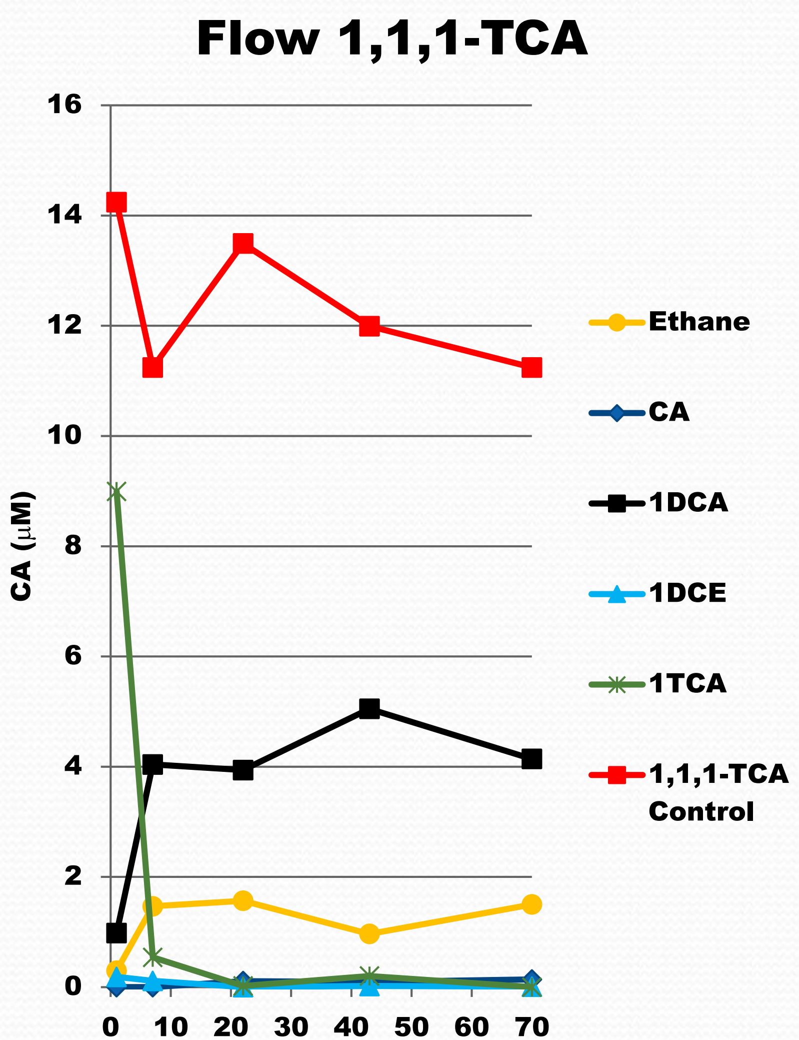
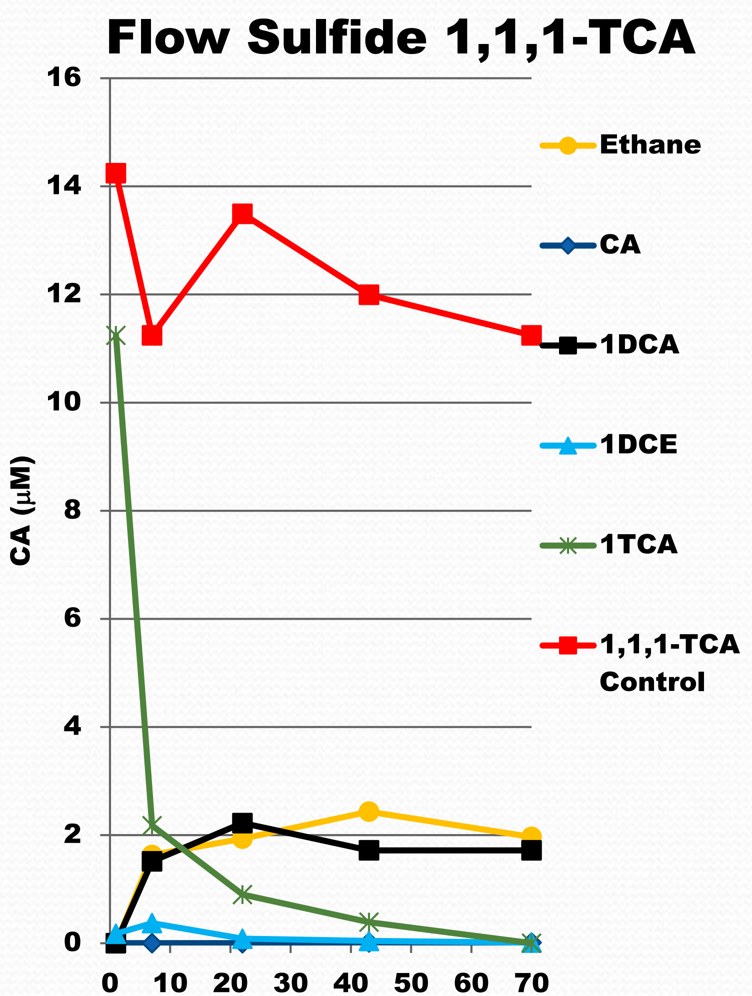
Chlorinated Ethanes





