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Using CSIA to Distinguish Abiotic and Biotic Degradation Mechanisms in ISCR-Assisted Bioremediation Systems

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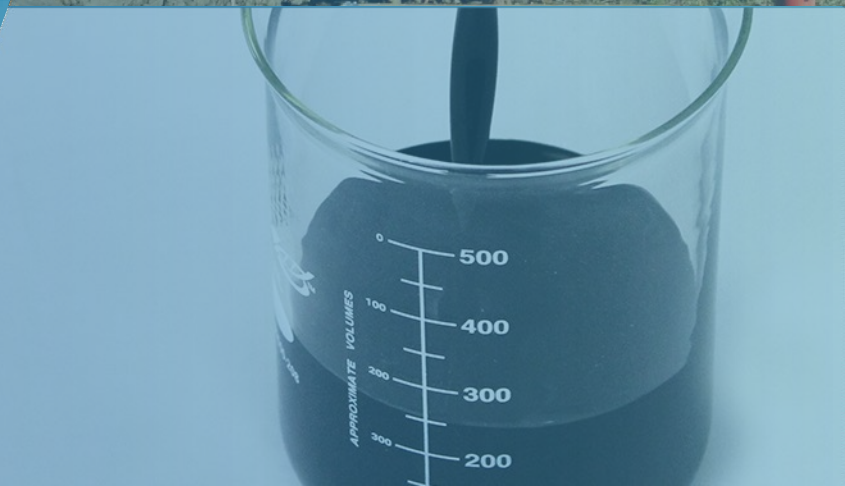
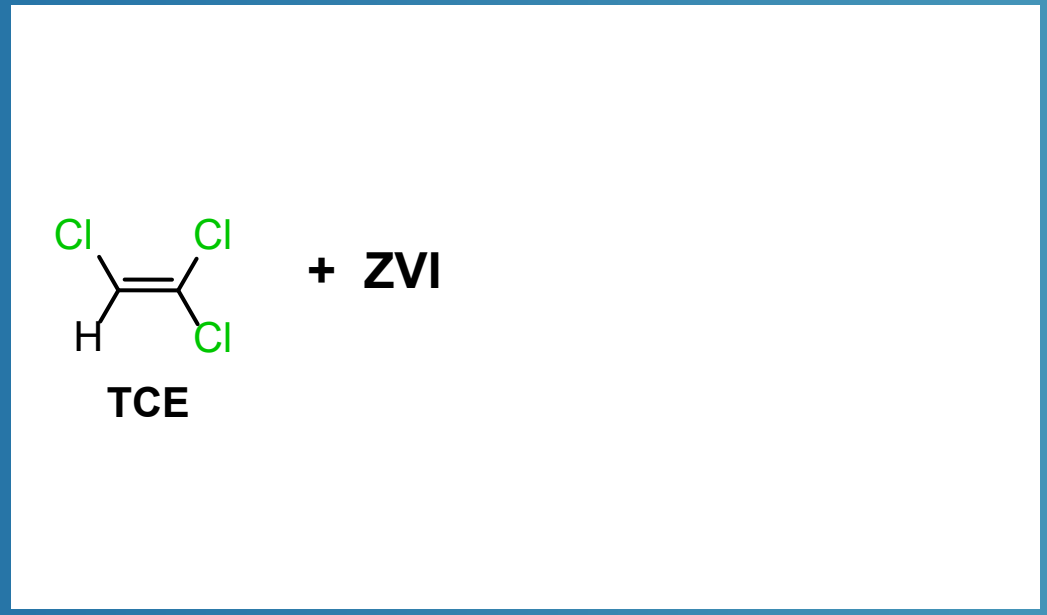


Summary

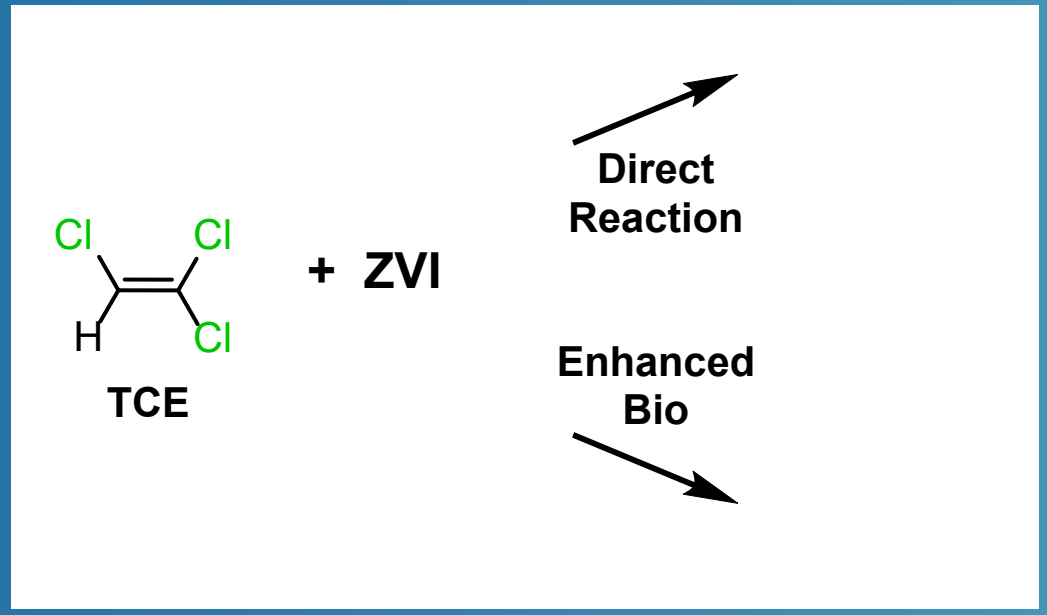
- ISCR-Enhanced Bioremediation: Introduction
  - ZVI and its impact on Enhanced Reductive Dechlorination (ERD)
  - CSIA and dual isotope plots as a tool to follow reaction pathways

- CSIA Study
  - Reporting $\delta^{13}C$ enrichment factor (ε_c) for S-ZVI
  - Dual-isotope plots to distinguish biotic/abiotic TCE degradation?

