Quantification of Abiotic Transformation Rates for cDCE Using a ^{14}C Assay

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Abiotic Processes and Chlorinated Ethenes

- The potential for abiotic processes to contribute to attenuation of large, dilute plumes is significant
- Before we can begin to fully realize the potential of abiotic processes, we need to better understand factors that impact the rates
- Keys to successful application include:
  - What are the best ways to document the occurrence of abiotic processes, considering that the products are difficult to discern from background?
  - How can we relate the mineralogy of the subsurface to the occurrence and rate of abiotic degradation?

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Objectives

- **Overall: Develop a deeper understanding for the role of magnetic materials in mediating abiotic degradation of chlorinated ethenes in aquifers**
- **Specific:**
  - Develop carbon isotope assay (^{14}C-assay) to measure abiotic degradation rates
  - Use ^{14}C-assay to measure abiotic degradation in water supply aquifers
  - Assess the proportion of abiotic degradation attributable to magnetic materials
  - Determine the proportion of magnetite in the aquifer sediments
  - Identity the mechanism(s) for abiotic degradation in aerobic and anaerobic aquifer material

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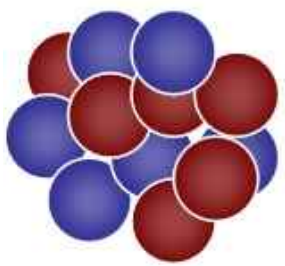
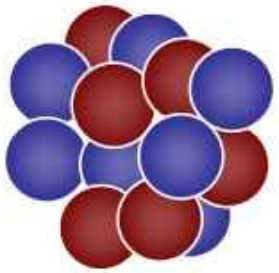
^{14}C Assay Background

- Isotopes of carbon: 12, 13, 14
- Focus today is on the radioactive isotope, carbon-14
- Half life is 5730 years
- Emits β energy during decay
- Use of ^{14}C-labeled compounds allows for
  - ❖ detection of ^{14}C-labeled products that are difficult to discern from background, including CO_2 and soluble, polar compounds
  - ❖ Measurement of degradation rates as low as ~0.007 yr^{-1} ($t_{½}$ ~ 100 yr)

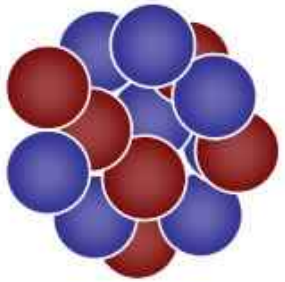


carbon-12
98.9%
6 protons
6 neutrons



carbon-13
1.1%
6 protons
7 neutrons

Measured by compound specific isotope analysis (CSIA)



carbon-14
<0.1%
6 protons
8 neutrons

Measured by photons emitted from scintillators excited by β energy from ^{14}C decay

^{14}C Assay Background

- Work must be done in a lab licensed to handle radioactive materials
- Only a few vendors provide ^{14}C-labeled material; custom synthesis $$$
- ^{14}C compounds usually delivered in a solvent (e.g., acetonitrile, butanol) making purification essential
- To quantify products, need to separate from the unreacted parent compound; with ^{14}C-cDCE, that is done by sparging to strip away cDCE
- Follow ^{14}C distribution by counting samples in liquid scintillation cocktail using a liquid scintillation counter
- Use of controls to account for background activity is essential

Site Selection

- Authentic aquifer sediment collected from
  - Former manufacturing site in Arizona
  - Site 102 at the former Twin Cities Army Ammunition Plant (TCAAP) near Arden Hills, MN
  - Site A at TCAAP, where degradation of cDCE was detected but not PCE and TCE
  - Vandenberg Air Force Base (California)
  - Plattsburgh Air Force Base (New York)

TCAAP plumes

Sediment Processing

Collect ~70 kg sediment

Deliver to Clemson

Dry at 103 °C

Sieve

- >850 µm not used
- <850 µm selected
  - Bar magnet
    - Magnetically enriched → Microcosm ^{14}C assay (enriched)
    - Magnetically depleted → Microcosm ^{14}C assay (depleted)
  - As-is → Microcosm ^{14}C assay (unaltered)

Magnetically enriched

Magnetically depleted

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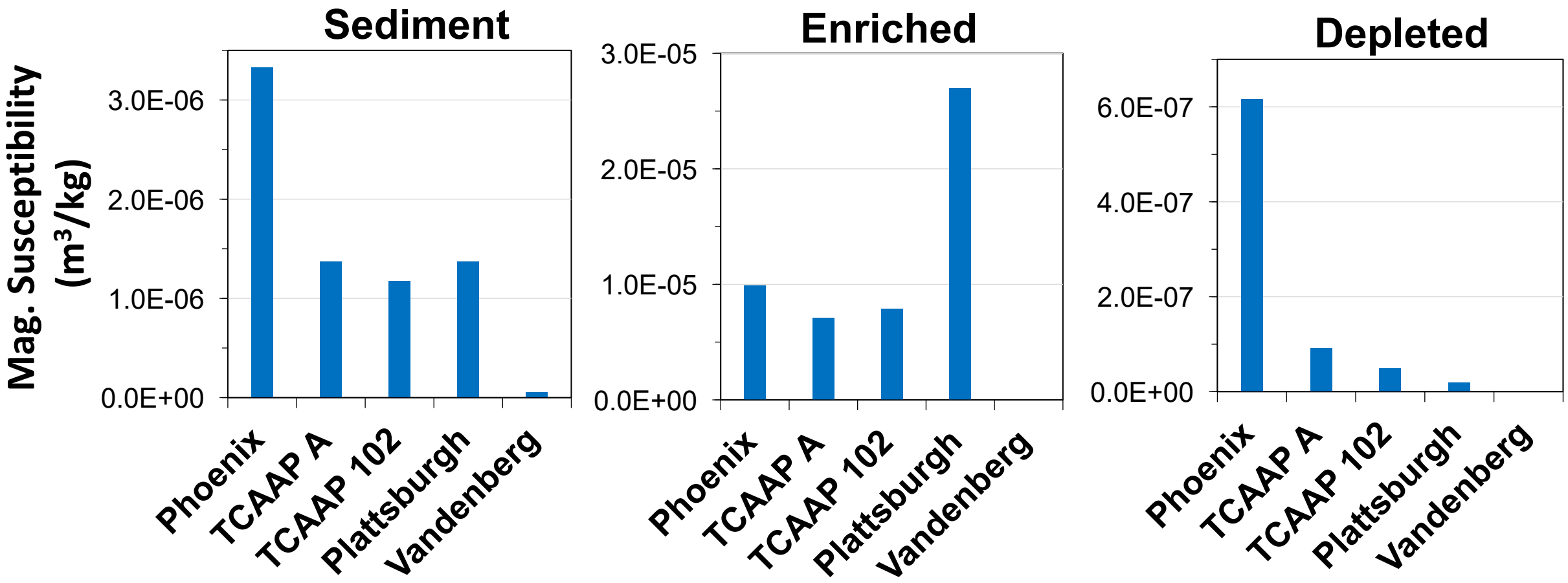
Magnetic Susceptibility

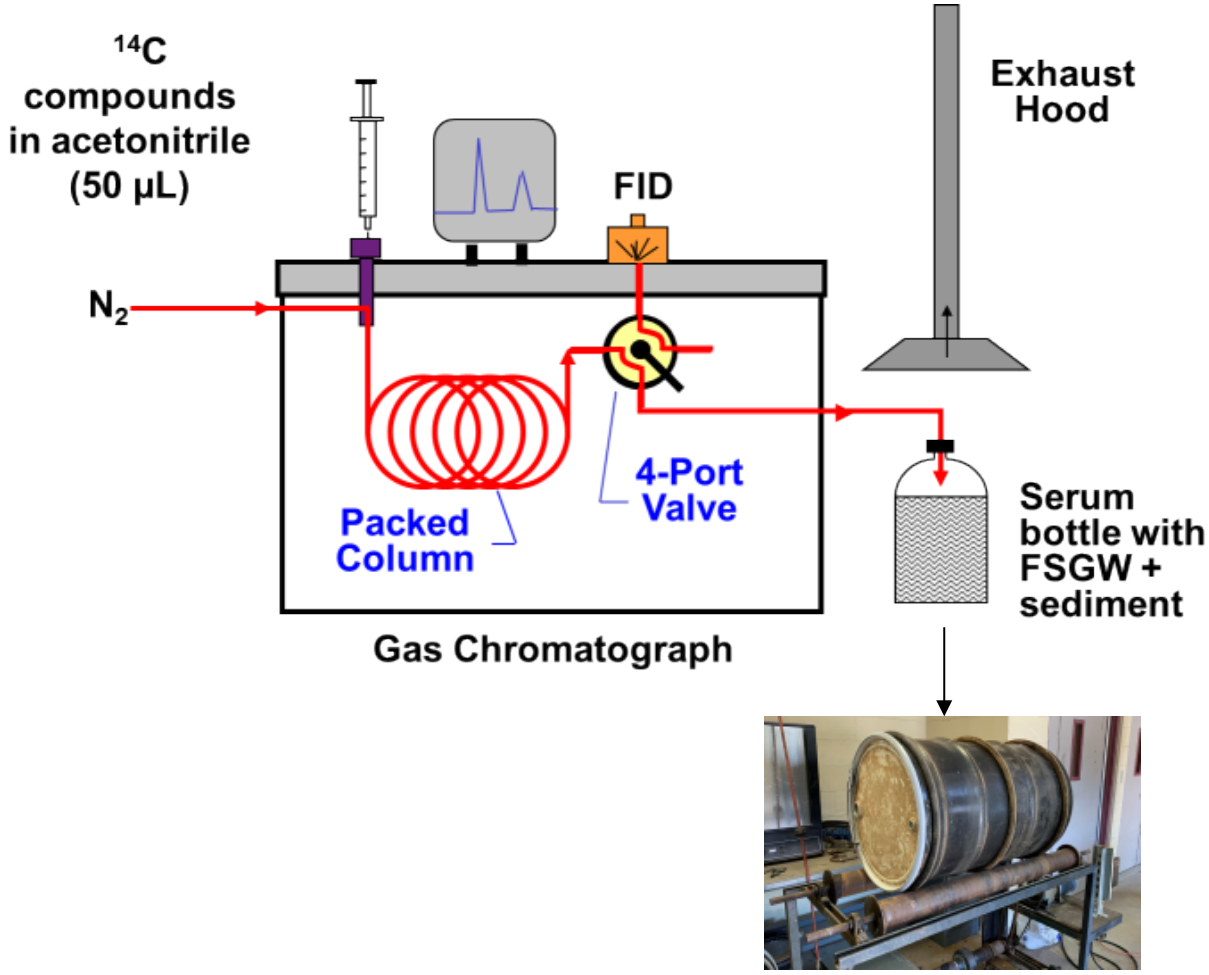


Magnetically Enriched Sediment > Unprocessed Sediment > Depleted Sediment

Microcosms

Preparation and Operation

- 160 mL serum bottles
- Teflon-faced butyl rubber septa
- ~100 g wet solids or 70 g dry solids + ~70 mL filter sterilized groundwater (FSGW)
- Add purified ^{14}C compound
- Add TCE or PCE saturated water to bring initial concentrations to ~700-1,000 µg/L
- Incubate on a tumbler
- Weekly measurements of polar products in 5 mL filtered samples
- Analyze ^{14}C product formation to determine rate constant



Experimental Design

Sites
- Phoenix
- TCAAP A
- TCAAP 102
- Plattsburgh
- Vandenburg

X

Treatments
- Enriched + FSGW*
- Unprocessed + FSGW
- Depleted + FSGW
- Wet sediment + FSGW
- FSGW alone

