

Use of a ^{14}C Assay to Determine Rates of TCE Co-oxidation in Groundwater

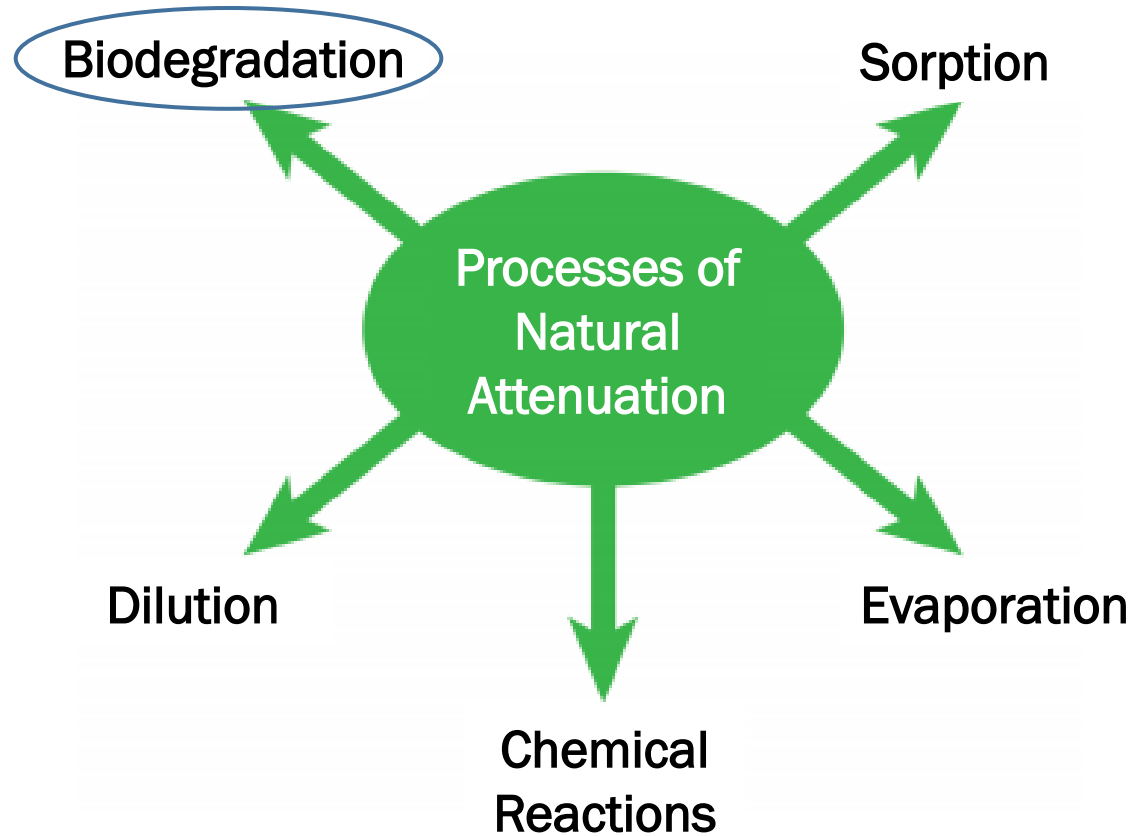
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Background



TCE biodegradation includes

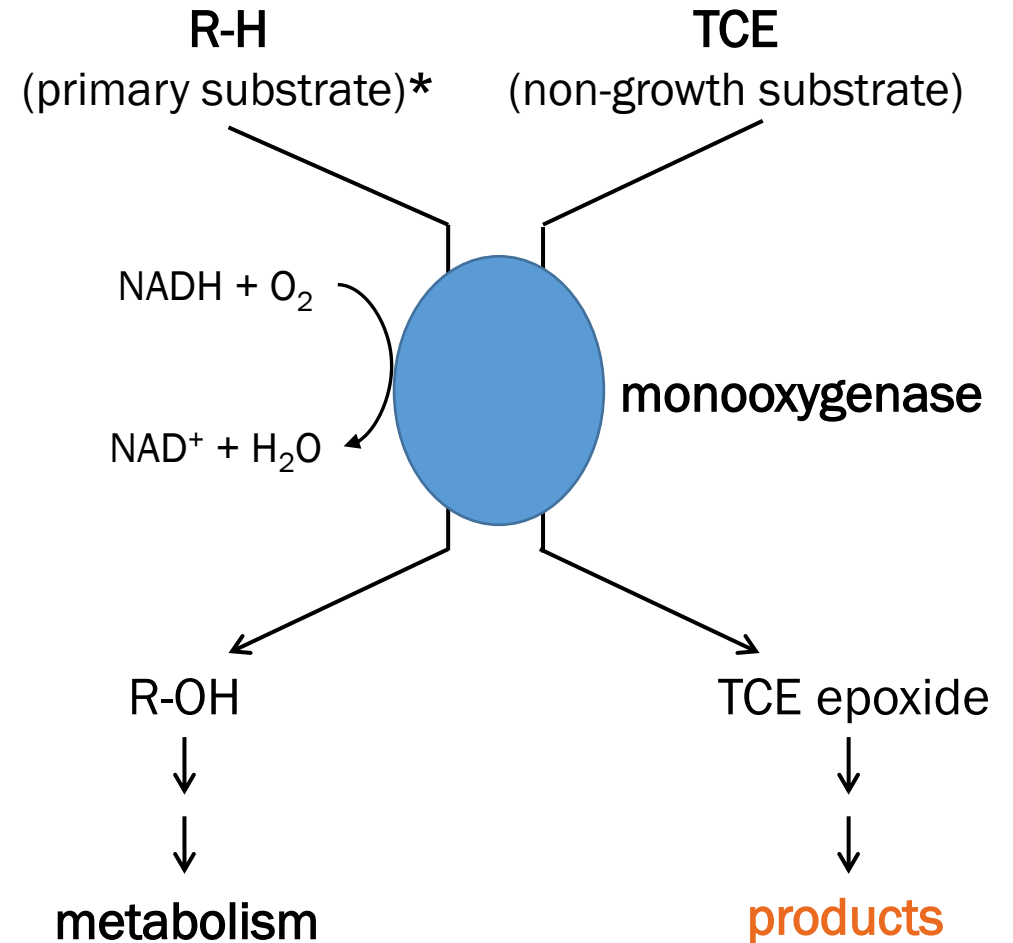
- **Reductive dechlorination**
 - Tools to document are well developed
 - Daughter products
 - Molecular
 - CSIA
- **Aerobic co-oxidation**
 - Tools to document are less developed

Background

Oxygenase enzymes

- Require oxic conditions
- Add oxygen atom(s) to compounds
- Mono- and dioxygenase varieties

Co-oxidation of TCE



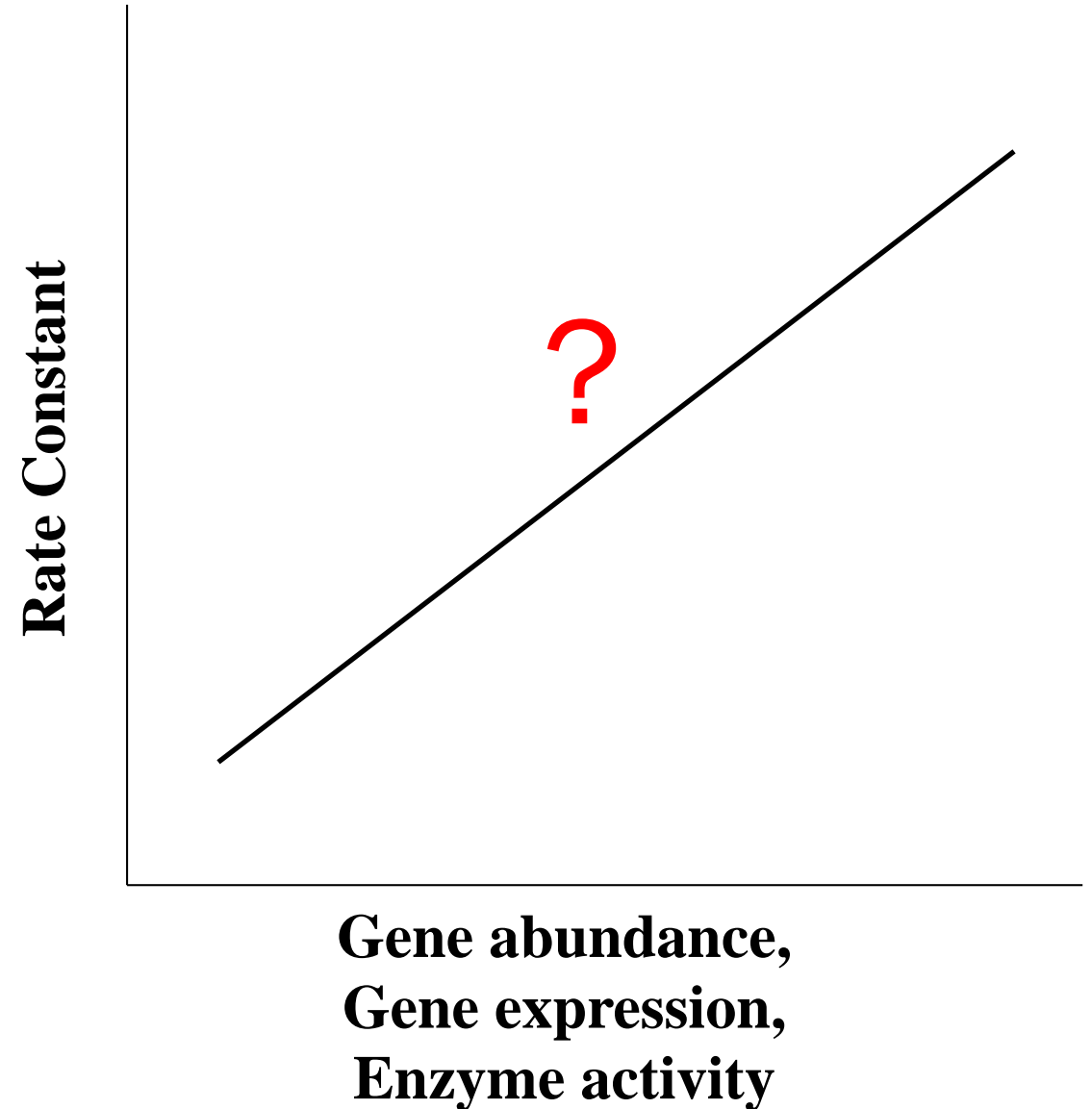
* Substrates may include: methane, natural organic matter (e.g. humic acids), ethene, vinyl chloride, BTEX

Background

Approaches to document aerobic co-oxidation

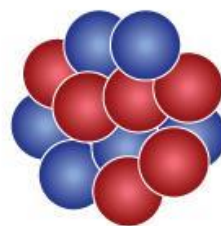
- Molecular (fast)
 - qPCR for specific oxygenases
 - qPCR for oxygenase expression
- Enzyme assay for specific oxygenases (fast)
- ^{14}C assay to determine rate constants (more time consuming)

Strength of correlation?

