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The Role of Carbonates in the Effectiveness of Biostimulatory Solutions for the Removal of Petroleum Hydrocarbon Contaminants in Cold Calcareous Soils

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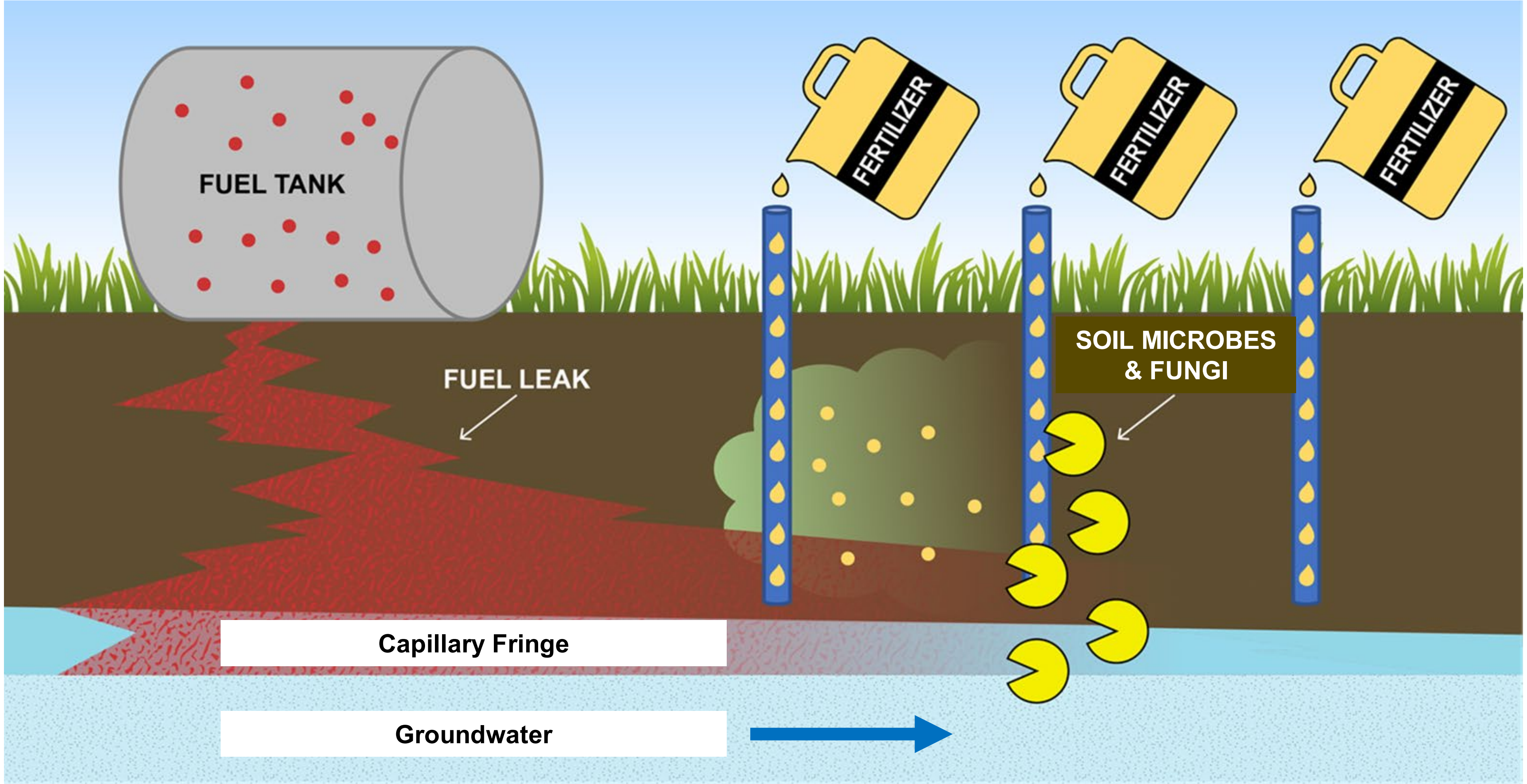
University of Saskatchewan

Project Background



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Project Background

- Data gaps surrounding effectiveness of in situ bioremediation
    - Influence of site-specific soil properties over looked in “off the shelf” remedies
- Recent studies have identified that biostimulation can work:
    - Understanding phosphorous bioavailability *(Siciliano et al., 2016; Hamilton et al., 2018; Bulmer et al., 2018)*
        - Sorption, complexation, precipitation
    - Addition of low molecular weight organic acids to chelate Ca and Mg ions increase availability of phosphorus *(Siciliano et al., 2016; Chen, 2018)*
- However, remediation at some sites has ***stalled***
    - Believed to be related to buffering capacity and carbonate mineralogy

A Note on Soil Buffering Capacity

- Ability of a soil system to resist changes in pH
  - Related to CEC, base saturation, and acid neutralizing capability.
- Stalling is likely associated with a failure of the soils to buffer against the biostimulatory solutions
  - Results in formation of Ca-P complexes that are stable compounds with relatively low solubilities

Project Objective

- Understand role of site-specific properties in the effectiveness of biostimulation techniques for the remediation of petroleum impacts in cold-region calcareous soils
  - **How geochemical parameters 'condition' biostimulatory solutions**

- **END GOAL**: create a conceptual model that integrate site-specific geochemical parameters and microbial activity to estimate hydrocarbon degradation rates.

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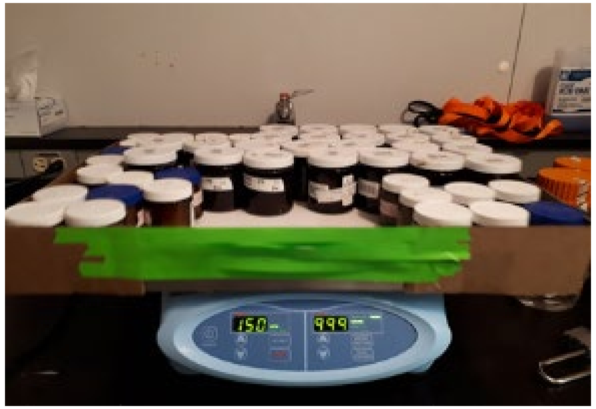
Experimental Design



Experimental Design

<u>Biostimulatory Solutions</u>

- Sodium triphosphate
- Nitric acid
- Magnesium sulphate / potassium sulphate
- Ammonium iron citrate

