Do chemical characteristics affect the potential of biochars to adsorb cations?

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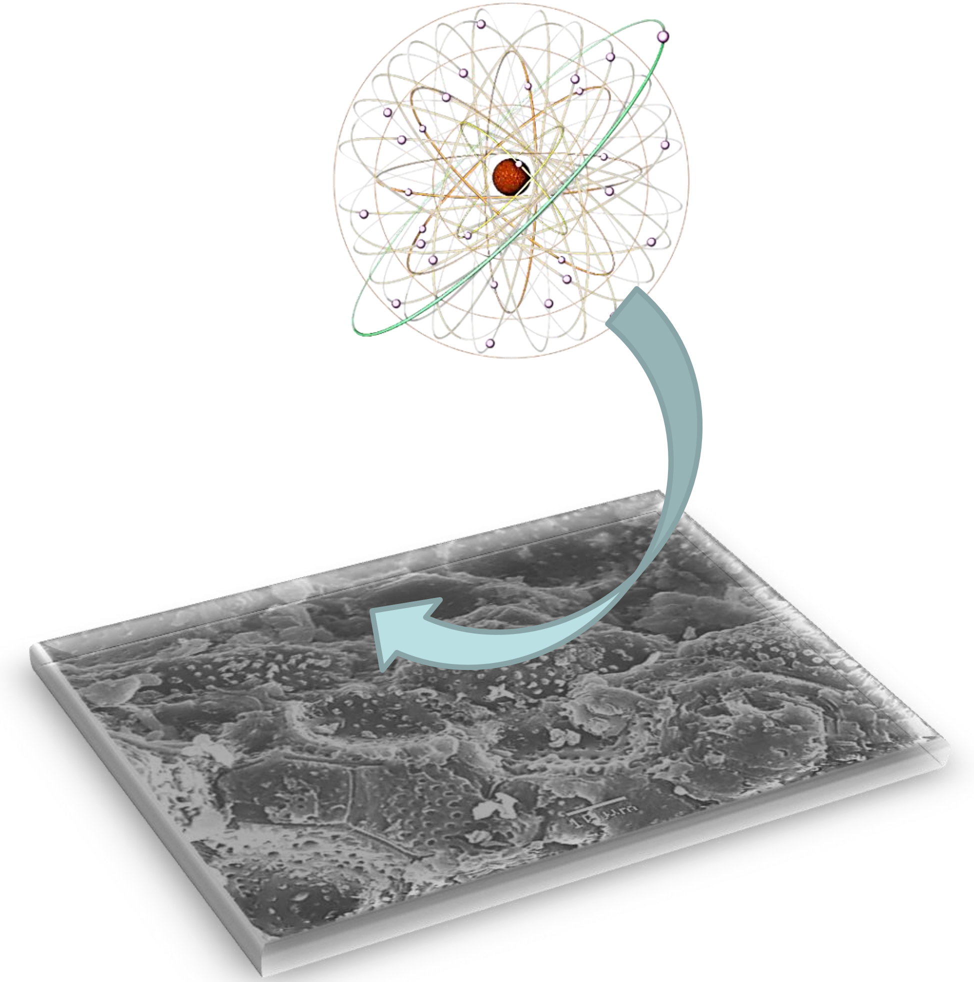
Summary: Reasoning

- ***Biochar adsorbs cations:***
  - use as filter for heavy metals
  - soil amendment with nutrients storage capacity
- ***As a paramagnetic Ion, Cu^{2+} shortens the Spin-Lattice Relaxation time (T_1)*** of the ^{13}C and its ^{1}H to which it is adsorbed.
- ***NMR Relaxometry*** on Cu^{2+}- doted pyrochars allows the determination of C-groups involved in the adsorption of cations
- ***Revealing relationship between chemical composition and adsorption efficiency***
  Using pyrochars with different aromaticity and chemical composition may contribute to a better understanding of the adsorption mechanism



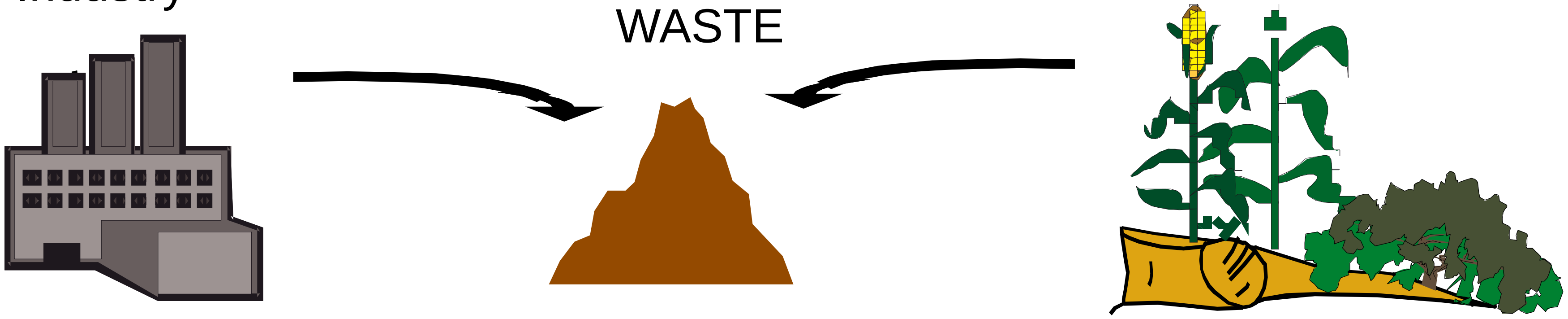
Summary: Results

- The Adsorption to the three pyrochars used in this study was best fitted with the **Freundlich model**
- The **adsorption efficiency increased with aromaticity** of the sample
- We found indications that **crystalline domains** of weakly charred pyrochars from cellulosic feedstock **did not allow Cu^{2+} to access** all potential adsorption sites
- Aside from charged functional groups, **π-orbitals of aromatic rings contributed to Cu^{2+} adsorption**

Porosity is not the main factor determining Cu^{2+} adsorption to pyrochar;

Accessibility of Cu^{2+} to pores and the availability of π-orbitals of aromatic rings seem also to play an important role.

Introduction: Organic Waste - a Valuable Resource



Valorization:
-Biochar

Pyrolysis (low oxygen)

Definition:
- Ecologically sustainable organic feedstock
- Heterogeneous substance
- High aromaticity
- High organic C content

EBC (2012)

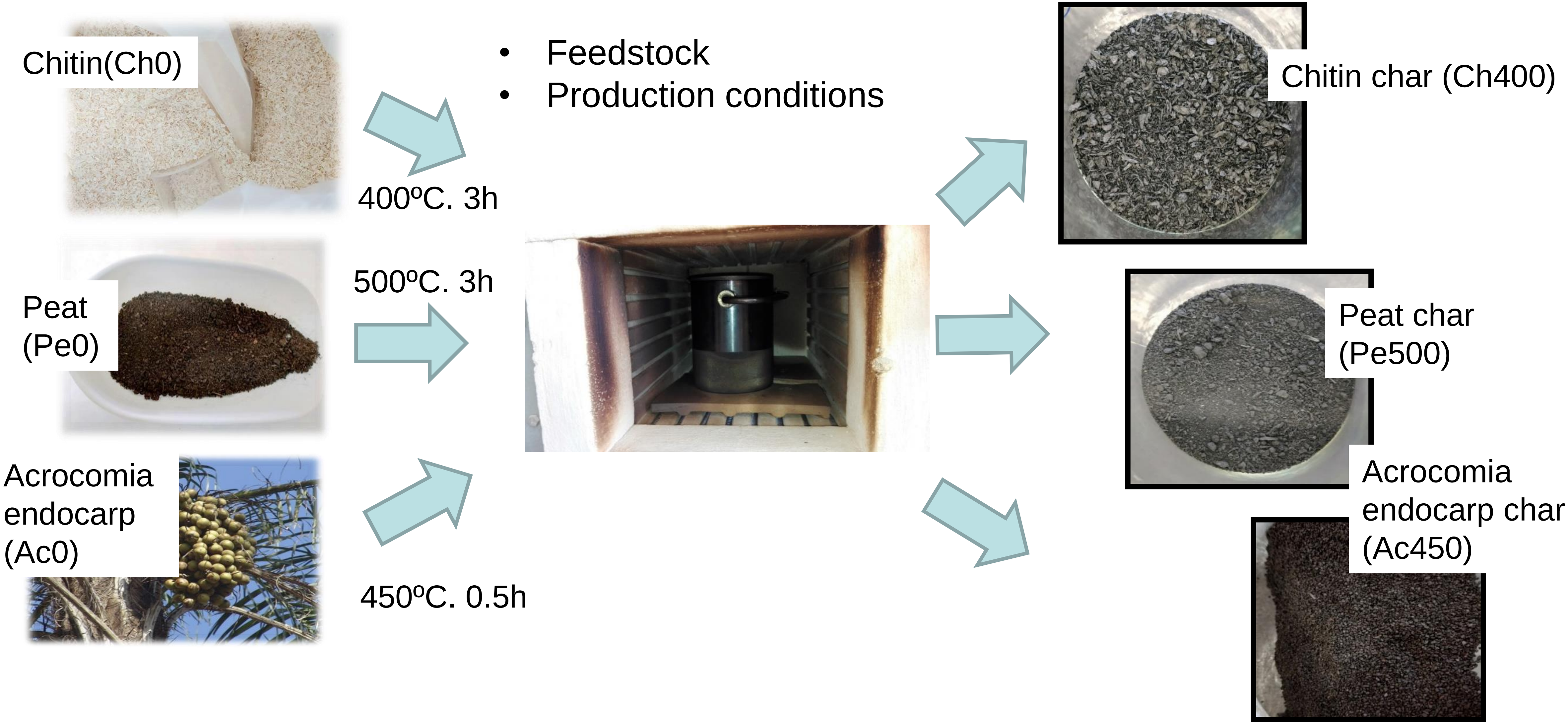
Material with:
- High porosity
- High waterholding capacity
- Cation adsorption

- Soil amendment
- Slow-release fertilizer
- Gardening soil
- Water clean-up
- Soil remediation
- Filter (water clean-up)
- etc.