X

Incubation Conditions
- Aerobic (AER)
- Anaerobic (ANA)
- ANA + 2-propanol (scavenger)

X

^{14}C Compounds
- PCE
- TCE
- cDCE
- VC

X triplicates ≈ 900 microcosms total

*FSGW = filter sterilized groundwater

Text in blue: results summarized today

Hypotheses

- Rate constants for magnetically enriched > unprocessed > depleted > Filter Sterilized Groundwater (FSGW)
- Rate constants for aerobic (AER) > anaerobic (ANA) > anaerobic + scavenger
- Based on magnetic susceptibility, rate constants for
  - Enriched: Plattsburgh > TCAAP A ≈ TCAAP 102 ≈ Phoenix
  - Unprocessed: Phoenix > TCAAP A ≈ TCAAP 102 ≈ Plattsburgh
  - Depleted: Phoenix > TCAAP A ≈ TCAAP 102 ≈ Plattsburgh

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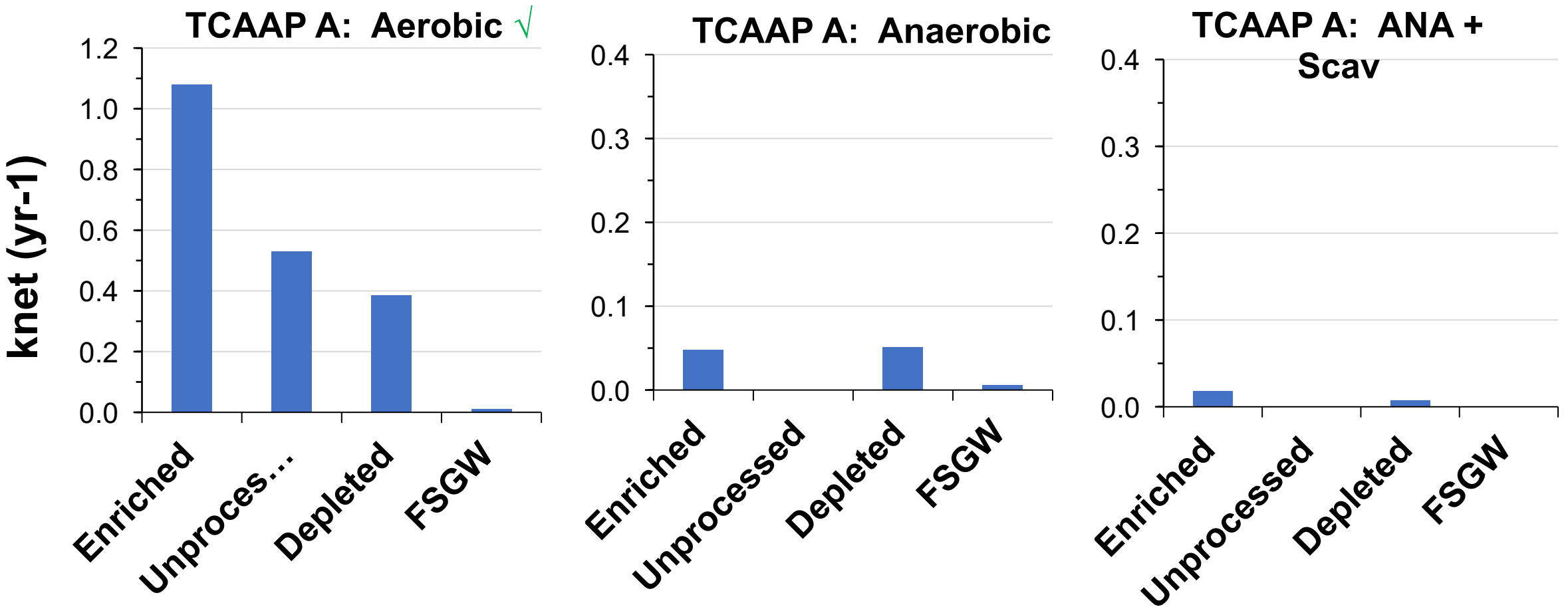
enriched > unprocessed > depleted > FSGW?



k = 0.1 yr^{-1} → $t_{½}$ = 6.9 yr; aquifer rate constant will be higher

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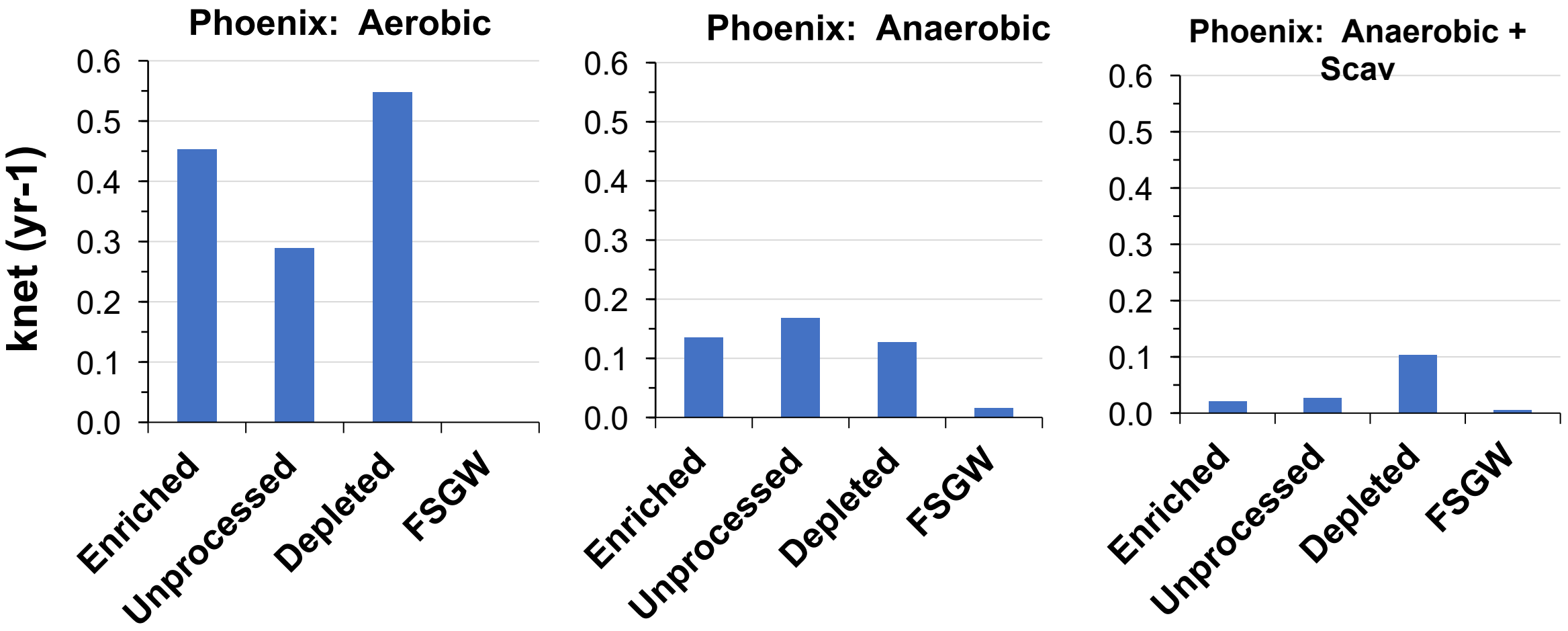
enriched > unprocessed > depleted > FSGW?



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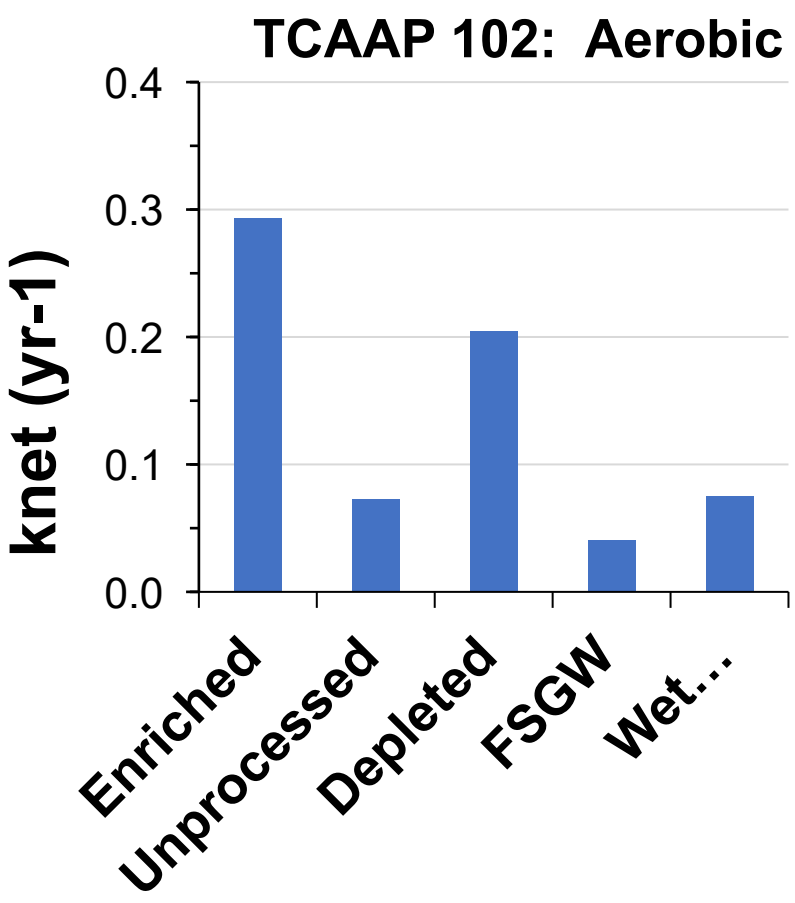