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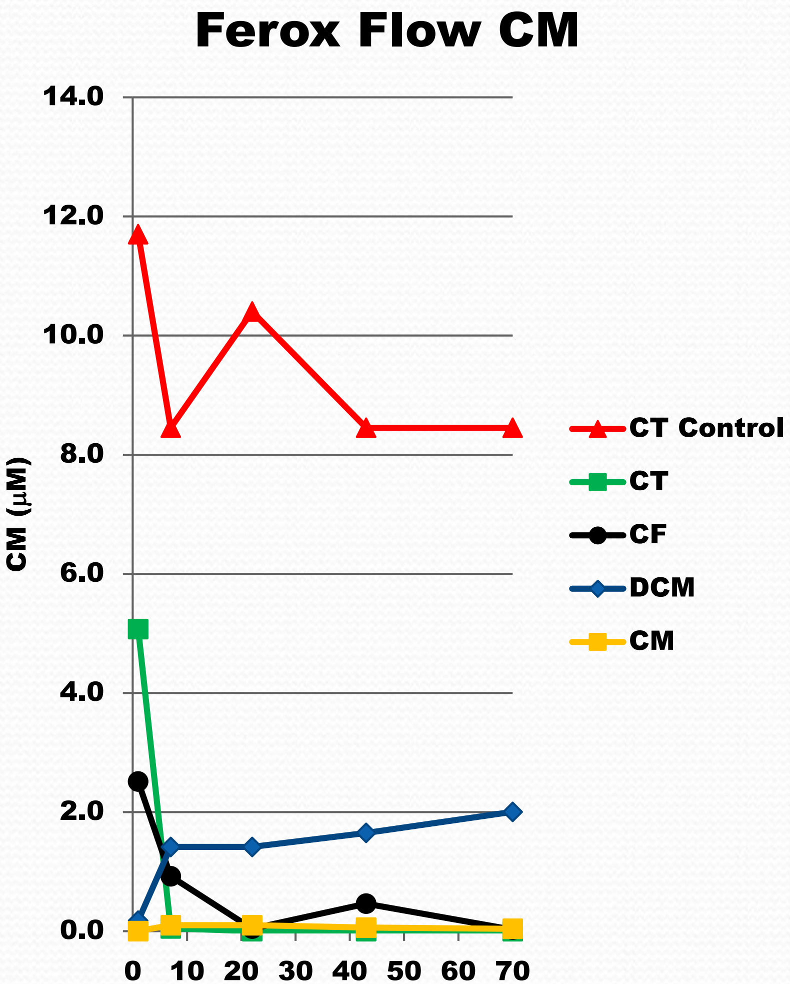
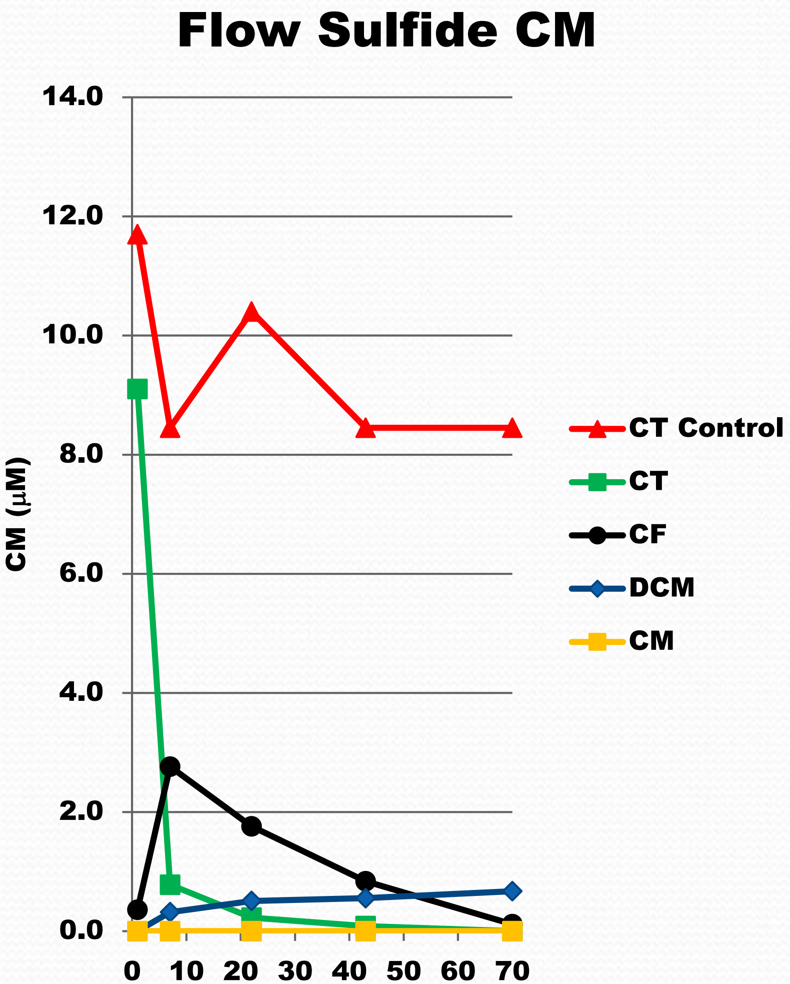