But: Biochar ≠ Biochar!

Biochar structure depends on:

- Feedstock
- Production conditions



Chitin(Ch0)

Peat
(Pe0)

Acrocomia
endocarp
(Ac0)

400ºC. 3h

500ºC. 3h

450ºC. 0.5h

Chitin char (Ch400)

Peat char
(Pe500)

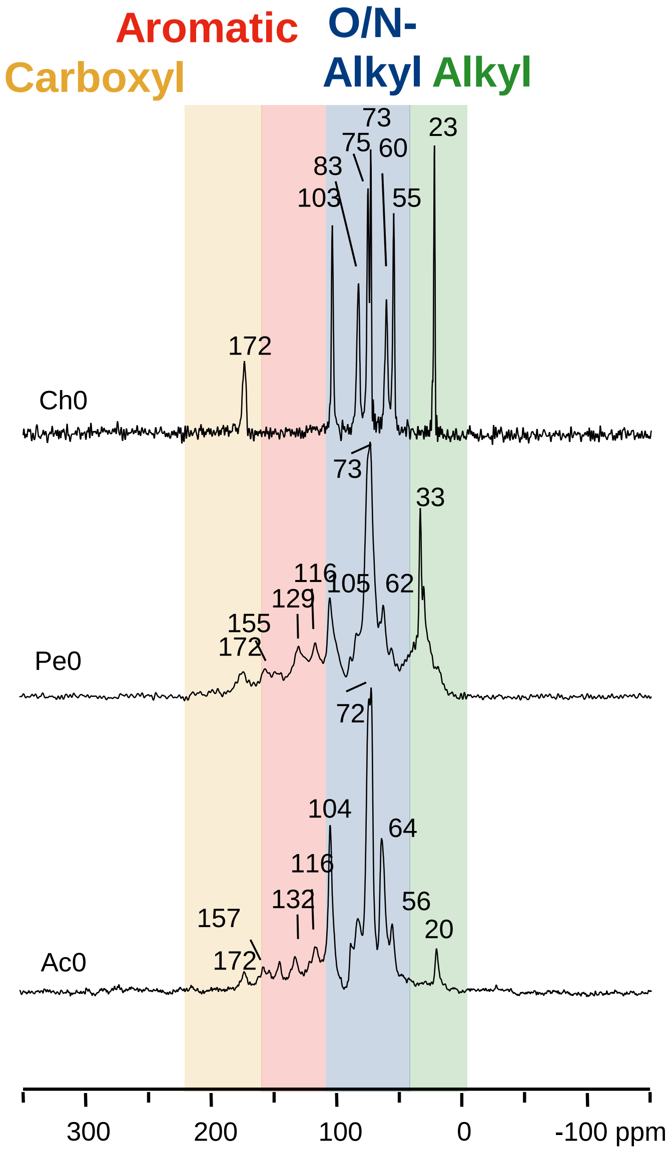
Acrocomia
endocarp char
(Ac450)

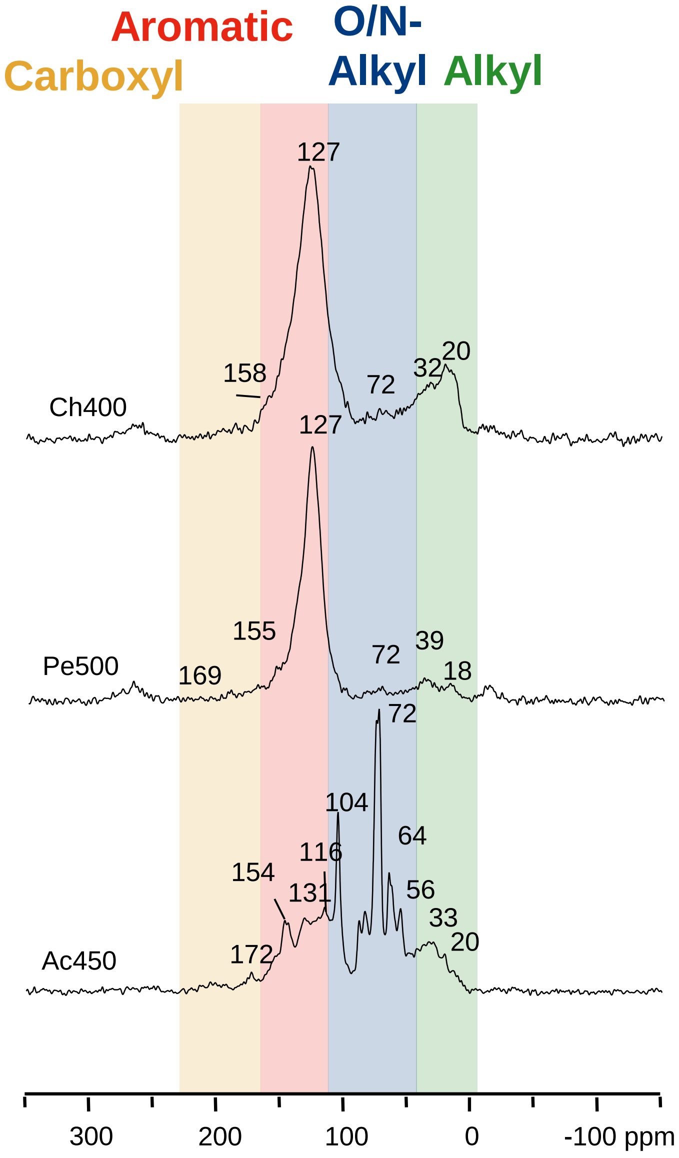
Table 1: Elemental composition of chitin, peat and Acrocomia endocarp and their chars produced at 400°C, 500°C and 450°C, respectively. the pH (H_2O) and the BET surface area (SA) (CO_2) of the chars.

Material	**C** g kg^{-1}	**H** g kg^{-1}	**N** g kg^{-1}	**Ash** g kg^{-1}	**O*** g kg^{-1}	**H/C$_{atm}$**	**C/N** (w/w)	**O/C$_{atm}$**	**pH (H_2O)**	**S$_{BET}$** m^{2}g^{-1}
Ch0	437.7 ± 2.0	64.4 ± 0.7	63.8 ± 0.4			1.8	6.9		6.9 ± 0.0	
Ch400	700.1 ± 2.2	28.0 ± 0.1	86.1 ± 1.0	11.8 ± 0.1	143.7	0.5	8.1	0.2	6.4 ± 0.0	216
Pe0	429.0 ± 8.8	49.5 ± 2.0	8.7 ± 0.3			1.4	49.2		6.2 ± 0.1	
Pe500	684.1 ± 3.7	26.8 ± 0.5	14.3 ± 0.3	140.1 ± 1.3	134.8	0.5	47.9	0.1	8.4 ± 0.1	192
Ac0	487.4 ± 1.7	55.8 ± 0.4	1.8 ± 0.0			1.4	264.4		5.9 ± 1.2	
Ac450	564.8 ± 2.5	46.7 ± 0.2	2.8 ± 0.1	16.8 ± 0.1	368.8	1.0	202.7	0.5	7.3 ± 0.1	178

*Calculated by the sum of ash. C. H. and N contents subtracted from 1000 g of sample material.

Chemical Composition Determined by Solid-state ^{13}C NMR Spectroscopy





Bruker Avance III 400 MHz

Cross-polarization: 1 ms

Magic angle spinning: 14 kHz

- *Difference in aromaticity (160-90 ppm):*

Pe500 > Ch400 > Ac450

- *Difference in polarity P:*

$$P = \frac{I(225\text{-}140\ \text{ppm}) + I(90 - 45\ \text{ppm})}{I(140\text{-}90\ \text{ppm}) + I(45\text{-}0\ \text{ppm})}$$

Ac450 > Ch400 > Pe500

Hypothesis:

Different chemical compostion, polarity, pH and BET surface (CO_2) may lead to:

Differences in the Cation Adsorption?

Differences in the Adsorption Mechanism?

