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Biochar + The Environment

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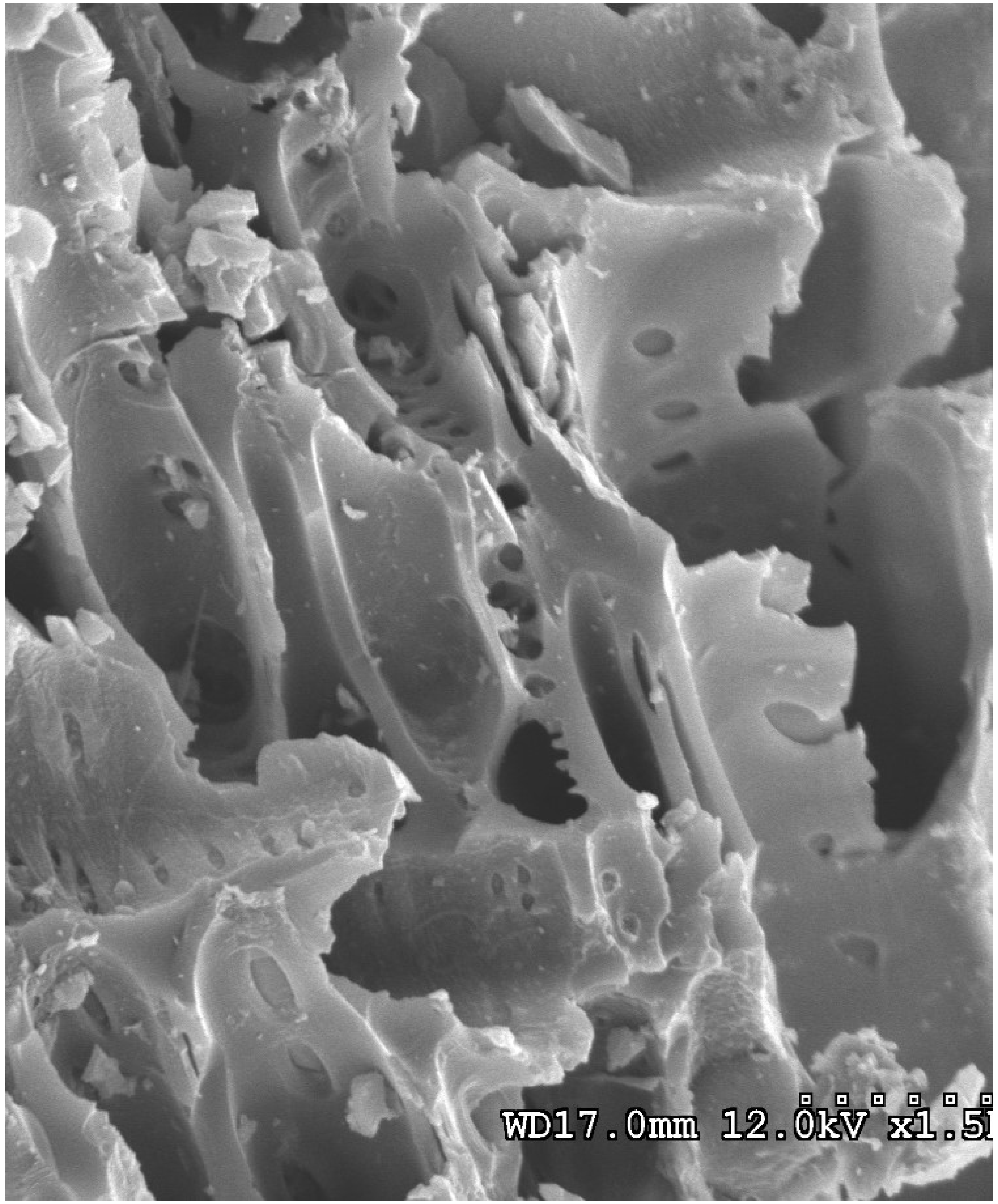

Minnesota BIOCHAR SUMMIT

Ancient Civilizations

Egyptians: 7,000 to 500 BC: Pyrolysis for embalming fluids

- Pyrolysis used to produce embalming fluids (wood vinegar)
- Charcoal - medicinal use on wounds
- Potential use as soil improver (?)

Romans: 1000 BC to 500 AD: Water Filtration & Direct Soil Use

- *"In burned vegetables, there are abundance of the salts of vegetables, so they must greatly contribute to enrich the land"*
  - Open "*stiff lands*" and included caution > "*not too frequently*"

Pre-Columbian America: 800 AD (?) – 1942 AD

- Wim Sombroek
  - Hypothesized that Amazonian natives purposely added biochar to improve soil fertility & productivity ("Terra Preta" Soil)
- Recent isotopic evidence question this hypothesis

[Silva, L.C.R., Corrêa, R.S., Wright, J.L. *et al.* A new hypothesis for the origin of Amazonian Dark Earths. *Nat Commun* **12**, 127 (2021). https://doi.org/10.1038/s41467-020-20184-2]

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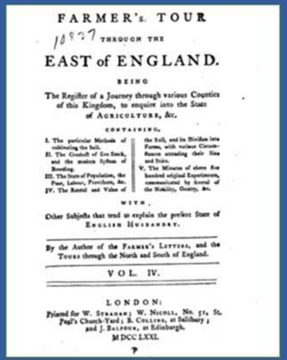
Start of Modern Science

Arthur Young : *A Course in Experimental Agriculture*

1770 – First documented biochar field plots

- Occasional yield improvements (not reproducible)
- Composed of plant nutrients = must be good for plants

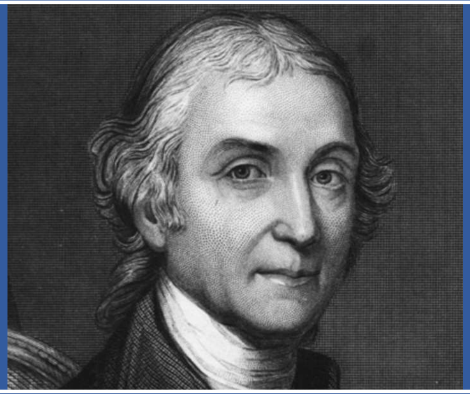


FARMER's TOUR
THROUGH THE
EAST of ENGLAND.

VOL. IV.

LONDON:

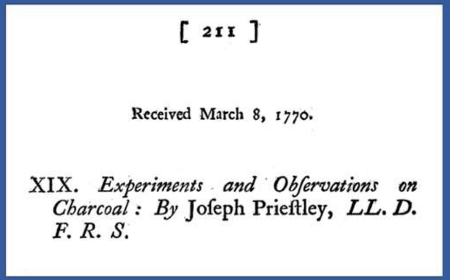
MDCCLXXI.



Joseph Priestley: *Experiments and Observations on Charcoal*

1770 – First scientific investigations into the properties of charcoal

- Primarily electrical properties
- Noted differences between and within batches of charcoal



[211]

Received March 8, 1770.

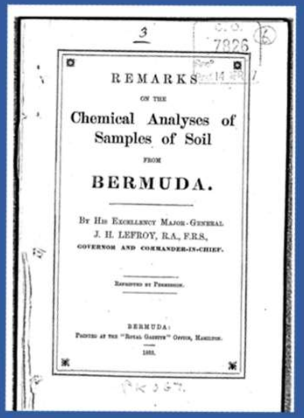
XIX. *Experiments and Obfervations on Charcoal*: *By* Jofeph Prieftley, *LL. D. F. R. S.*

John Henry LeFroy: *Chemical Analysis of Samples of Soil from Bermuda*

1883 – Documentation of actual use in agriculture

Application rate (5000 lb/ac);

However, "lose much of their value" with storage



REMARKS
ON THE
Chemical Analyses of Samples of Soil
FROM
BERMUDA.

Biochar Use in Agriculture (1800-1950)

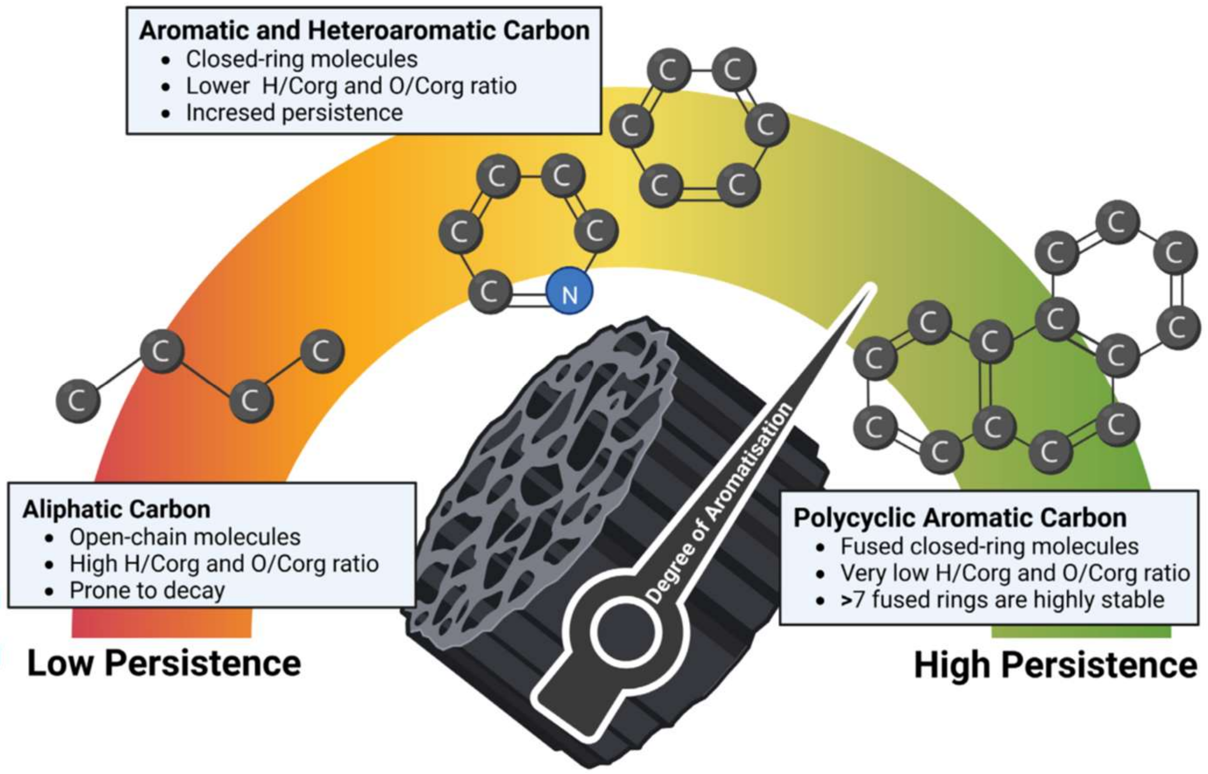
- **Improving yields (peat charcoal)**
  - Oats – 2-fold increases reported (1770)
  - Grasses - improved growth & color (1800)
  - Potatoes – Improved yield 2-fold (1880)
- **Increasing soil temperature**
  - Earlier crop germination/emergence (1730/1800)
- **Charcoal mixed with manures (co-composting & co-applying)**
  - "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)
- **Patents in the 1850's for charcoal "Antiseptic fertilizer"**
- **"Aging" of biochar under laboratory conditions changed sorption properties**

