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Optimizing Biostimulatory Solutions Using Site Specific Conditions to Enhance Petroleum Hydrocarbon Degradation Rates

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ems

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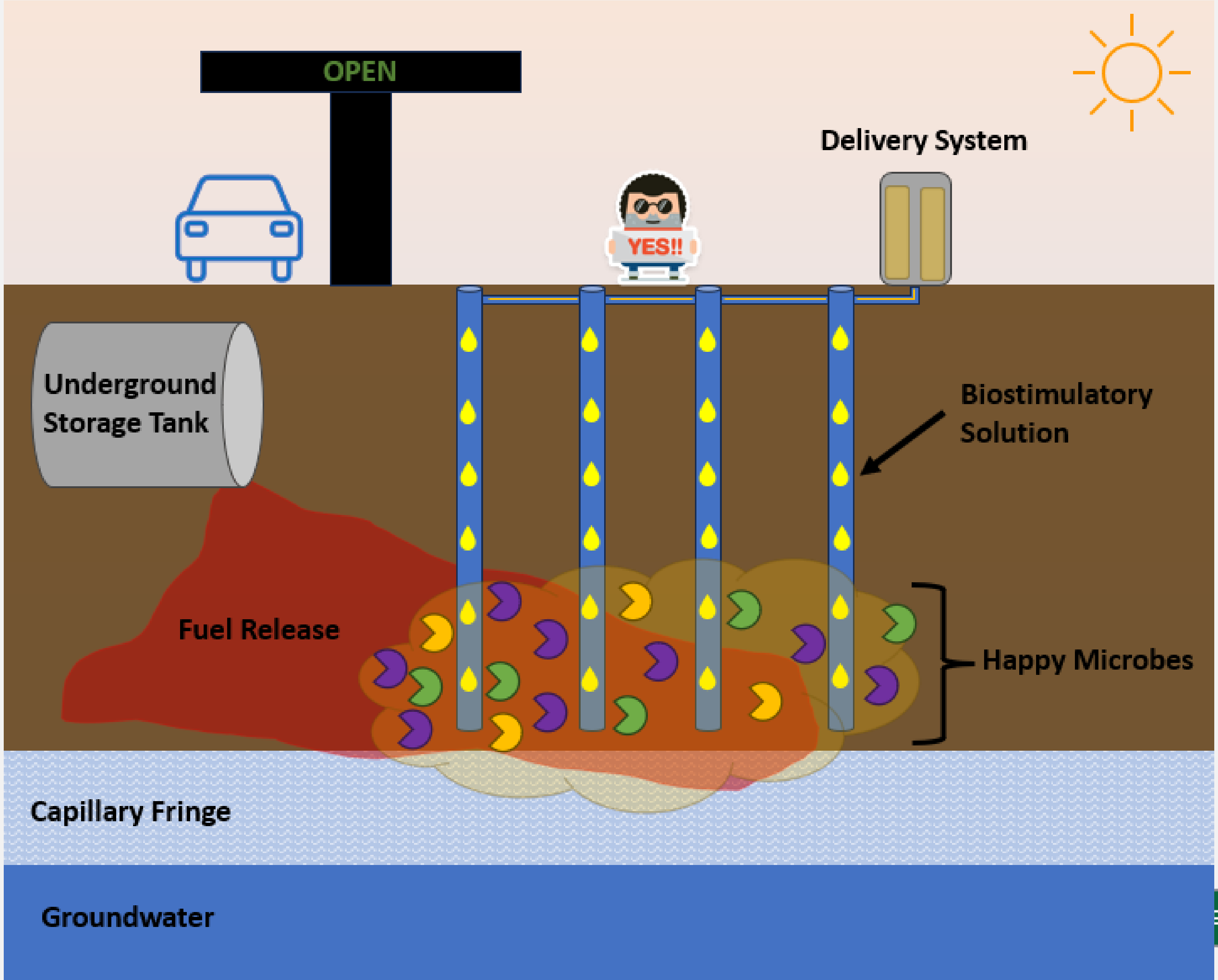
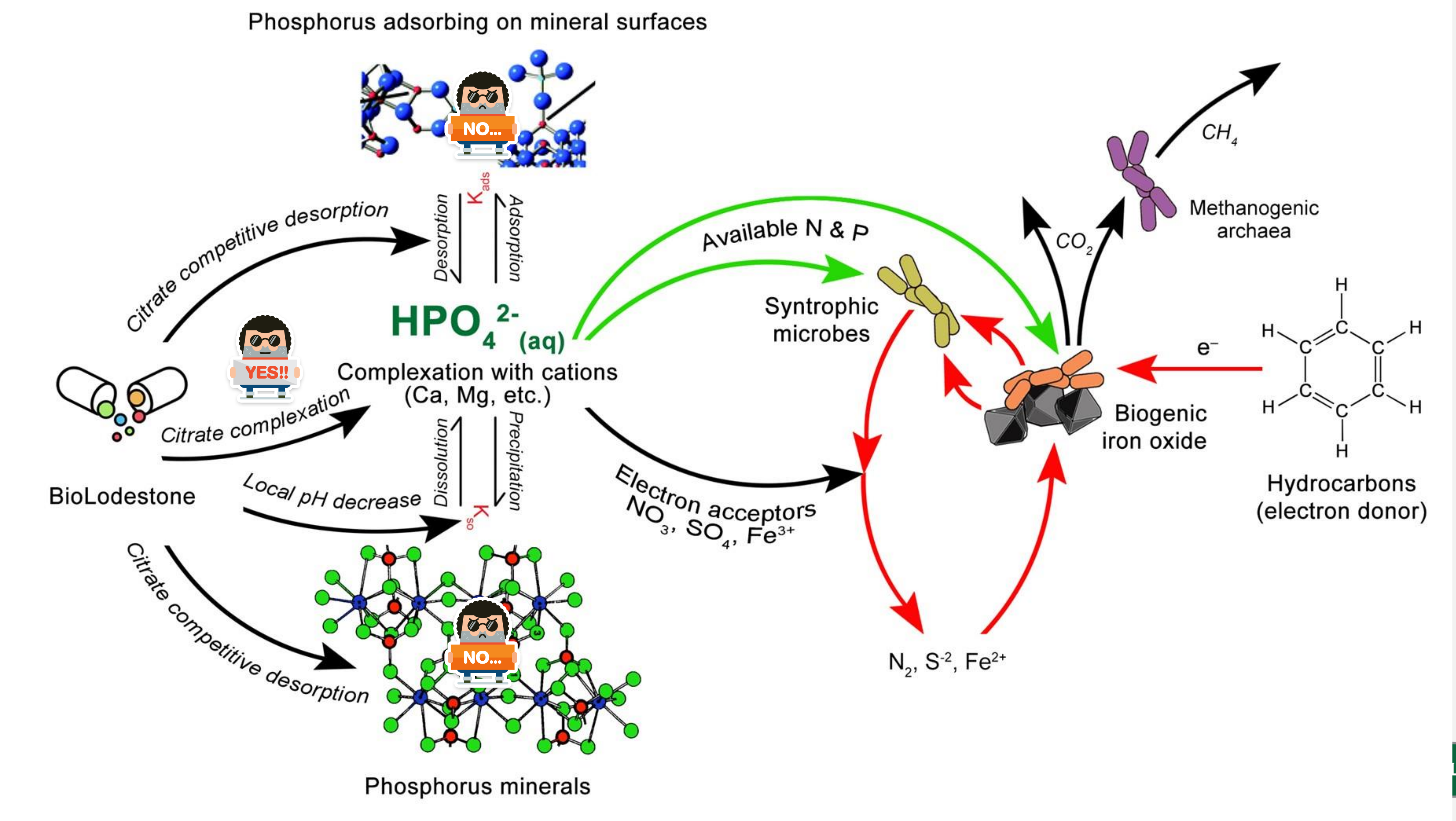
Project Background



Biostimulatory Solution



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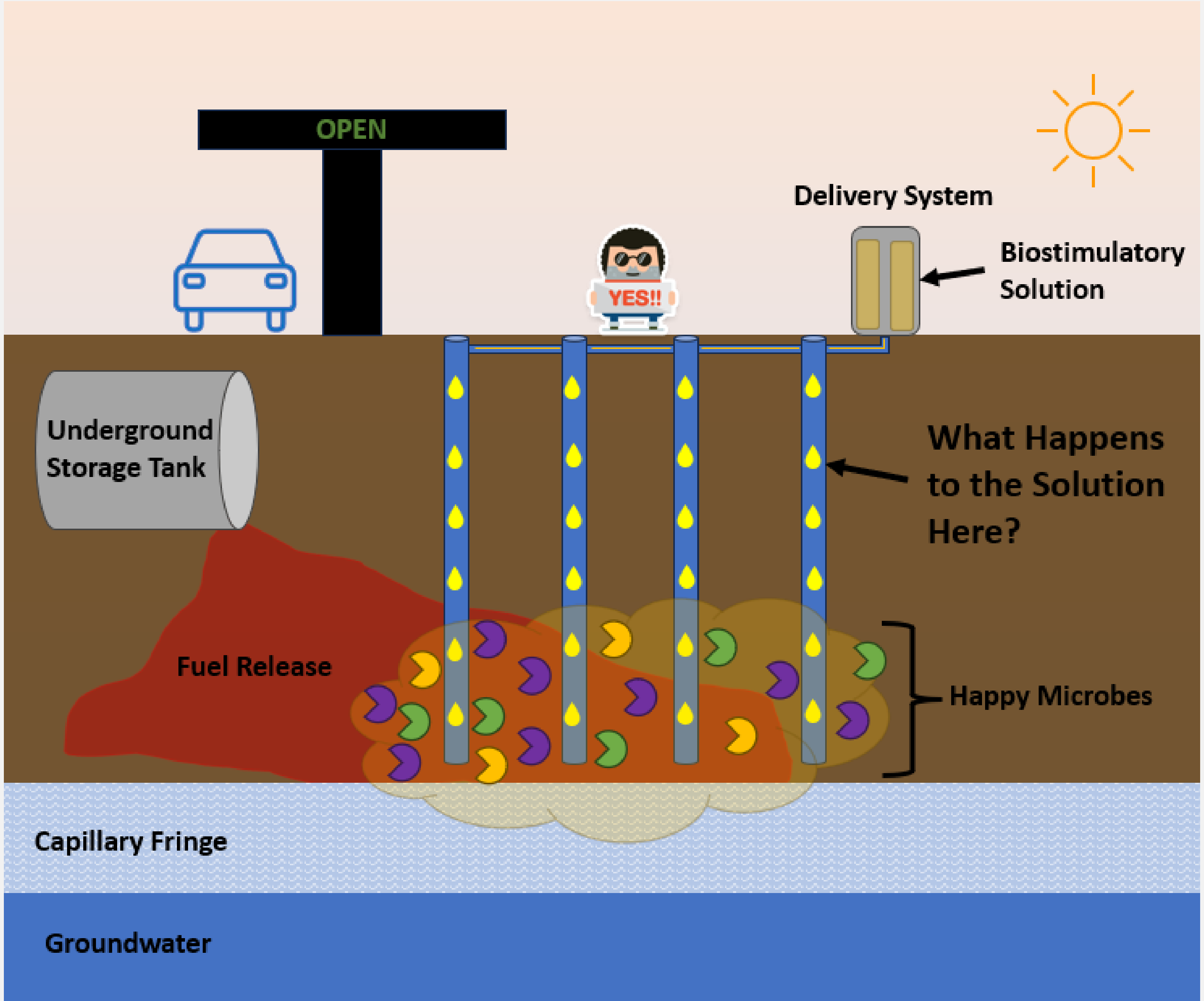
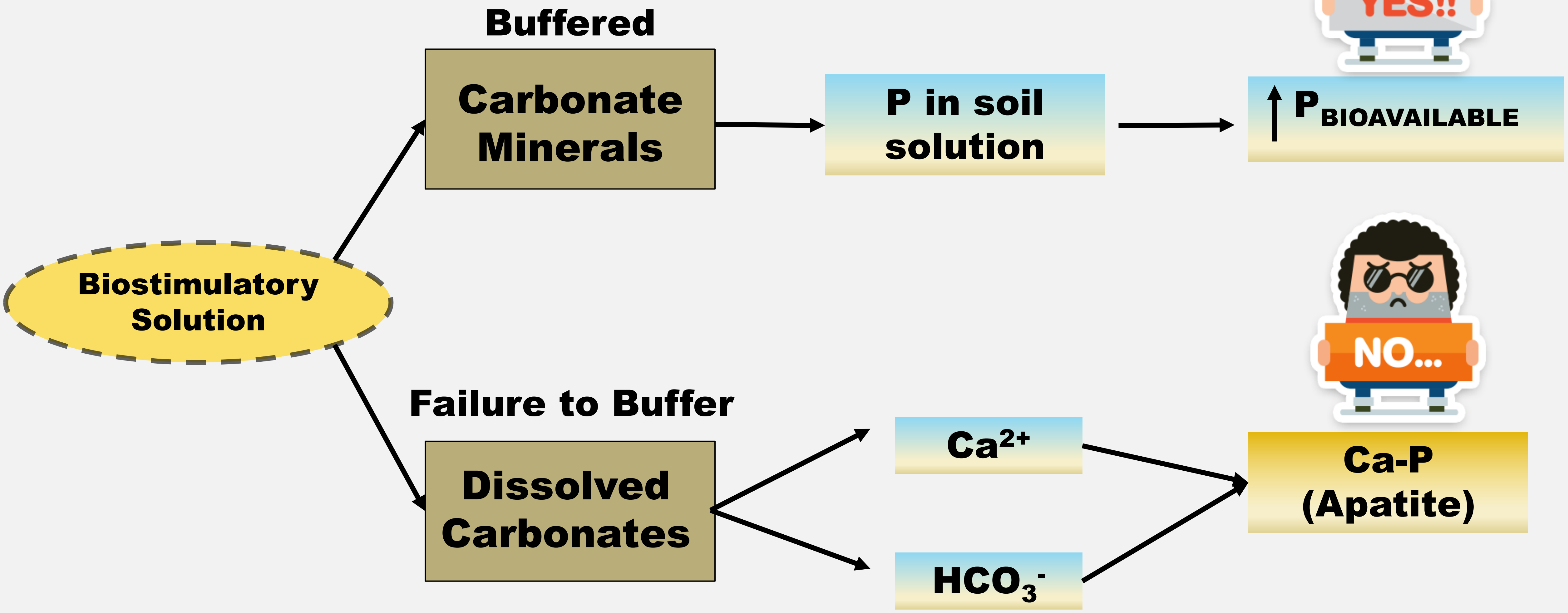
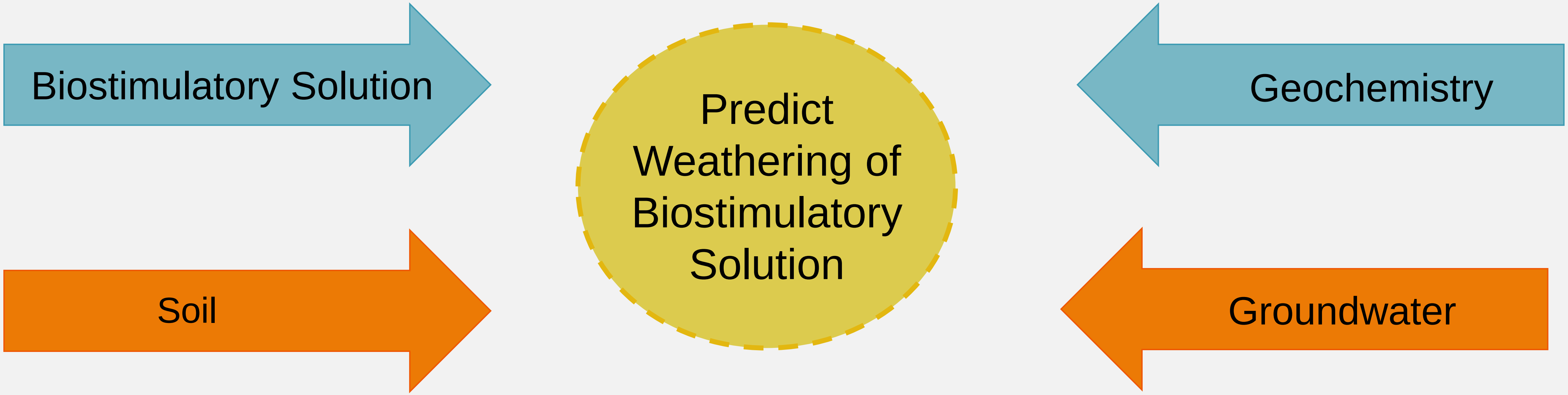


