La Scienza in un Bicchiare
Bassano del Grappa 22.02.2013

UNIVERSITÀ DEGLI STUDI DI PALERMO

VICOLO GAMBA

BIOCHAR

UNA RISORSA PER LA PRODUTTIVITÀ DEI SUOLI E LA MITIGAZIONE DEL CAMBIAMENTO CLIMATICO

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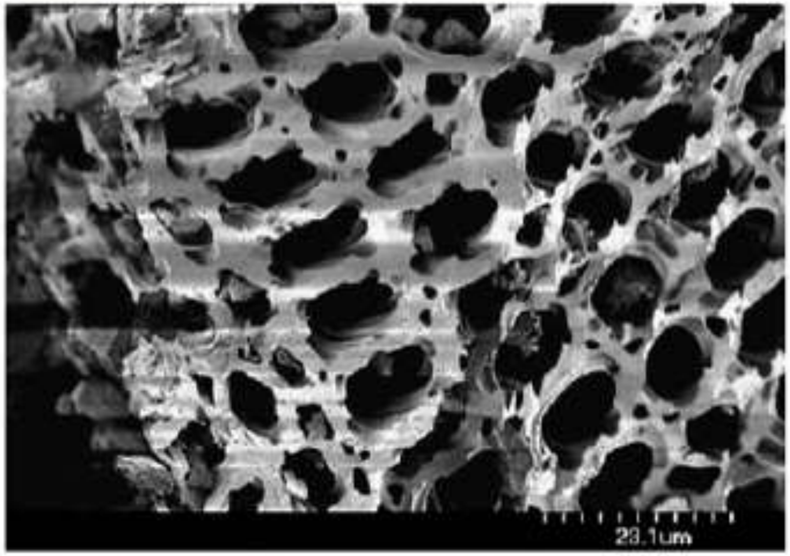
Cos'è il biochar


(c) Can Stock

Biochar is a type of charcoal with specific properties obtained from gasification/pyrolysis of biomass. Instead of burning standing biomass from cleared forest, the resource is charred.

Potentials for worldwide carbon sequestration via biochar production and dispersion over agricultural land.

Item	Value	Comments
Net primary production (NPP)	60.6 GtC/yr	...
Percentage of NPP for biochar	10.00%	
Resultant biochar production	3 GtC/yr	Assume 50% of biomass carbon is converted into biochar
Carbon offset via combustible products (60% of 50% biomass)	1.8 GtC/yr	Assume 60% emission displacement efficiency of the combustion portion (50% of biomass). The remaining 40% (1.3 GtC/yr) is used up for running pyrolysis
Annual increase in atmospheric C due to fossil fuels and cement industry	4.1 GtC/yr	Amount of CO_2 that remains in the atmosphere, out of the total of 7.2 GtC/yr released by humans.



An electron micrograph of charcoal collected from a ponderosa pine forest in Northern Idaho, U.S., which was exposed to fire 79 years prior to collection.

Matovick D. Biochar as a viable carbon sequestration option. Energy 2010 in Press

The two pillars that make biochar revolutionary are:
- the affinity of nutrients and water retention (adsorption)
- the high persistence (stability).