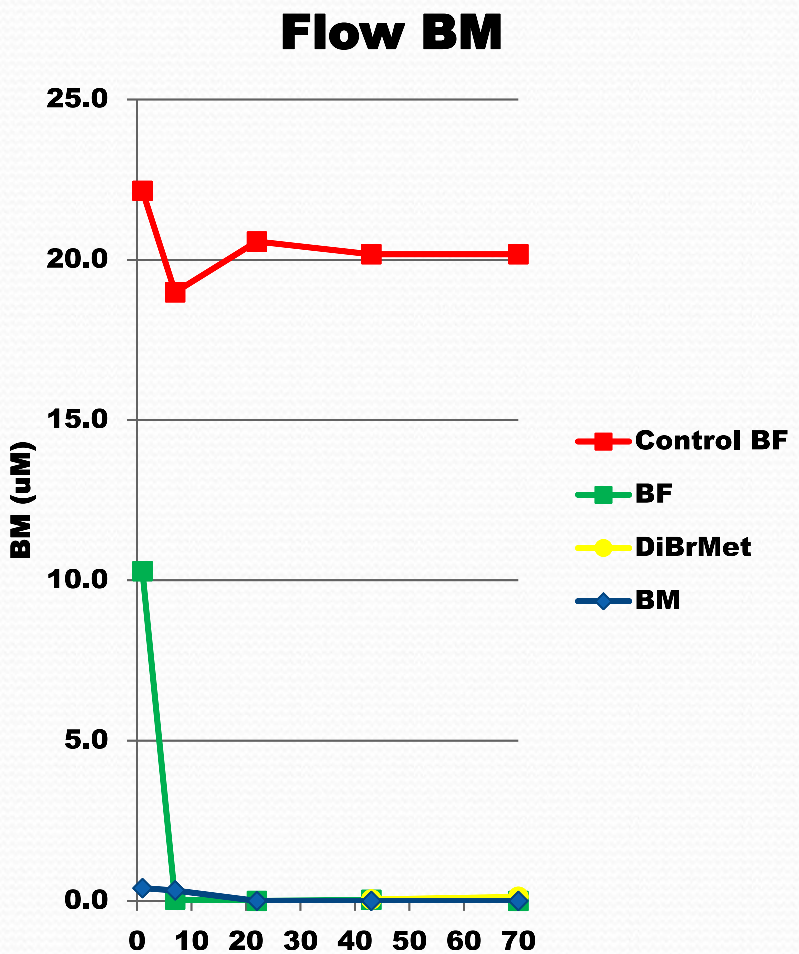
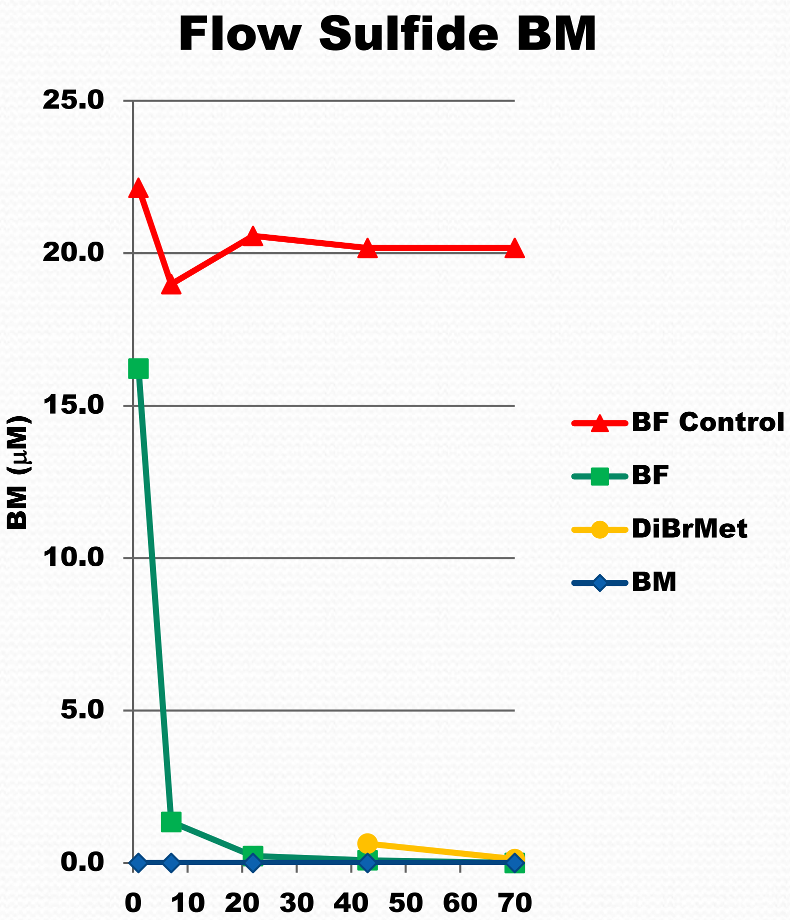
Chlorinated Methanes