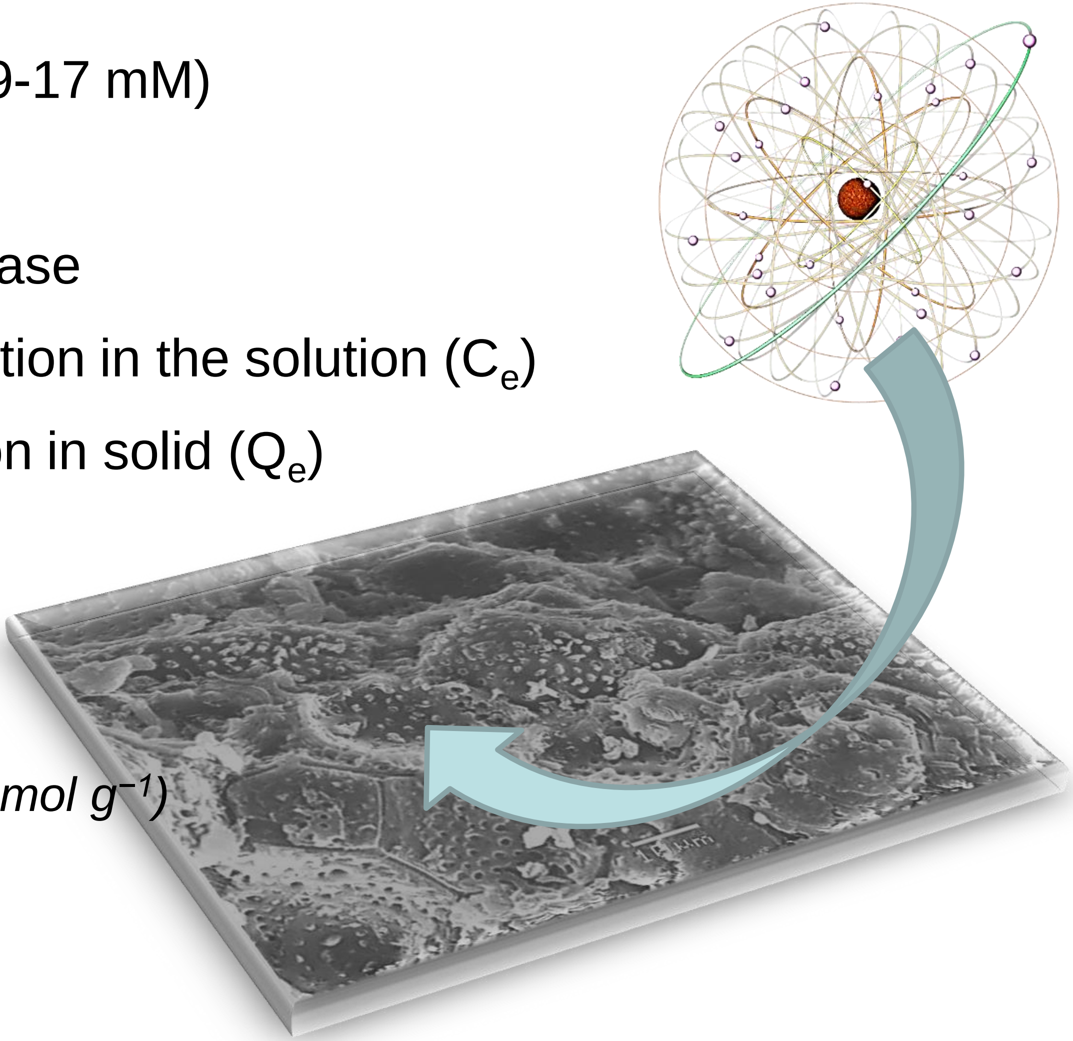
<u>Adsorption experiments</u> with paramagnetic Cu^{2+}

<u>NMR-Relaxometry:</u>

- Relaxation time is affected by paramagnetic Cu^{2+}
- Determination of affected C group allows identification of binding site

Adsorption of Cu^{2+} onto Biochar: Experimental Design

- 200 mg biochar + $Cu(NO_3)_2$ (0.9-17 mM)
- Shaking for 24 h at 25ºC
- Separation of solid and liquid phase
- Determination of Cu^{2+} concentration in the solution (C_e)
- Calculation of Cu^{2+} concentration in solid (Q_e)



Langmuir

$$\frac{C_e}{Q_e} = \frac{1}{K \cdot Q_{max}} + \frac{C_e}{Q_{max}}$$

Freundlich

$$Q_e = K_d\, {C_e}^{1/n}$$

$$lnQ_e = \ln K_d + \frac{1}{n} lnC_e$$

$Q_{max:}$ maximum adsorption capacity (mmol g^{-1})

K: Langmuir constant (L mg^{-1})

K_{d}: Freundlich distribution coefficient.

n: correction factor constant

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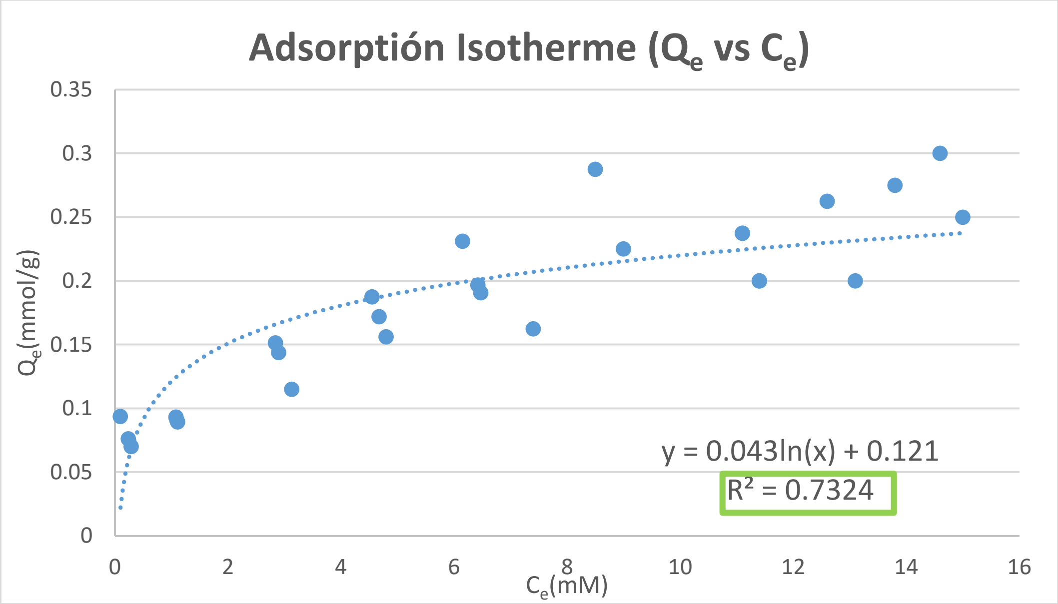
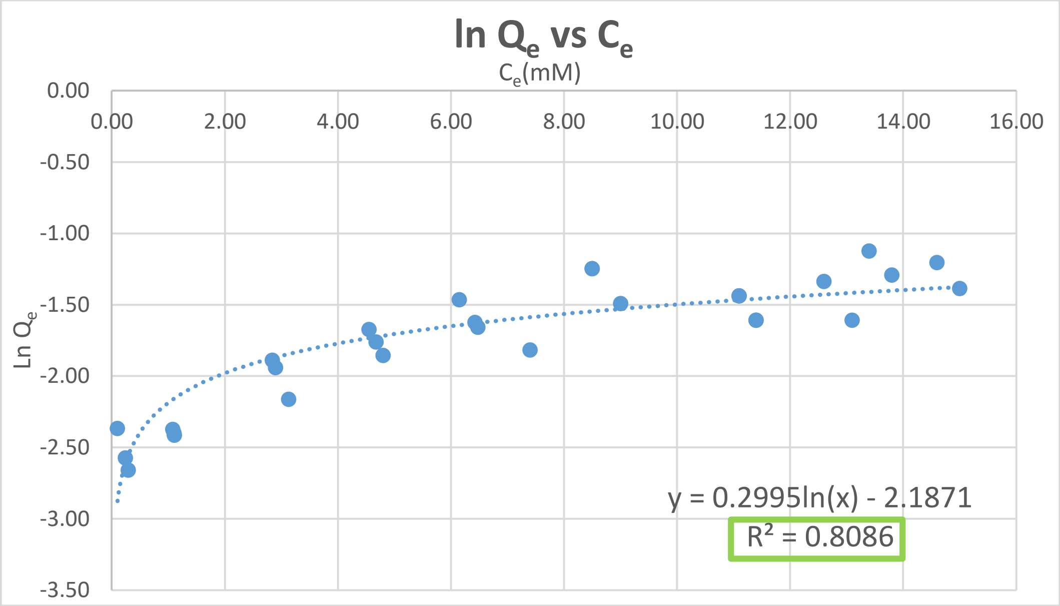
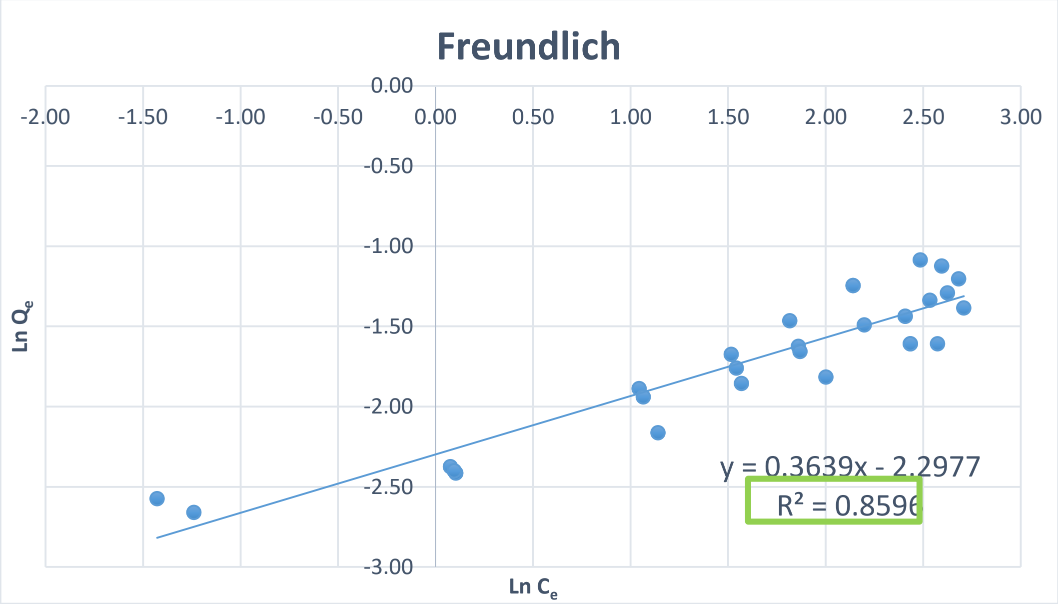
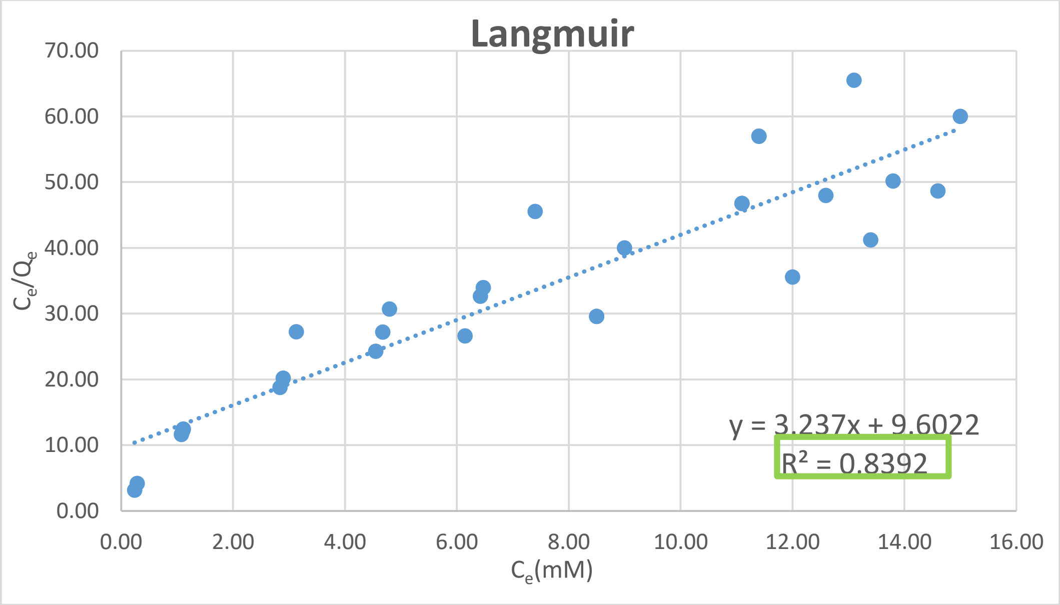
Adsorption Isotherms of Cu^{2+} to Ch400









