OBG PRESENTS:

Role of Iron and Vitamin B12 Amendments in Stimulating Reductive Dechlorination of TCE in High Sulfate Groundwater

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OUTLINE

Iron and Sulfate Geochemistry

Previous Microcosm Work

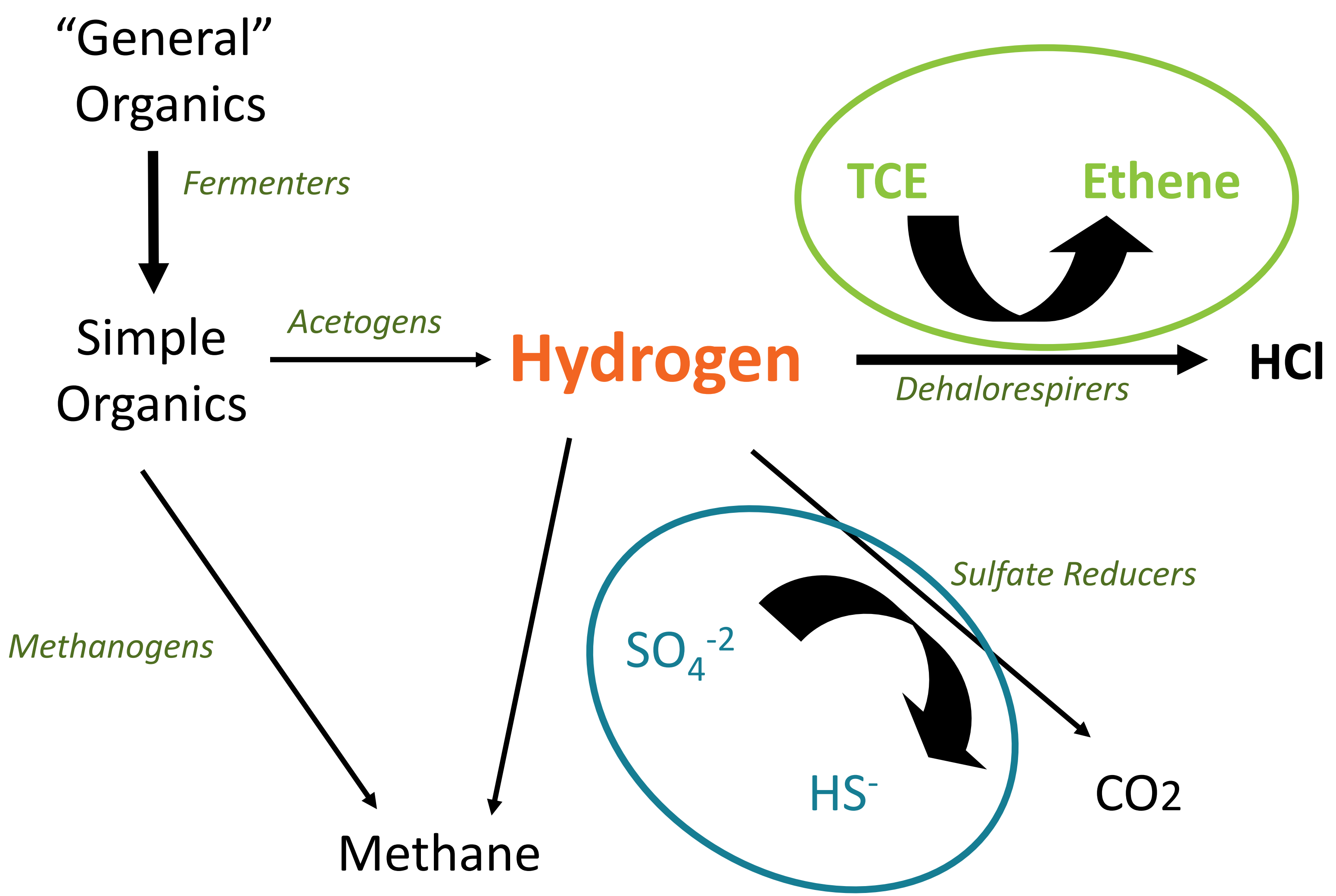
Column Study Set-up and Design

Column Operation

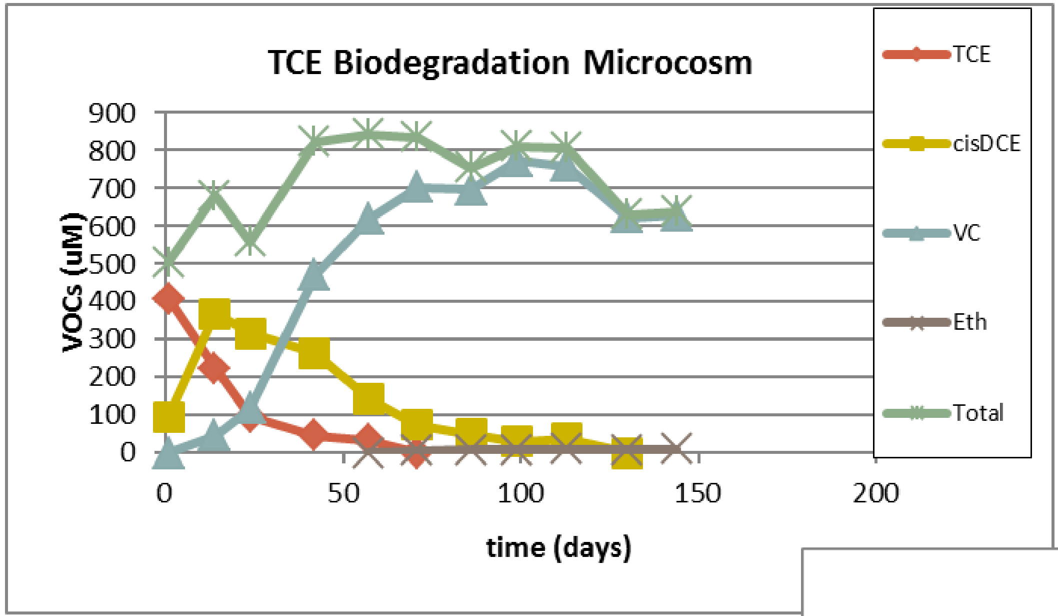
Role of Nutrients in Supporting Complete Biodegradation

Conclusions

Problems with High Sulfate Groundwater

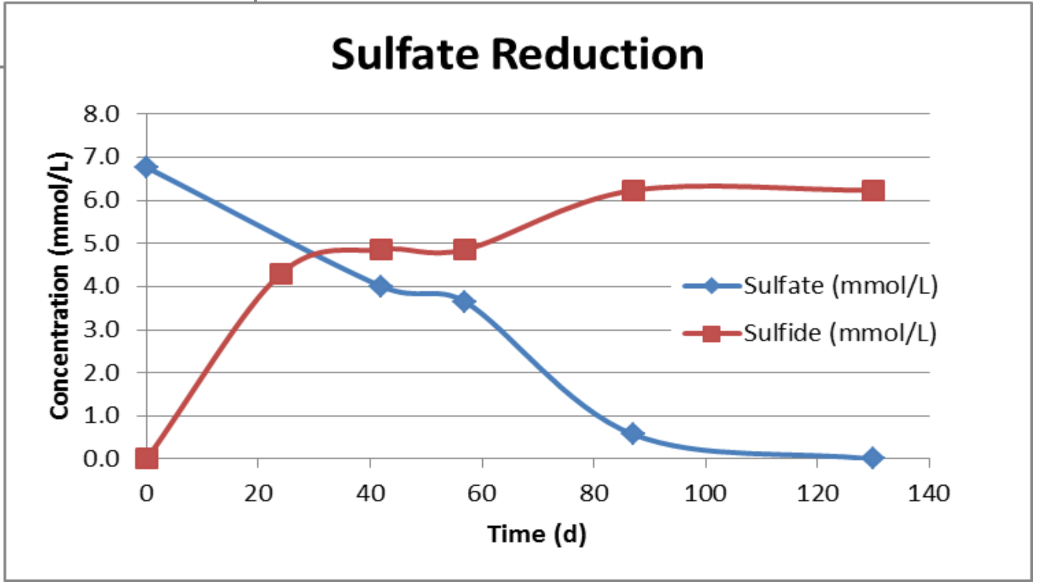


Problems with High Sulfate Groundwater



Biological degradation of TCE:
TCE → cDCE → VC → ethene

Complete biodegradation of TCE to ethene inhibited by high sulfide concentrations