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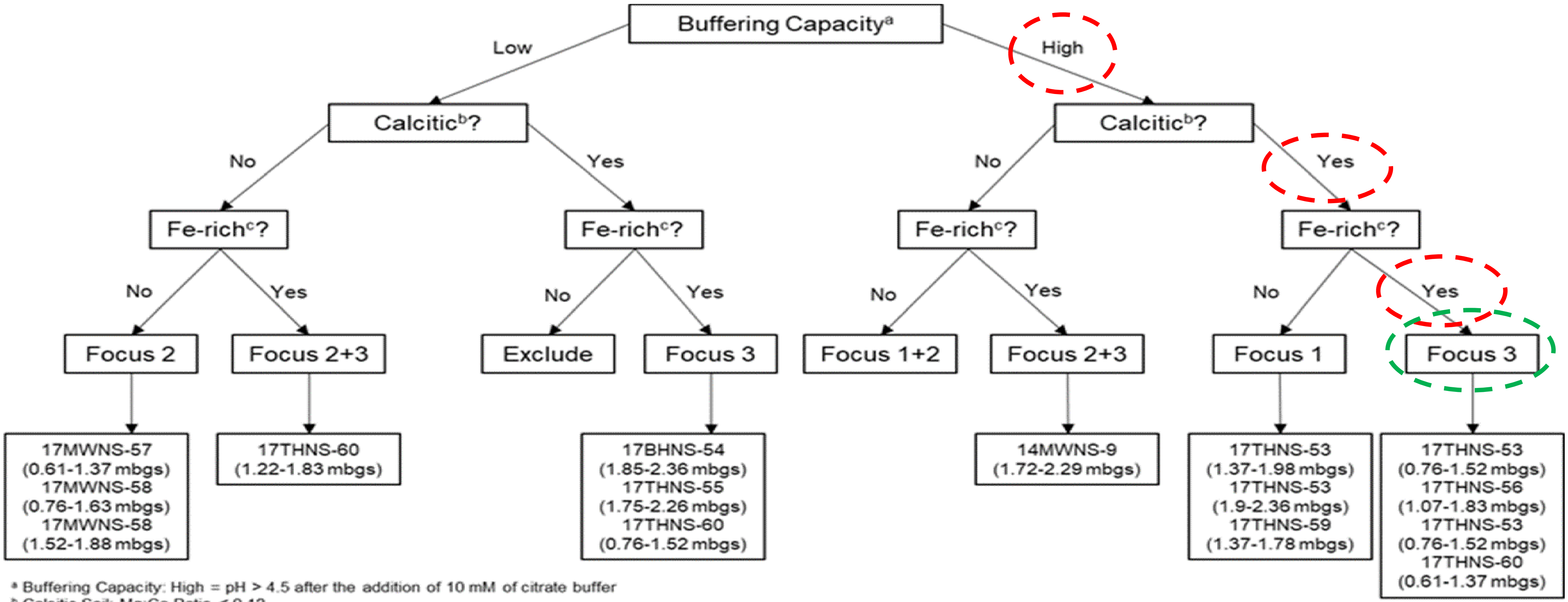
Experimental Design

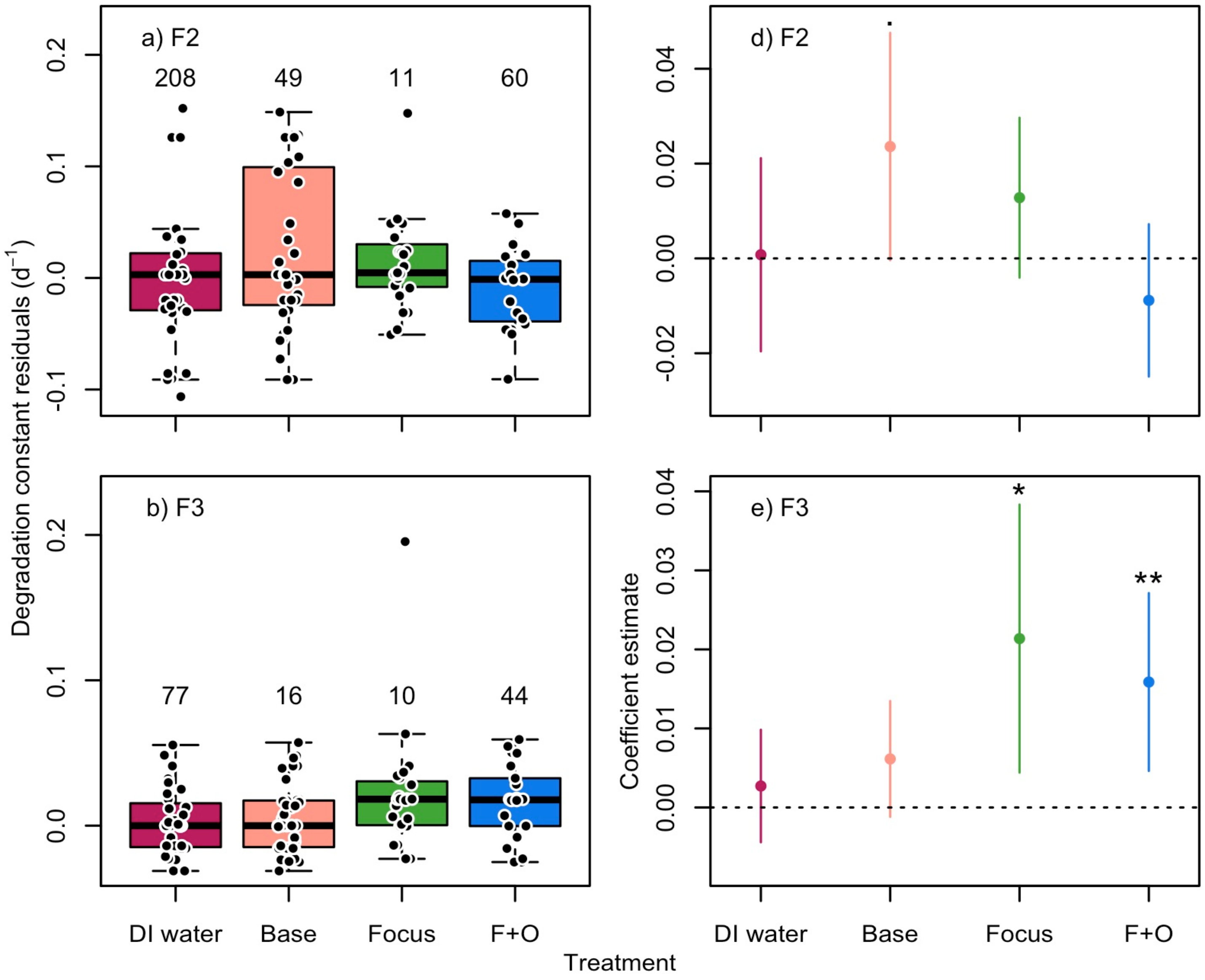


[a] Buffering Capacity: High = pH > 4.5 after the addition of 10 mM of citrate buffer
[b] Calcitic Soil: Mg:Ca Ratio < 0.12
[c] Fe-rich soil: $Fe_{solution}$ > 30 mg/L