  3-fold increase after 4 yr on laboratory shelf (Shelton, 1920)

Biochar Stability/Permanence

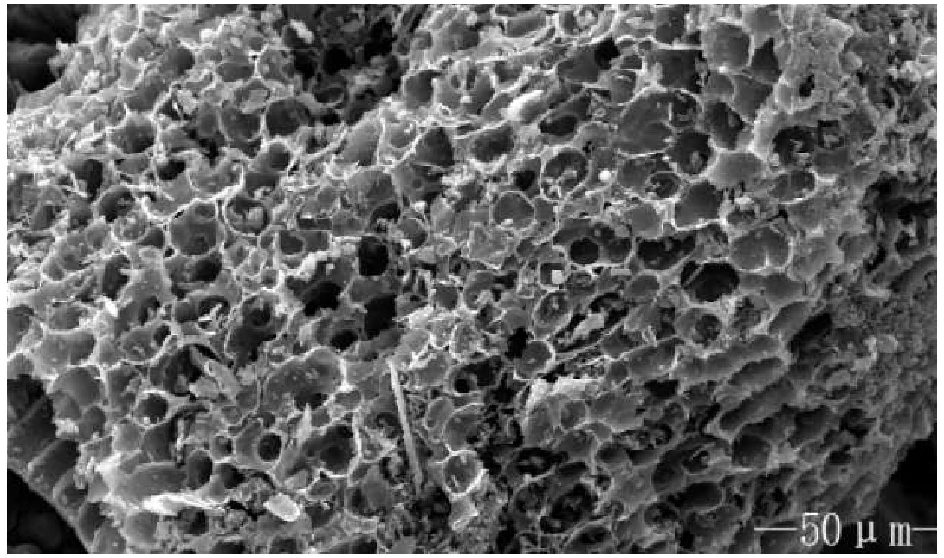
"Biochar that was produced at **pyrolysis temperatures above 550°C** and presenting a **molar H:C ratio below 0.4** is highly persistent when applied to soil. 75% of such biochar carbon consists of stable polycyclic aromatic carbon (PAC) and will persist after soil application for more than 1000 years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



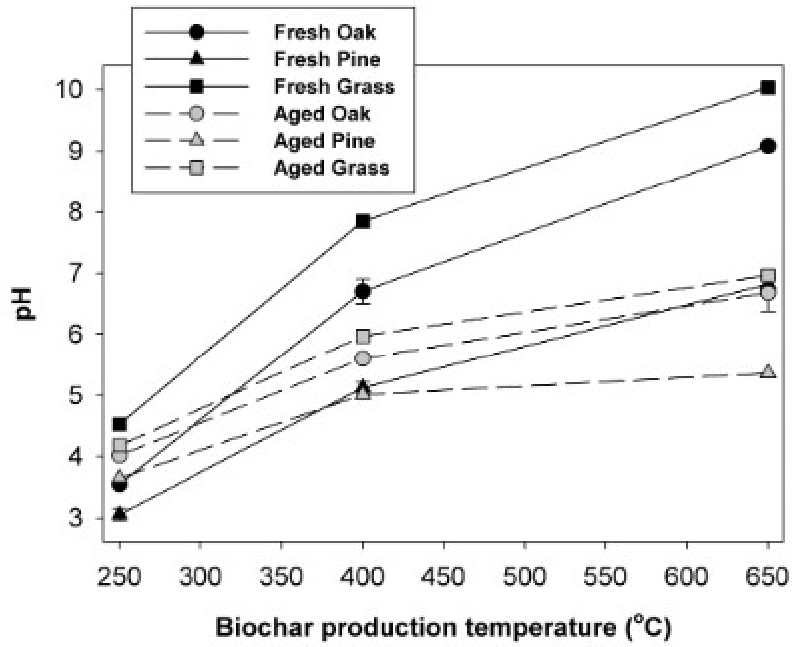
Can Soil Interactions be Dismissed?

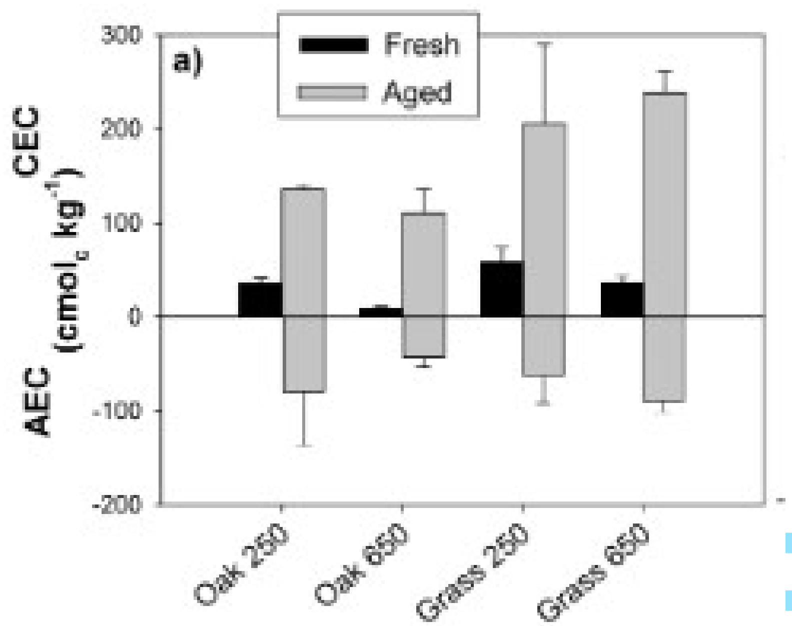
- Field aging biochar leads to changes in behavior

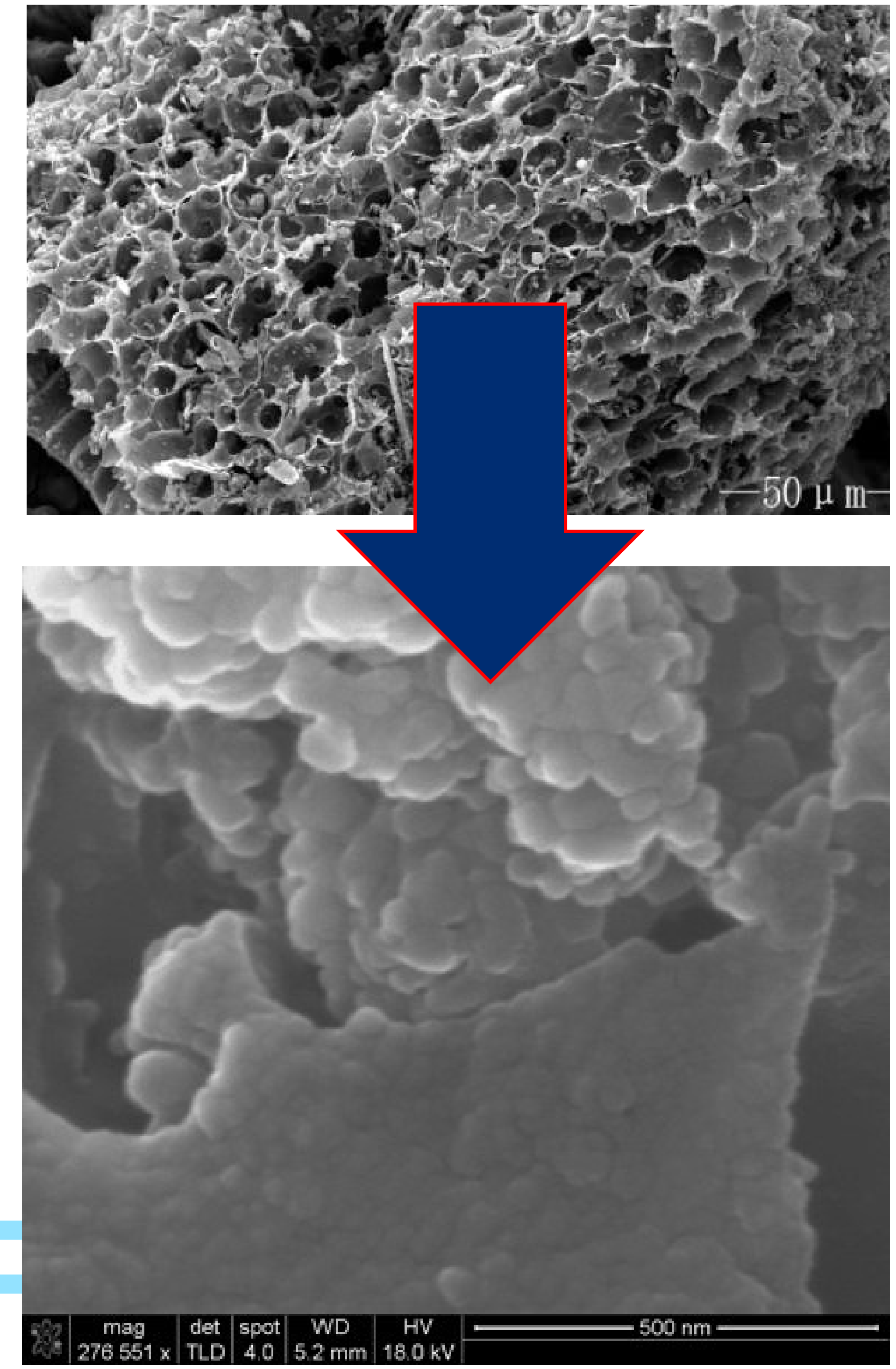
  Studies detailing alterations to:

  - 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.

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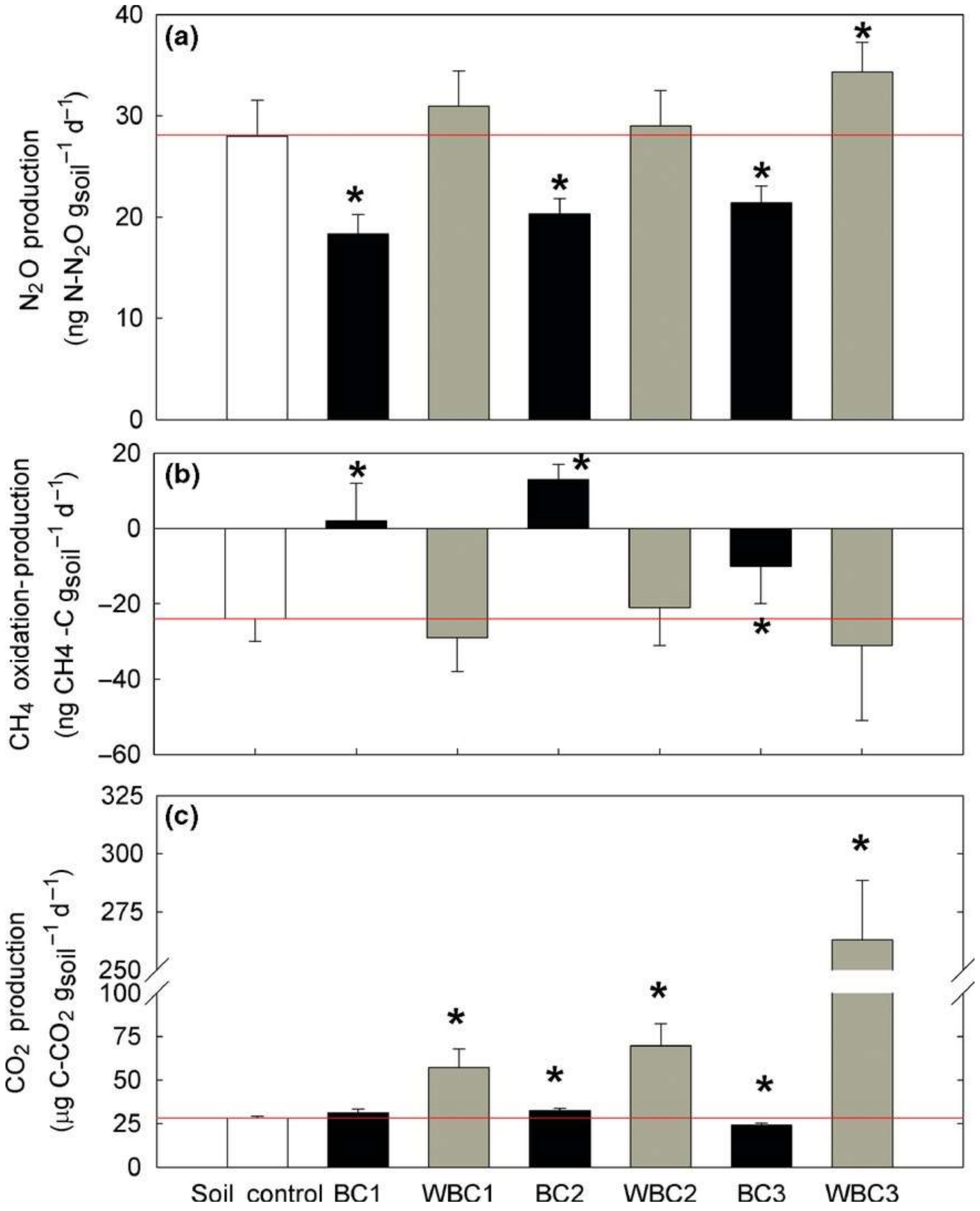

Rosemount, MN Biochar Plots

- One of the longest running field experiments examining the impact of field applied biochar (started 2008)
- Biochar collected 3 years after application

BC1 – Hardwood biochar
BC2 – Pine chip biochar
BC3 – Macadamia nutshell biochar
W – Weathered (3 yr)

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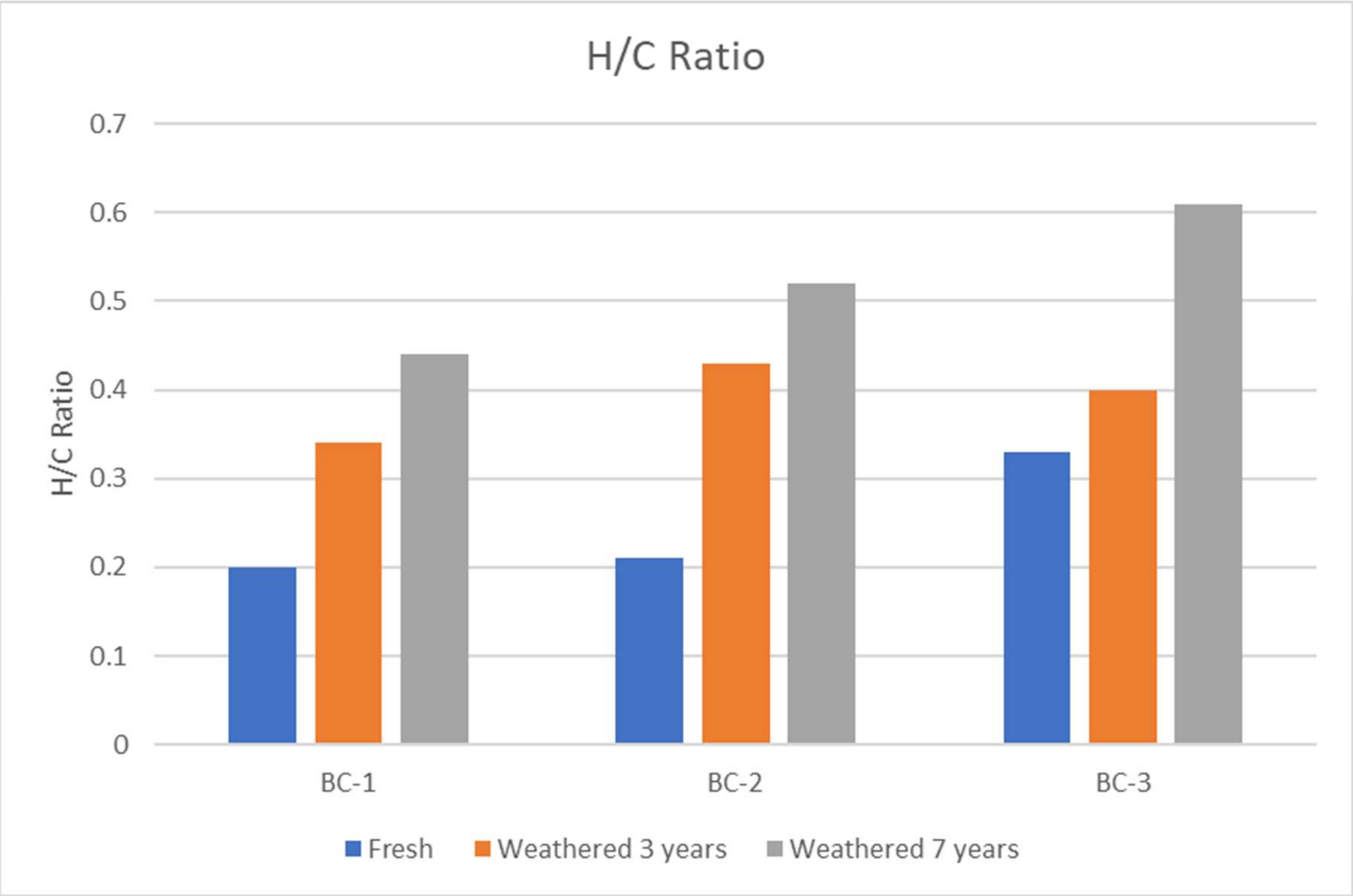