Buffering Capacity and Calcareous Soils



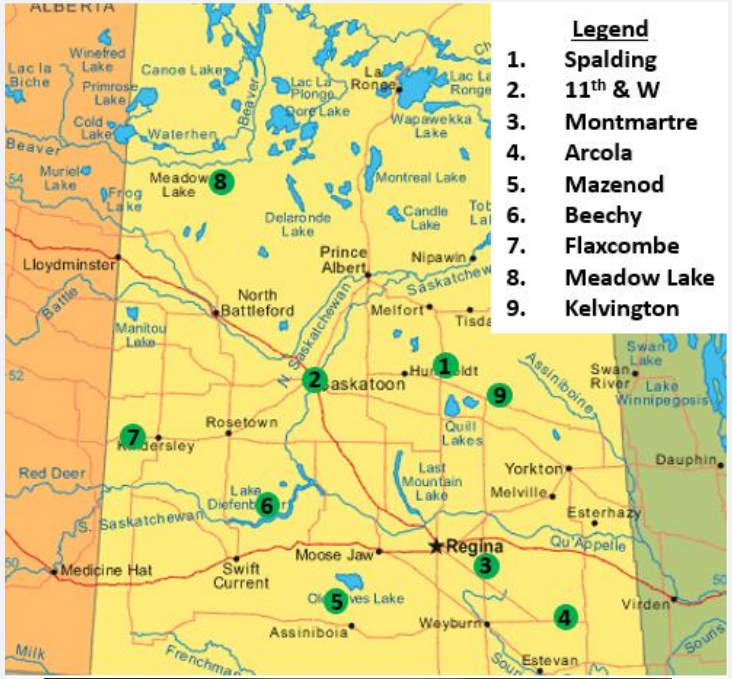
Project Objective

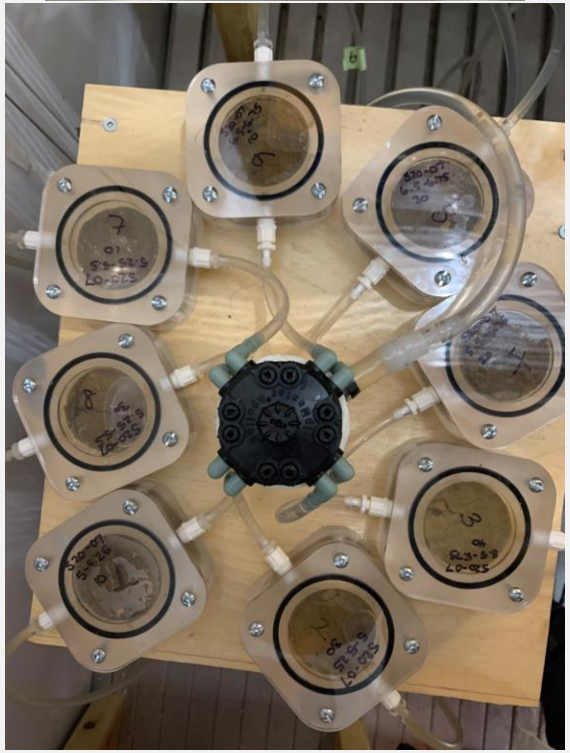
Laboratory **Field**



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

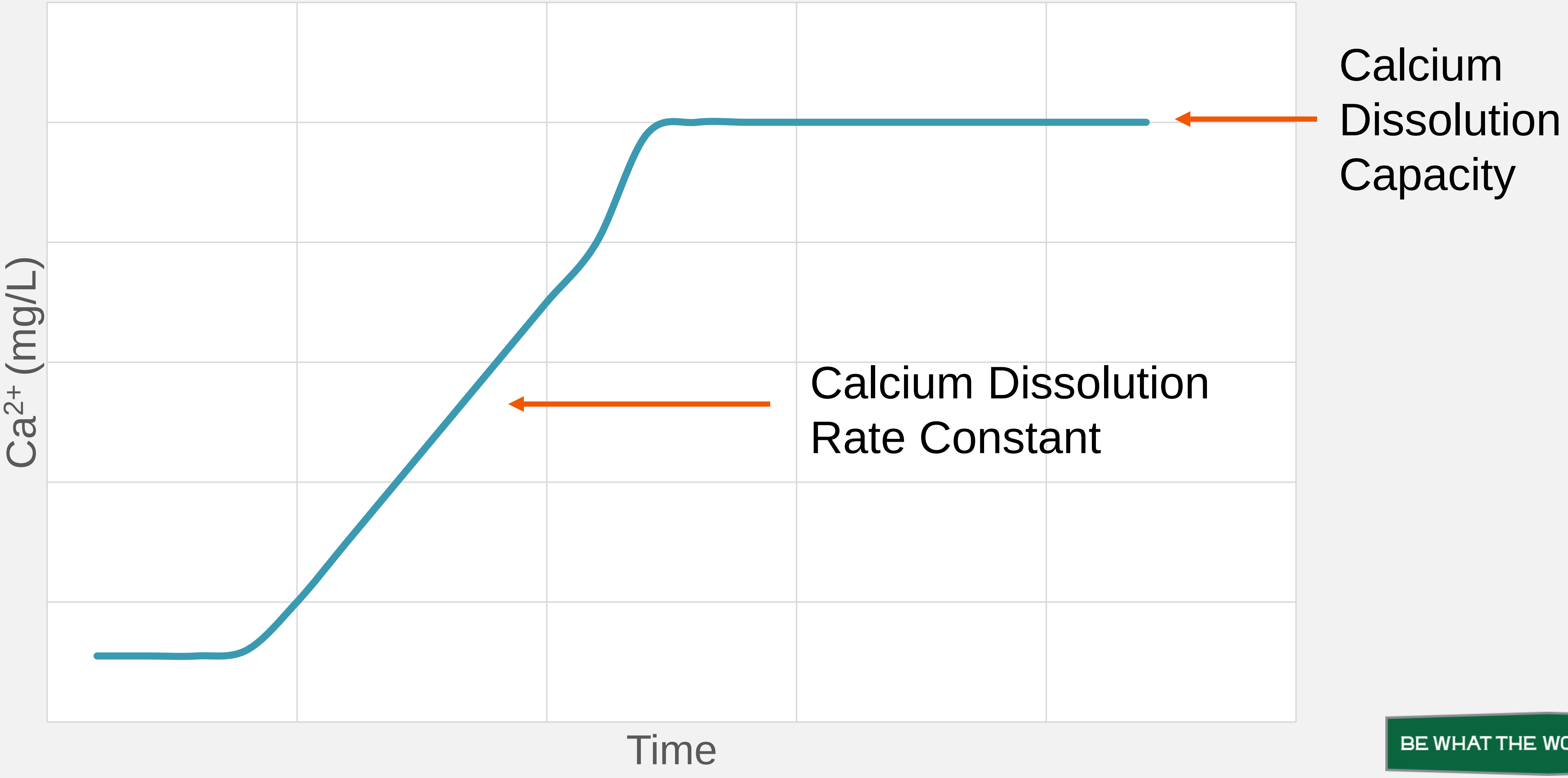
Laboratory Experimental Design





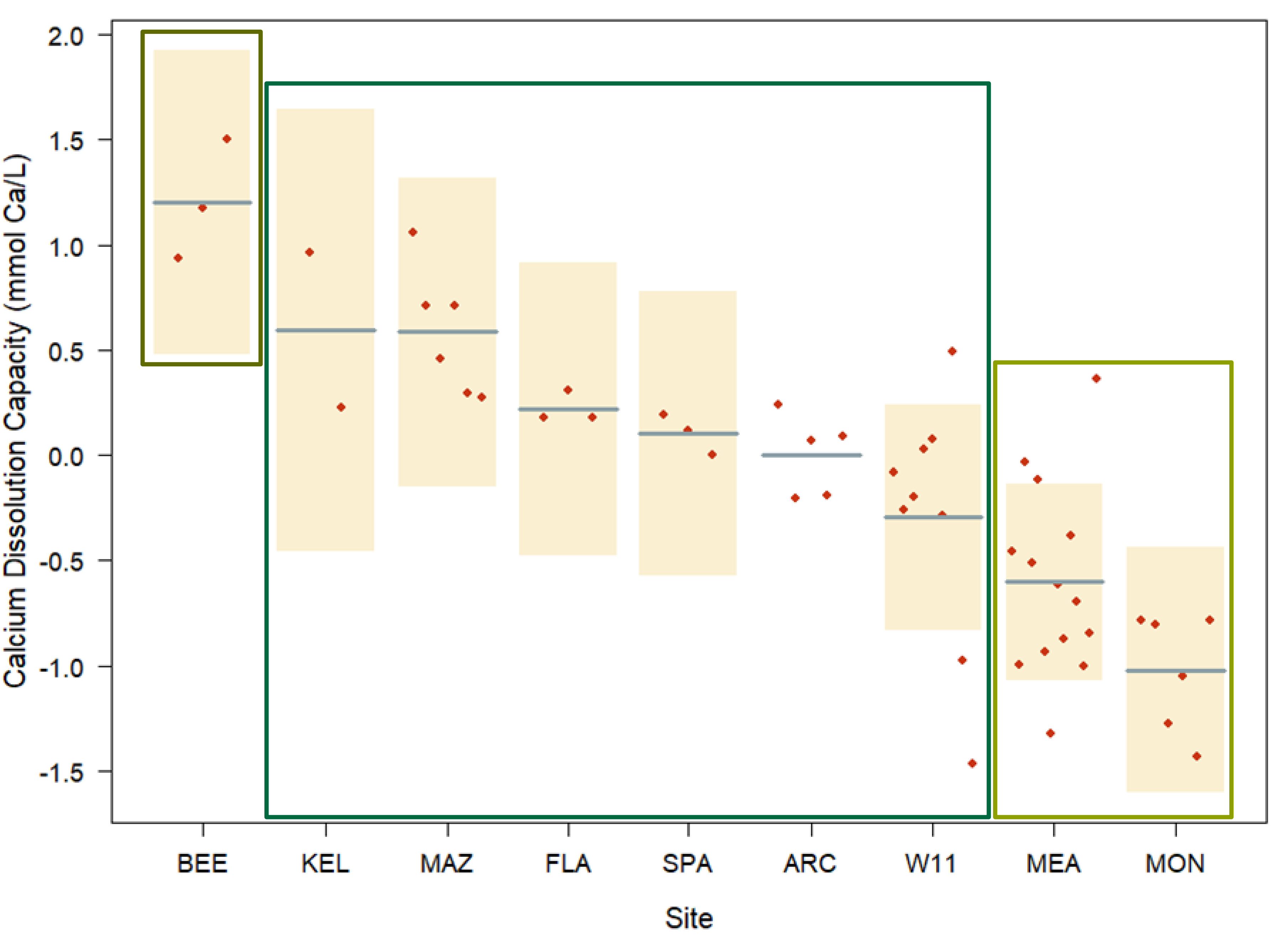
Calcium as a Surrogate for Buffering Capacity

