2024 NORTH AMERICAN BIOCHAR CONFERENCE

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USDA Agricultural Research Service
U.S. DEPARTMENT OF AGRICULTURE

Biochar + Soil: Uncovering the Driving Mechanisms

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Biochar + Soil

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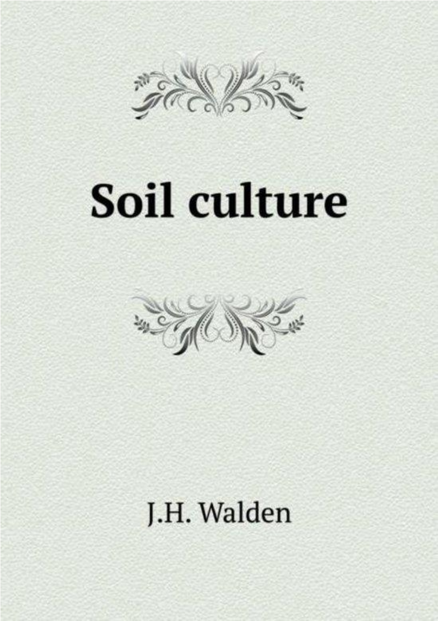
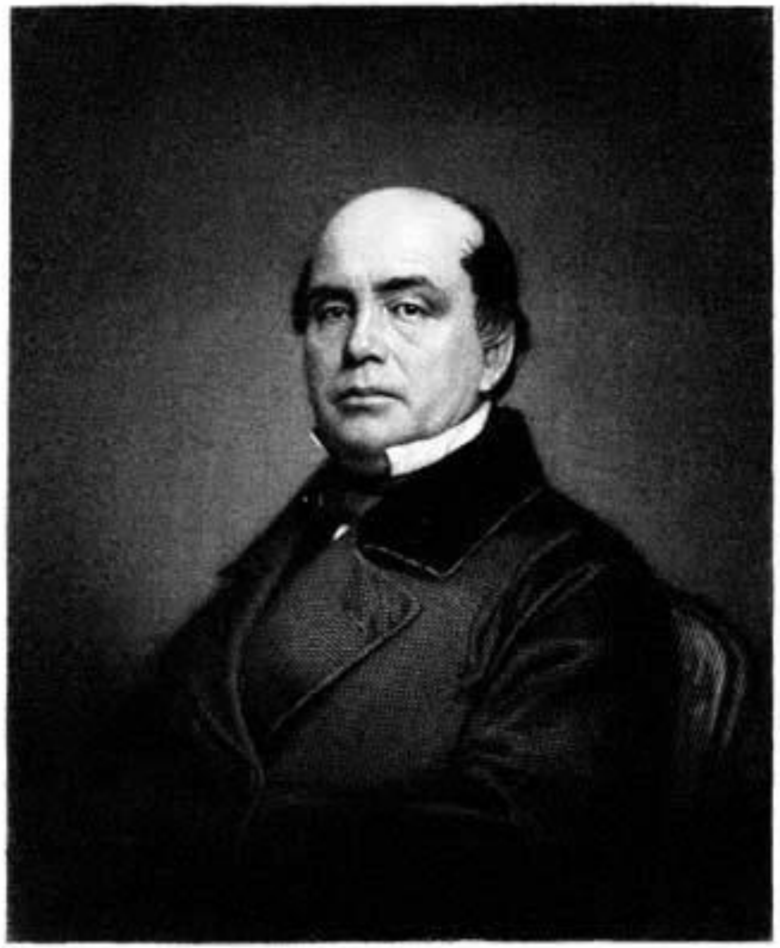
-**Soil Culture – J.H. Walden (1860)**



Majority of observations of charcoal and plant interactions can be traced back to 1790-1850's

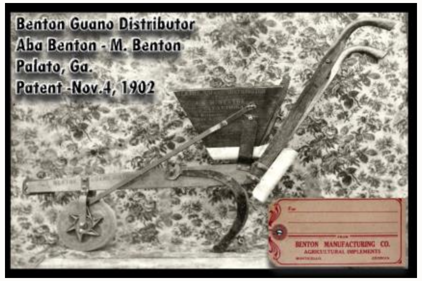


Charcoal Use in 1800's

- **Occasional improvement in yields** (1770-1880)
- **Increasing soil temperature**
  - Earlier crop germination/emergence (1730/1800)
- **Charcoal mixed with manures**
  - "Improved fertilization action" (1834)
  - "Deodorizing animal manures for fertilizers" (1873)
- **Reducing plant pathogens**
  - Particularly for potatoes, peach trees
  - "One handful of charcoal with each seed" (1834)
- **Patent in the 1850's for "antiseptic fertilizer"**
- **Variability of charcoal in kiln** (1730)

Biochar + Soil – Historical Hurdles

- **If charcoal was being used – What happened?**



- **1800's** – The benefit of charcoal did not outweigh the cost (time/money)
  - Basic laboratory analysis of soils started, which eventually lead to application guidelines for phosphorus and potassium rich materials ("natural" fertilizers)

- **1900's** – Agricultural implements developed for charcoal application / coal fines
  (Benton Manufacturing Co: manure (guano) + charcoal during planting)

  1) Great Depression

  2) 1921 first ammonia plant in US – Advancements in soil testing and N-fertilizer recommendations – "synthetic fertilizers" **= predictable response**

- **2000's** – Biochar Renaissance : Charcoal for climate mitigation

Biochar + Soil – Still lacking mechanisms

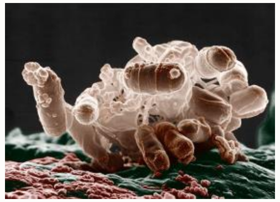
- Biochar impact depends on

  Soil x Weather x Crop (1800's)



- Interesting to note that in 200+ years we have added 2 more complicating factors:

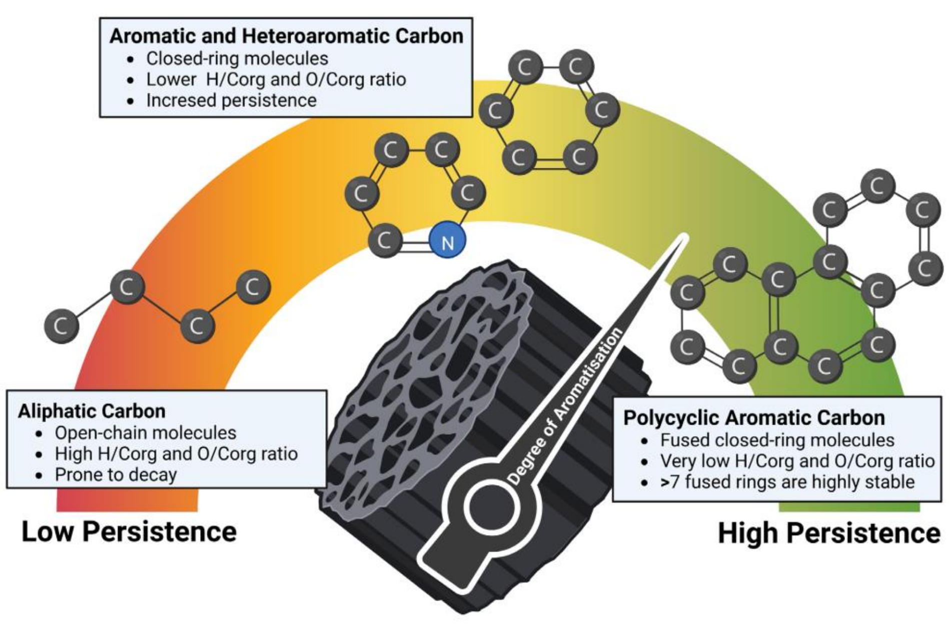
  Soil x Climate x Crop x Biochar Type x Microbial