Potential Solution – Add Iron

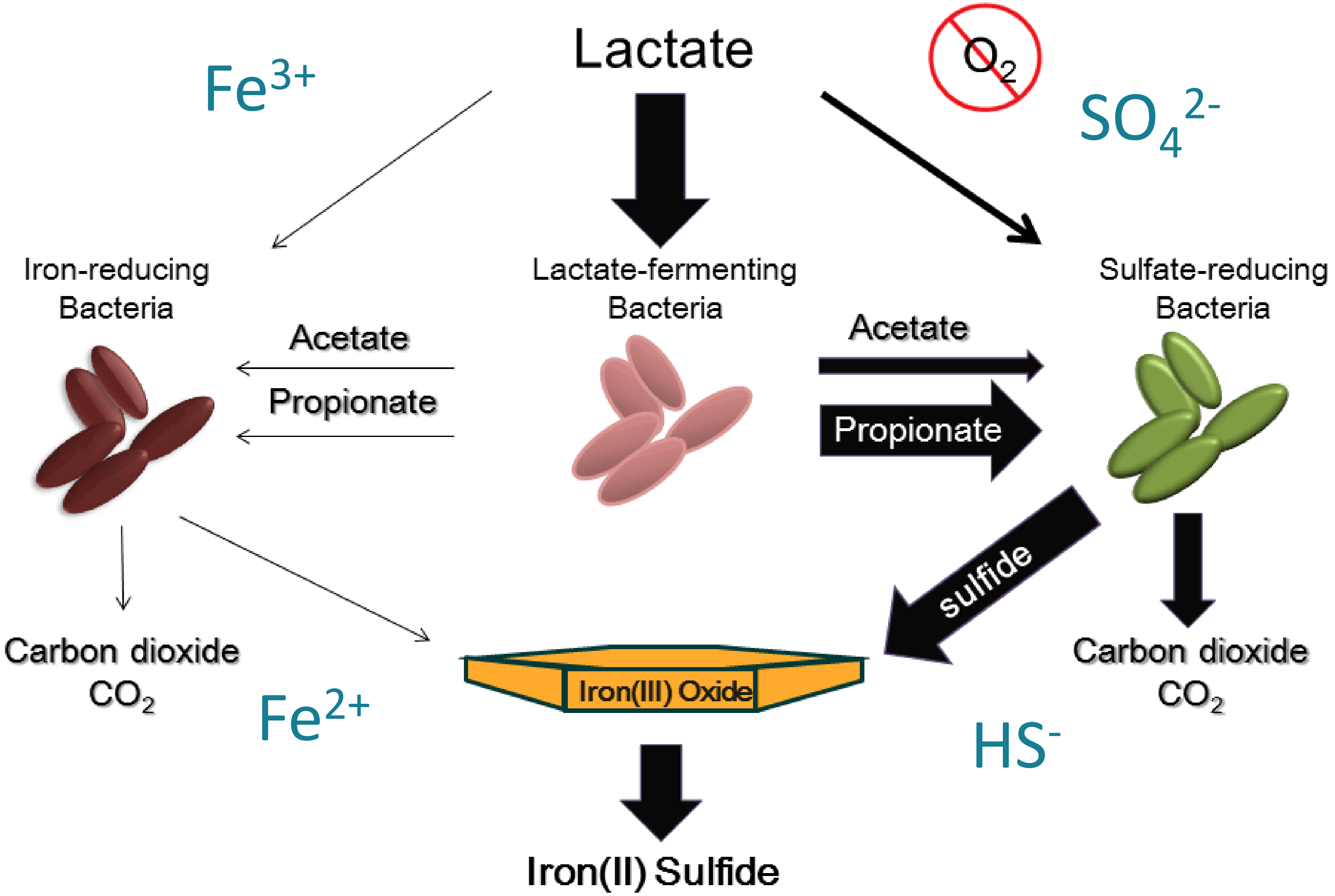


Image Source: http://www.bio.anl.gov/images/environbio/subsurface/reduction_iron.gif

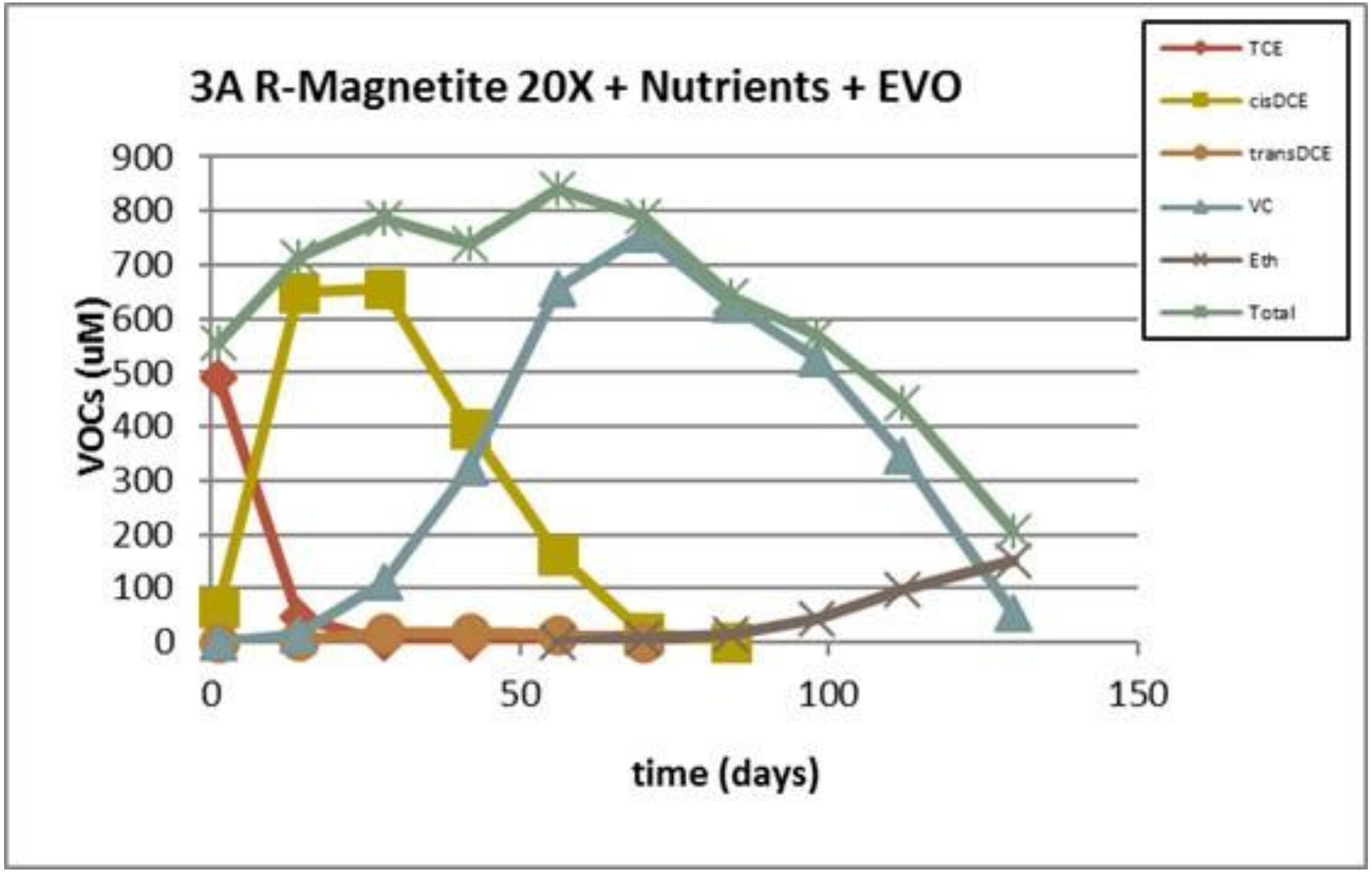
Microcosm Study Design

Study performed in serum bottles (125 mL groundwater, 25 g crushed gypsum-rich bedrock, 5 g sediment), in duplicate

Treatments:

- Killed controls
- Unamended
- Magnetite (Fe3O4) (Rockwood)
- Magnetite (Fe3O4) (Alfa Aesar)
- Ferric citrate
- Ferric sulfate
- Ferrous chloride
- Ferrous lactate
- Ferrous sulfate

