Can biochar’s thirst be satisfied ?

USDA

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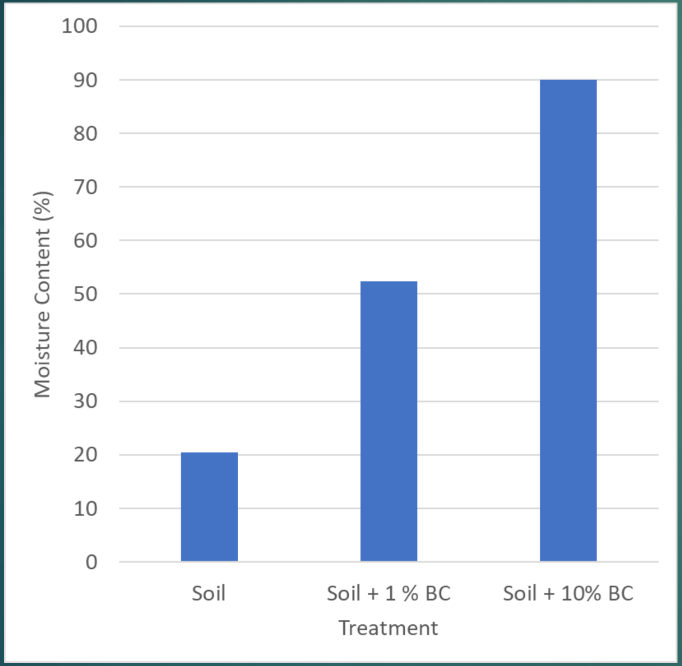
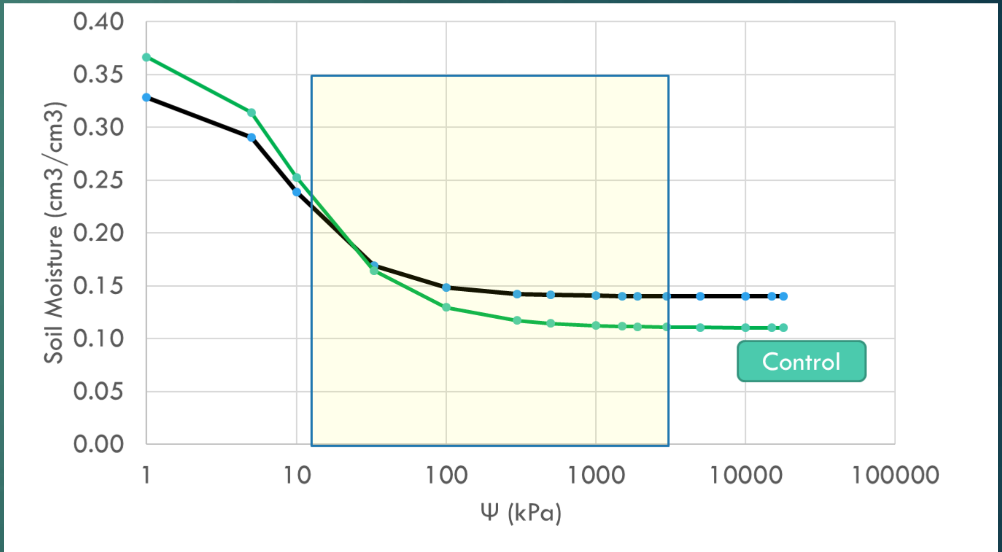
Biochar and Soil Moisture

- **Typical observation**
  - Higher gravimetric moisture following biochar additions



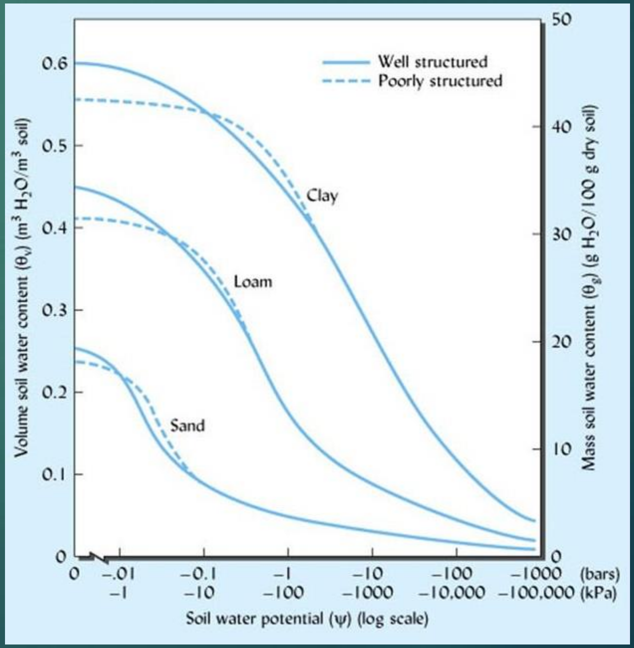


- **Foundation for biochar's application for improving soil water availability**

Total Soil Water Potential

- When looking at soil moisture: Need to remember total soil moisture potential

$$\psi_{smp} = \psi_{matrix} + \psi_{gravitational} + \cdots$$



Total Soil Water Potential

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

OFTEN "DROPPED" TERMS OF SOIL MOISTURE POTENTIAL:

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

Typically not important components in the soil environment….
But what about biochar ?

Osmotic Potential Component

$$\Psi_{osmotic} = C\ R\ T$$

Osmotic Potential Component

$$\psi_{osmotic} = C\ R\ T$$

- For a soil moisture potential equal to the wilting point (-1500 kPa)

$$-1500\ kPa = C\ \left[8.314\ x\ 10^{-3}\ \frac{kPa\ m^3}{mol\ K}\right]\ (298\ K)$$

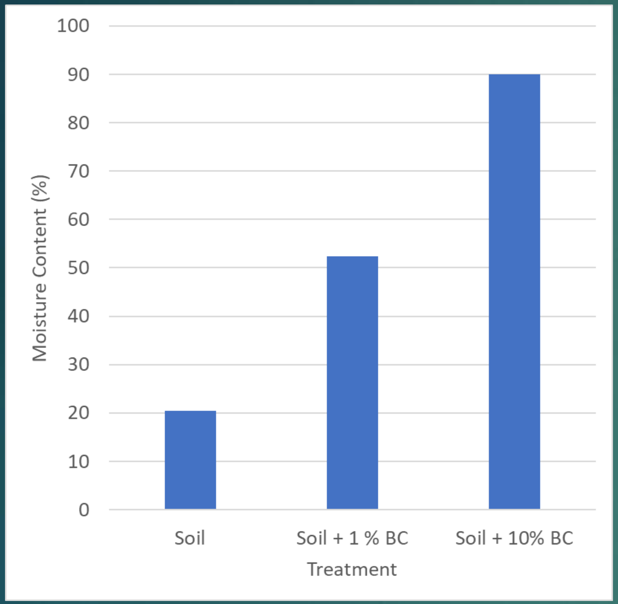
C = 605.43 mol m^{-3} = **0.605 mole** L^{-1}

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

An electrical conductivity > 41.6 µS/cm ➔ wilting point

Osmotic Effects:

- Remember the initial data :



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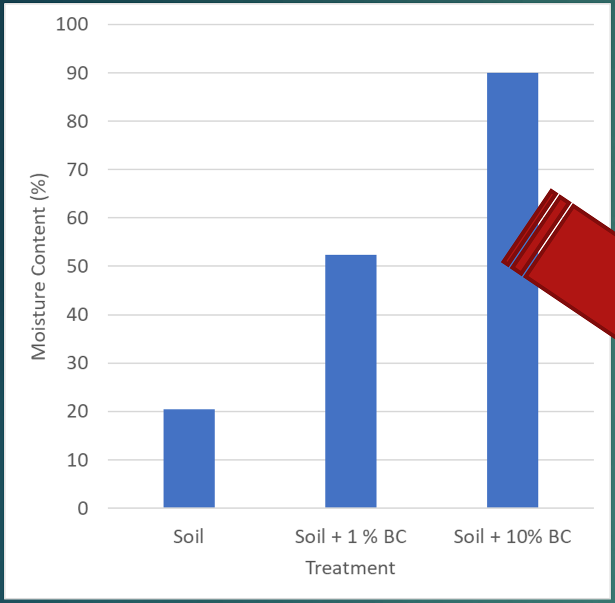
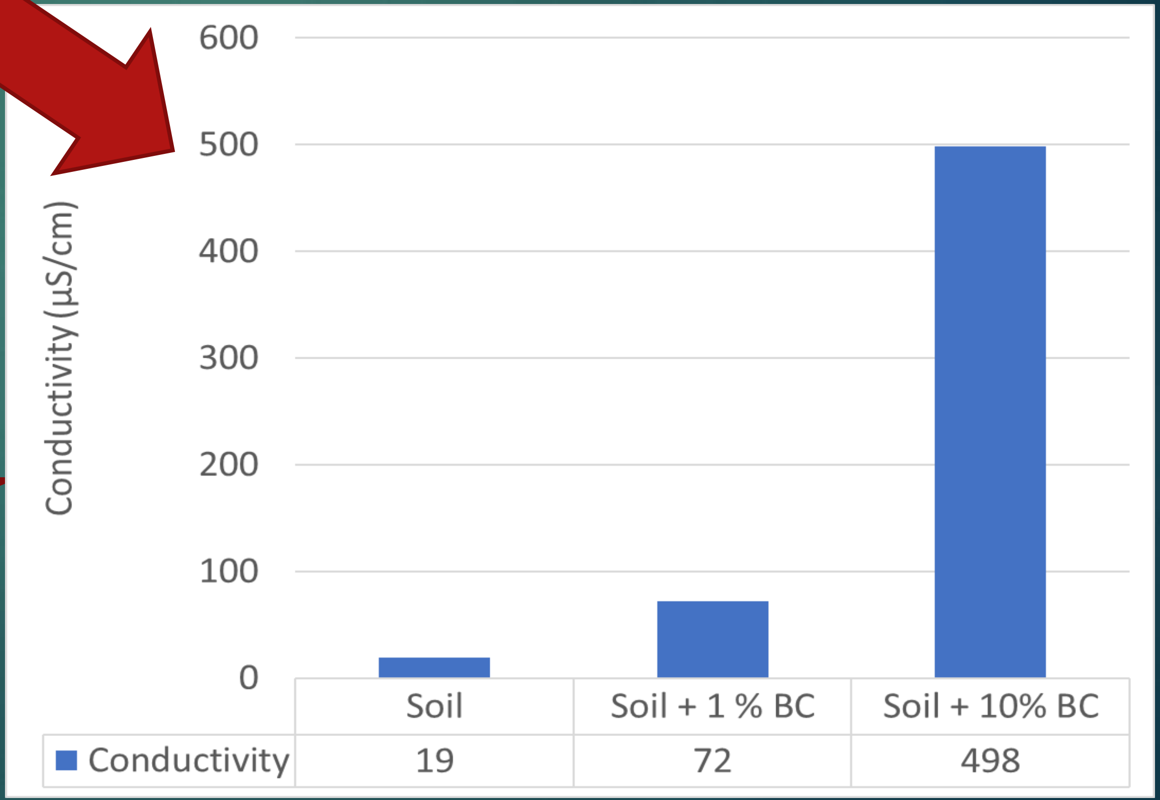
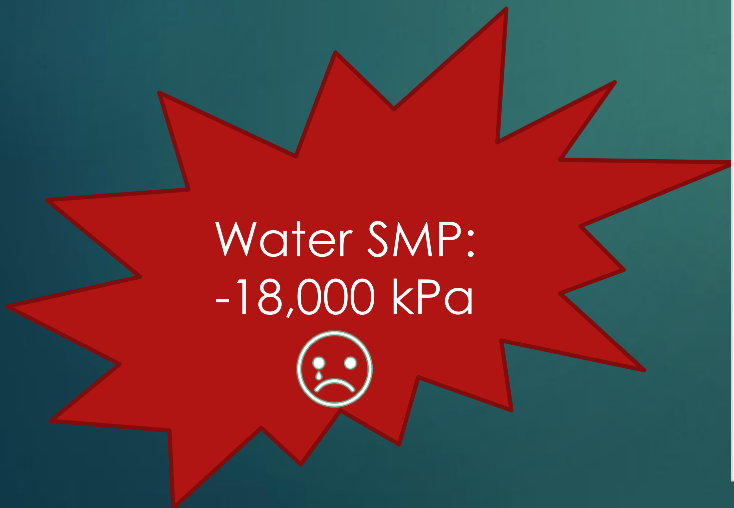


$$\psi_{osmotic} = -36 * (EC)\ kPa$$

Electrical conductivity > 41.6 µS/cm is at the wilting point





Relative Humidity (RH)

$$\boldsymbol{\Psi}_{RH} = \frac{RT}{M_w} \, ln(h_r)$$

Relative Humidity (RH)

$$\psi_{RH} = \frac{RT}{M_w} ln(h_r)$$

- For a soil moisture potential equal at the wilting point (-1500 kPa)

$$h_r = \exp(7.3\ x\ 10^{-6} * \psi)$$

$$h_r = 0.989 \quad [98.9\% \text{ relative humidity}]$$

- < 98.9% RH is below the wilting point

Research Question →

- Which sorbs quicker to biochar : Water vapor or liquid ?