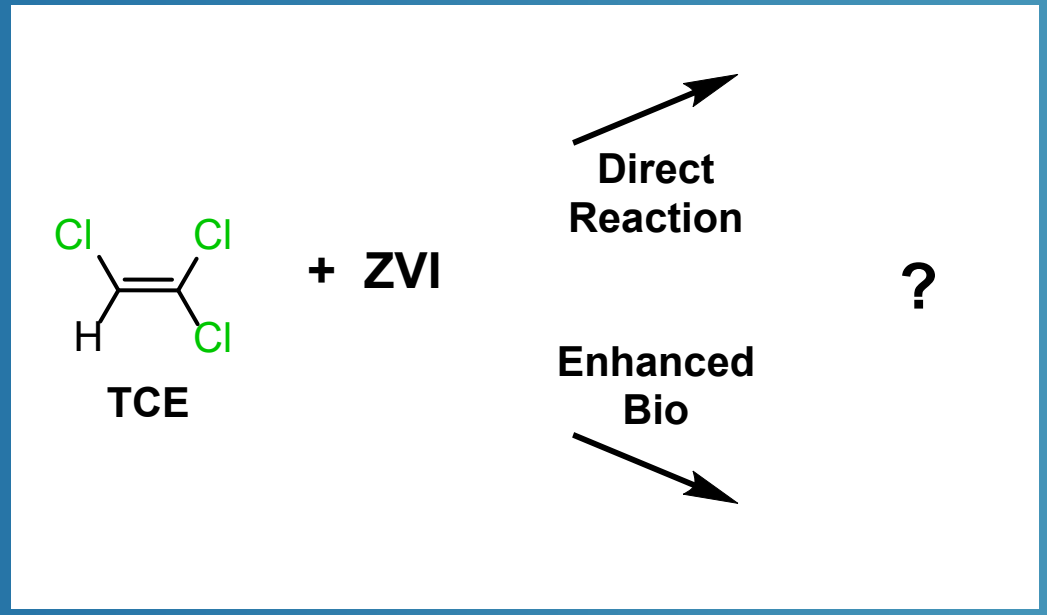
ISCR-Enhanced Bioremediation



ISCR-Enhanced Bioremediation



ISCR-Enhanced Bioremediation



Efficiency of direct ZVI reaction?

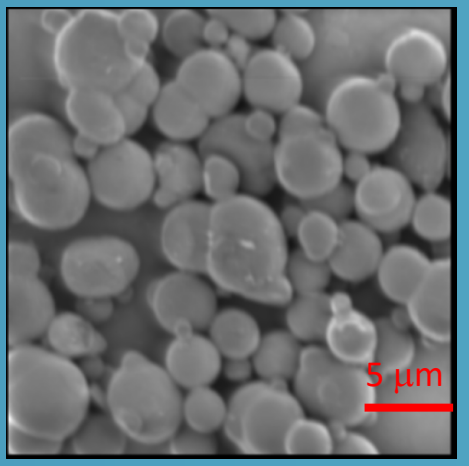
Are both pathways active?

What can we learn using CSIA?

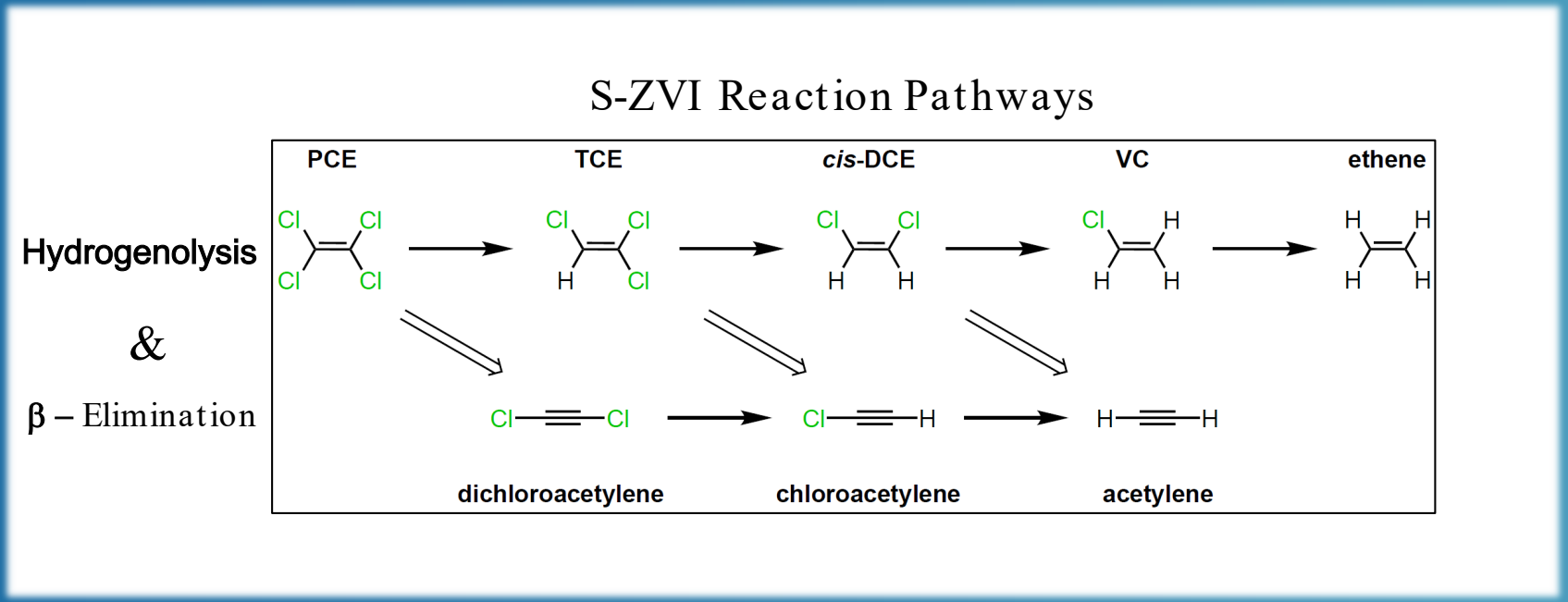
ISCR-Enhanced Bioremediation

Sulfidated Zero-Valent Iron (S-ZVI)

- Abiotic pathway reduces formation of *cis*-DCE, VC
- S-ZVI application primes aquifer for anaerobic bioremediation



SIMS image of S-ZVI



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ISCR-Enhanced Bioremediation: Column Study

Experimental design and analysis by REGENESIS R&D

BIOTIC COLUMN

- Sodium Lactate: 1000 mg/L
- Nutrients: 10 mg/L
- Dehalococcoides: 10^9 cells/L

ISCR-ASSISTED COLUMN

- Sodium Lactate: 1000 mg/L
- Nutrients: 10 mg/L
- Dehalococcoides: 10^9 cells/L
- Colloidal ZVI: 10 g/L

- 15 µM TCE (2 mg/L) at 1 Pore Volume/Week

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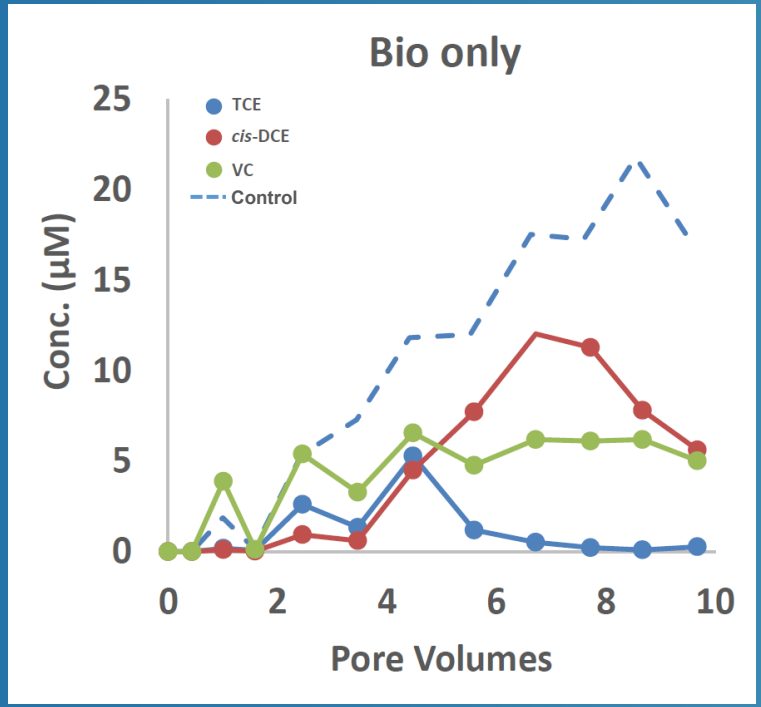
ISCR-Enhanced Bioremediation: Column Study