Biochar + Soil -

- "Biochar that was produced at **pyrolysis temperatures above 550°C** and presenting a **molar H:C ratio below 0.4** is highly persistent when applied to soil. 75% of such biochar carbon consists of stable polycyclic aromatic carbon (PAC) and will persist after soil application for more than 1000 years **independent of the soil type and climate**."

Schmidt HP, Abiven S, Hageman N, Meyer zu Drewer J: Permanence of soil applied biochar. An executive summary for Global Biochar Carbon ink certification, The Biochar Journal 2022, Arbaz, Switzerland, www.biochar-journal.org/en/ct/109, pp 69-74

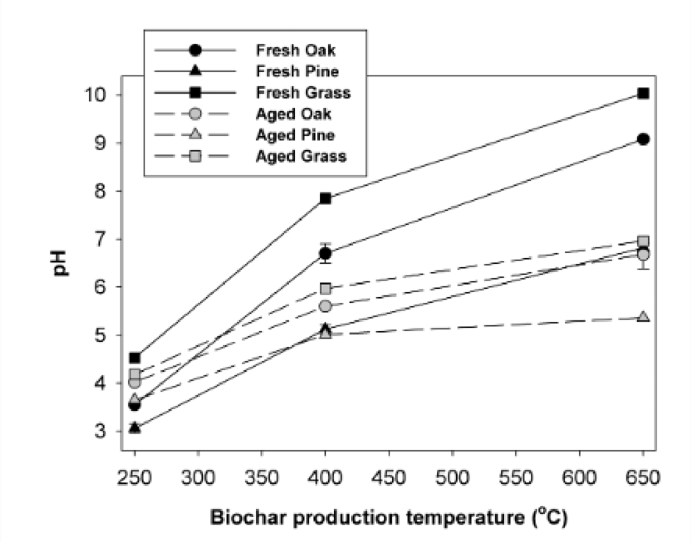


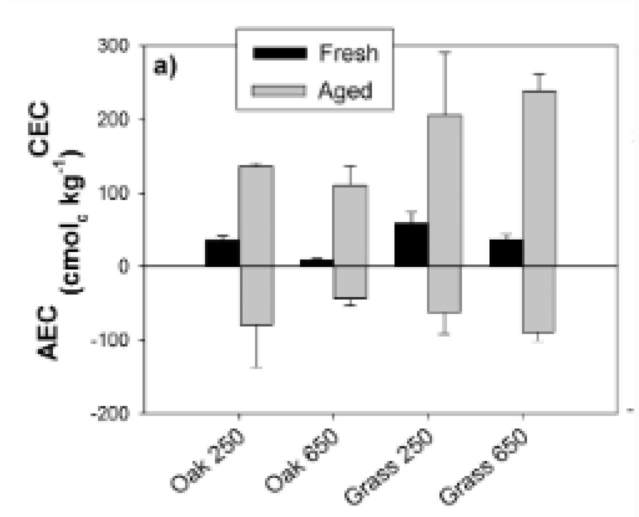
Can Soil Interactions be Dismissed?

- Field aging biochar leads to changes in behavior – both chemical and physical

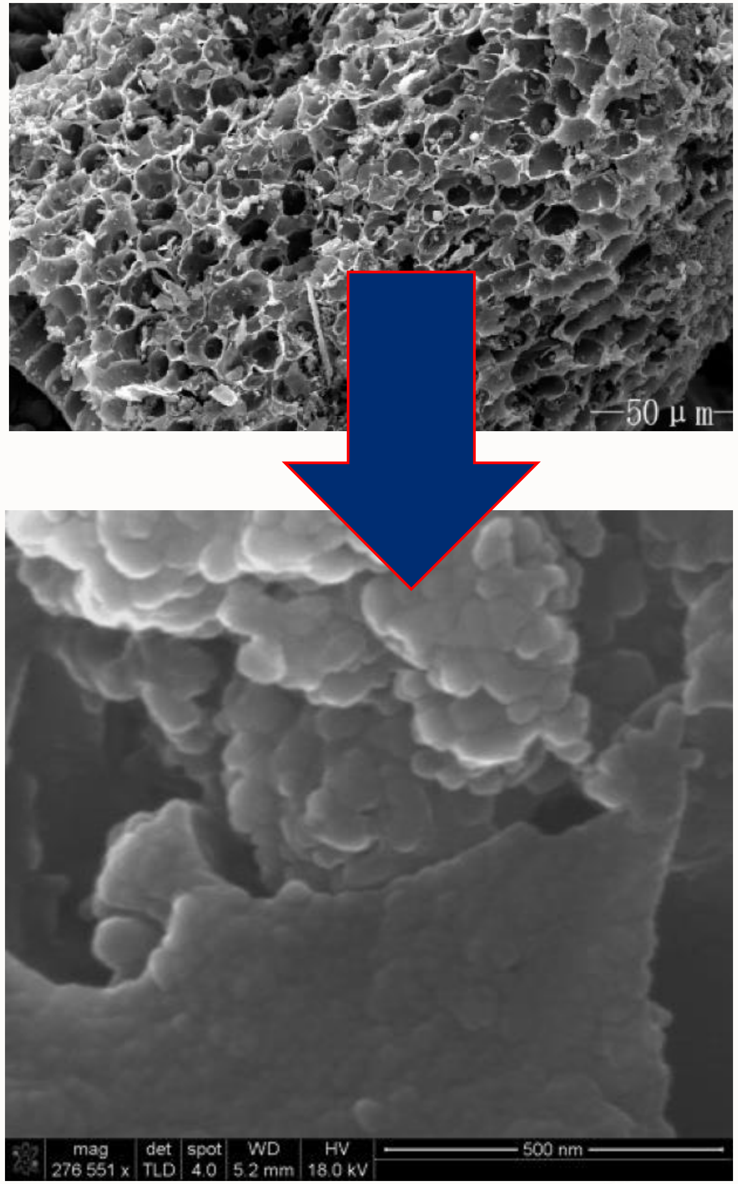
Studies detailing alterations to:
- pH (decreases) & CEC (increases)
- Agrochemical sorption (positive/negative)