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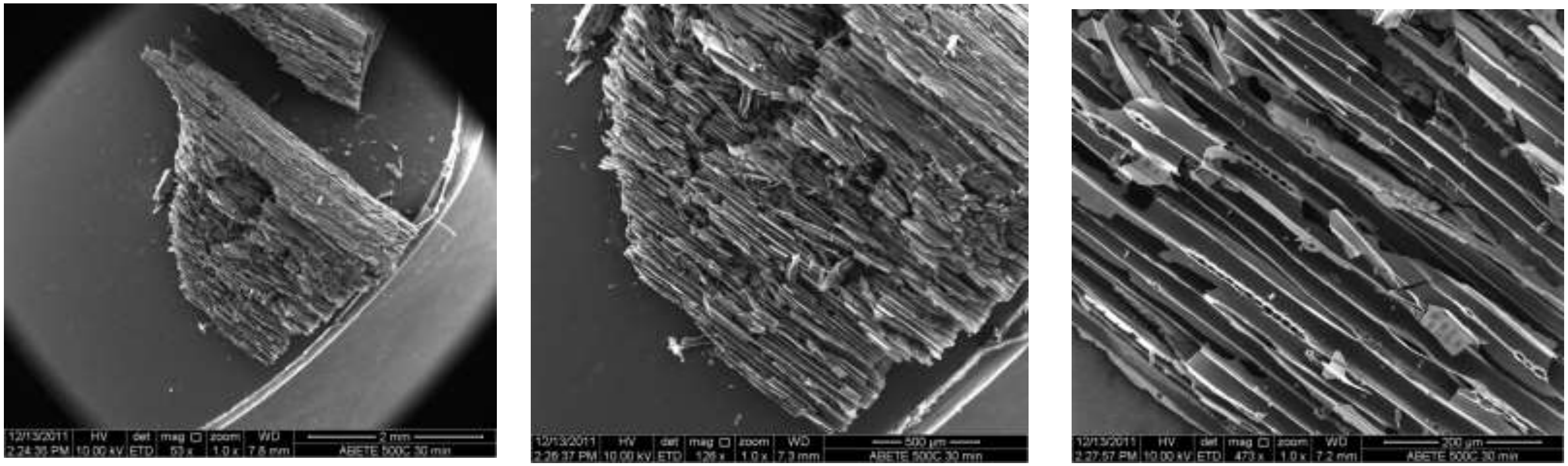
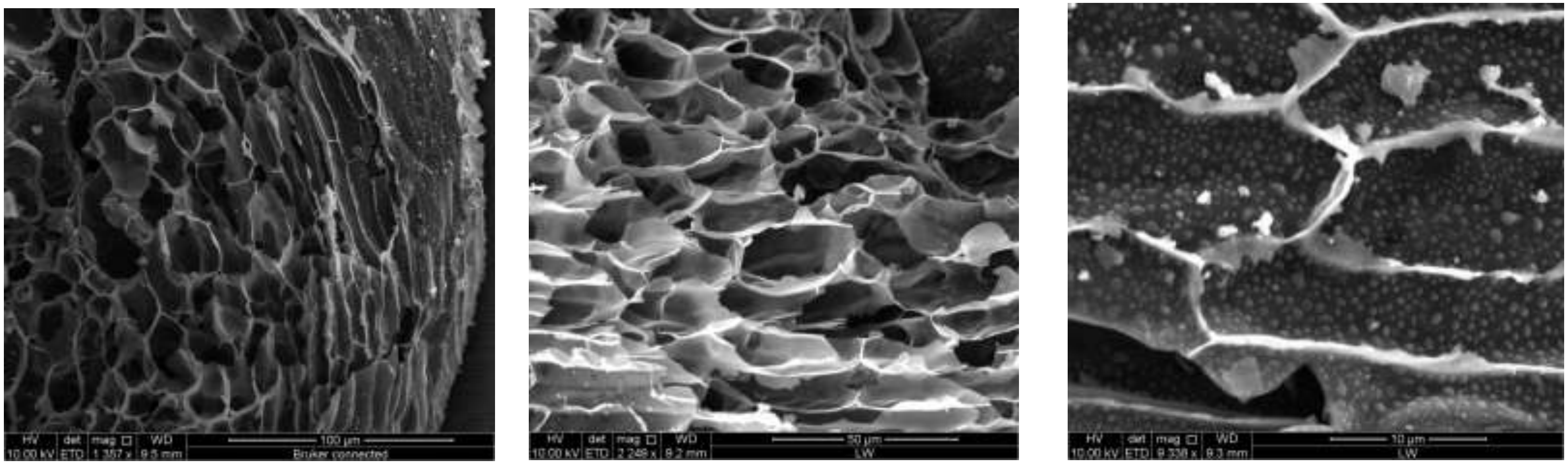
Char from fir wastes (500°C/30 min)



Char from chicken manure (600°C/45 min)



AMAZONIAN DARK EARTH SOILS (TERRA PRETA)

Recognised hypothesis

- Agricultural activity of ancient populations;
- Deposition of plant residues;
- Deposition of ashes and coal produced from use of fires;
- All those factors contribute to the formation of dark soils in Amazonia basin. These soils result very fertile due to the large amounts of C, P, Ca, Mg, Zn and Mn.