Adsorption Parameters of Cu^{2+} to Ch400, Pe500, Ac450

	Freundlich			**Langmuir**		
	R^2	K_d	n	R^2	Q_{max} (mg/g)	K (l/mg)
Ch400	0.8596	0.1122	2.7480	0.8392	19.63	2.142
Pe500	0.8854	0.1177	2.4624	0.848	25.73	1.973
Ac450	0.568	0.0144	1.0618	0.3426	12.84	1.227

Better R^2 with Freundlich:	***non-ideal adsorption on a heterogeneous surface***
$n > 1$:	***higher Cu^{2+}-concentration decreases relative adsorption***
K_d (Adsorption affinity):	***Pe500> Ch400 > Ac450 (very low adsorption)***

Relation between Adsorption of Cu^{2+} with Surface Area, pH and Aromaticity

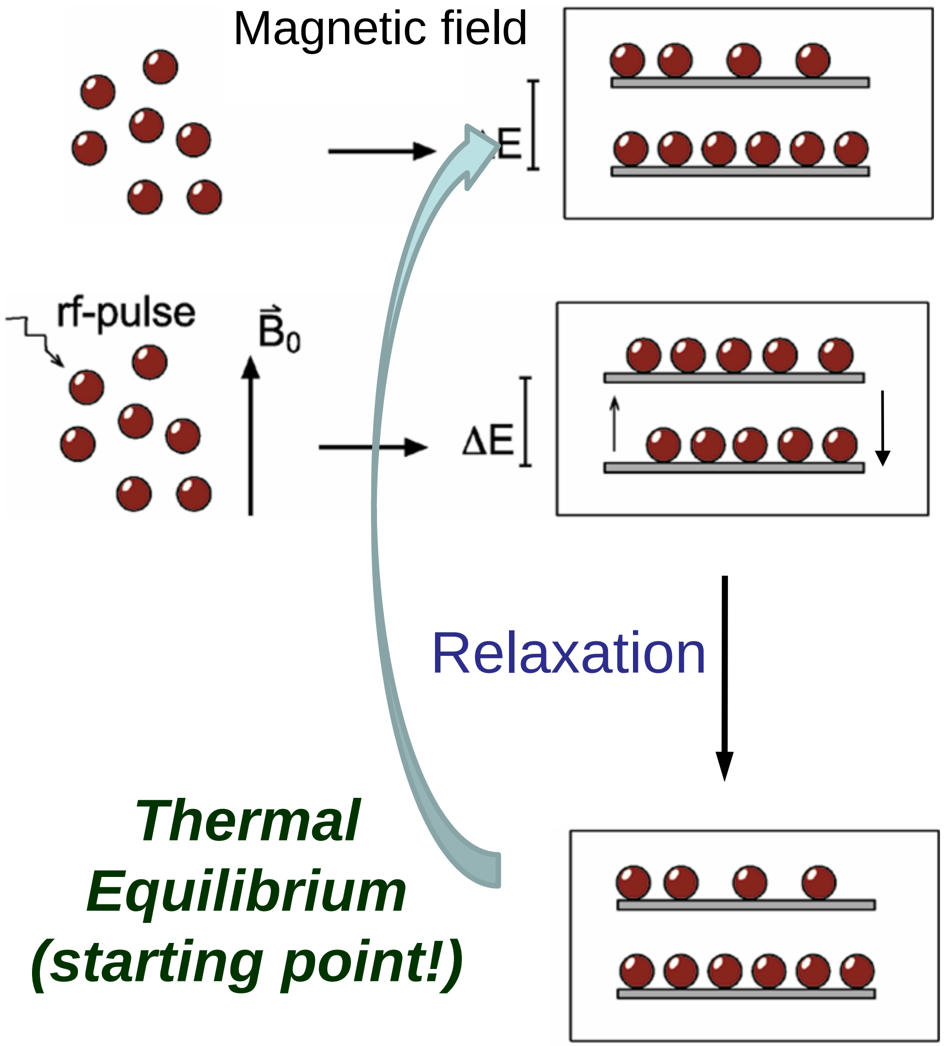
Biochar	Single point surface area at P/Po (m^2/g)	BET Surface Area (CO_2)	pH	Aromaticity	Polarity
Quitina (Ch)	163.36	216.13	6.4	74	0.32
Turba (Pe)	158.89	192.41	8.4	88	0.27
Acrocomia (Ac)	140.02	177.62	7.3	26	1.18

- ***No evident relationschip between K, K_d and surface area or pH***
- ***Adsorption efficiency increases with aromaticity and decreasing polarity***

Adsorption to charged groups as main mechanism is unlikely!!!