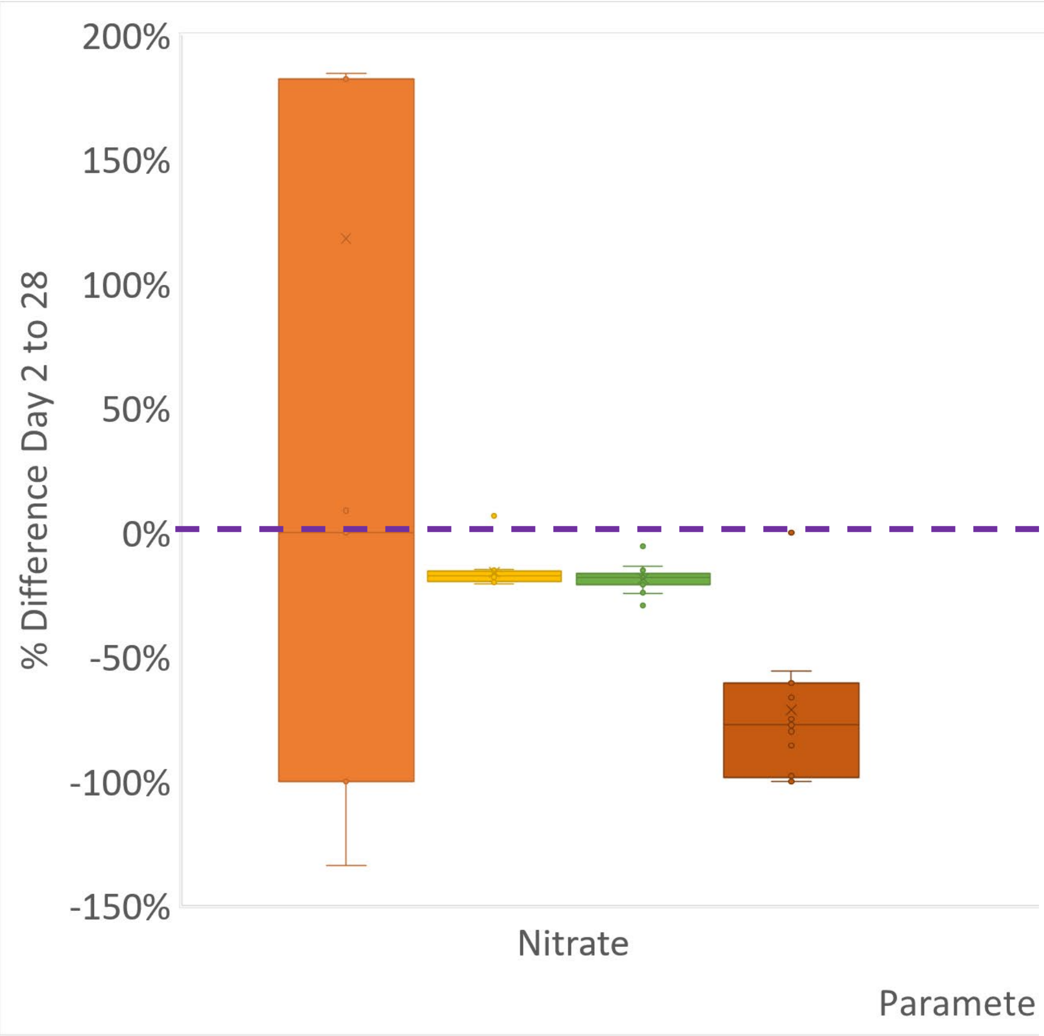
Notes:

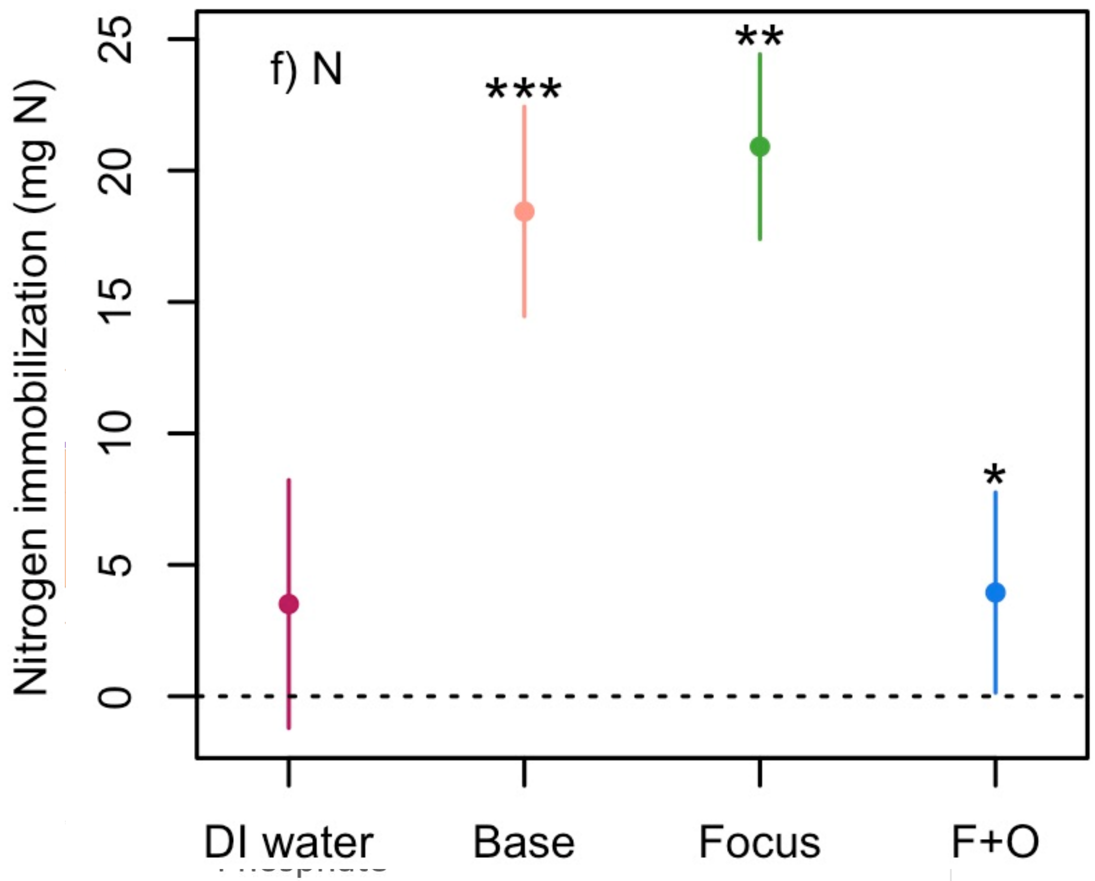
17THNS-53 (1.9-2.36 mbgs) was not used for the final microcosm test because it did not follow the same flow as the other cores (unusual place on decision tree)
> = greater than
< = less than
Ca = calcium
Mg = magnesium