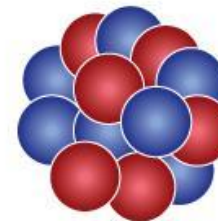


Research Objective

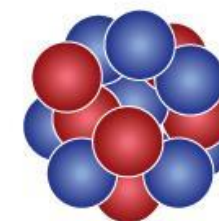
- Develop ^{14}C assay to detect first-order rate constants from groundwater samples
- Reasons to develop ^{14}C assay
 - In situ concentrations difficult to measure
 - Sensitivity of ^{14}C signal above background levels ‡
 - More complete mass balances



carbon-12
98.9%
6 protons
6 neutrons



carbon-13
1.1%
6 protons
7 neutrons



carbon-14
<0.1%
6 protons
8 neutrons

Site Locations



^{14}C Assay

Controls:

- Distilled deionized (DDI) water
- Filter-sterilized groundwater (FSGW)

Total ^{14}C :

- Determine total ^{14}C in bottles

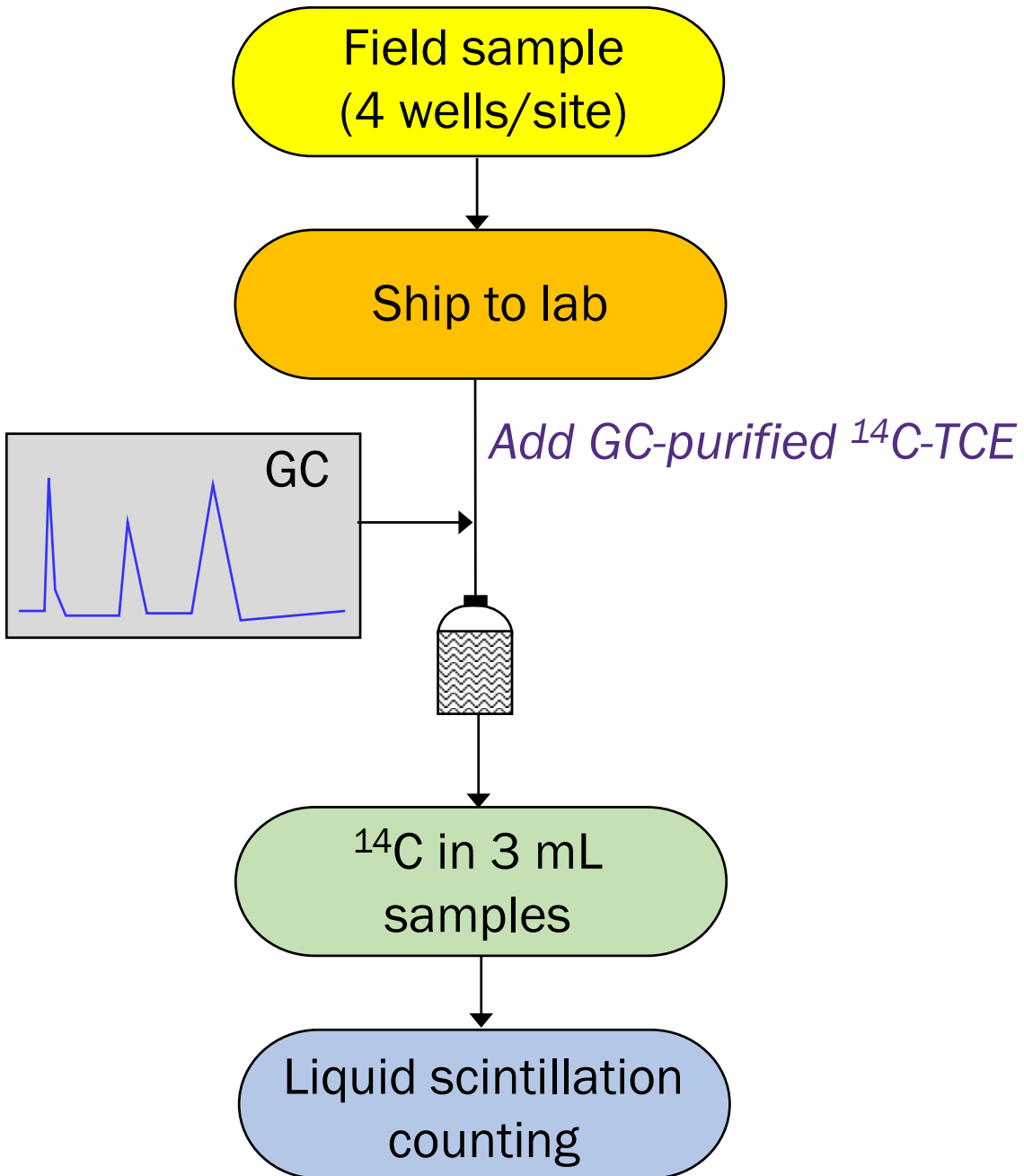
Total ^{14}C products:



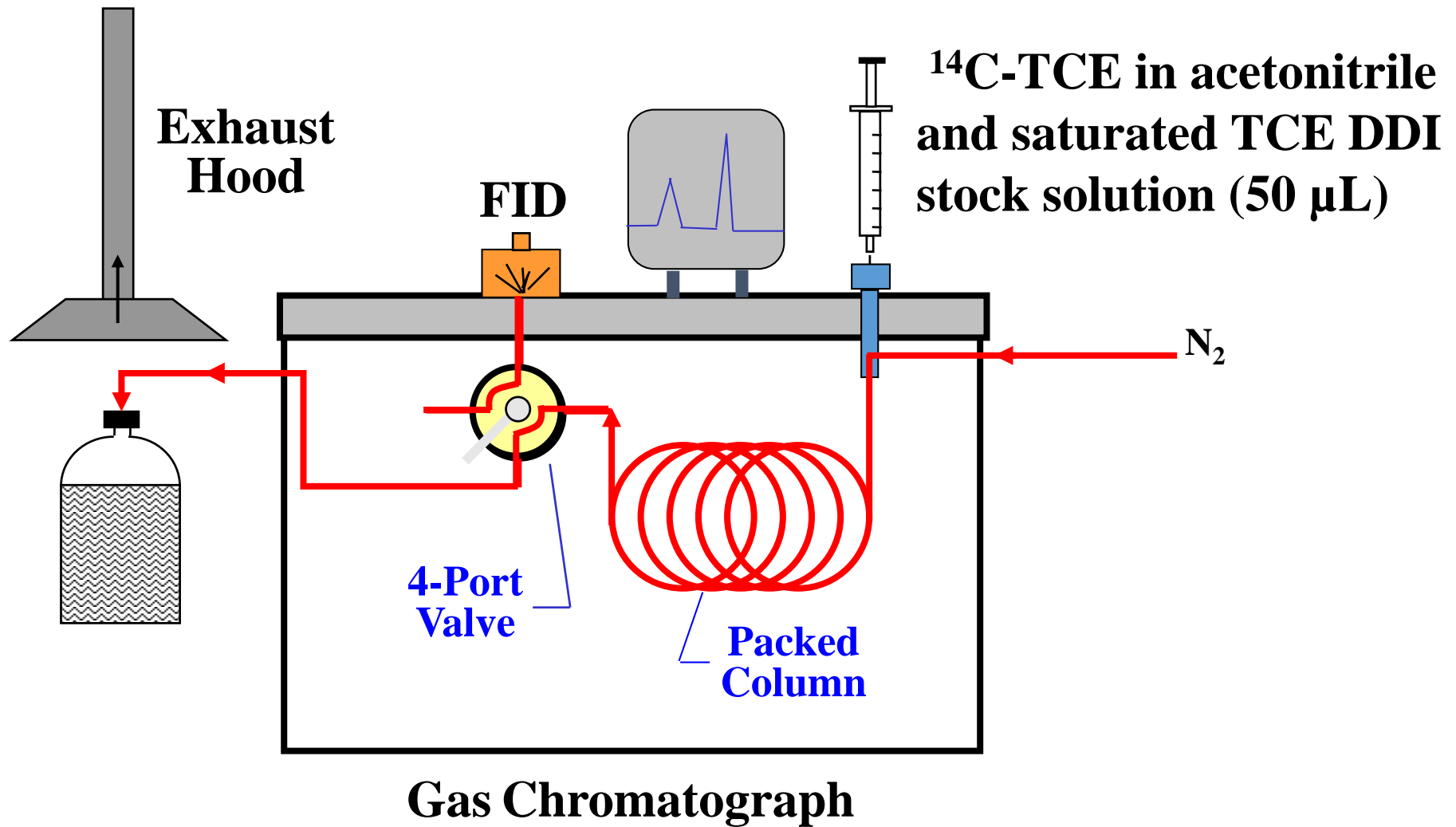
- Removed 3 mL aqueous samples
- Raised pH > 10 using NaOH to retain $^{14}\text{CO}_2$
- Sparged samples for 30 min with N_2

End-of-incubation products:

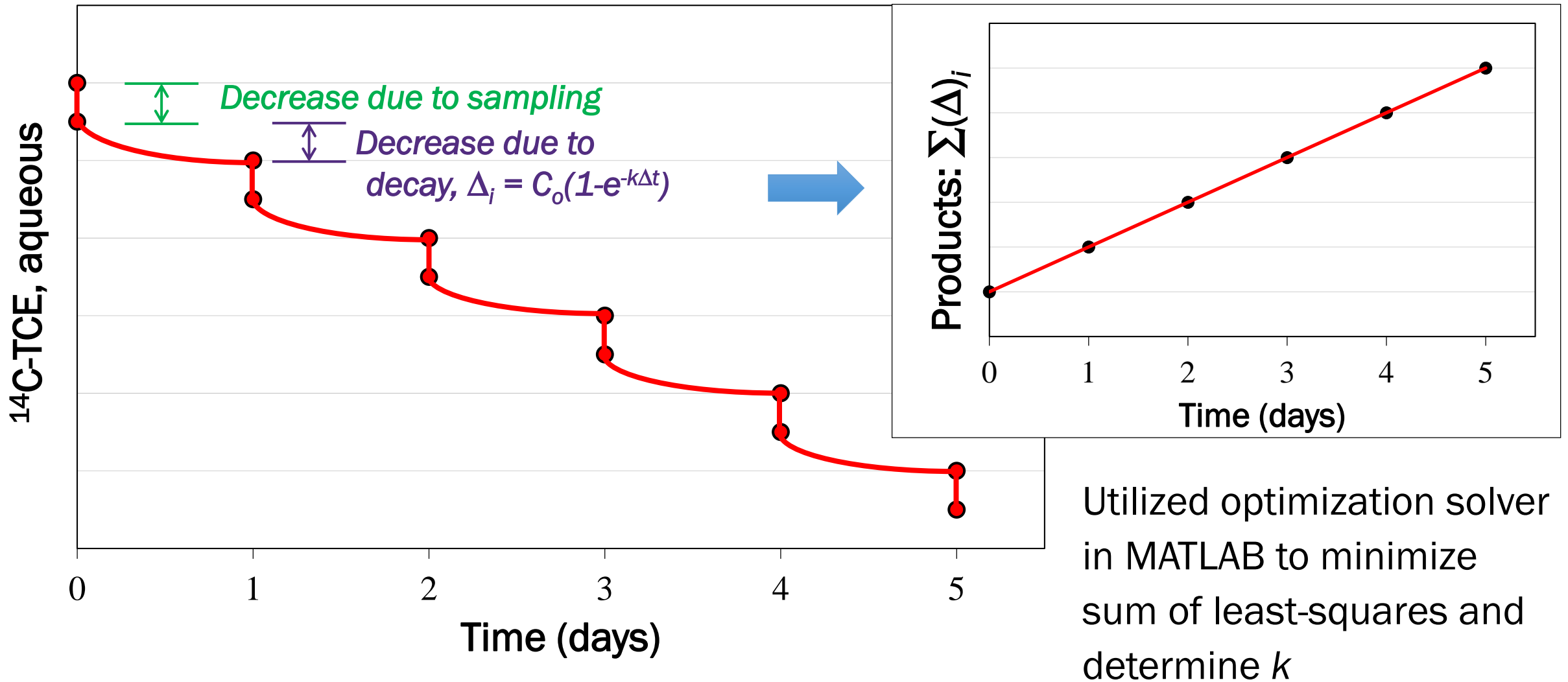
- Precipitated $^{14}\text{CO}_3^{-2}$ using $\text{Ba}(\text{OH})_2$
- Determined percent $^{14}\text{CO}_2$



