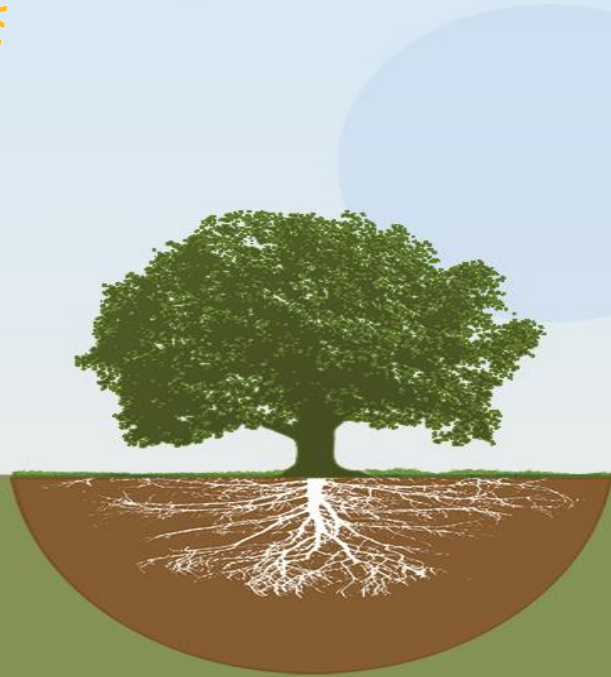


# Do chemical characteristics affect the potential of biochars to adsorb cations?



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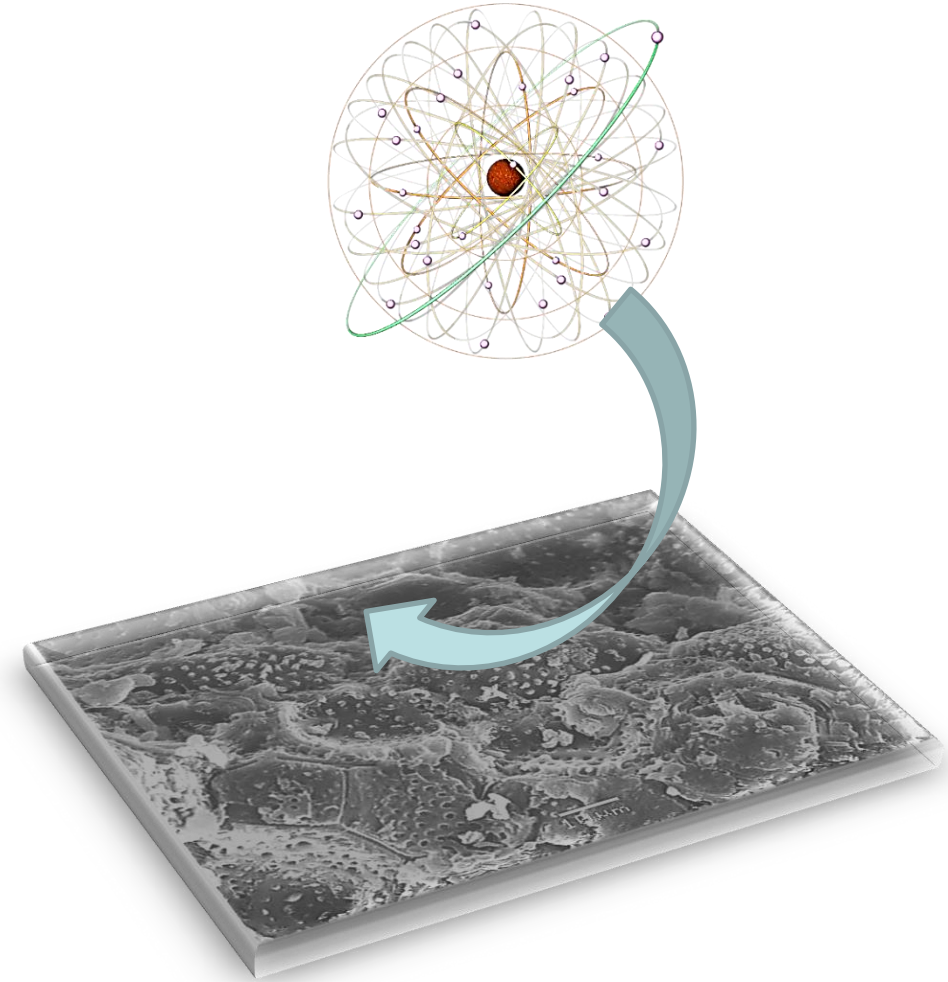
<sup>3</sup> Consult Michael Knicker (CMK). München. Germany

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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,  $\text{Cu}^{2+}$  shortens the Spin-Lattice Relaxation time ( $T_1$ )** of the  $^{13}\text{C}$  and its  $^1\text{H}$  to which it is adsorbed.
- **NMR Relaxometry** on  $\text{Cu}^{2+}$ -doped 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



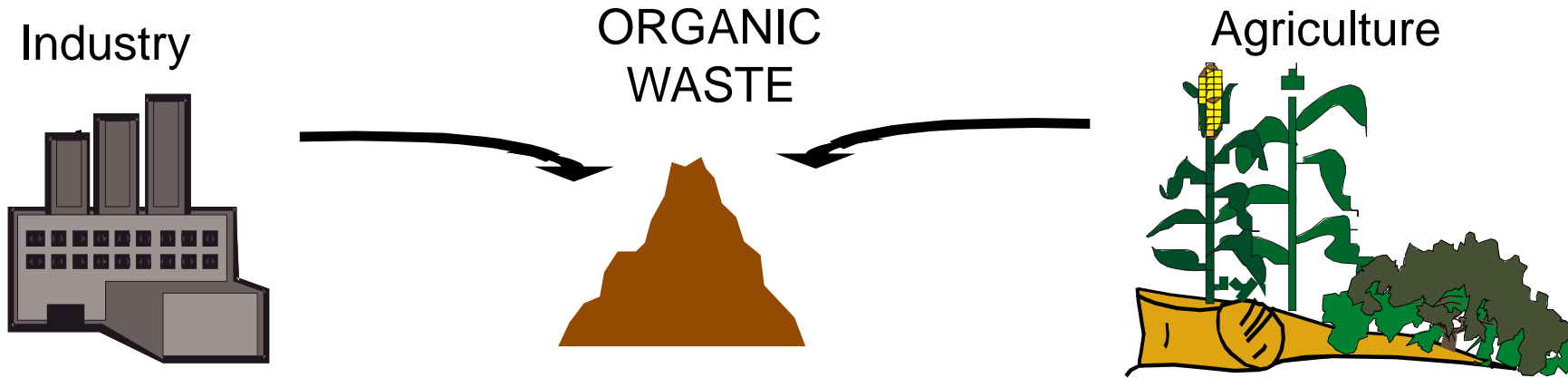
# Summary: Results

- 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<sup>2+</sup> to access** all potential adsorption sites
- Aside from charged functional groups,  **$\pi$ -orbitals of aromatic rings contributed to Cu<sup>2+</sup> adsorption**

***Porosity is not the main factor determining Cu<sup>2+</sup> adsorption to pyrochar;***

***Accessibility of Cu<sup>2+</sup> to pores and the availability of  $\pi$ -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

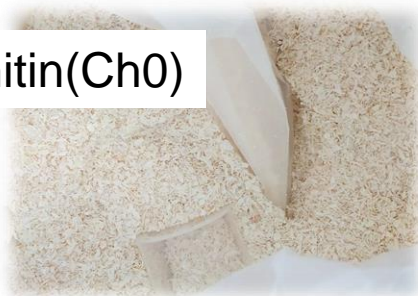
- Soil amendment
- Slow-release fertilizer
- Gardening soil
- Water clean-up
- Soil remediation
- Filter (water clean-up)
- etc.