NMR Relaxometry for the Identification of Cu^{2+} Adsorption Sites:

Theoretical Background



Relaxation

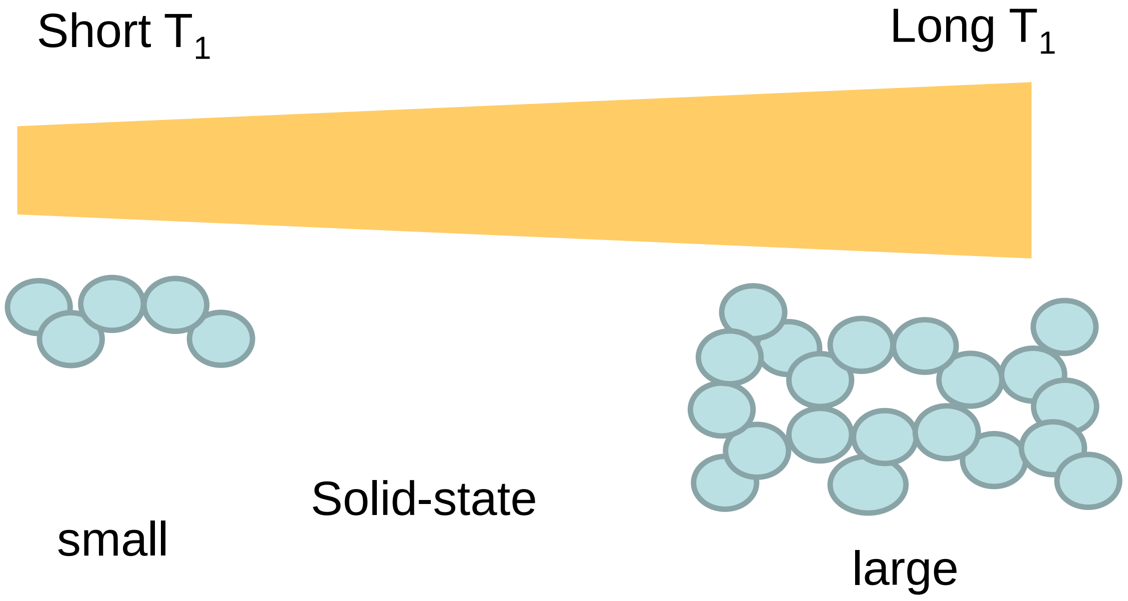
Thermal Equilibrium (starting point!)

1. Nuclear spins given into a static magnetic field will align themselves on two different energy levels according to the thermal equilibrium
2. A radio frequency-pulse (rf) moves spins from the lower to the higher energy level
3. Termination of the pulse allows the spins to return (relax) to their thermal equilibrium with the spin-lattice relaxation time rate, T_1.

Theoretical Background: T_1 and Molecular Properties

T_1 depends on:

- Molecular size / mobility:

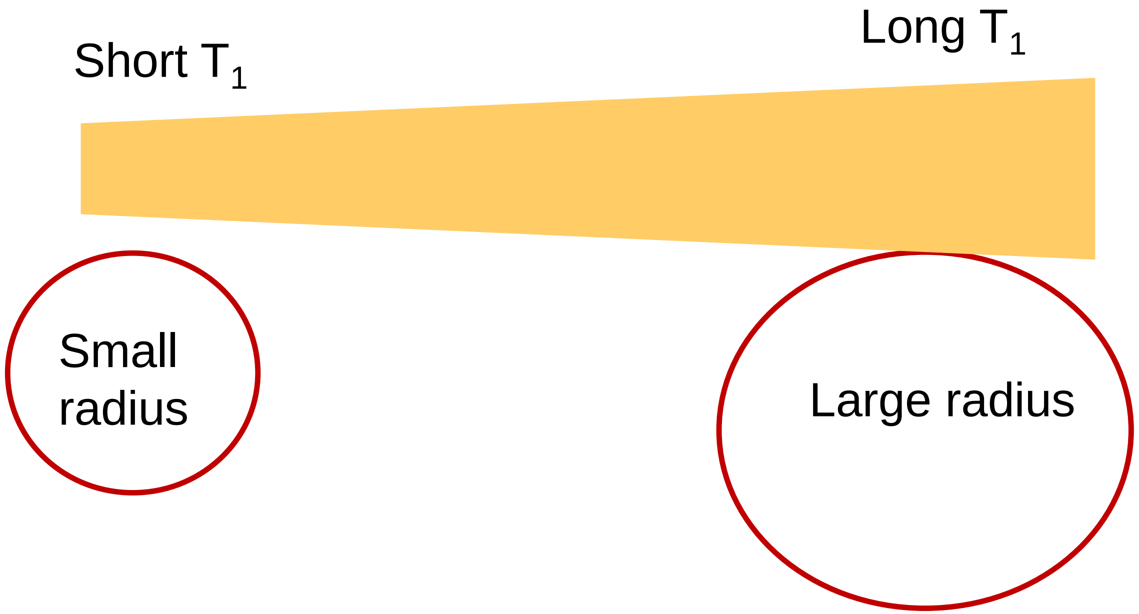


- Interaction with paramagnetics at a distance < 1 nm decreases efficiently T_1

Theoretical Background: T_1 and Domaine Size

Spin Diffusion: Spins in close neighborhood “communicate” their relaxation behavior among each other, which results in **one** common T_1:

The size of the „communication radius. L“ depends on T_1:



Kind and range of T_1s used in the present study:

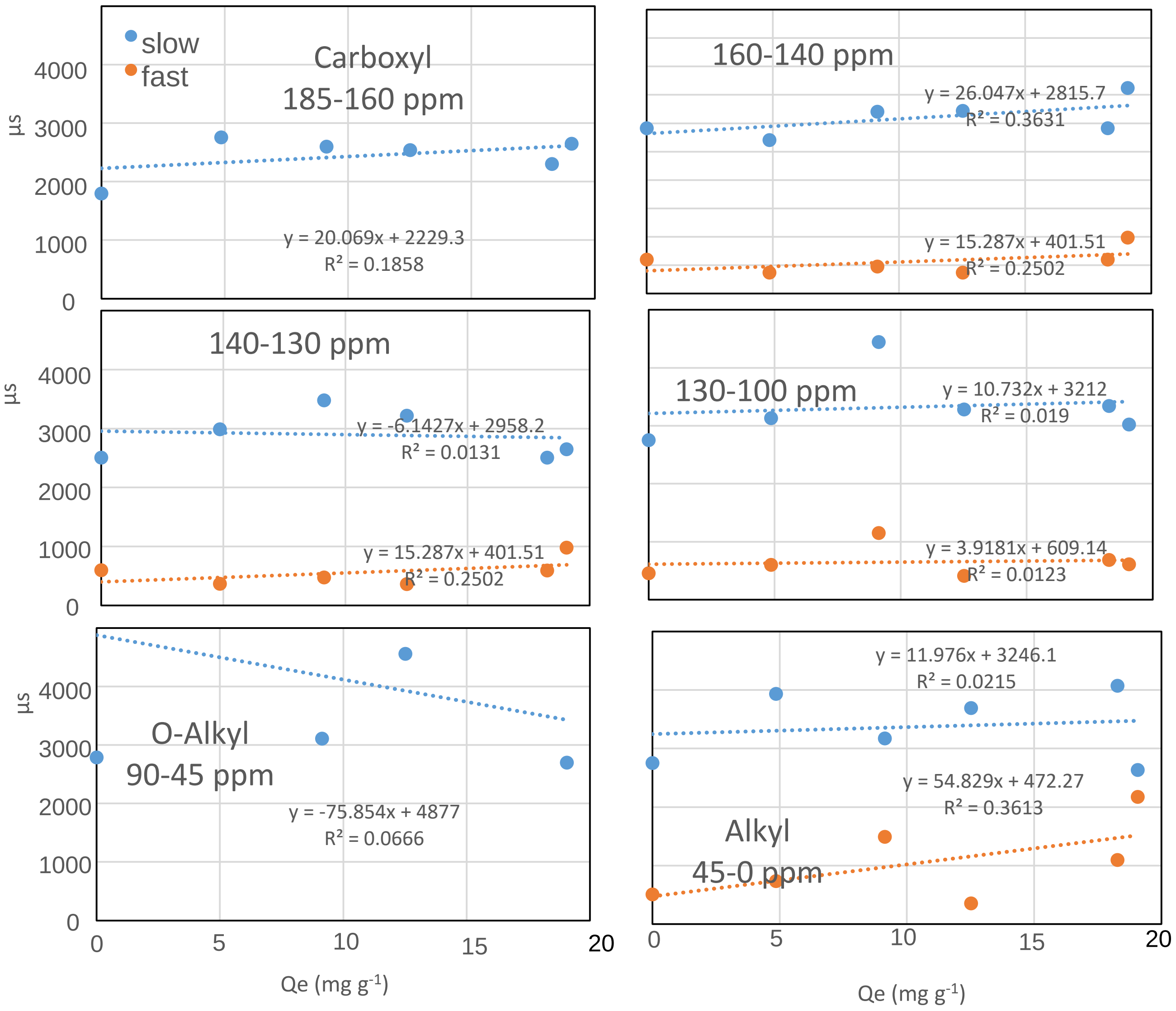
Kind of T_1	Time (ms)	L (nm)
$T_{1roh\text{-}H}$	0.1 – 20	2 - 30
T_{1H}	20-940	30 -160
T_{1C}	2000 -34000	Non*

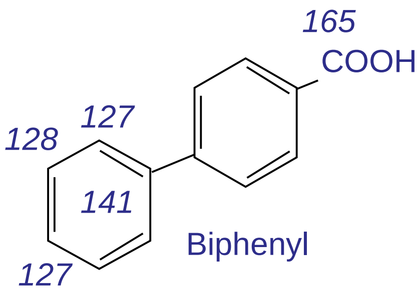
* The low natural abundance of ^{13}C does not allow spin-diffusion

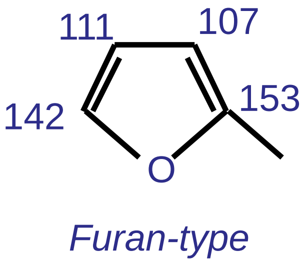
Information Obtainable from the Determination of T_1:

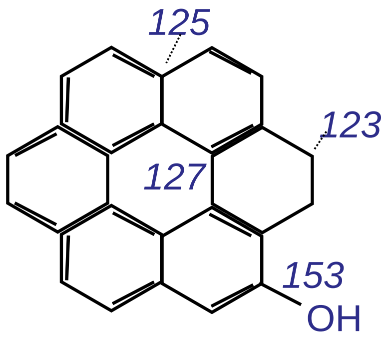
1. Identification of C groups which are affected by Cu^{2+} adsorption: T_{1C}
2. Changes in molecular mobility: T_{1H}, T_{1Hroh}
3. Minimal distance between domaines: T_{1H}, T_{1Hroh}
4. Chemical composition of fast and slowly relaxing pool
5. Selecting an adsorption mechanism according to the results

T_{1Hroh} versus Q_e (Cu^{2+}) in Ch400









T_{1Hroh} versus Q_e (Cu^{2+}) - conclusions

- None or only weak but positive correlations between T_{1Hroh} and Q_e:
  - Decrease of domain mobility after Cu^{2+} Adsorption overcomes shortening due to paramagentic interaction?