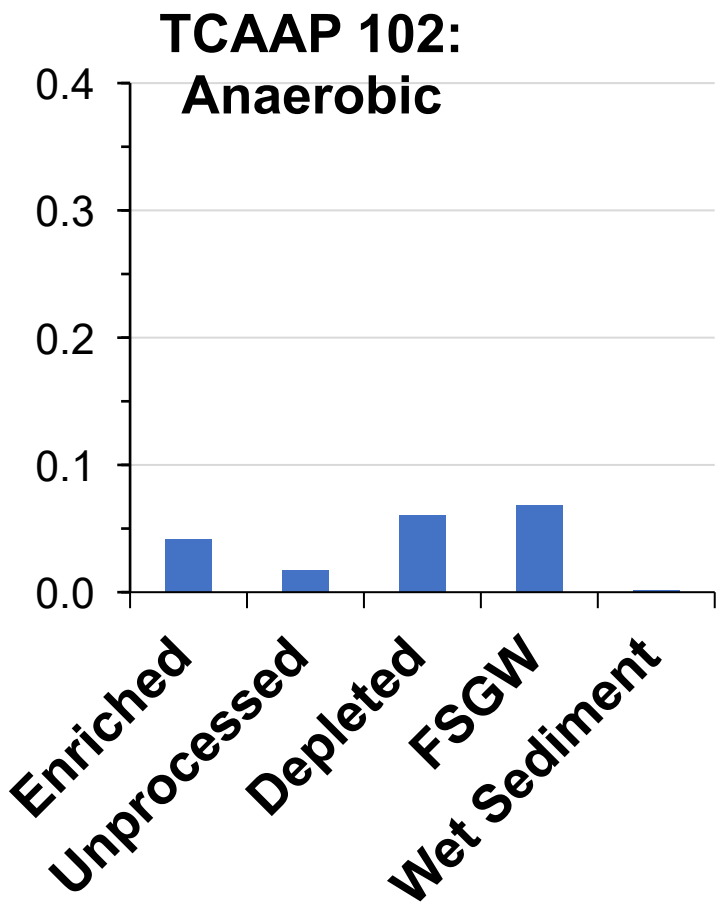

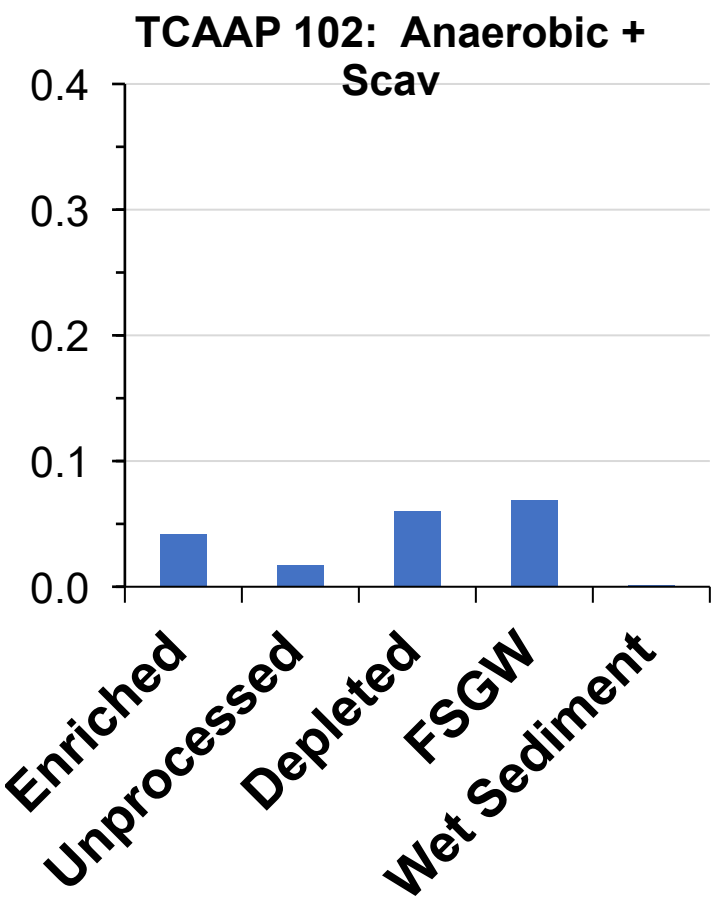

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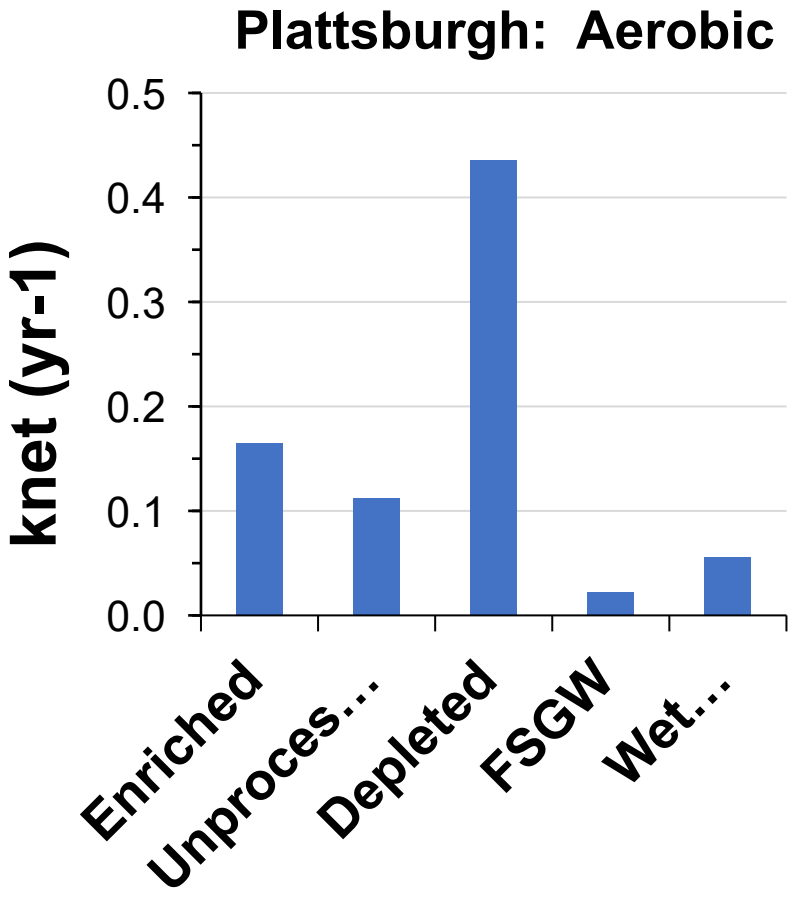

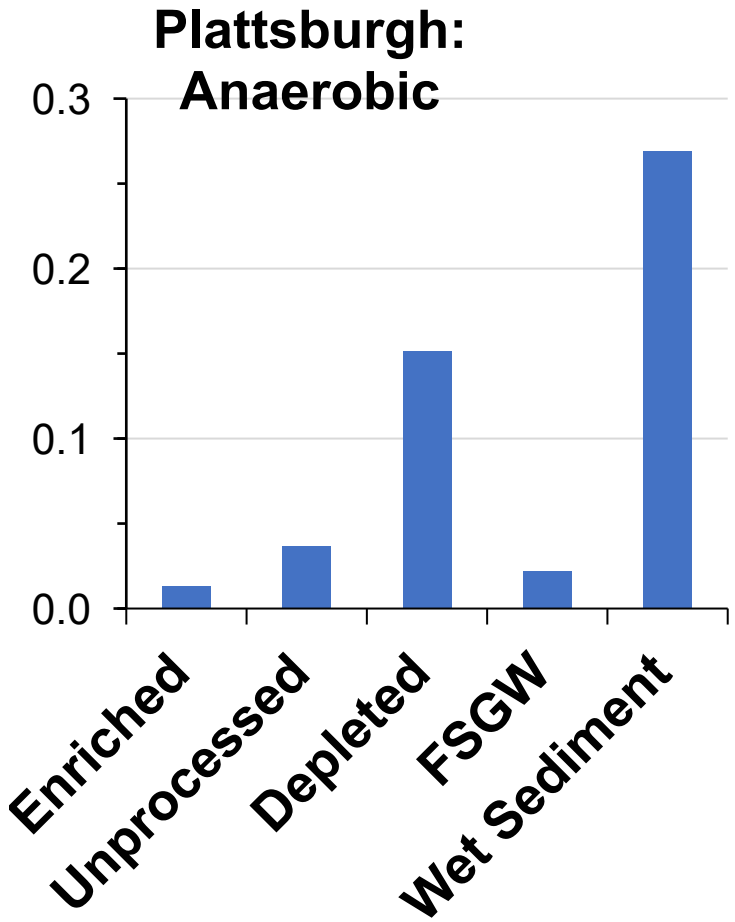

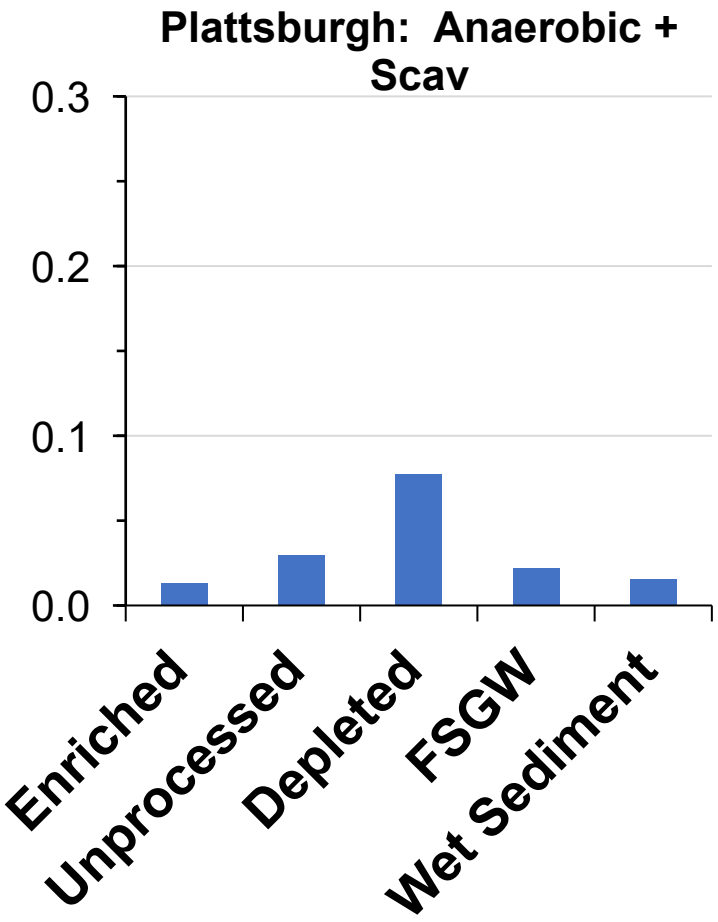

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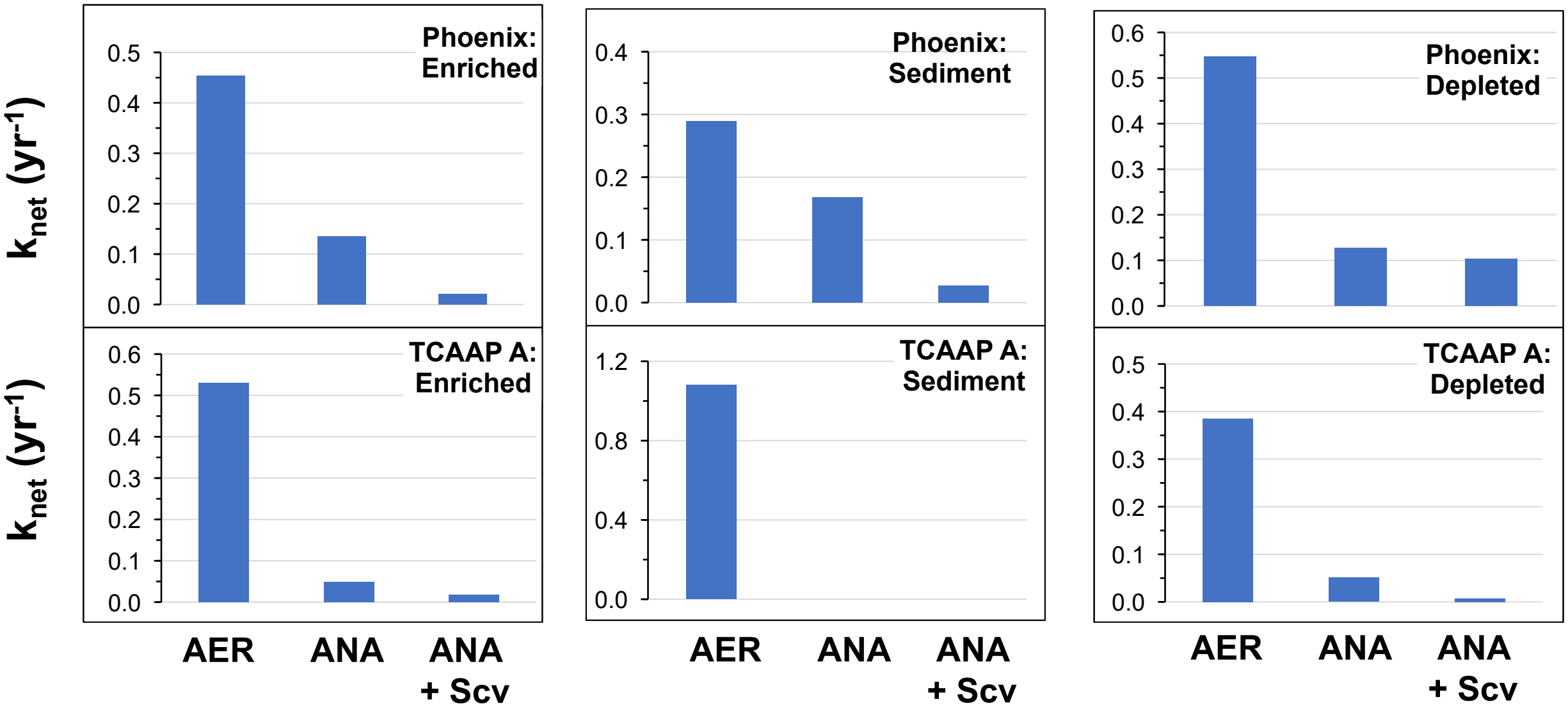
Aerobic > Anaerobic > Anaerobic + Scavenger?