# But: Biochar ≠ Biochar!

Biochar structure depends on:

- Feedstock
- Production conditions

Chitin(Ch0)



400°C. 3h

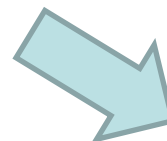
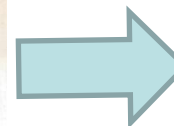
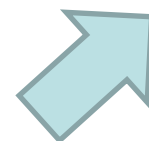
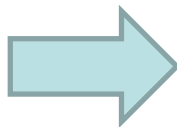


Chitin char (Ch400)

Peat (Pe0)



500°C. 3h

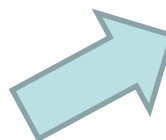


Peat char (Pe500)

Acrocomia endocarp (Ac0)



450°C. 0.5h



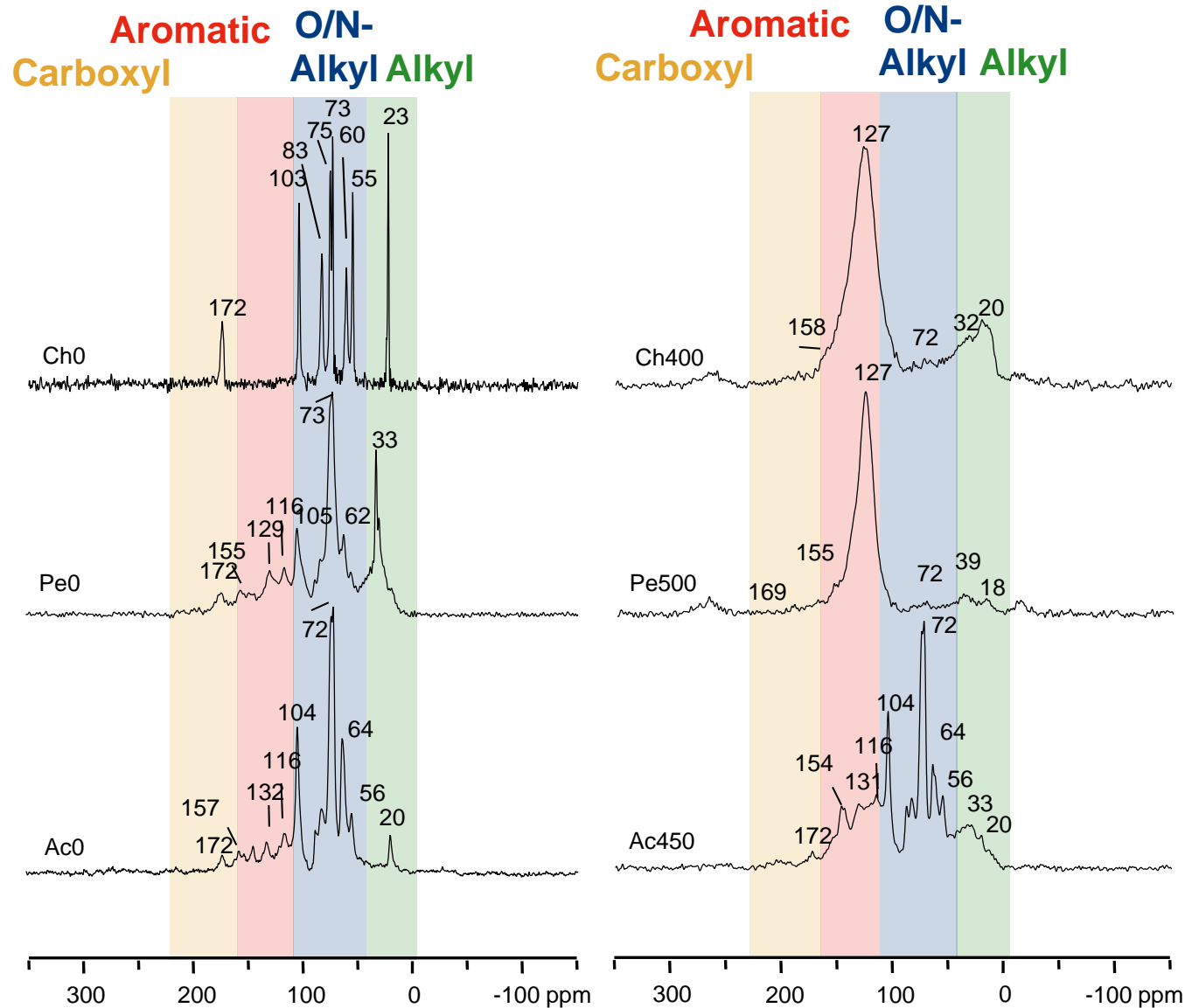
Acrocomia endocarp char (Ac450)

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<sub>2</sub>O) and the BET surface area (SA) (CO<sub>2</sub>) of the chars.

Material	C		H		N		Ash		O*	H/C <sub>atm</sub>	C/N (w/w)	O/C <sub>atm</sub>	pH (H <sub>2</sub> O)		S <sub>BET</sub> m <sup>2</sup> g <sup>-1</sup>
	g kg <sup>-1</sup>		g kg <sup>-1</sup>		g kg <sup>-1</sup>		g kg <sup>-1</sup>								
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 $^{13}\text{C}$ 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  $P$ :

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

*Ac450 > Ch400 > Pe500*

# Hypothesis:

Different chemical composition, polarity, pH and BET surface (CO<sub>2</sub>) may lead to:

*Differences in the Cation Adsorption?*



Adsorption experiments with  
paramagnetic Cu<sup>2+</sup>

*Differences in the Adsorption Mechanism?*



NMR-Relaxometry:

- Relaxation time is affected by paramagnetic Cu<sup>2+</sup>
- Determination of affected C group allows identification of binding site



# Adsorption of $\text{Cu}^{2+}$ onto Biochar: Experimental Design

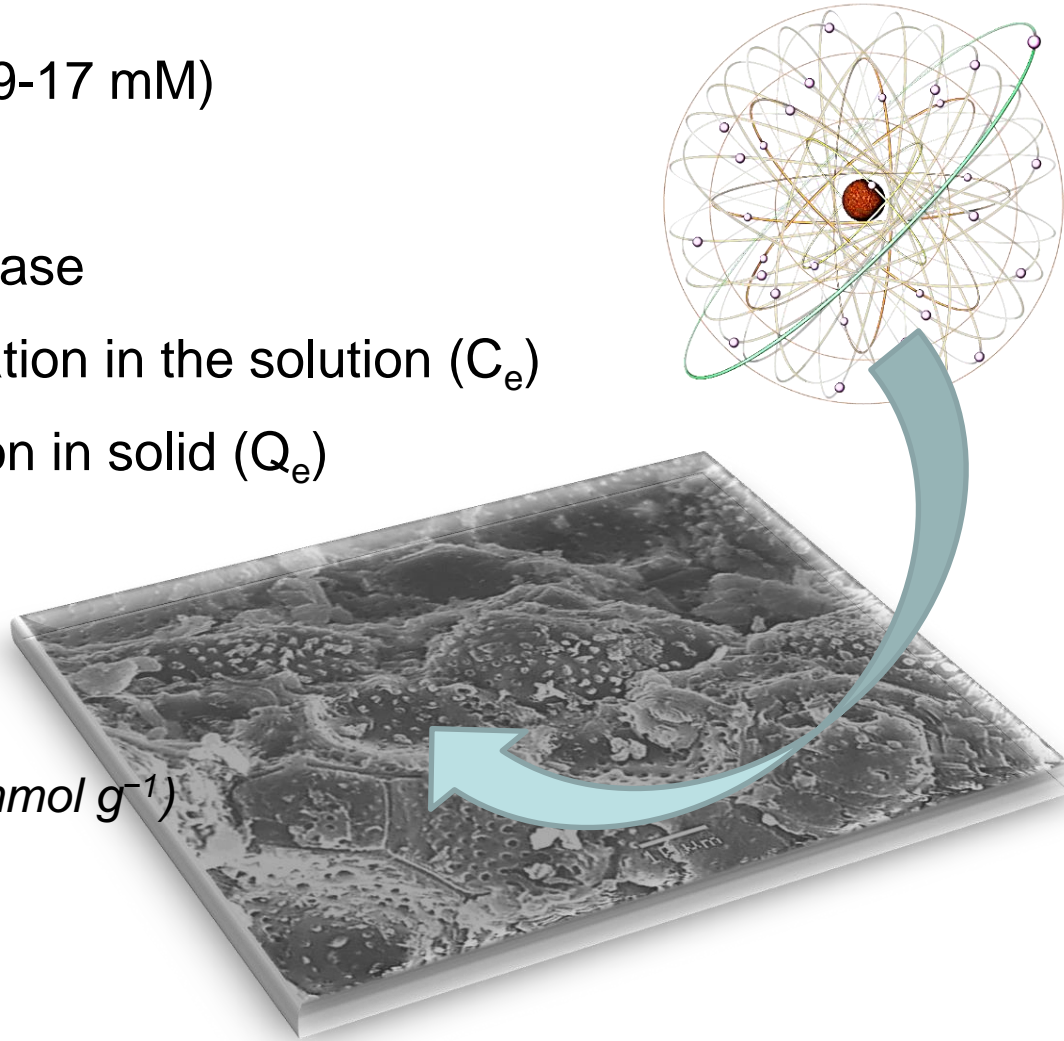
- 200 mg biochar +  $\text{Cu}(\text{NO}_3)_2$  (0.9-17 mM)
- Shaking for 24 h at  $25^\circ\text{C}$
- Separation of solid and liquid phase
- Determination of  $\text{Cu}^{2+}$  concentration in the solution ( $C_e$ )
- Calculation of  $\text{Cu}^{2+}$  concentration in solid ( $Q_e$ )