Method to Purify ^{14}C -TCE

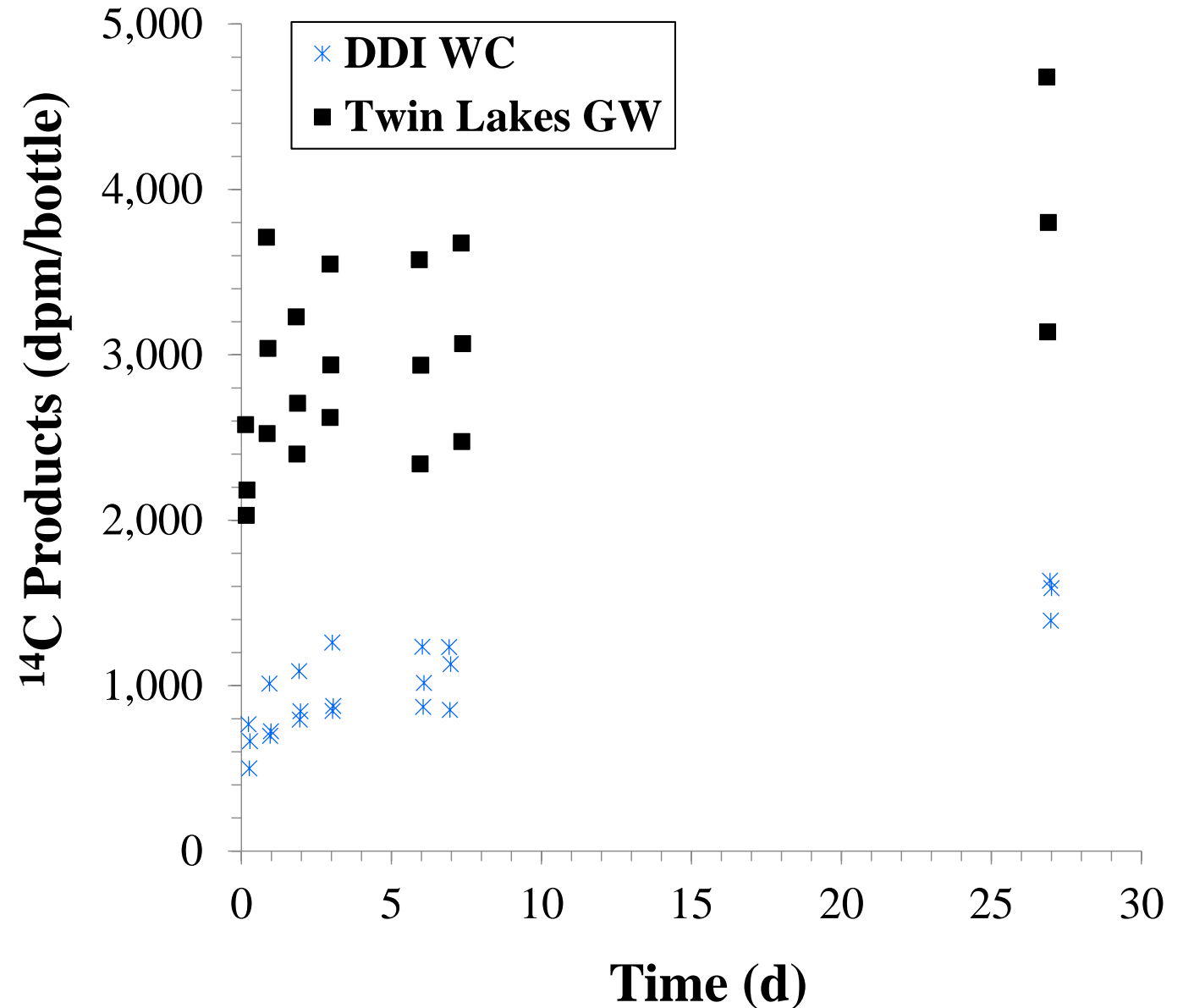


First-Order Modeling

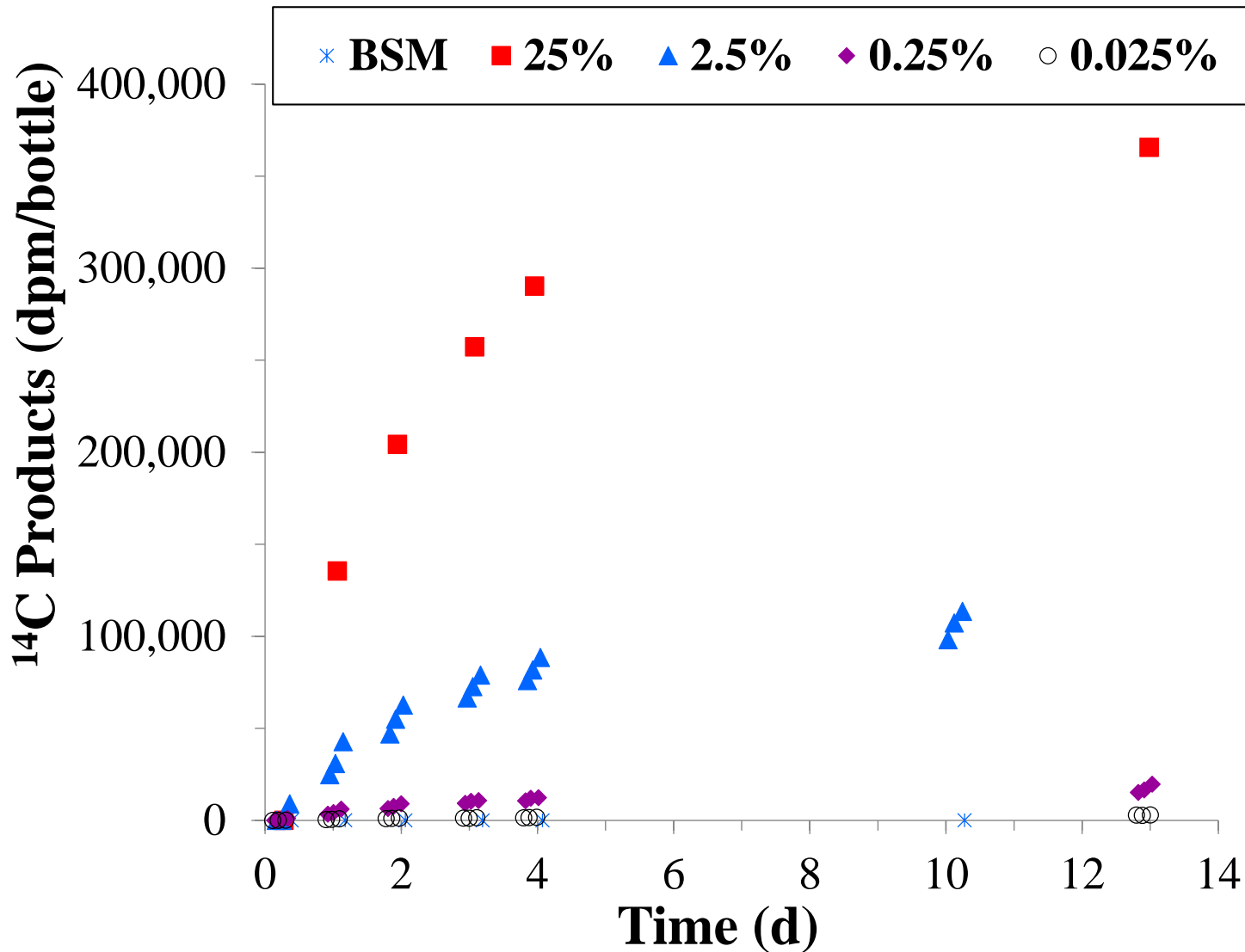


Positive Controls

- Groundwater from natural source
- Collected at seep near Twin Lakes Recreation Area in Pendleton, SC
- Used to validate ^{14}C assay with natural groundwater
- $k = 0.024 \text{ yr}^{-1}$
- $t_{1/2} = 29.0 \text{ yr}$