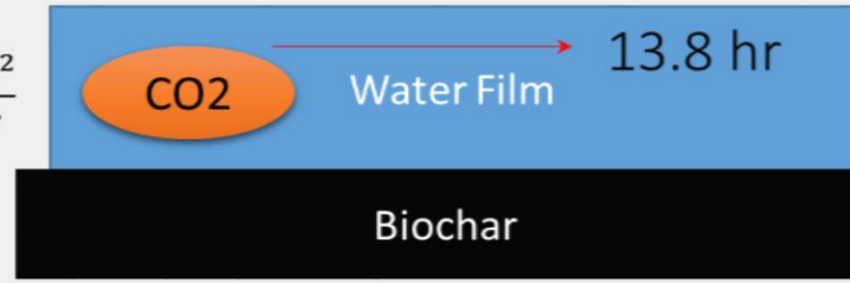
Transport of species in water and gas phases

- Estimate the time for diffusion of 1 cm in liquid and gaseous phases

Diffusion of CO_2

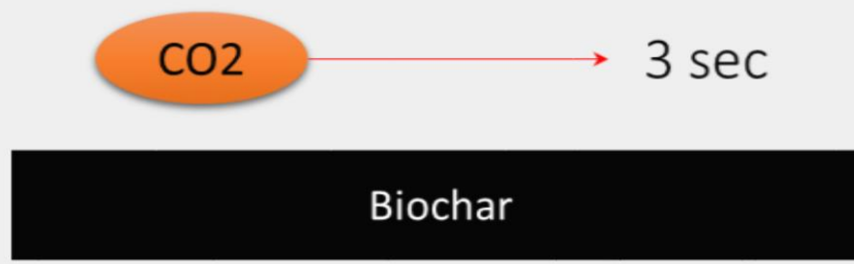
A) In liquid phase

$$D_L = 1.6\,x\,10^{-3}\,\frac{mm^2}{sec}$$



B) In gas phase

$$D_G = 16\,\frac{mm^2}{sec}$$

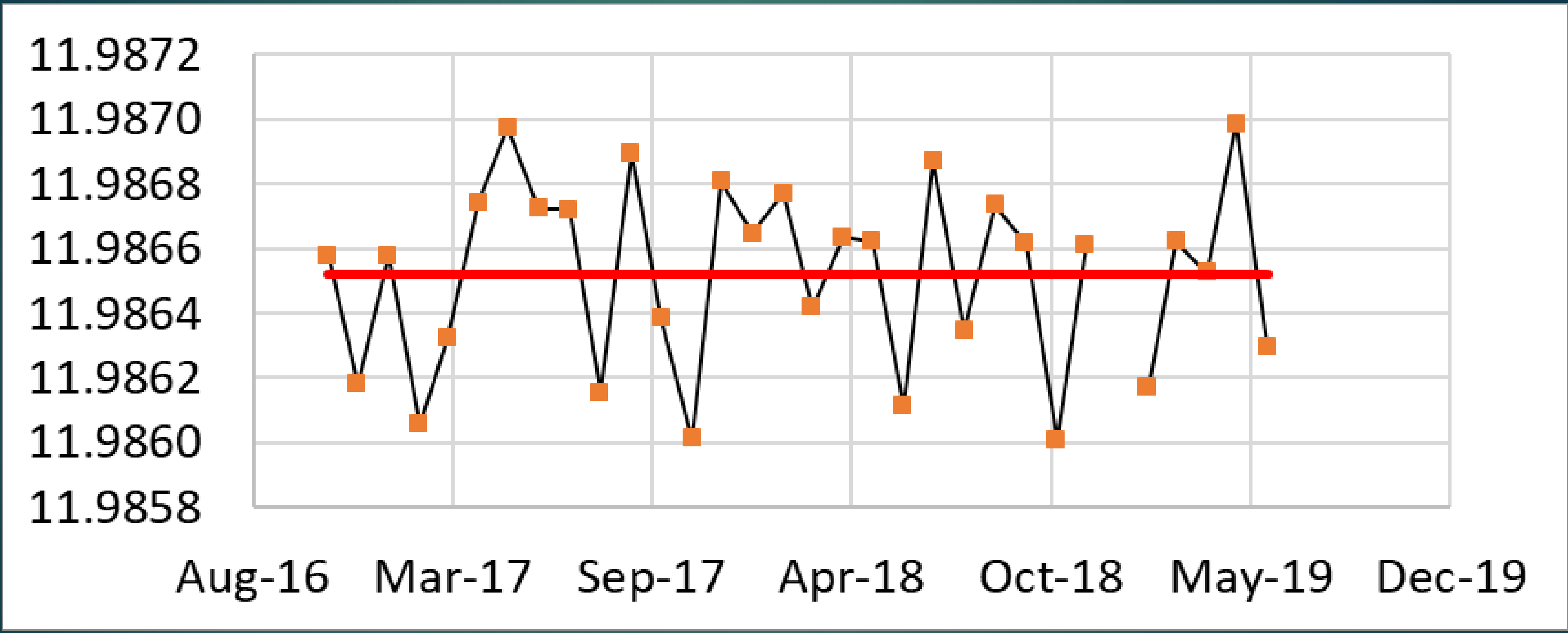


$$t \approx \frac{x^2}{2D}$$

Gravimetric Determinations

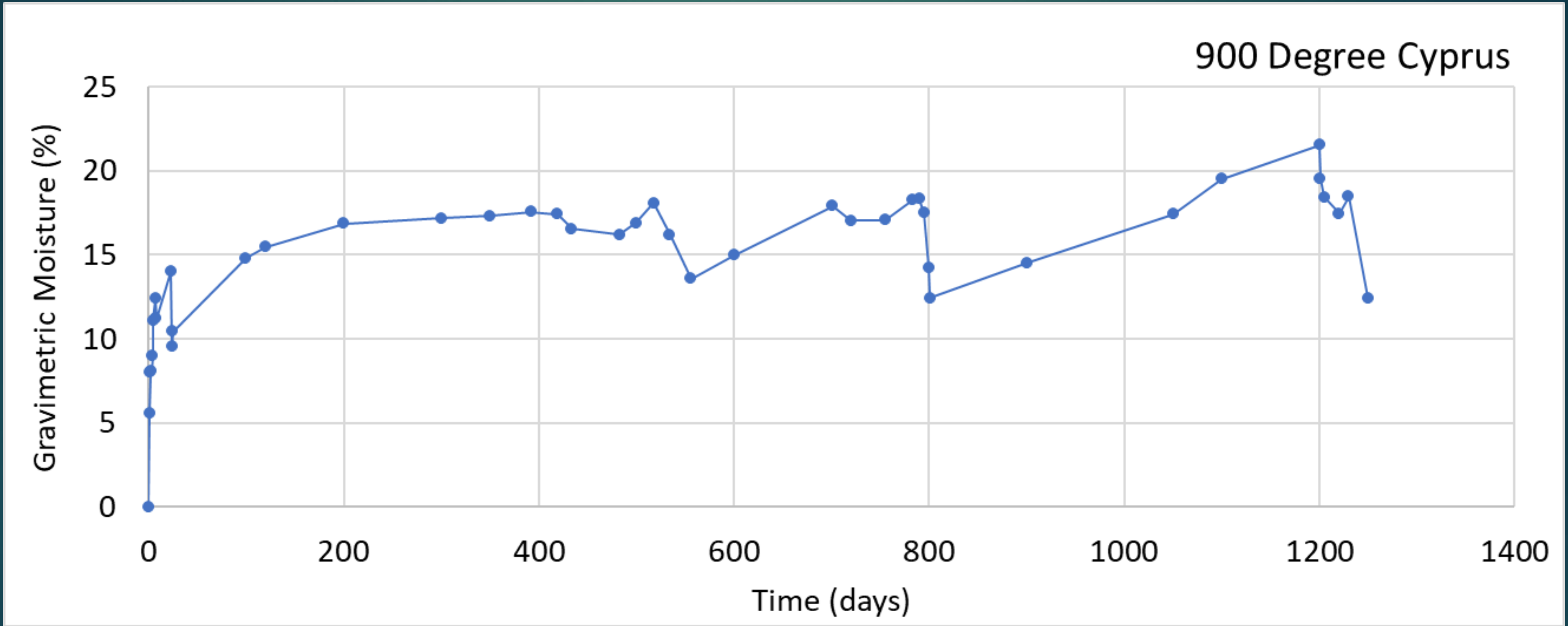
- Sealed environment: Saturated salt solutions (Greenspan, 1989) or specialized water vapor packs (i.e., Boveda)
- Biochar contained in open glass vials
- Empty glass vials controls [started Oct 2016]
- Weighed periodically
  (5 decimal place balance)
- Longest running for 3.5 years.