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

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

$K_d$ : Freundlich distribution coefficient.

$n$ : correction factor constant



Langmuir

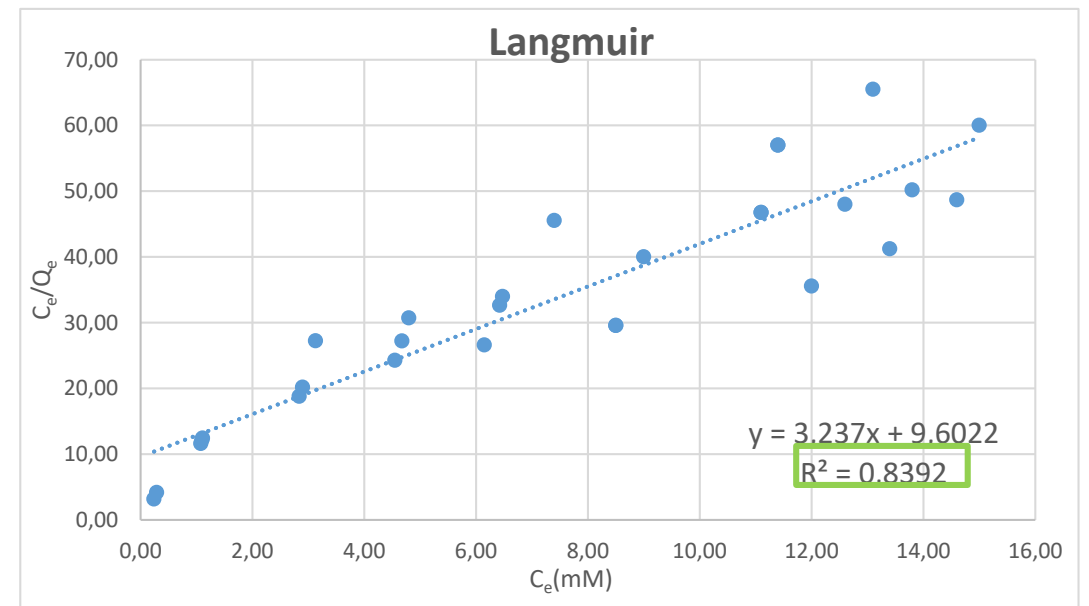
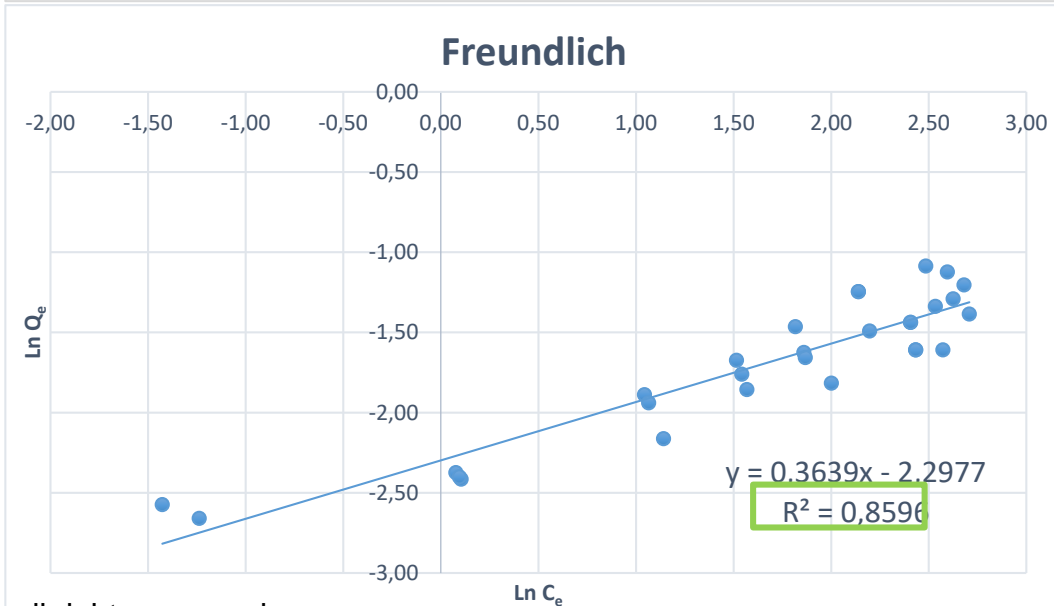
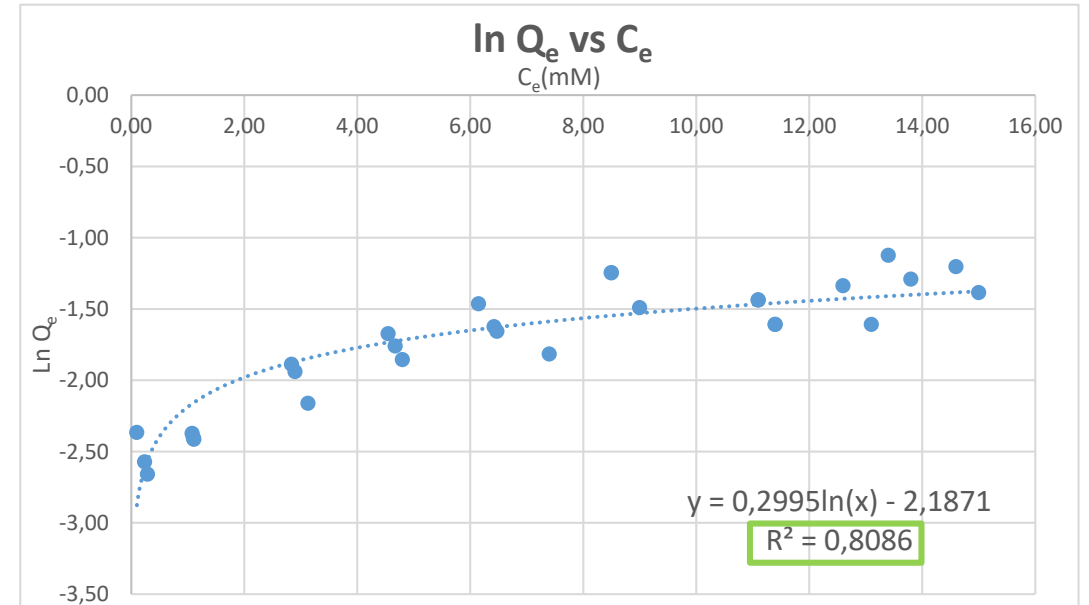
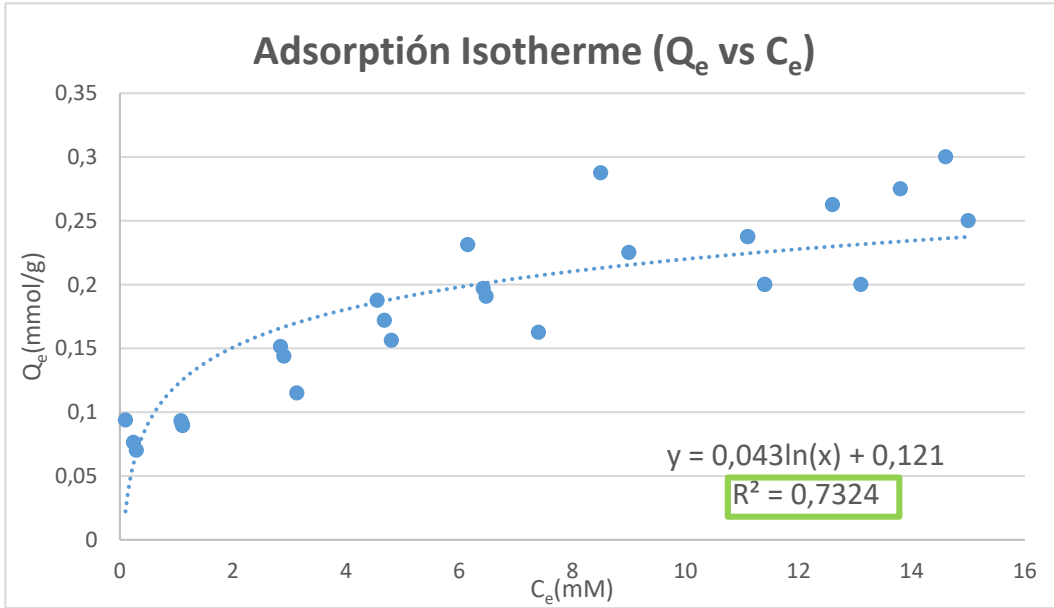
$$\frac{C_e}{Q_e} = \frac{1}{K \cdot Q_{\max}} + \frac{C_e}{Q_{\max}}$$