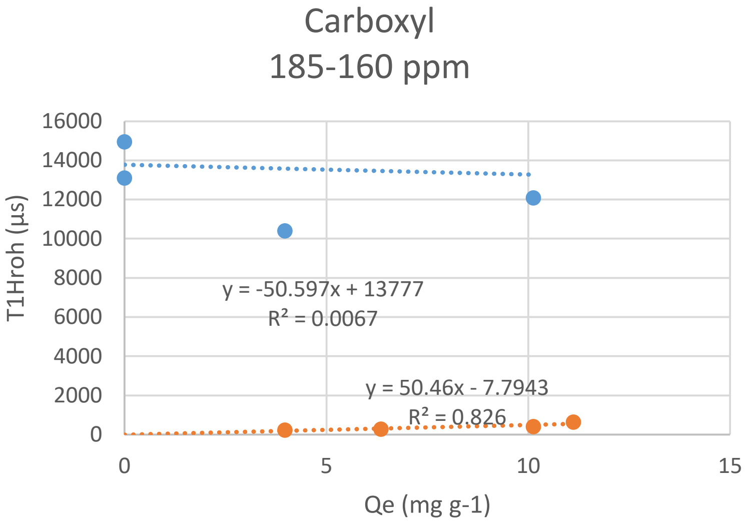
- Aromatic C and alkyl C show pools with fast and slow T_{1Hroh} (no spin diffusion among them, thus no interactions)
  - Domains with small and large molecules: Distance: > 7.5 nm

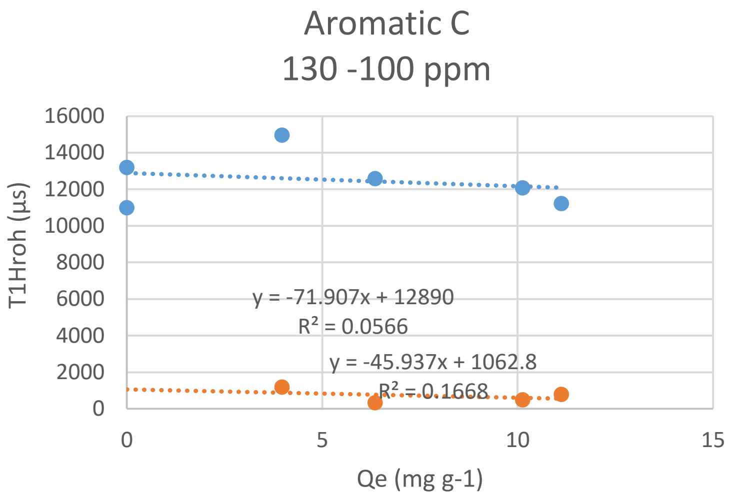
- Carboxyl C and O-alkyl C is only present in the slow fraction with higher molecular weight
  - Located mostly in ether and ester bonds. This makes them unlikely to serve as cation-adsorption site

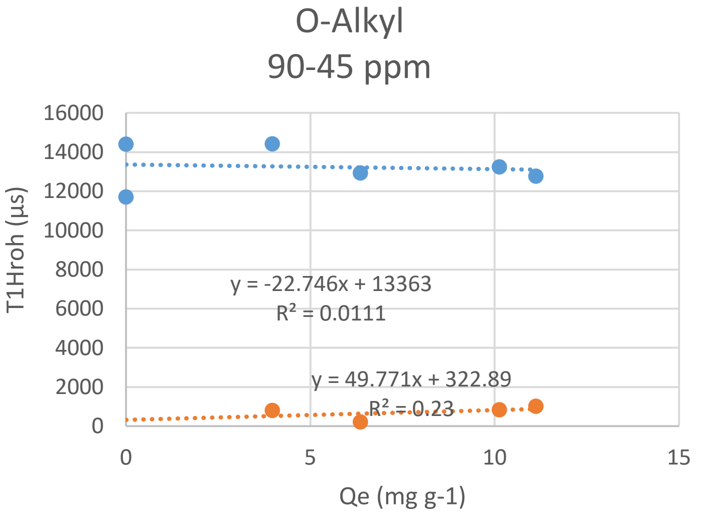
- T_{1Hroh} is comparable for all peaks within one domain
  - Efficient spin ^1H spin diffusion does not allow the identification of a specific adsorption site