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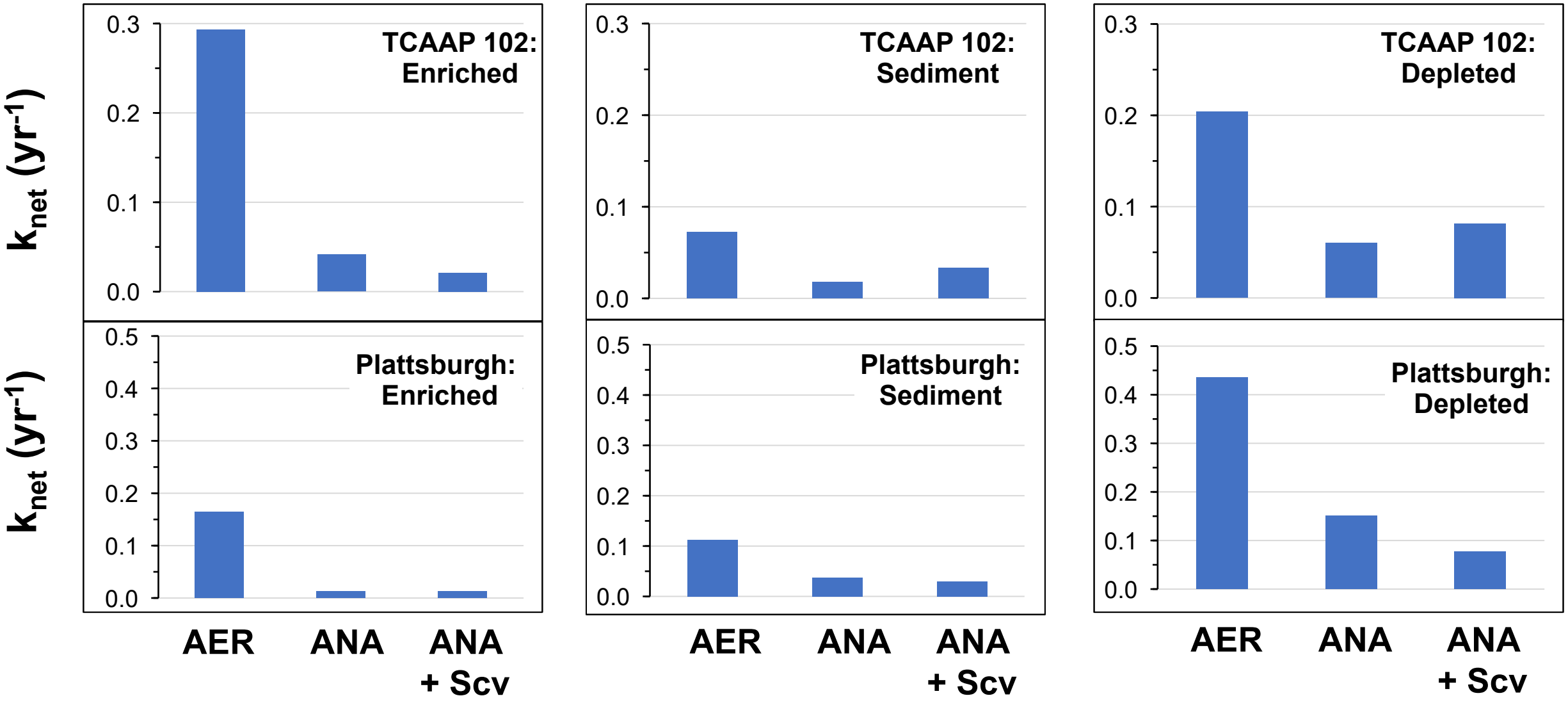
Aerobic > Anaerobic > Anaerobic + Scavenger?



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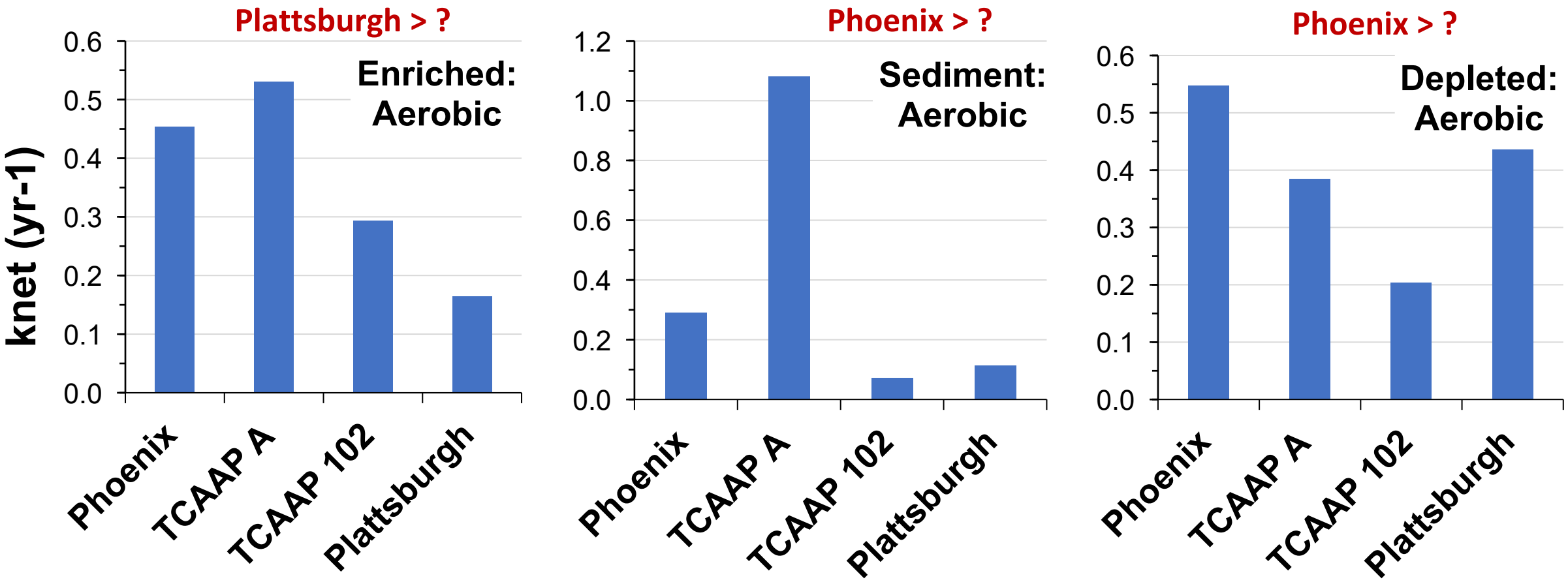
Variations by Site, Aerobic Treatment



k = 0.1 yr^{-1} → $t_{½}$ = 6.9 yr; aquifer rate constant will be higher

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Summary

- With cDCE, the rate constants for magnetically enriched sediment were not consistently higher than for unprocessed and depleted sediment
- However, there is overall correspondence between rate constants and magnetic susceptibility; see talk later this morning by John Wilson
- Rate constants for aerobic incubation were generally higher than anaerobic
- Rate constants for anaerobic with a 2-propanol added were generally lower than anaerobic alone; suggests a role for a free radical in anaerobic degradation
- Rate constants for FSGW alone were generally lower than with sediment present
- For all of the sites, rate constants are high enough to suggest that abiotic degradation can have a meaningful impact on natural attenuation; measurement of rates based on accumulation of ^{14}C products provides compelling line of evidence for degradation

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Acknowledgement:

Funding from SERDP, project #ER20-1368

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Extra Slides

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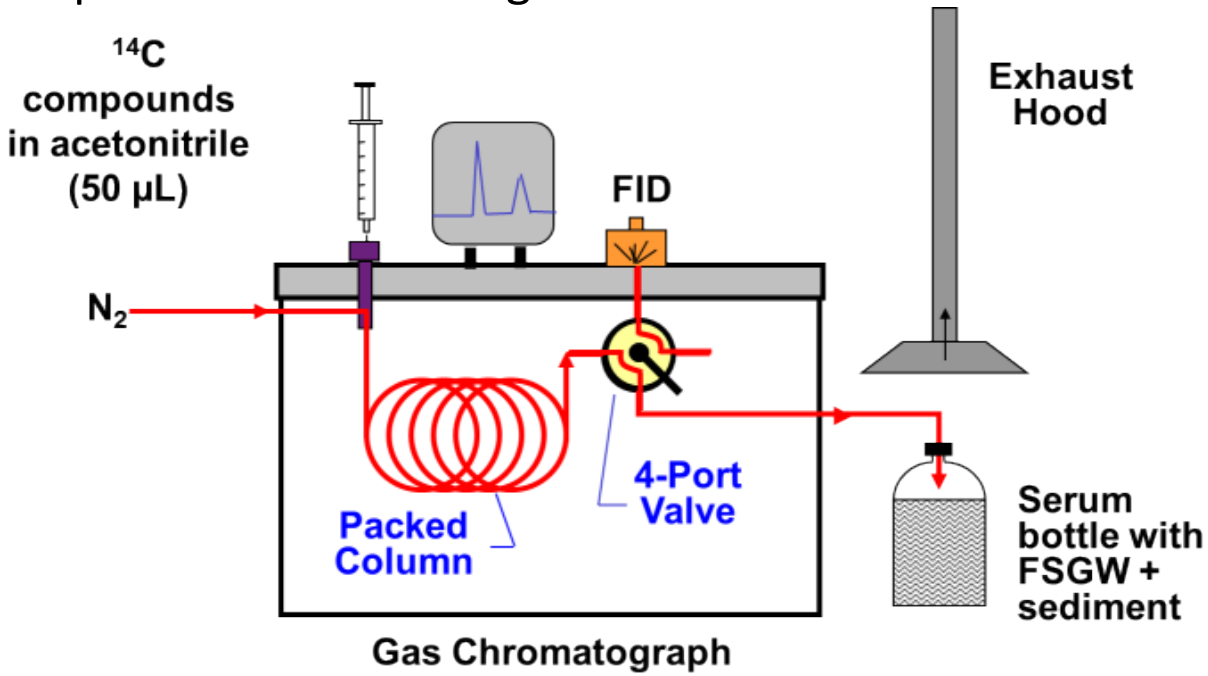
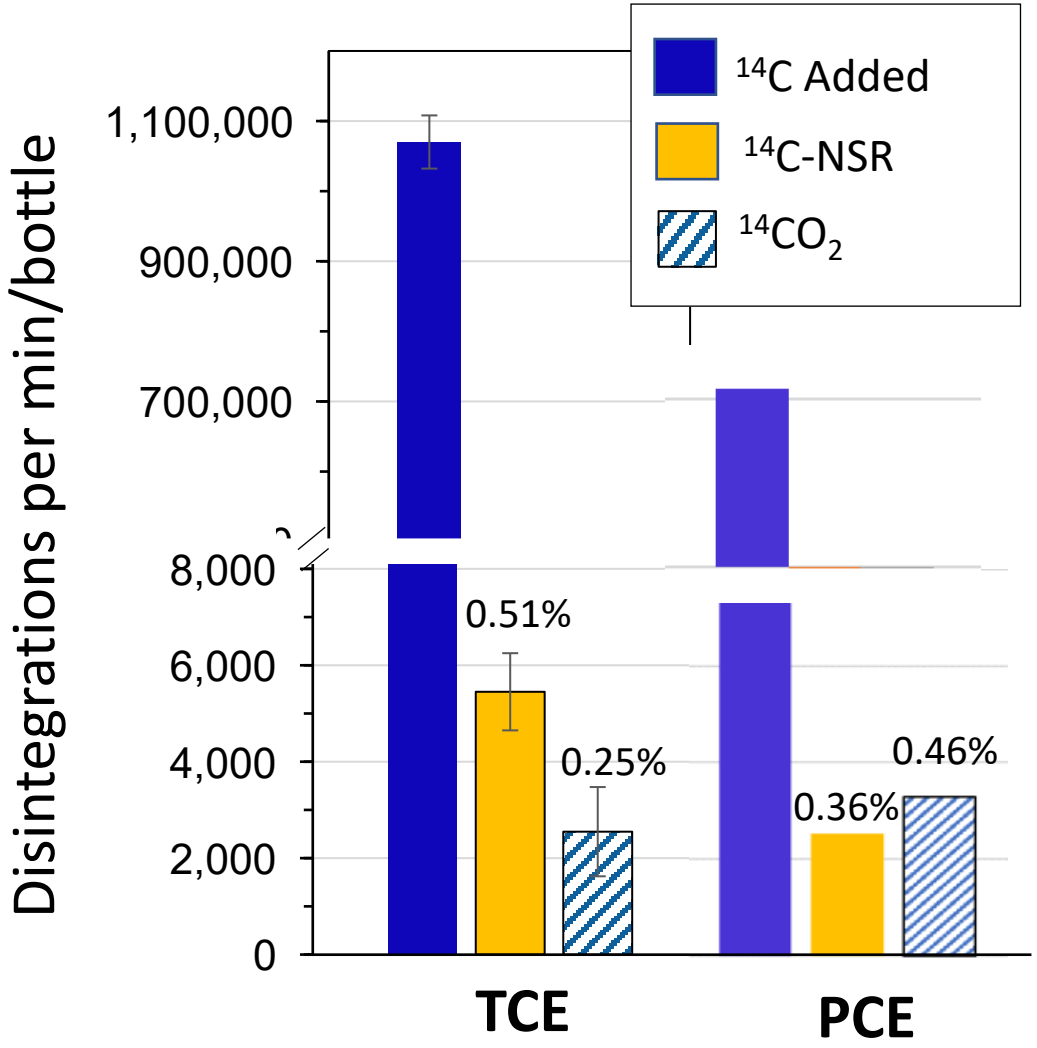
Experimental Design

Solids Present	Water Present	Oxygen Present	Scavenger Present	Compounds Tested	Analysis Performed
Sediment (Unaltered)	FSGW	No	No	PCE, TCE, cDCE, VC	^{14}C
		No	Yes	PCE, TCE, cDCE, VC	^{14}C
		Yes	No	PCE, TCE, cDCE, VC	^{14}C
Sediment Enriched in MM	FSGW	No	No	PCE, TCE, cDCE, VC	^{14}C
		No	Yes	PCE, TCE, cDCE, VC	^{14}C
		Yes	No	PCE, TCE, cDCE, VC	^{14}C
Sediment Depleted in MM	FSGW	No	No	PCE, TCE, cDCE, VC	^{14}C
		No	Yes	PCE, TCE, cDCE, VC	^{14}C
		Yes	No	PCE, TCE, cDCE, VC	^{14}C
Synthetic Magnetite	FSGW	No	No	PCE, TCE, cDCE, VC	^{14}C
		No	Yes	PCE, TCE, cDCE, VC	^{14}C
		Yes	No	PCE, TCE, cDCE, VC	^{14}C
Synthetic Magnetite + Sorbed Fe^{2+}	FSSGW	No	No	PCE, TCE, cDCE, VC	^{14}C
		No	Yes	PCE, TCE, cDCE, VC	^{14}C
		Yes	No	PCE, TCE, cDCE, VC	^{14}C
Sediment	FSGW	Ambient	No	PCE, TCE, cDCE, VC, tDCE, 1,1-DCE	CSIA
Sediment Enriched in MM	FSGW	Ambient	No	PCE, TCE, cDCE, VC, tDCE, 1,1-DCE	CSIA
Sediment Depleted in MM	FSGW	Ambient	No	PCE, TCE, cDCE, VC, tDCE, 1,1-DCE	CSIA

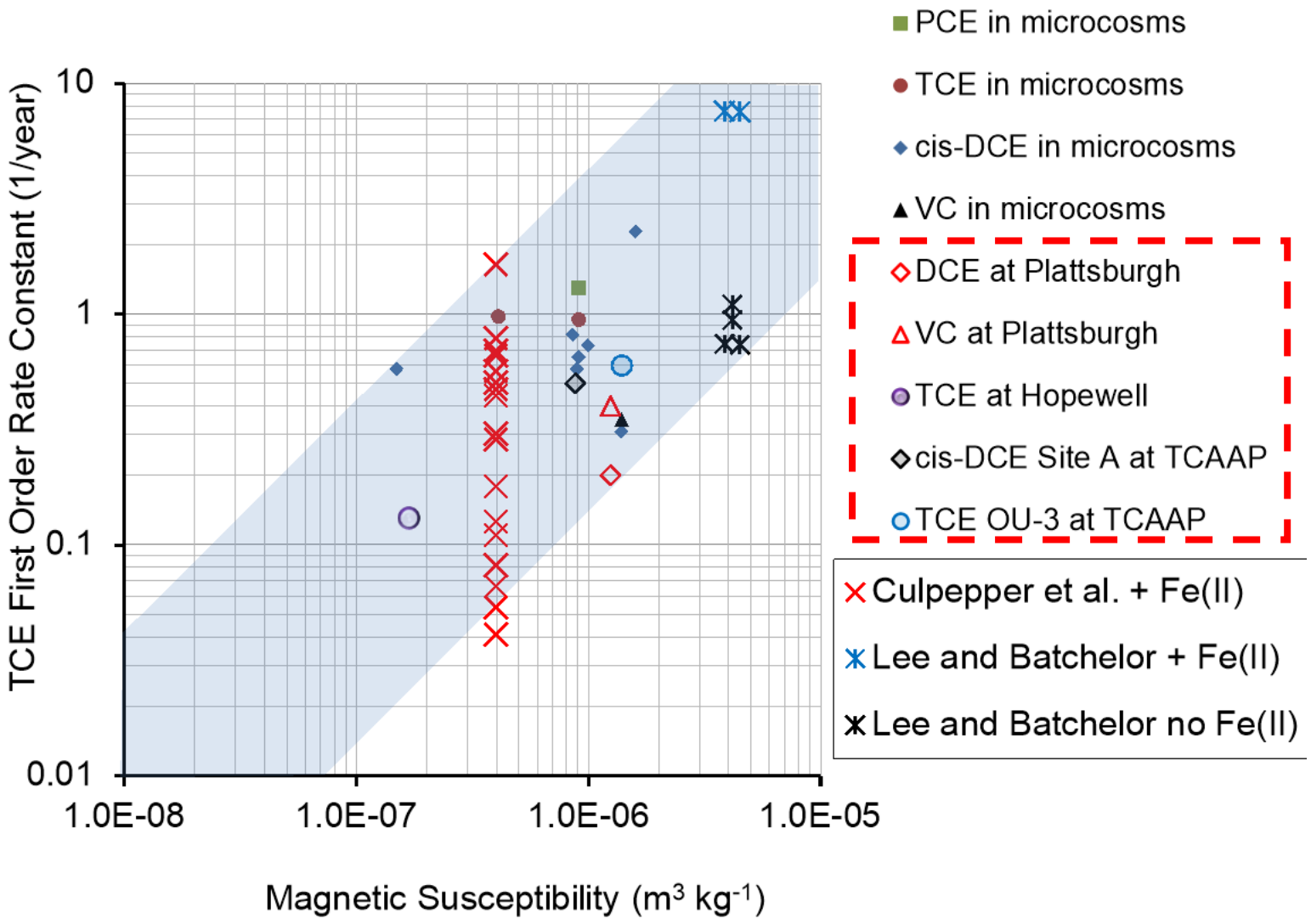
^{14}C-TCE, ^{14}C-PCE Purity

- 1 mCi each of ^{14}C-PCE, TCE, and cDCE received from Moravek Biochemicals, dissolved in acetonitrile
- Stock solutions of ^{14}C-TCE and ^{14}C-PCE prepared so far
- Purity checked: >99%
- ^{14}C-VC will be produced from ^{14}C-cDCE with a low pH reductive dechlorinating culture
- ^{14}C purified while adding to microcosms





Site Selection: Potential Activity Related to Magnetic Materials



- Output from BioPIC worksheet: *MagneticSusceptibility.xlsx*

Lee and Batchelor. 2002. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. Pyrite and Magnetite. *Environ. Sci. Technol.* 36(23): 5147–5154.

Culpepper et al. 2018. Reduction of PCE and TCE by magnetite revisited. *Environ. Sci. Processes & Impacts.*

Soil Preparation

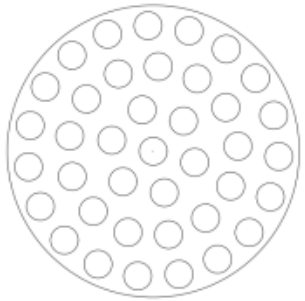
Factors considered

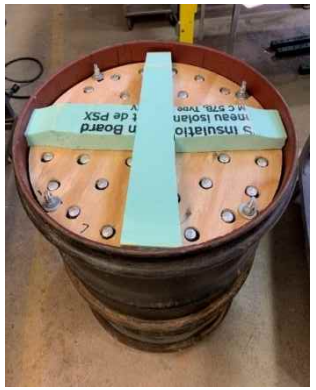
- Homogenizing, drying, homogenizing of the sediment
- Grinding: Decided against this based on alteration of naturally occurring surfaces
- Sieving: Evaluated 3 sizes: 850, 594, and 150 µm
- Optimization of the Frantz magnetic barrier laboratory separator
- Calculation of the degree of enrichment based on the ratio of magnetic materials in enriched versus depleted sediment