$$CaCO_3 + H_2CO_3 \leftrightarrow \boxed{Ca^{2+}} + 2HCO_3^-$$



Calcium Dissolution Kinetics

Higher
Ca dissolution
capacity
=
Higher soil buffering
capacity



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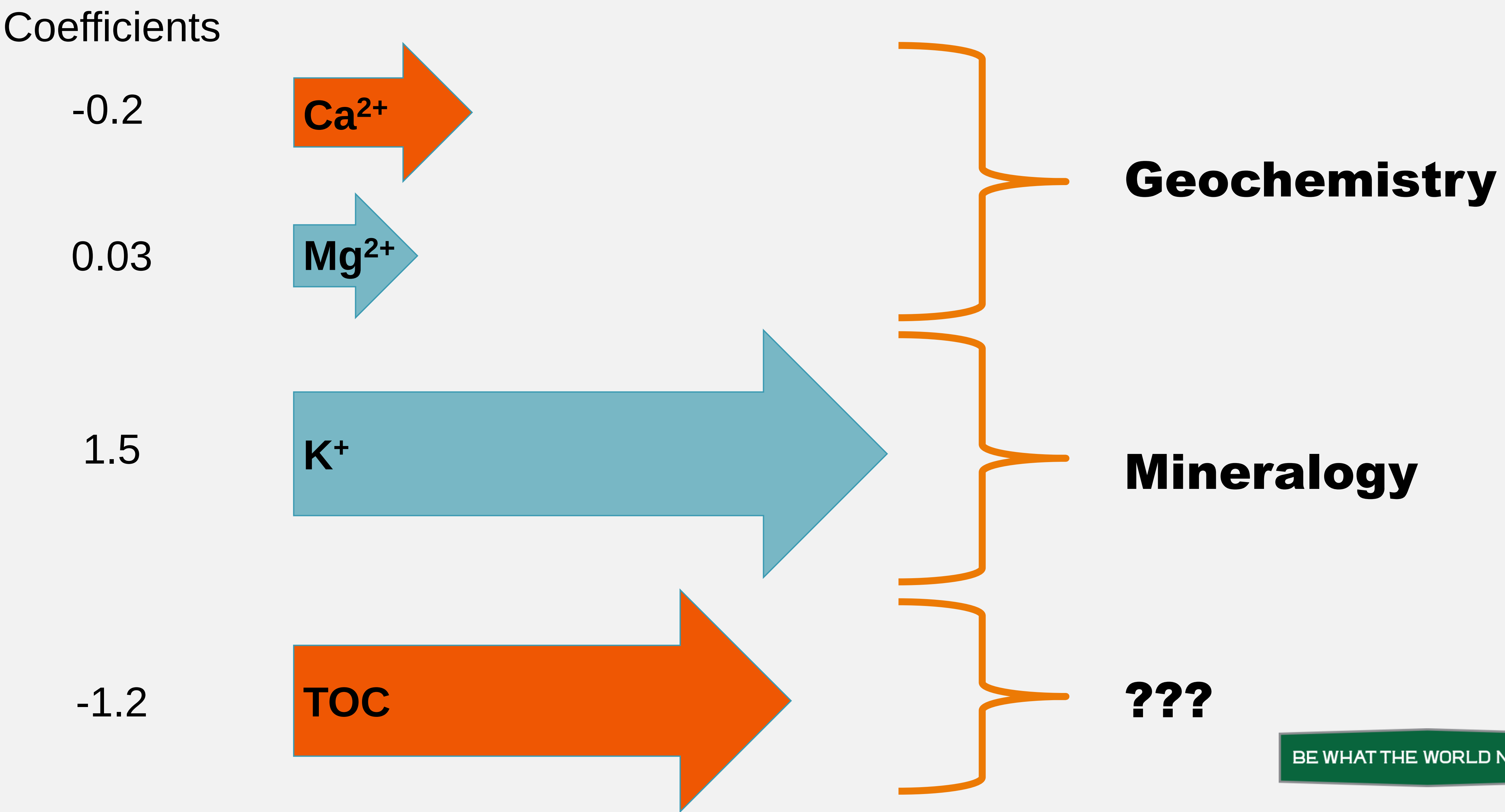
Assessing Influence of Site-Specific Parameters



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Field Study: Experimental Design

- Collect groundwater samples from 16 Sites across Alberta, Saskatchewan and Manitoba
  - 2^{+} years of ongoing in-situ biostimulation
  - Minimum of five monitoring wells at each site
  - Collected samples from across the PHC footprint
  - Analyzed for routine water quality parameters

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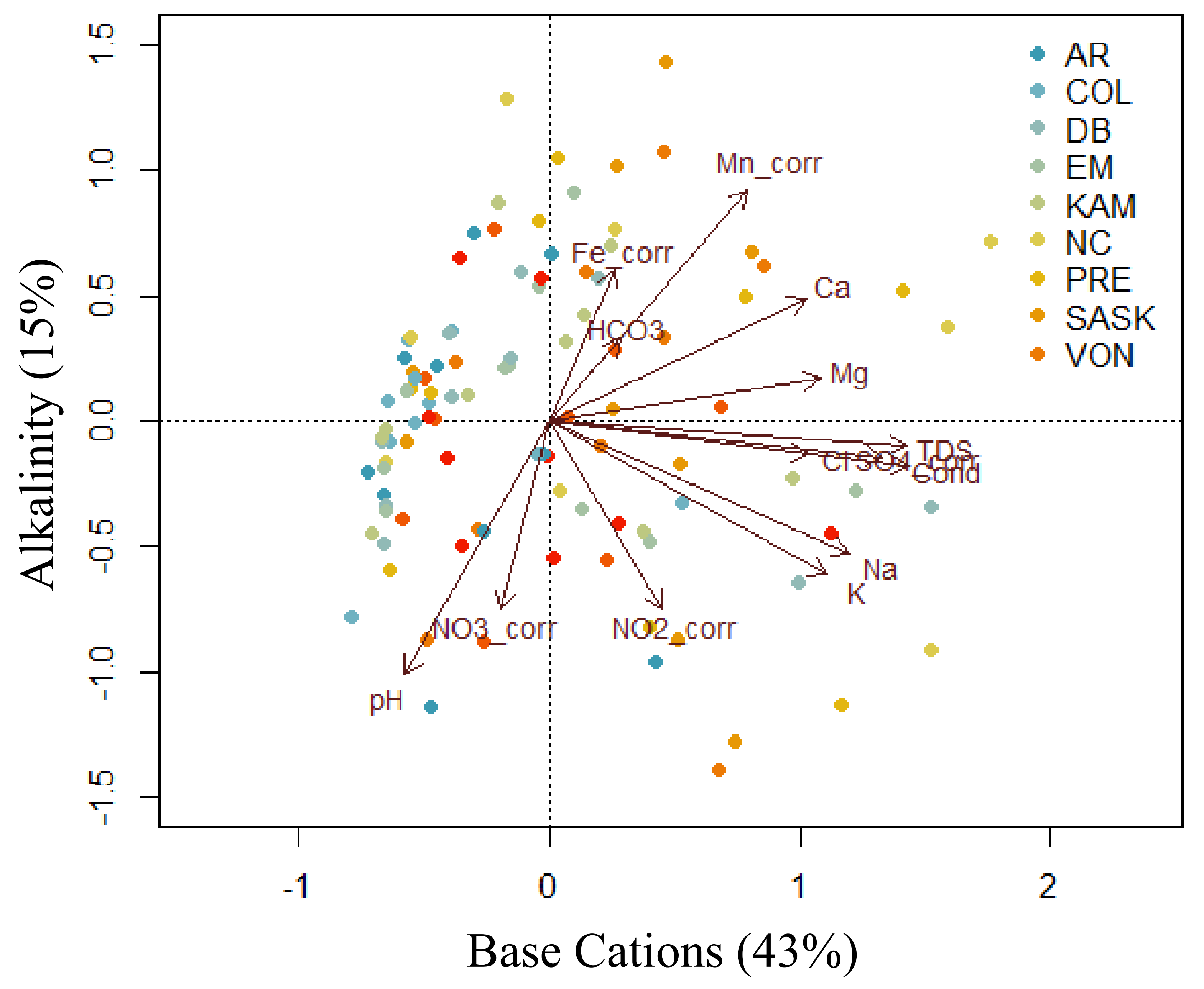
Field Study: Preliminary Results



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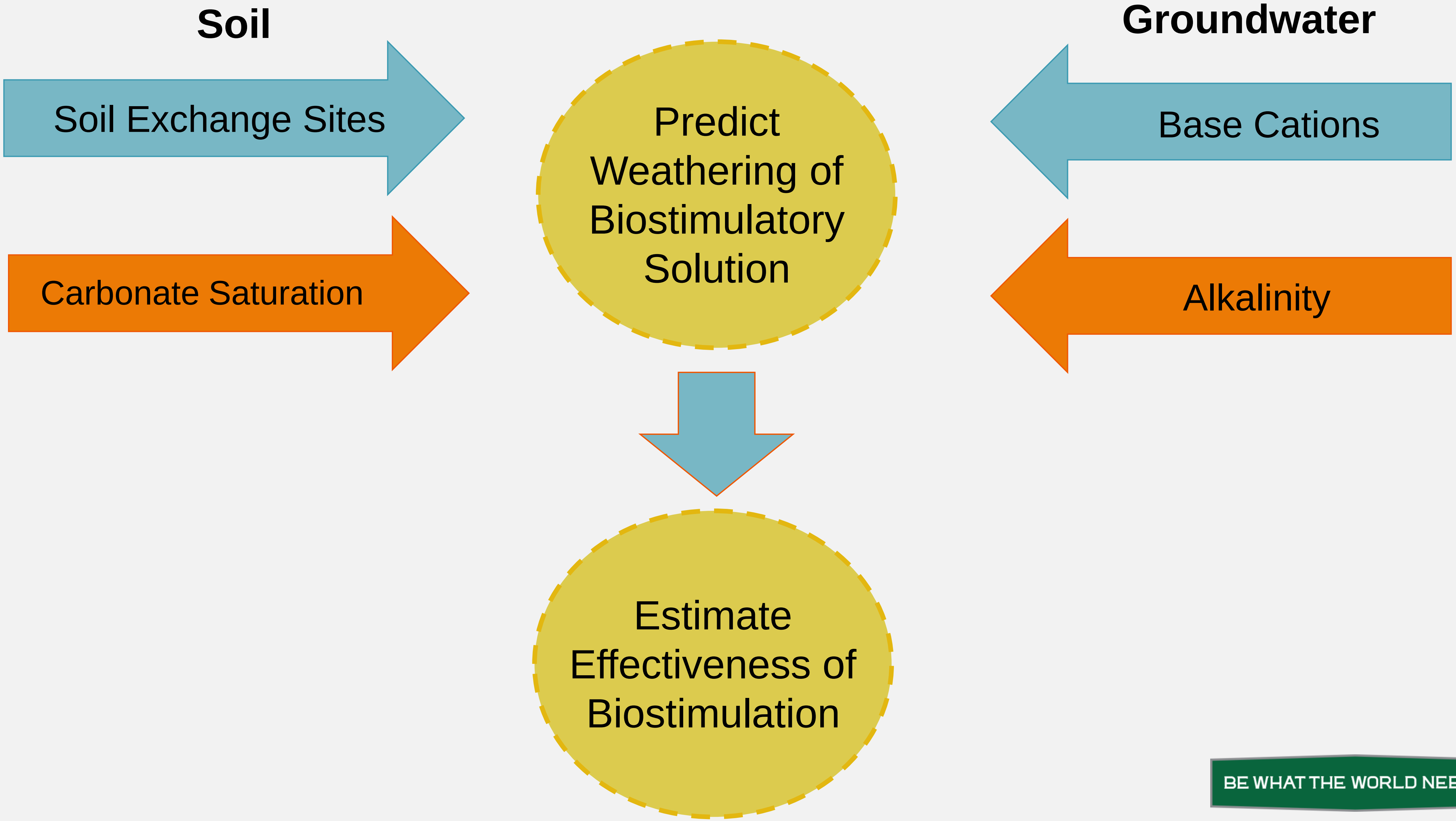
Conclusions



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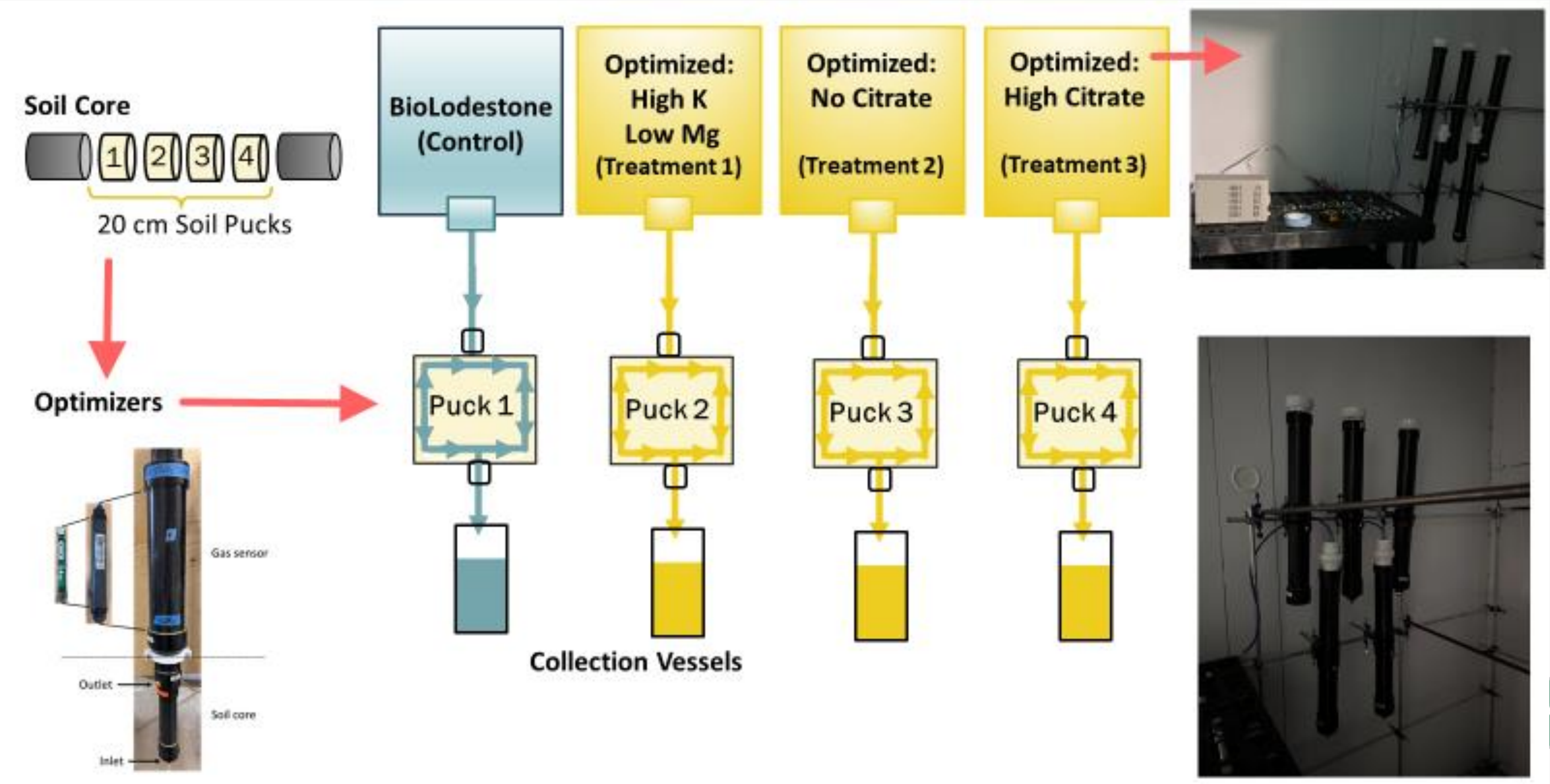
Next Steps