Available research and trials mainly show that biochar amendments result in appreciable improvements of soil fertility:

1. soil cation exchange capacity is increased.
2. soil microbial functions are enhanced; the porous structure of biochar forms a safe haven for microbes that make nutrients available to crops.
3. nutrient retention capacity of soils is improved thus preventing leaching and erosion; this allows farmers to reduce organic and inorganic fertilizers.
4. water retention capacity of soils is improved; the porous structure of biochar holds water and prevents the moisture from evaporating.
5. biochar variously affects soil pH depending on inorganic and organic soil constituents.

Biochar persistence

It is undisputed that biochar is much more persistent in soil than any other form of organic matter that is commonly applied to soil. Therefore, all associated benefits with respect to nutrient retention and soil fertility are longer lasting than with alternative management.

The long persistence of biochar in soil makes it a prime candidate for the mitigation of climate change as a potential sink for atmospheric carbon dioxide.

1. biochar soils are stable manageable and measurable carbon sinks; they can be built up over time and remove CO_2 from the atmosphere; soils can accumulate hundreds of tonnes of C while improving soil functions;
2. biochar systems halt slash-and-burn agriculture, and thus slow deforestation;
3. biochar produced in efficient pyrolysis plants offers clean, renewable electricity without polluting emissions.

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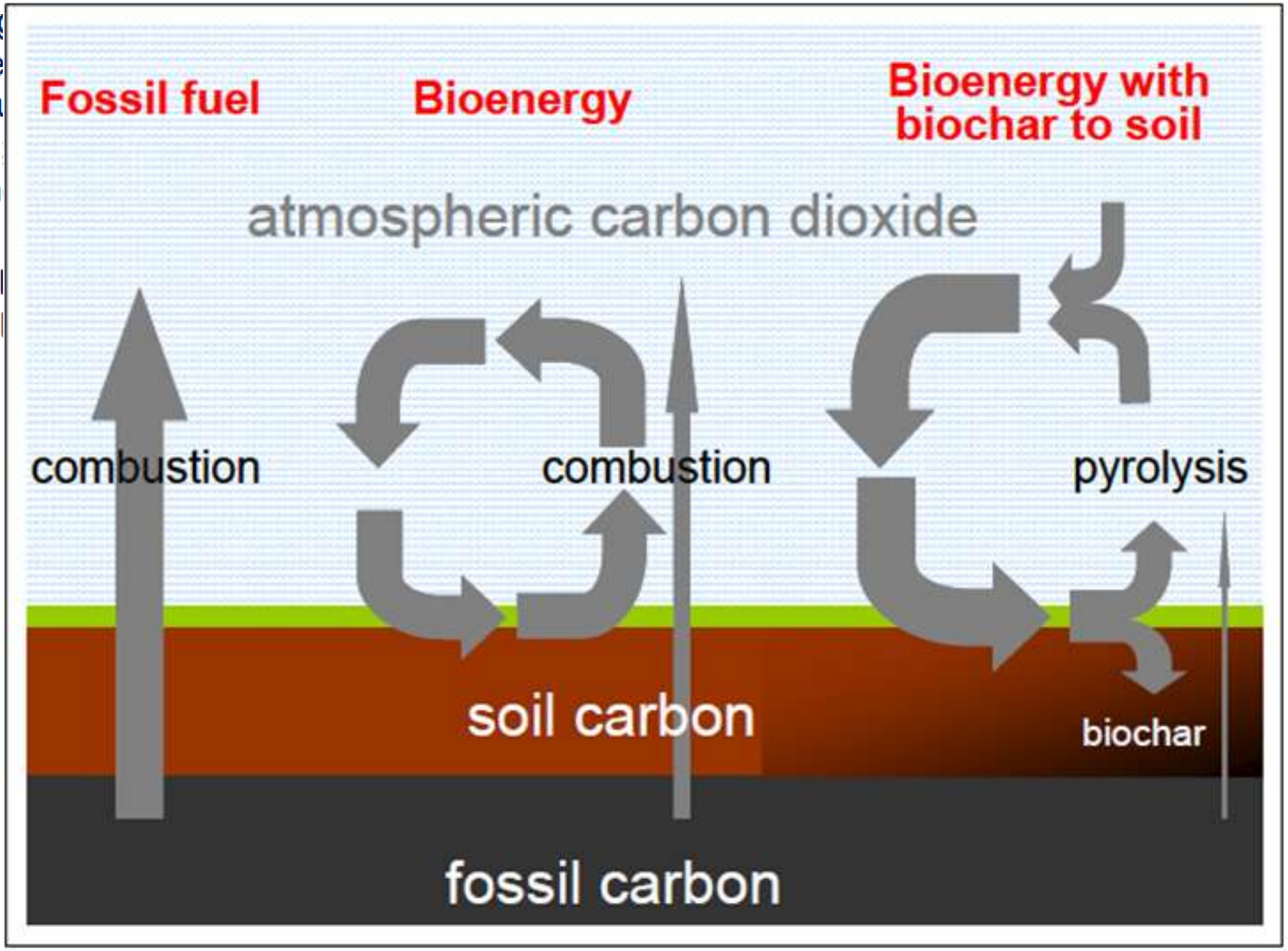
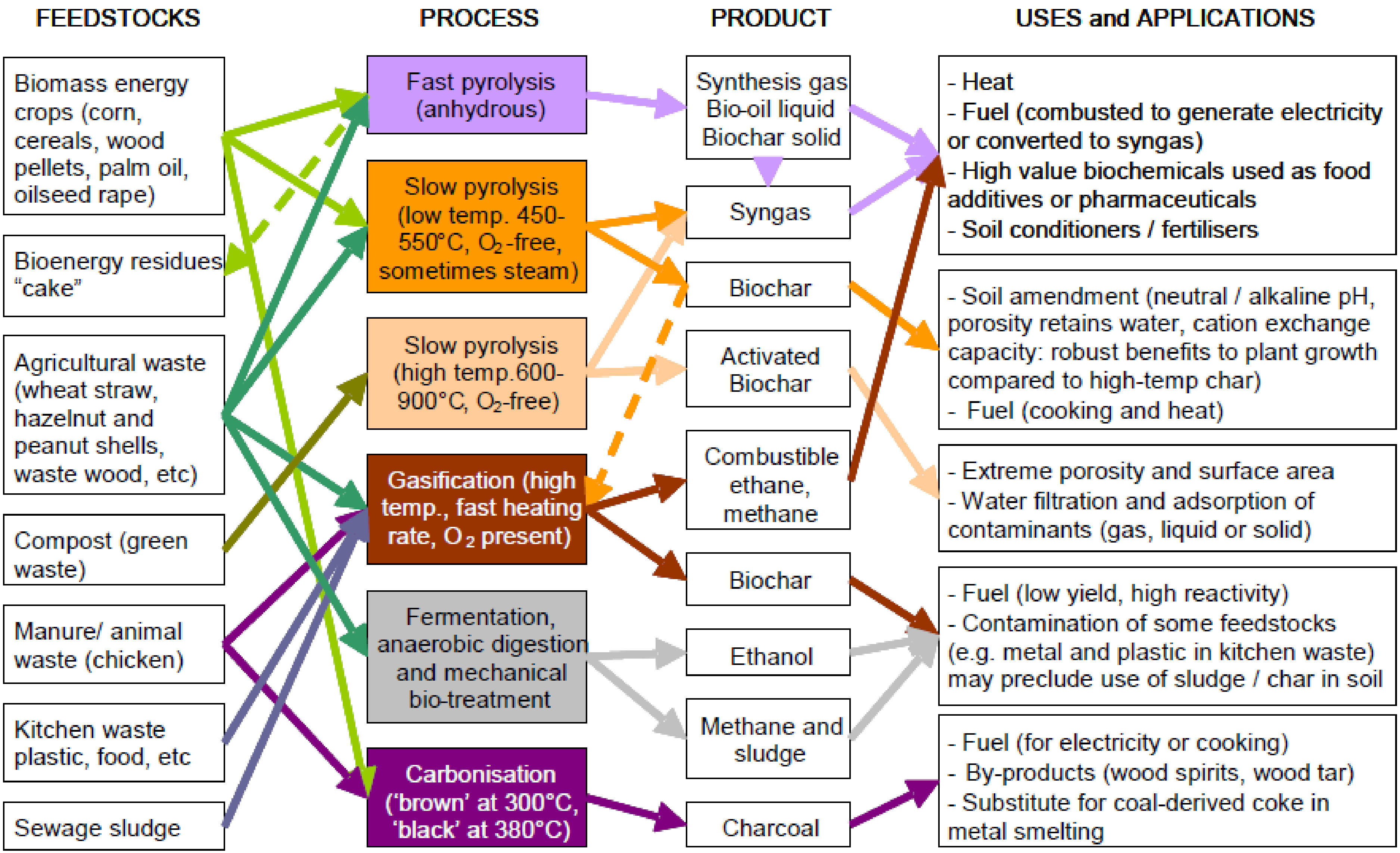