Results


a) F2
208
49
11
60
b) F3
77
16
10
44
d) F2
e) F3
*
**
Degradation constant residuals (d⁻¹)
Coefficient estimate
0.2
0.1
0.0
-0.1
0.04
0.02
0.00
-0.02
0.03
0.01
DI water
Base
Focus
F+O
Treatment

Results

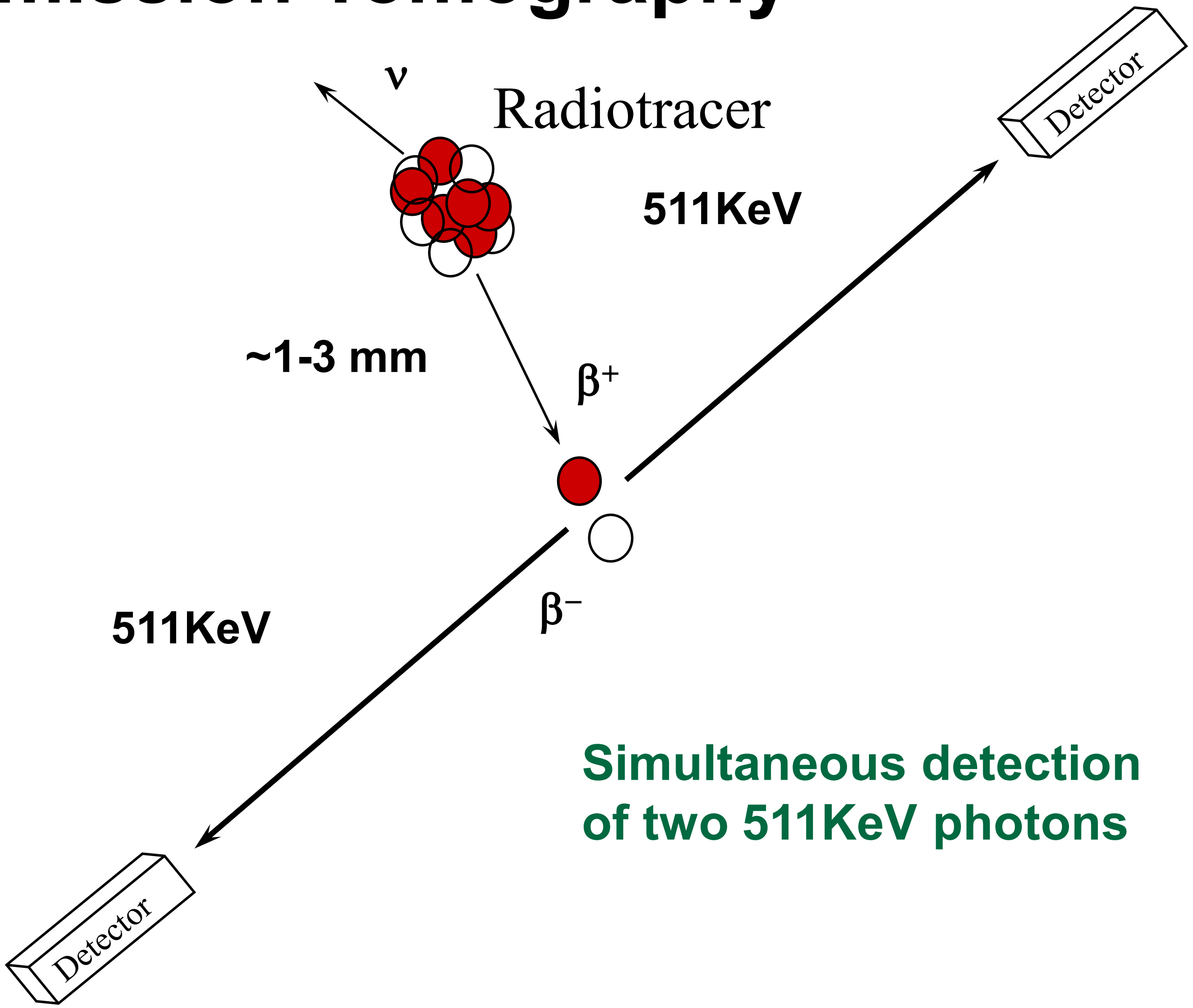

200%
150%
100%
50%
0%
-50%
-100%
-150%
% Difference Day 2 to 28
Nitrate
Paramete


f) N
Nitrogen immobilization (mg N)
0
5
10
15
20
25
***
**
*
DI water
Base
Focus
F+O

Positron Emission Tomography

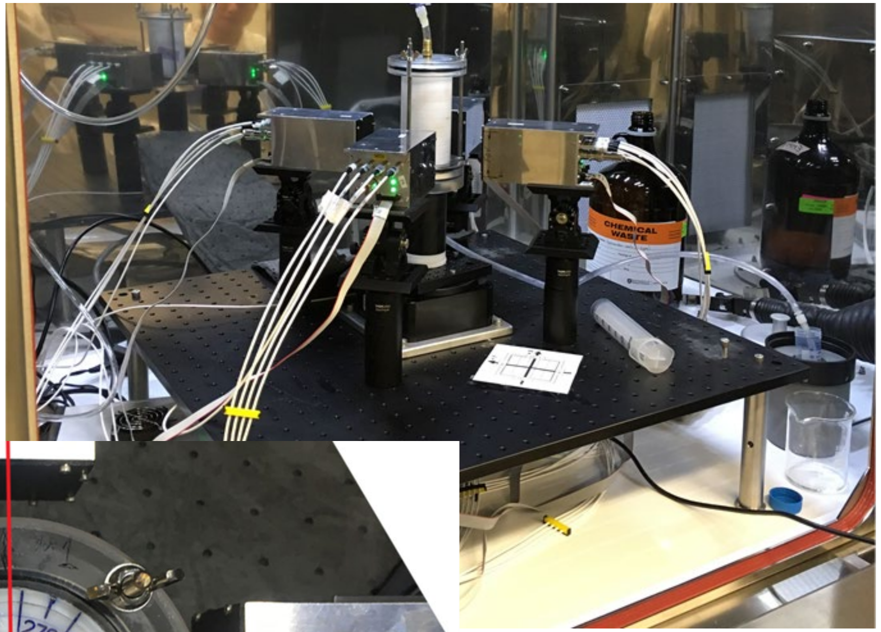
Positron travels 1-3 mm before annihilation (depending on energy)