- Laboratory experiment using hydrocarbon impacted soils to determine if solution ‘weathering’ impacts degradation rates
  - Real time monitoring of PHC degradation, depletion by-products (O_2, CO_2, CH_4) & ions at select intervals



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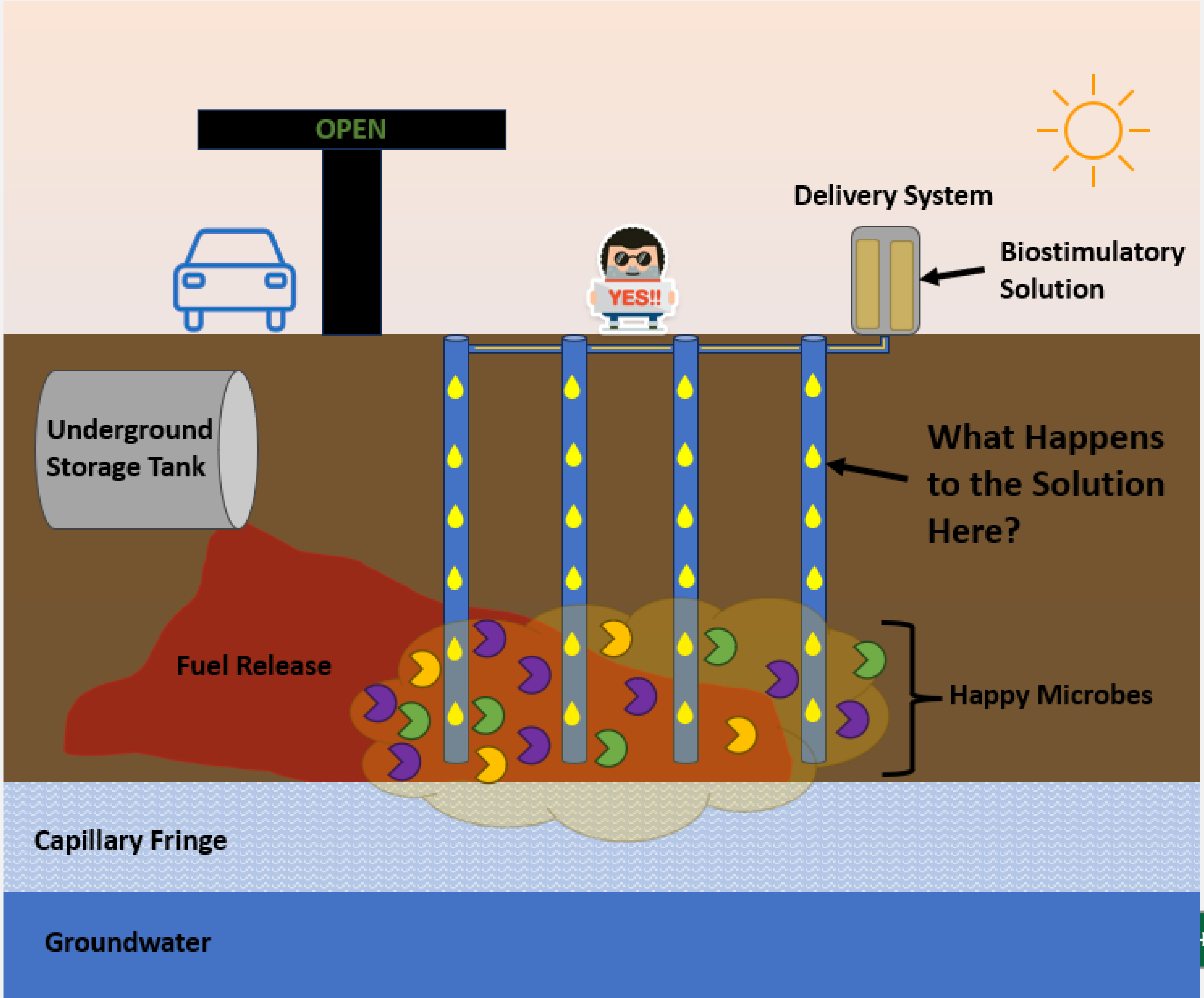

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- Advisory Committee:
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NSERC CRSNG

CO-OP

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Thank you!

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Project Background

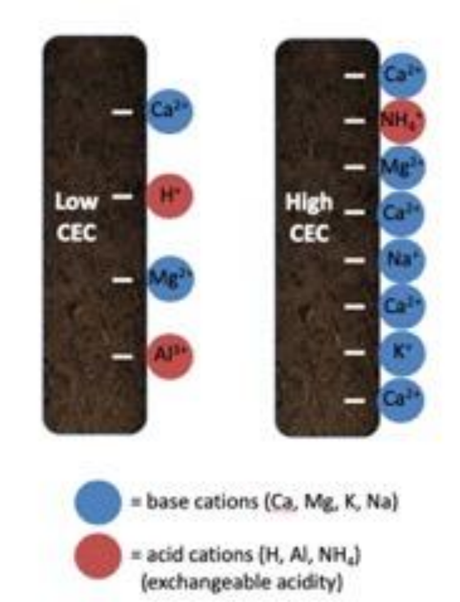
- Data gaps surrounding effectiveness of in situ bioremediation
  - Influence of site specific properties over looked in “off the shelf” remedies

- 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)*

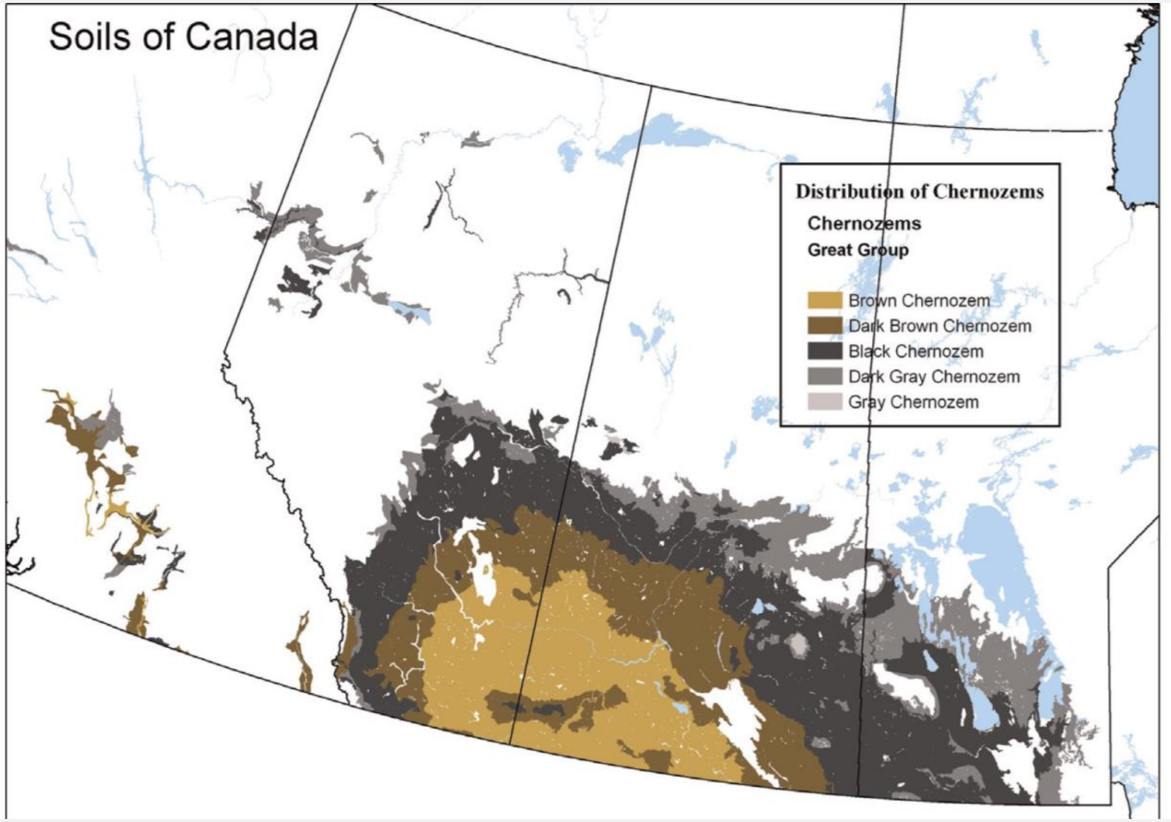
- However, remediation at some sites has ***stalled***
  - Believed to be related to buffering capacity and carbonate mineralogy

Buffering Capacity and Calcareous Soils

- 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



https://ohioline.osu.edu/factsheet/anr-81



- Neutral to Alkaline Soils
- $CaCO_3$ and $MgCO_3$ minerals

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^-$$

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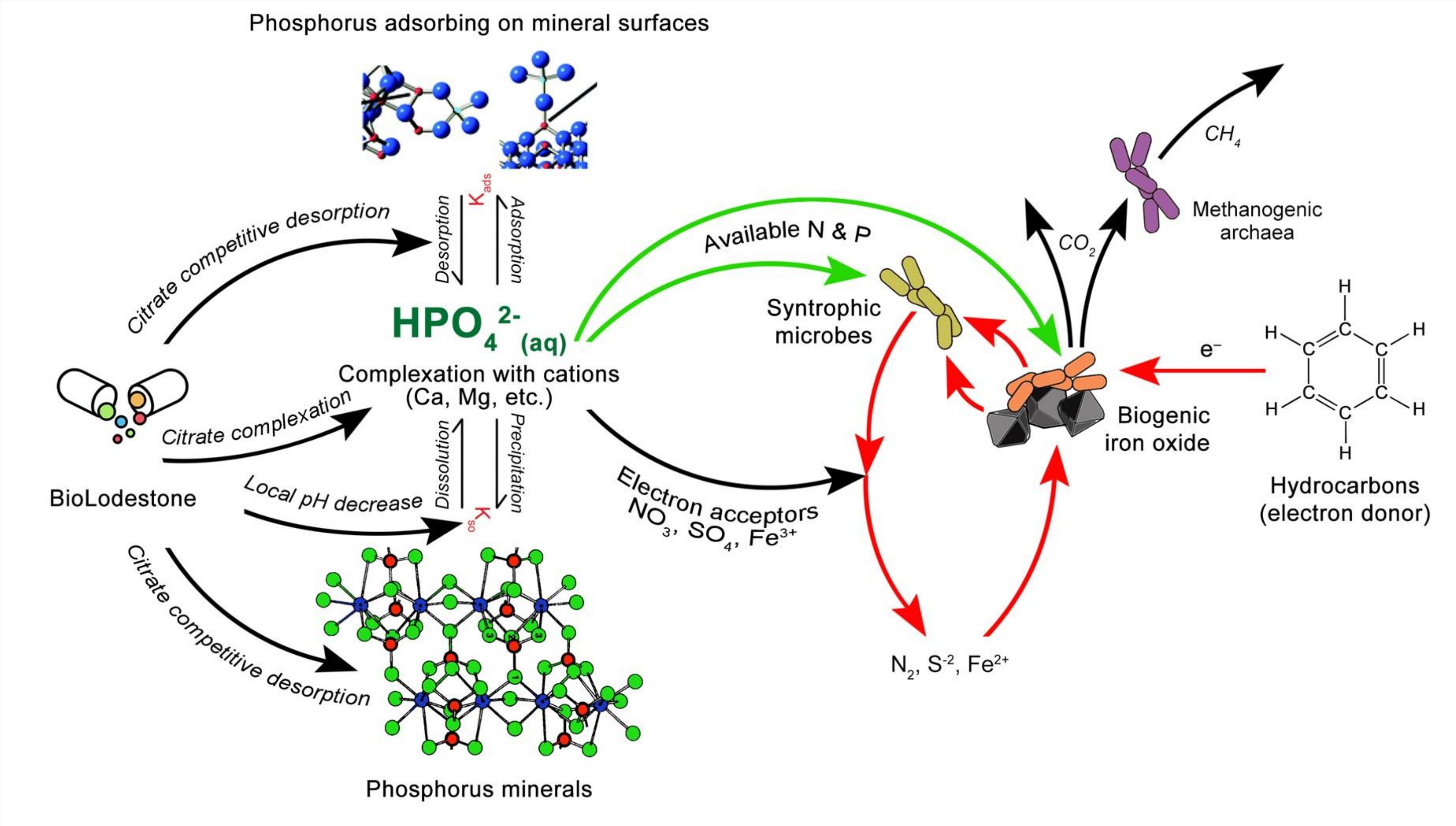
Image : https://bioone.org/journals/canadian-journal-of-soil-science/volume-91/issue-5/CJSS10022/Chernozemic-soils-of-Canada-Genesis-distribution-and-classification/10.1139/CJSS10022.short

Biostimulatory Solution

Readjust the C:N:P ratio to 100:11:1
- Additional P
- Additional N

Citrate
- Chelate Ca^{2+} & Mg^{2+}

Terminal Electron Acceptors
- Fe^{2+}
- SO_4^{2-}



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Assessing Influence of Site-Specific Soil Parameters