Control Vials -

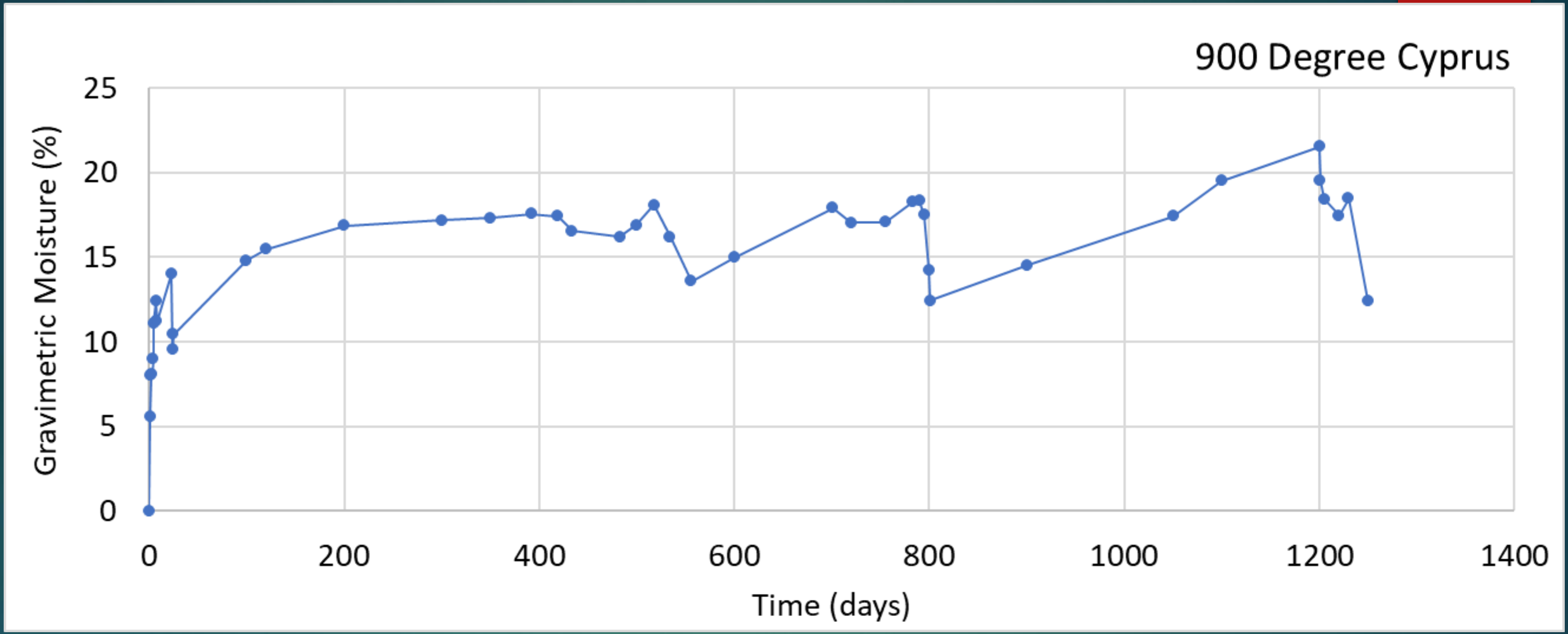


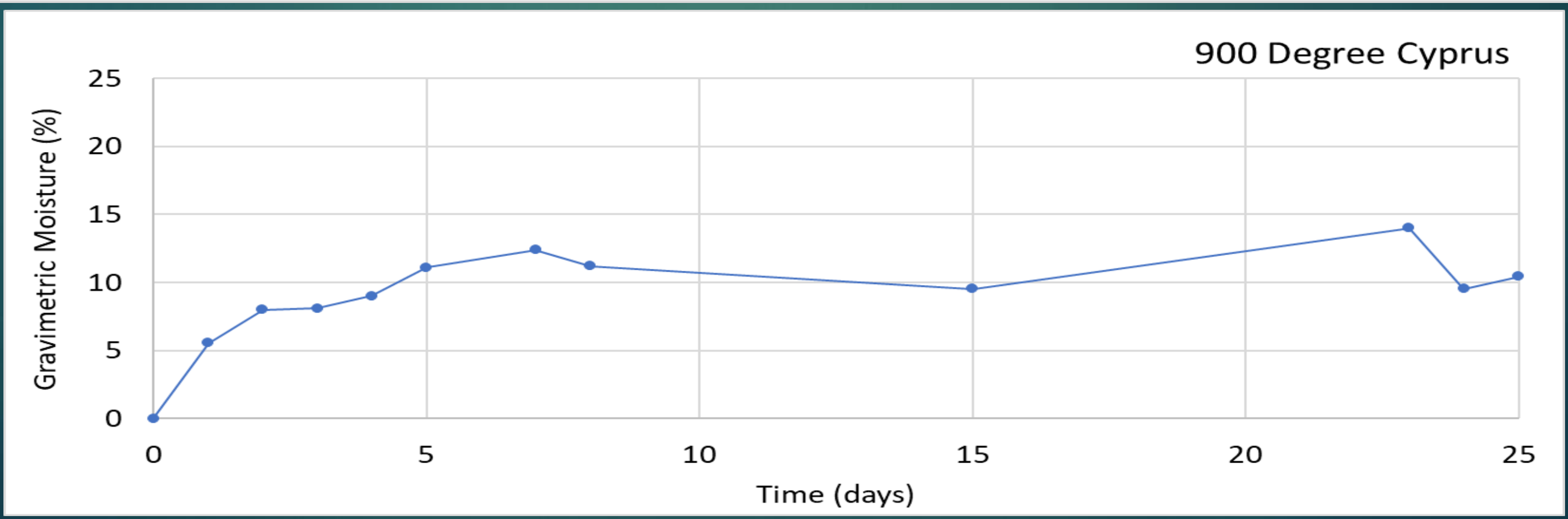
Standard Deviation = 0.3 mg (0.0003 g)

Cyprus 900 Biochar : 50% RH



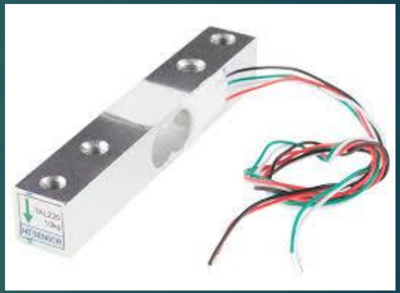
Cyprus 900 Biochar



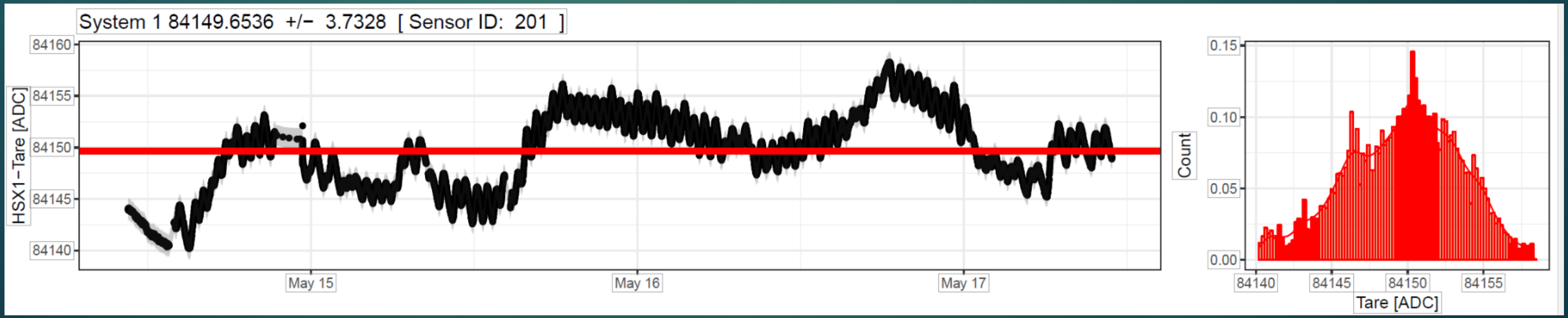


Arduino-based balances

- Need an inexpensive system to monitor milligram differences in mass with time and could be enclosed in a controlled environment

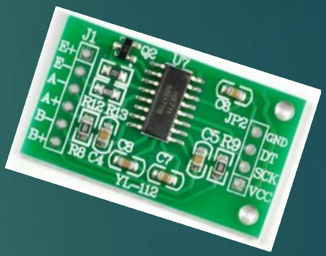


- **Problems:**
  - Stability of strain gauges:
    - Temperature / Zero Offset / Tare drifts
    - Often limits the accuracy of inexpensive beam strain gauges

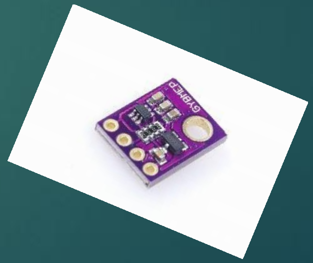


Arduino Balance Systems

- Based on Arduino Uno and Nano microcontroller boards
  - Using 0-100 g strain gauge balances
  - HX-711 24-bit ADC chip
  - Stepper motor (sample lifter)
  - BMP280E – temp/humidity/barometric pressure
  - nRF24 boards (multi-point wireless communication)

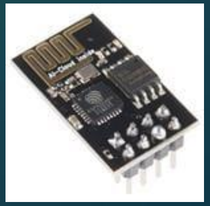


- Total system cost < $15.00 per system



- Data sent over a 2.4 GHz radio mesh network

  Simplifies data archiving



Arduino Balance System

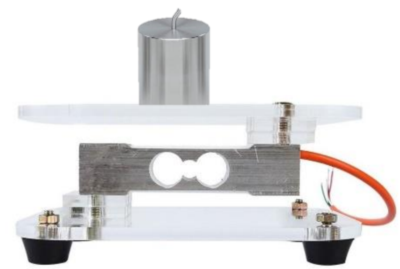
- **Compounding of errors**

  – Lead to lack of sensitive measurement

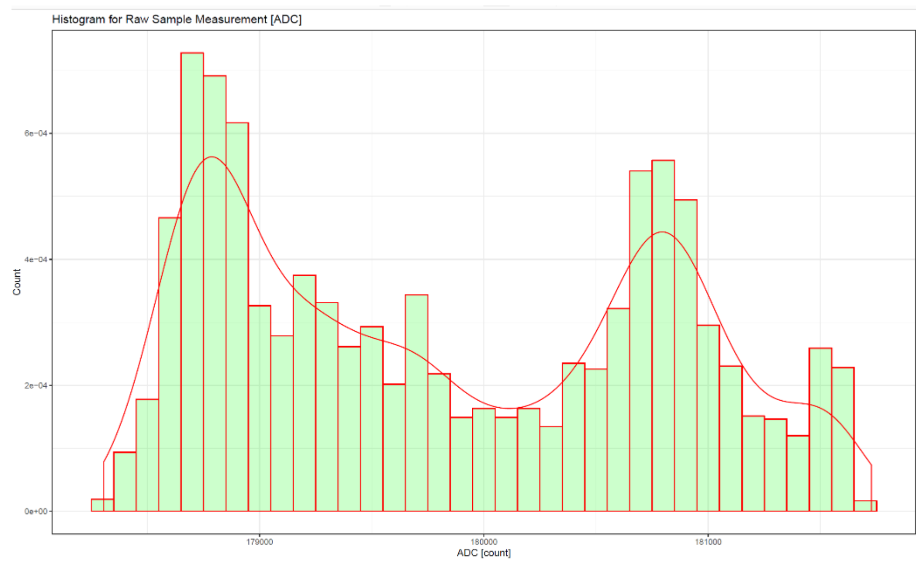
  - **100 g mass**
  - **Mass recorded every 10 seconds over 24 hours**

Overall error ± 1.5 g (<2%)

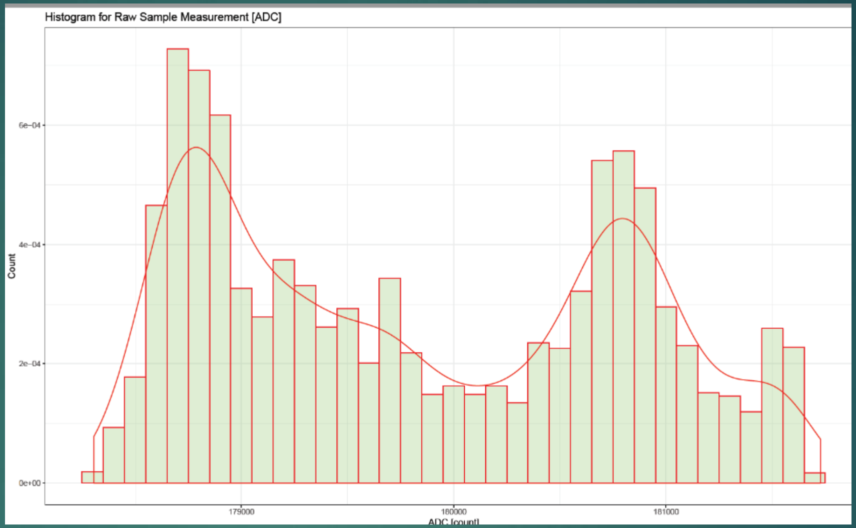
  - **Can we do better?**



Load Cell temp drift/zero errors:
2% full scale



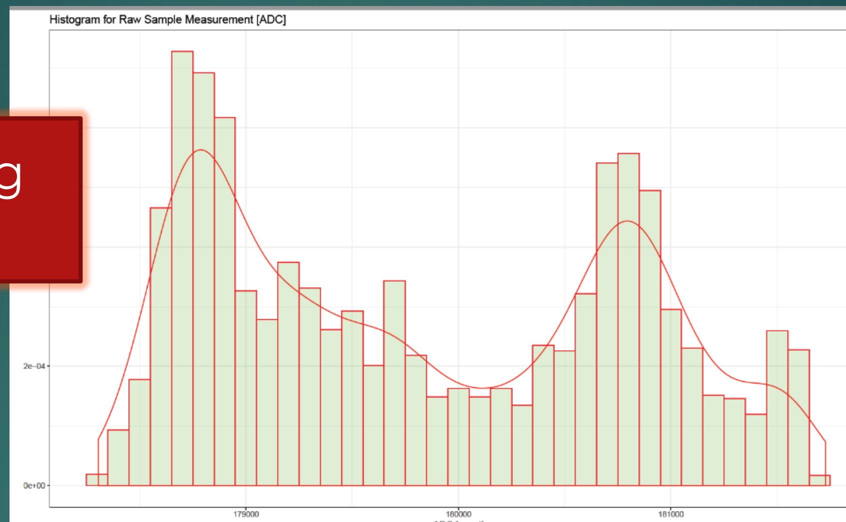
Mechanical Solution:



- How do lab bench balances achieve higher accuracy ?