Summary of pyrolysis processes in relation to their common feedstocks, typical products, and the applications and uses of these products



GASIFICATION

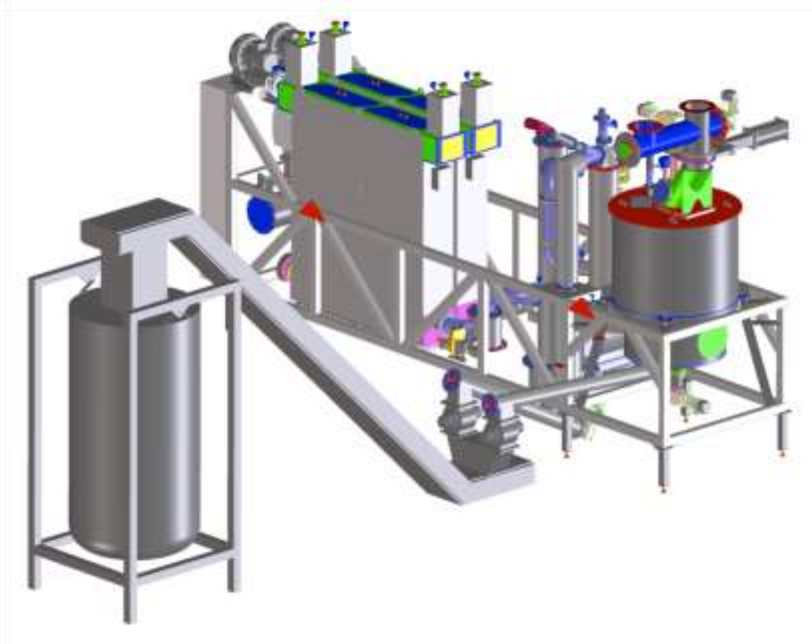
Gasification is a thermo chemical conversion process in wich a biomass (or other different organic matrices) is partially oxidized by heating at **high temperatures** in a gas and charcoal.

The gas (generally called **syngas**) is a mix of **carbon monoxide and dioxide**, **hydrogen**, **methane** and **nitrogen**.
Syngas is used to power a diesel-cycle endothermic engine in order to produce electricity and heat or as fuel for direct use.

Gasification creates a **fine-grained**, **highly porous charcoal** that may significantly vary in its chemical and physical properties depending on the process typology and starting material.

Industrial gasification process: ***biochar is only a by-product***

Scheme of the reactions during gasification



The steps occurring during gasification in a temperature gradient can be distinguished as: drying completion, pyrolysis, combustion (i.e., oxidation), and gasification (i.e., reduction). The first step is simply the removal of biomass moisture. Pyrolysis heats up the carbonaceous particles producing volatile compounds and char. After pyrolysis, combustion of volatile compounds and part of the char occurs according to the following reactions:

$O_2 + C \rightarrow CO_2$	$\Delta H = -393\ kJ\ mol^{-1}$
$2H_2 + O_2 \rightarrow 2H_2O$	$\Delta H = -242\ kJ\ mol^{-1}$

The energy obtained by the aforementioned reactions is used in the last gasification step. It consists in the reduction of the products of combustion (i.e., CO_2, H_2O, and some non-combusted partially cracked pyrolysis products) into carbon monoxide, hydrogen, and methane through the catalytic action of a red-hot charcoal bed. The reactions involved in the gasification step are as follows:

$C + CO_2 \rightarrow 2\ CO$	$\Delta H = +165\ kJ\ mol^{-1}$
$C + H_2O \rightarrow CO + H_2$	$\Delta H = +123\ kJ\ mol^{-1}$
$CO + H_2O \rightarrow CO_2 + H_2$	$\Delta H = -42\ kJ\ mol^{-1}$
$CO_2 + H_2 \rightarrow CO + H_2O$	$\Delta H = +42\ kJ\ mol^{-1}$
$C + 2\ H_2 \rightarrow CH_4$	$\Delta H = -75\ kJ\ mol^{-1}$