Site	pH	CEC	Alkalinity[1]	Ca	Mg
	unitless	meq/100g	mg/L	mg/kg	mg/kg
Arcola	8.43	4.74	248	5.5	16.3
Beechy		12.3	40		
Kelvington	7.48	16.8	76	374	152
Mazenod		19.2	36		
Montmartre	7.94	10.8	47	244	546
Meadow Lake	7.81	8.44	87	32.4	20.8
Spalding	7.42	6.42	36	237	124
11th & W	7.61	4.87	46	97.0	43.3

[1]Total Alkalinity (as $CaCO_3$)

**Also analyzed for TOC, N, S, P, Fe, Mn*

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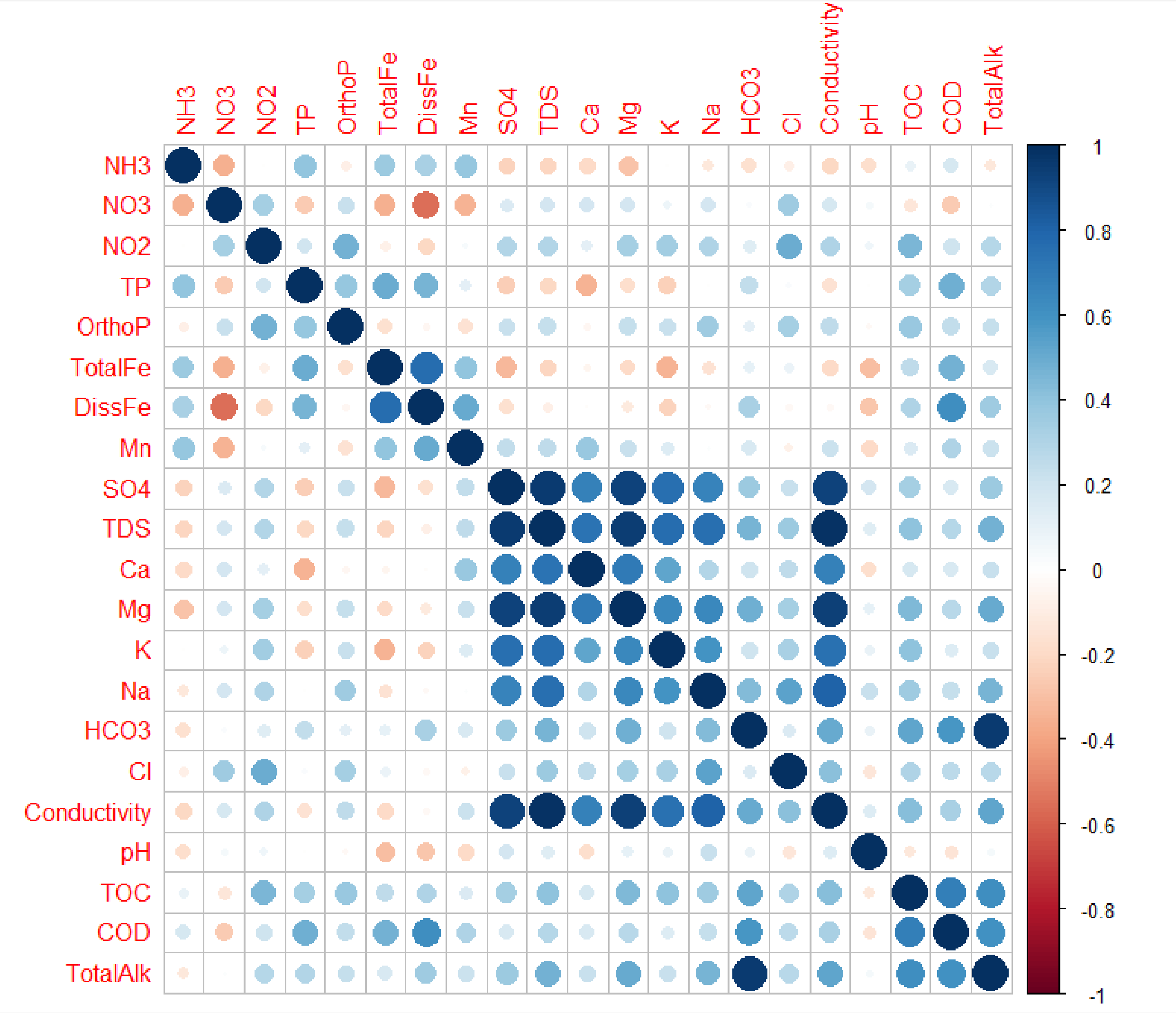
Assessing Influence of Site-Specific Groundwater Parameters



VIF > 10

- Conductivity
- TDS
- Total Alkalinity
- Orthophosphate
- SO_4

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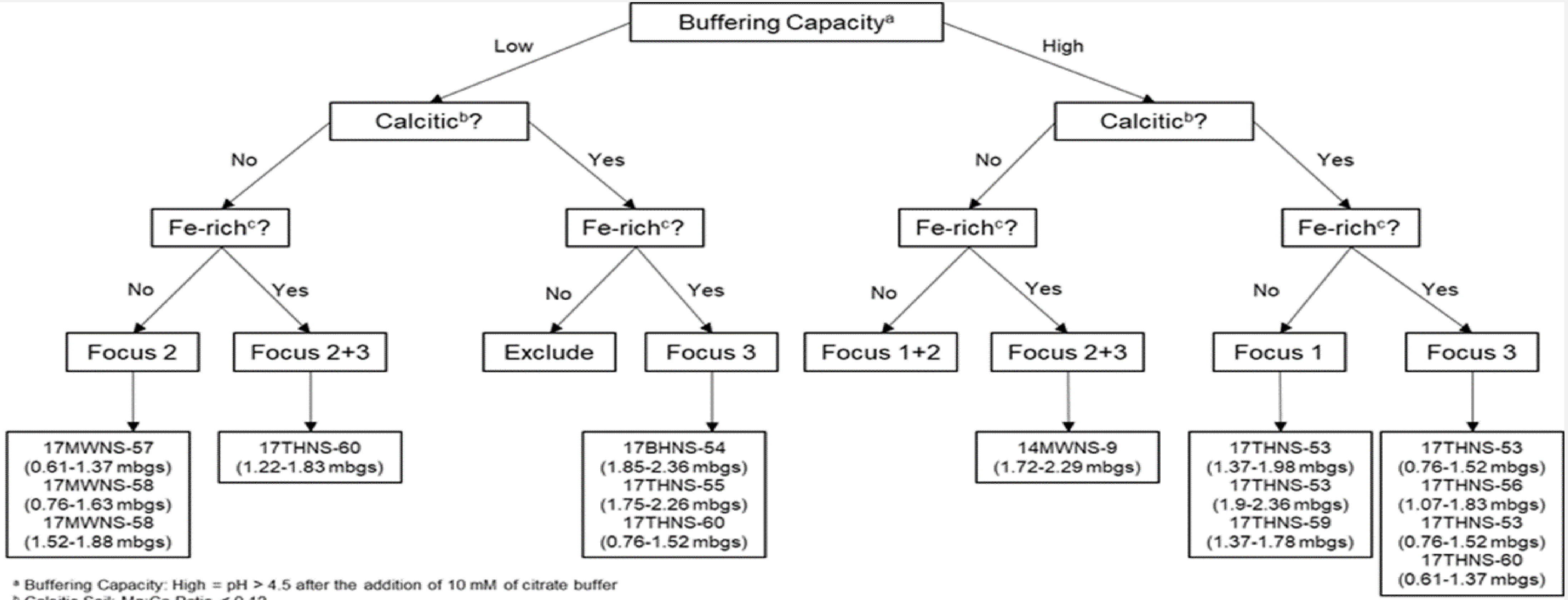
Decision Tree

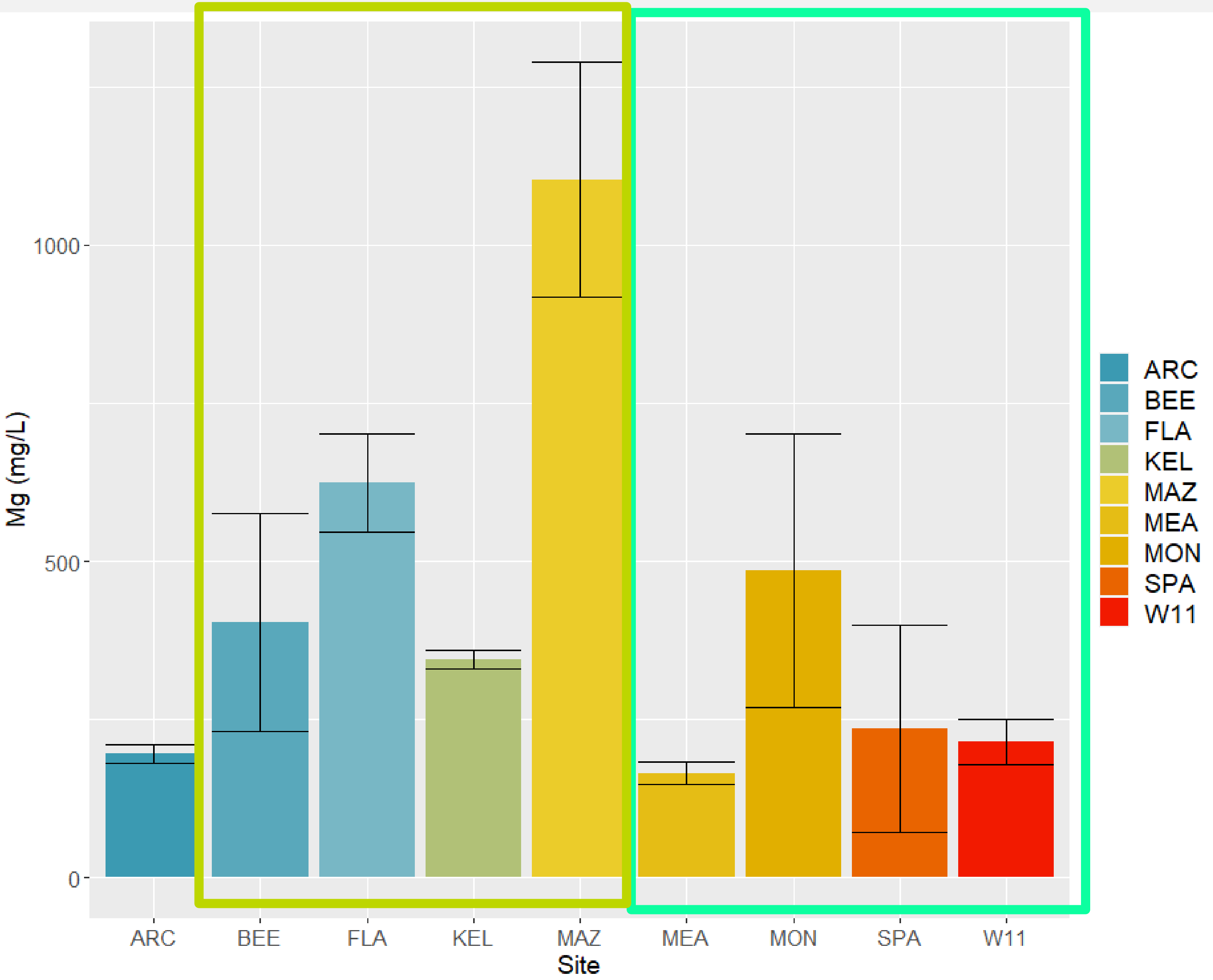


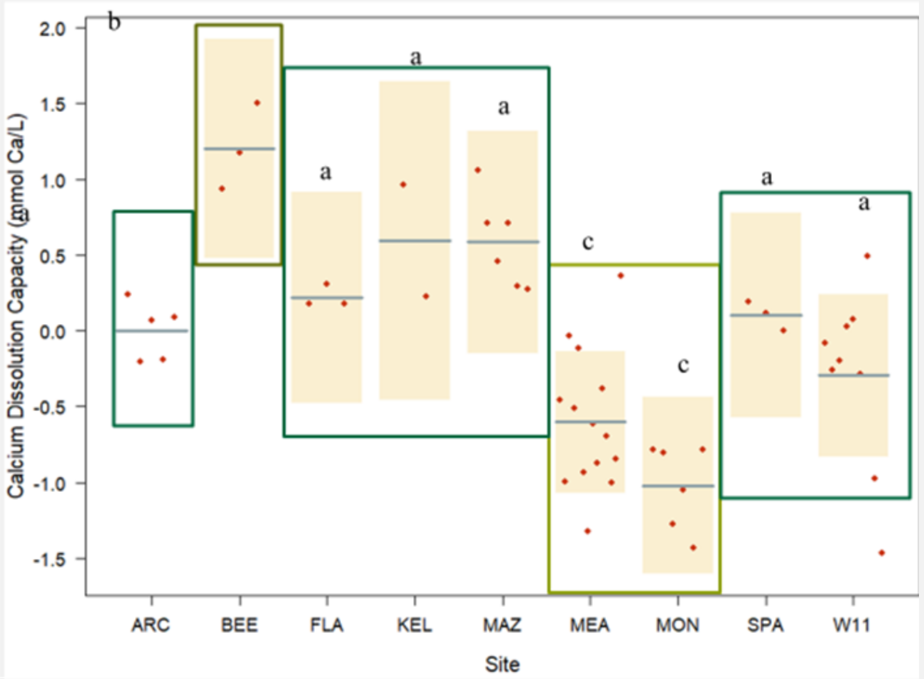
[a] Buffering Capacity: High = pH > 4.5 after the addition of 10 mM of citrate buffer
[b] Calcitic Soil: Mg:Ca Ratio < 0.12
[c] Fe-rich soil: $Fe_{solution}$ > 30 mg/L