Microcosm Results

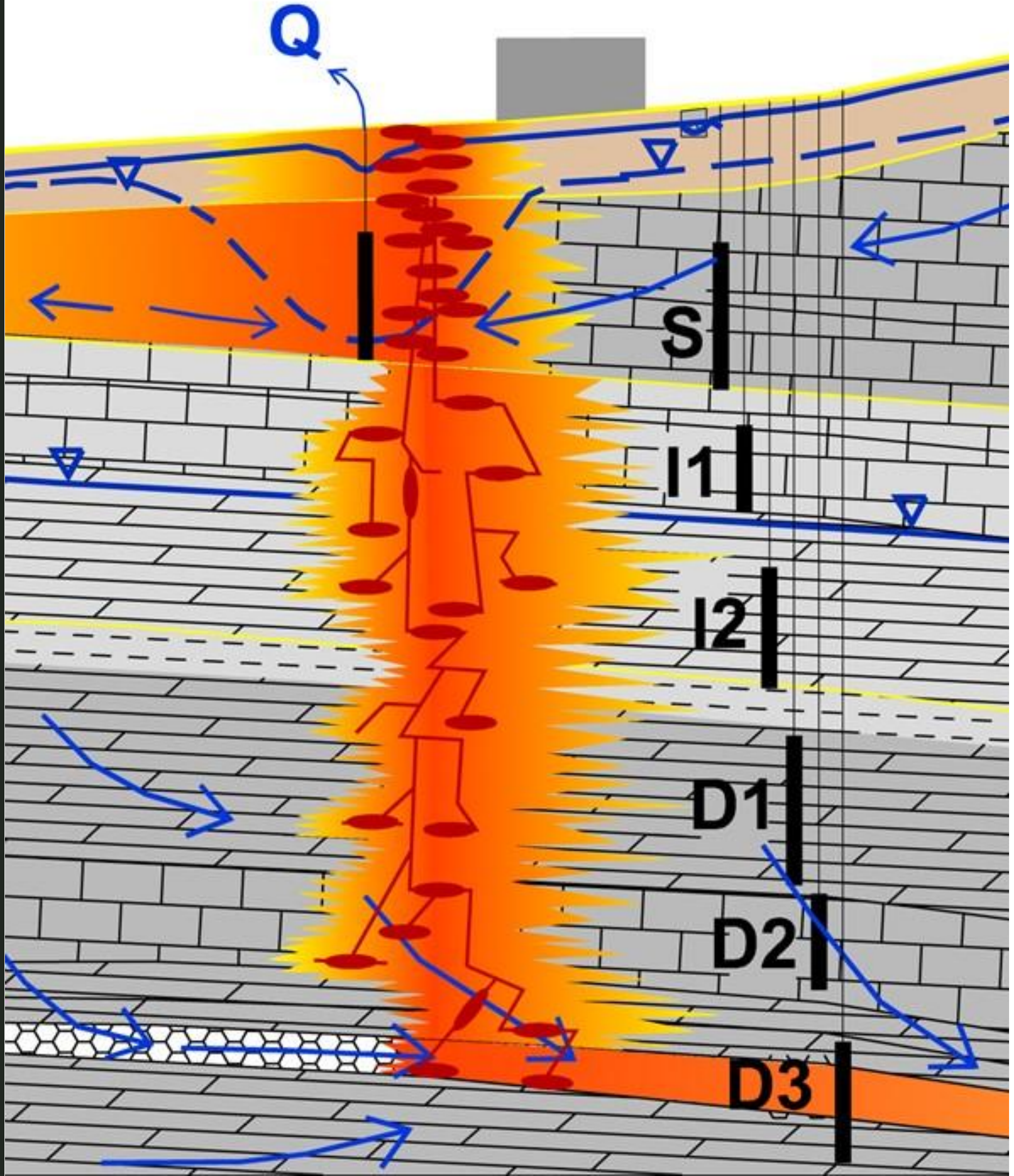


Complete reductive dechlorination of TCE to ethene observed with EVO and magnetite

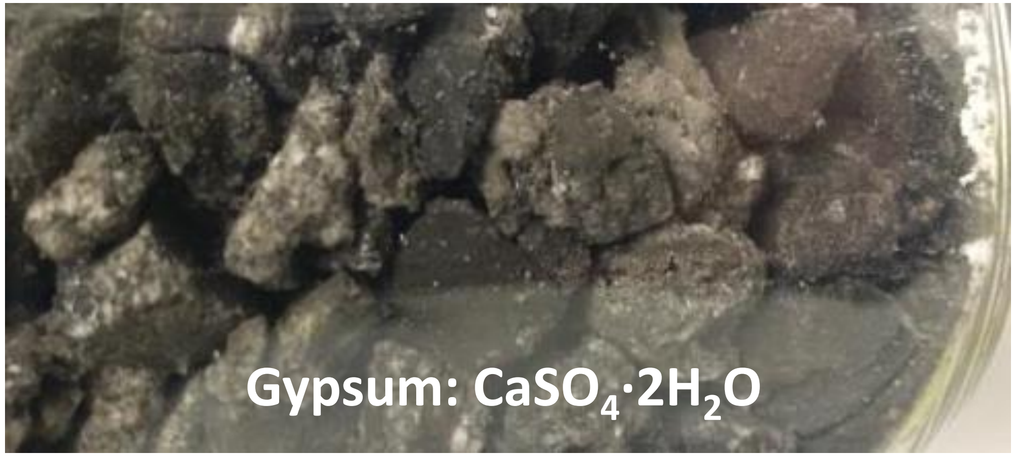
Site Description

- Former plant site
- Electrical components manufactured from 1951-1990
- 55 acre site
- Waste solvents (TCE, acetone, methanol) disposed into evaporation pit(s)

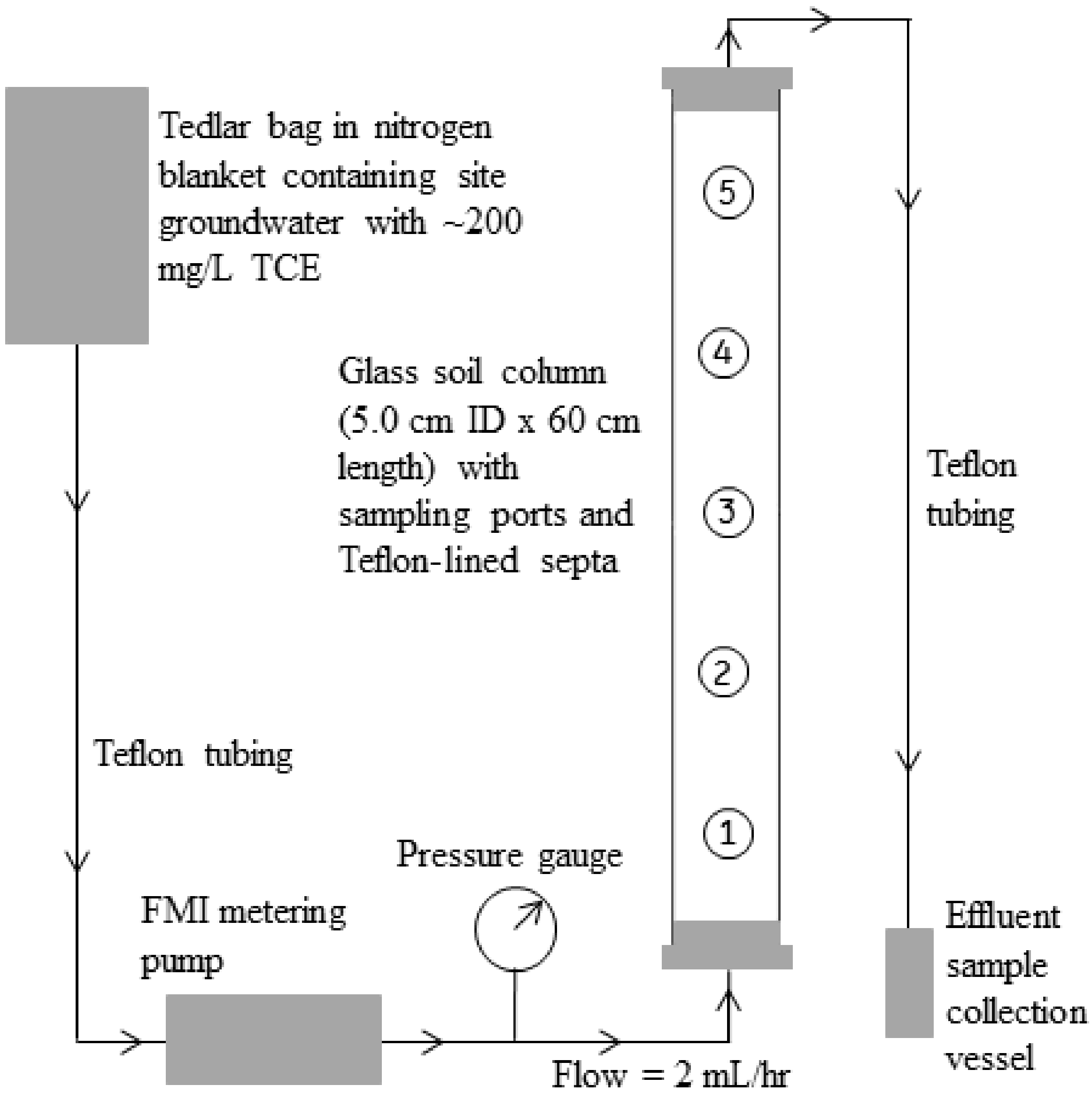
Site Description – Gypsum-Rich Bedrock Layer



Primary GW flow in gypsum-rich D3 unit located ~ 46 meters bgs



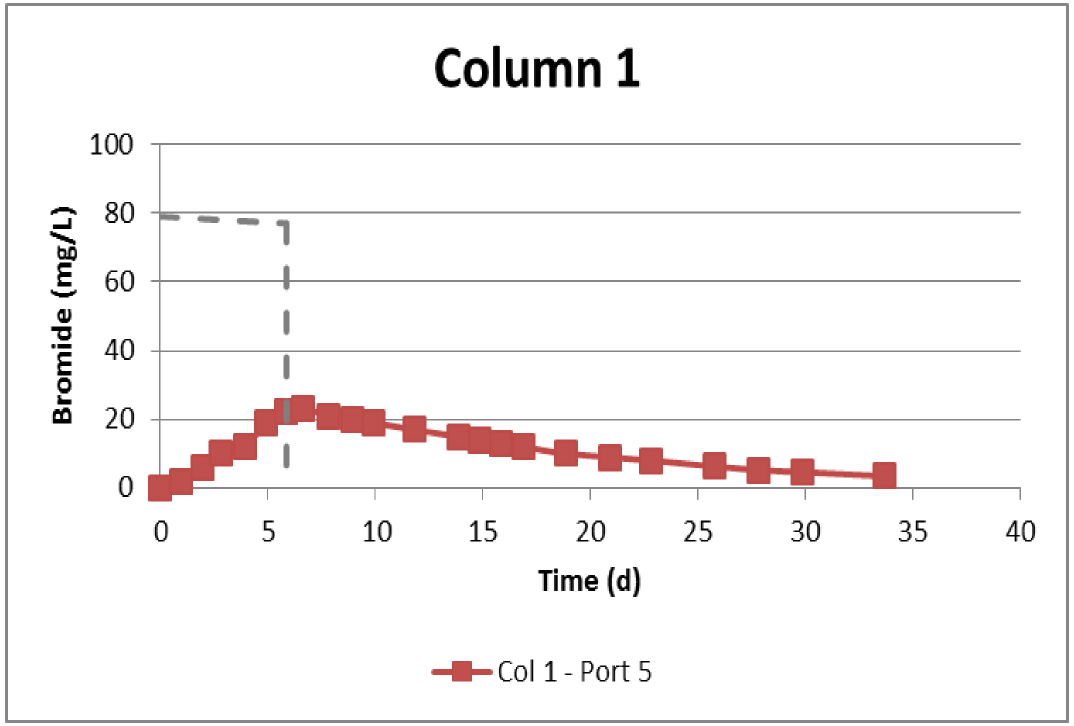
Column Set-Up



Experimental Design

Column	Type	Rock Added (g)	Magnetite Added (g)	Oil Retained (g)
1	Control	1553	None	N/A
2	Active	1573	12.2	15.9
3	Active	1582	48.8	15.8