Positive Controls



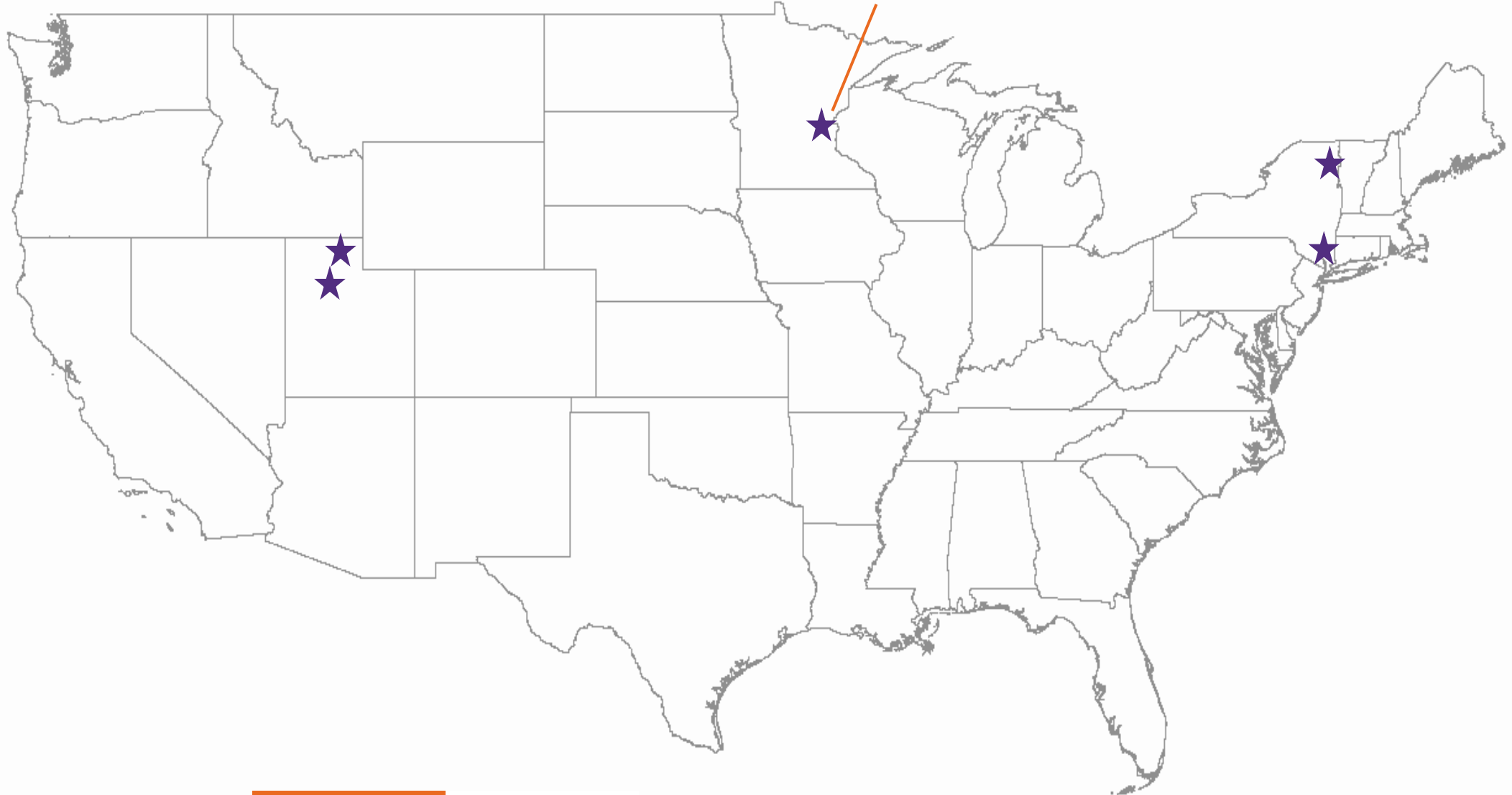
Propanotrophic Culture

- Cultured from ENV487 (courtesy CB&I)
- Known to degrade TCE using oxygenase enzymes
- Grown in basal salts medium
- Used to validate ¹⁴C assay

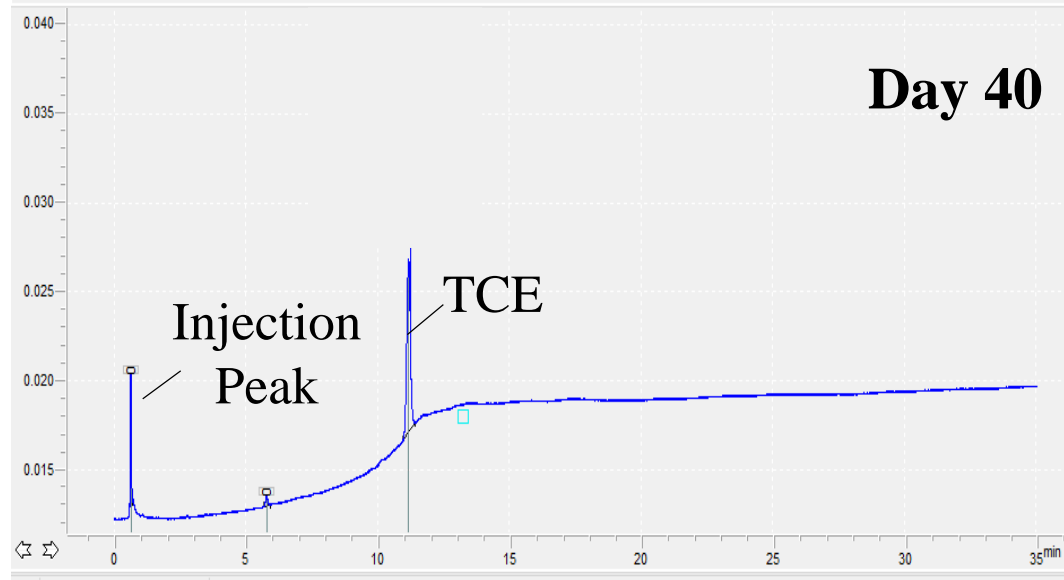
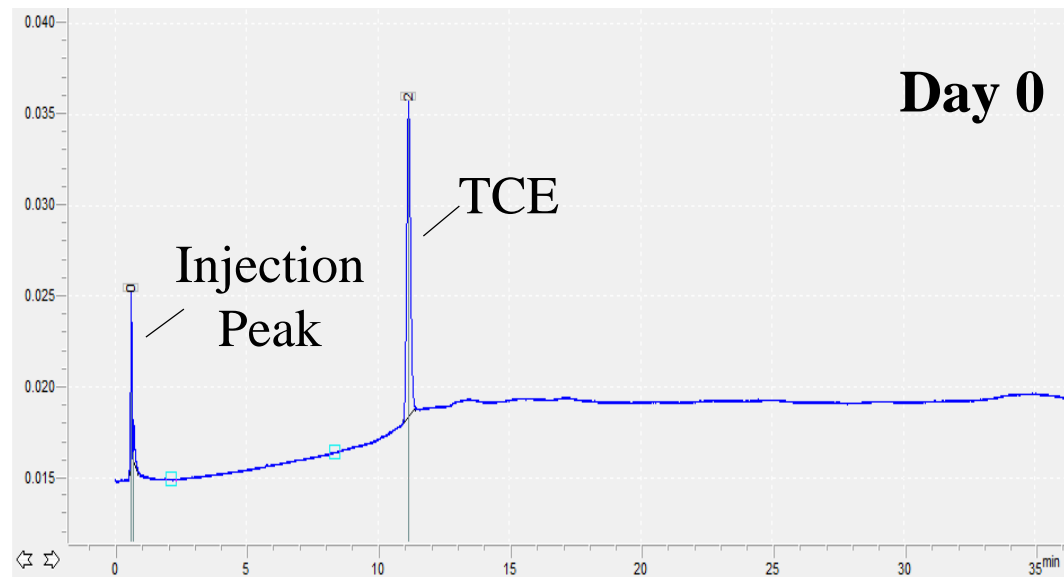
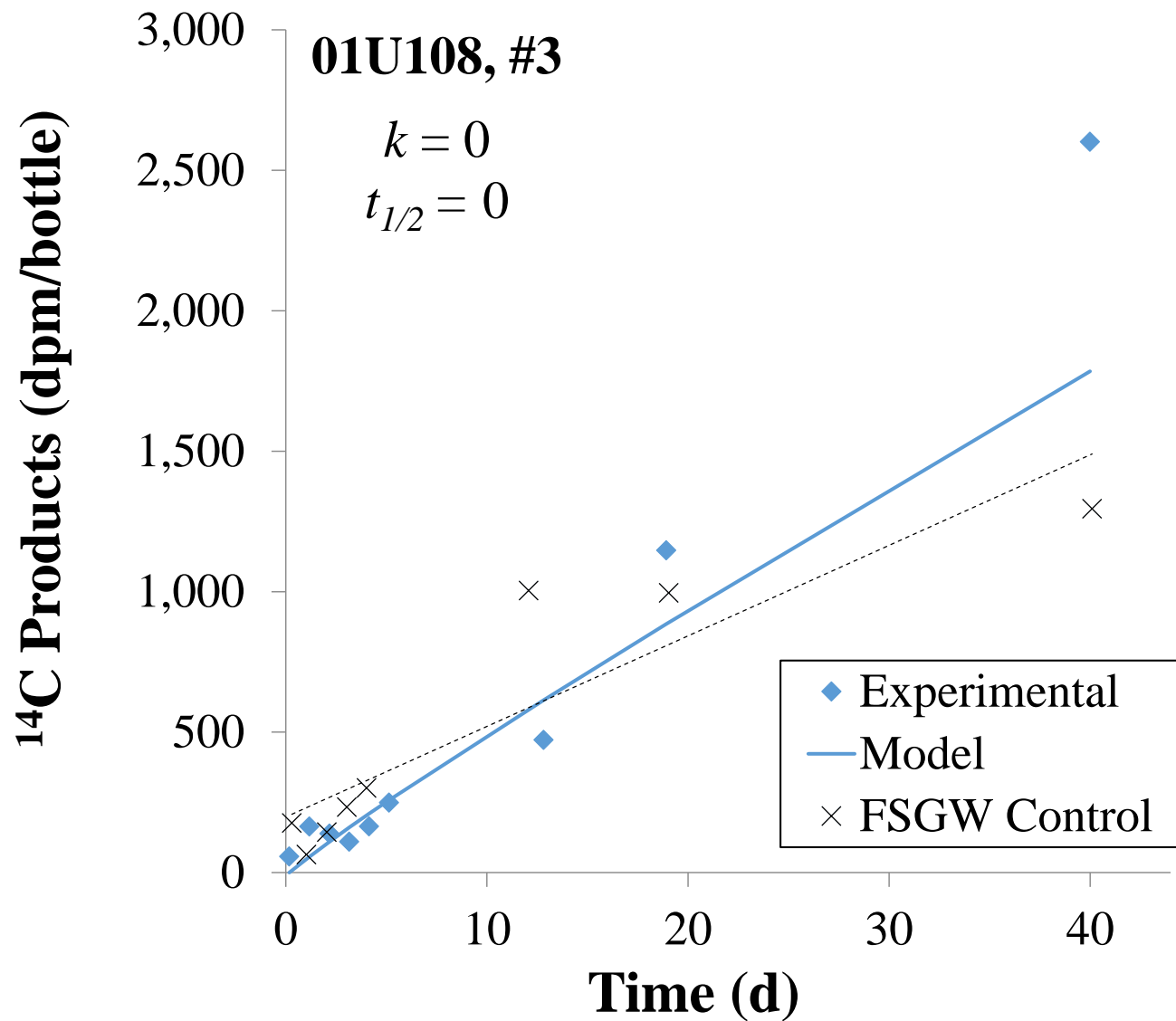
Dilution	t _{1/2} (yr)
25 %	0.010
2.5 %	0.068
0.25 %	0.62
0.025 %	4.0