- TCE elution until week 7
- Daughter products peaked at week 7
- 10 µM daughter products at week 10

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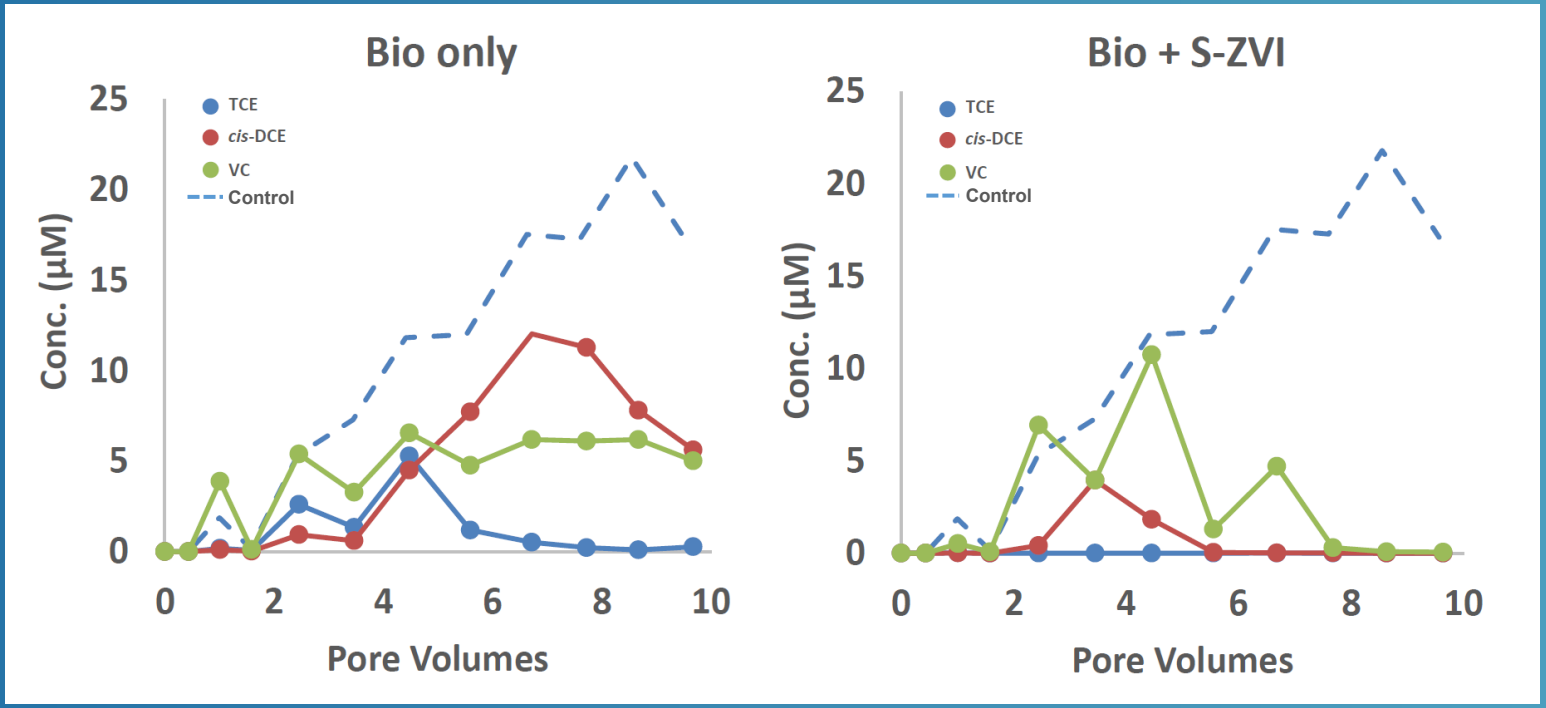
ISCR-Enhanced Bioremediation: Column Study



- TCE elution until week 7
- Daughter products peaked at week 7
- 10 µM daughter products at week 10

- TCE never eluted
- Daughter products peaked at week 5
- No daughters after week 7

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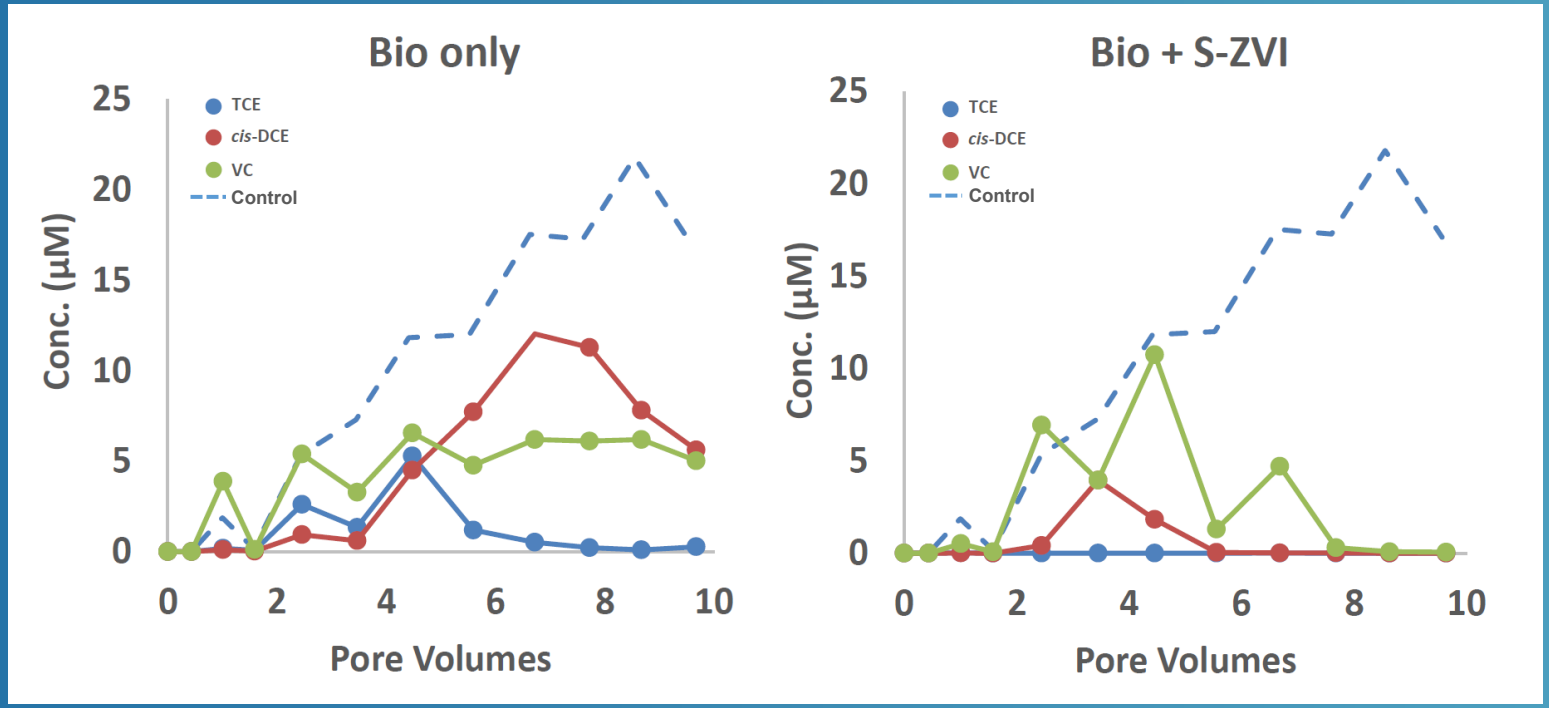
ISCR-Enhanced Bioremediation: Column Study