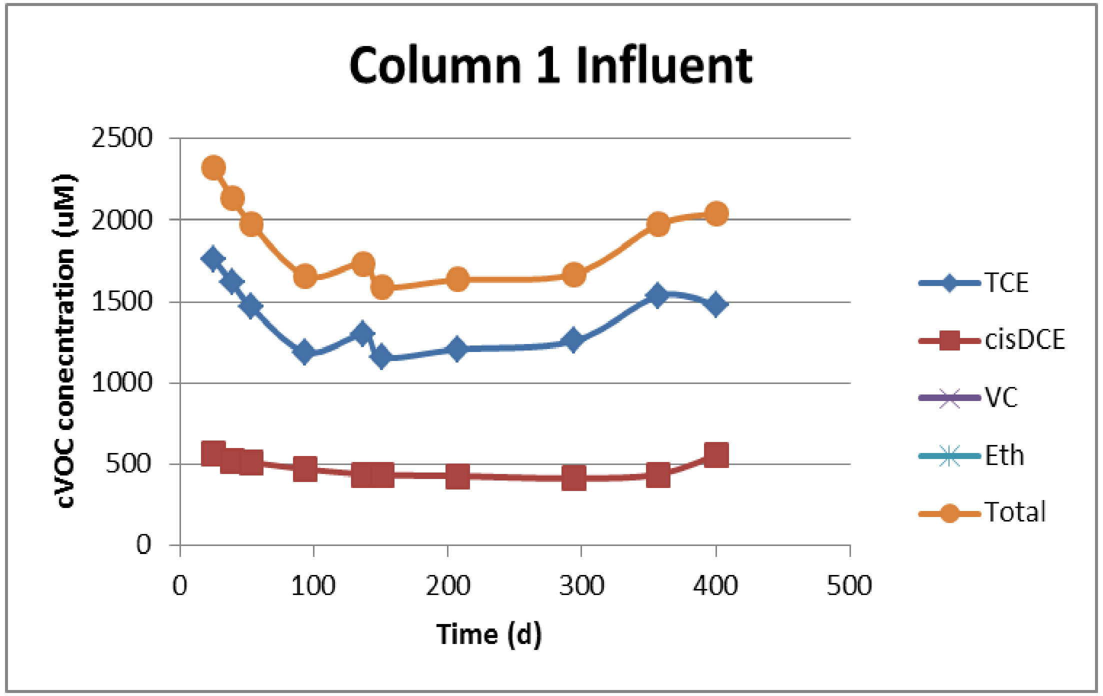
Bromide Tracer Testing Results

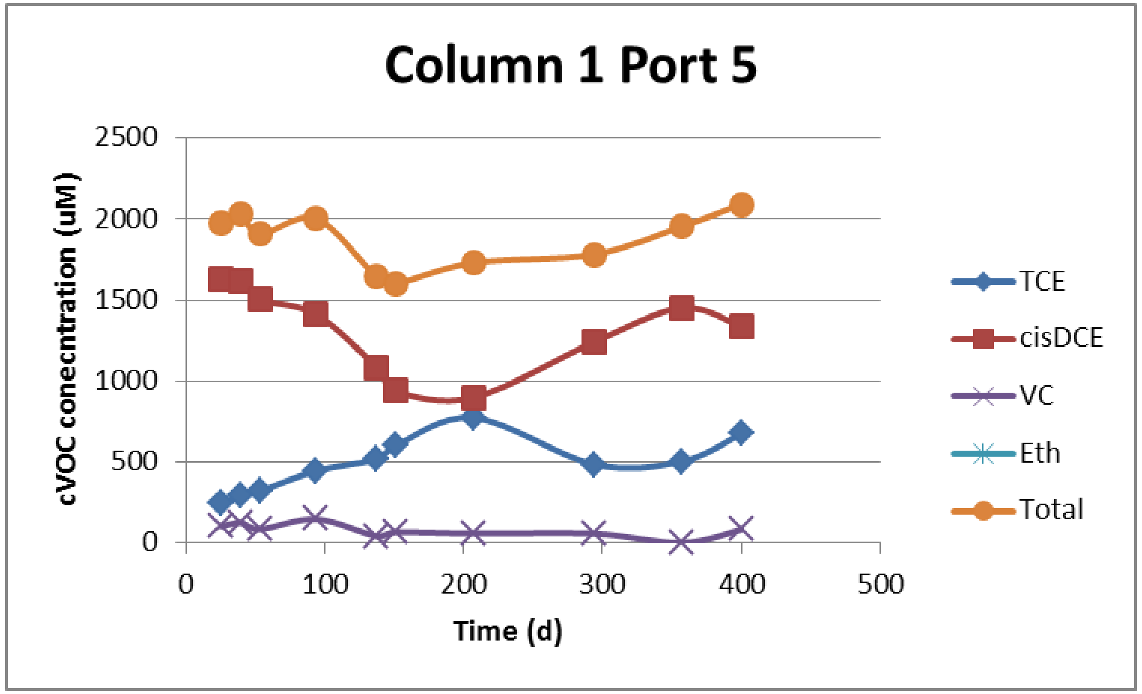


Mean residence time matched theoretical, but breakthrough was early and long tail was present

Column	Bedrock mass (grams)	Pore volume (mL)	Total porosity	Calculated MRT (days)	Total bromide feed (mL)	Measured MRT (days)
1 (control)	1553	550	0.475	11.5	261	11.6
2	1573	542	0.466	11.2	259	11.6
3	1582	539	0.456	11.0	277	12