Freundlich

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

$$\ln Q_e = \ln K_d + \frac{1}{n} \ln C_e$$

# Adsorption Isotherms of $\text{Cu}^{2+}$ to Ch400



# Adsorption Parameters of Cu<sup>2+</sup> to Ch400, Pe500, Ac450

	Freundlich			Langmuir		
	R <sup>2</sup>	K <sub>d</sub>	n	R <sup>2</sup>	Q <sub>max</sub> (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<sup>2</sup> with Freundlich:**  
**n > 1:**  
**K<sub>d</sub> (Adsorption affinity):**

**non-ideal adsorption on a heterogeneous surface**  
**higher Cu<sup>2+</sup>-concentration decreases relative adsorption**  
**Pe500 > Ch400 > Ac450 (very low adsorption)**

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

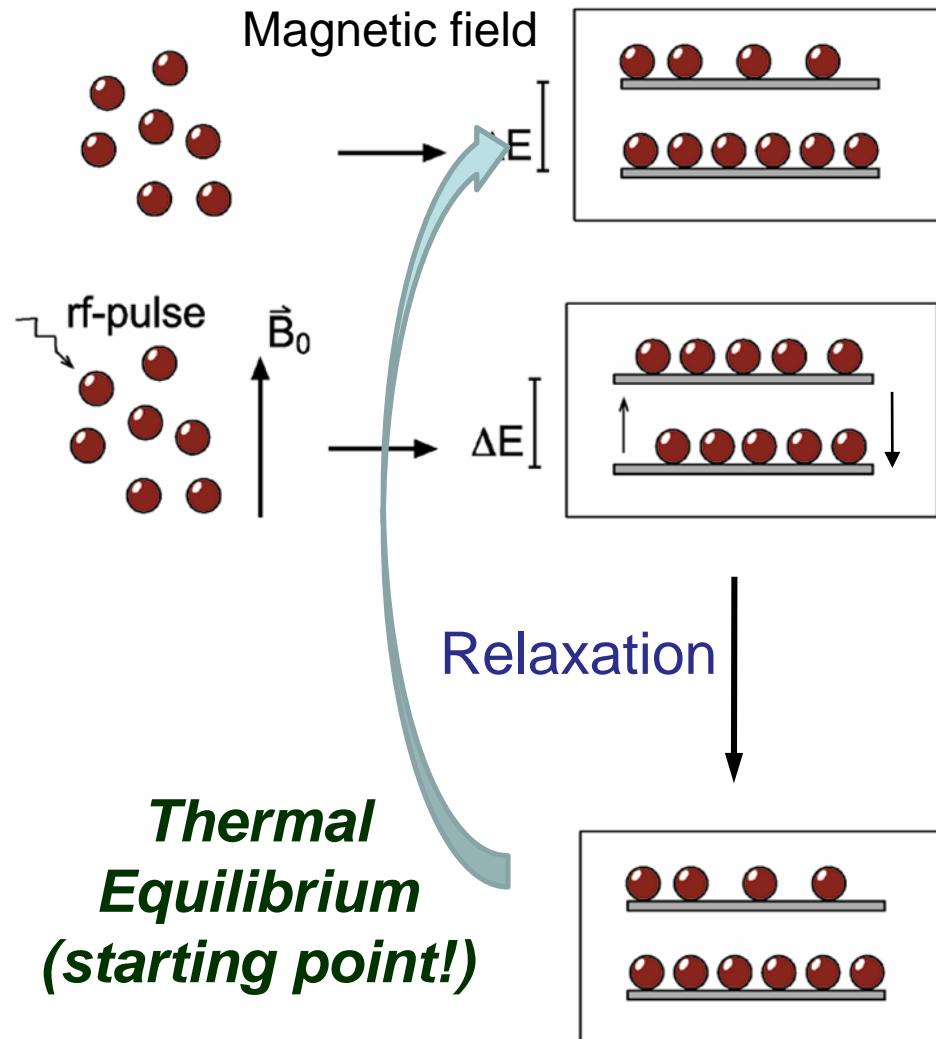
Biochar	Single point surface area at P/Po ( $\text{m}^2/\text{g}$ )	BET Surface Area ( $\text{CO}_2$ )	pH	Aromaticity	Polarity
Quitina (Ch)	163.36	216.13	6.4	74	0.32
Turba (Pe)	158.89	192.41	8.4	88	0.27
Acrocomia (Ac)	140.02	177.62	7.3	26	1.18

- *No evident relationship 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 $\text{Cu}^{2+}$ Adsorption Sites:

## Theoretical Background

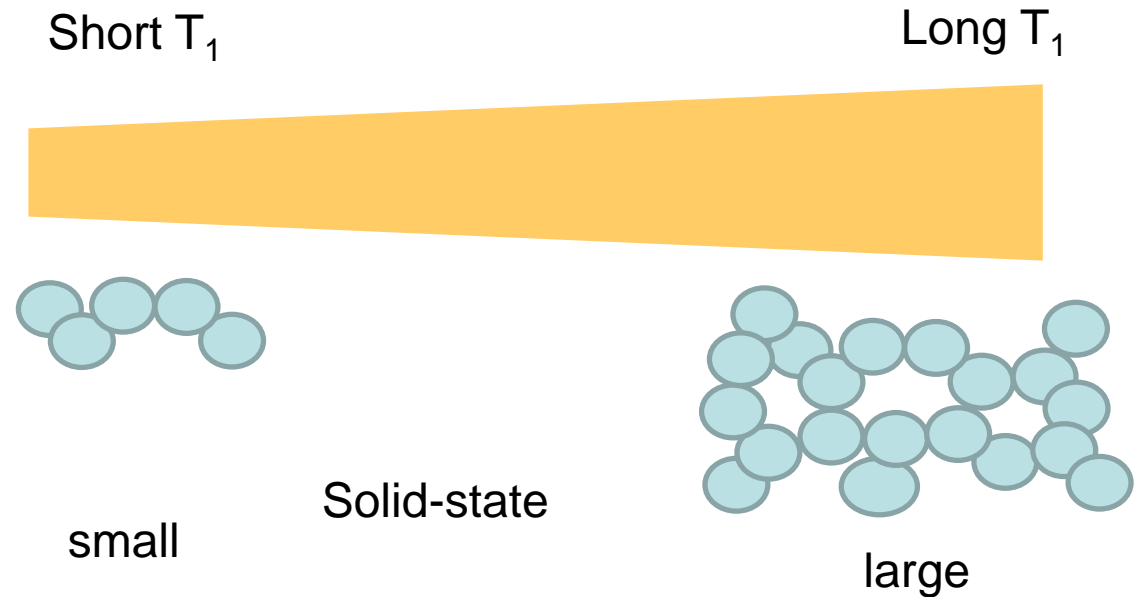


1. Nuclear spins given into a static magnetic field will align themselves on two different energy levels according to the thermal equilibrium
2. A radio frequency-pulse (rf) moves spins from the lower to the higher energy level
3. Termination of the pulse allows the spins to return (relax) to their thermal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