Improvement From:

Abiotic?

Enhanced bio?

Both?

- TCE elution until week 7
- Daughter products peaked at week 7
- 10 µM daughter products at week 10

- TCE never eluted
- Daughter products peaked at week 5
- No daughters after week 7

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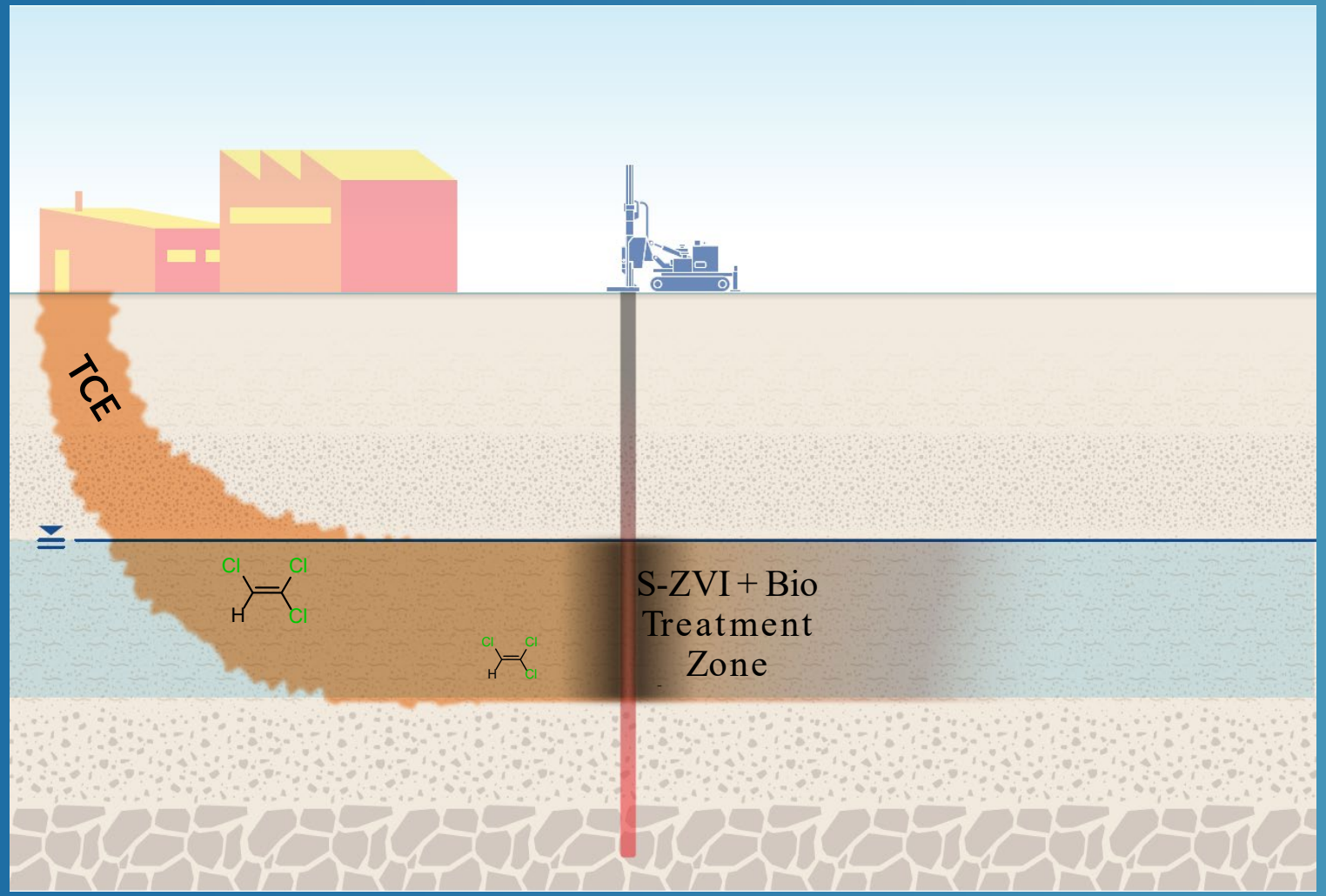
Tracking ISCR Progress with CSIA

- Compound-Specific Isotope Analysis
  - Bonds involving lighter isotopes are slightly weaker
  - Transformation *might* change the isotopic fraction in remaining molecules

δ "Delta" Value: fraction of heavy isotope is present relative to std.