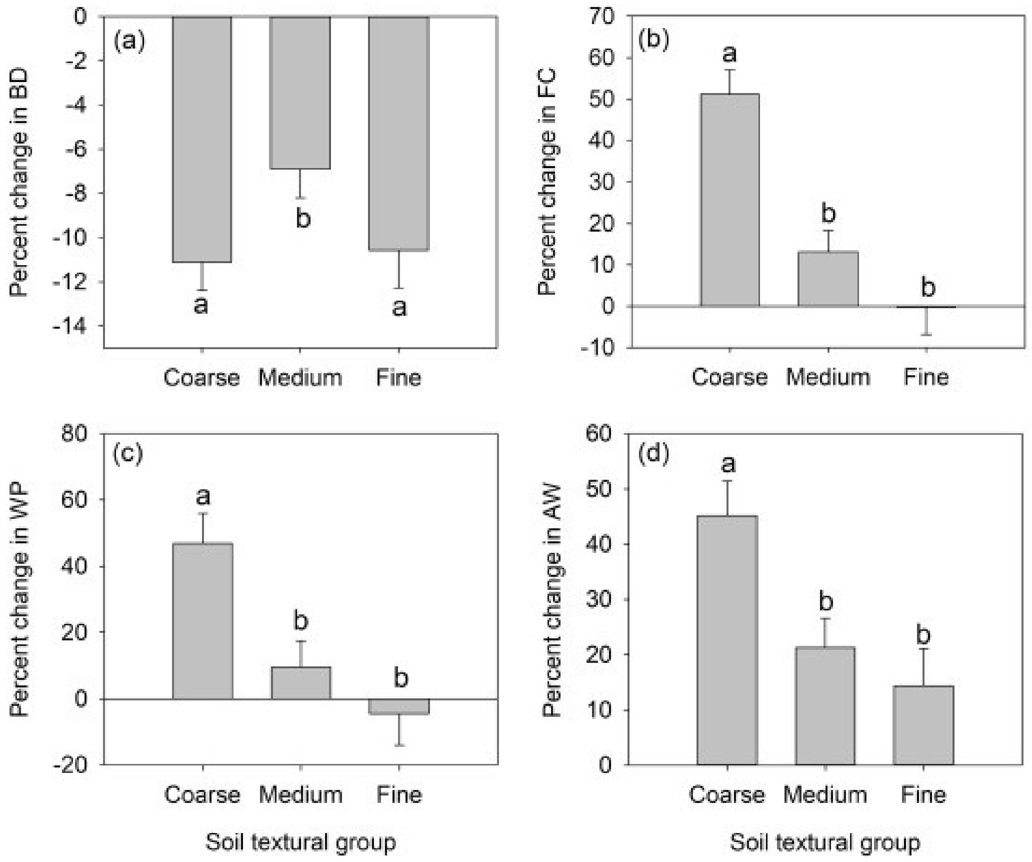
Alteration in Chemical Composition of Field Retrieved Biochar

- Increasing H:C ratio – (remember <0.4 threshold)
- With previous increase in CO_2 production : Suggests reduced resistance to microbial and chemical mineralization with time
- However, is H attached to biochar-C, “new” carbon sorbed to biochar or something else ?
- 15-year time point this Fall

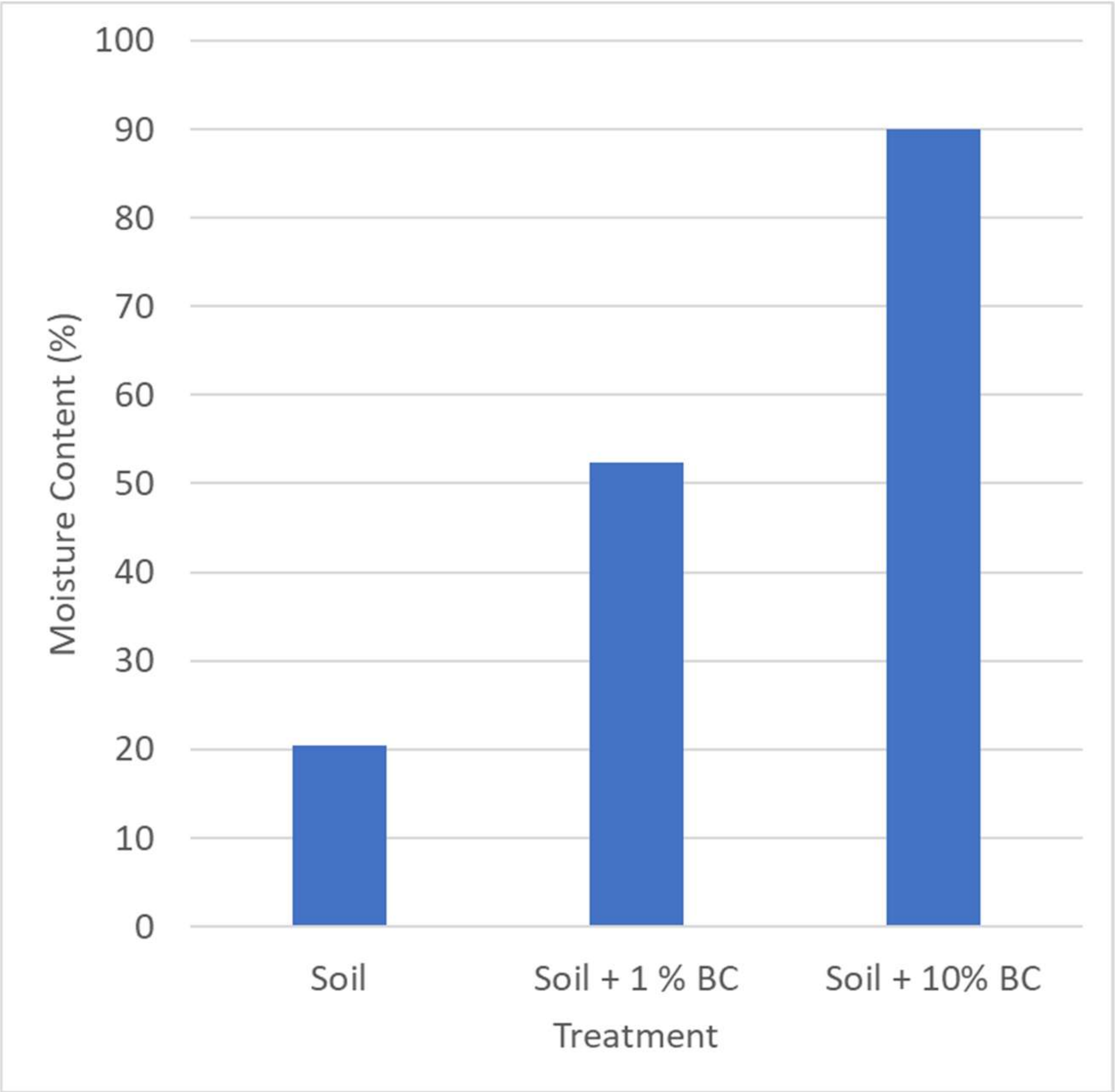
Soil Moisture Improvements

Higher gravimetric moisture observed following biochar additions

- **Foundation for biochar's application for improving soil water availability**



Statistically significant for coarse textured (sandy) soils only



-- Saturated soil moisture content sandy soil (Becker, MN) (pine chip 500 °C biochar)

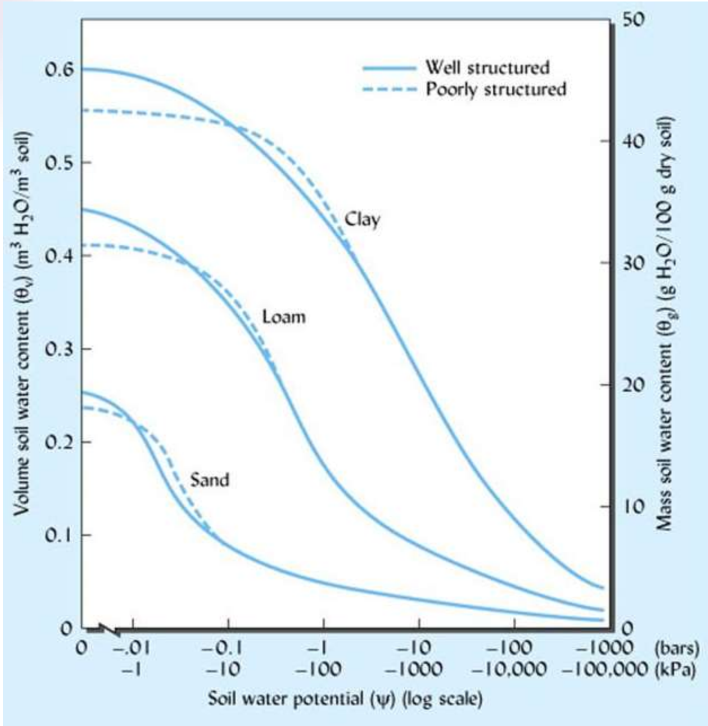
Razzaghi, F., P.B.Obour, E. Arthur, Does biochar improve soil water retention? A systematic review and meta-analysis, Geoderma, Volume 361, 2020, 114055, ISSN 0016-7061, https://doi.org/10.1016/j.geoderma.2019.114055

Total soil water potential

- When looking at soil moisture:

  Need to remember **total soil moisture potential**

$$\Psi_{smp} = \Psi_{matrix} + \Psi_{gravitational}$$



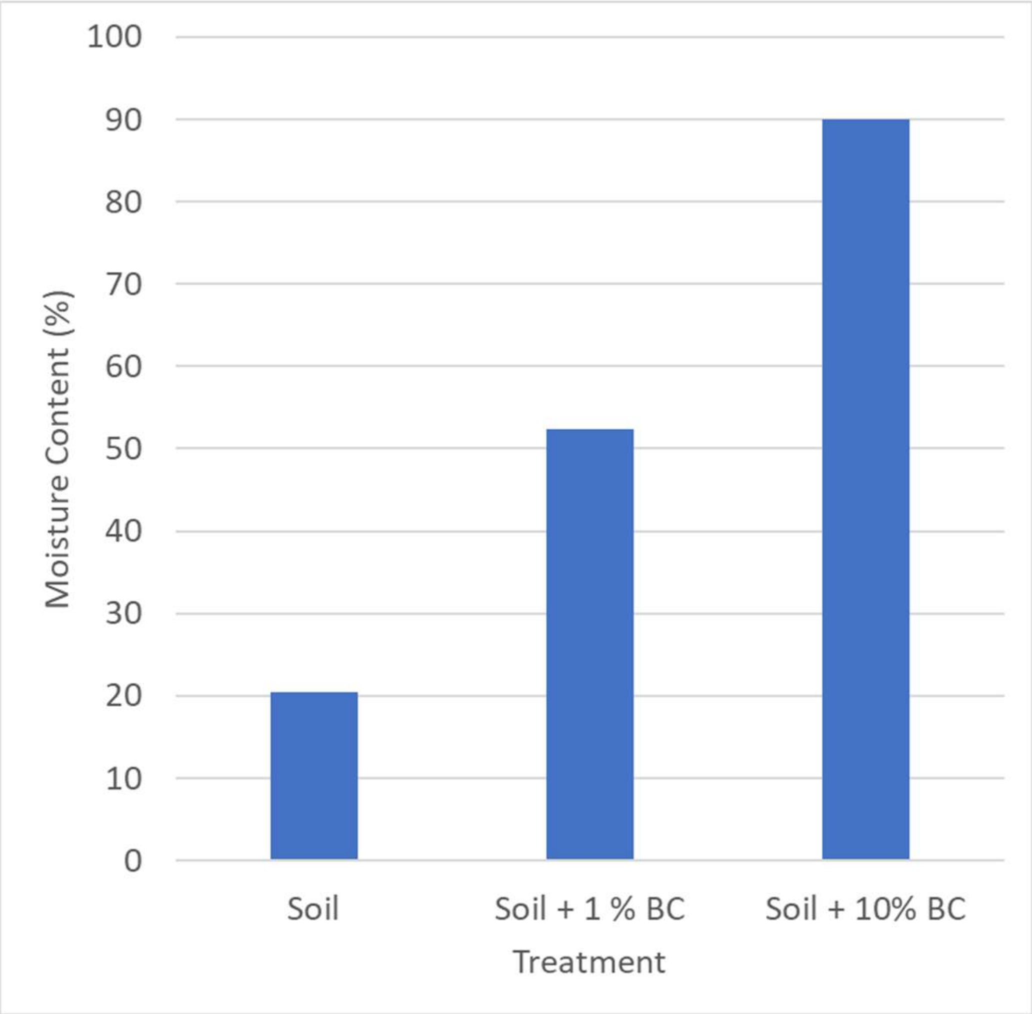
Often "dropped" terms of soil moisture potential:

$$\Psi_{smp} = \Psi_{matrix} + \Psi_{gravitational} + \boxed{\Psi_{osmotic} + \Psi_{RH} + \Psi_{electrostatic} + \cdots}$$

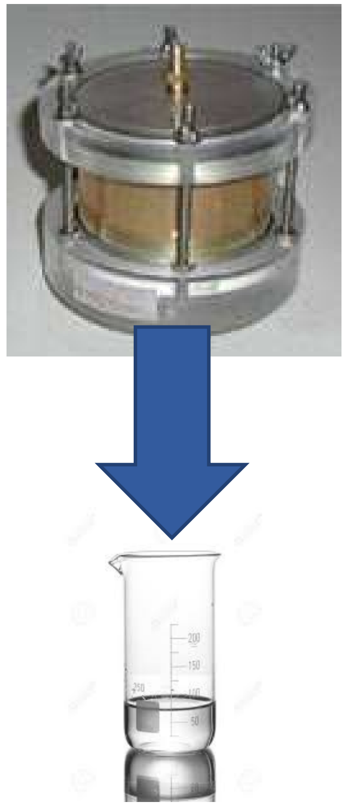
Typically, not important drivers in the soil environment
But what about biochar ?

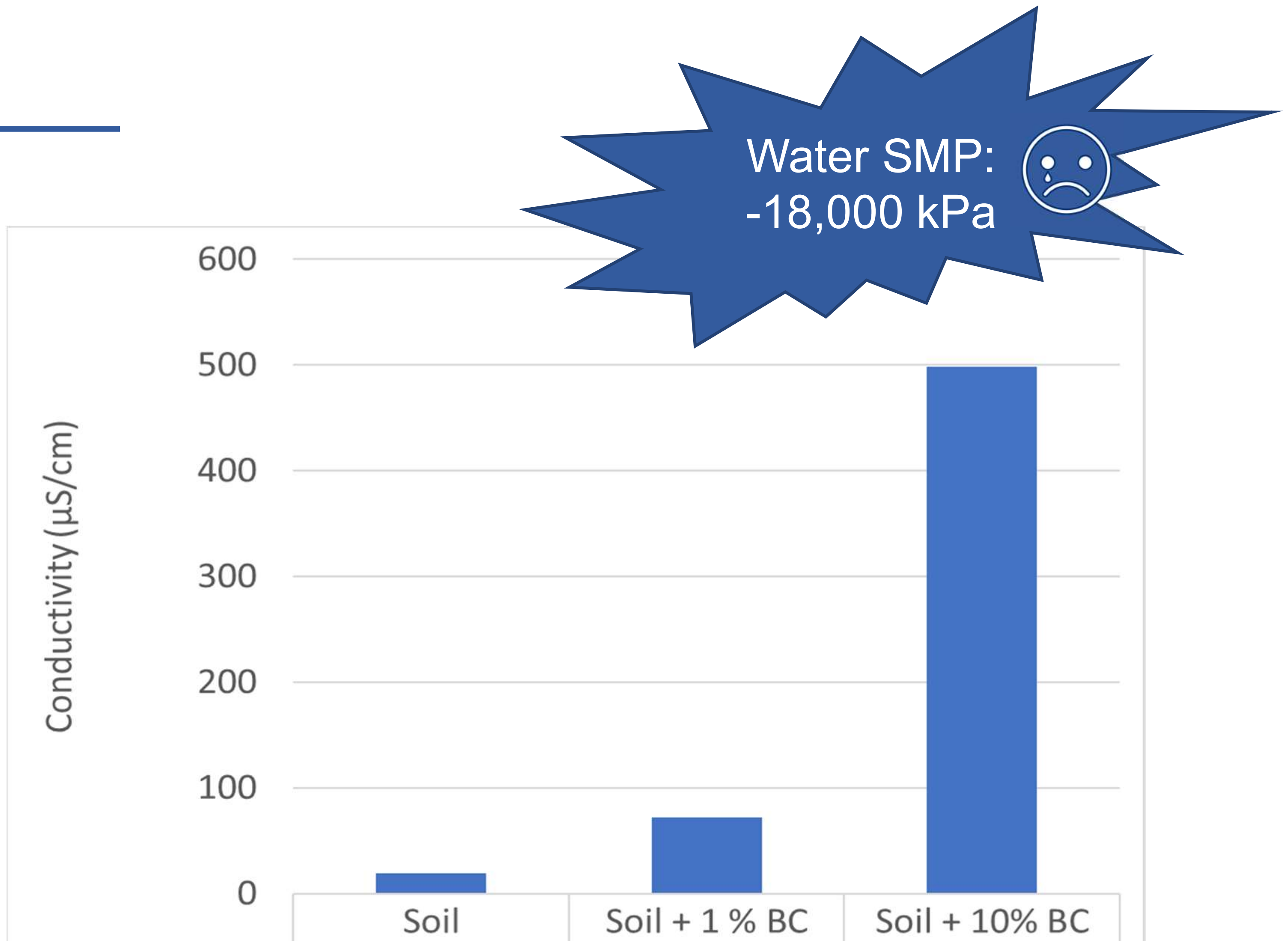
Osmotic Effects

- Remember the initial data :



Pine chip biochar (500 C)





	Soil	Soil + 1 % BC	Soil + 10% BC
Conductivity	19	72	498

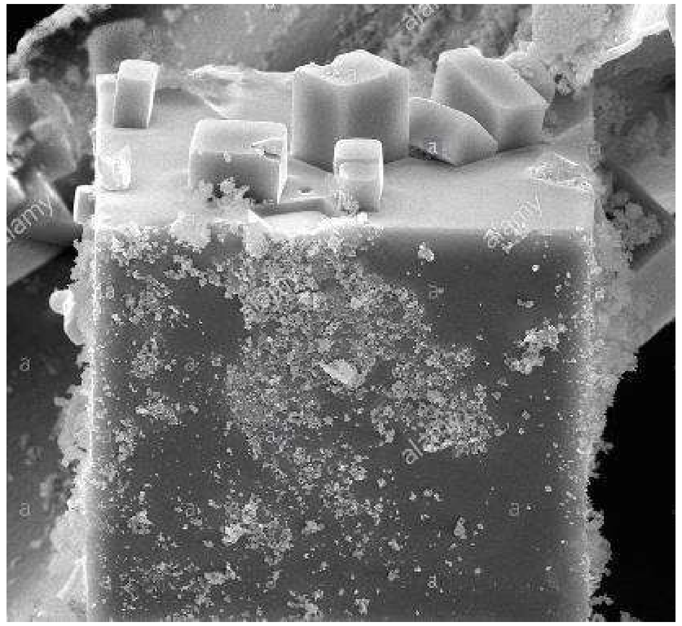
$$\Psi_{osmotic} = -36 * (EC)\ kPa$$

An electrical conductivity > 41.6 µS/cm is at the wilting point (-1,500 kPa)