Site Locations

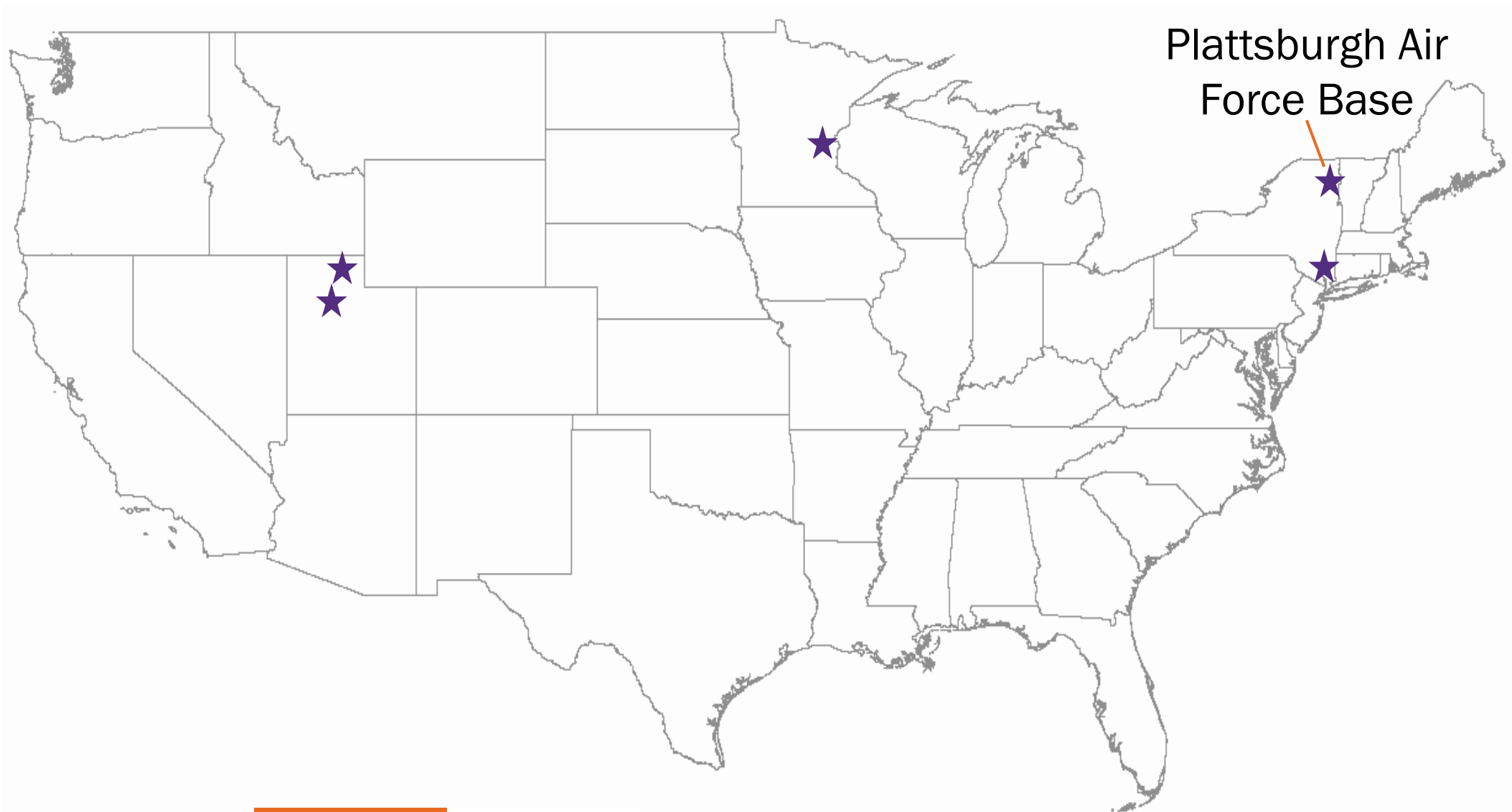
Twin Cities Army
Ammunition Plant



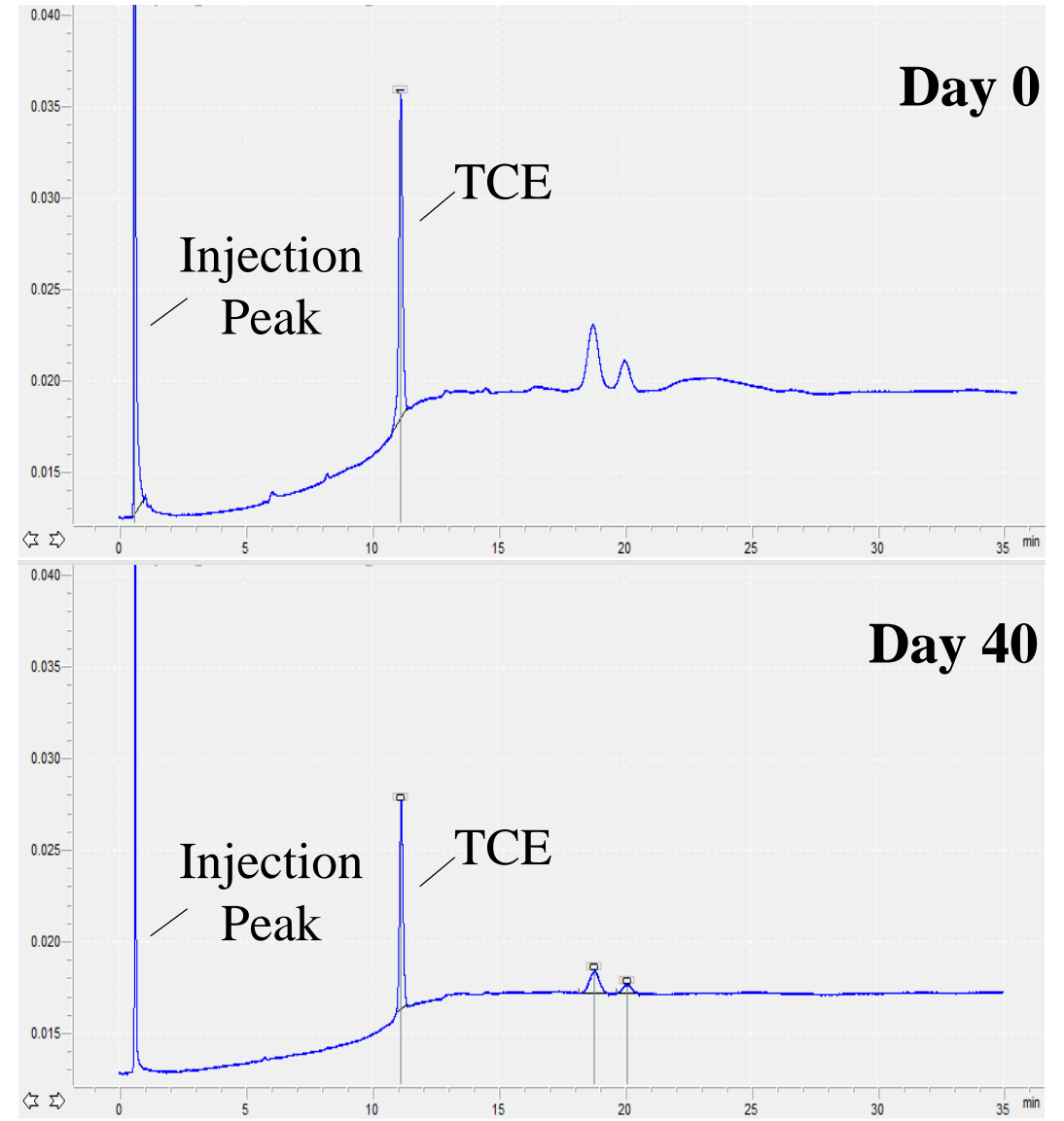
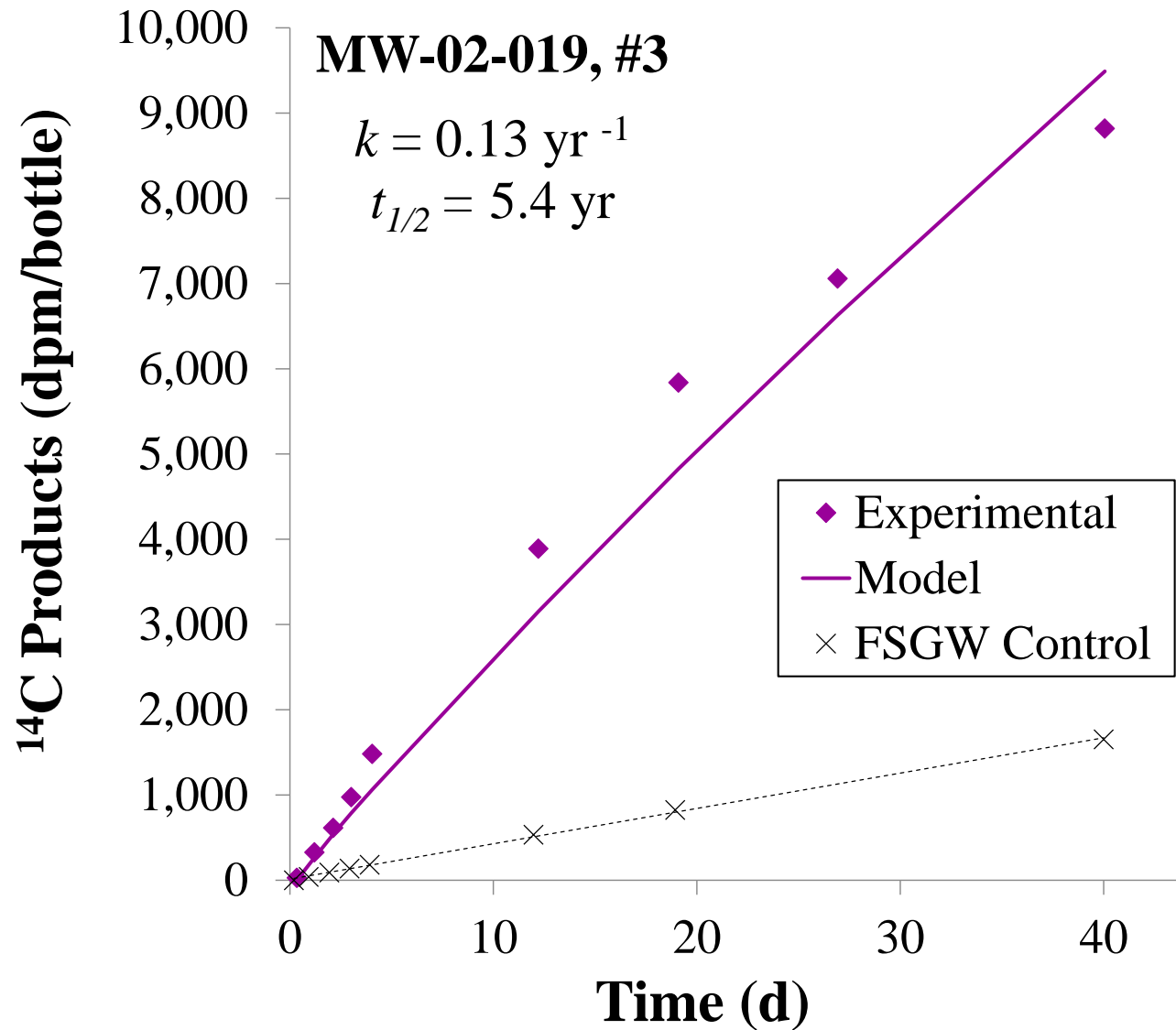
Results: TCAAP, MN