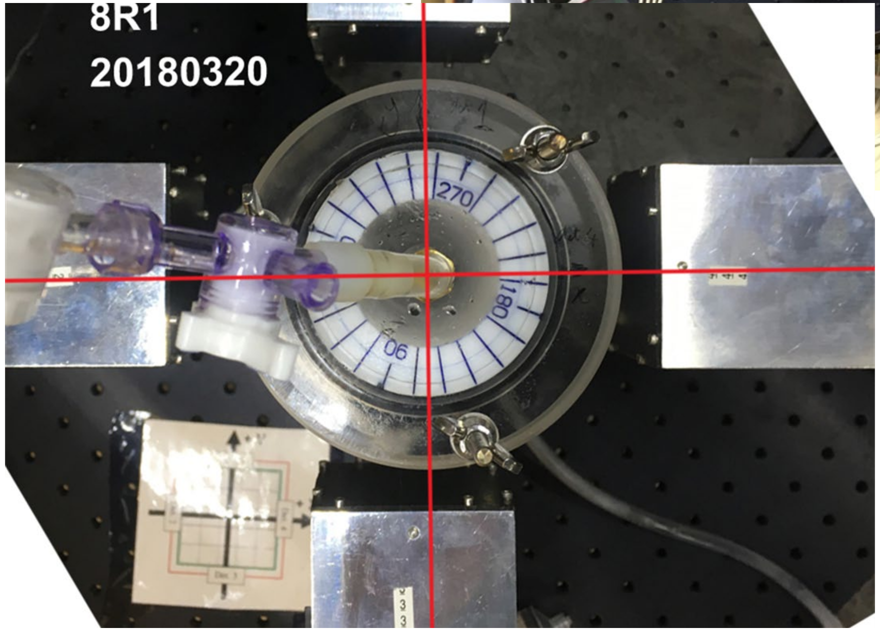
Energy and Momentum conservation
- 511 keV Photons and back-to-back



Simultaneous detection of two 511KeV photons

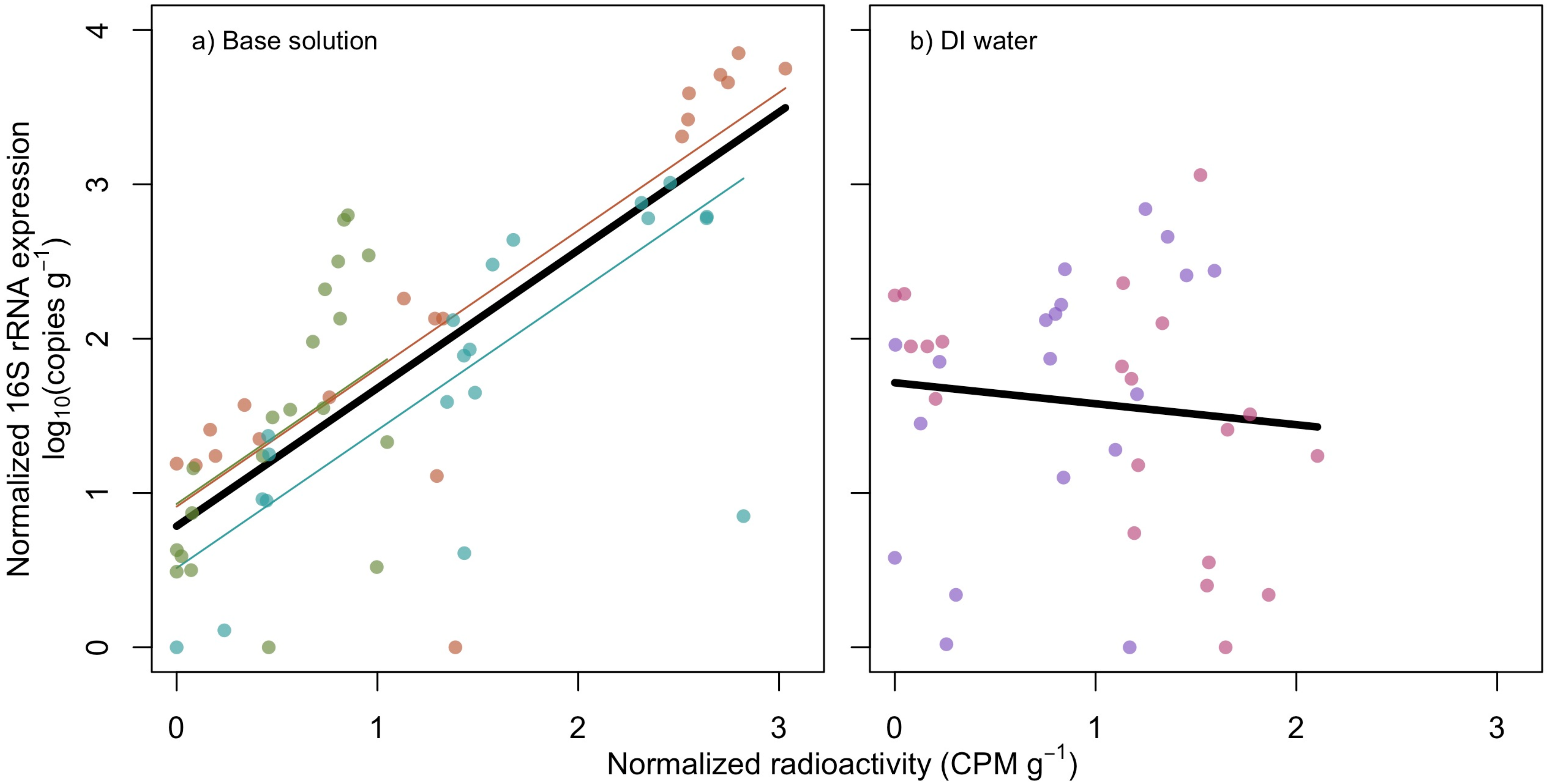
^{18}F-fludeoxyglucose
(^{18}F-FDG)
→





You measure what stays in the system!