Biochar + Salt Solutions

- 500 ^oC 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

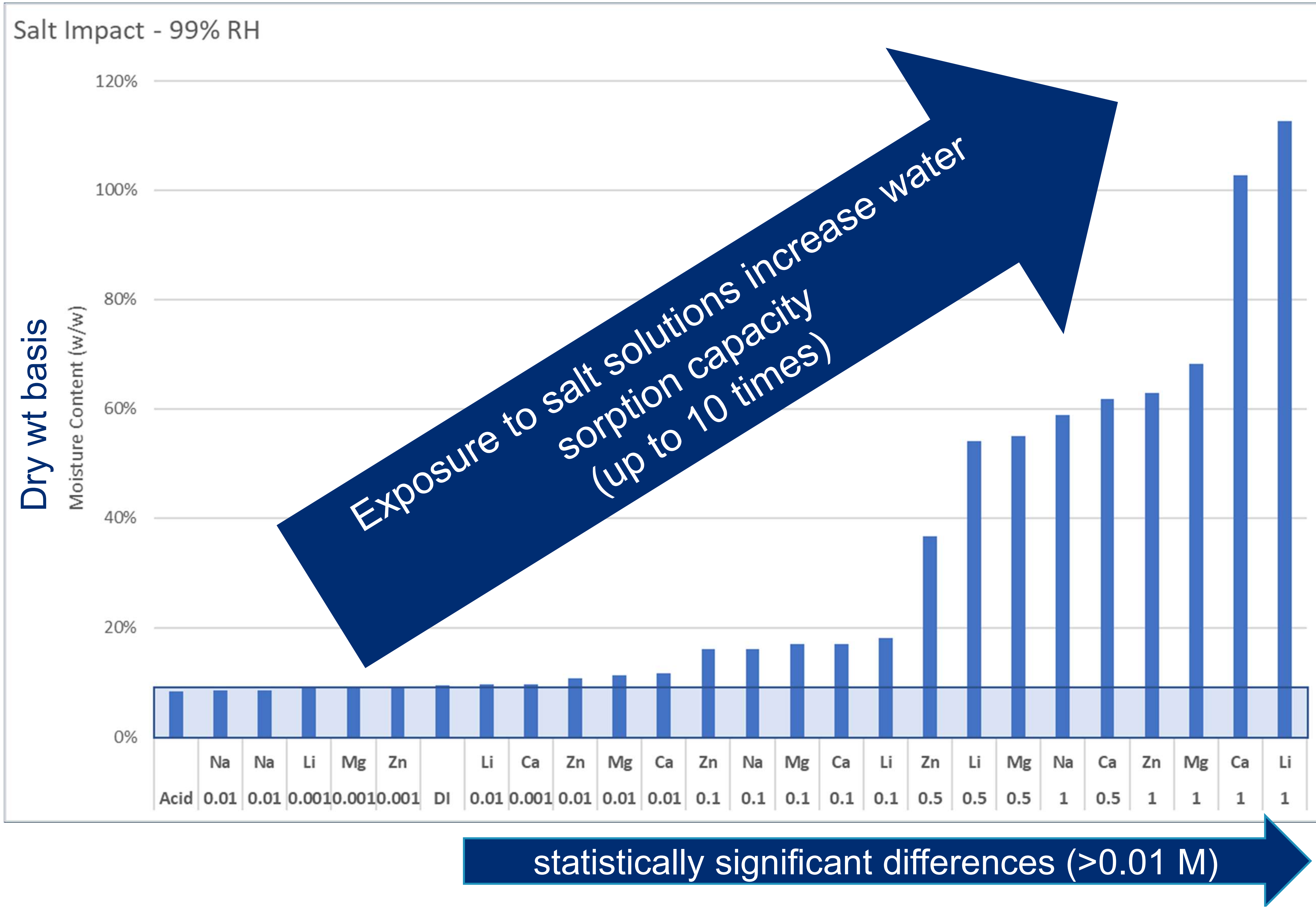


- Soaked for 30 days (reciprocating shaker 180 rev/min)

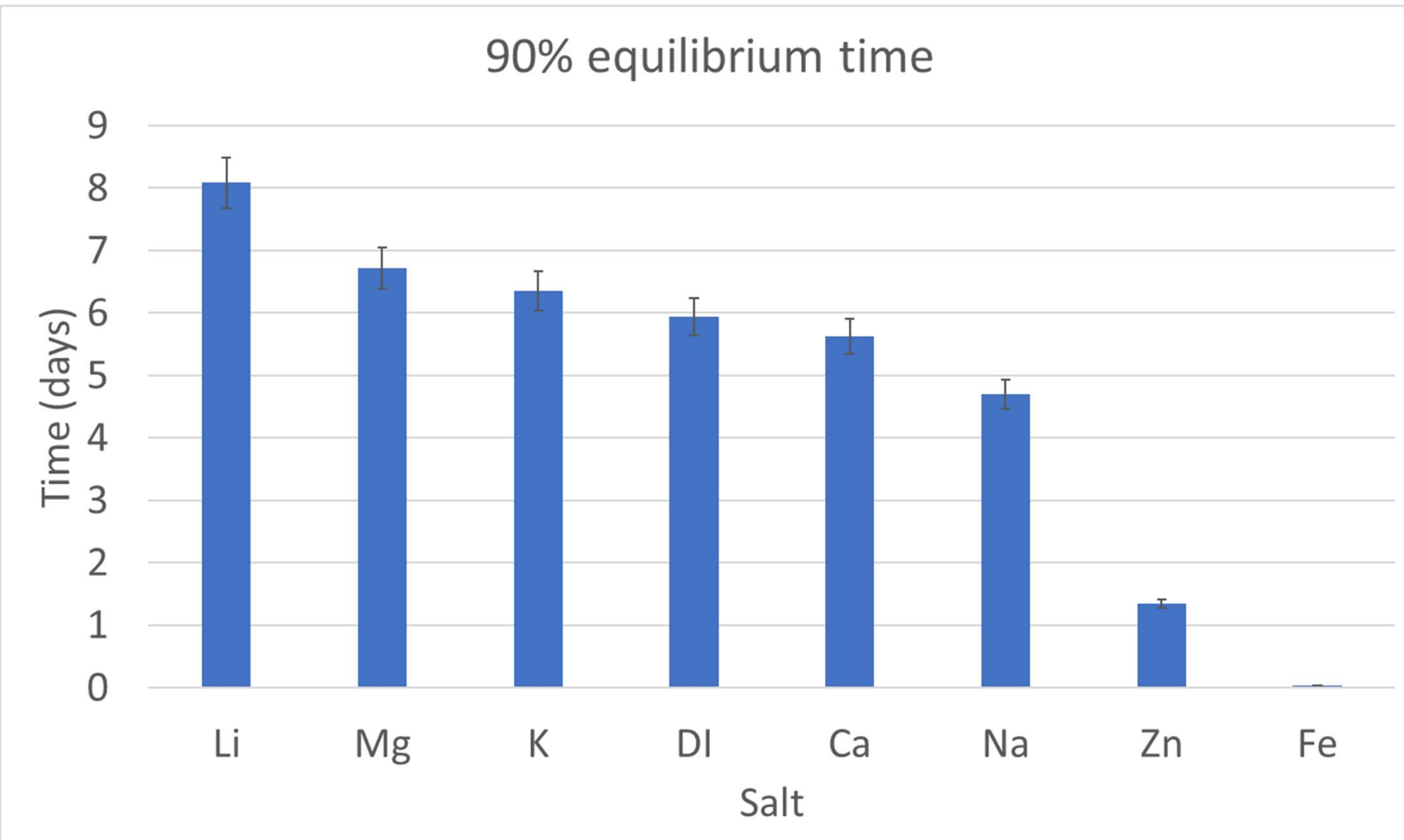
- Biochar was then rinsed with DI water in funnel with filter paper until <15 µS/cm conductivity