Brominated Methanes





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Percent Removals over 70 Day Study Compared to Control Day 1

Treatment	Control	Flow	Flow + Sulfide	Target	Target+ Sulfide	SRS Flow	SRS+ Flow + Sulfide
PCE	0.0	72.5	95.5	76.7	97.9	73.3	80.8
Sum Chlorinated Ethenes w/o Gases	0.0	54.7	87.1	73.2	91.8	73.3	80.2
1,1,1-TCA	21.1	>99.97	>99.97	99.8	>99.97	91.1	>99.7
Sum Chlorinated Ethanes wo Gases	12.0	32.5	28.2	31.0	34.2	60.6	51.5
1.2-DCA	9.1	20.5	9.1	18.2	15.9	52.3	38.6
CT	27.8	>99.97	>99.97	>99.97	>99.97	>99.7	>99.7
Sum Chlorinated Methanes wo Gases	25.9	82.8	93.4	81.8	94.9	92.9	96.3
BF	8.9	>99.99	>99.99	>99.98	>99.99	>99.9	>99.9
Sum Brominated Methanes wo Gases	8.3	99.4	99.4	99.9	99.8	97.5	100.0

First Order Half-Lives (Days) for Treatability Study

Compound	Control	Flow	Flow + Sulfide	Target	Target + Sulfide	SRS + Flow	SRS + Flow + Sulfide
PCE	517	39	16	33	12	37	22
1,1,1-TCA	236	6.6	8.6	8.0	4.9	22	10
1,2-DCA	446	282	753	717	866	75	86
CT	172	0.9	6.3	1.6	2.2	11	8.7
BF	795	0.8	5.5	1.6	1.1	22	4.7

Batch Studies Conclusions

- **Addition of sulfide increased the reactivity of the ZVI against PCE and 1,1,1-TCA and increased the rate of reaction against CT and BF.**
- **1,2-DCA treatment was low; best for combination of SRS, Flow ZVI, and bioaugmentation culture.**
- **Treatment of the ZVI with sodium sulfide was effective in these studies.**