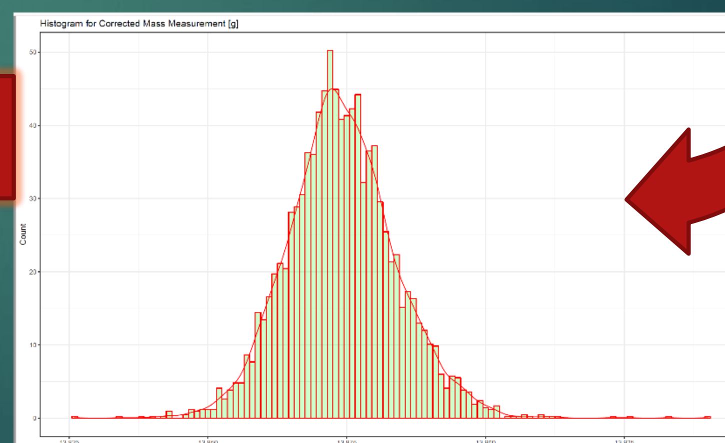
Mechanical Solution

Overall error ± 1.5 g (<2%)



- Raise-Lower samples onto balances each weighing period

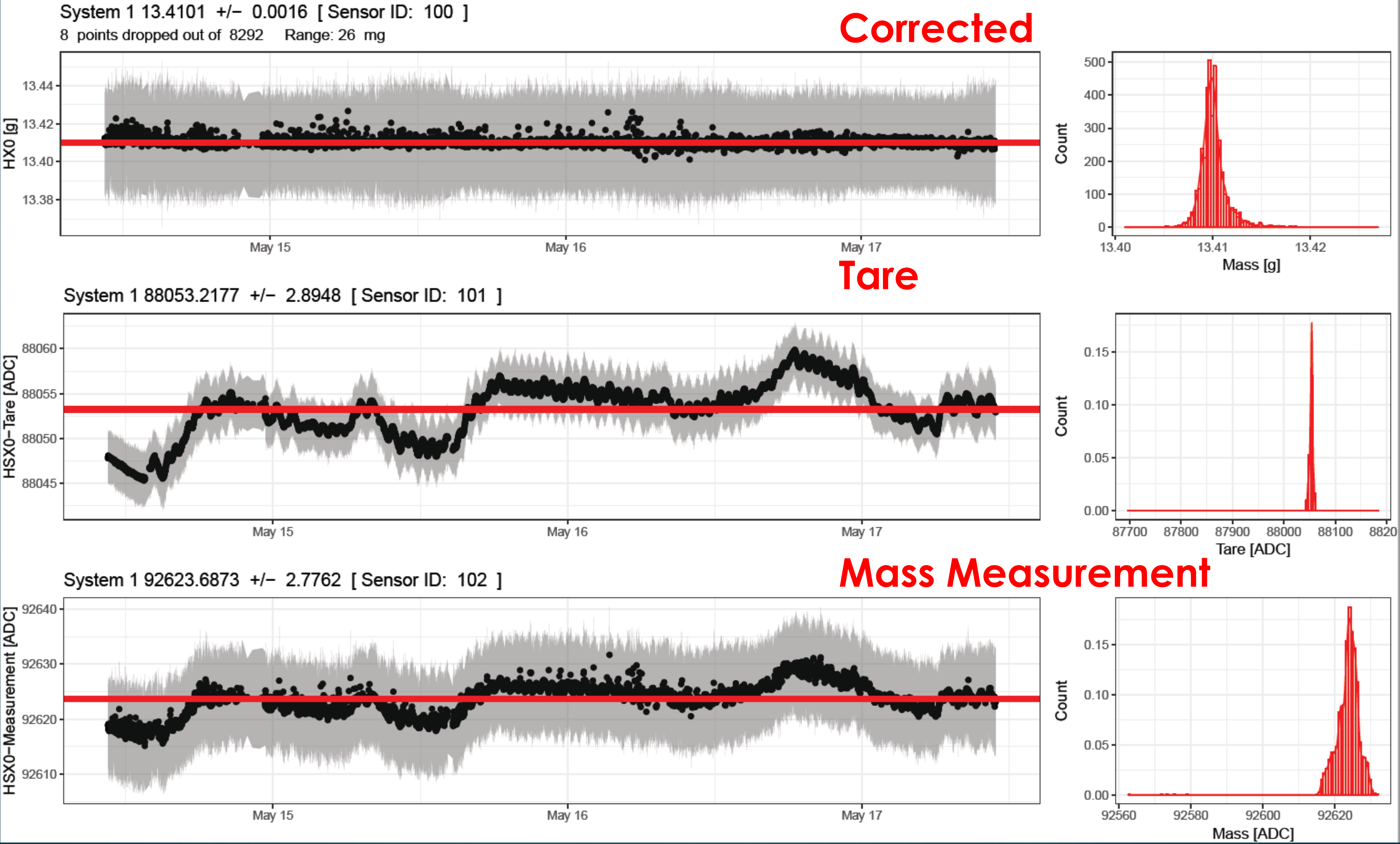
Overall error ± 0.005 g



Provides a tare measurement synched to each measurement

Mechanical Corrected Balances

Empty sample container



Solid State Physics – Reduced Time Graphs

- Any process can be represented by the kinetic relationship:

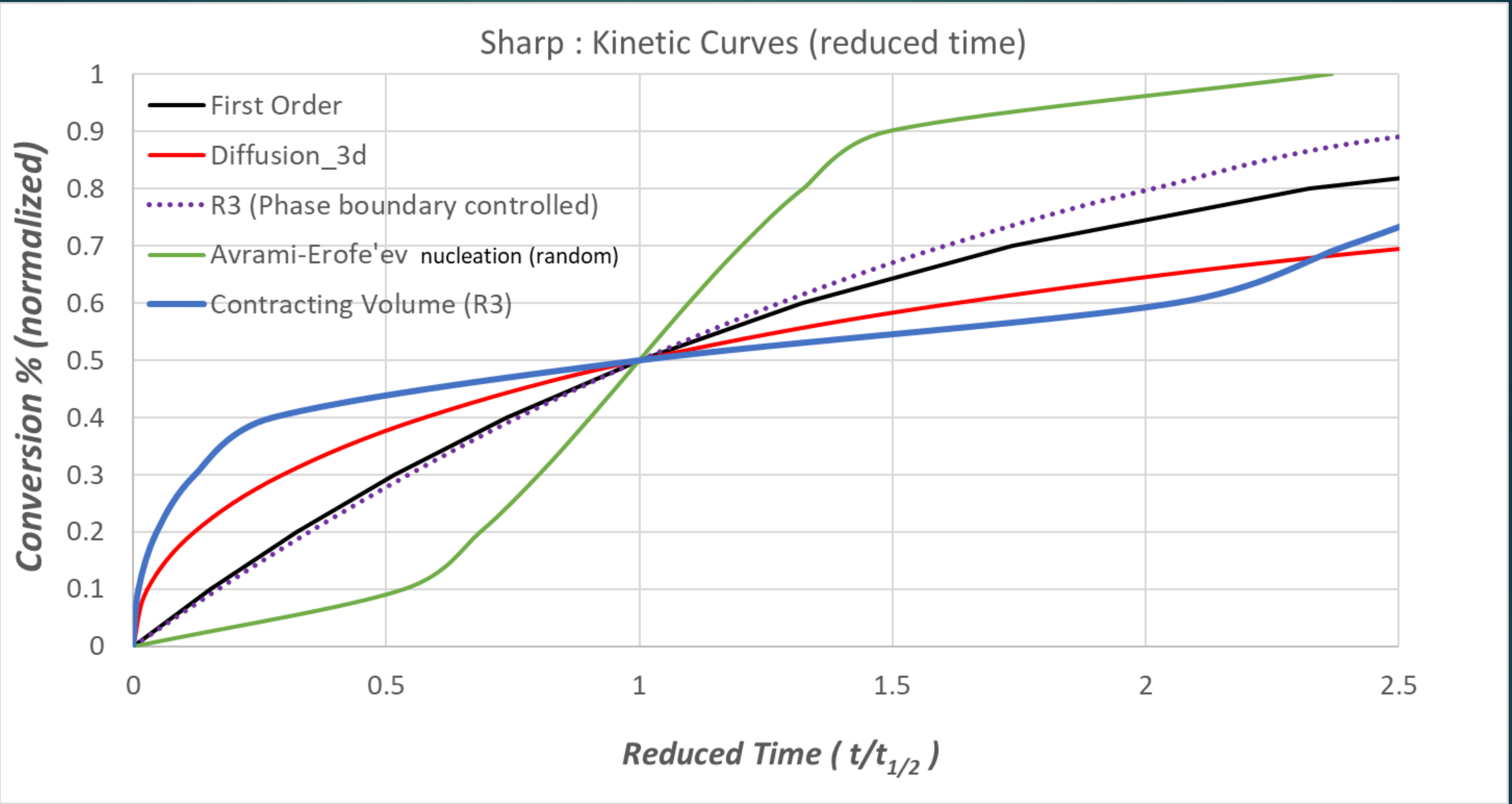
$$g(\alpha) = k\,t$$

(α) – percent complete

Mechanism Kinetics	$g(\alpha)$
Zero Order	α
First Order	$-\ln(1-\alpha)$
Diffusion (3D)	$[1-(1-\alpha)^{1/3}]^2$
Contracting Volume (sphere)	$[1-(1-\alpha)^{1/3}]$
Nucleation Model (A2)	$[-\ln(1-\alpha)]^{1/2}$

(Khawam and Flanagan, 2006)