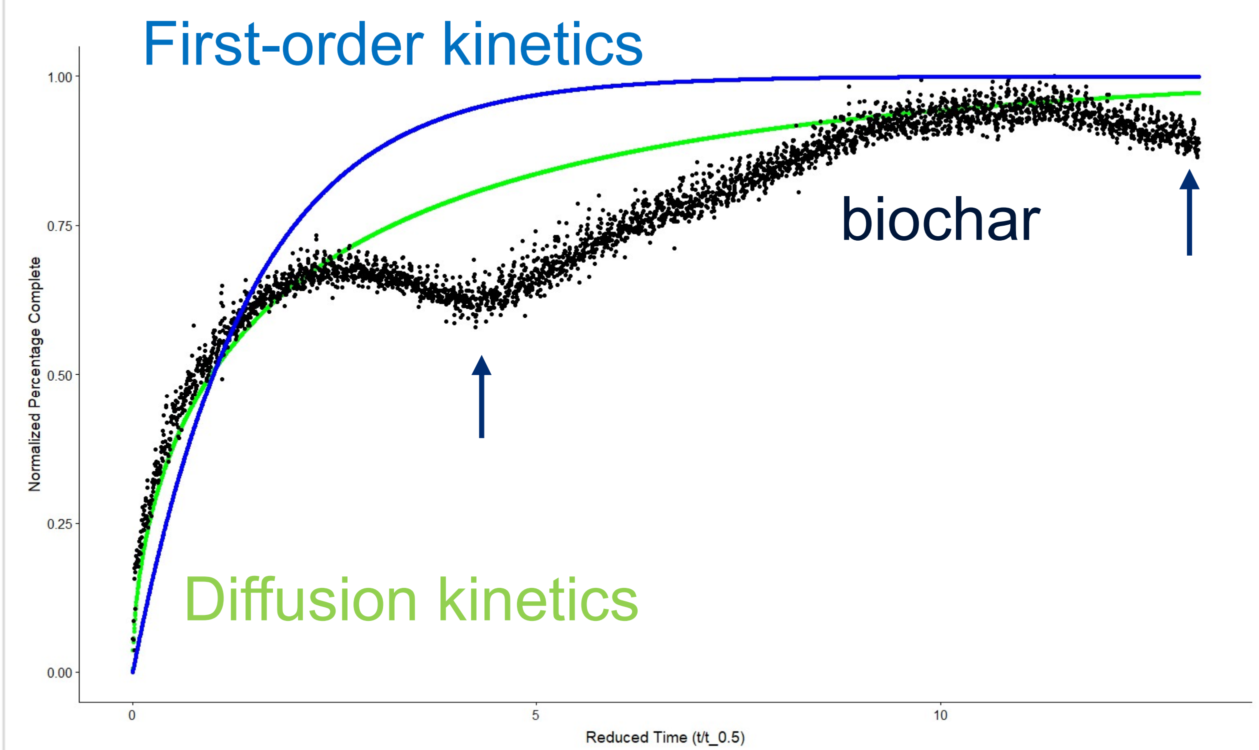
- Oven dried at 125 ^oC and then subjected to various tests

Moisture Content (99% RH)



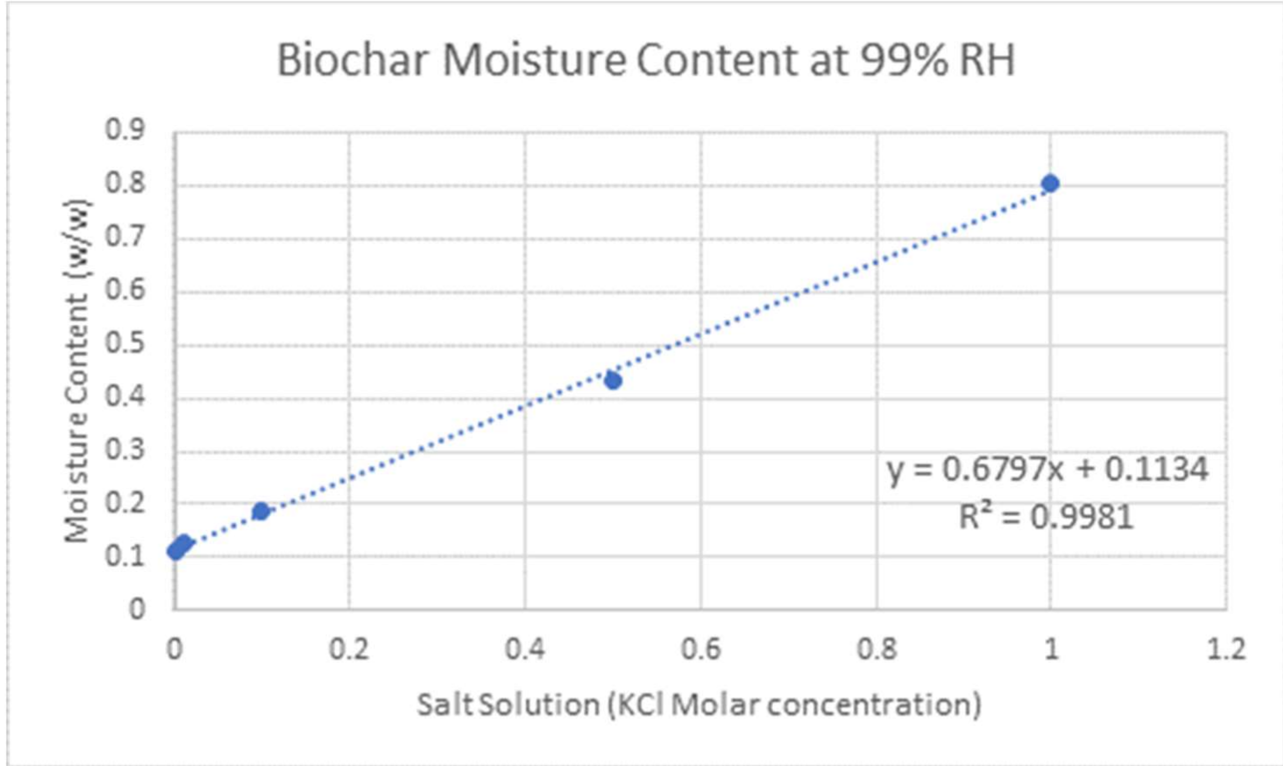
Alteration in water drying equilibrium time





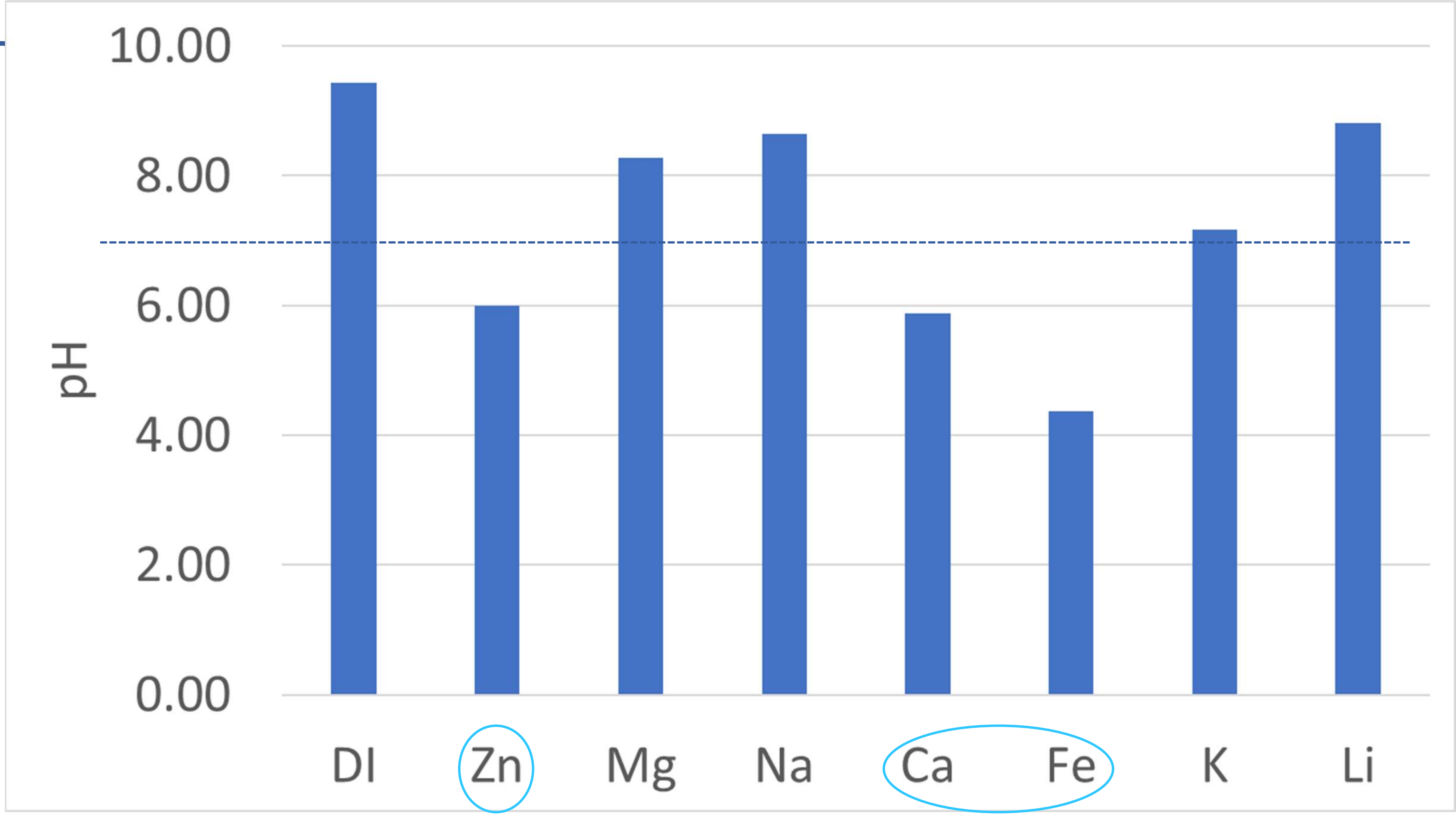
Predictable impact of salt concentration on biochar

- For each salt, there is an excellent correlation between the salt concentration that the biochar was exposed to and the observed moisture content at 99% RH
- $R^2 > 0.98$ for all salts
- However, the exact mechanisms for this are unknown.