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

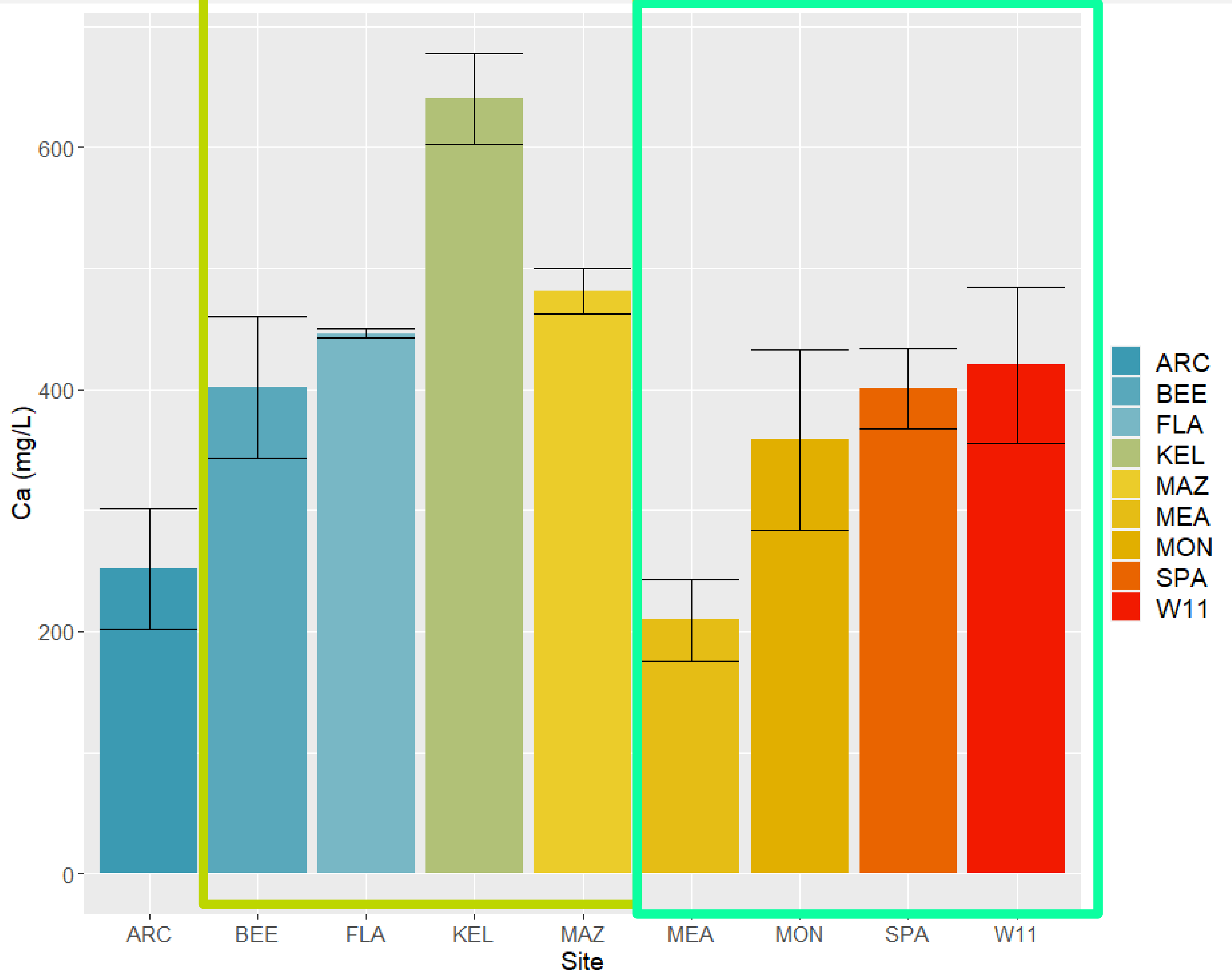
Assessing Influence of Site-Specific Parameters

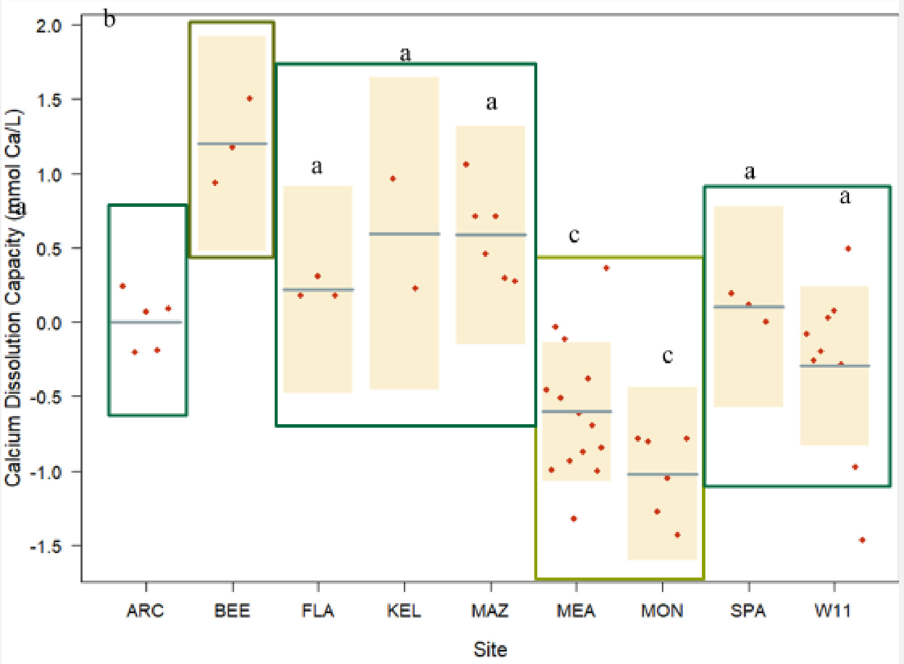




Multiple Linear Regression
(~57% of the variance was explained)
TOC, Ca, Mg & K were highly significant ($p>0.05$)

Assessing Influence of Site-Specific Parameters





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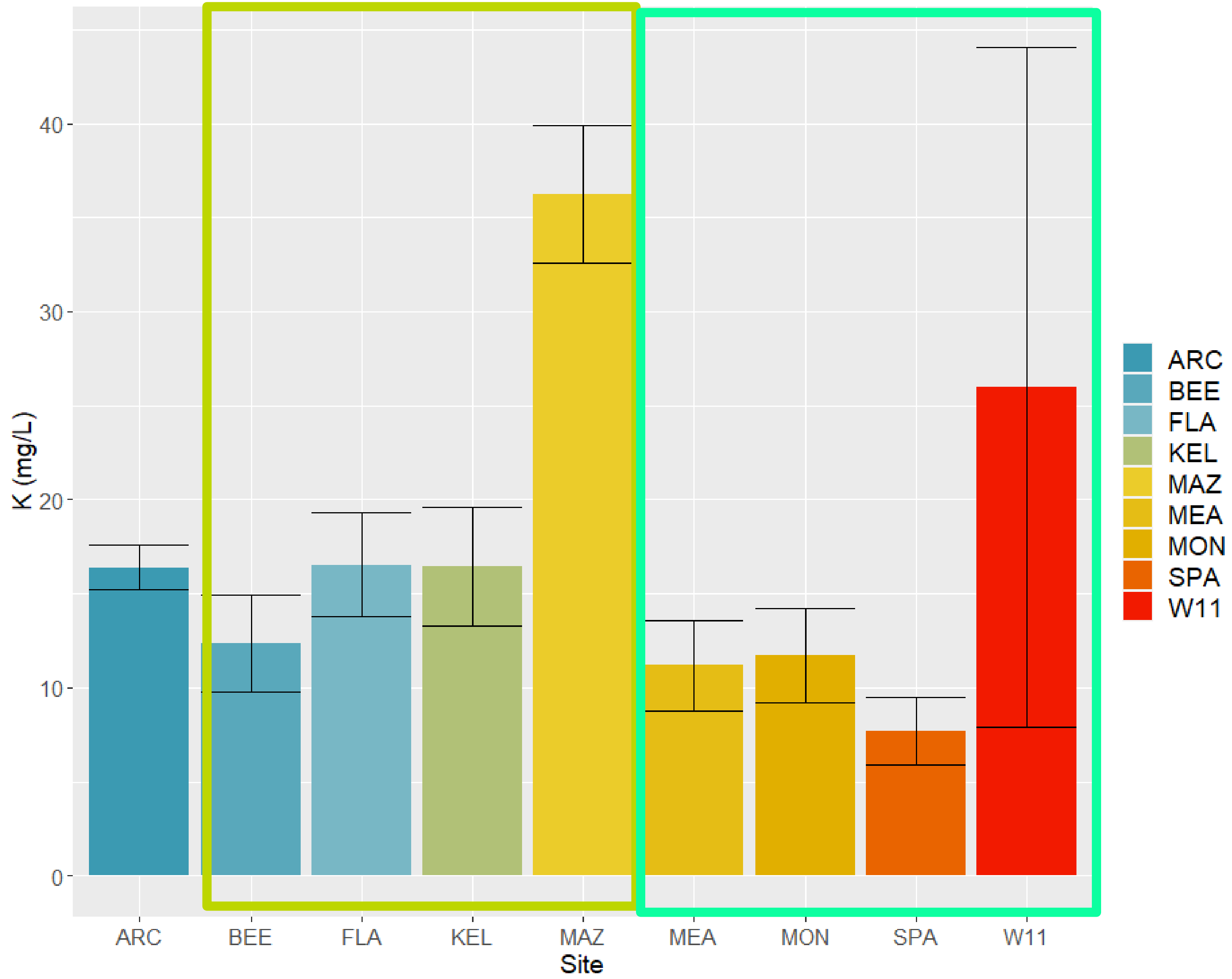

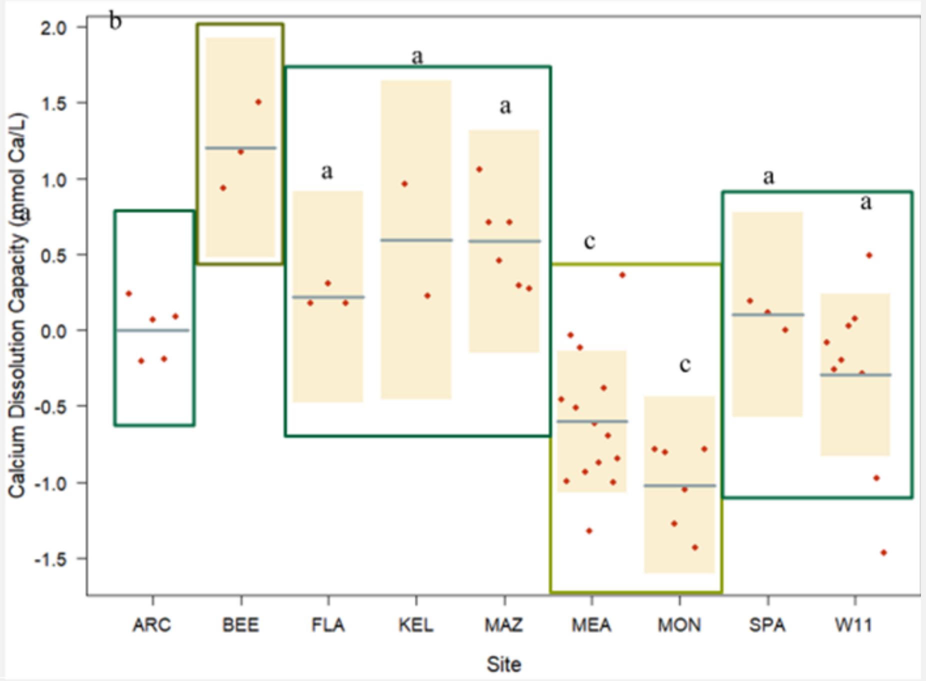

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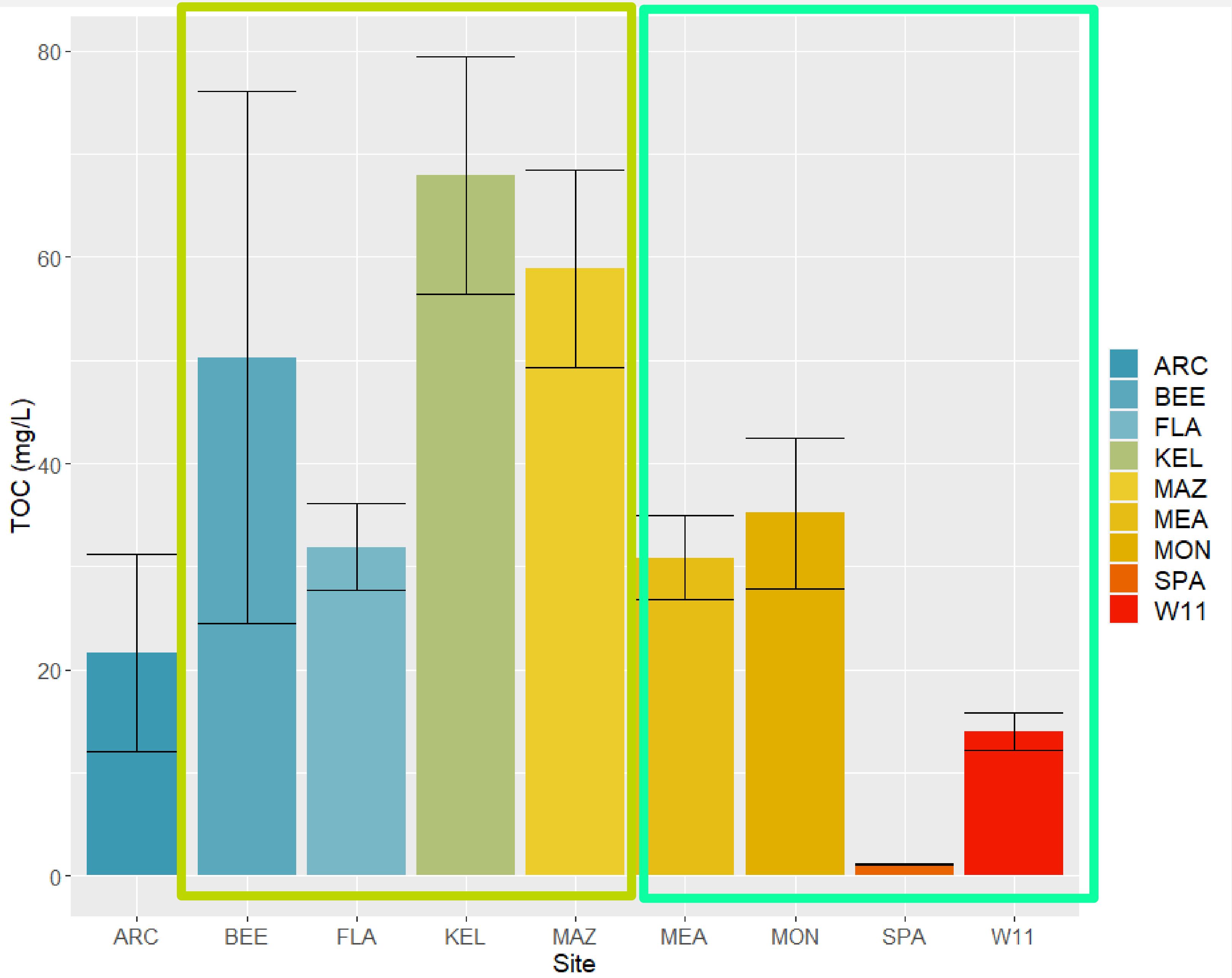