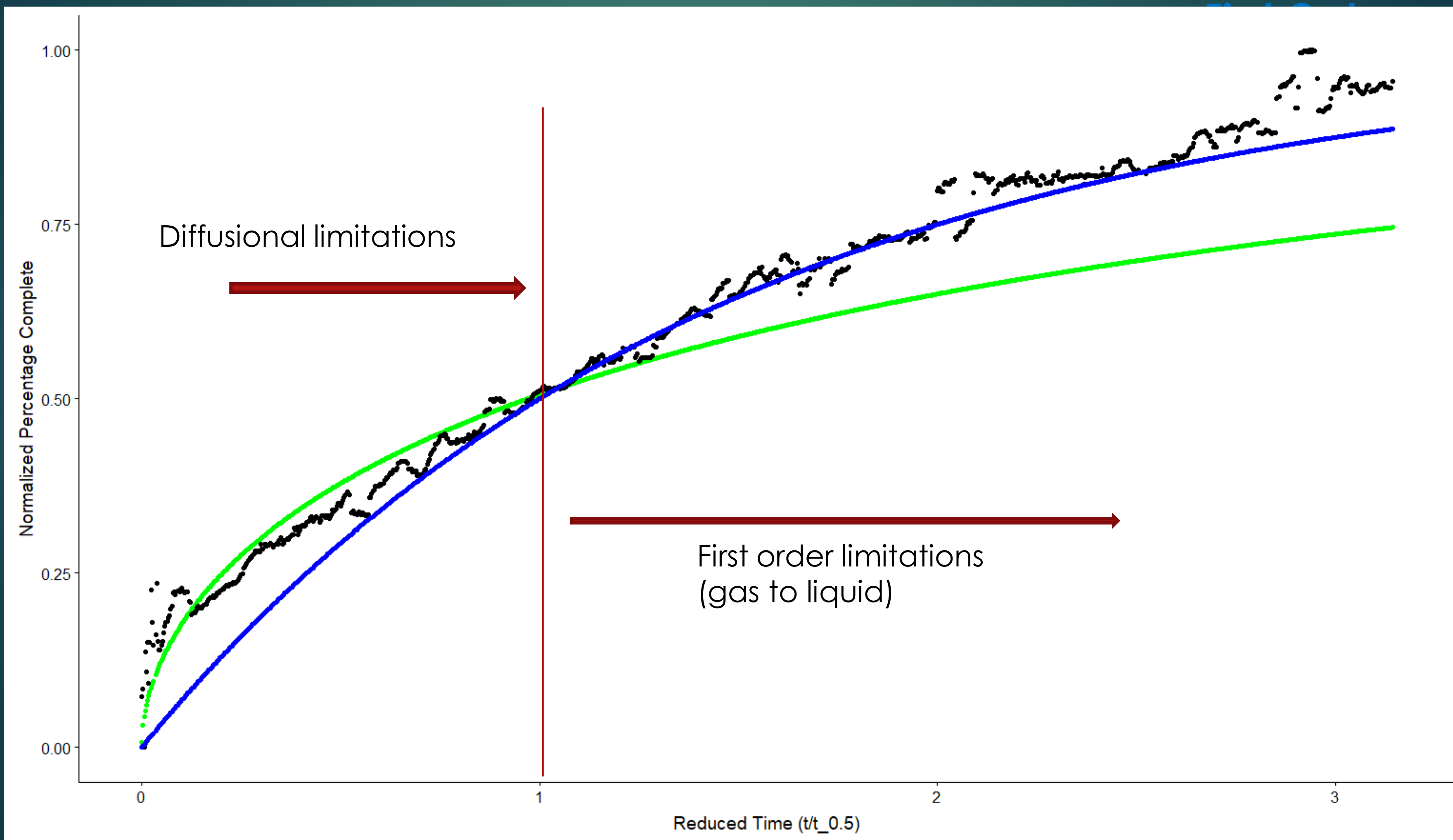
Reduced Time Graphs



Shape of curve is controlled by the rate limiting mechanism

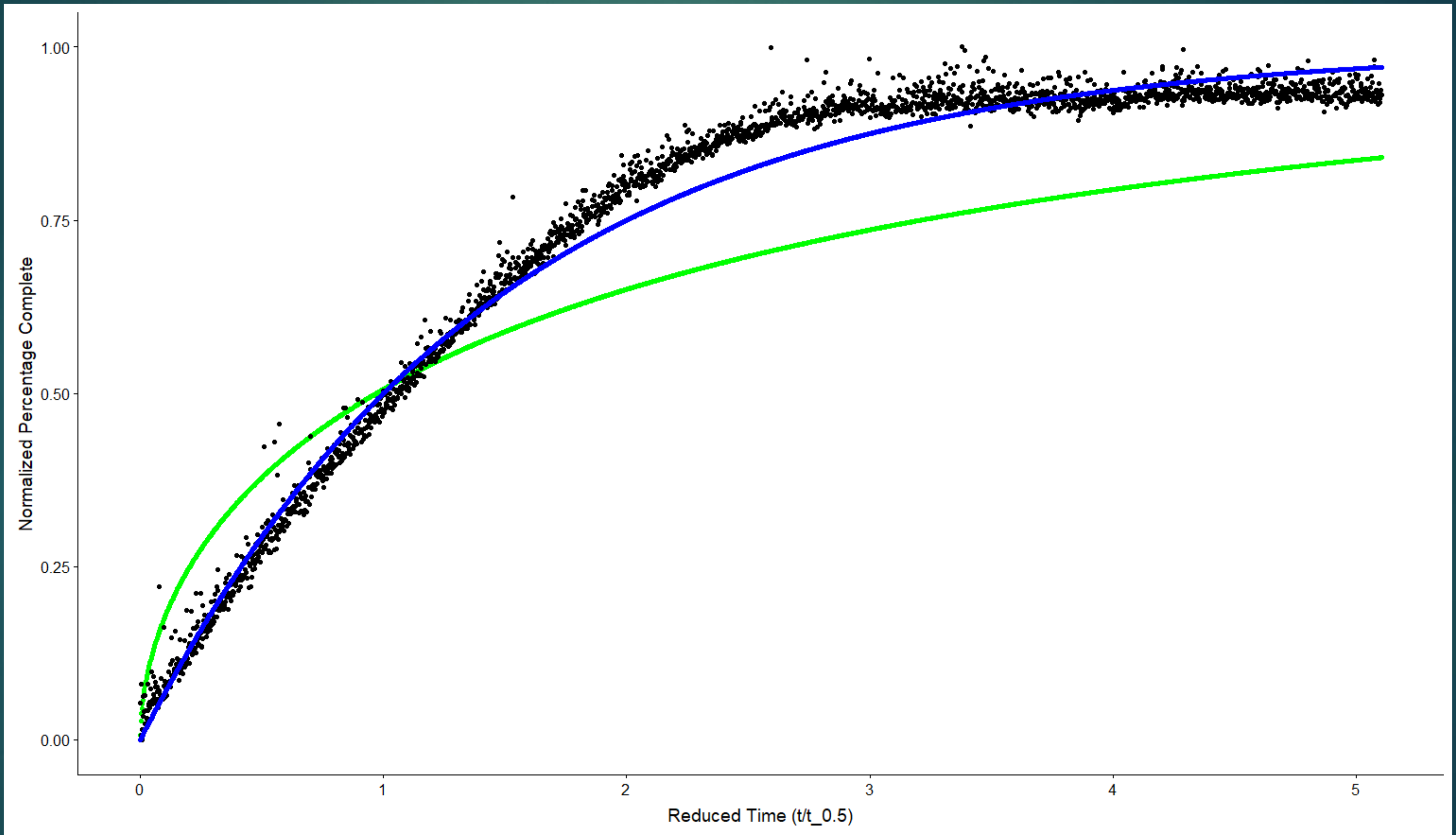
Activated Charcoal

Reduced Time Plot
– Rate limitations (water sorption)



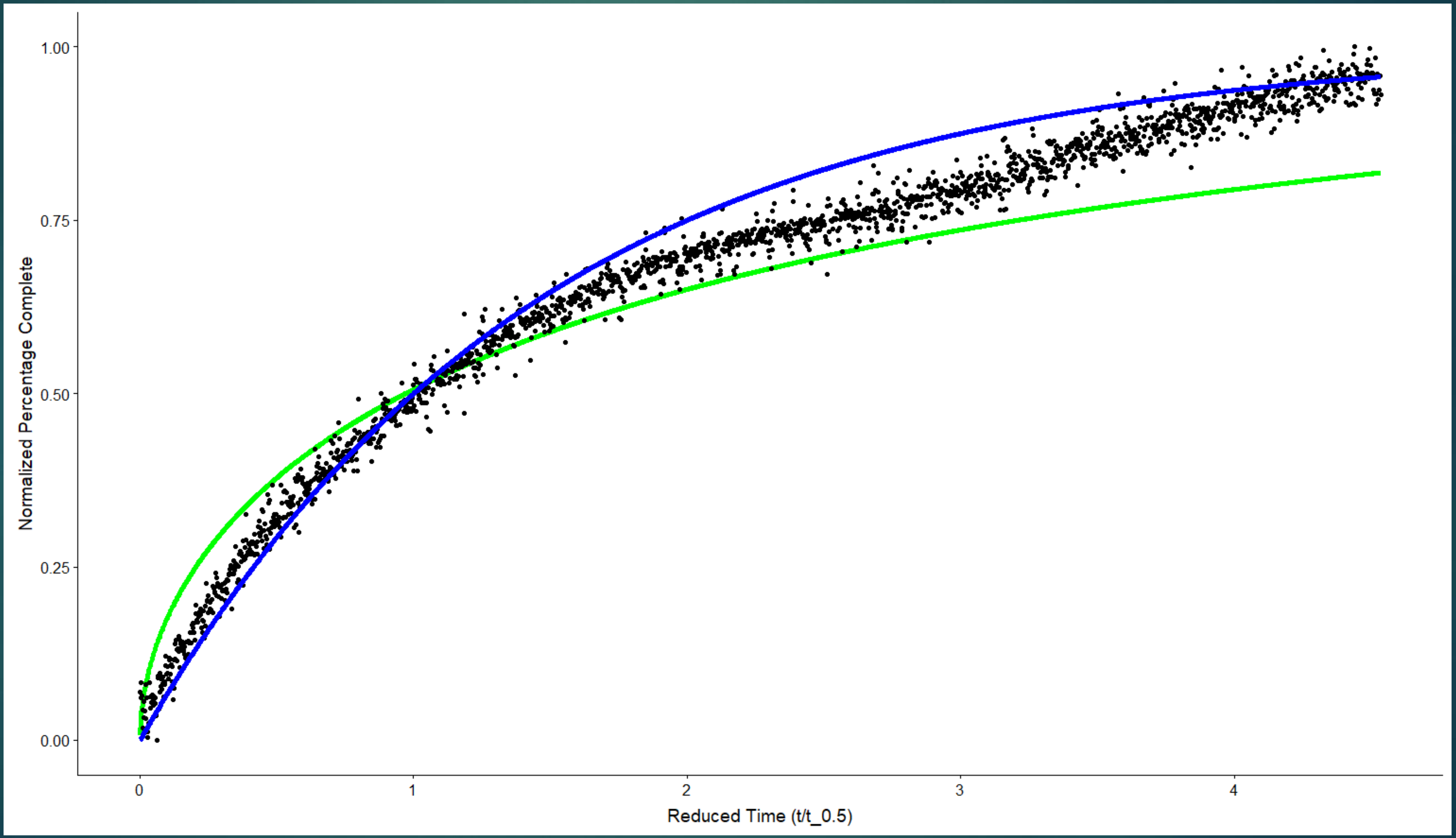
Molesieve Materials -

- 4A (First order limitation – no suggestion of diffusional limitation)