Site Locations



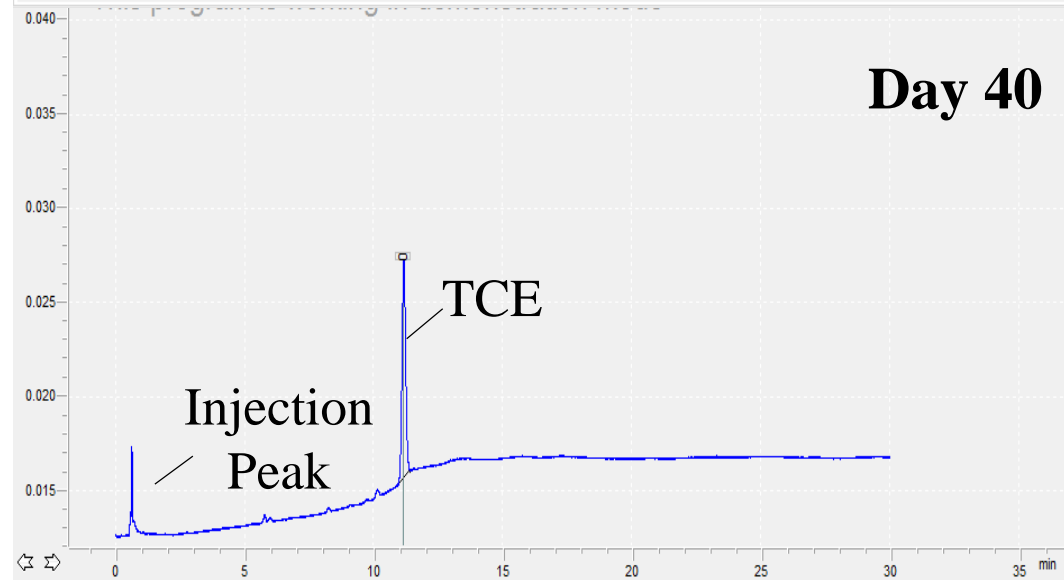
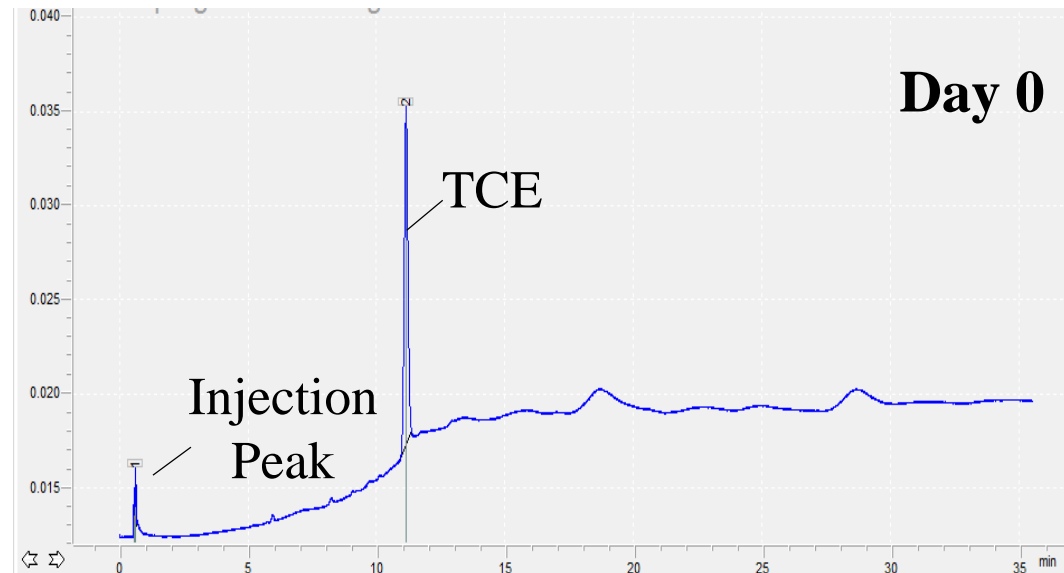
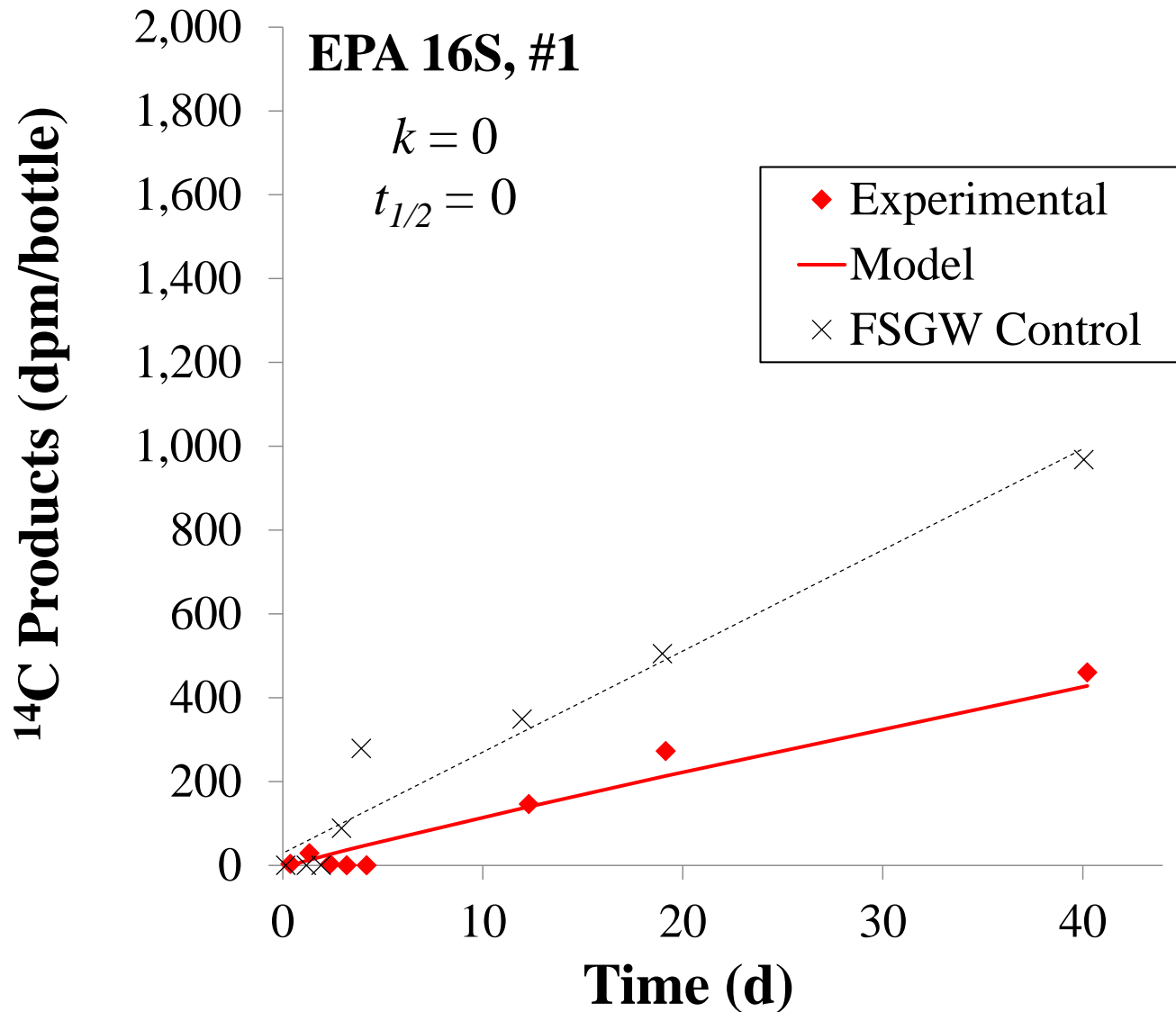
Results: Plattsburgh AFB, NY