“*Organic*” plaque formation on biochar



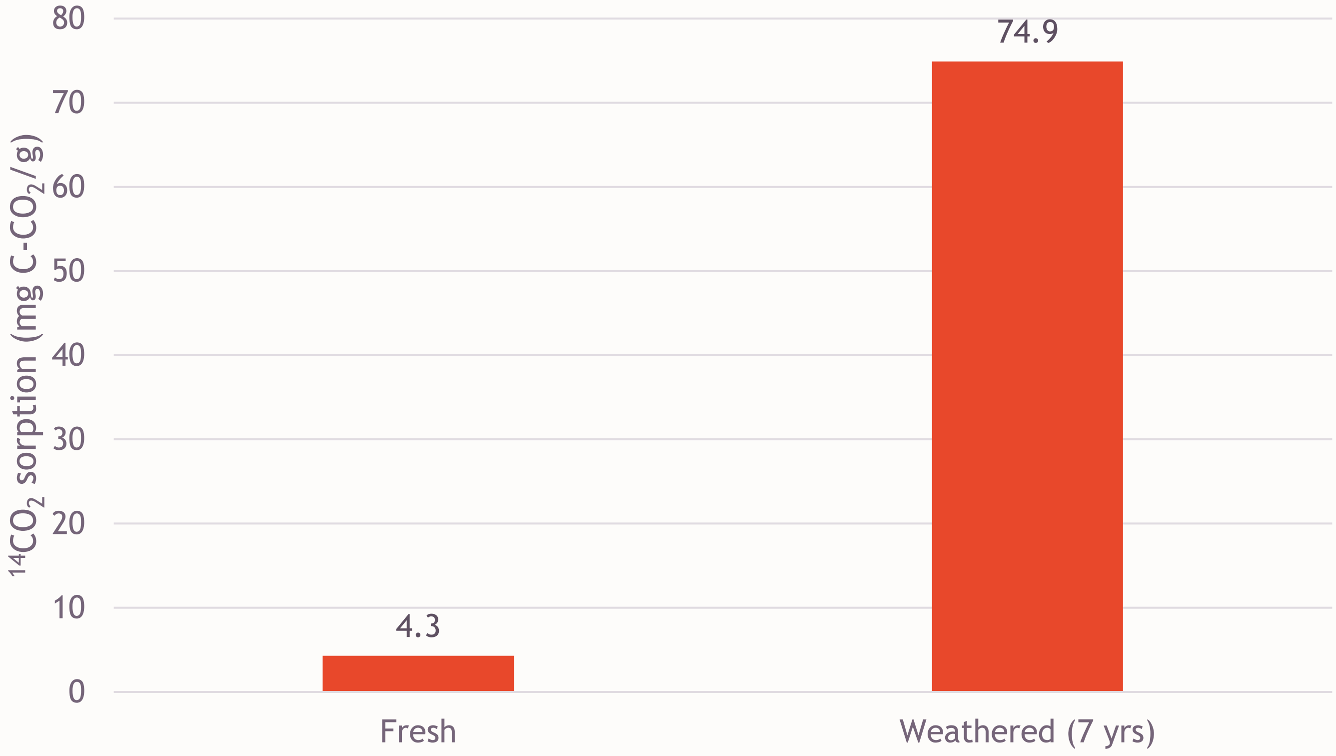


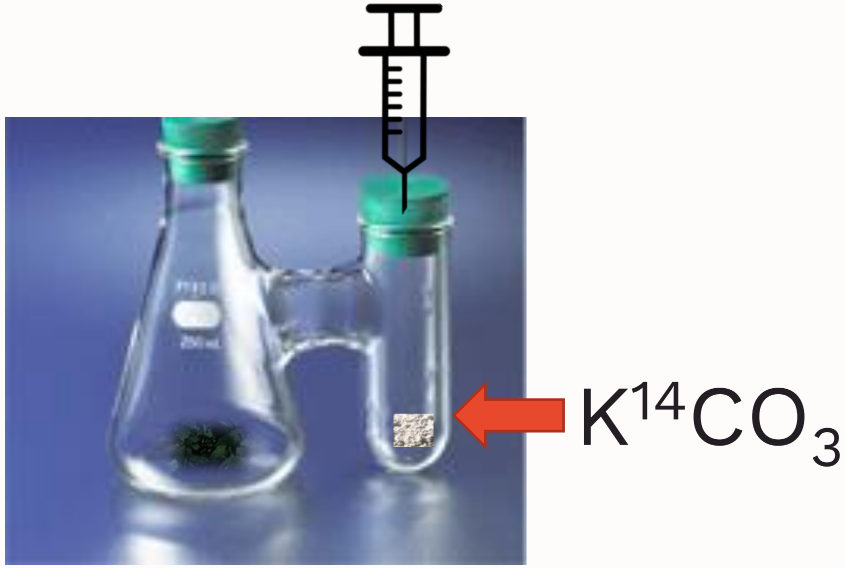
Mukherjee, A., Zimmerman, A. R., Hamdan, R., and Cooper, W. T.: Physicochemical changes in pyrogenic organic matter (biochar) after 15 months of field aging, Solid Earth, 5, 693–704, https://doi.org/10.5194/se-5-693-2014, 2014.



Weathered biochar – Increased CO_2 sorption

- Carbon might not be “organic” in plaque
- Weathered and fresh biochar (Oak-550 °C)