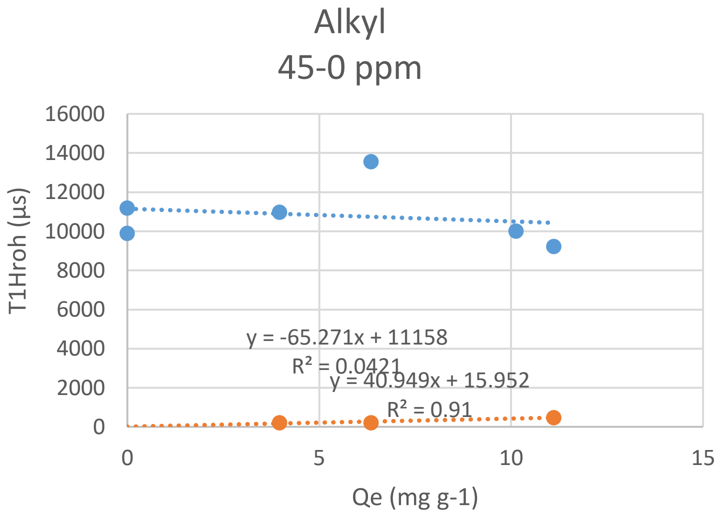
- Comparable results for Pe500

T_{1Hroh} versus Q_e (Cu^{2+}) – Ac450



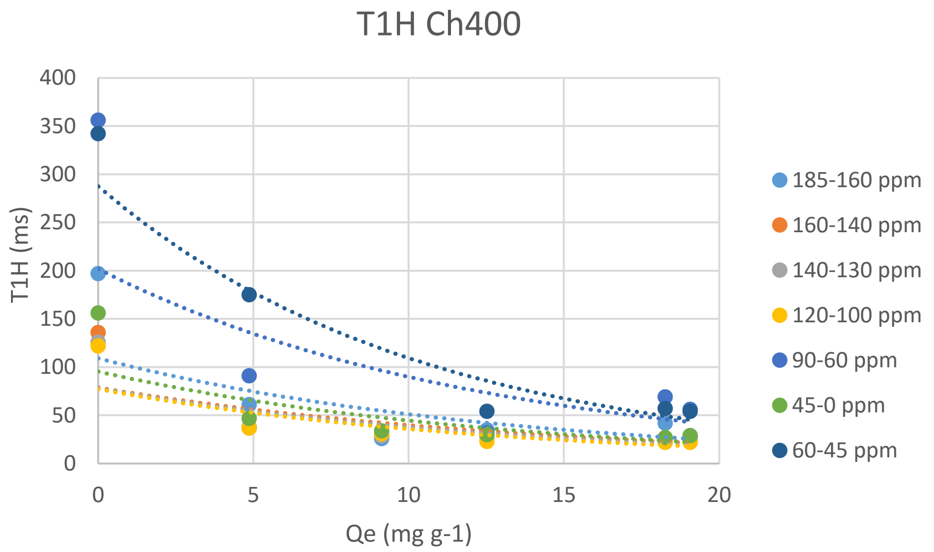


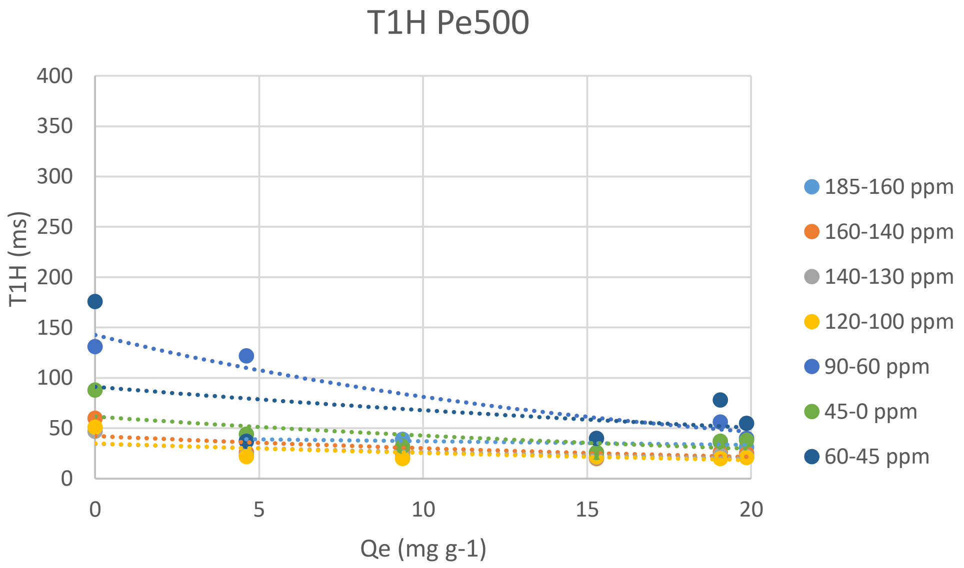




- T_{1Hroh} Ac450 >> T_{1Hroh} Ch400 = T_{1Hroh} Pe500:
  - ➢ Remaining crystalline cellulose-like units in Ac450
- Carboxyl, O-alkyl and alkyl show two domains
  - ➢ Presence of amorphous units (short T_{1Hroh})
- T_{1Hroh} short (carboxyl, alkyl) increases with Q_e
  - ➢ “Stabilization“ of amorphous domains?
- T_{1Hroh} versus Q_e of aromatic C shows no correlation

T_{1H} versus Q_e (Cu^{2+}) – Ch400, Pe500

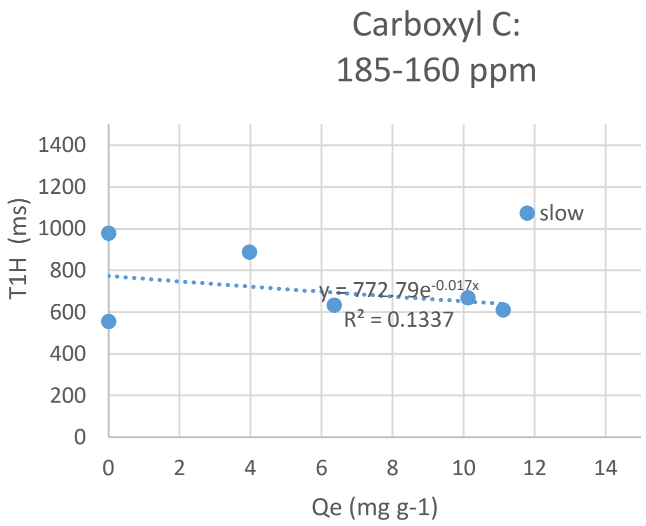


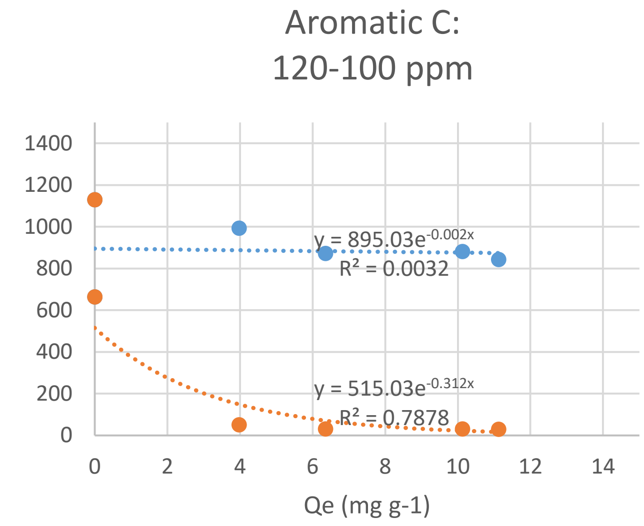


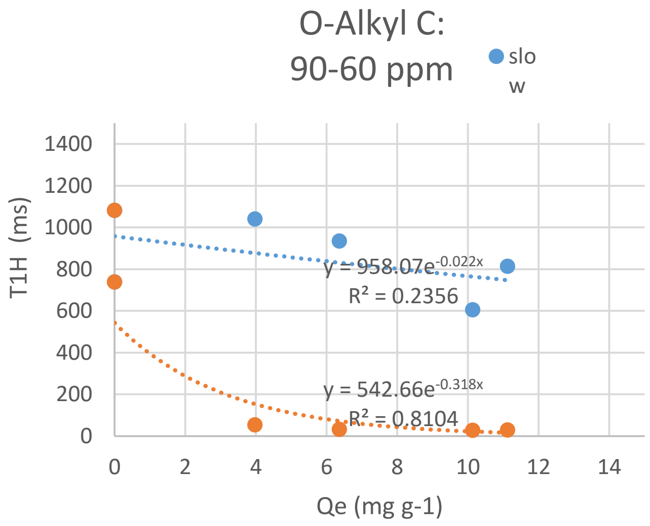
- For all C-groups the “one-pool”–fit works best
- T_{1H} O/N-alkyl (ether, N-alkyl; 90 – 45 ppm) > T_{1H} aromatic C (160-100 ppm)
- T_{1H} of all C-groups are affected by Cu^{2+}
- Minimum T_{1H}: aromatic C (20-30 ms) < O/N-alkyl C (50 – 60 ms)

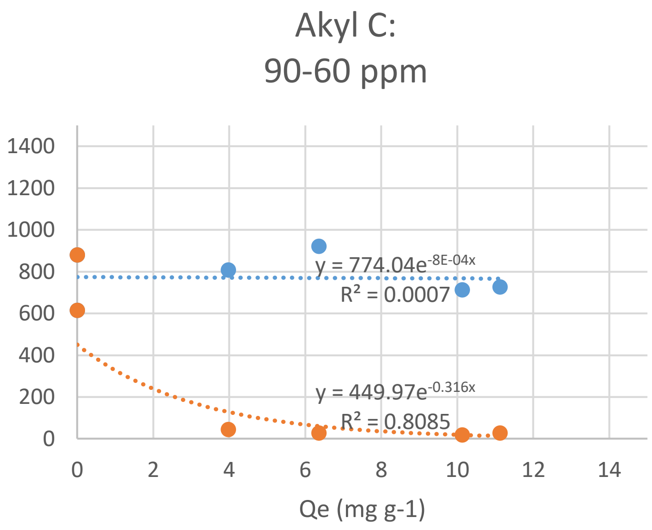
→ ***aromatic C as the preferential adsorption site ?***