Site Locations



Results: Hopewell, NY

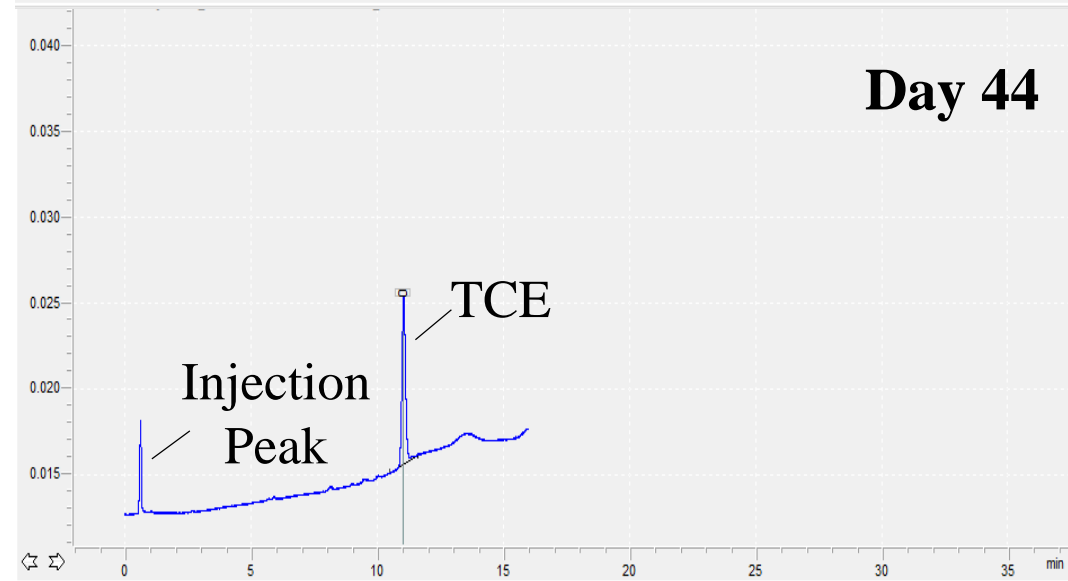
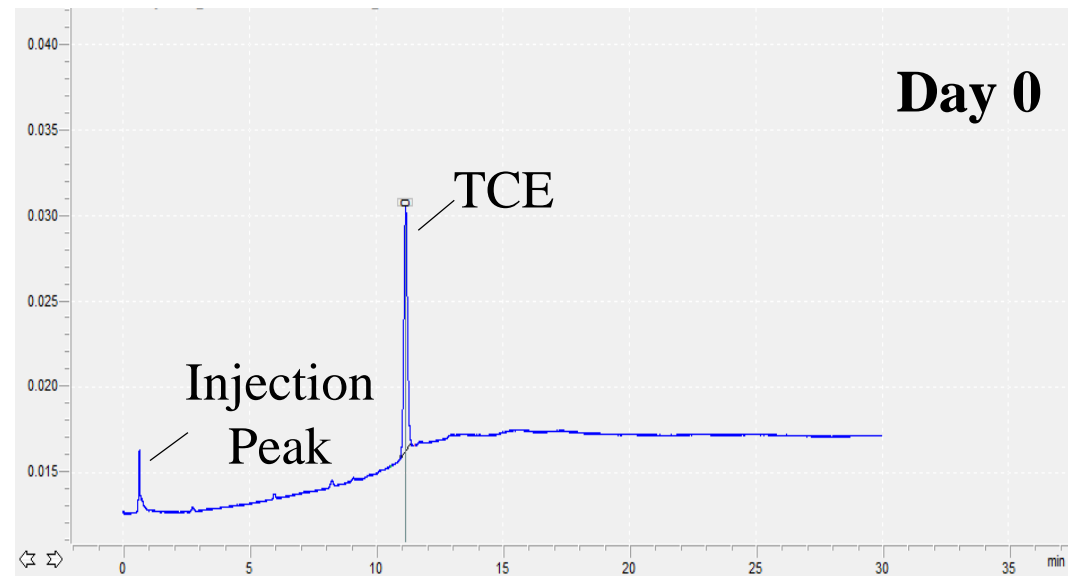
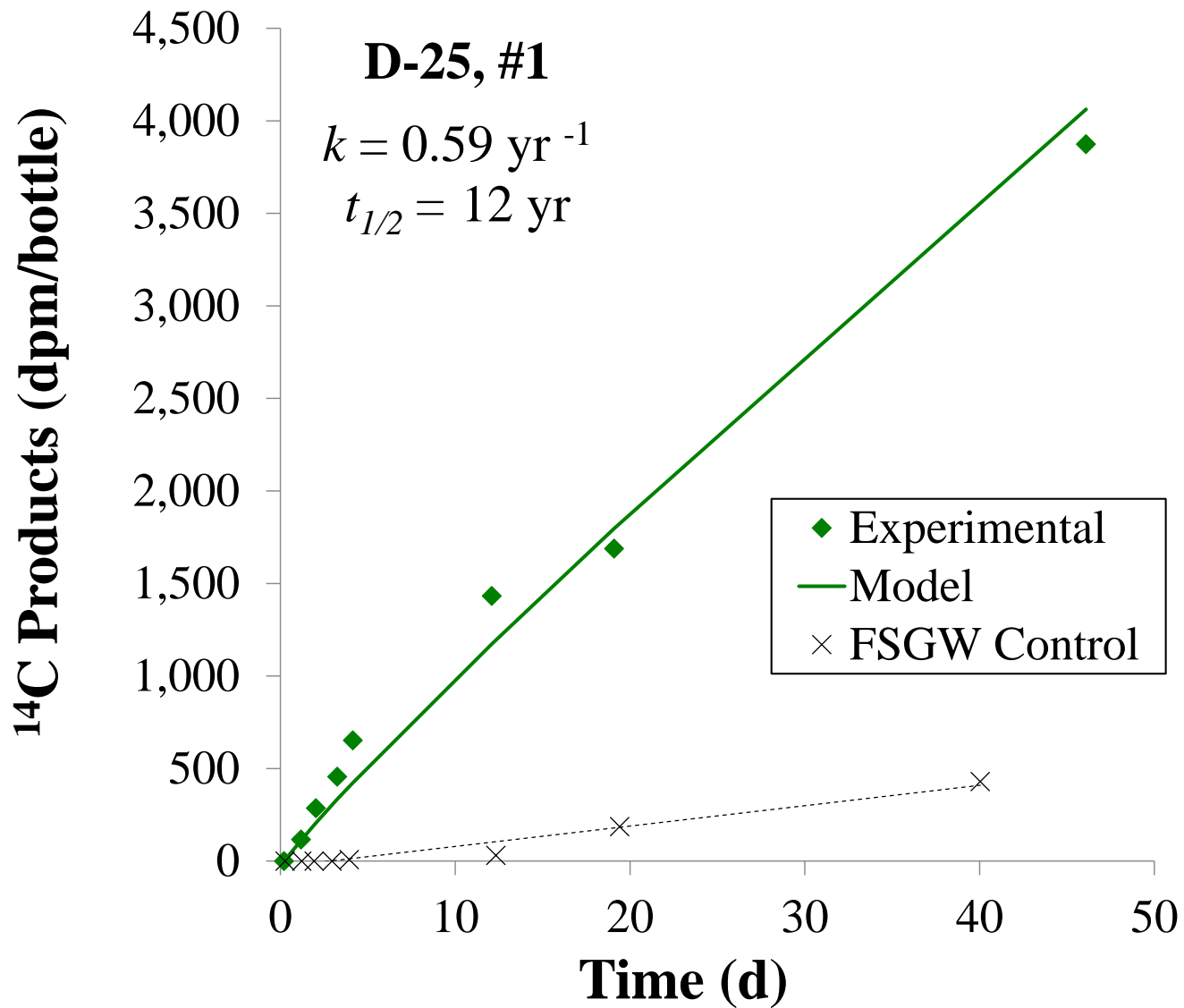


Site Locations



Tooele Army
Depot

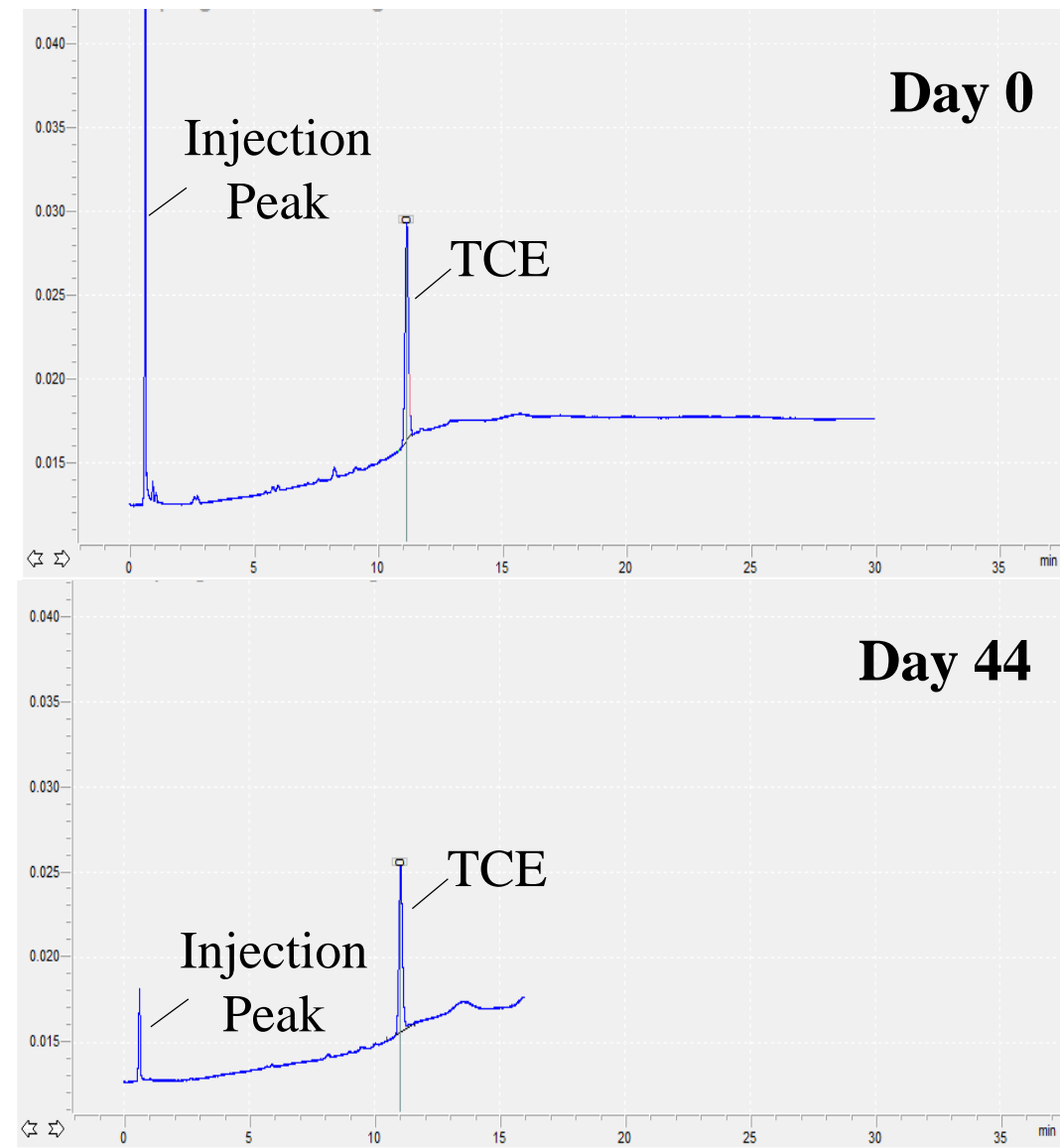
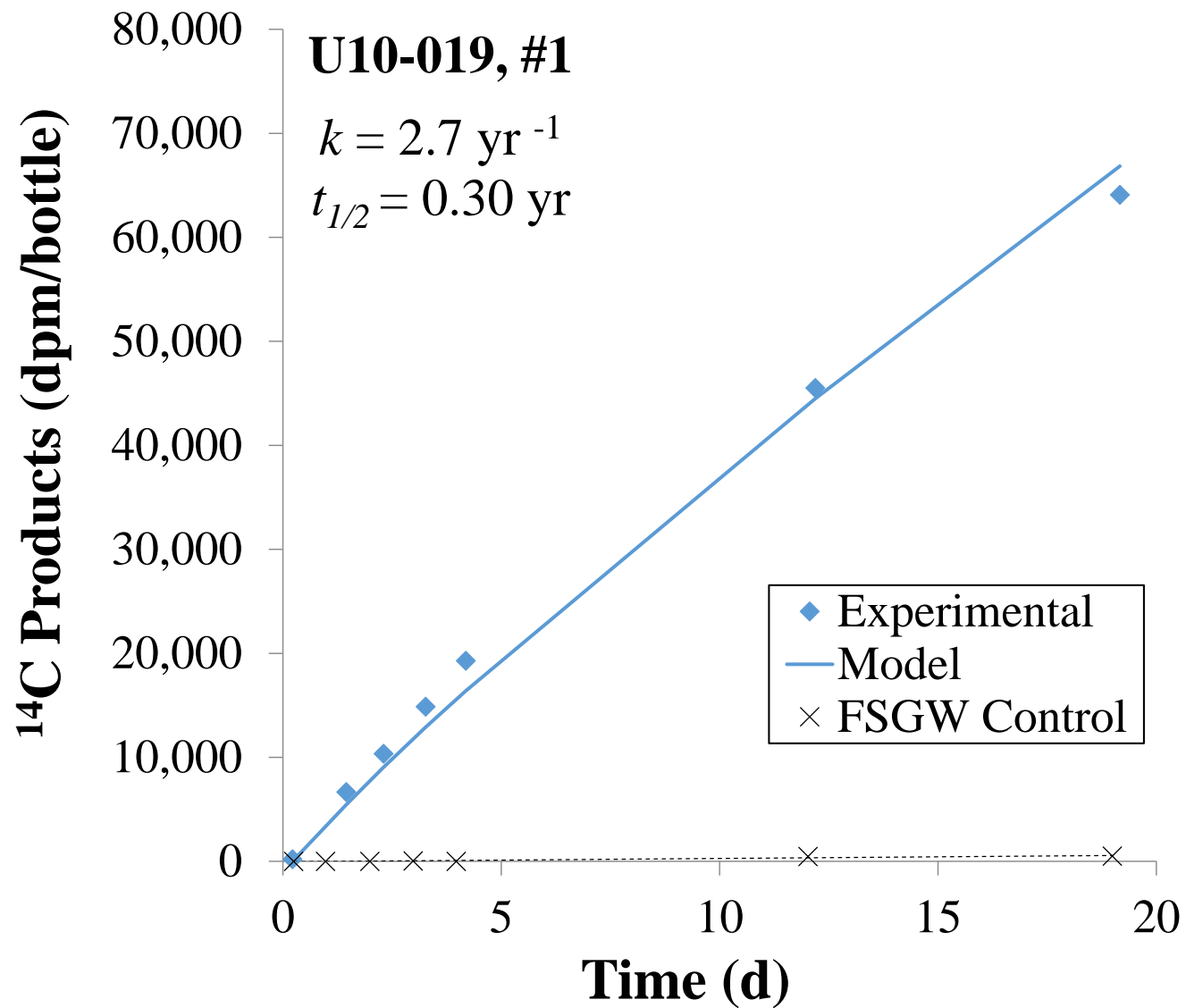
Results: Tooele, UT