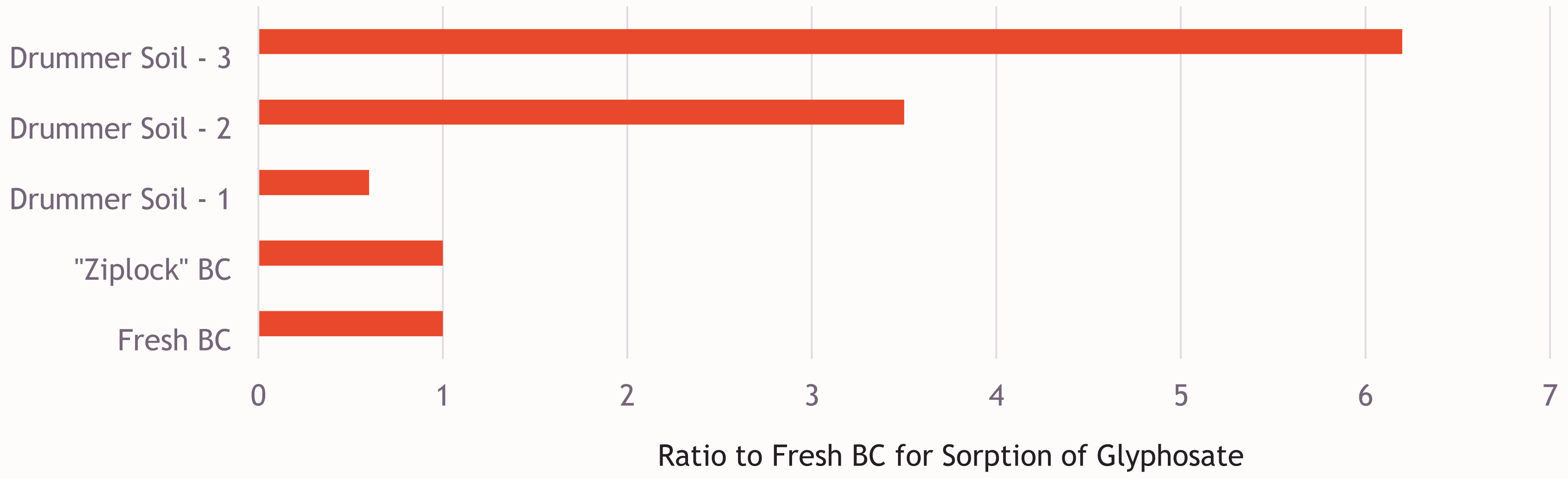




CO_2 in soil gas averages around 1% in gas phase

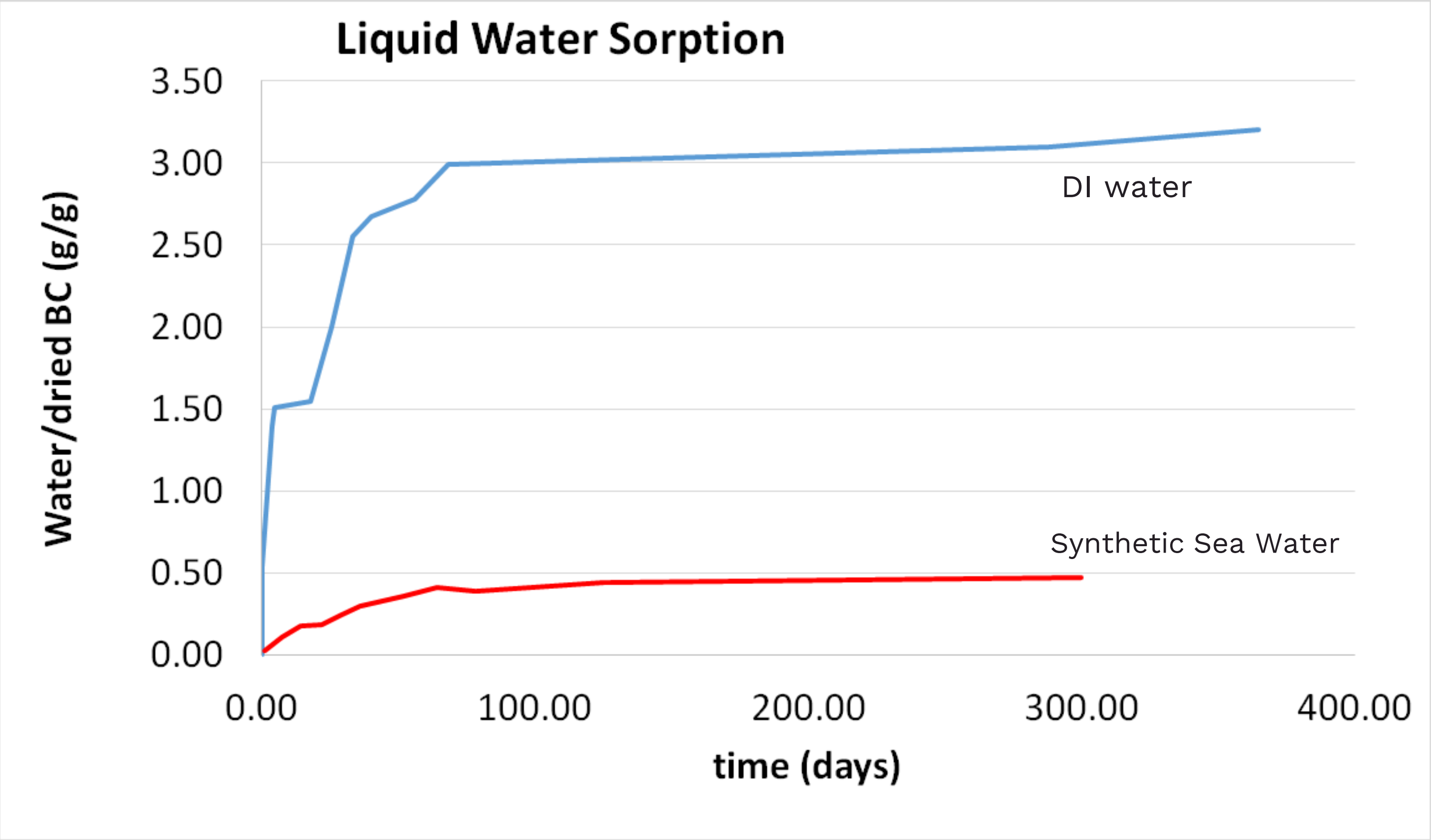
Biochar + Soil:

- **Citizen Science Project – 10+ years**
  - Shipping the same biochar (550 °C; Oak wood) to locations
  - Burial in mesh bags (1 year) and then returned
    - Same soil type = drastically different results for agrochemical sorption alteration after retrieval



Why Salts?