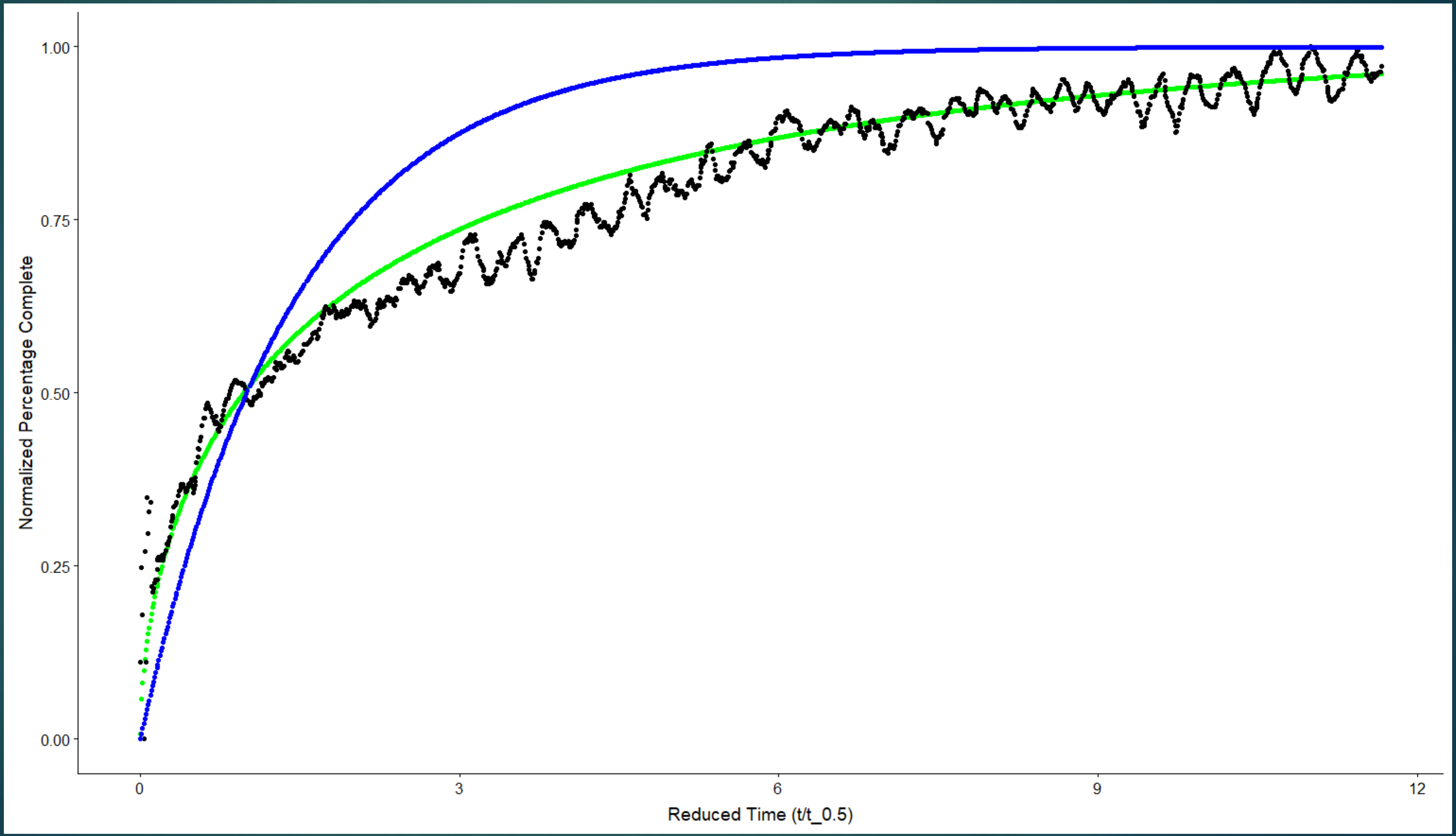
Biochar: Cherry [350 °C]

Typically follows first order kinetics (rate limiting)

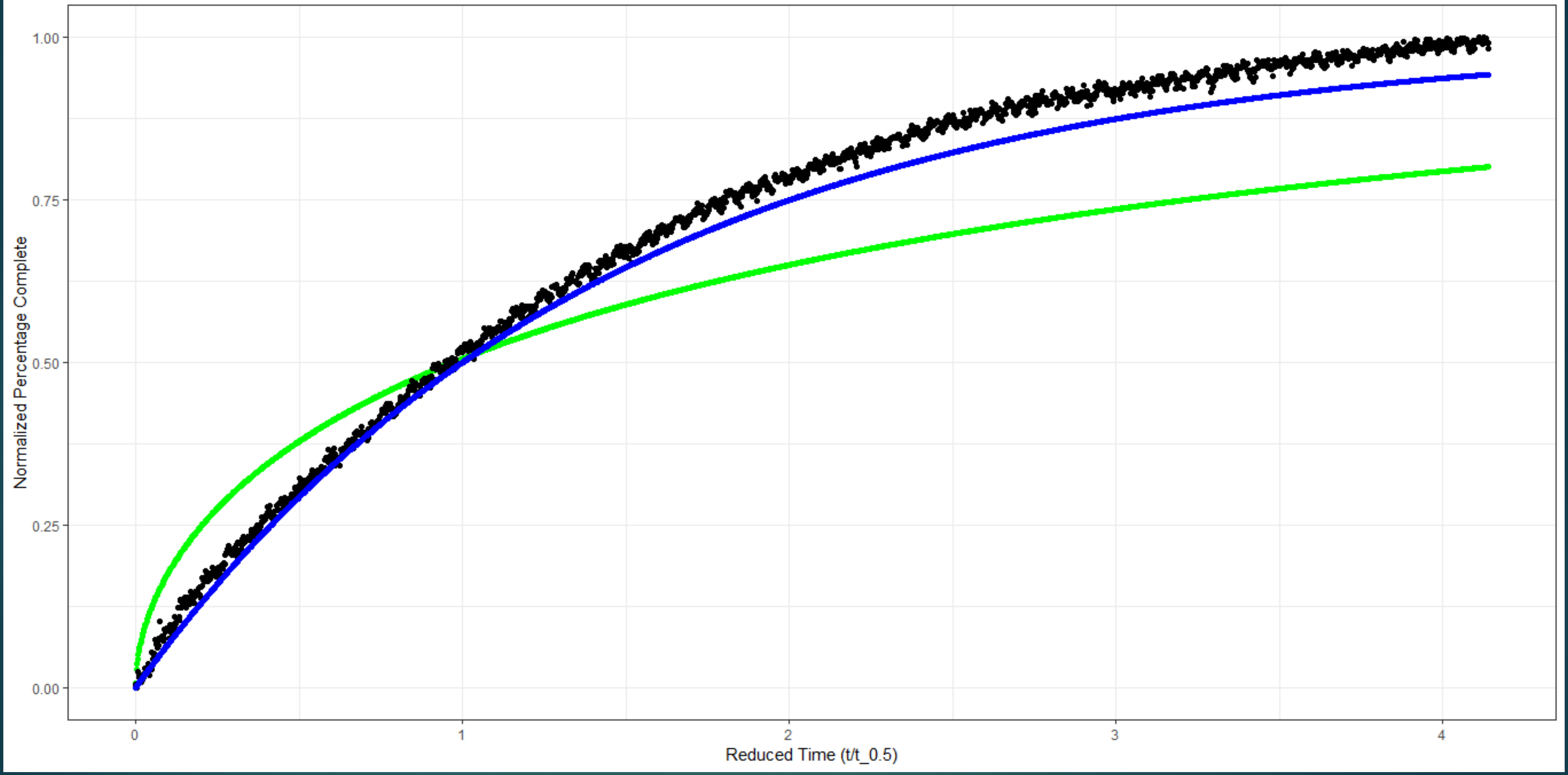


Biochar: Cherry [500 °C]