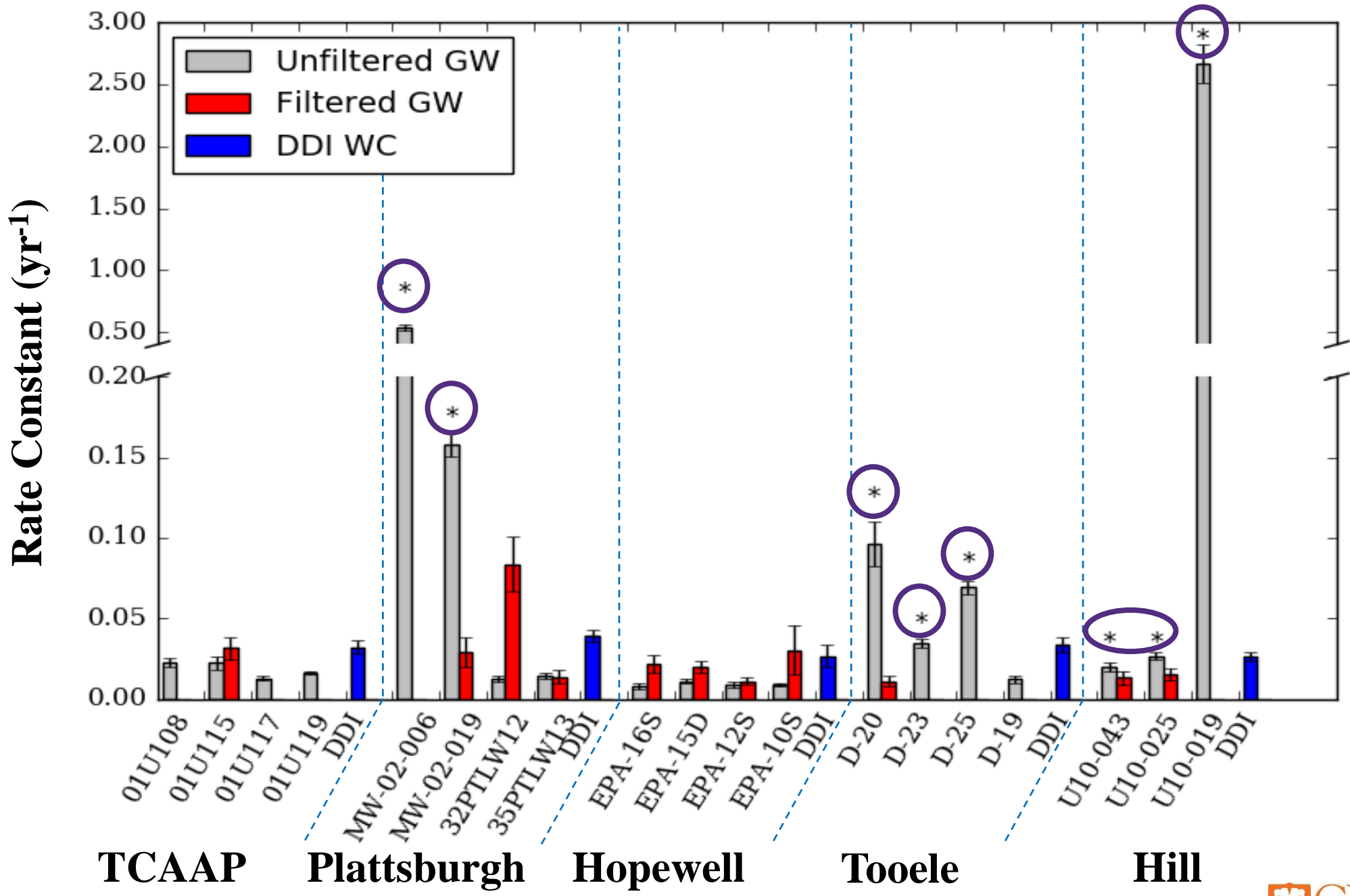


Site Locations

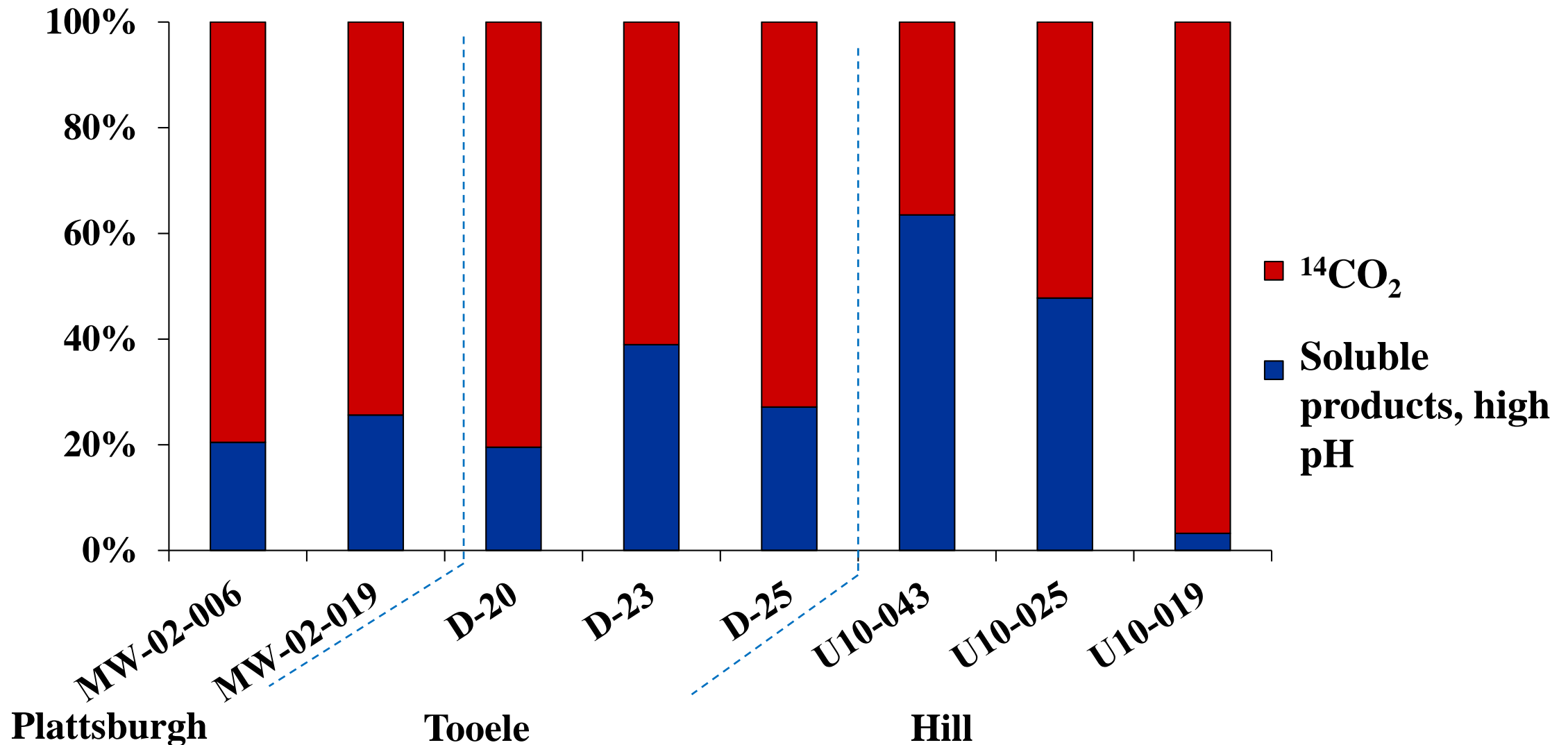


Results: Hill AFB, UT





^{14}C Product Distribution

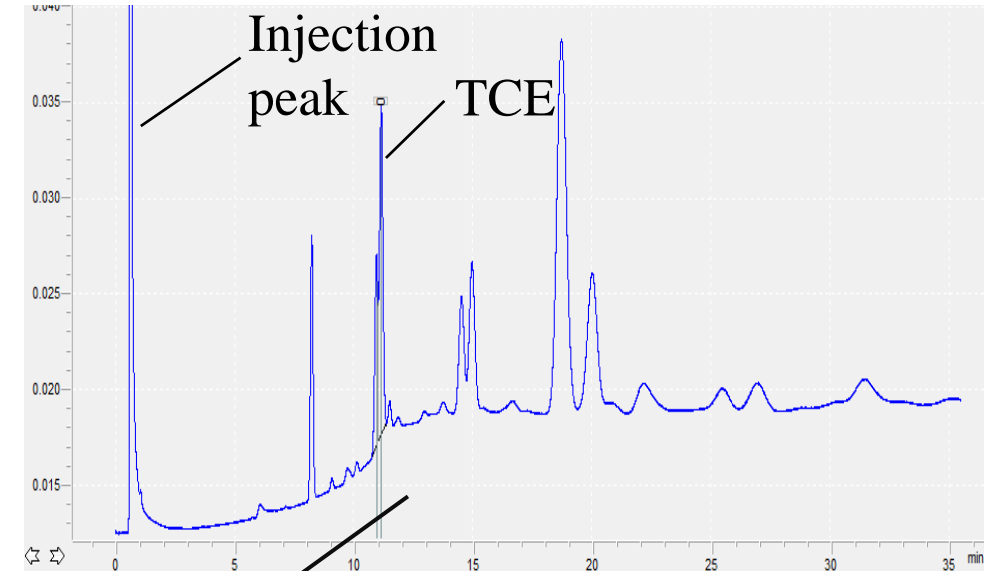


Conclusions

- ^{14}C assay provides quantitative evidence for aerobic TCE co-oxidation; provides rate constants that can be used as a second line of evidence to assess MNA
- Capable of predicting first-order constants for TCE degradation as low as 0.0066 yr^{-1} = half-life up to 105 yr
- ^{14}C product distribution was 37-97% $^{14}\text{CO}_2$ with remainder as soluble products

Next presentations

- Enzyme activity probe response:
Brady Lee
- Gene abundance and expression:
Dora Ogles-Taggart
- Application to abiotic degradation:
John Wilson



Contaminant plume, Plattsburgh AFB

Acknowledgments

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Dr. David Freedman

Dr. John Wilson

Todd Wiedemeier



Questions?