Results



a) Base solution
b) DI water
Normalized 16S rRNA expression
$\log_{10}$(copies g^{-1})
Normalized radioactivity (CPM g^{-1})
0
1
2
3
4

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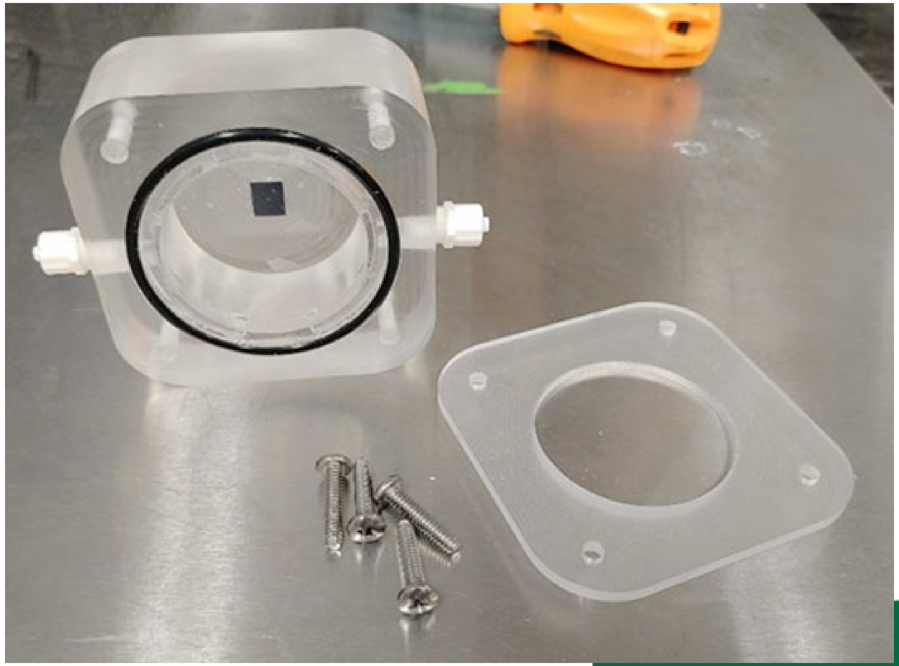
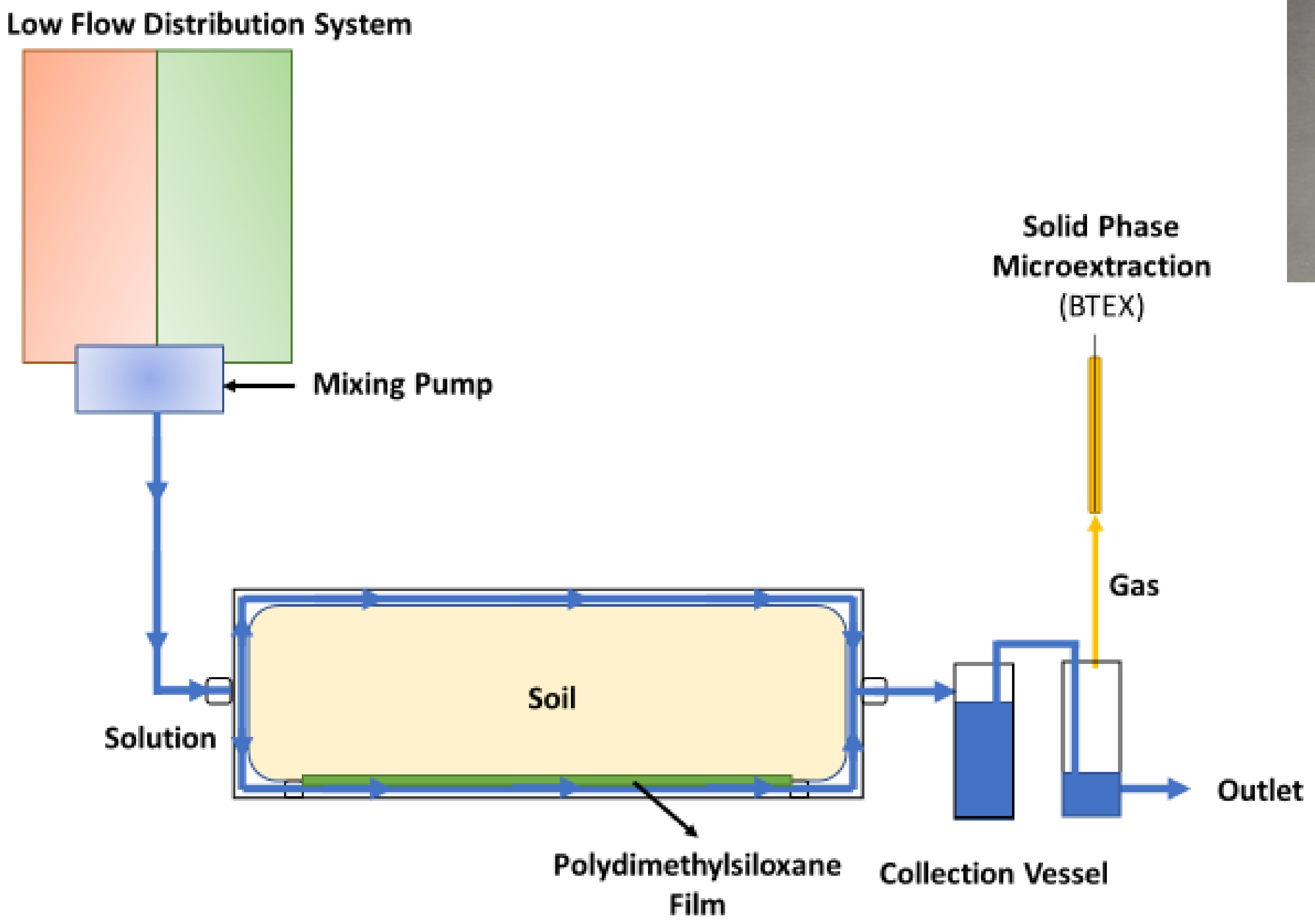
Conclusions and Next Steps

- General trends were evident
  - Interference/Dilution effects due to microcosm design
- Further development of the focus solutions is warranted
- Evaluate sorption kinetics in these systems