Control Column – VOC Results

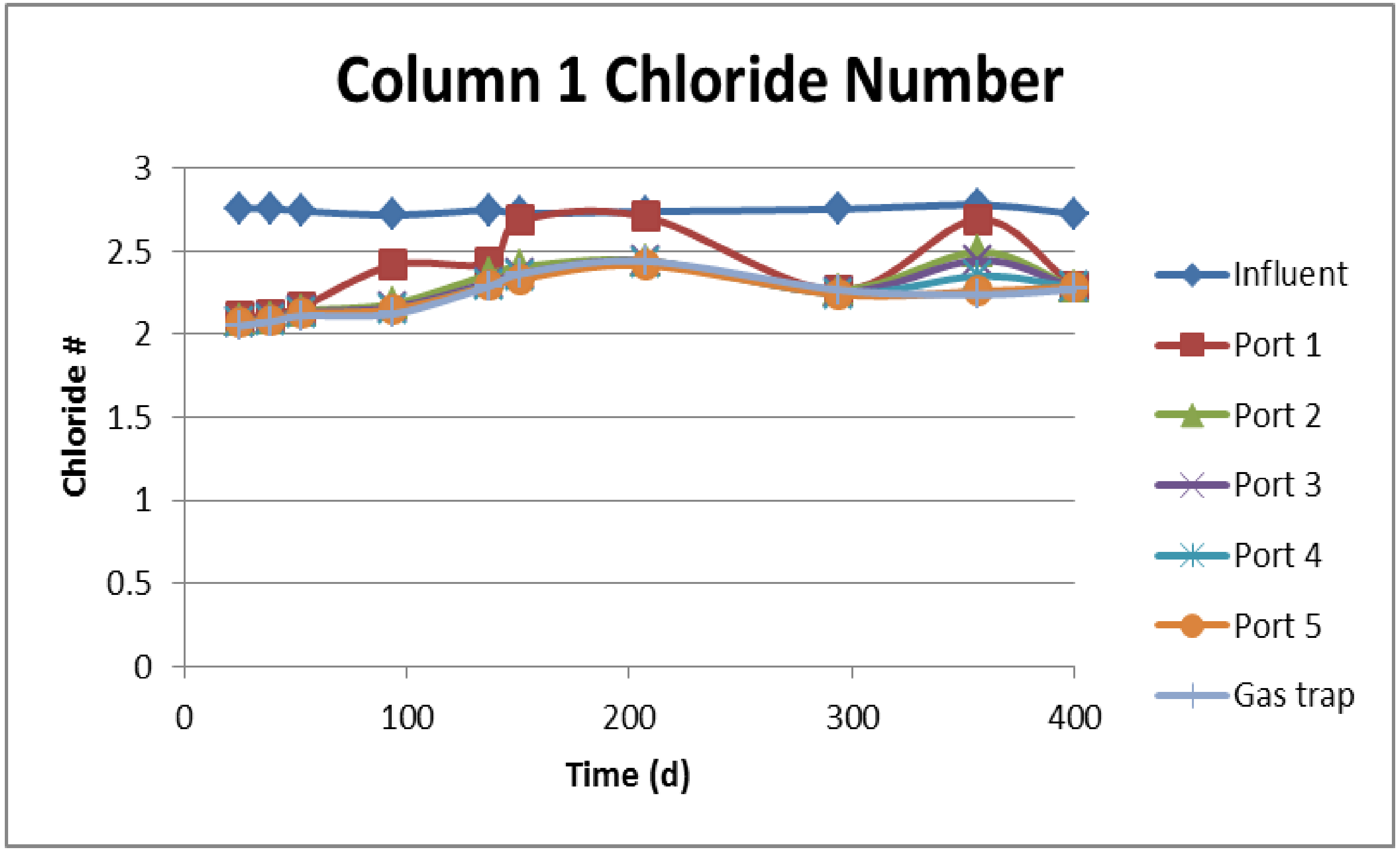




Influent mostly TCE with lower amounts of cisDCE

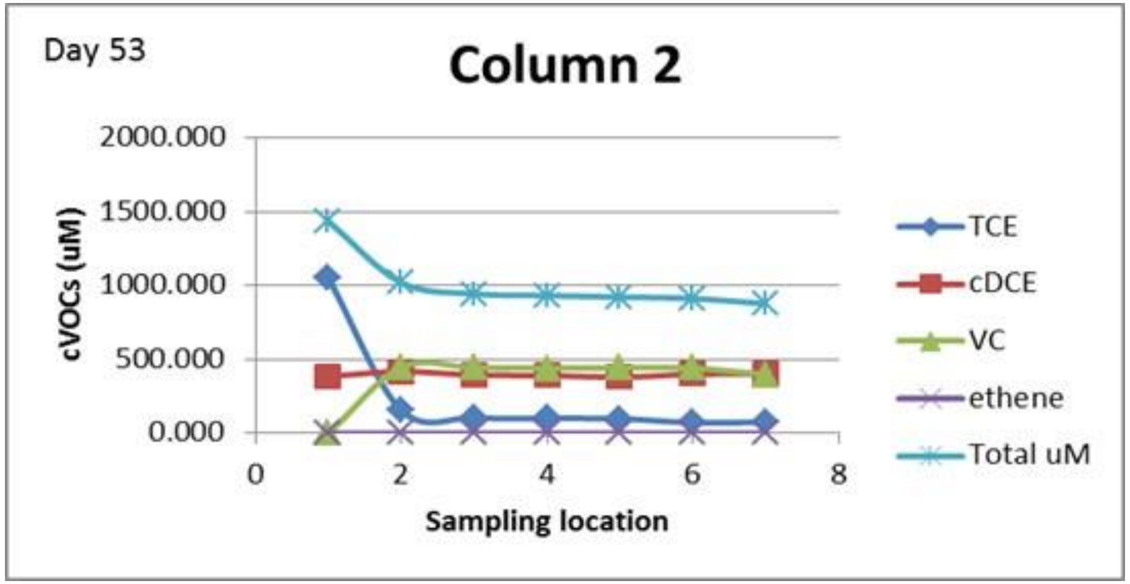
Effluent mostly cisDCE with lower of amounts of TCE and minor VC

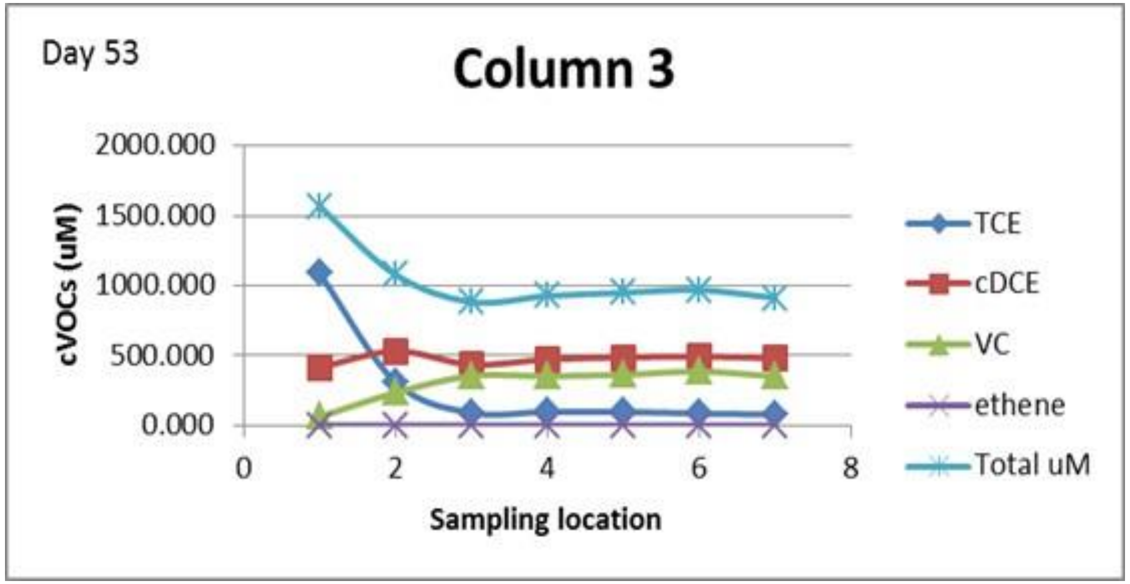
Control Column – Chloride Number



$$\text{Cl \#} = \frac{(mol\ TCE\ x\ 3)+(mol\ cDCE\ x\ 2)+(mol\ VC)}{(total\ mol\ chlorinated\ ethenes+ethene)}$$