Column Studies

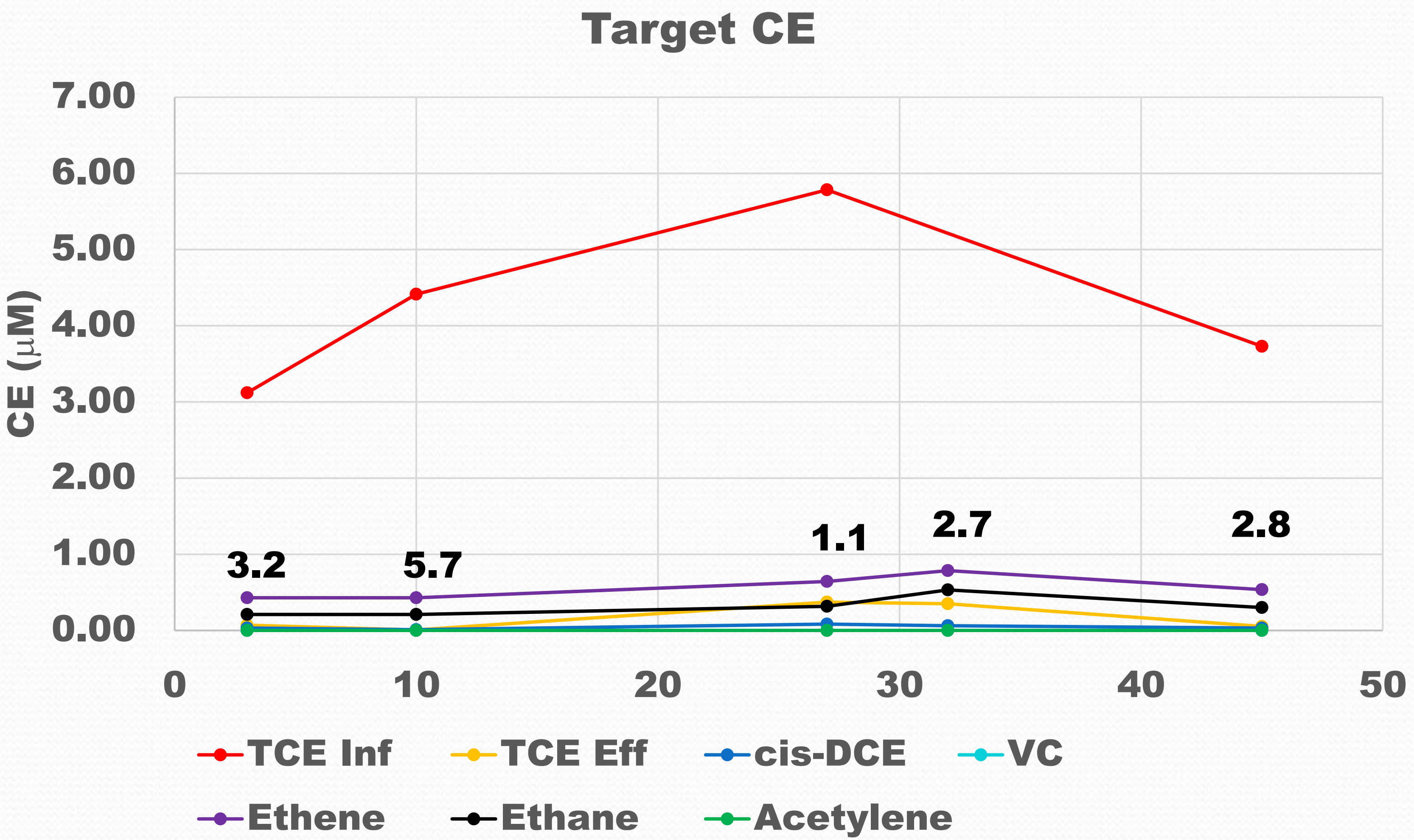
- **Column studies using**
  - **40% PRB (297 to 2,380 microns) and 60% Flow (<37 to 149 microns)**
  - **Target (<37 microns)**
  - **40% PRB/60% Flow treated with calcium polysulfide at S:Fe molar ratio of 0.11**
- **24 inch long columns prepared with 4% ZVI 96% sand**
- **Tapwater spiked with TCE and CF pumped through columns at 0.02 to 0.32 mL/min or retention times of 1 to 11 days**