Follows a diffusional limitation

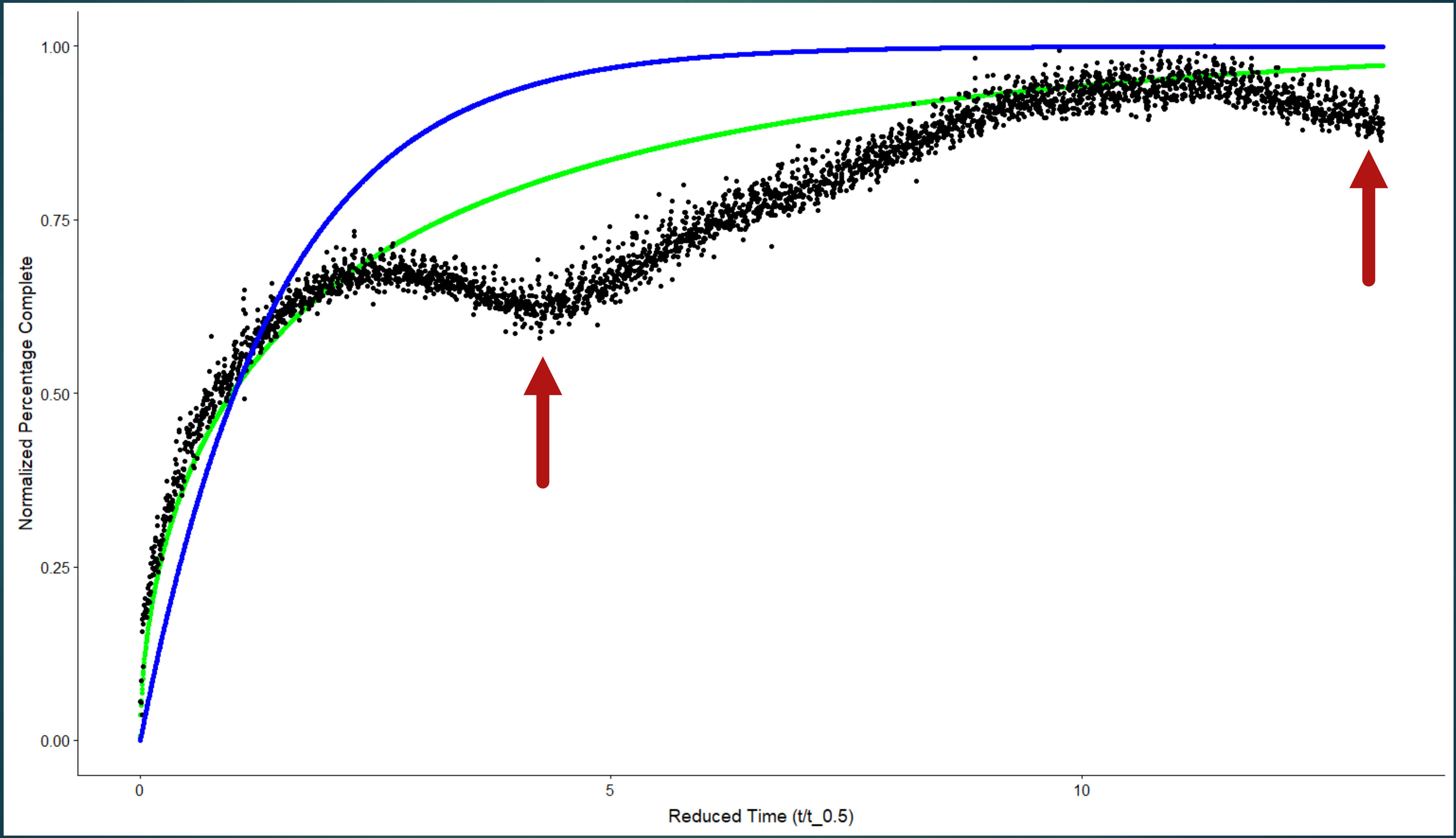


Not all biochar behave the same – Hardwood 550 C

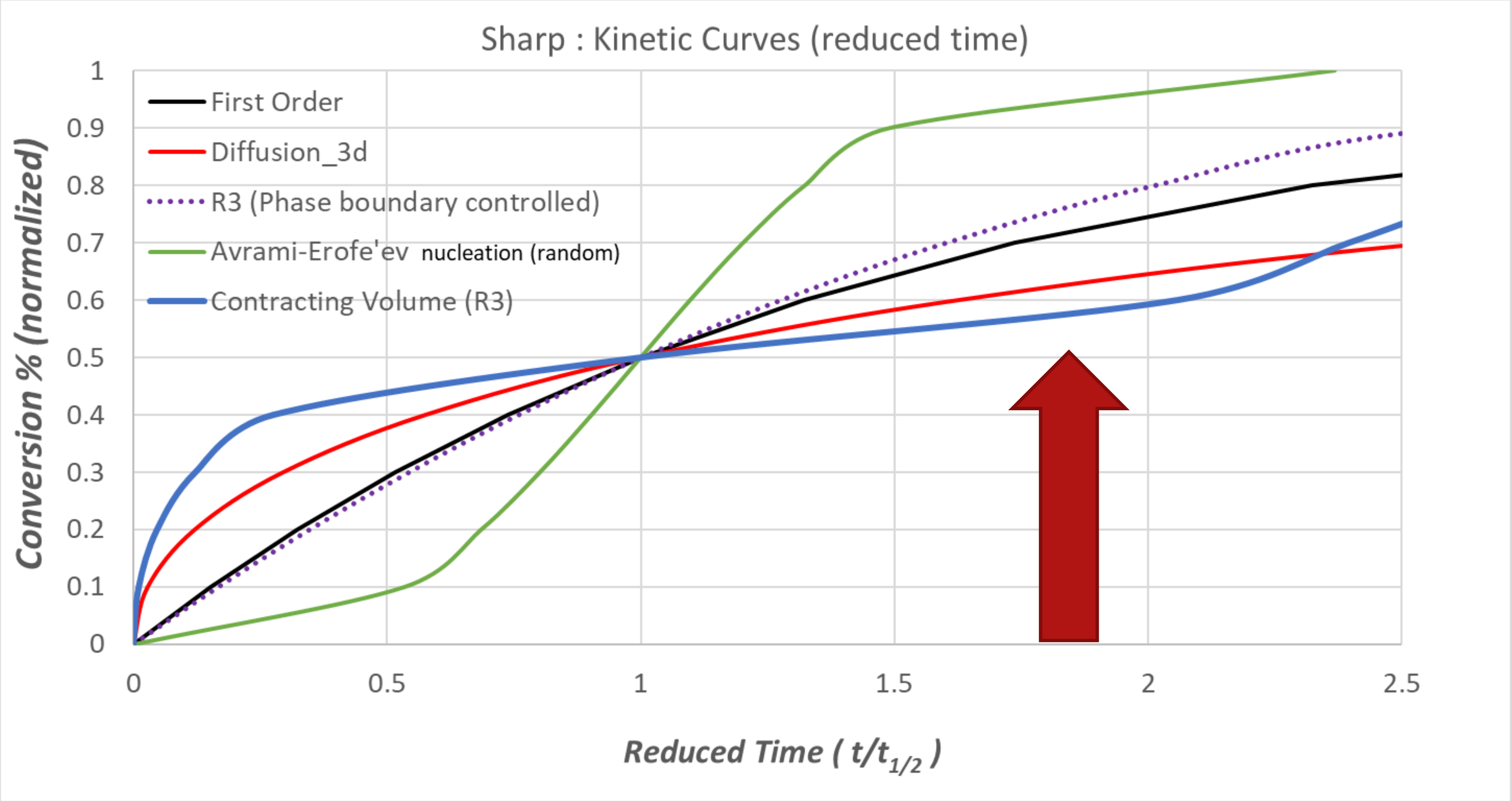


No diffusional limitation observed

Biochar: Cherry [700 °C]

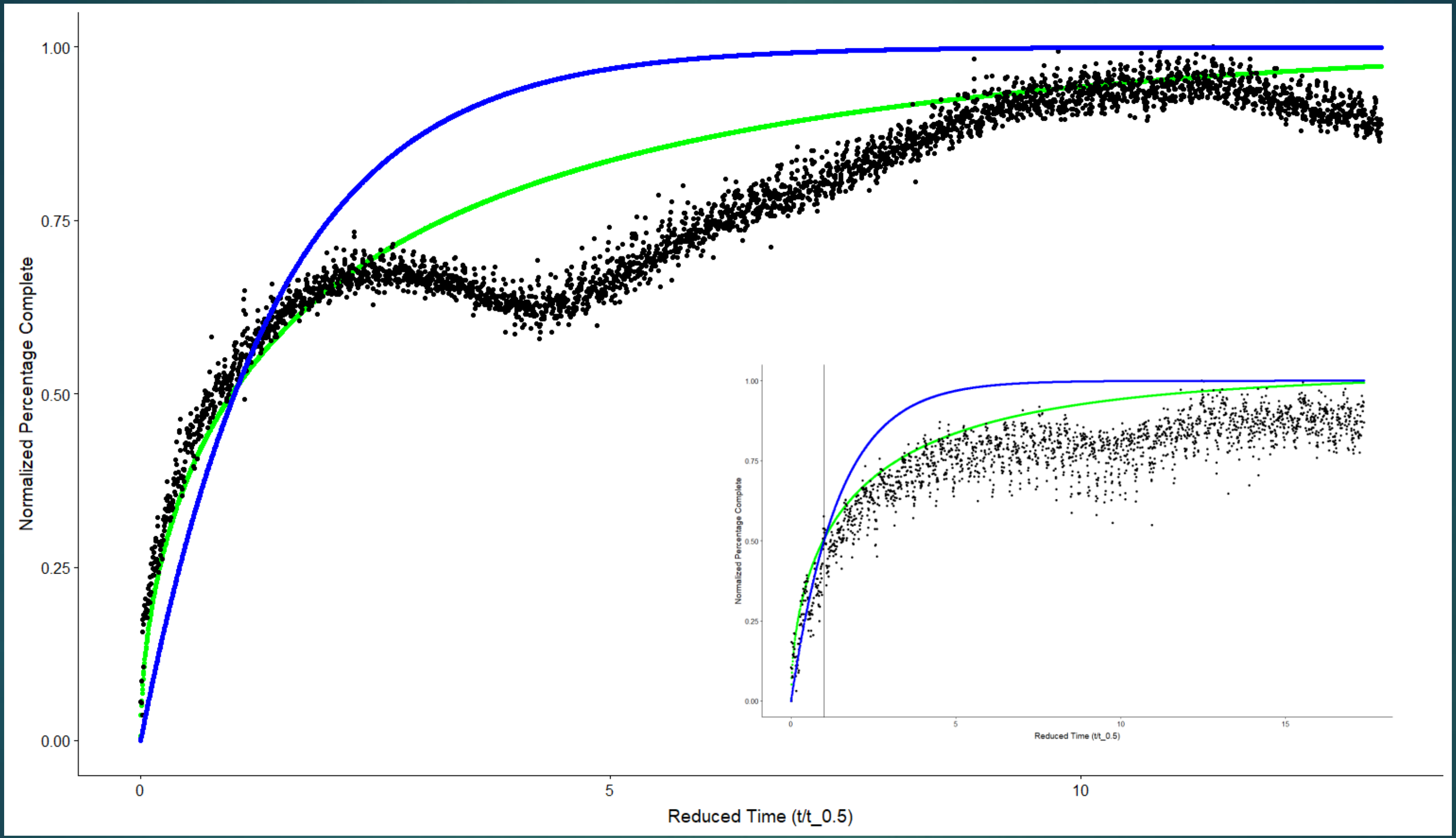


Reduced Time Graphs



Shape of curve is controlled by the rate limiting mechanism

Cherry 700 °C



From theoretical curves

-- Diffusion + potential volume shrinkage/physical shape alterations

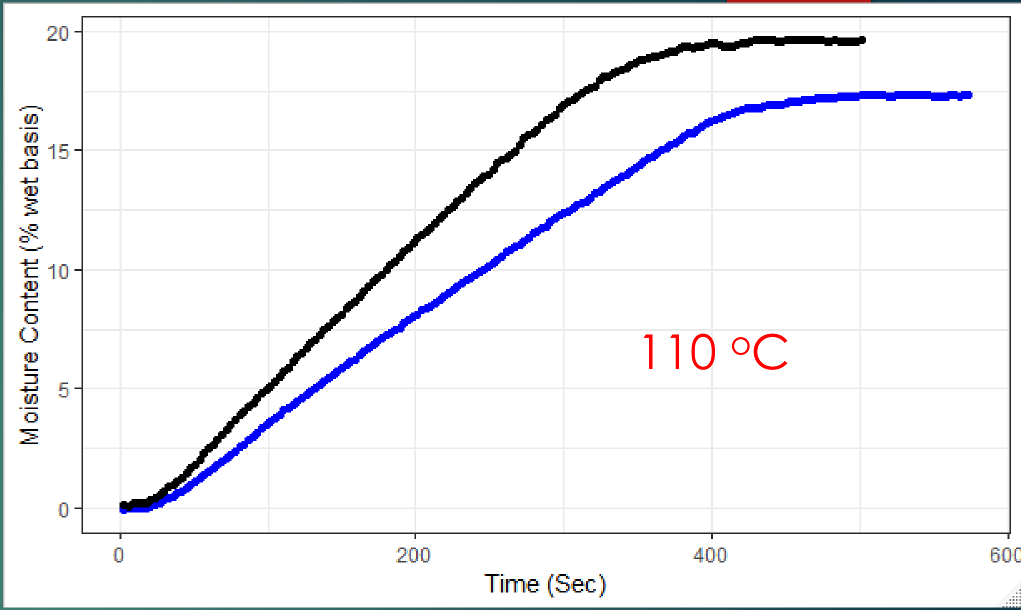
>> Not repeatable sample to sample

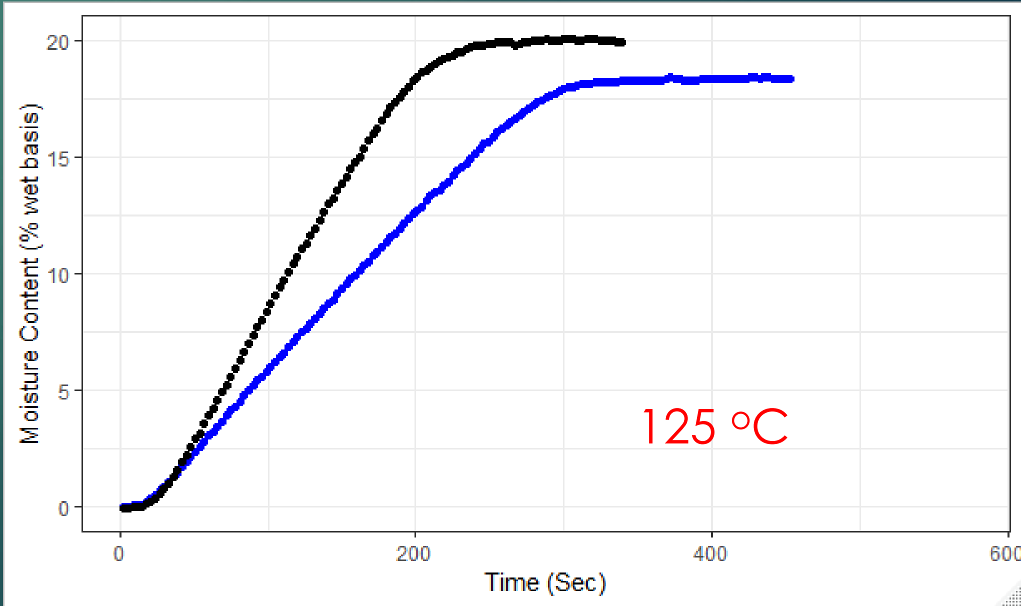
Cherry wood pellets – Kinetics summary Water uptake (initial rates)

Temperature (°C)	µ_max (rate : hr^{-1})	K (maximum moisture content)	Time (hours) (50%)	Time (hours) (90%)
25	0.07	0.08	14.99	60.10
350	0.37	0.07	3.60	11.63
500	0.42	0.07	3.07	10.35
700	0.05	0.10	9.10	66.58

Drying Rate Comparisons

- Drying rates compared for sand and sand+5% biochar (hardwood – 500 C)
- Biochar amended sand dries quicker at elevated temperatures
- Does not hold at room temp
  (BC+Soil slower than soil)