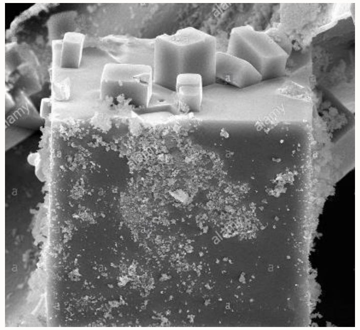
550 °C Oak biochar



DI water

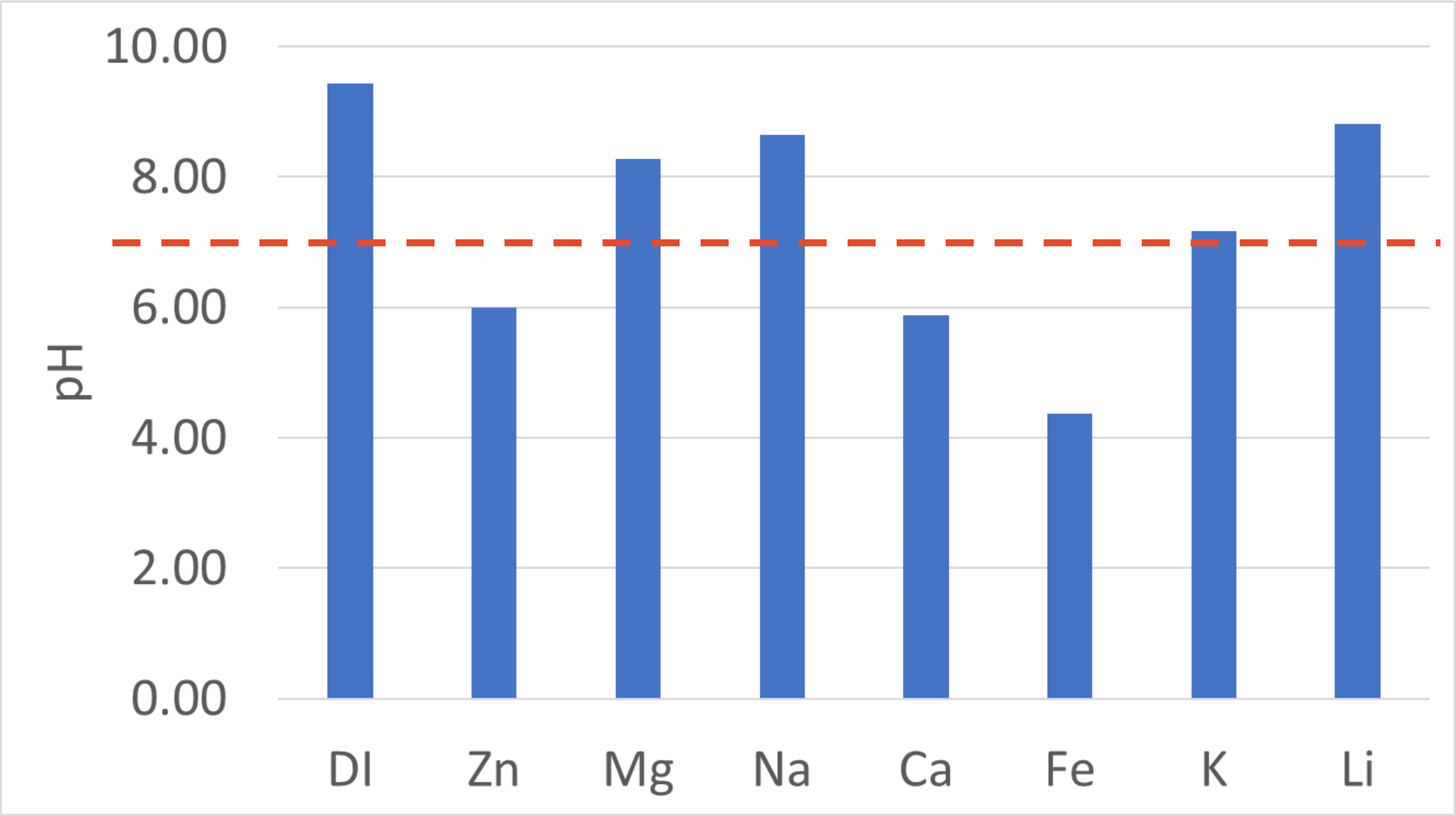
Synthetic Sea Water

Biochar + Dissolved Salts



- 500 ^{o}C grape wood biochar
- Soaked in various salt solutions :
  - $CaCl_2$, $MgCl_2$, $ZnCl_2$, $AlCl_3$, LiCl, NaCl, & KCl
  - Concentrations : 0.001, 0.01, 0.1, 0.5, and 1.0 M
- Soaked for 30 days (22 ^{o}C; dark; reciprocating shaker 60 rev/min)
- Biochar was then rinsed with DI water in funnel with filter paper
- Oven dried at 125 ^{o}C and then subjected to various tests