ε Enrichment Factor : The rate a degradation process changes δ

Tracking ISCR Progress with CSIA



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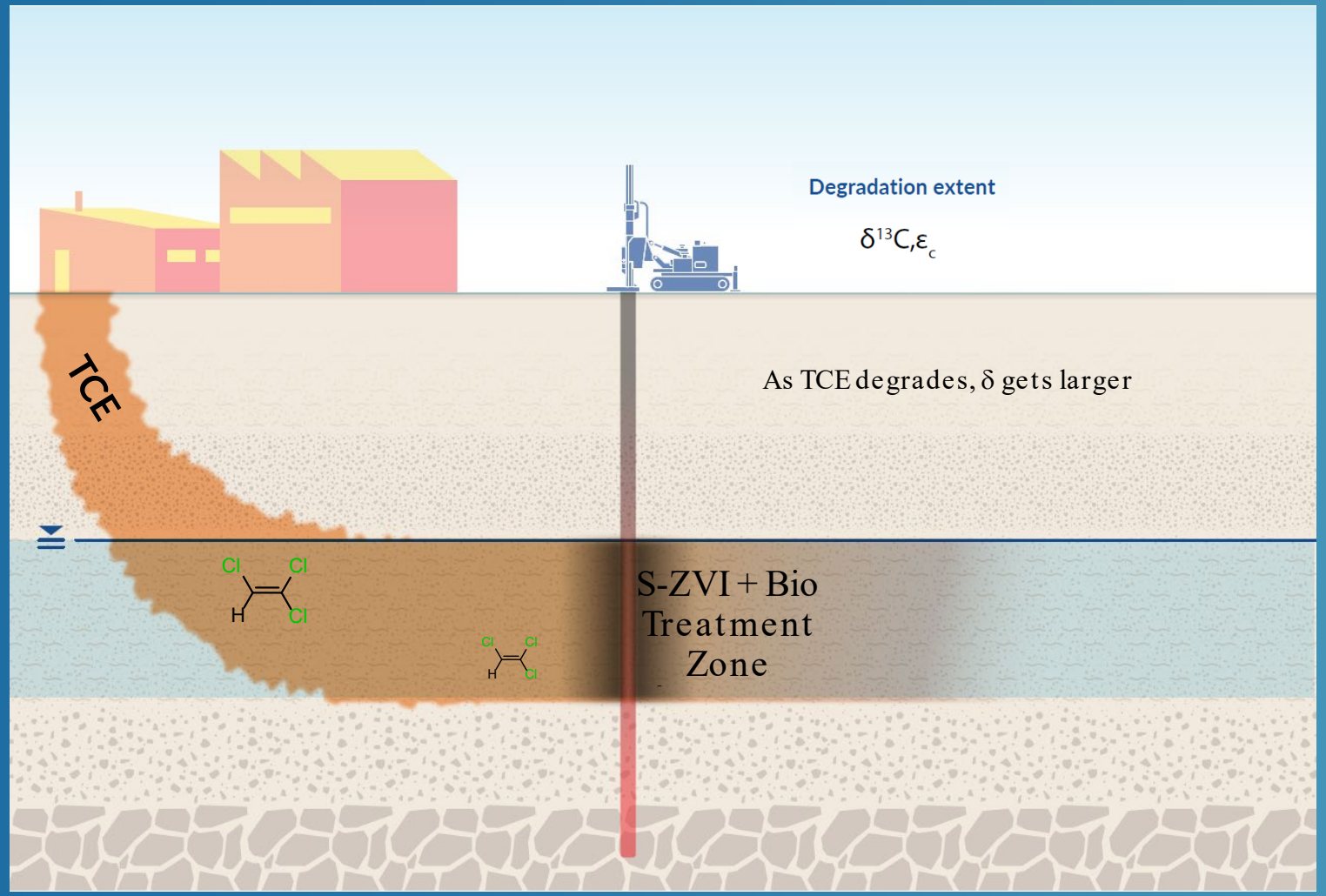
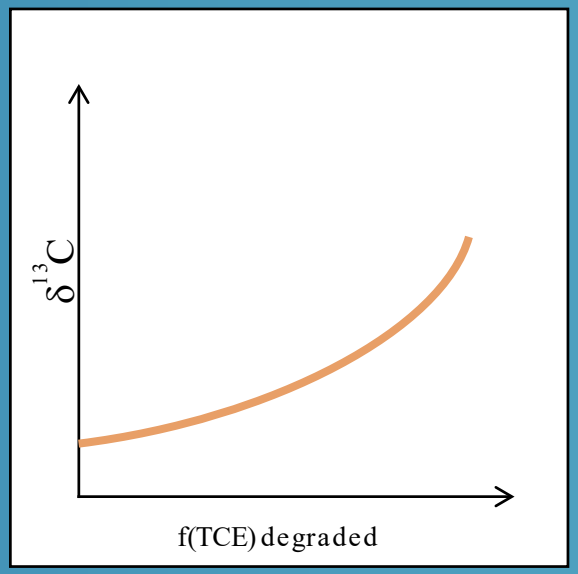
Tracking ISCR Progress with CSIA



Monitoring $\delta^{13}C$ shows TCE is degrading

Rules out dilution, evaporation , etc.

Cannot determine mechanism unless amount degraded is known



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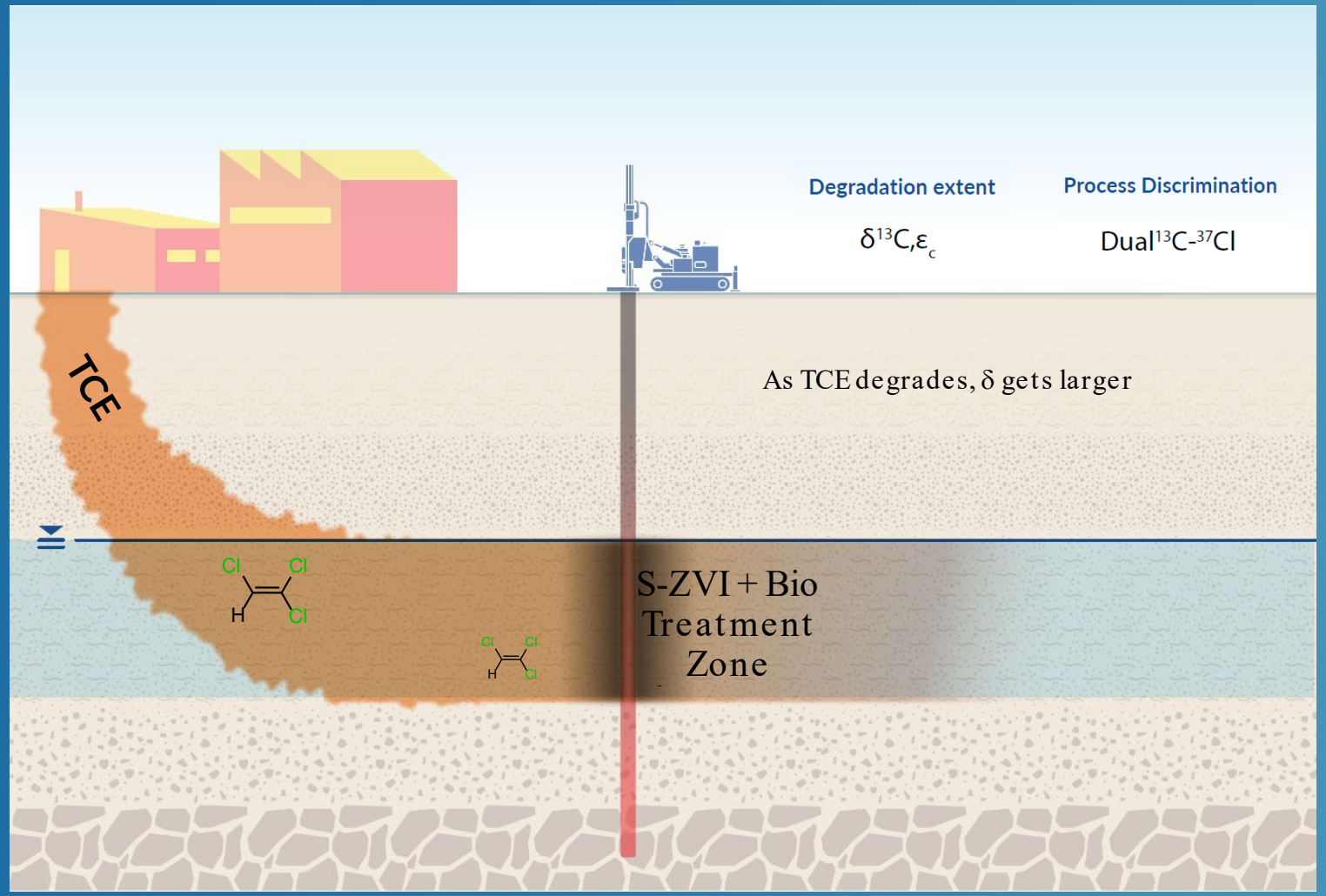
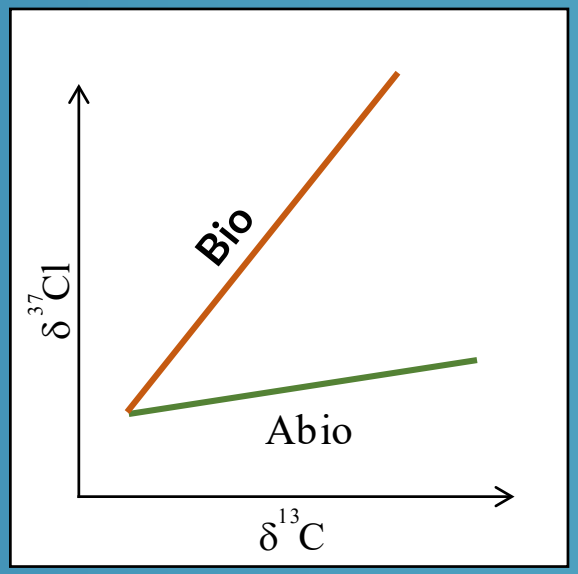
Tracking ISCR Progress with CSIA