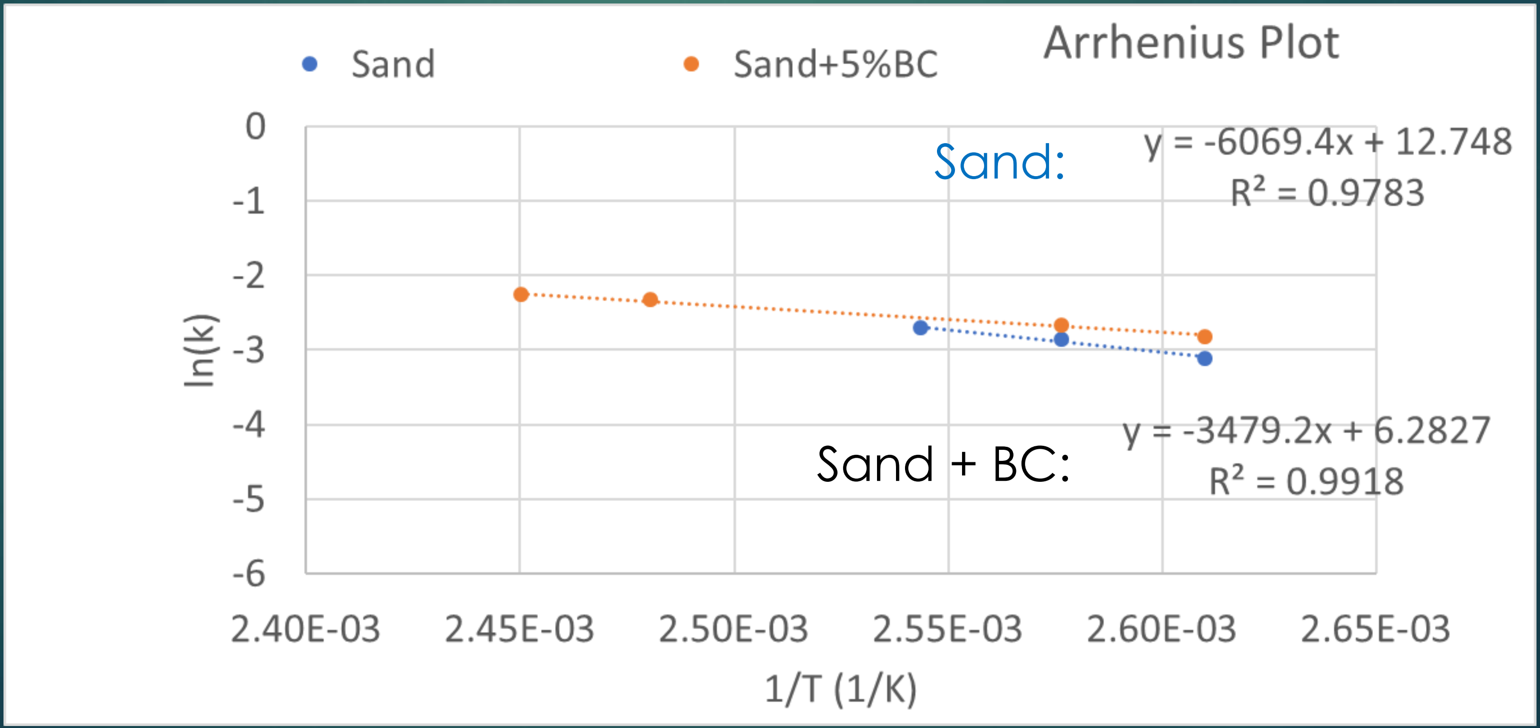
Comparisons of Activation Energy for Drying

E_a Sand + 50.5 kJ/mole

Free Water Evap = + 41.4 kJ/mole

E_a Sand + BC + 28.9 kJ/mole

$$m = -\frac{E_a}{R}$$



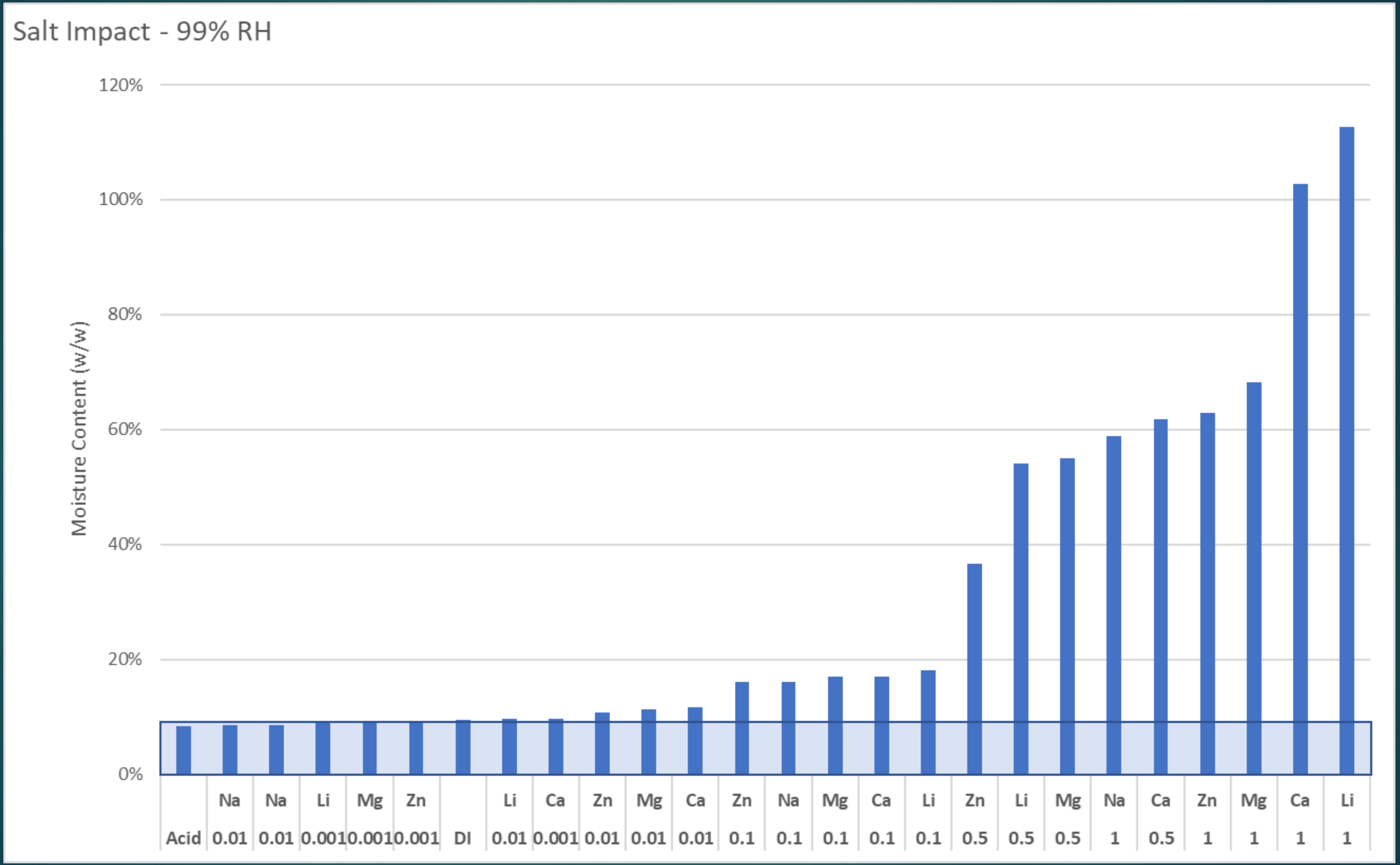
Biochar + Salts

- 500 °C pine chip biochar

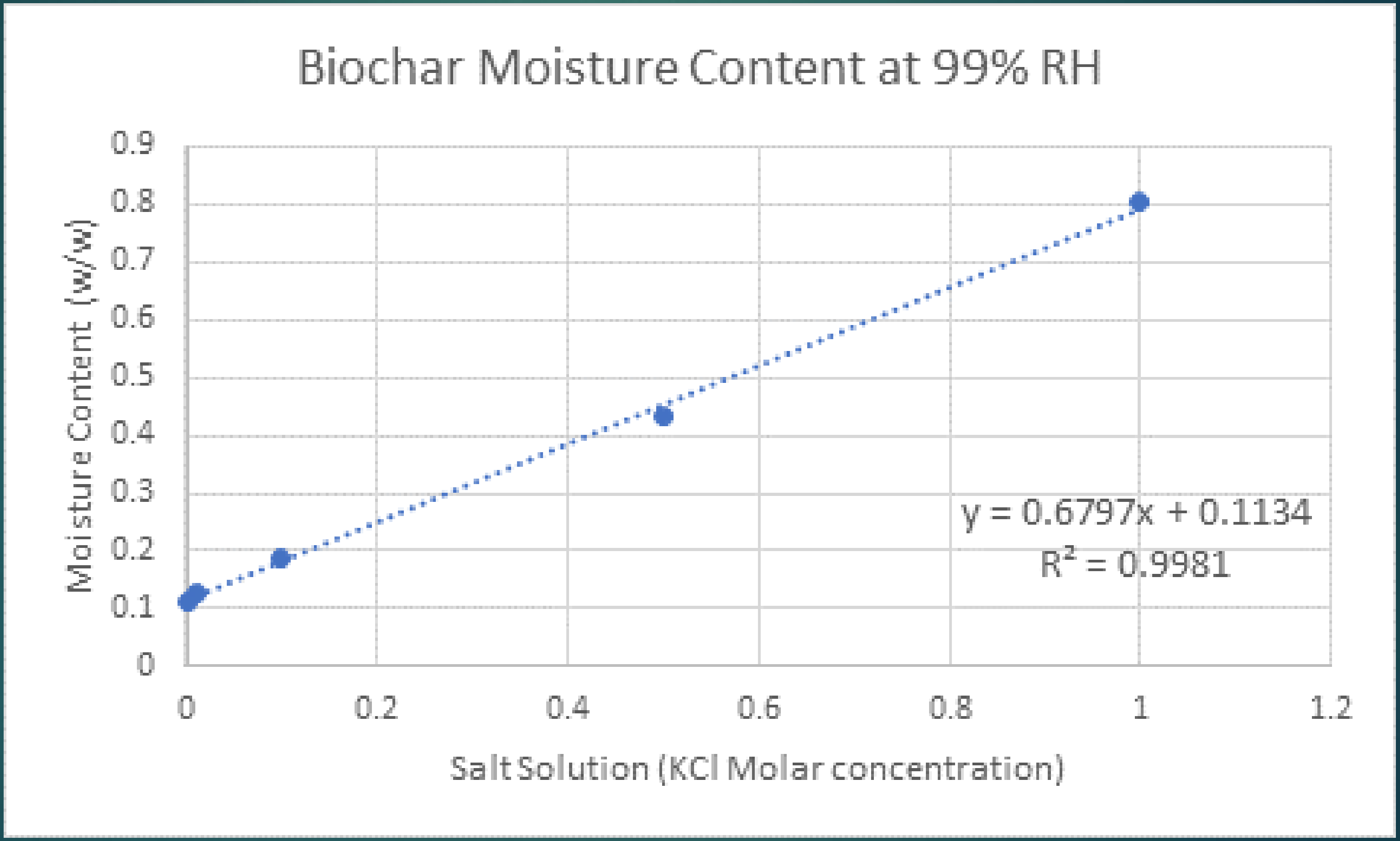
- Soaked in various salt solutions :
  - $CaCl_2$, $MgCl_2$, $ZnCl_2$, LiCl, NaCl, & KCl
  - Concentrations : 0.001, 0.01, 0.1, 0.5, and 1.0 M
  - Soaked for 30 days
  - Biochar was then rinsed with DI water until <5 µS/cm conductivity was achieved

  - Oven dried biochar was then placed in various relative humidity for 120 days

Moisture Content (99% RH)



Examining KCl effects:



Wrap-up & Conclusions

- No crystalline structures have been located with XRD on surface
- Attracts an amorphous cation rich layer to the surface of biochar: not easily removed
  - Carbonate + Oxides of Minerals: C from atmospheric CO_2 and not biochar C !
- Significantly alters water sorption, agrochemical sorption, etc…
- >1200 days and still changing
- **Maybe change in mass is not solely water**