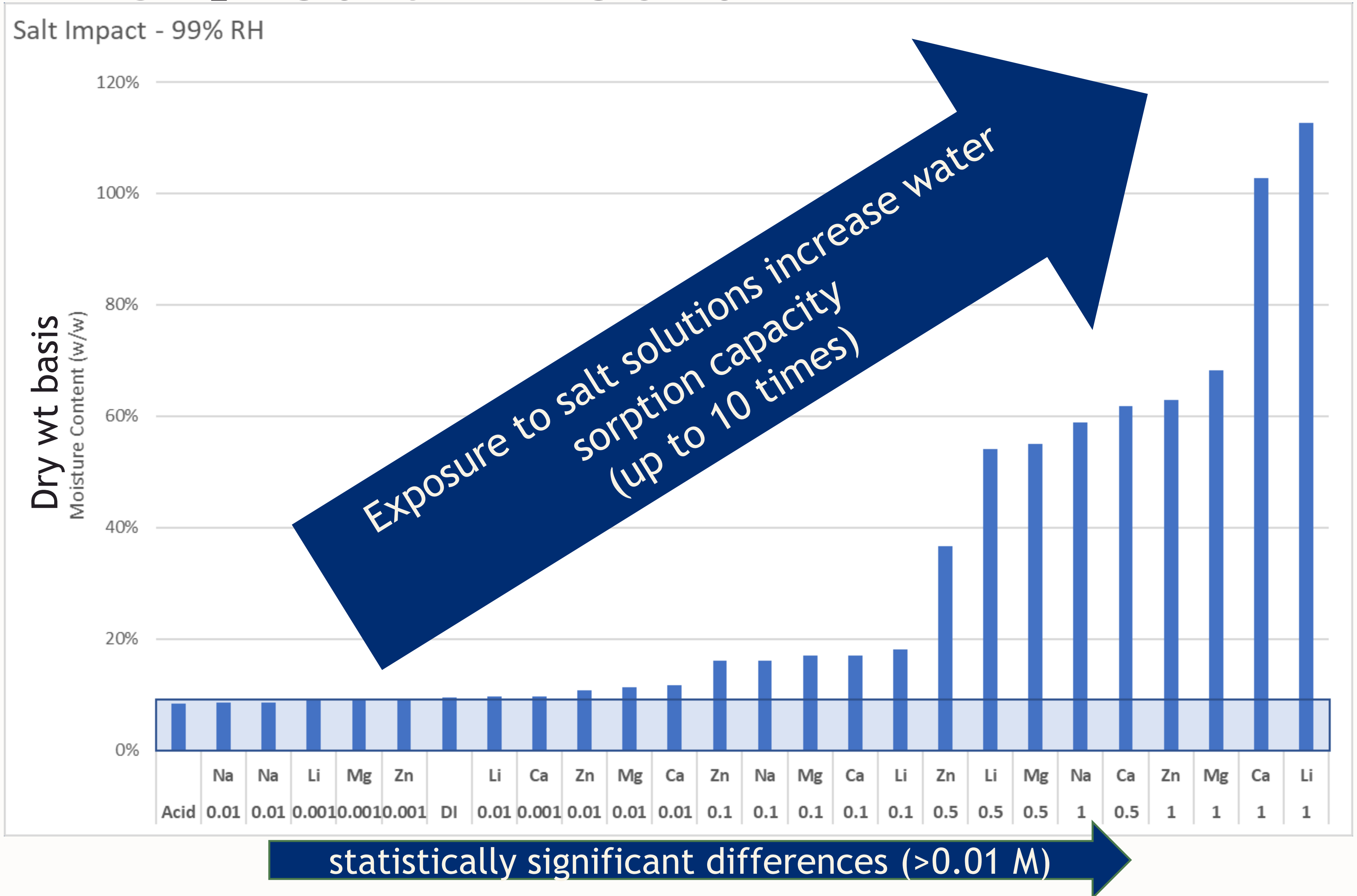
pH Impacts



1:10 BC:DI water ratio

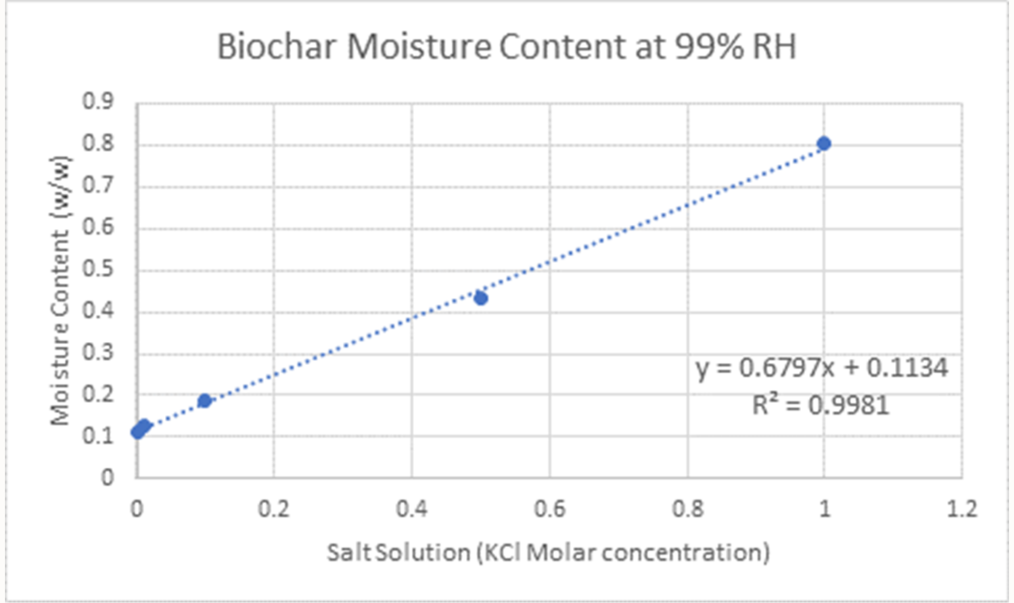
All salts reduced the pH of the biochar, but differing degrees