Incubation of Microcosms

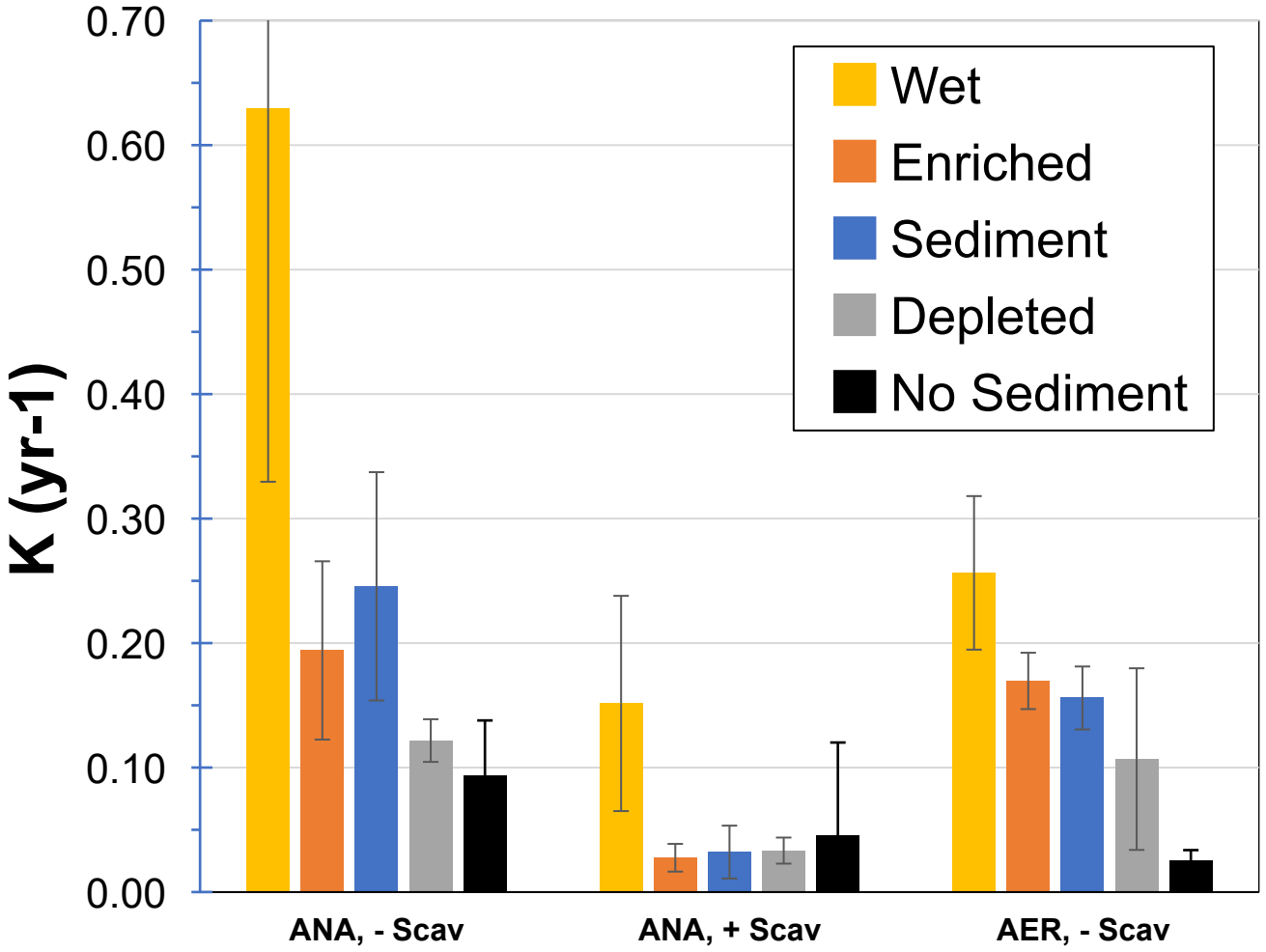
- Developed system to gently stir microcosms
- 55-gallon drum
  - Holds 39 serum bottles per layer
  - 7 layers = 273 serum bottles

Variable speed DC drive



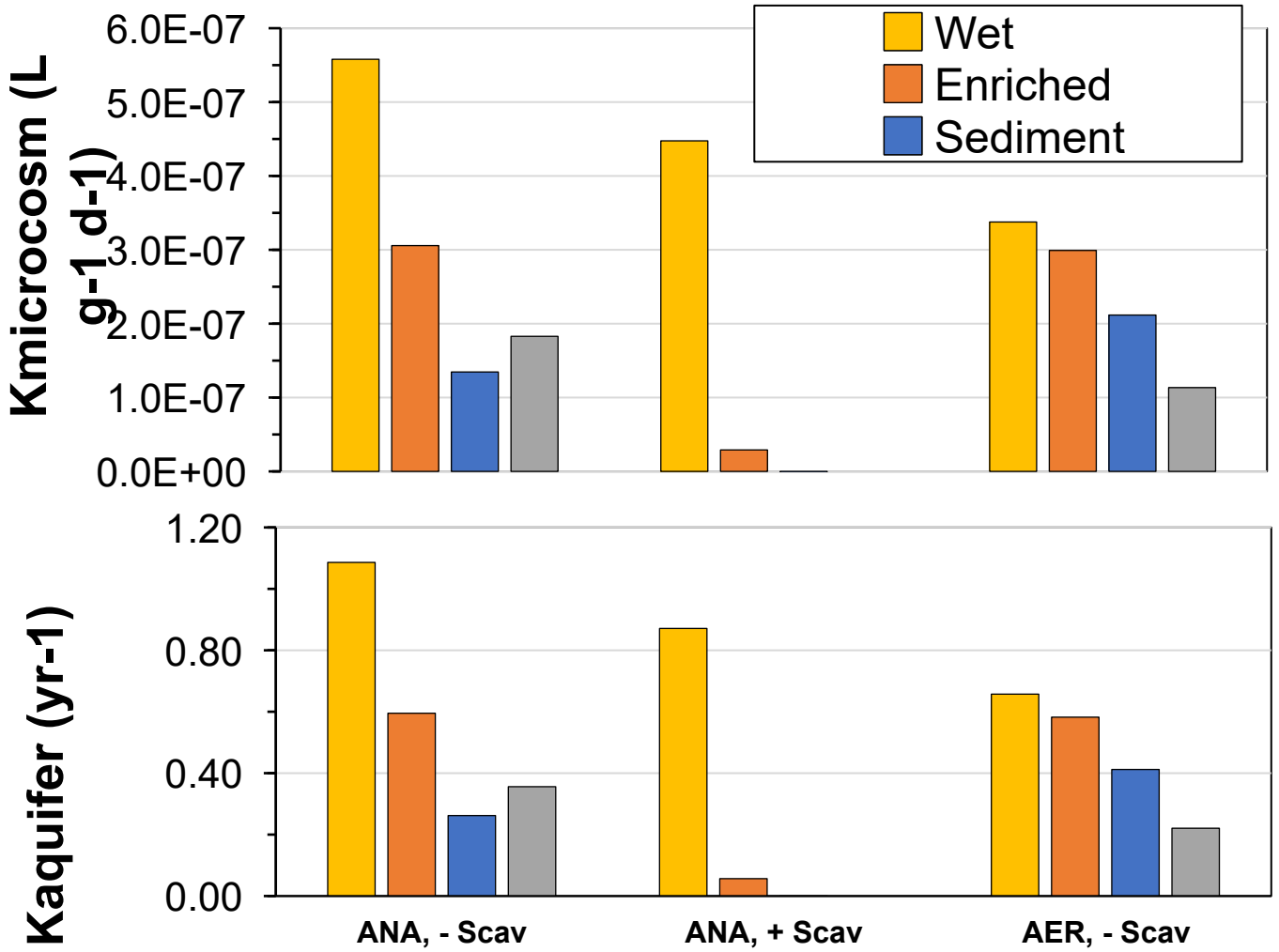


Summary of Results: ^{14}C-TCE for Arizona



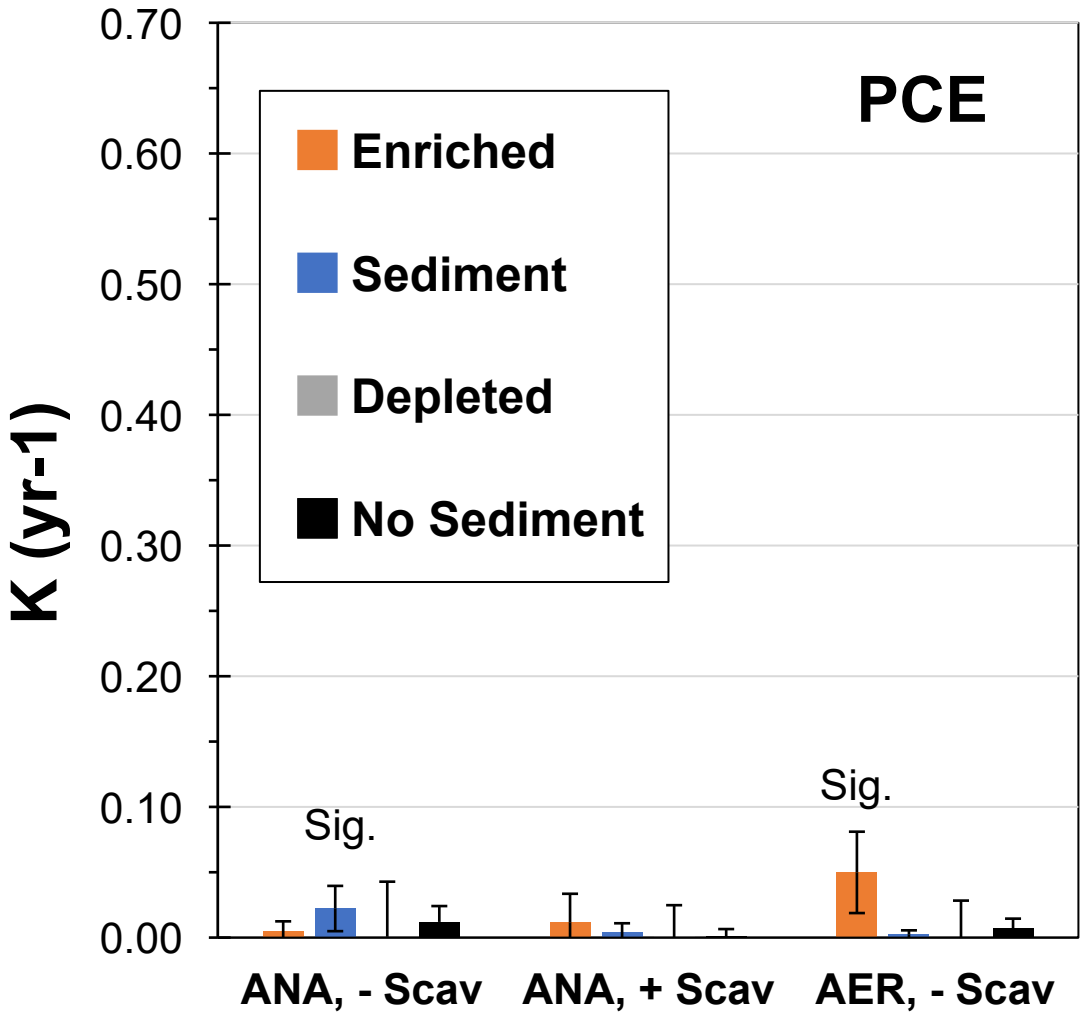
- Highest *K* with original wet sediment
- Minor differences between magnetically enriched and unaltered sediment
- Magnetically depleted sediment lower in anaerobic and aerobic treatments without scavenger
- Scavenger results suggest a possible role for a radical
- "Raw" *K* needs to be related to the ratio of soil to GW in the aquifer
- Modified method developed to calculate soil-normalized values for *K*