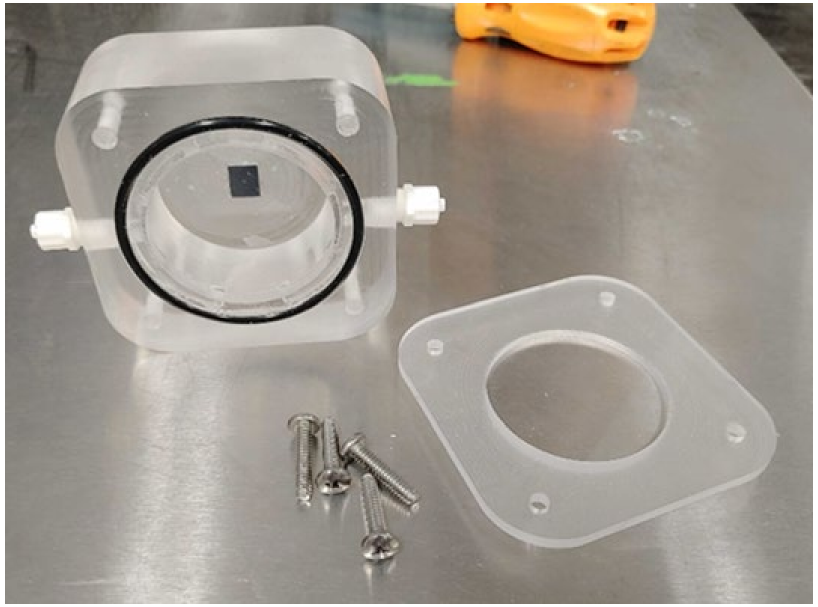


- **Comparing to sorption kinetics experimental set-ups**
- **Assess sorption of PO_4**

Next Steps



Low Flow Distribution System
Mixing Pump
Solid Phase
Microextraction
(BTEX)
Gas
Soil
Solution
Outlet
Polydimethylsiloxane
Film
Collection Vessel



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Summary

- Assess biostimulation holistically to develop conceptual model to estimate degradation rates
  a) Site specific geochemistry
  b) Microbial activity

- Goal: create a model that can predict an effective solution for all sites
  - Understand which geochemical parameters influence or condition biostimulatory solutions

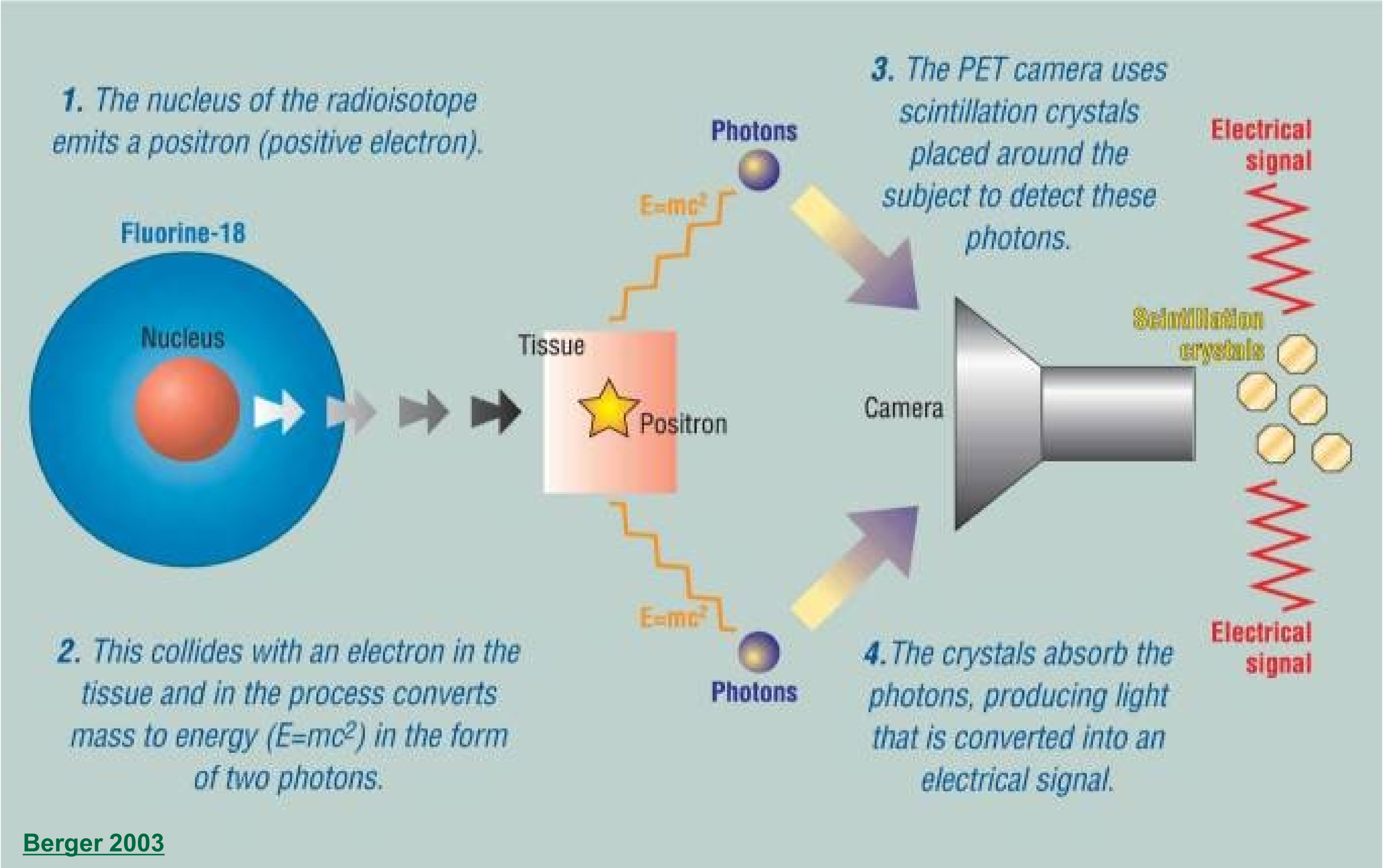
Thank you!

Acknowledgements:

Analysis: Drs. Steven Siciliano and Steven Mamet

University of Saskatchewan’s Environmental Soil Toxicology Laboratory
Government of Yukon’s Site Assessment and Remediation Unit
Jacobs Engineering

How do we trace PET isotopes?



Assessing Microbial Activity

Increasing Benzene Biodegradation via Delivery of a Conditioned Biostimulatory Solution

- **Objective:** estimate the influence of 'conditioned' biostimulatory solutions on benzene degradation.

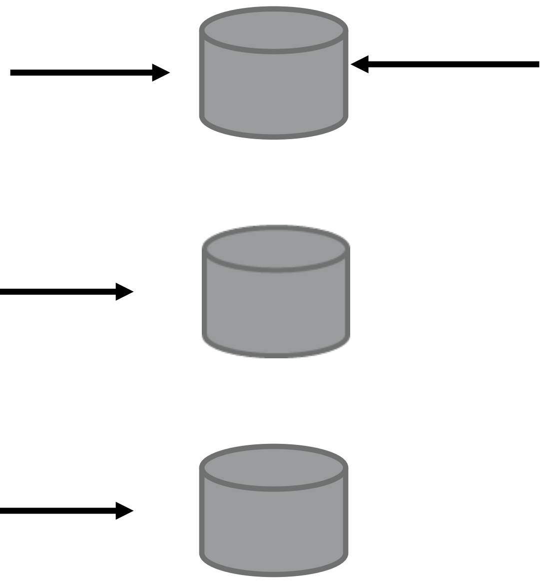
Assessing Microbial Activity

- **Objective:** estimate the influence of 'conditioned' biostimulatory solutions on benzene degradation.