T_{1H} versus Q_e (Cu^{2+}) – Ac450


Carboxyl C:
185-160 ppm


Aromatic C:
120-100 ppm

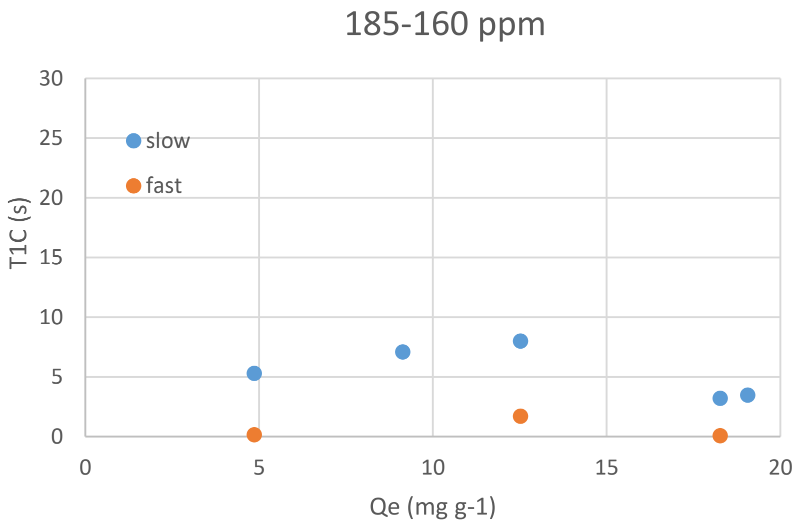

O-Alkyl C:
90-60 ppm

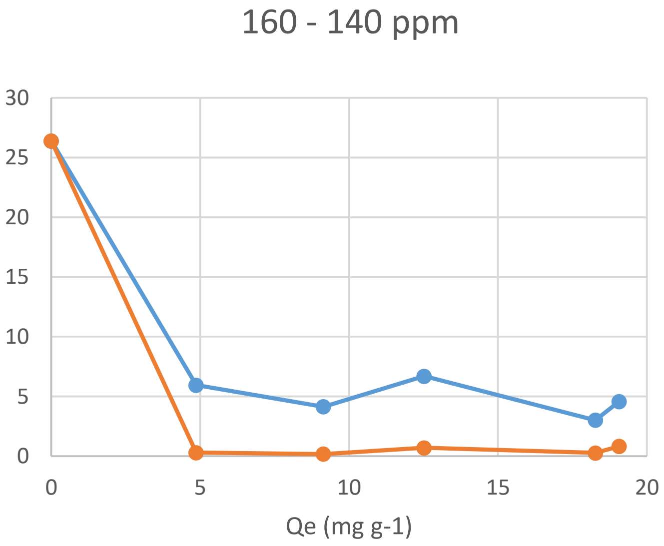

Akyl C:
90-60 ppm

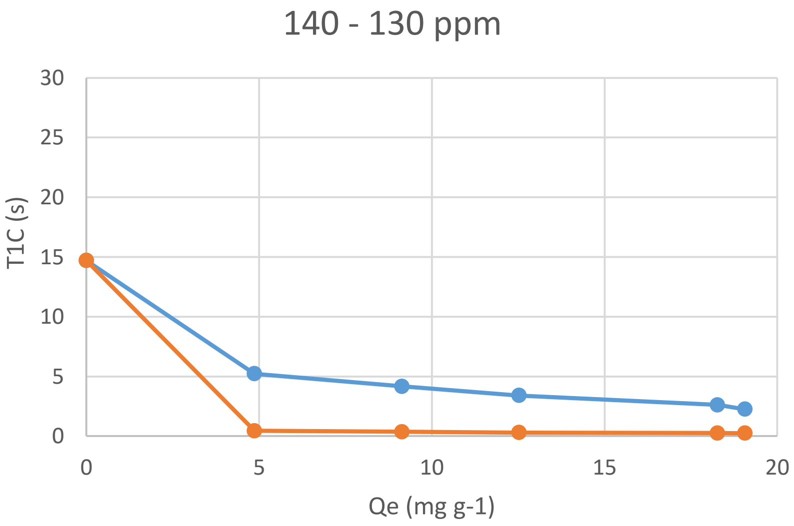
- **Without Cu^{2+}, there is only one "pool"**
- **Cu^{2+} (4 mg g^{-1}) → 2 pools (T_{1H} ≈ 50 ms → efficient spin diffusion < 35 nm)**
- **T_{1H}-slow stays almost constant**
- **T_{1H}-fast decreases with Q_e**
- **Minimum T_{1H} for all C groups: 30 ms**

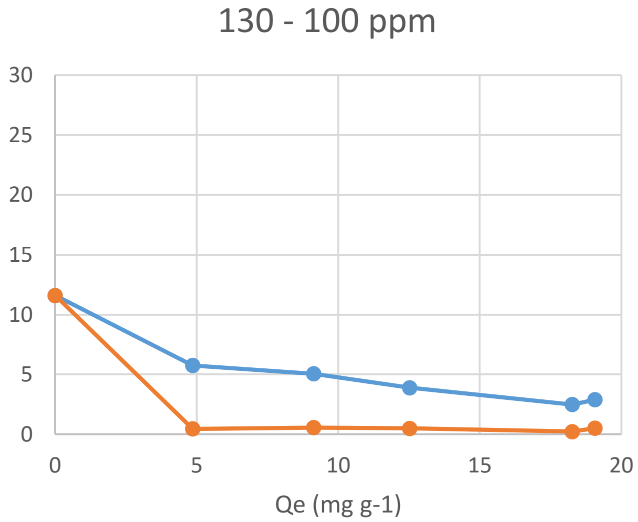
- ***Cu^{2+} adsorbs only on certain surfaces (pores are to small for entrance of Cu^{2+}?)***
- ***^{1}H spin diffusion affects only C in a radius < 35 nm***
- ***Core C (T_{1H}-slow) with a distance > 35 nm is not affected by Cu^{2+} adsorption***

T_{1C} versus Q_e (Cu^{2+}) – ChCu400







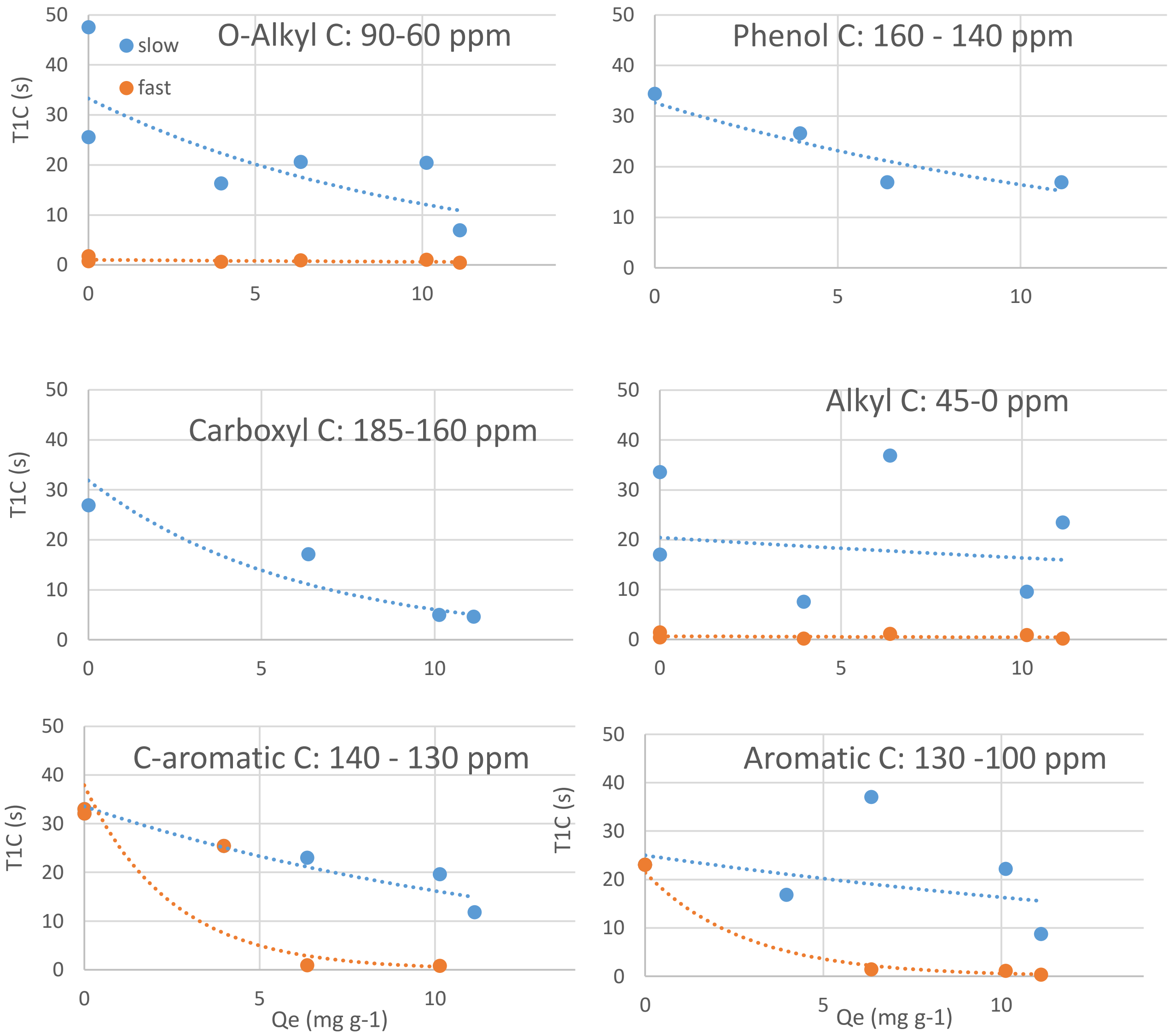


- **Without Cu^{2+}, there is only one “pool”**
- **Cu^{2+} (4.8 mg g^{-1}) → 2 pools**
- **All aromatic C are affected by Cu^{2+}**
- **O-Alkyl C shows no evidence for adsorption**

➢ ***NO evidence for C with preferential sorption***

Cation adsorption to π-orbitals of the aromatic rings?

T_{1C} versus Q_e (Cu^{2+}) – AcCu450



- **O-substituted groups show adsorption**
- **No evidence for adsorption on alkyl C**
- **Aromatic C shows 2 pools after Cu^{2+} addition**

➢ ***Cu^{2+} adsorption is different for Ac450 and ChCu400***

Conclusions

- Cu^{2+} adsorption correlates best with aromaticity of the char, possibly because in the highly aromatic pyrochars, charged groups such as carboxyl or ether are involved in bridging the aromatic domains or within an crystalline domaine (Ac450) and thus not accessible for Cu^{2+}.

- Cu^{2+} did not or only slightly affect T_{1Hroh}:
  - ➢ *Effect of decreasing mobility due to chelating is more pronounced than the paramagnetic effects?*

- Smaller domain size (indicated by smaller T_{1H}) of the highly aromatic chars offer more surface and thus more sites for adsorption than slightly charred material derived from woody residues (showing large T_{1H}).

Conclusions

- In Ac450 containing both polar groups and aromatic structures, both groups are involved in the adsorption.
- We have no evidence that alkyl C or methoxyl C were involved in the adsorption

Low Cu^{2+} adsorption in Ac450 may be best explained by crystalline structures, reducing the accessibility of Cu^{2+} to adsorption sites and the low content of aromatic C offering binding do their π-orbitals

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