Summary of Results: ^{14}C-TCE for Arizona

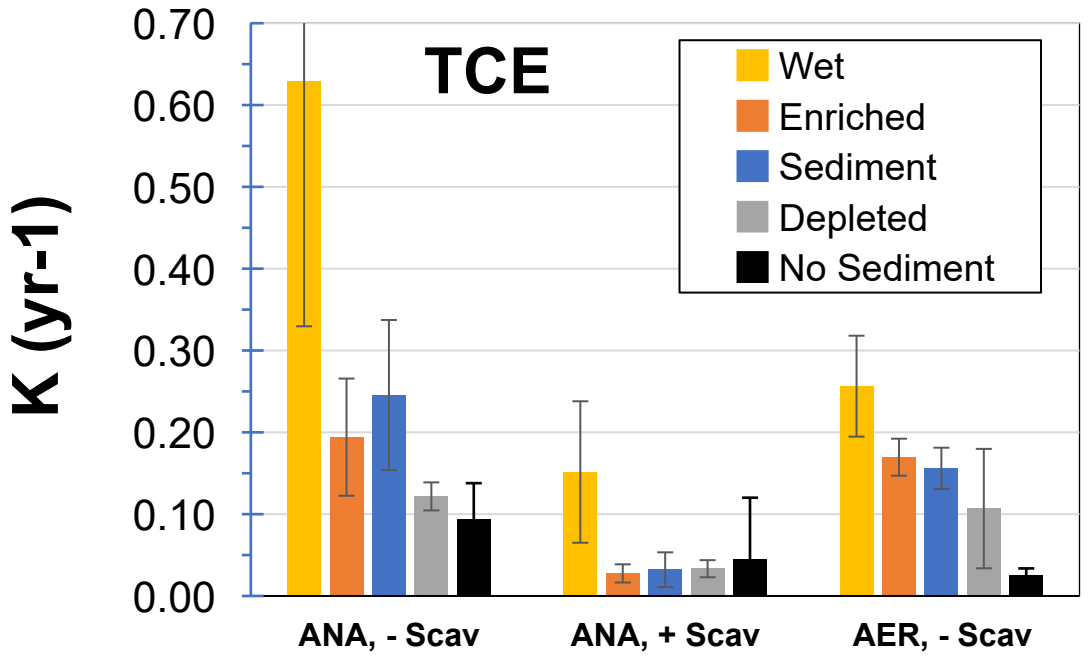


- Normalized *K* to the amount of soil and FSGW at each time step, corrected for activity in FSGW-only treatment
- Normalized *K* follows similar trends for "raw" *K*
- $K_{microcosm}$ converted to $K_{aquifer}$ using the ratio of soil mass to groundwater found in the aquifer
- Aquifer half-life for aerobic wet soil ~1 year

Summary of Results: ^{14}C-PCE for Arizona



- Much lower *K* compared to ^{14}C-TCE
- *K* is statistically significant for only two treatments
- Wet sediment not available for PCE



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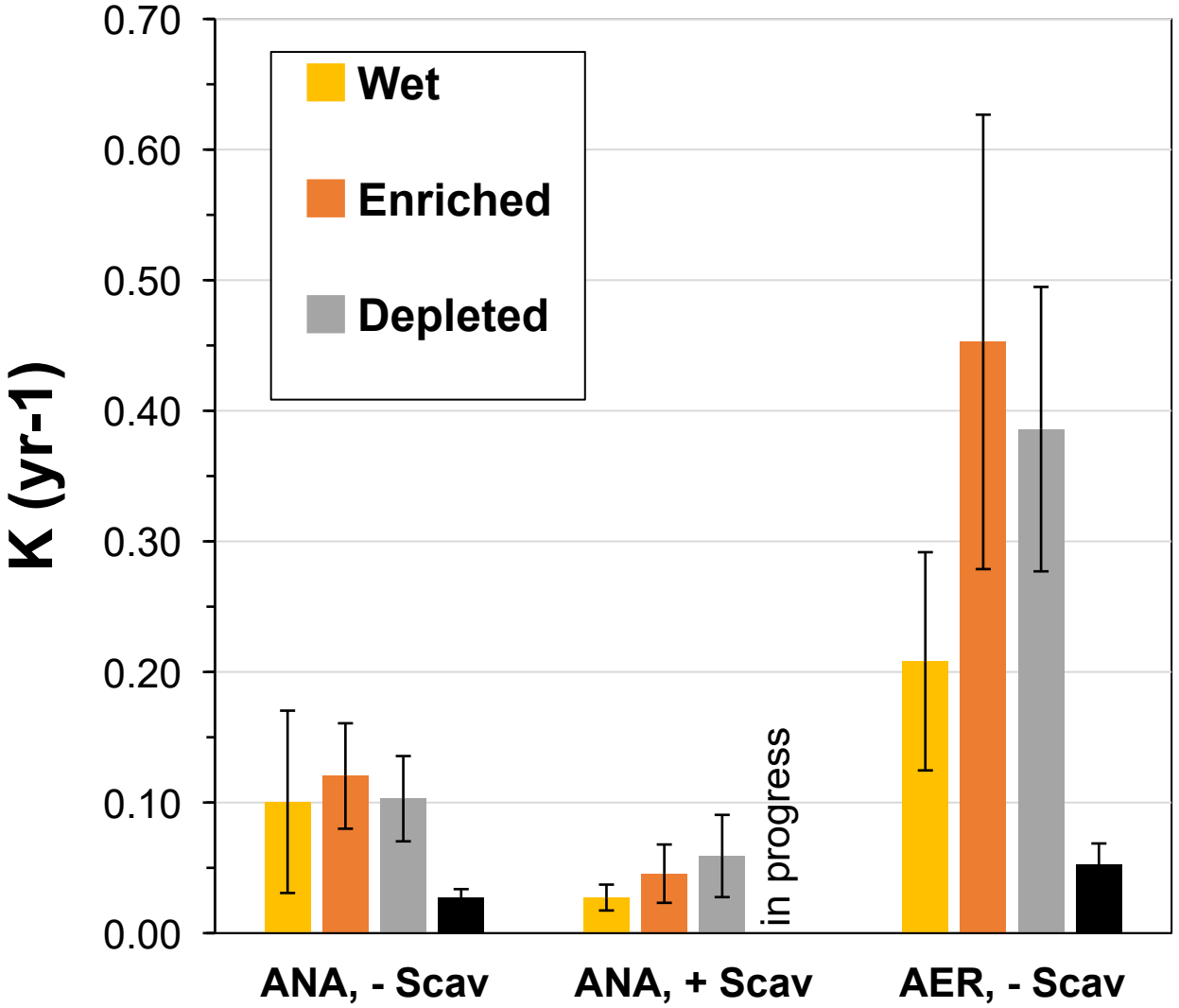
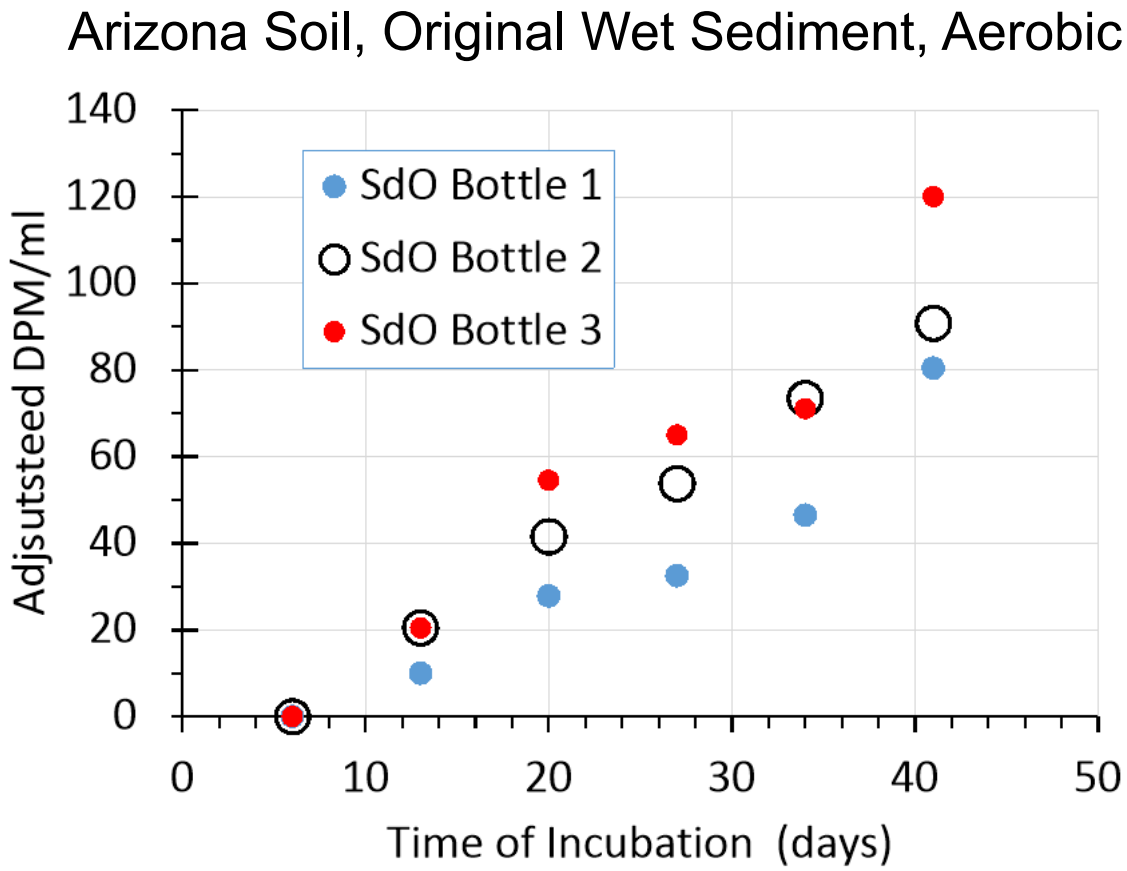
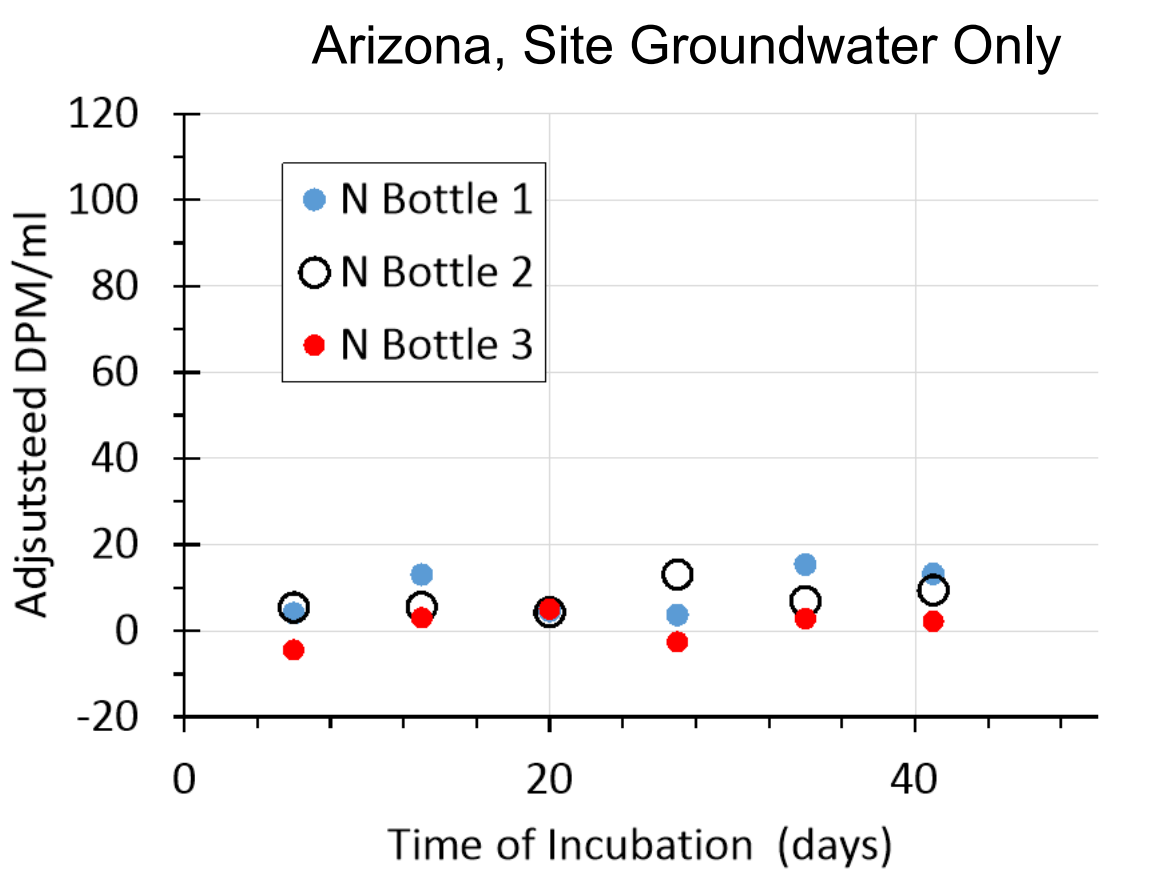
Summary of Initial Results: ^{14}C-TCE for TCAAP A