Slopes are different for each cation

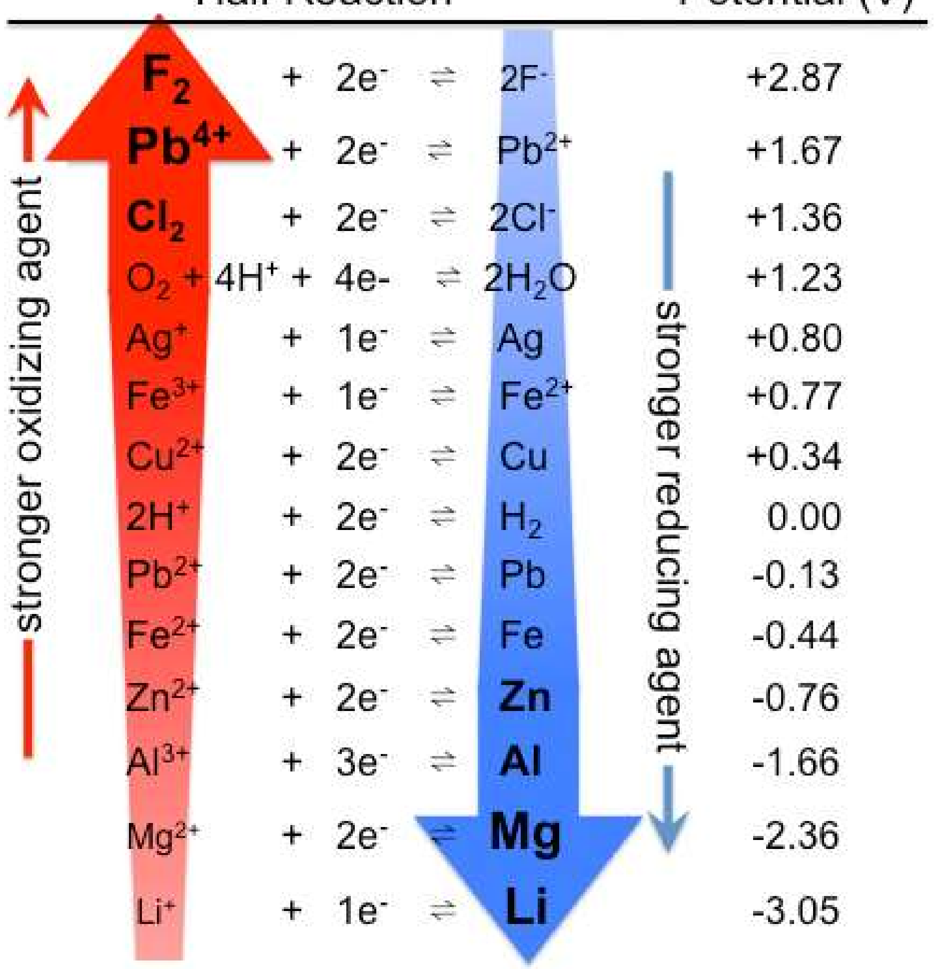
pH Impacts on Biochar



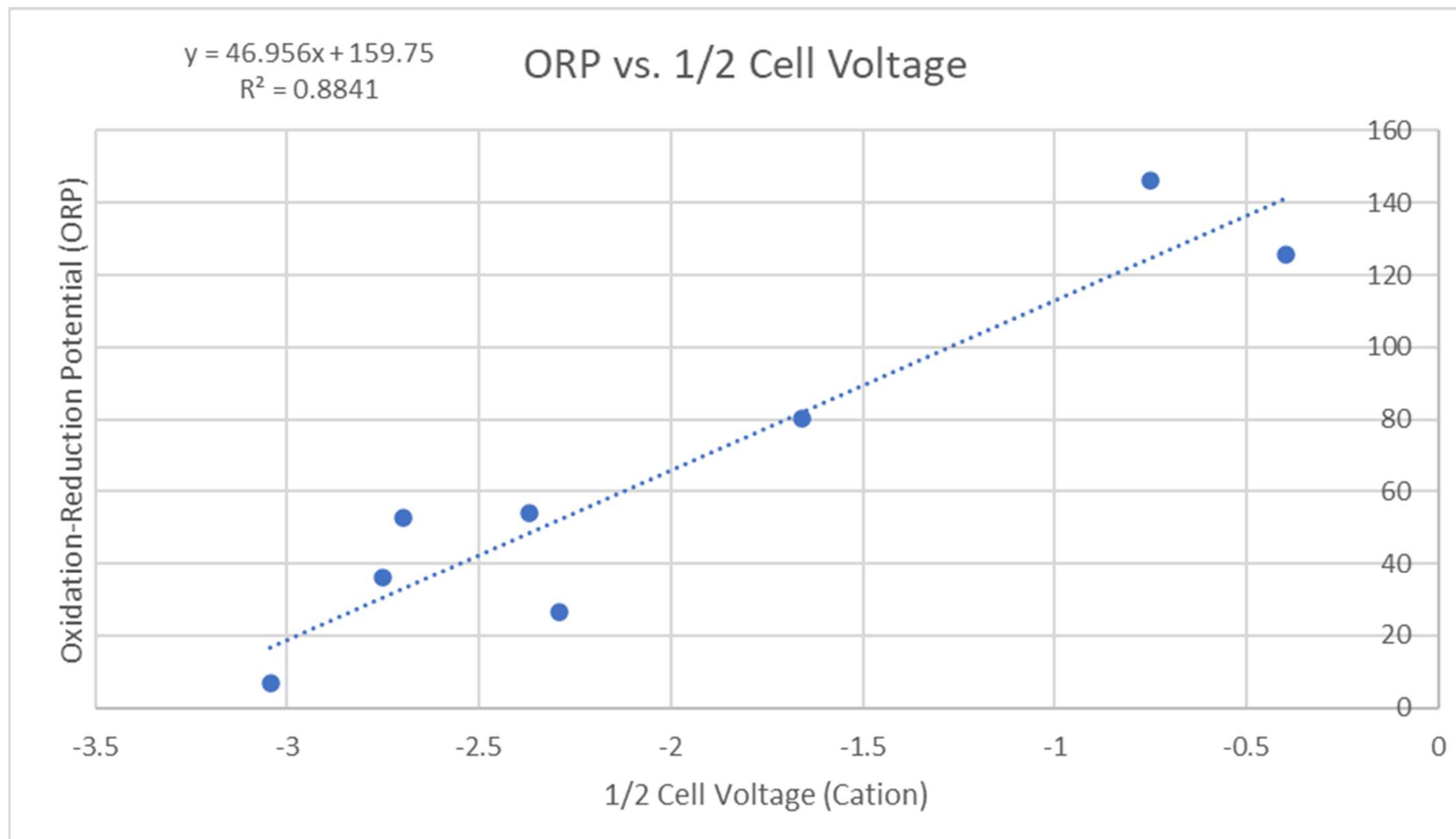
- All salts significantly altered pH of biochar

1:10 BC:DI water ratio

ORP vs. ½ Cell REDOX Potentials



Half Reaction				Standard Potential (V)
F_2	+ $2e^-$	⇌	$2F^-$	+2.87
Pb^{4+}	+ $2e^-$	⇌	Pb^{2+}	+1.67
Cl_2	+ $2e^-$	⇌	$2Cl^-$	+1.36
O_2 + $4H^+$	+ 4e-	⇌	$2H_2O$	+1.23
Ag^+	+ $1e^-$	⇌	Ag	+0.80
Fe^{3+}	+ $1e^-$	⇌	Fe^{2+}	+0.77
Cu^{2+}	+ $2e^-$	⇌	Cu	+0.34
$2H^+$	+ $2e^-$	⇌	H_2	0.00
Pb^{2+}	+ $2e^-$	⇌	Pb	-0.13
Fe^{2+}	+ $2e^-$	⇌	Fe	-0.44
Zn^{2+}	+ $2e^-$	⇌	Zn	-0.76
Al^{3+}	+ $3e^-$	⇌	Al	-1.66
Mg^{2+}	+ $2e^-$	⇌	Mg	-2.36
Li^+	+ $1e^-$	⇌	Li	-3.05



Original biochar was 130 mV ORP

Could biochar ORP be involved in microbial responses ?

Biochemical Reactions and Corresponding ORP Values

Biochemical Reaction	ORP, mV
Nitrification	+100 to +350
cBOD degradation with free molecular oxygen	+50 to +250
Biological phosphorus removal	+25 to +250
Denitrification	+50 to -50
Sulfide (H_2S) formation	-50 to -250
Biological phosphorus release	-100 to -250
Acid formation (fermentation)	-100 to -225
Methane production	-175 to -400

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Conclusions

- Lack of crystalline/clear structures on biochar’s surface after soil exposure
- Attracts an amorphous cation rich layer to the surface of biochar:

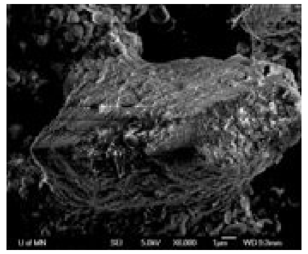
  Not easily removed –-> maybe C-Metal bonds (organo-metalic)

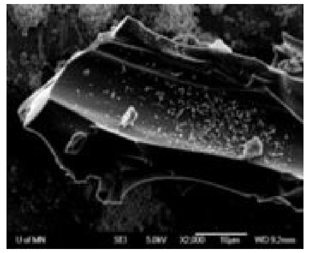
  Carbonates + Oxides of Salt Minerals (Ash): C from atmospheric CO_2 and not biochar C **($CaO \rightarrow CaCO_3$)**

- Dissolved salts/soil solutions → Significantly alters water sorption, agrochemical sorption, and other properties/behaviors
- Changes in redox chemistry could be vital to the mechanisms of biochar interaction

  Redox controls nutrient availability, cation solubility, microbial enzymes, …

- Just like cooking -> “***Not all biochars are equal***”





Thank-you for your attention.