PRB Flow

Target

PRB Flow Sulfide

Target CE



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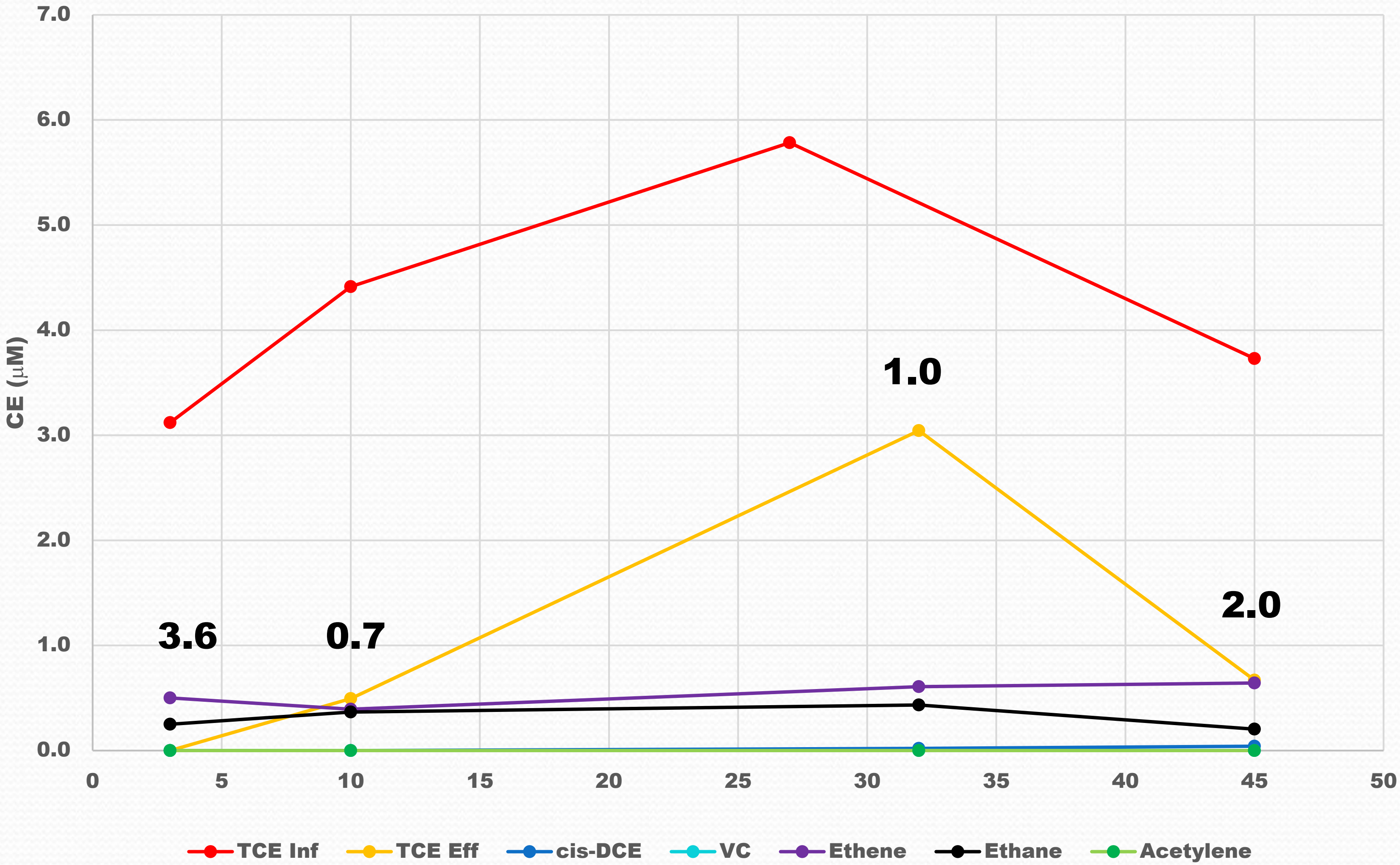
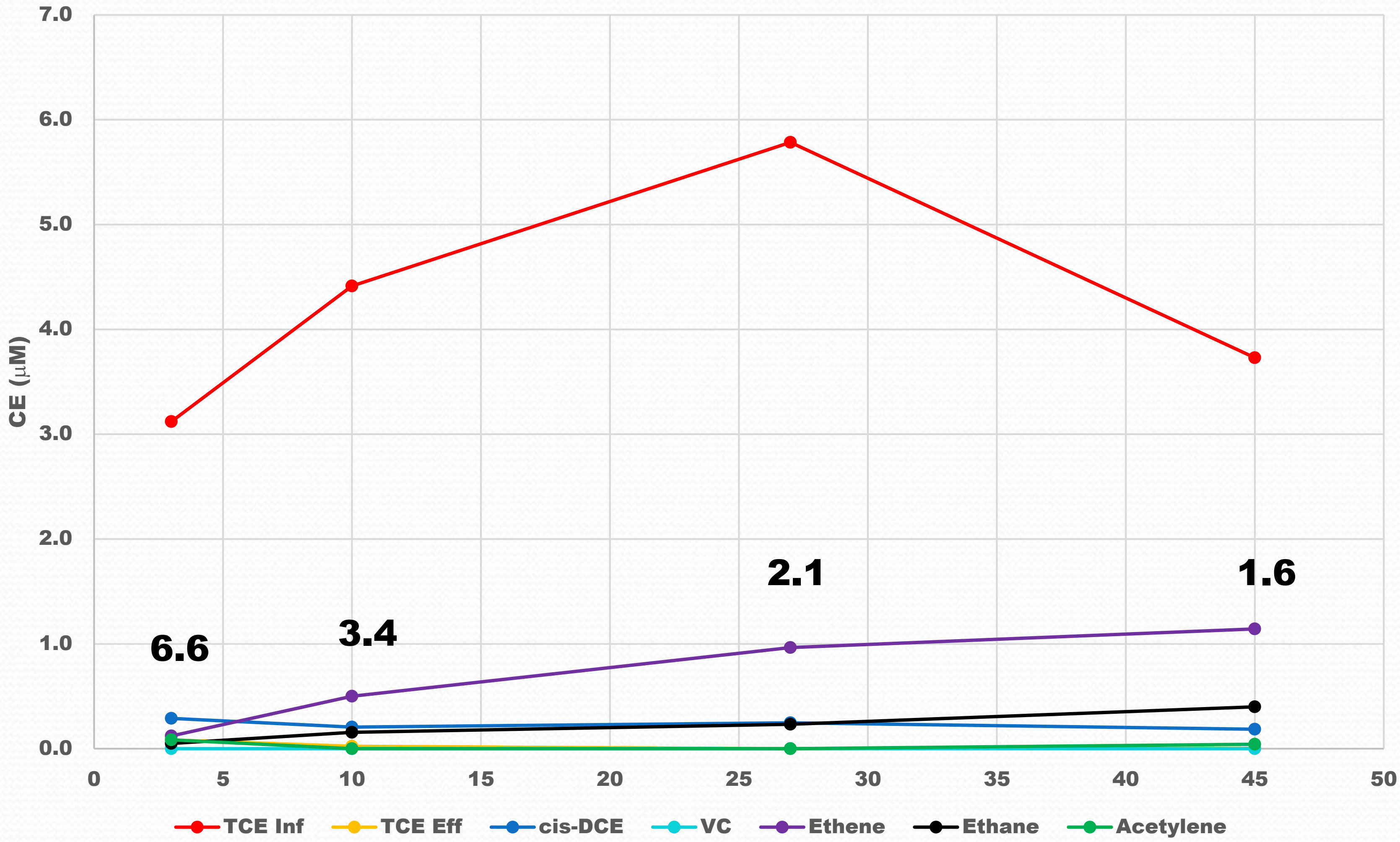
PRB/Flow CE