Dual $\delta^{13}C$ - ^{37}Cl plots can reveal pathway independent of % removed



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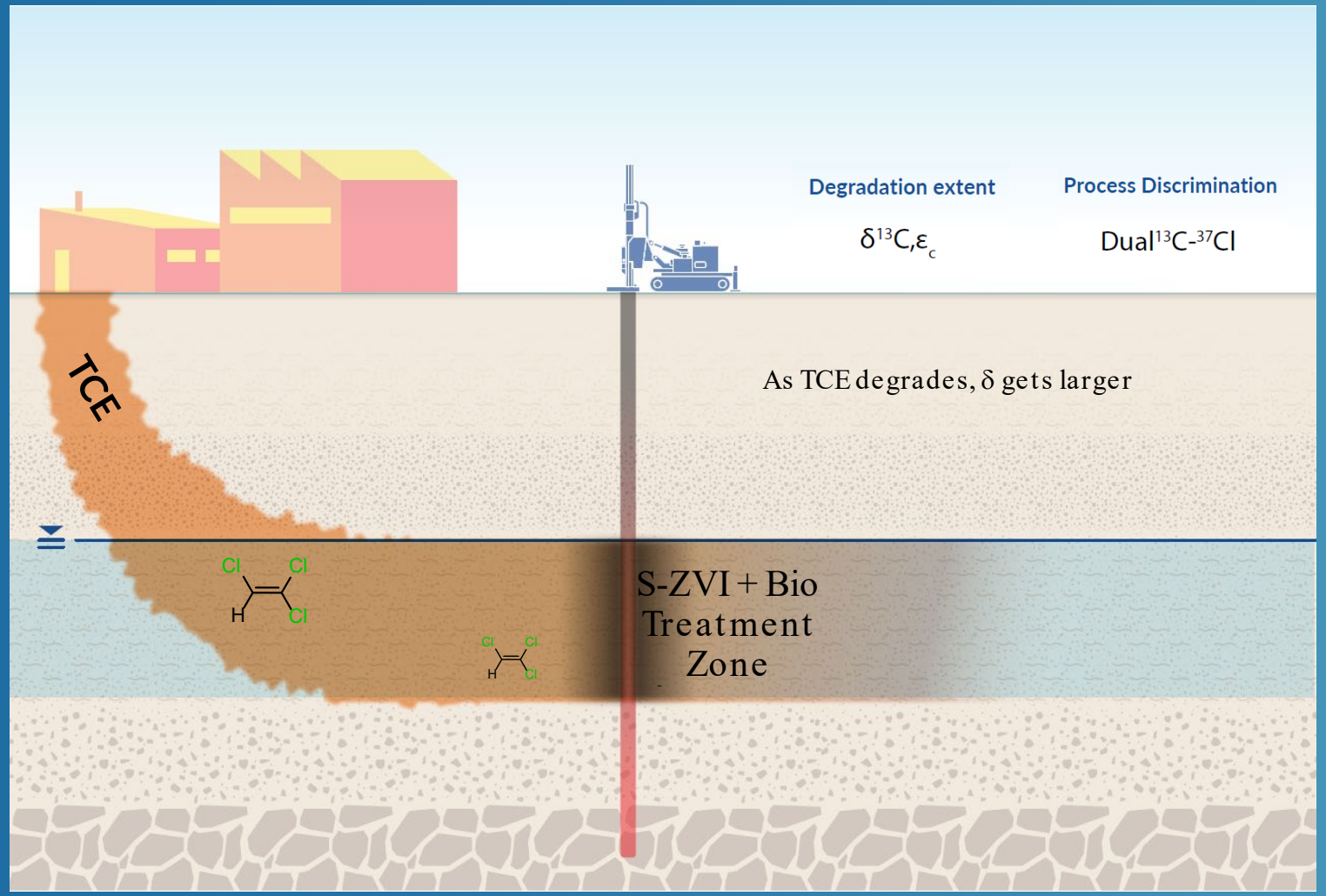
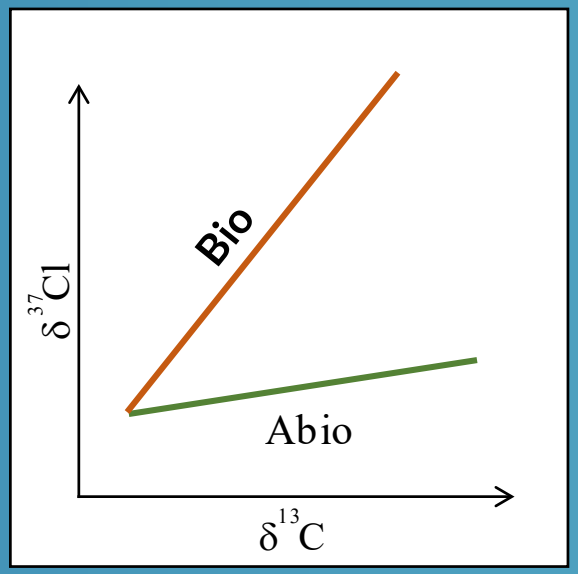
Tracking ISCR Progress with CSIA