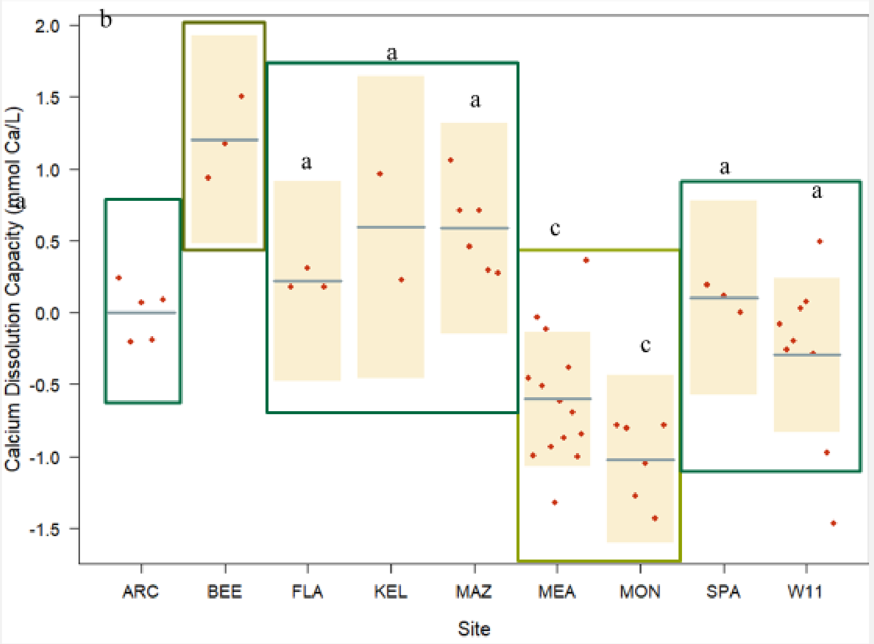

Multiple Linear Regression
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TOC, Ca, Mg & K were highly significant (p>0.05)

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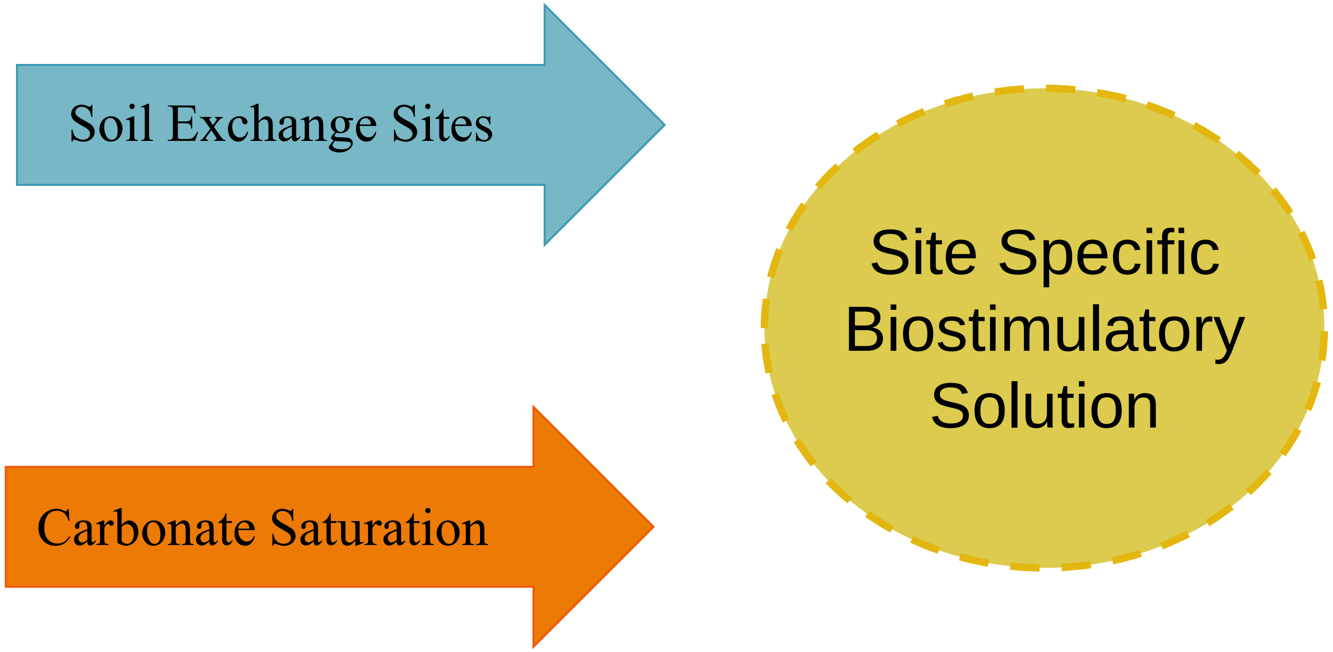
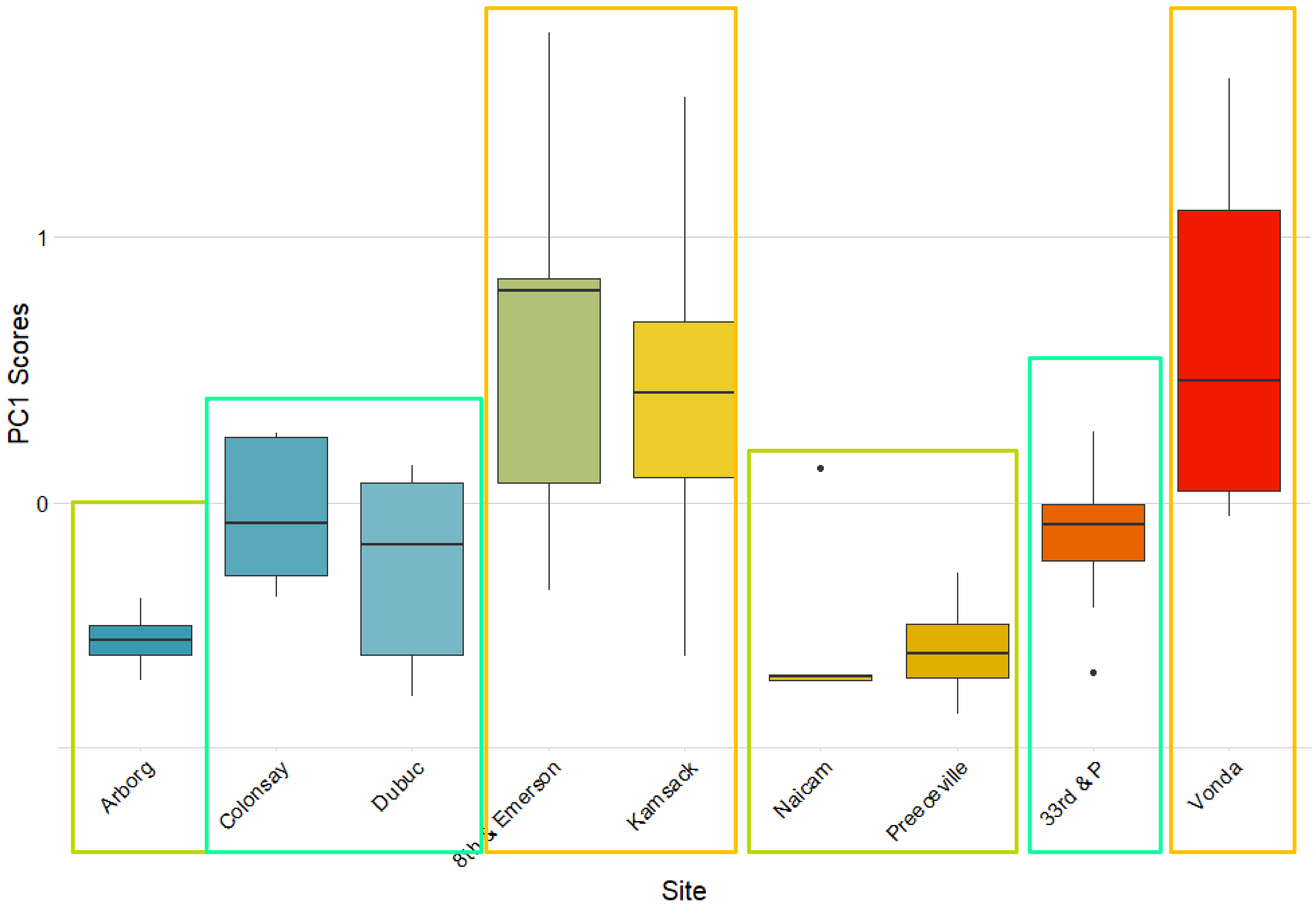
Laboratory Study Findings

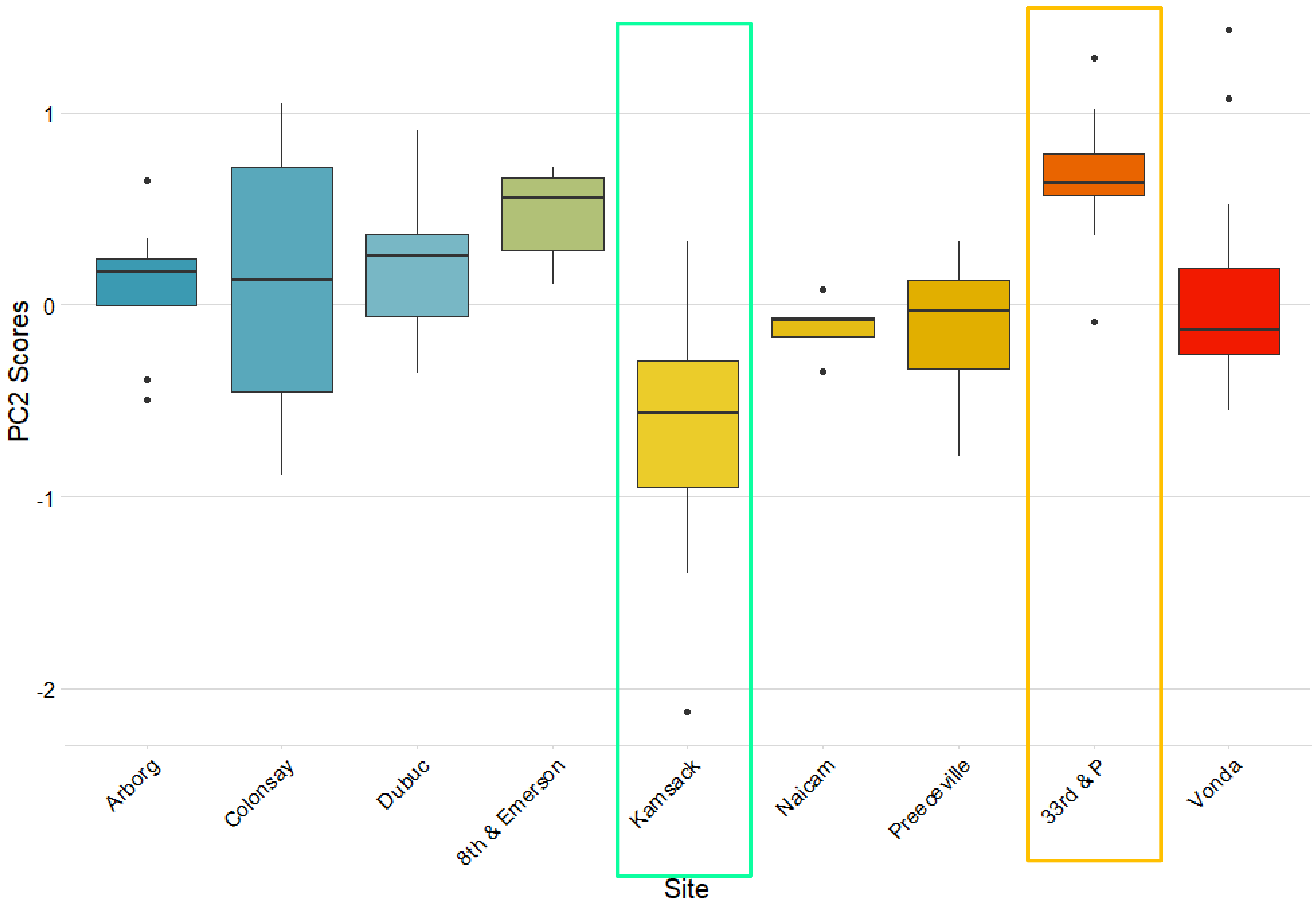
- Differences in calcium dissolution at different sites driven by:
  - Calcium, Magnesium, Potassium, Total Organic Carbon

Higher CEC means more Ca is available for dissolution

Carbonate and pH are intrinsically linked to P availability




PC1 Scores
1
0
Arborg
Colonsay
Dubuc
Emerson
Kamsack
Naicam
Preeceville
33rd & P
Vonda
Site



PC2 Scores
1
0
-1
-2
Arborg
Colonsay
Dubuc
8th & Emerson
Kamsack
Naicam
Preeceville
33rd & P
Vonda
Site