7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
CE (µM)
0
5
10
15
20
25
30
35
40
45
50
3.6
0.7
1.0
2.0
TCE Inf
TCE Eff
cis-DCE
VC
Ethene
Ethane
Acetylene

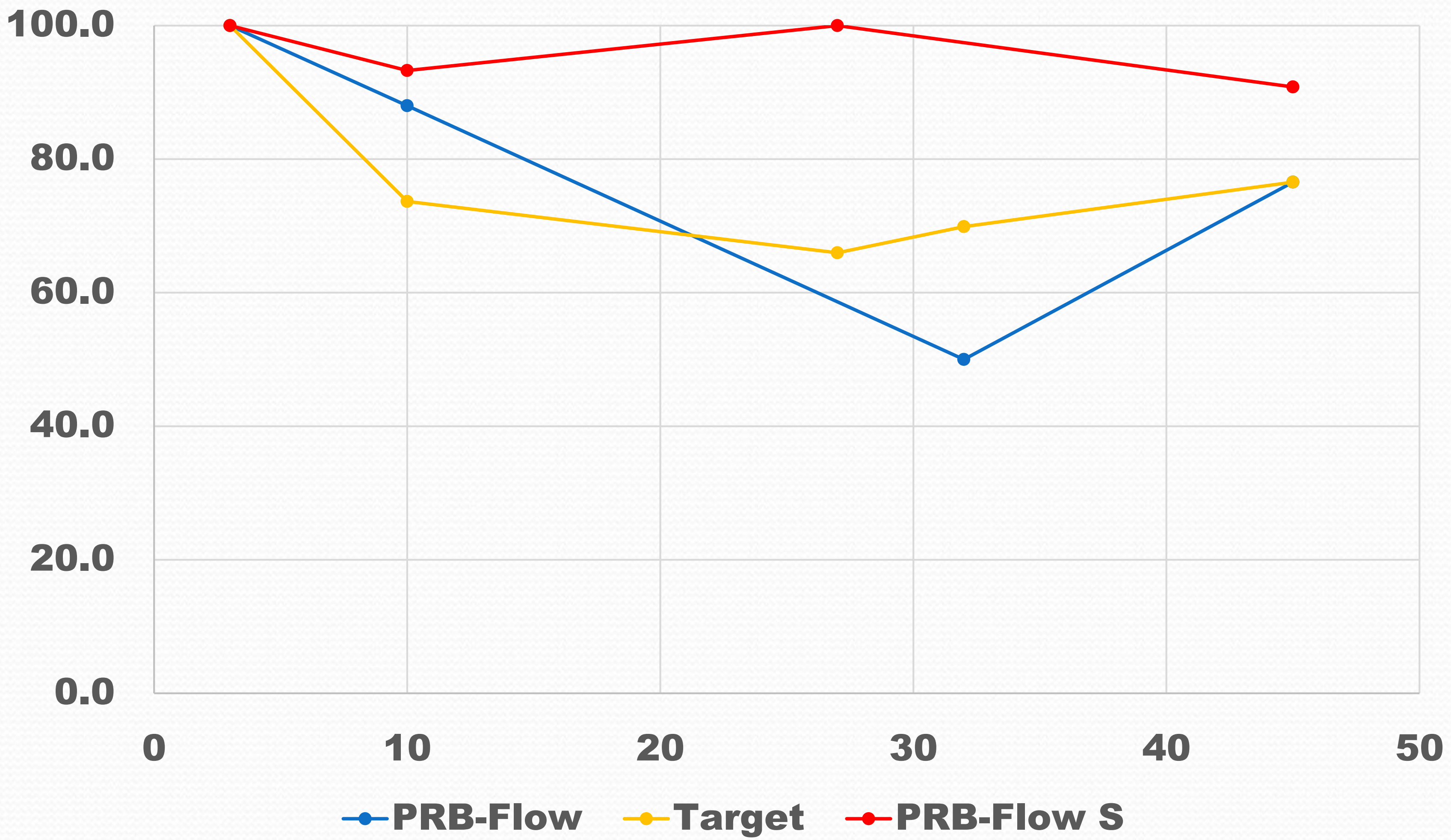
PRB/Flow Sulfide CE



Column Kinetics

Avg Half-Life (hrs)	Hepure PRB/Flow	Hepure Target	PRB/Flow Sulfide
TCE	16.2	12.5	12.3
CF	18.5	14.1	23.6

CM % Reduction



Column Summary

Avg Percent Removal	Hepure PRB/Flow	Hepure Target	PRB/Flow Sulfide
Chlorinated Ethenes	79.2	95.8	93.3
Chlorinated Methanes	78.6	77.2	96.0

Column Conclusions

- **PRB/Flow ZVI + sulfide promoted more complete removal of the TCE and CF than PRB/Flow ZVI alone.**
- **The smaller Target ZVI generally gave higher removal efficiencies for the chlorinated ethenes than the PRB/Flow + Sulfide, but the PRB/Flow + Sulfide gave more complete removal of the chlorinated methanes.**
- **The addition of sulfide also seemed to alter the daughter products with less TCE, but more cis-DCE, ethene, and acetylene than the column with only the PRB/Flow ZVI.**
- **When the retention time on the column was less than about 2 days, the performance of the ZVI columns, suffered particularly for the PRB/Flow column. The retention times had a variable effect on the Target ZVI TCE effluent concentrations.**

Overall Conclusions

- **Column study half-lives were hours for chlorinated ethenes and chlorinated methanes versus days for batch tests.**
- **Comparing PCE for batch versus TCE for column and CT for batch and versus CF for column and different ZVI loadings.**
- **ZVI treatments with sulfide generally had lower half-lives than ZVI without sulfide.**

Questions?

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