Conditioned Solutions
from Study #1

Base IRC Solution
positive control

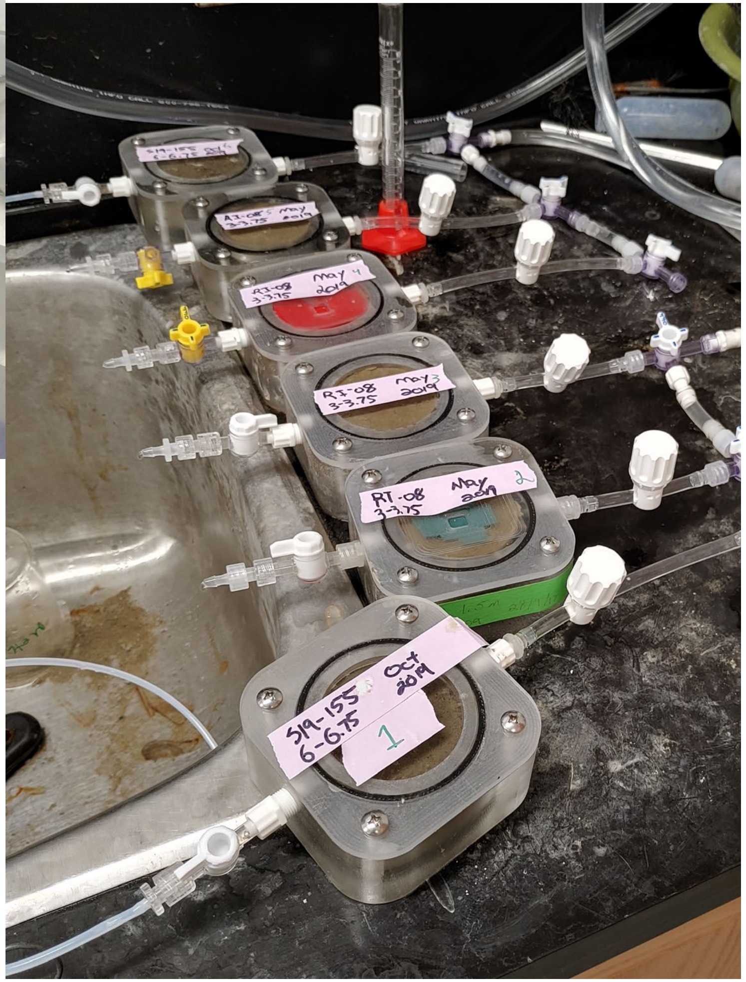
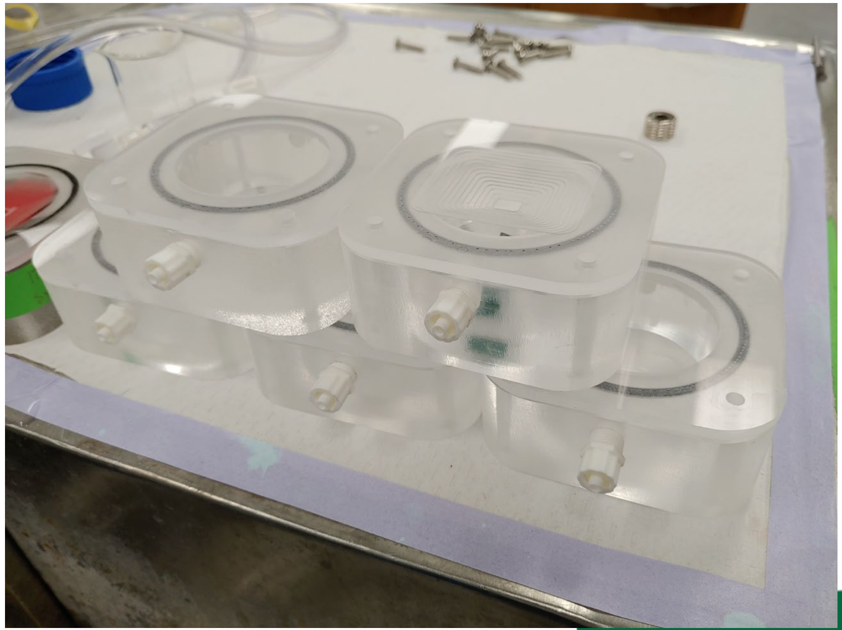
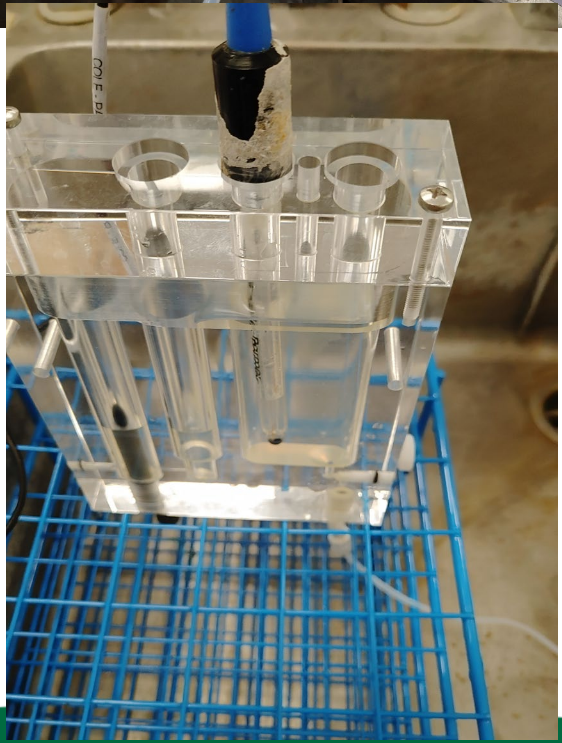
Deionized Water
negative control



20 mL Serum Bottle
- **1 mL benzene (0.4 – 1 ppm)**
- **2 mL Ulrich culture**
- **9 mL solution**

- **Minimum three replicates per solution**
- **30 day trial**
  - **Benzene concentrations**
  - **Gene expression**


Purell
HEALTHY SOAP
Groundwater
RRM


S19-155
6-6.75
Oct
2019
1



Lessons Learned