Soil + BC → Salt *x* Biochar

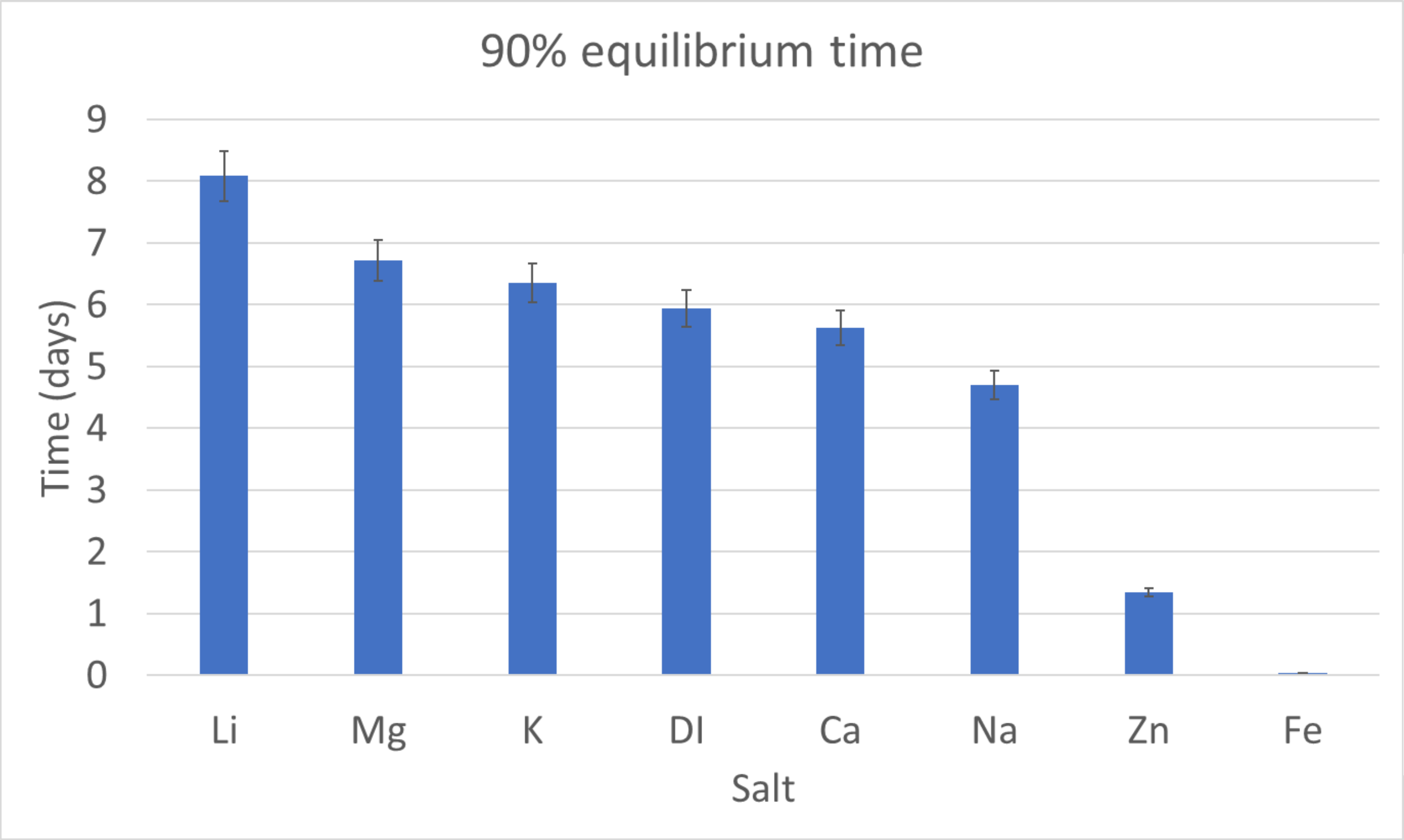


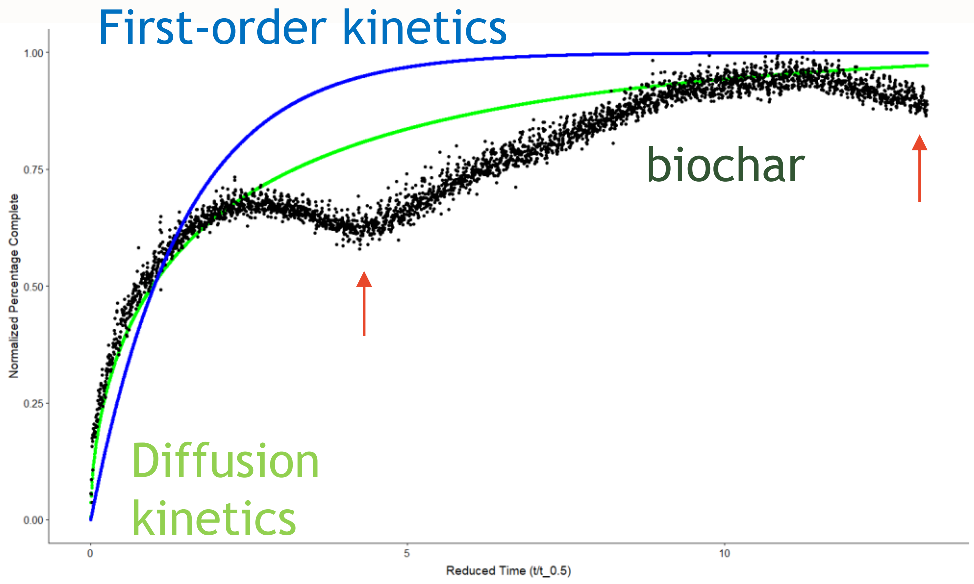
Predictable biochar impact of salt concentration

- For each salt, there is an excellent correlation between the salt concentration that the biochar was exposed to and the observed equilibrium moisture content at 99% RH
- $R^2 > 0.98$ for all salts
- However:
  - No clear relationship across biochar types
  - Exact mechanisms for this are uncertain