# Theoretical Background: $T_1$ and Molecular Properties

$T_1$  depends on:

- Molecular size / mobility:

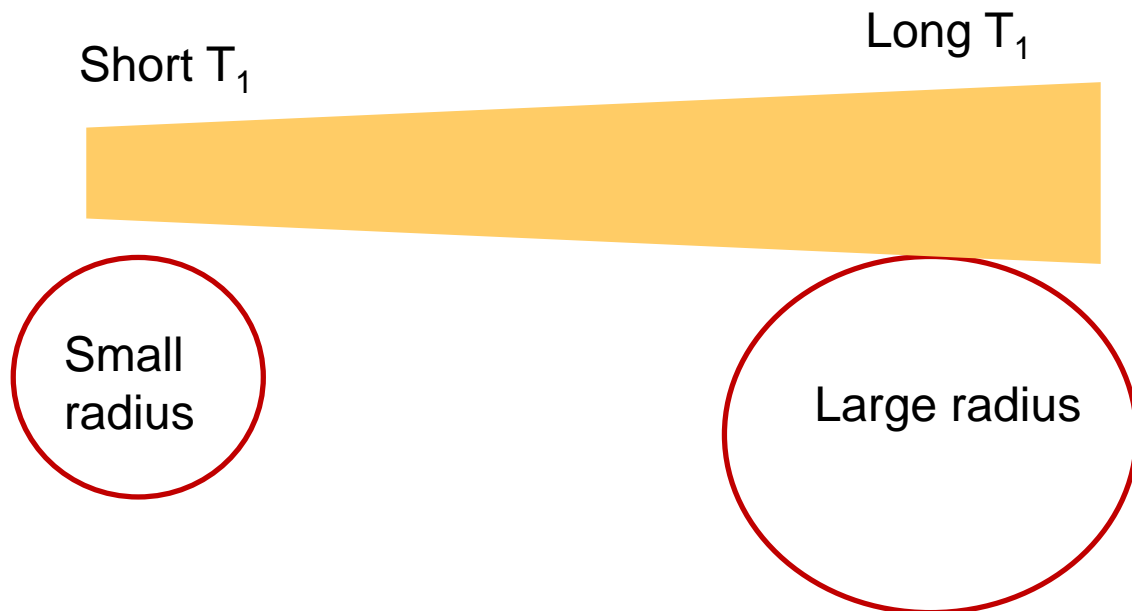


- Interaction with paramagnetics at a distance  $< 1$  nm decreases efficiently  $T_1$

# Theoretical Background: $T_1$ and Domain 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  $T_1$ s used in the present study:*

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

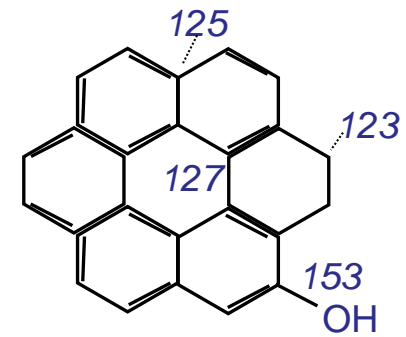
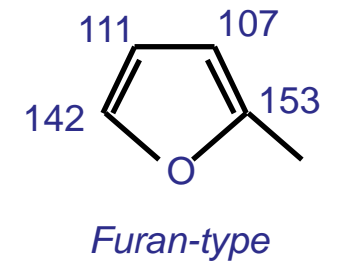
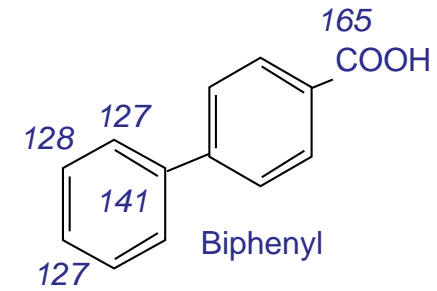
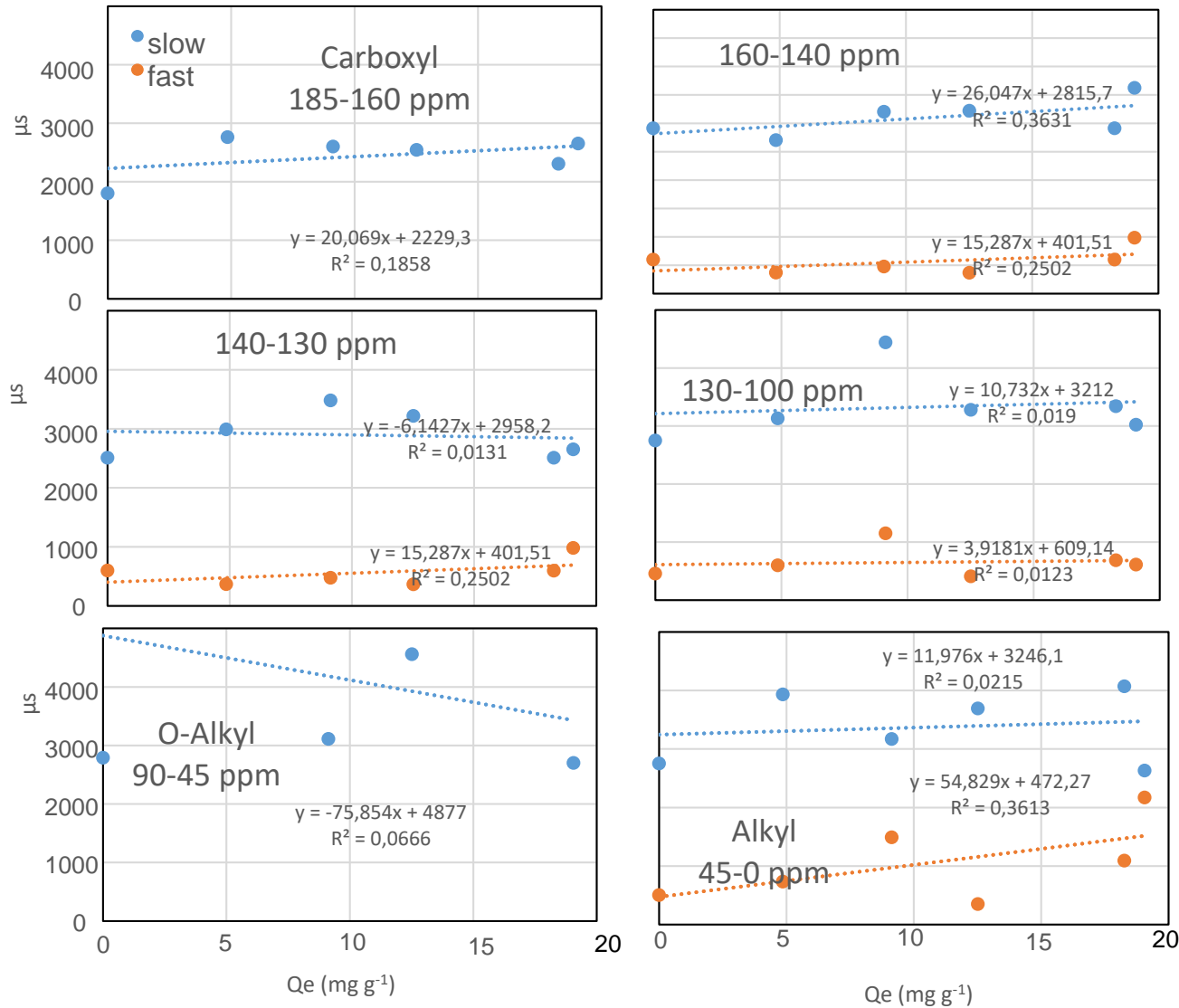
\* The low natural abundance of  $^{13}\text{C}$  does not allow spin-diffusion