Dual $\delta^{13}C$ - ^{37}Cl plots can reveal pathway independent of % removed

Process A and B<u>must</u> have different slopes



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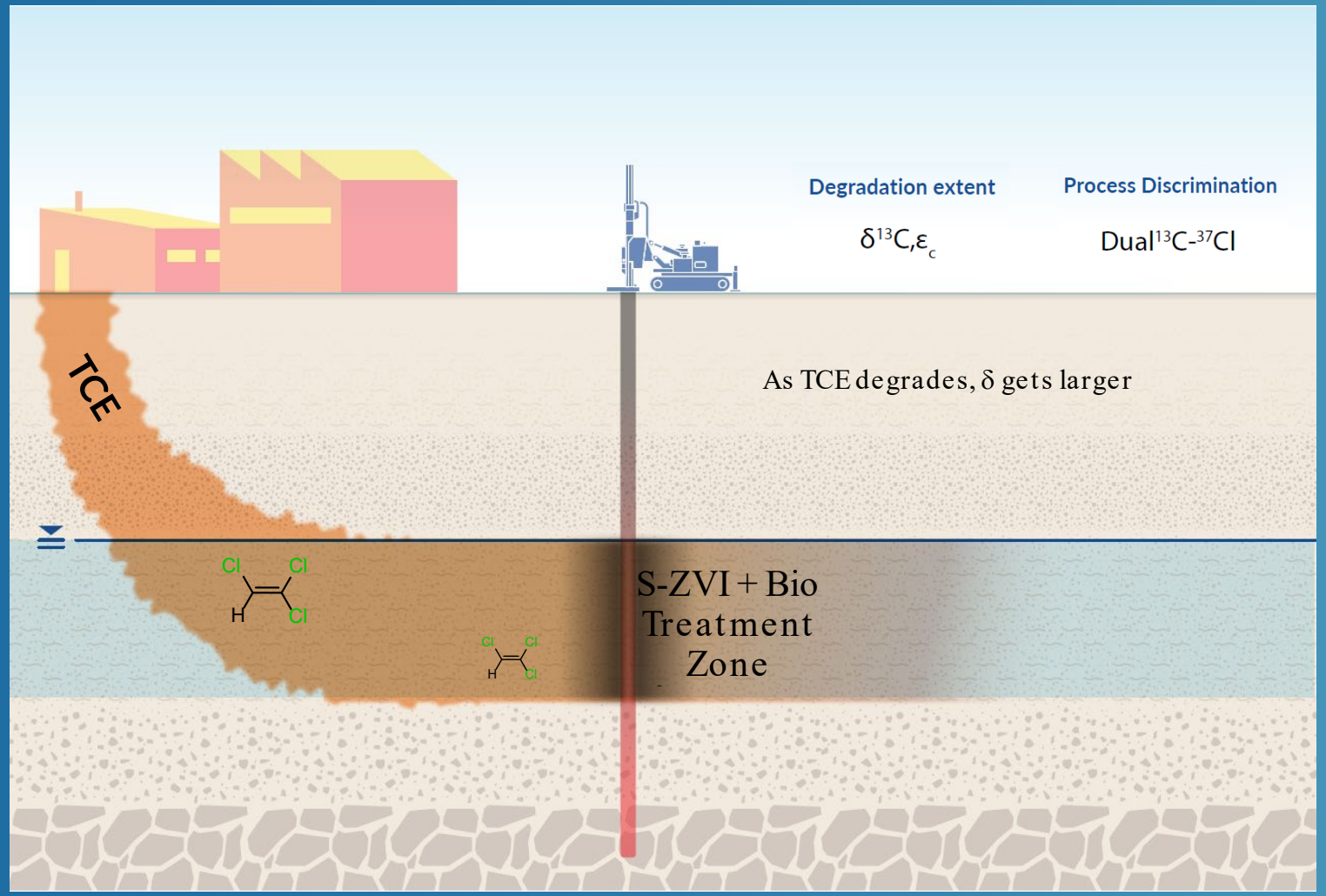
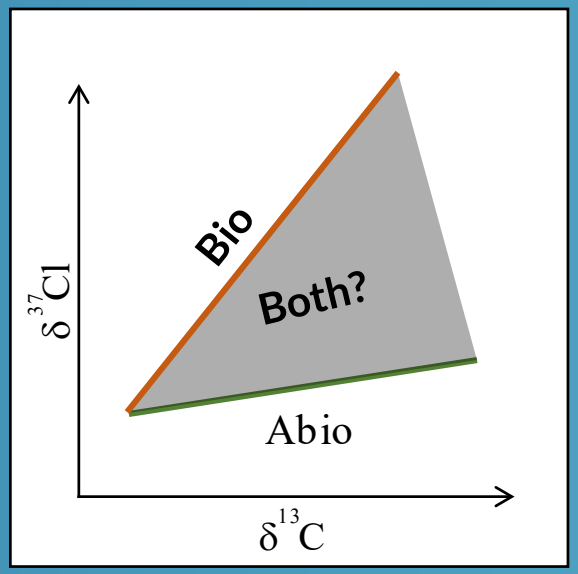


Dual $\delta^{13}C$ - ^{37}Cl plots can reveal pathway independent of % removed

Process A and Bmust have different slopes

Contribution from each process may be distinguished



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Study Objectives

- Determine enrichment factor ε_c for S-ZVI
  - ε_c to compare with bare ZVI
  - Previously unreported value
- Determine ability to resolve degradation pathways
  - Biotic or abiotic removal dominating?
  - Can dual $\delta^{13}C$-^{37}Cl plots provide the answer?