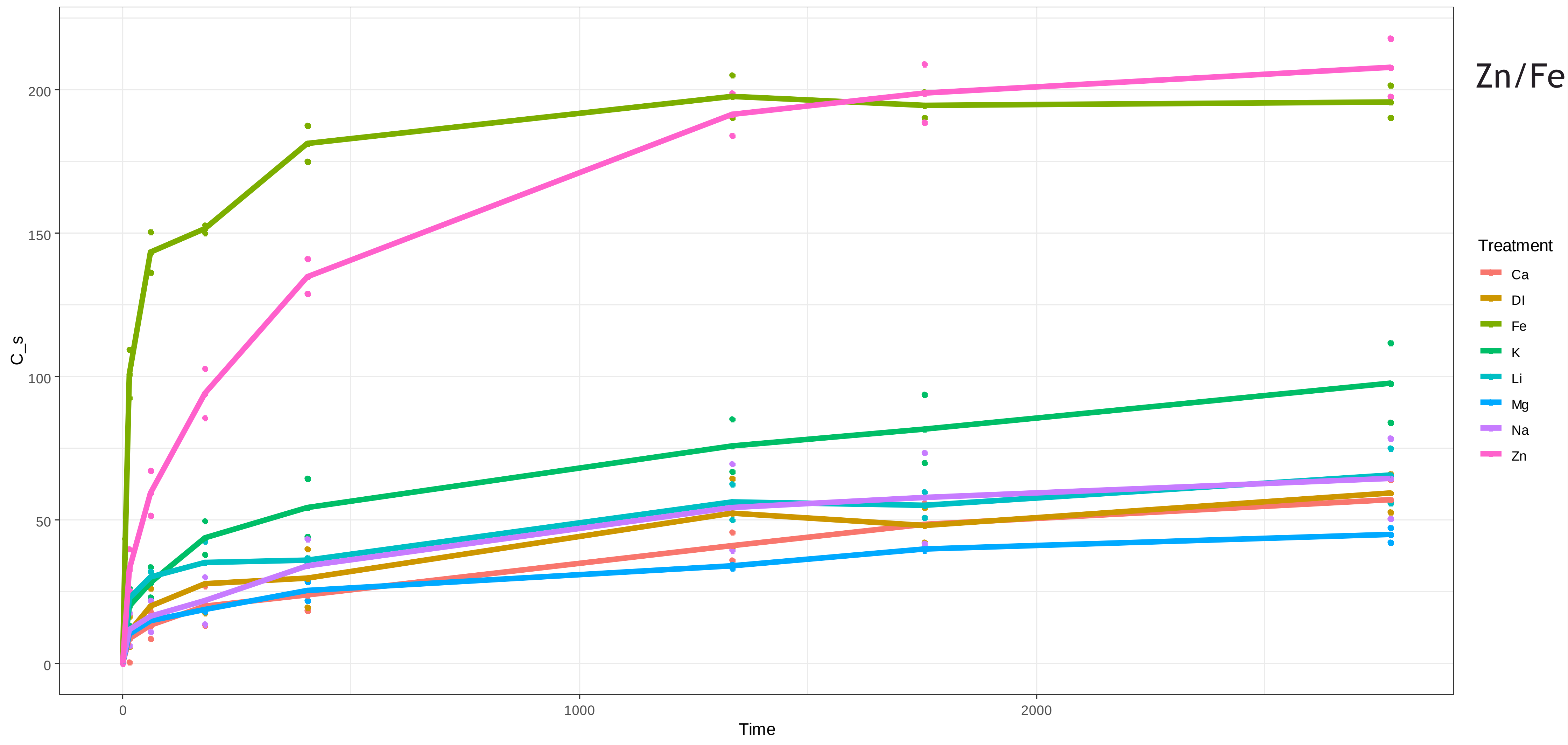


Kinetics are also impacted





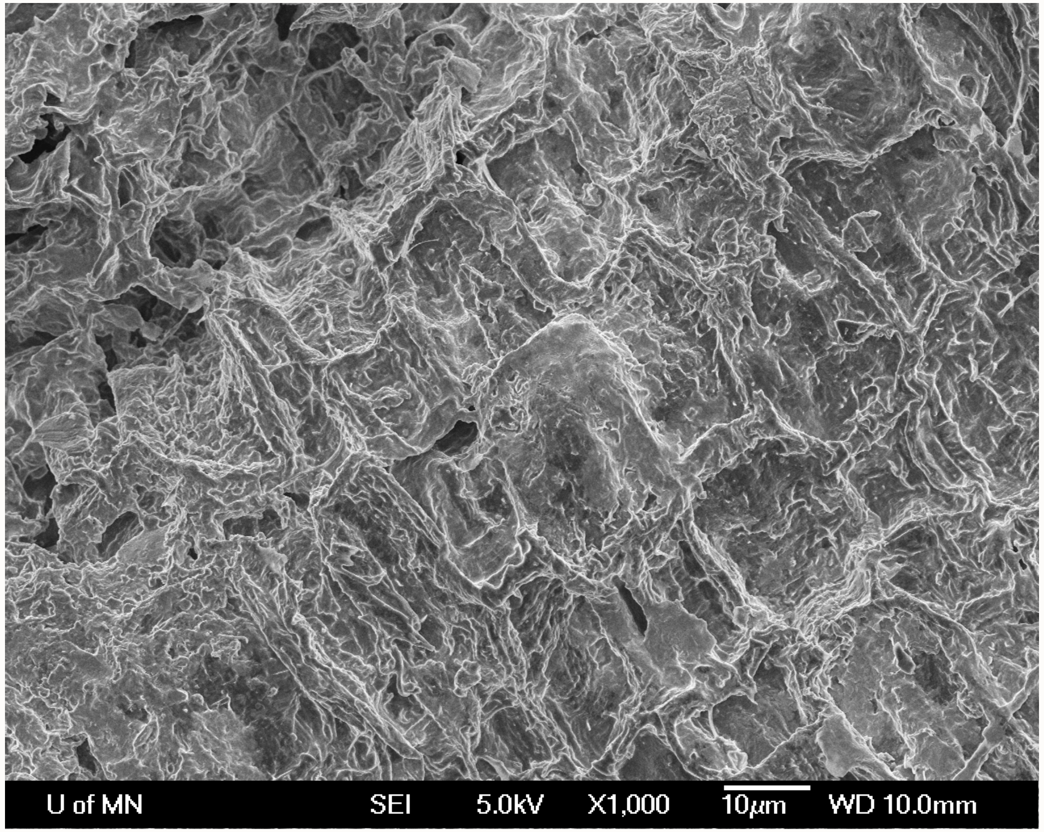
^{14}C - Glyphosate : Kinetic Analysis



Original BC

Element	Wt%
C	81.56
O	15.80
Cl	0.08
Zn	--

Zn^{+2} exposed BC

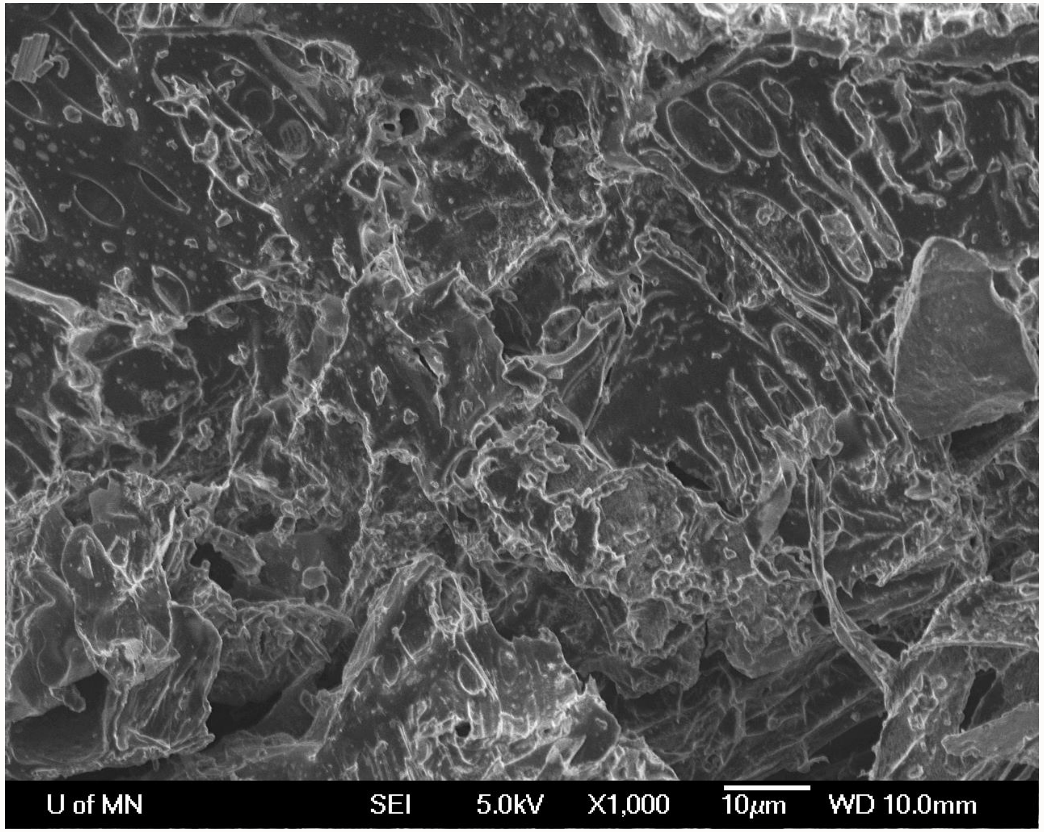


Element	Wt%
C	57.44
O	15.00
Cl	11.23
Zn	11.25

Original BC

Element	Wt%
C	81.56
O	15.80
Cl	0.08
Ca	0.30

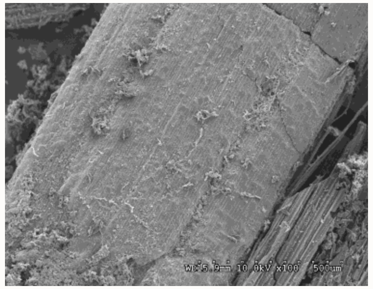
Ca^{+2} exposed BC



Element	Wt%
C	79.82
O	11.01
Cl	7.05
Ca	0.66

?

Devil is in the details; or the plaque?



- Biochar plaque formation observed with co-composting (Joseph et al., 2018)
- Differing biochar behavior based on dissolved salts
- Cd^{+2} sorption improved overall BC-carbon stability (Jing et al, 2021)
- Reaction with humic acids (HA) alters weathering (Hammerschmiedt et al., 2021)
- Fertilizer addition alters surface plaque formation in the same soil (Ivanova et al., 2023)

Could these nanoscale alterations to biochar particles in soil be the reason for the lack of historical predictable and reproducible response?

Wrap-up & Conclusions

- No crystalline structures have been located to date with XRD on surface
- Attracts an amorphous cation rich layer to the surface of biochar:
  - Spatially very uniform (thickness/coverage)
  - Not easily removed –-> C-Metal bonds (organo-metalic)?

Carbonates + Oxides of Salt Minerals (Ash): **C & O** from atmospheric/soil CO_2 and not necessarily biochar

(i.e. $CaO \rightarrow CaCO_3$)

- **Soil solution chemistry** more important than **soil type**

  → Significantly alters water sorption, agrochemical sorption, mechanical particle strengths, dissolution/exfoliation mechanisms, etc.

  → Analogous to studies examining soil carbon databases – where exchangeable Ca^{+2} is a better predictor of soil C across soils (Rasmussen et al., 2018)