# Information Obtainable from the Determination of $T_1$ :

1. Identification of C groups which are affected by  $\text{Cu}^{2+}$  adsorption:  $T_{1C}$
2. Changes in molecular mobility:  $T_{1H}$ ,  $T_{1Hroh}$
3. Minimal distance between domains:  $T_{1H}$ ,  $T_{1Hroh}$
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

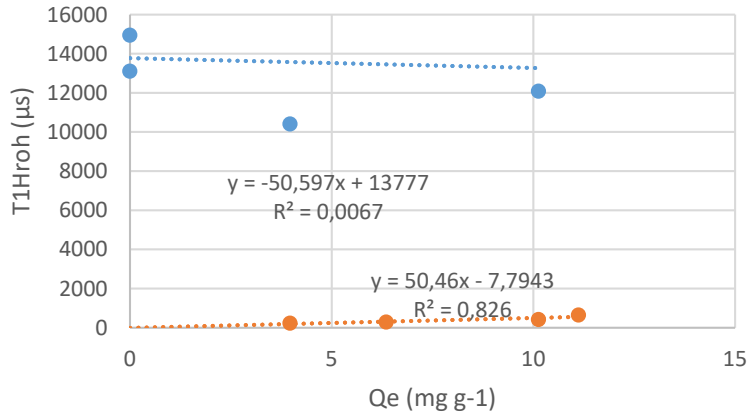


# $T_{1Hroh}$ versus $Q_e$ ( $Cu^{2+}$ ) - conclusions

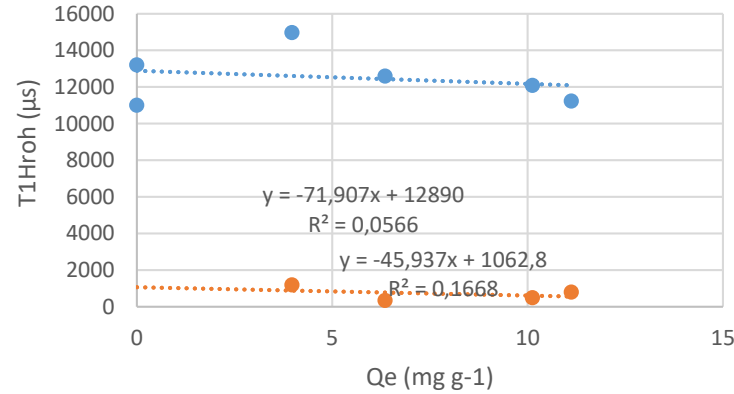
- None or only weak but positive correlations between  $T_{1Hroh}$  and  $Q_e$ :
  - Decrease of domain mobility after  $Cu^{2+}$  Adsorption overcomes shortening due to paramagnetic interaction?
- Aromatic C and alkyl C show pools with fast and slow  $T_{1Hroh}$  (no spin diffusion among them, thus 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

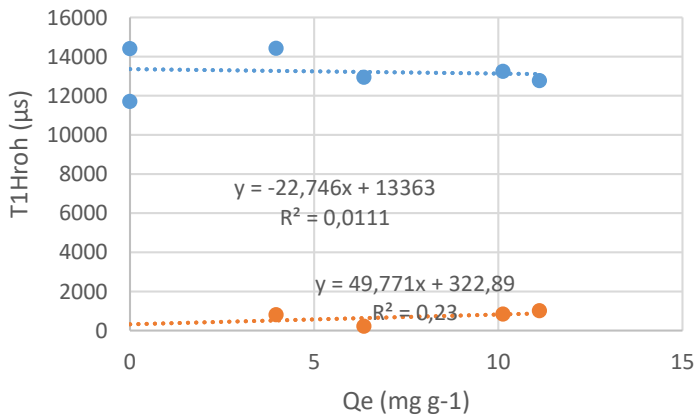
Carboxyl  
185-160 ppm



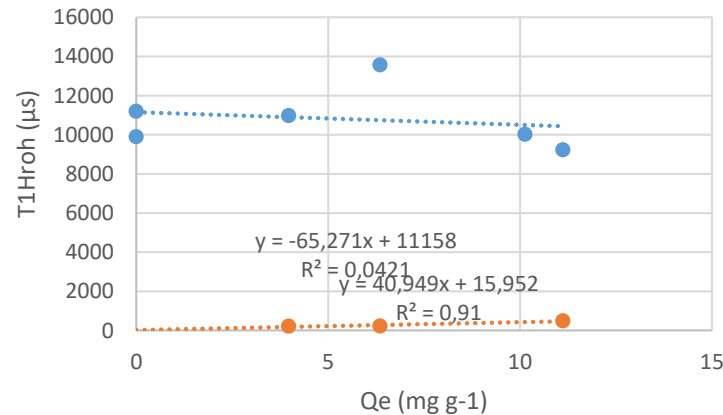
Aromatic C  
130 -100 ppm



O-Alkyl  
90-45 ppm

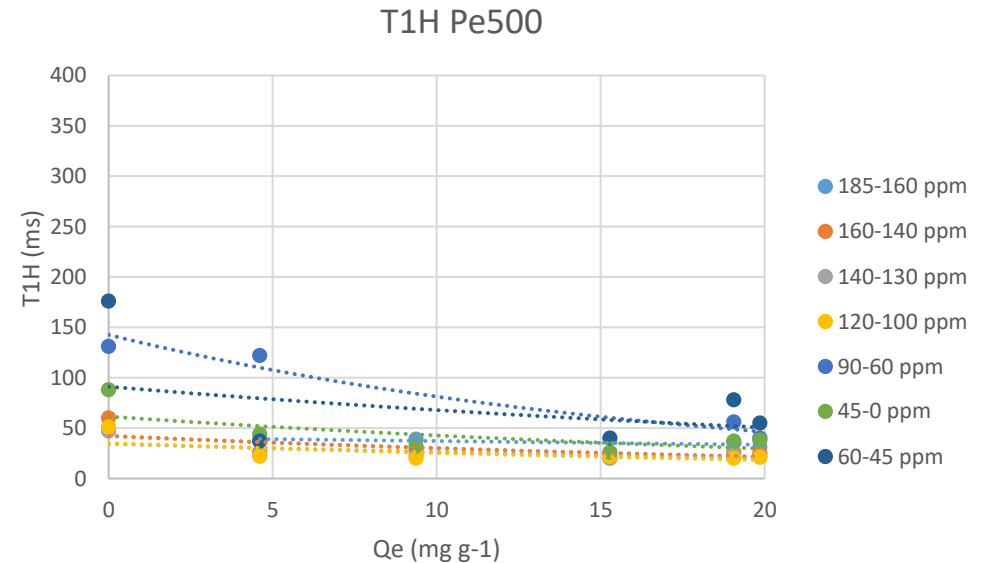
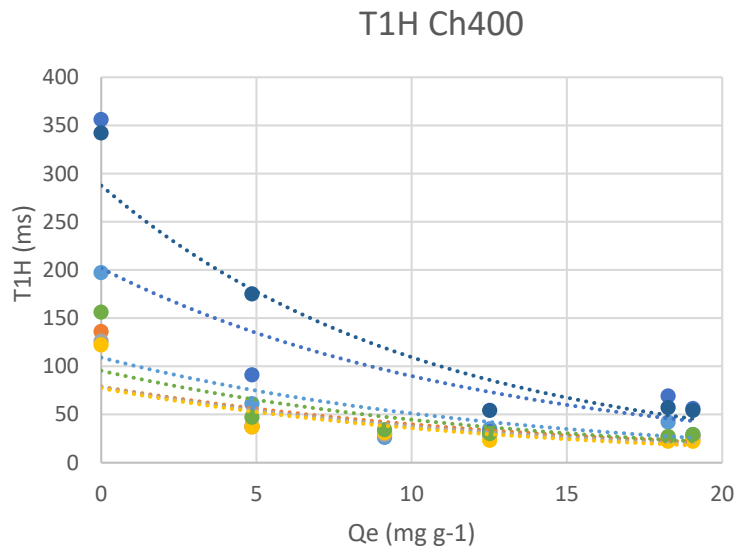