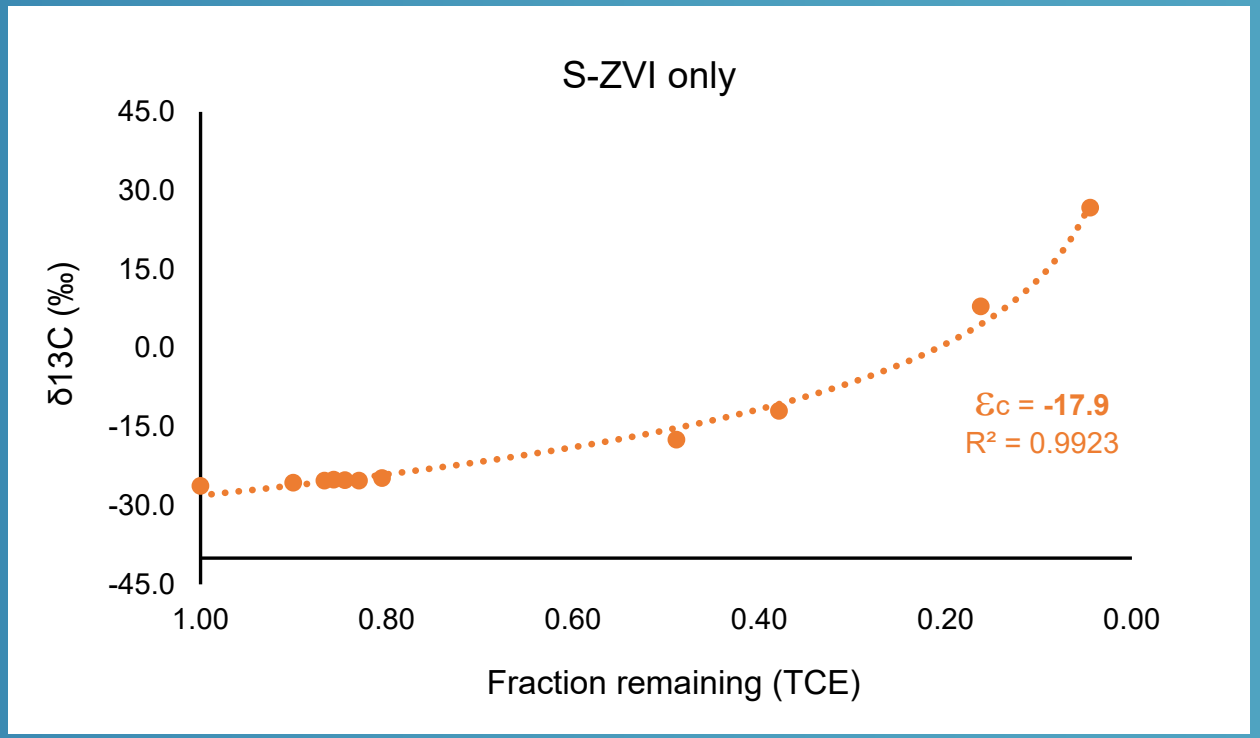
Study Experimental Design

- TCE degradation batch study conditions
  - S-ZVI alone
  - DHC (BDI) bioaugmented
  - ZVI + Bio combined treatment

- Replicate bottles prepared with amendments for sacrificing
- Bottles sampled by headspace to follow f(TCE) remaining with time
- Sent to Microbial Insights for C, Cl CSIA analysis at appropriate timepoints, 0-41 days

Study Results

- Strong ^{13}C fractionation seen with S-ZVI
  - TCE becomes ^{13}C enriched when reacting directly with S-ZVI
- ε_c comparable to reported bare ZVI values
  - Reported ZVI ε_c range is -9 to -27‰ *
  - Suggests shared reaction pathway



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*Audi-Miro et al. Applied Geochemistry, 2013 (32) 175-183

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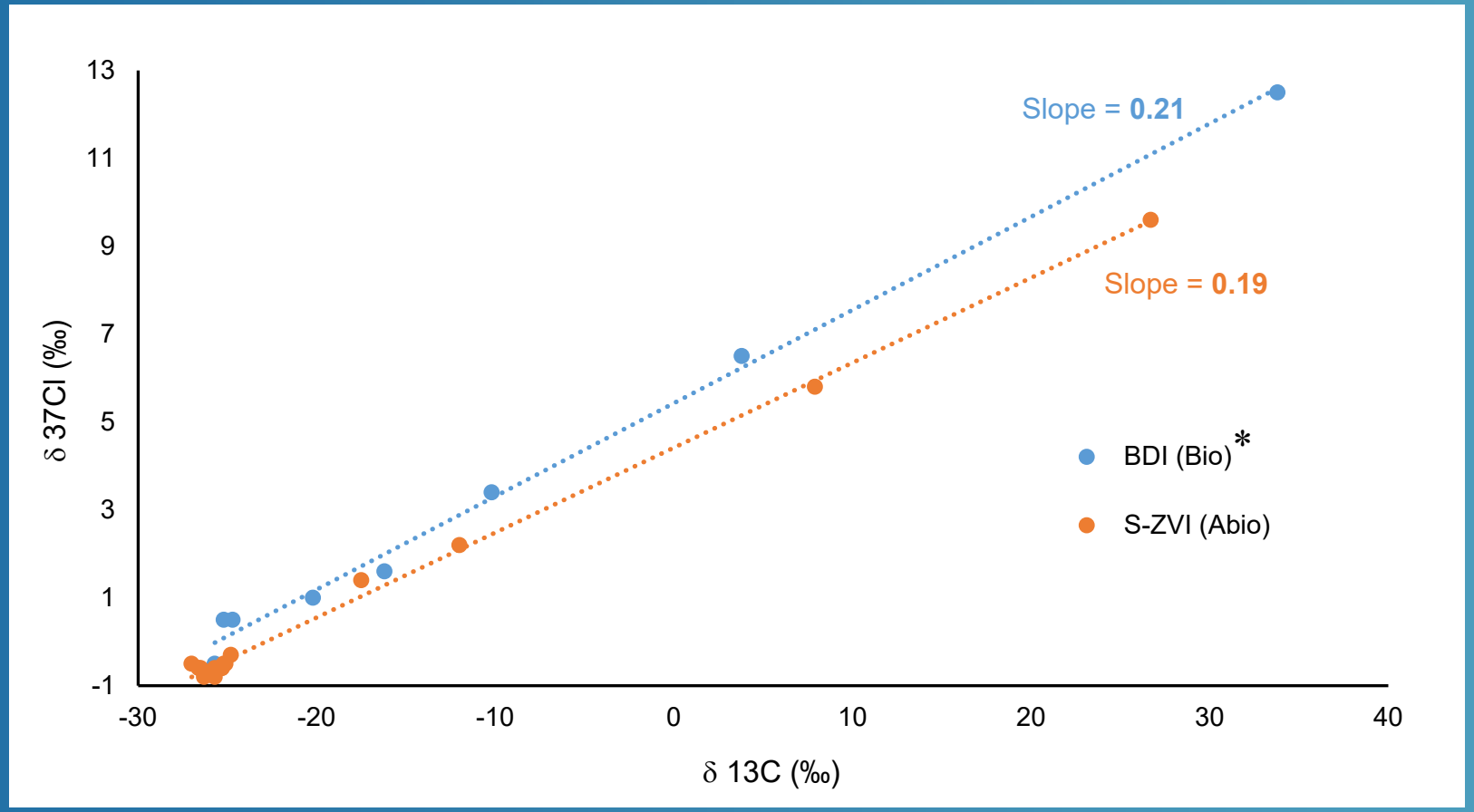
Study Results

- Dual isotope plot less revealing
  - $\delta^{13}C$ - ^{37}Cl slopes for both pathways are very similar
  - Bio/ S-ZVI differentiation would be difficult for this system



- *BDI data adapted from:

Kuder, et al. ES&T **2013**, (47), 9668-9677

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Conclusions

- CSIA revealed S-ZVI and bare ZVI share reaction pathway
  - Predictable behavior with enhanced reactivity and longevity
- Dual C-Cl plots may not differentiate ZVI/Bio pathway
  - Result will be site specific
  - Possibly better with native microbial consortium

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Thank you

Questions?