- Similar range of *k* values for enriched and depleted to Arizona site
- Acetylene inhibition test with aerobic wet sediment indicates some of the degradation activity is cometabolic
- Acetylene inhibition will also be tested with dry sediment
- Unaltered sediment is up next

Results: ^{14}C Product Accumulation

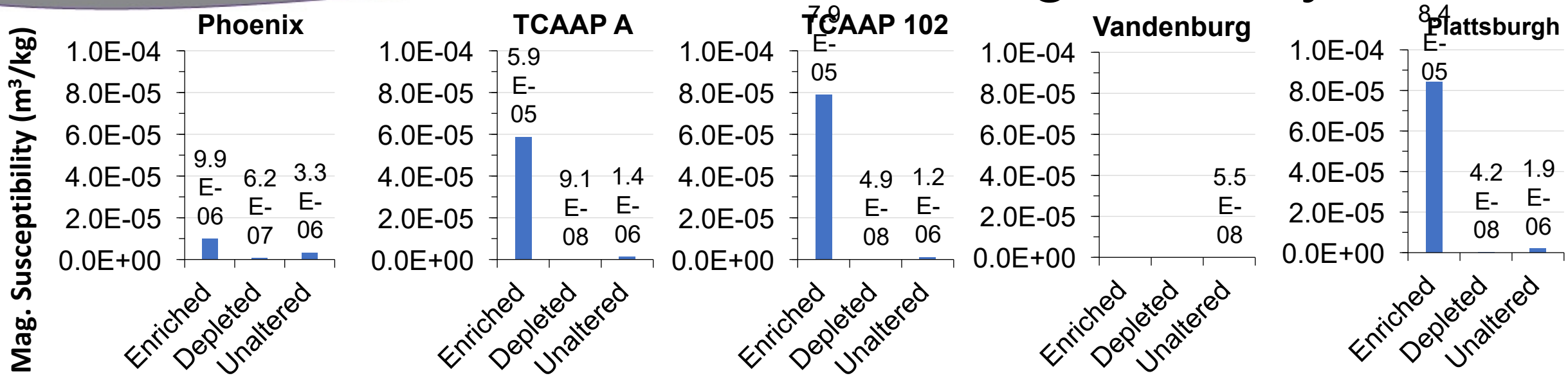


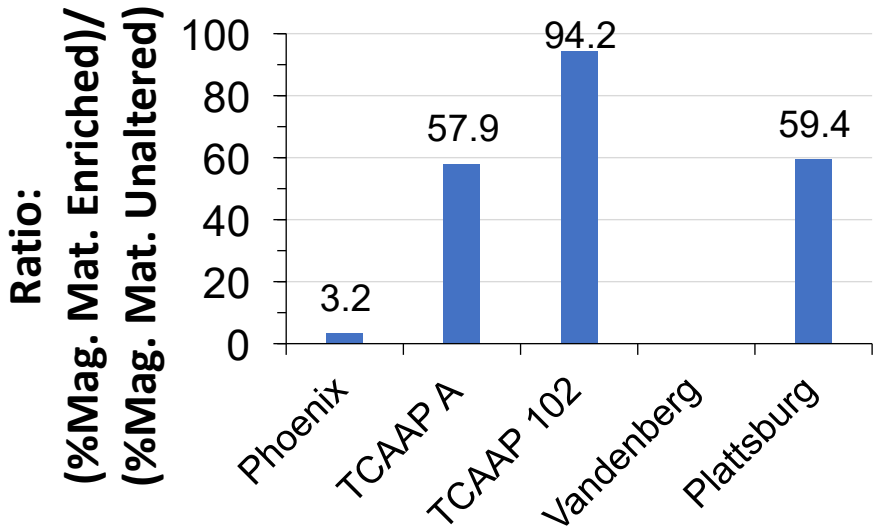


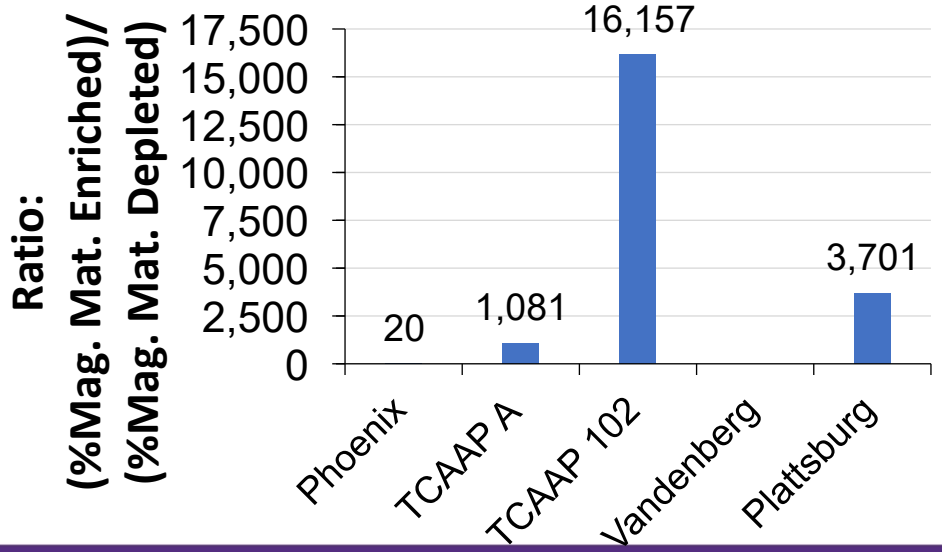
^{14}C products from abiotic degradation of ^{14}C-TCE accumulated in the microcosms with the original sediment present, but not in the controls without sediment

DPM = disintegrations per minute (i.e., a measure of ^{14}C activity)

Mag. Mat. by Site







TCAAP 102 >
Plattsburg ~
TCAAP A >
Phoenix >>>
Vandenburg

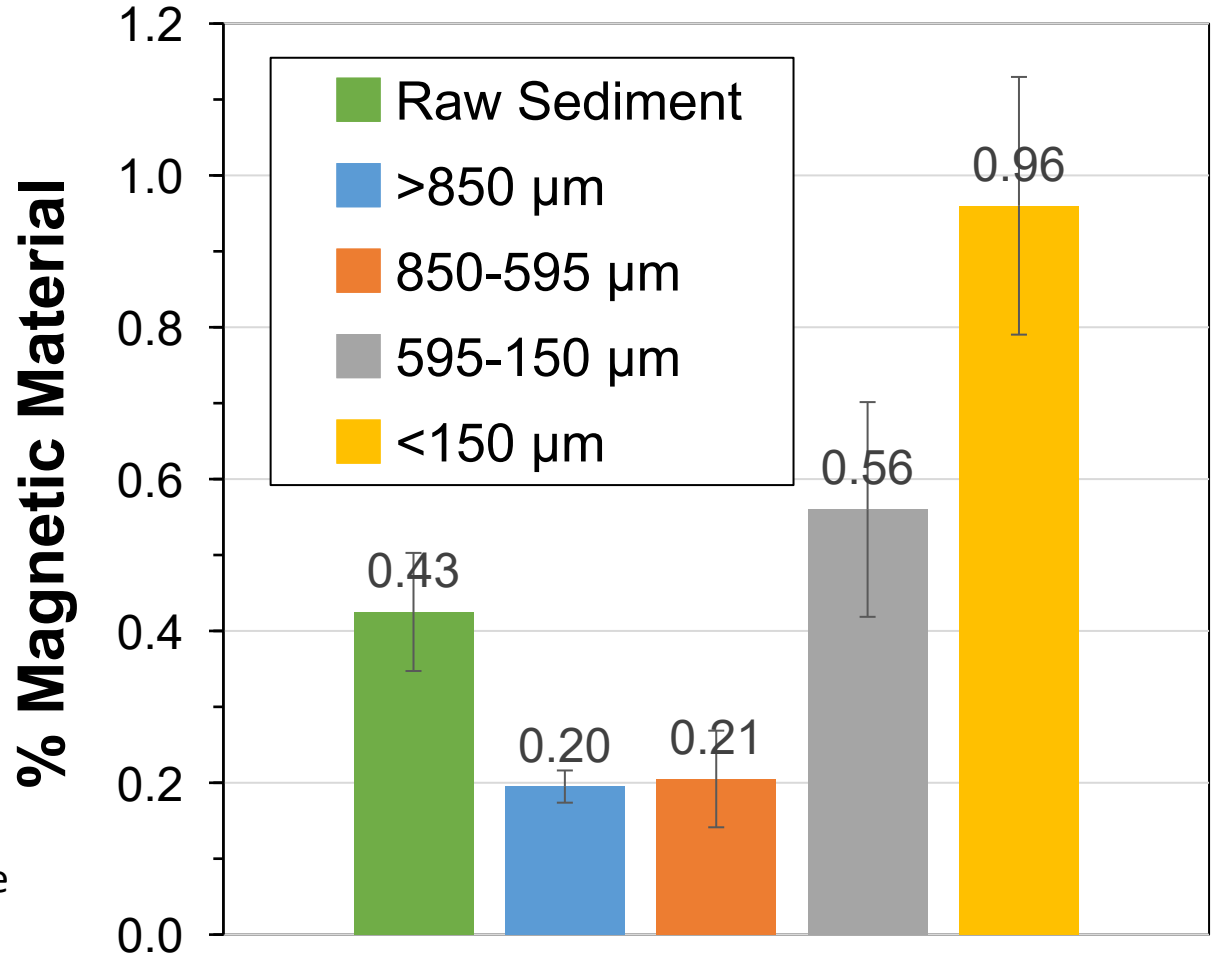
Separation of the Magnetic Component of Soils

- Measure the magnetic susceptibility (MS) of each fraction and convert to percent magnetic material (MM)

$$MS = \frac{(SI\ Units)(Volume\ of\ the\ ce}{Weiaht\ of\ the\ sample}$$

$$MM = 10^{(1.0803 * Log(MS) + 9.7038)}$$

$$\%MM = \frac{(100)(MM)}{10^6}$$



He et al. 2009. Identification and characterization methods for reactive minerals responsible for natural attenuation of chlorinated organic compounds in ground water. *US EPA*.

Separation of the Magnetic Component of Soils

Arizona Soil

- ~50% is >850 µm