Alkyl  
45-0 ppm



- $T_{1Hroh}$  Ac450  $\gg$   $T_{1Hroh}$  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 $Q_e$ ( $\text{Cu}^{2+}$ ) – Ch400, Pe500

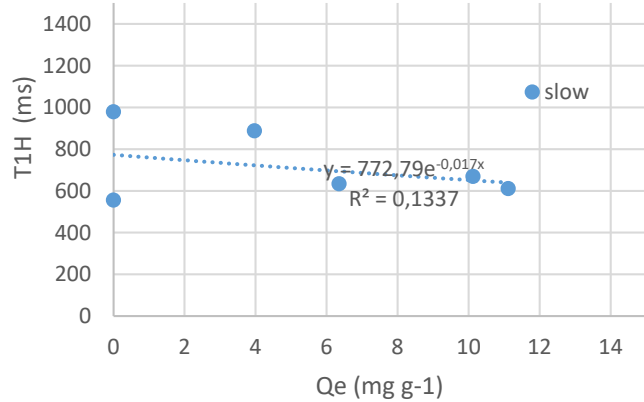


- For all C-groups the “one-pool”–fit works best
- $T_{1H}$  O/N-alkyl (ether, N-alkyl; 90 – 45 ppm) >  $T_{1H}$  aromatic C (160-100 ppm)
- $T_{1H}$  of all C-groups are affected by  $\text{Cu}^{2+}$
- Minimum  $T_{1H}$ : aromatic C (20-30 ms) < O/N-alkyl C (50 – 60 ms)

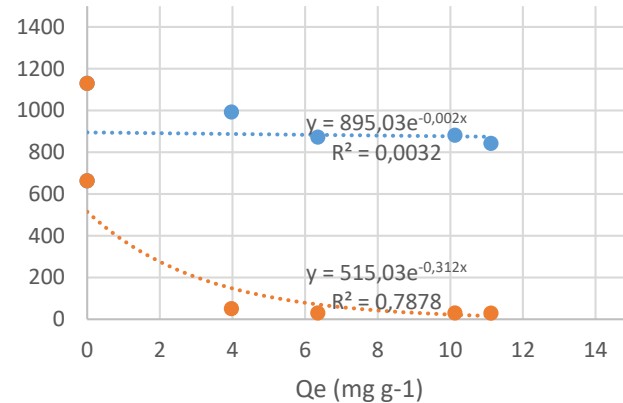
→ **aromatic C as the preferential adsorption site ?**

# $T_{1H}$ versus $Q_e$ ( $Cu^{2+}$ ) – Ac450

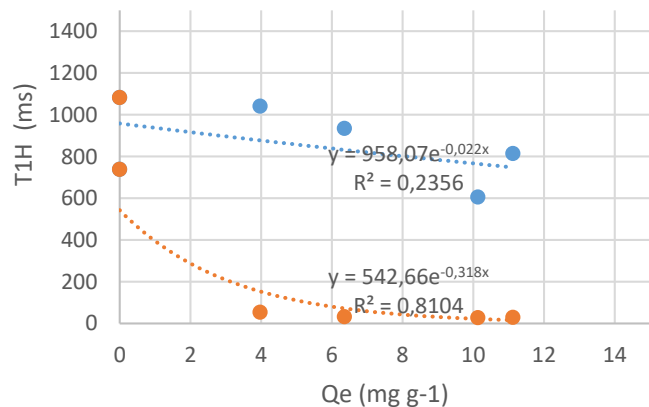
Carboxyl C:  
185-160 ppm



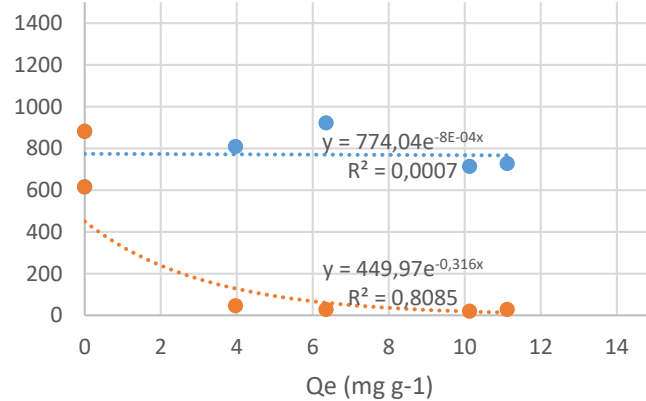
Aromatic C:  
120-100 ppm



O-Alkyl C:  
90-60 ppm



Akyl C:  
90-60 ppm



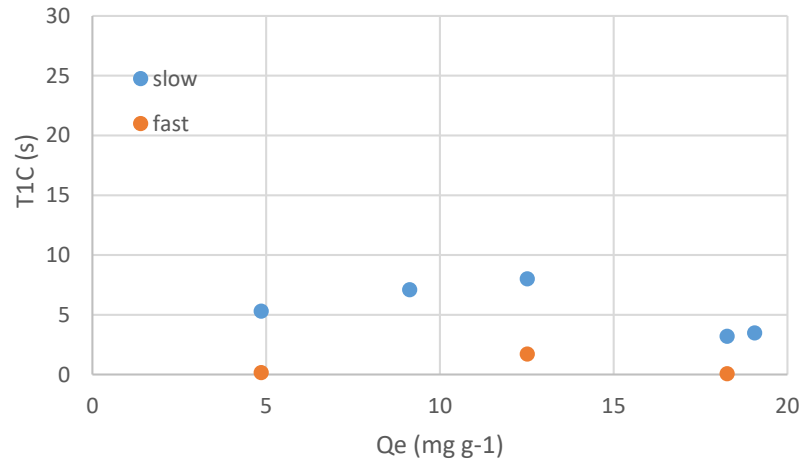
- Without  $Cu^{2+}$ , there is only one “pool”
- $Cu^{2+}$  (4 mg g<sup>-1</sup>) → 2 pools ( $T_{1H} \approx 50$  ms → efficient spin diffusion < 35 nm)
- $T_{1H}$ -slow stays almost constant
- $T_{1H}$ -fast decreases with  $Q_e$
- Minimum  $T_{1H}$  for all C groups: 30 ms



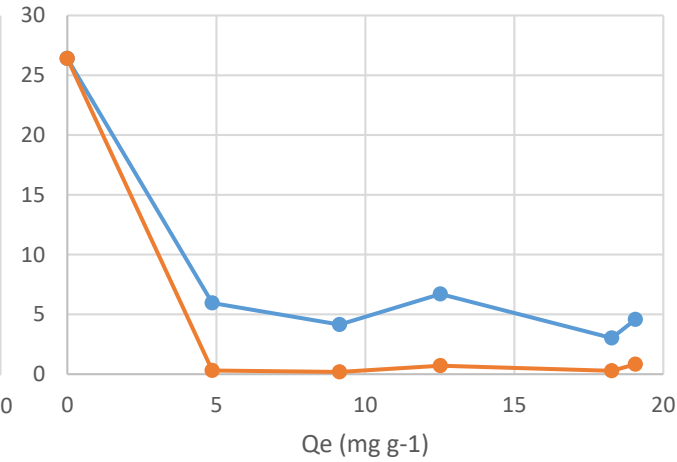
- $Cu^{2+}$  adsorbs only on certain surfaces (pores are too small for entrance of  $Cu^{2+}$ ?)
- $^1H$  spin diffusion affects only C in a radius < 35 nm
- Core C ( $T_{1H}$ -slow) with a distance > 35 nm is not affected by  $Cu^{2+}$  adsorption