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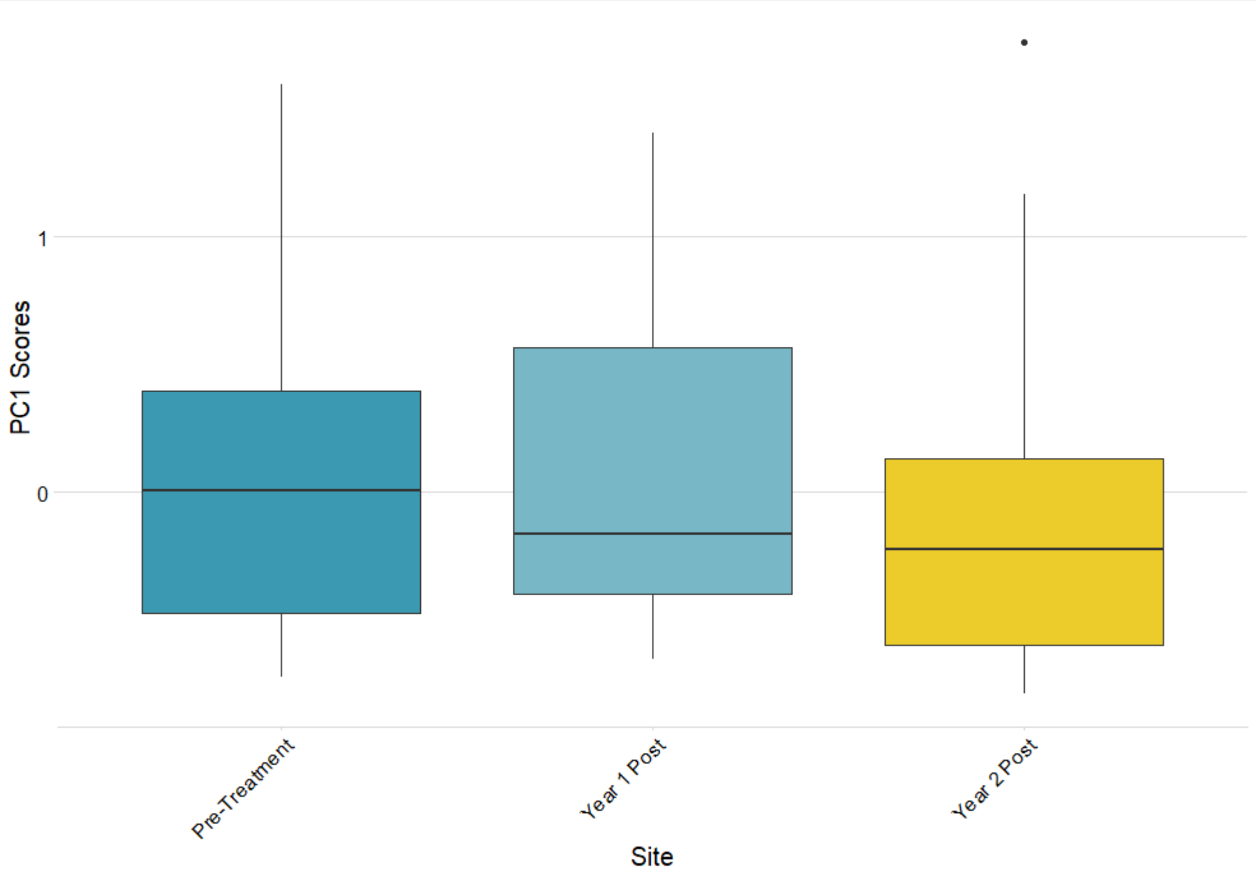
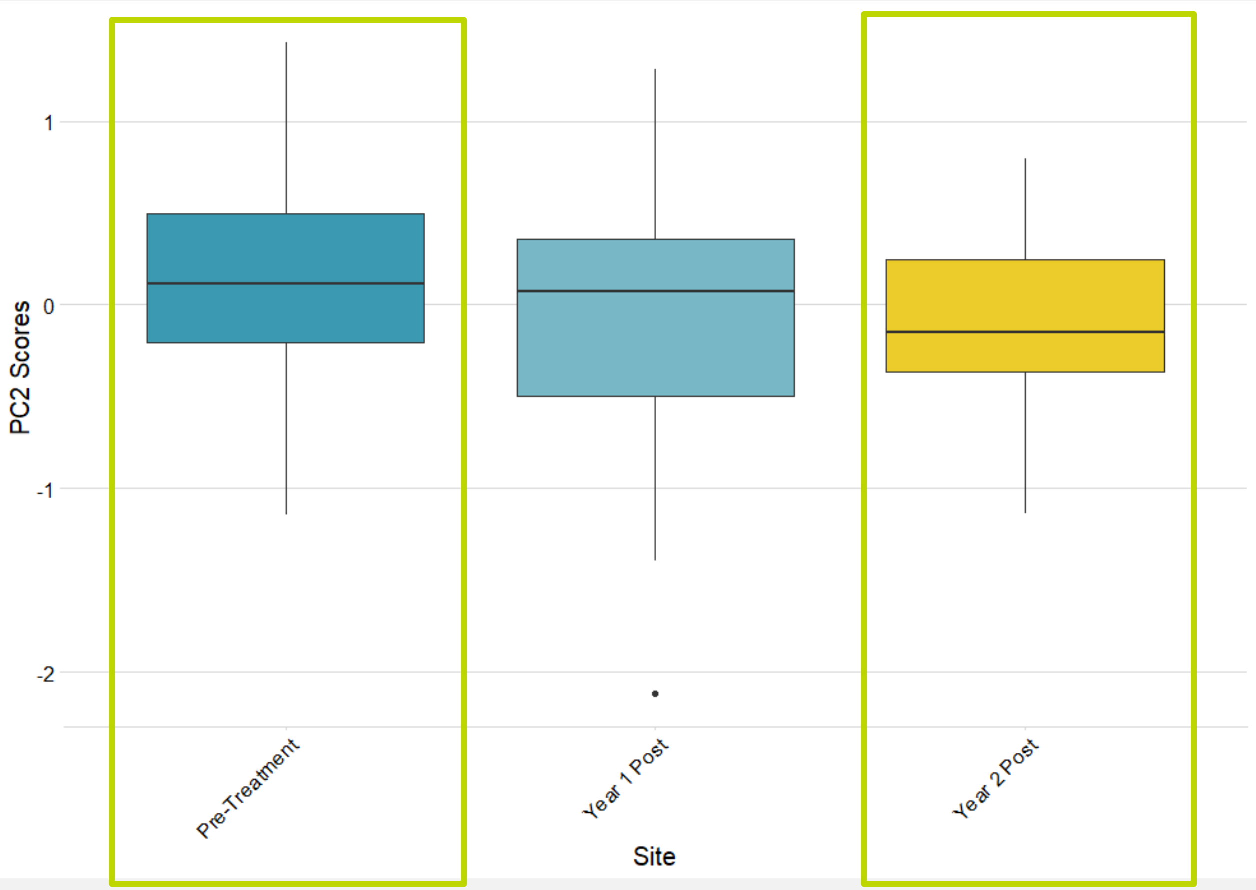
Field Study: Preliminary Results





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Calcium Dissolution Kinetics

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Higher
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Higher soil buffering
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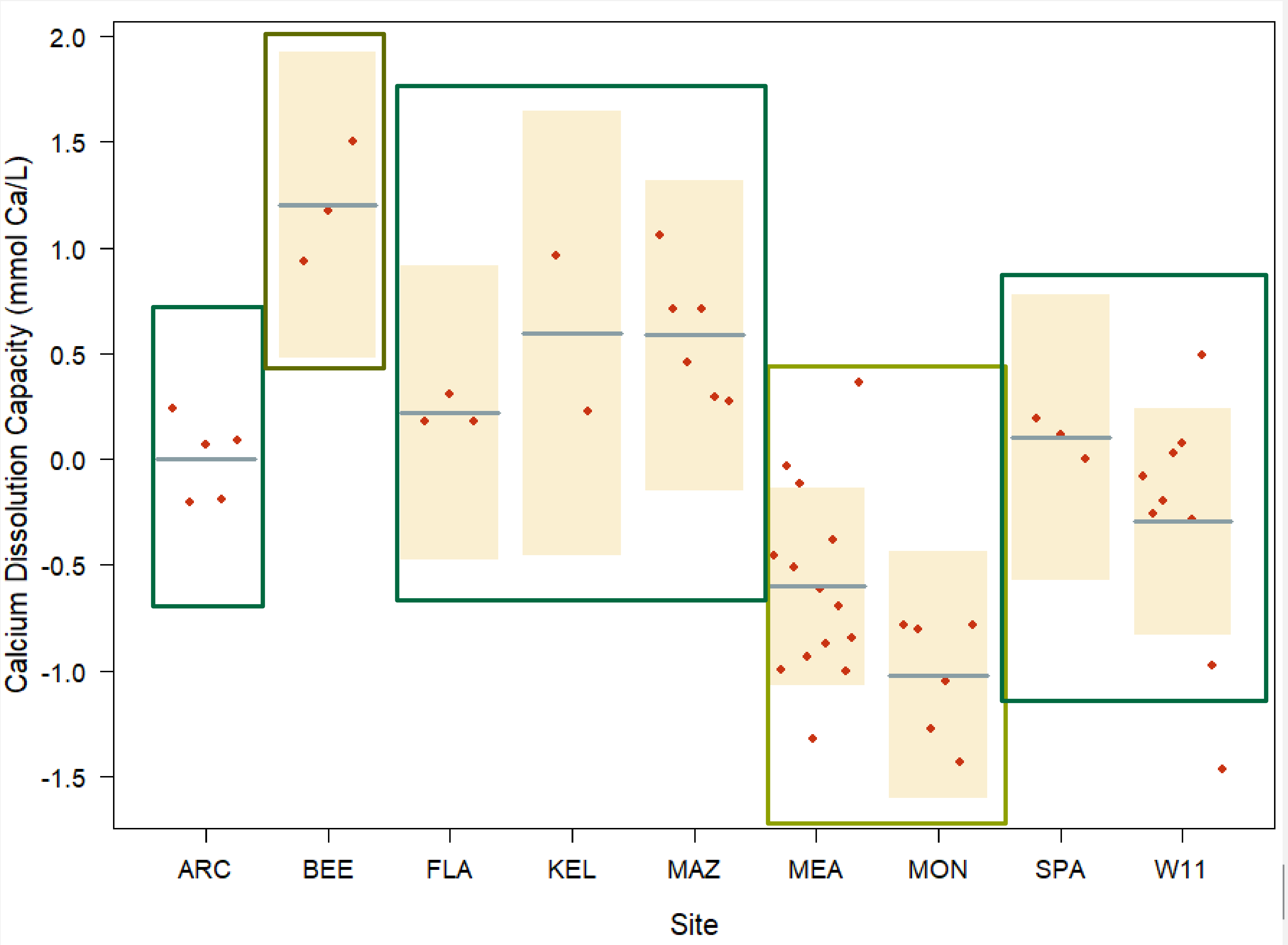

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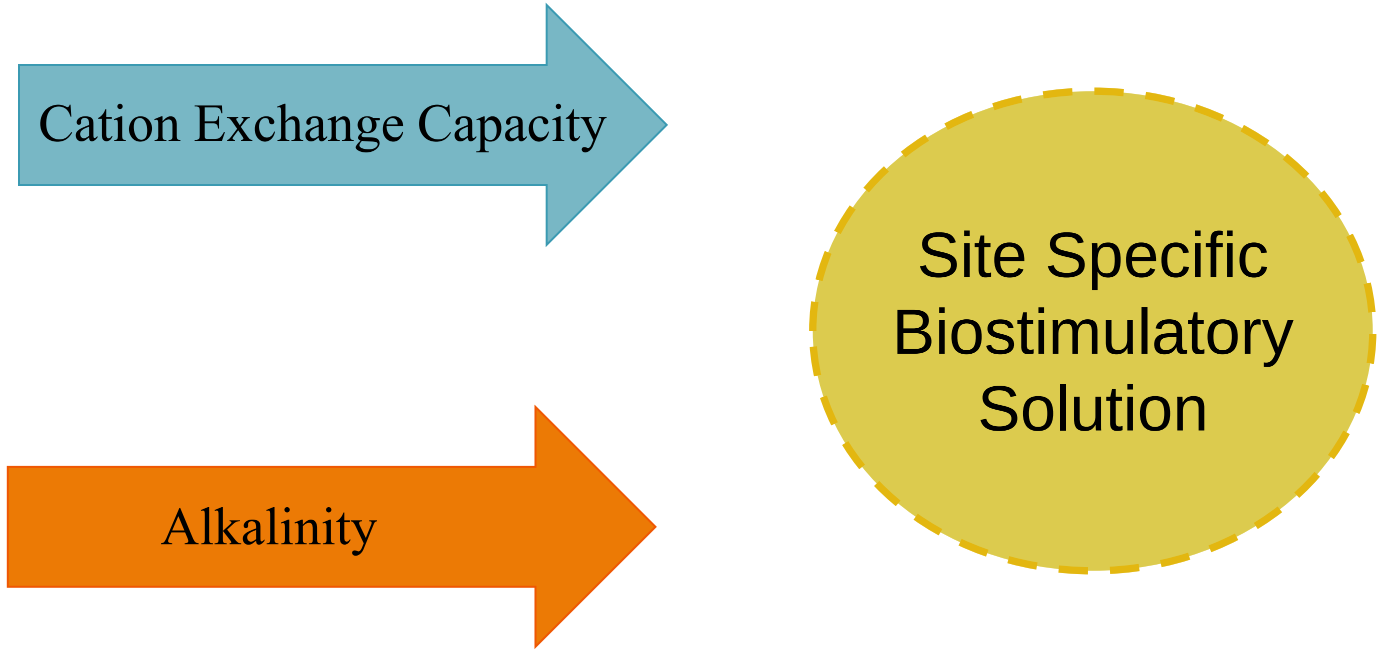
Field Study: Preliminary Findings

- Differences in groundwater geochemistry at different sites driven by:
  - Base cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}), Conductivity, TDS and SO_4^{2-}
  - pH and HCO_3^-

Ions drive site differences

Positive correlation between HCO_3^- & pH



Conclusions

Laboratory

- Soil Exchange Sites
- Carbonate Saturation

Field

- Cation Exchange Capacity
- Alkalinity

Site Specific Biostimulatory Solution

Soil Buffering Capacity plays an important role in weathering of biostimulatory solutions

BUT, how can we use this information to predict effectiveness?