Active Columns – Early VOC Results

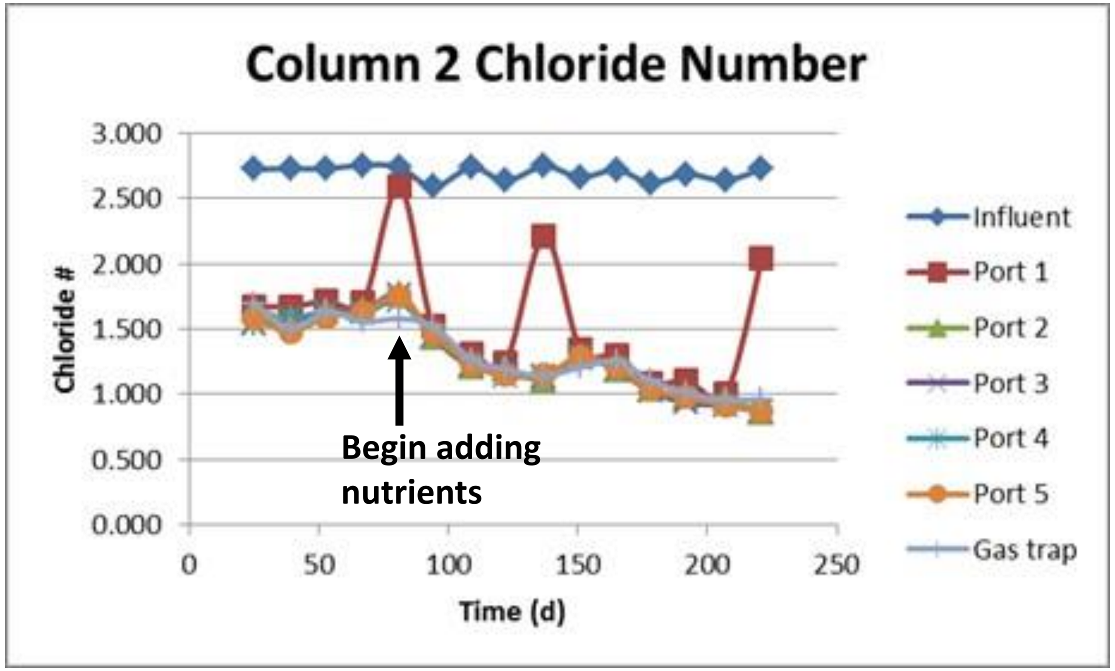


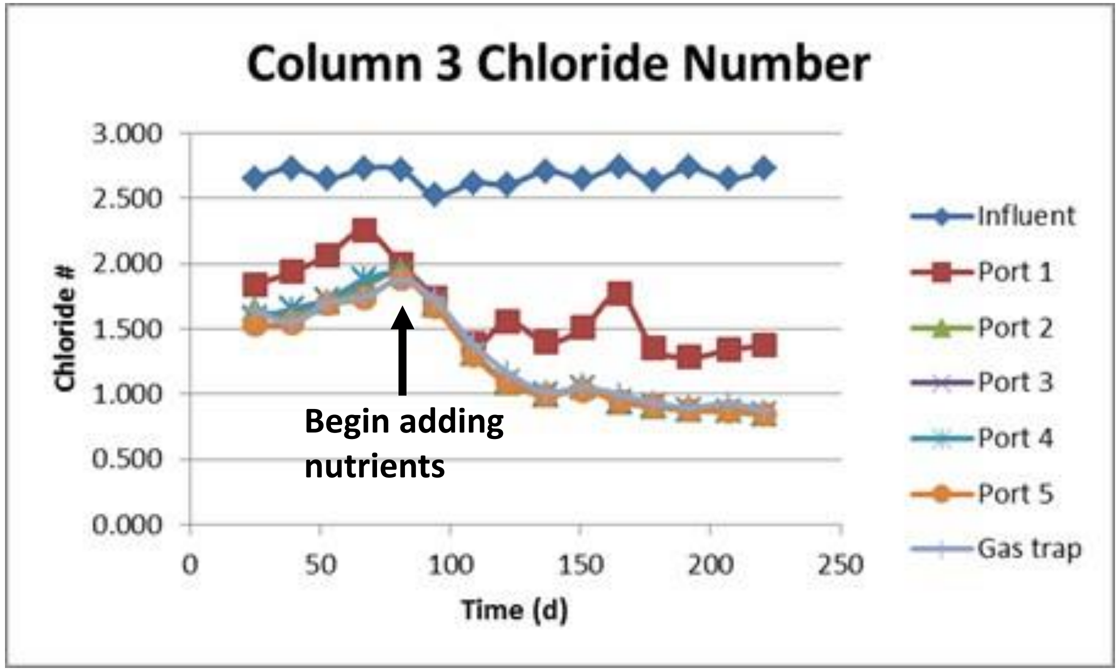


? *Why is dechlorination stopping at cDCE and VC?*

? *Why is dechlorination not progressing throughout the column?*

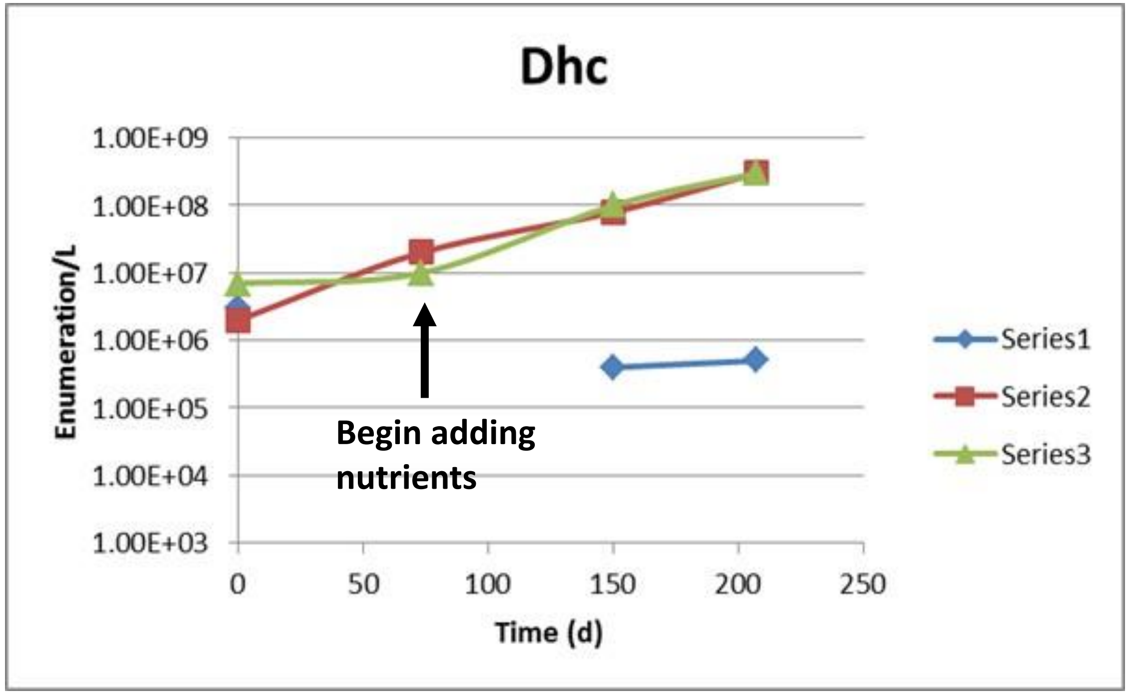
Active Columns – Mid-Point VOC Results

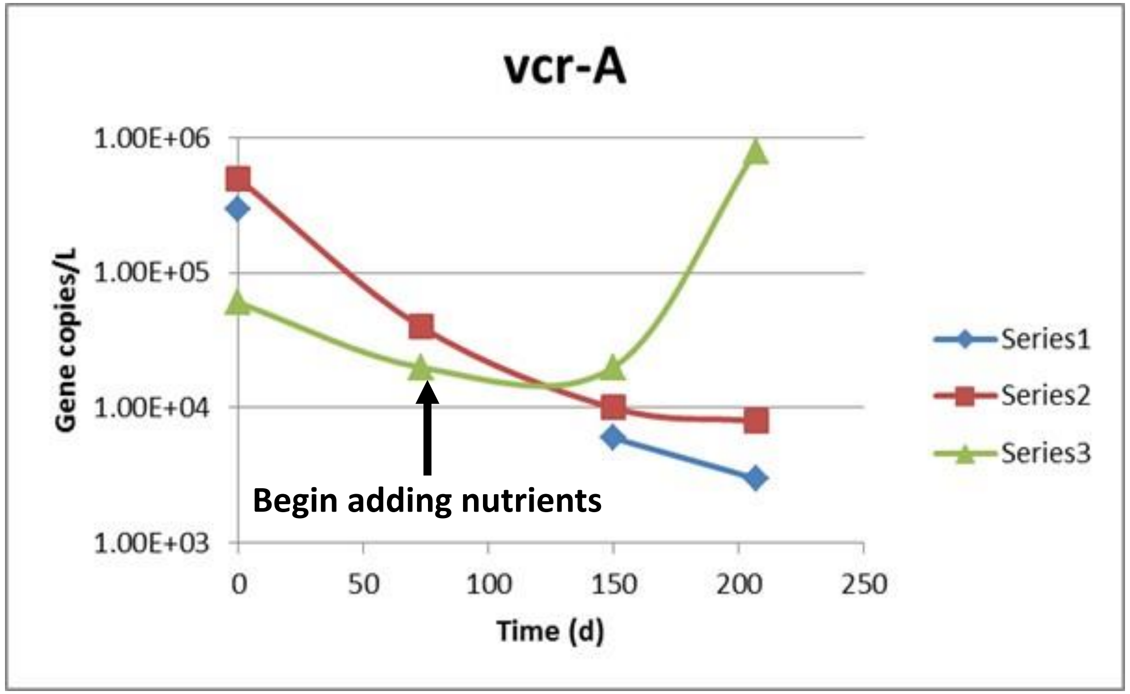




Periodic nutrient amendment (N/P, YE, vitamin B12) beginning on Day 77 improved dechlorination performance