# $T_{1\rho}$ versus $Q_e$ ( $\text{Cu}^{2+}$ ) – ChCu400

185-160 ppm

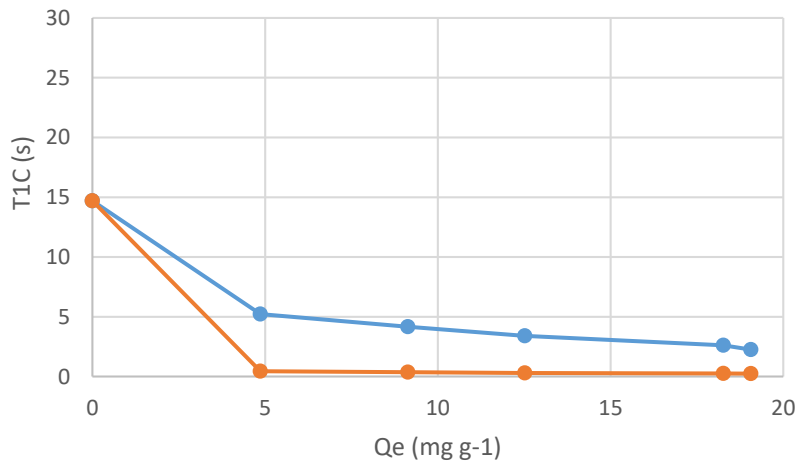


160 - 140 ppm

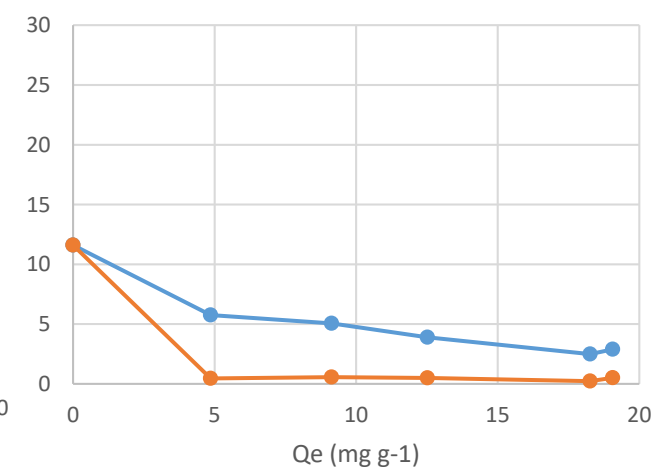


- Without  $\text{Cu}^{2+}$ , there is only one “pool”
- $\text{Cu}^{2+}$  ( $4.8 \text{ mg g}^{-1}$ )  $\rightarrow$  2 pools
- All aromatic C are affected by  $\text{Cu}^{2+}$
- O-Alkyl C shows no evidence for adsorption

140 - 130 ppm



130 - 100 ppm

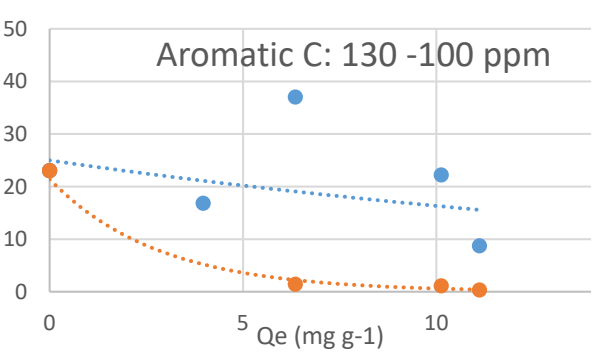
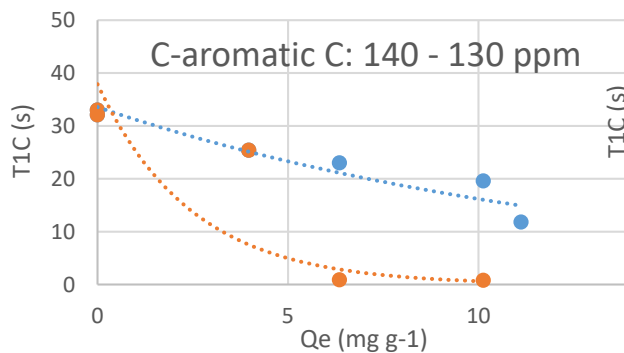
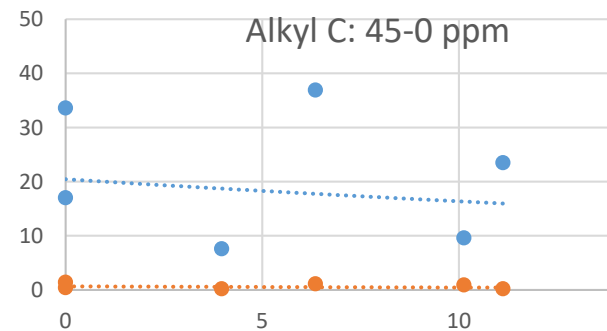
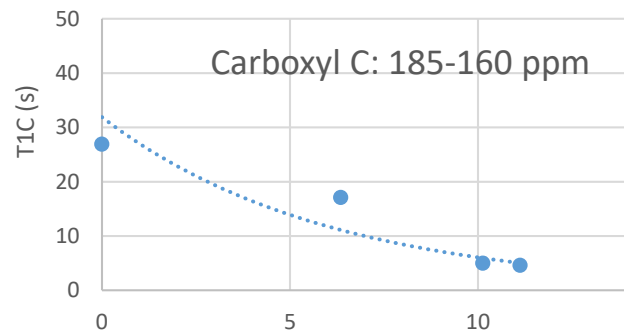
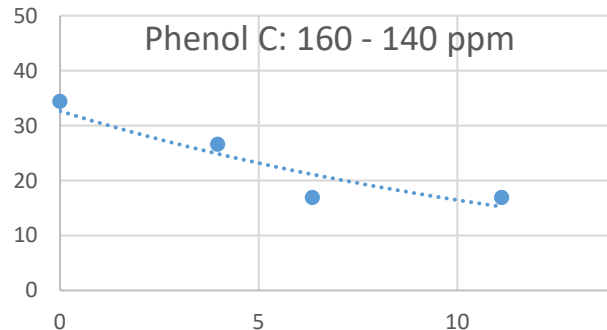
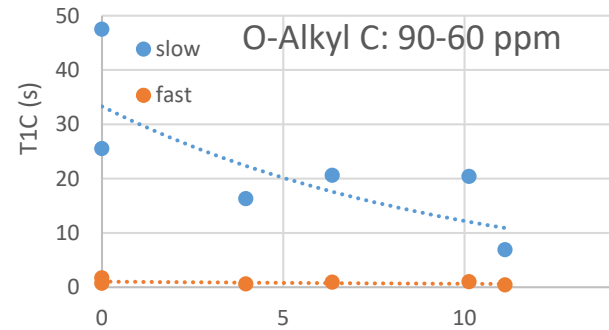


➤ *NO evidence for C with preferential sorption*



*Cation adsorption to  $\pi$ -orbitals of the aromatic rings?*

# $T_{1C}$ versus $Q_e$ ( $\text{Cu}^{2+}$ ) – AcCu450



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

➤  *$\text{Cu}^{2+}$  adsorption is different for Ac450 and ChCu400*

# Conclusions

- $\text{Cu}^{2+}$  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 domain (Ac450) and thus not accessible for  $\text{Cu}^{2+}$ .
- $\text{Cu}^{2+}$  did not or only slightly affect  $T_{1\text{HroH}}$ :
  - *Effect of decreasing mobility due to chelating is more pronounced than the paramagnetic effects?*
- Smaller domain size (indicated by smaller  $T_{1\text{H}}$ ) of the highly aromatic chars offer more surface and thus more sites for adsorption than slightly charred material derived from woody residues (showing large  $T_{1\text{H}}$ ).



# 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<sup>2+</sup> adsorption in Ac450 may be best explained by crystalline structures, reducing the accessibility of Cu<sup>2+</sup> to adsorption sites and the low content of aromatic C offering binding do their  $\pi$ -orbitals**

# Thanks

- *To the organizers that made this online conference possible*
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