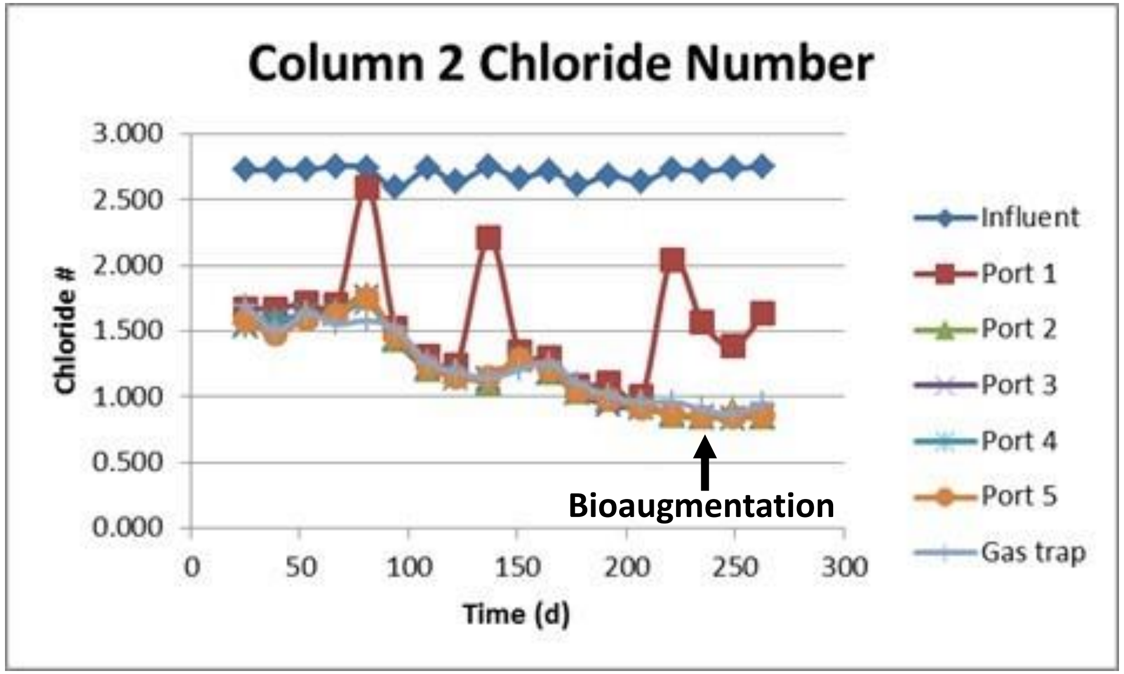
Microbial Characterization Results

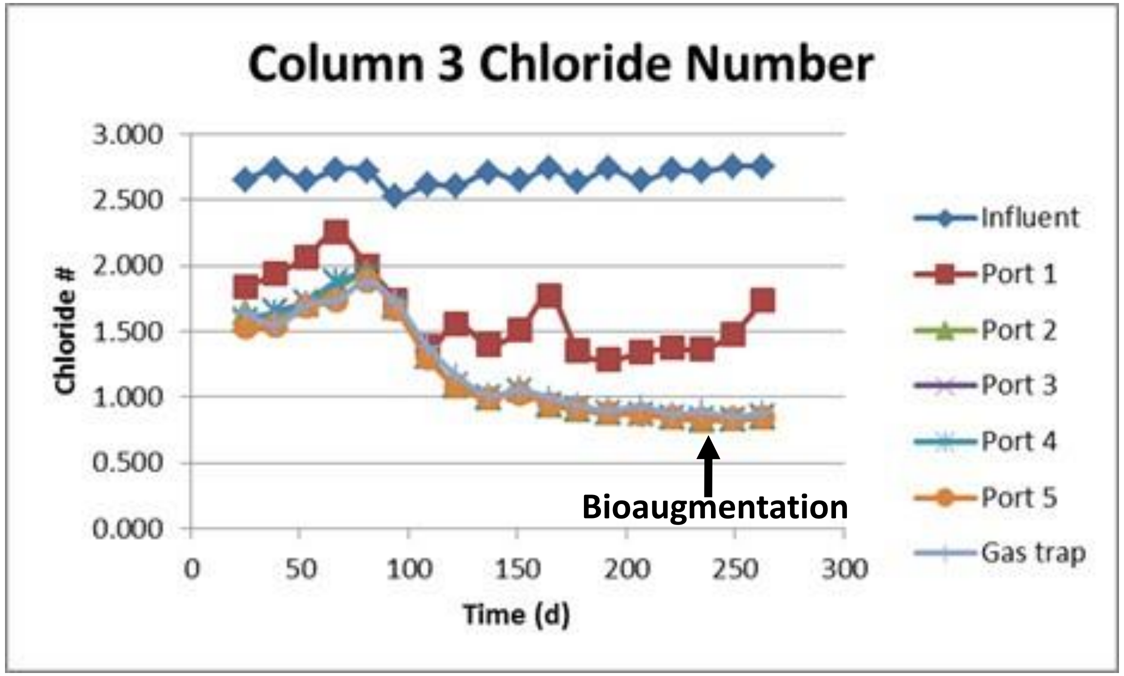




Dhc counts increasing in active columns, while vcr-A results are mixed

Active Columns – Post-Bioaug Degradation Results

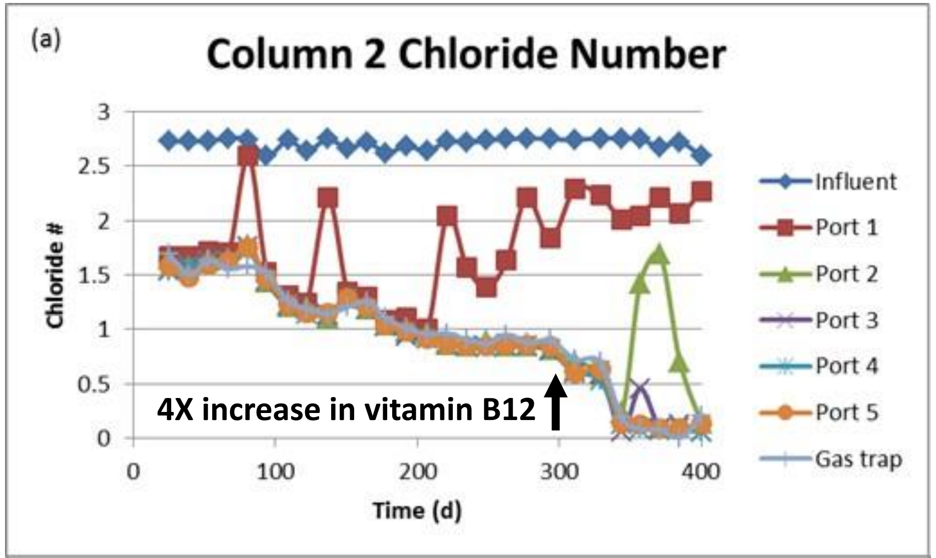


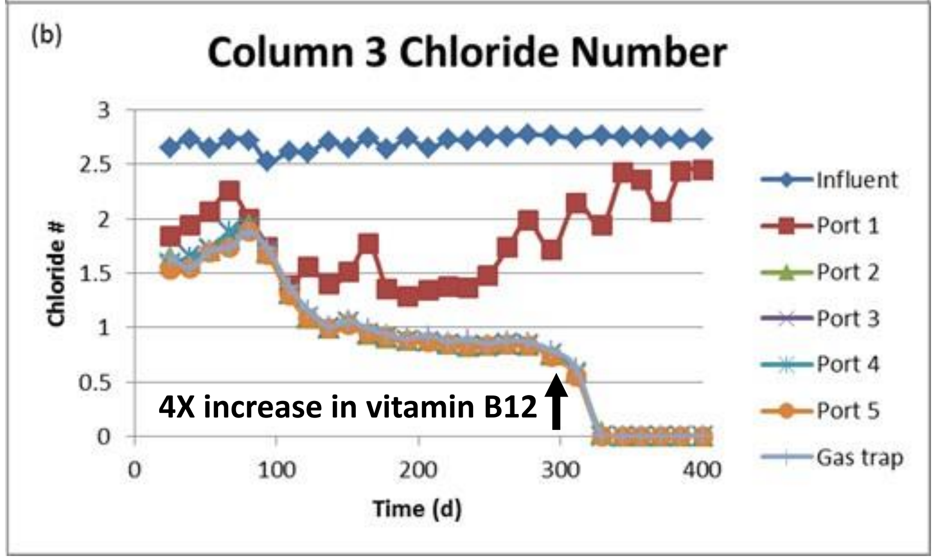


Dechlorination progress slowed after 200 days

Bioaugmentation with SDG-9™ on Day 238 did not improve performance

Active Columns – Degradation Results





4X increase in amount of vitamin B12 on Day 295 resulted in improved dechlorination performance

Column 2 – 90% conversion of TCE to ethene

Column 3 – Complete conversion of TCE to ethene

Chemical Structure of Vitamin B12

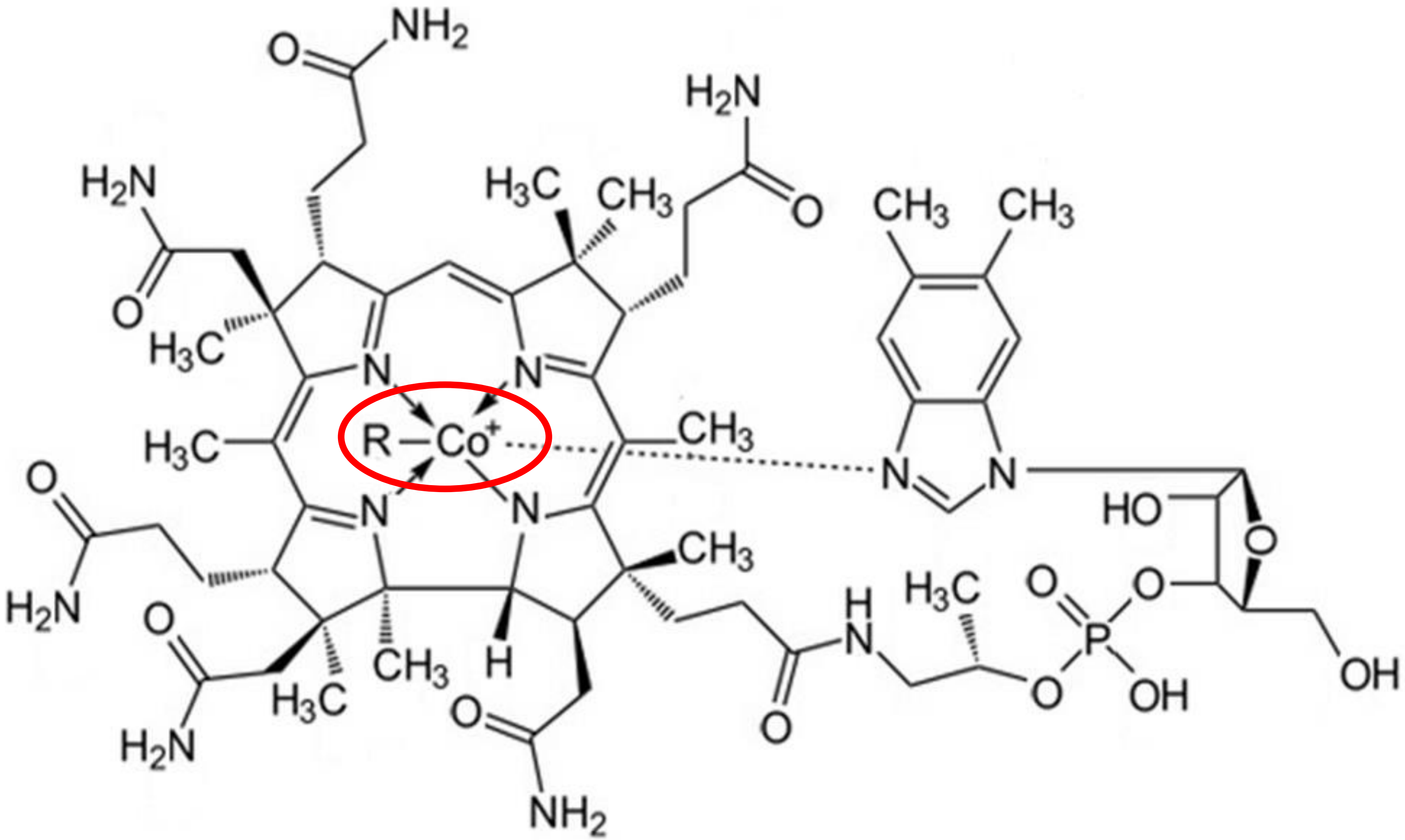
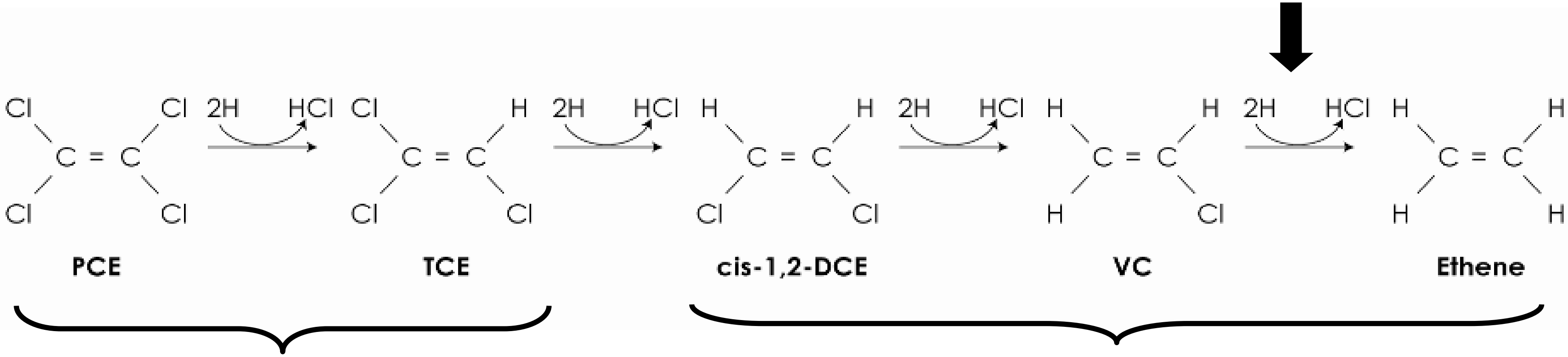


Figure Source: www.chemicalbook.com

Role of Cobalt in Reductive Dechlorination

Vinyl Chloride
Reductase Enzyme



Multiple strains within a single group *(Dehalococcoides)*

Cobalt is critical for VCR enzyme function

Figure Source: SABRE training class

Potential Cobalt Removal Mechanisms

$Co^{2+} + H_2S \longrightarrow$ Cobalt sulfide (CoS)

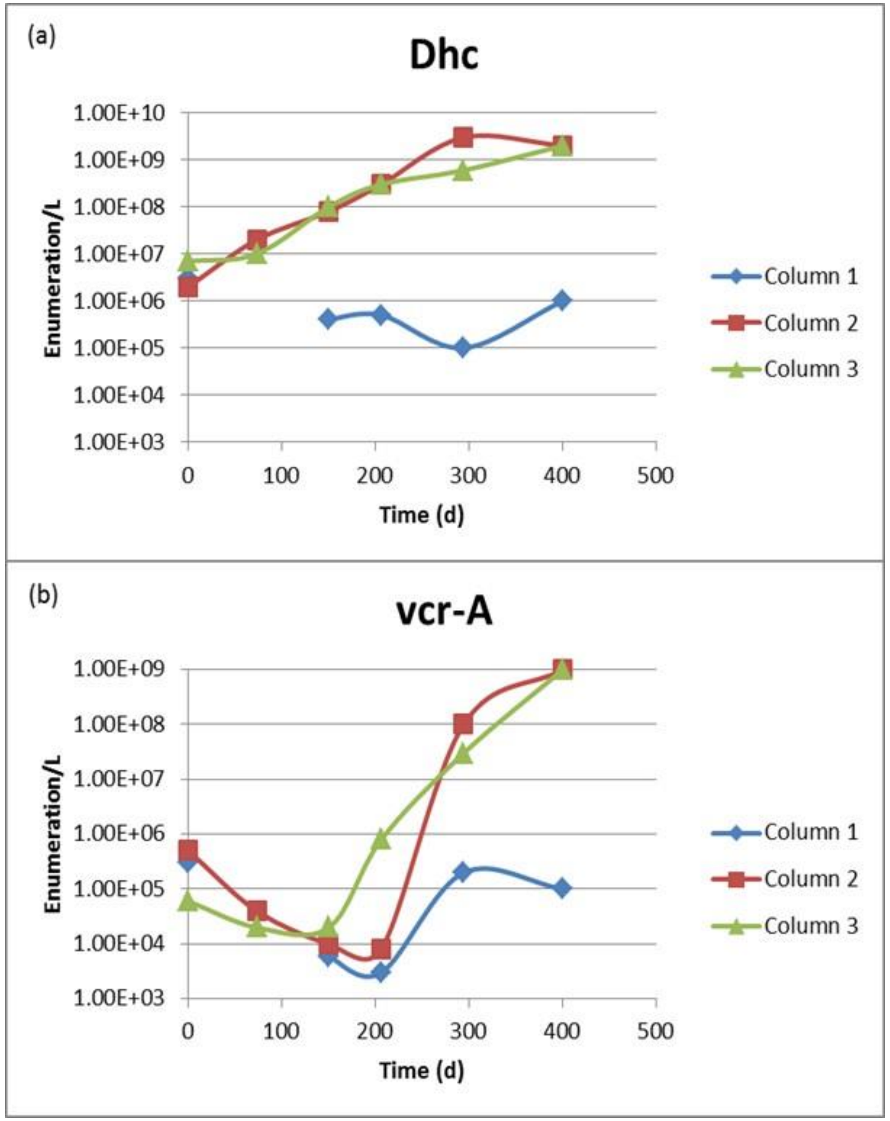
$Fe^{2+} + H_2S \longrightarrow$ Iron sulfide (Fe_xS_xCo)

$\uparrow$ Adsorption and Co-precipitation

Co^{2+}

Image Source: http://www.bio.anl.gov/images/environbio/subsurface/reduction_iron.gif

Final Microbial Characterization Results

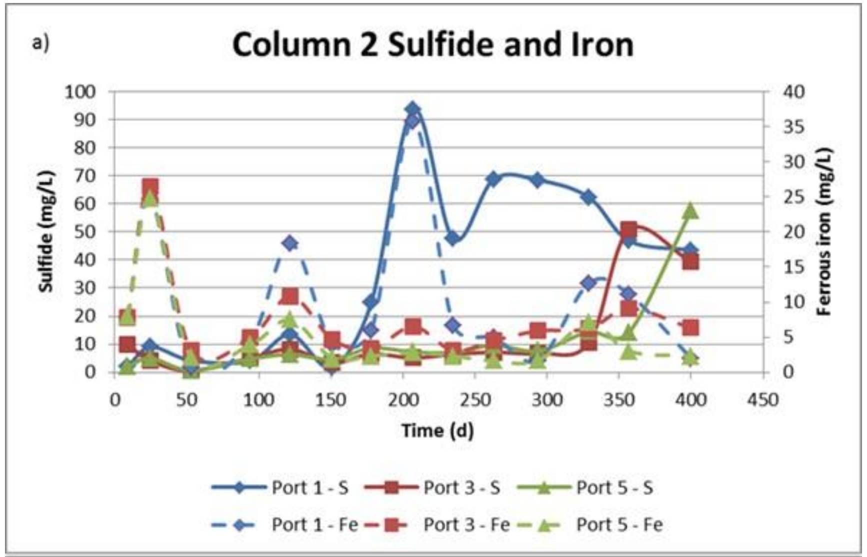


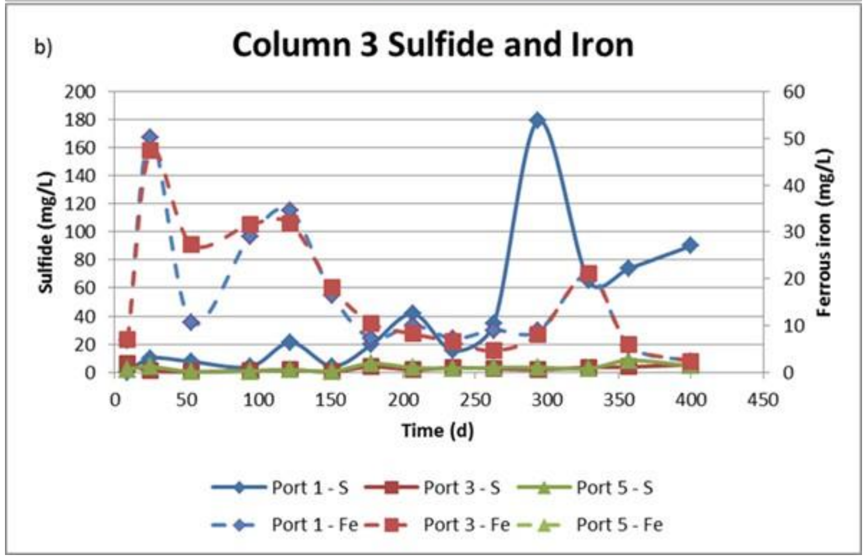
Positive response to nutrient addition (incl. vitamin B12)

Addition of nutrients (N/P, YE) increased Dhc

Addition of vitamin B12 increased vcr-A

Active Columns – Final Results





Why did Column 2 have 90% conversion of TCE to ethene, when Column 3 had complete conversion?

Sulfide levels in Column 2 consistently higher during last 50 days of study – suggests Fe limitation

Conclusions

Complete reductive dechlorination of TCE to ethene was achieved in active columns containing EVO and magnetite

The periodic addition of supplemental nutrients was critical to process

Vitamin B12 (cobalt) was particularly important

Availability of cobalt potentially affected by co-precipitation with iron-sulfide minerals

Moving forward with a pilot test in the deep bedrock to demonstrate process in-situ and collect data for full-scale design

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Thank you!

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