Industrial gasifier

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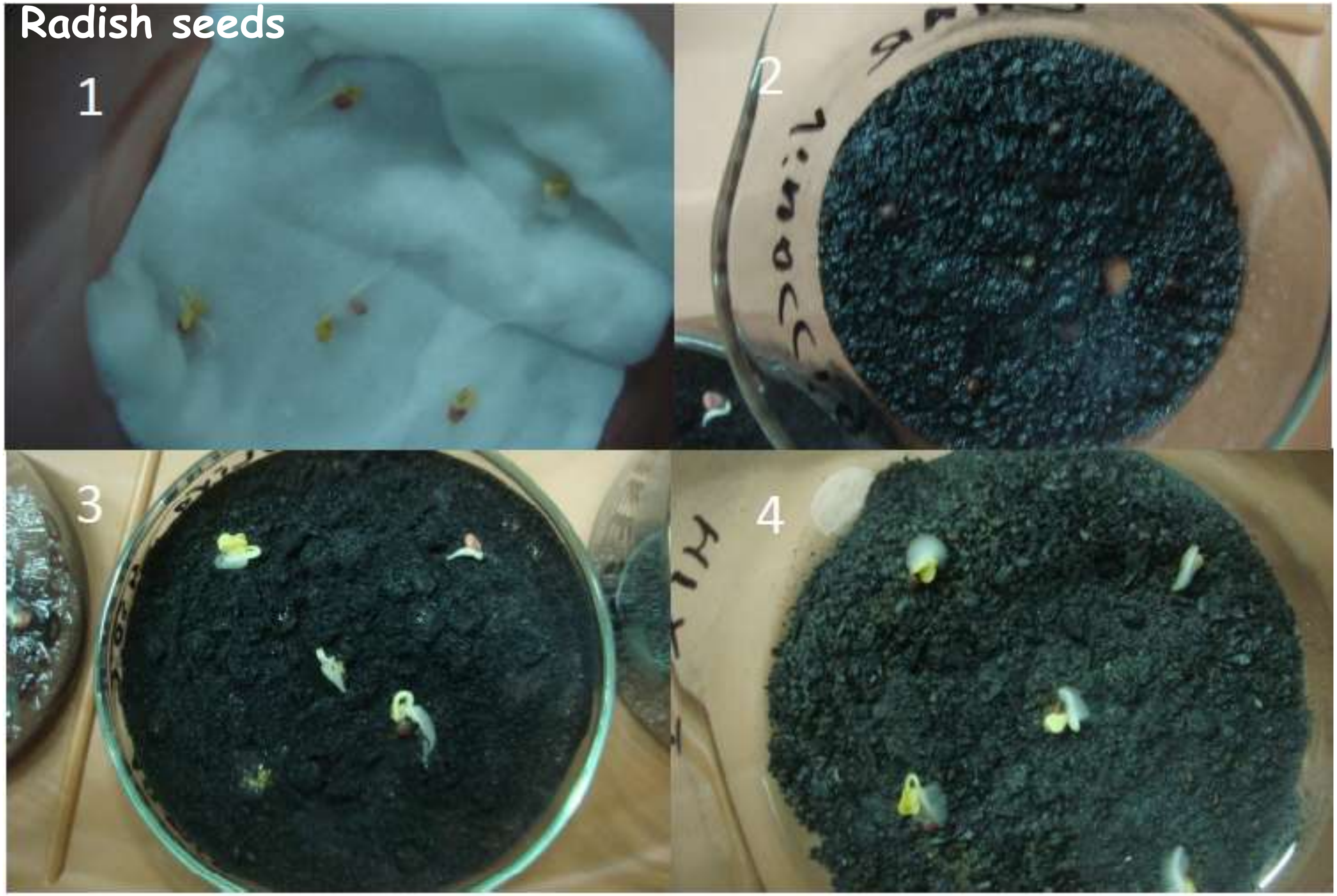
Effects of biochars on plant growth



1) cotton; 2) marc; 3) poplar; 4) conifer

Radish plants after 5 days

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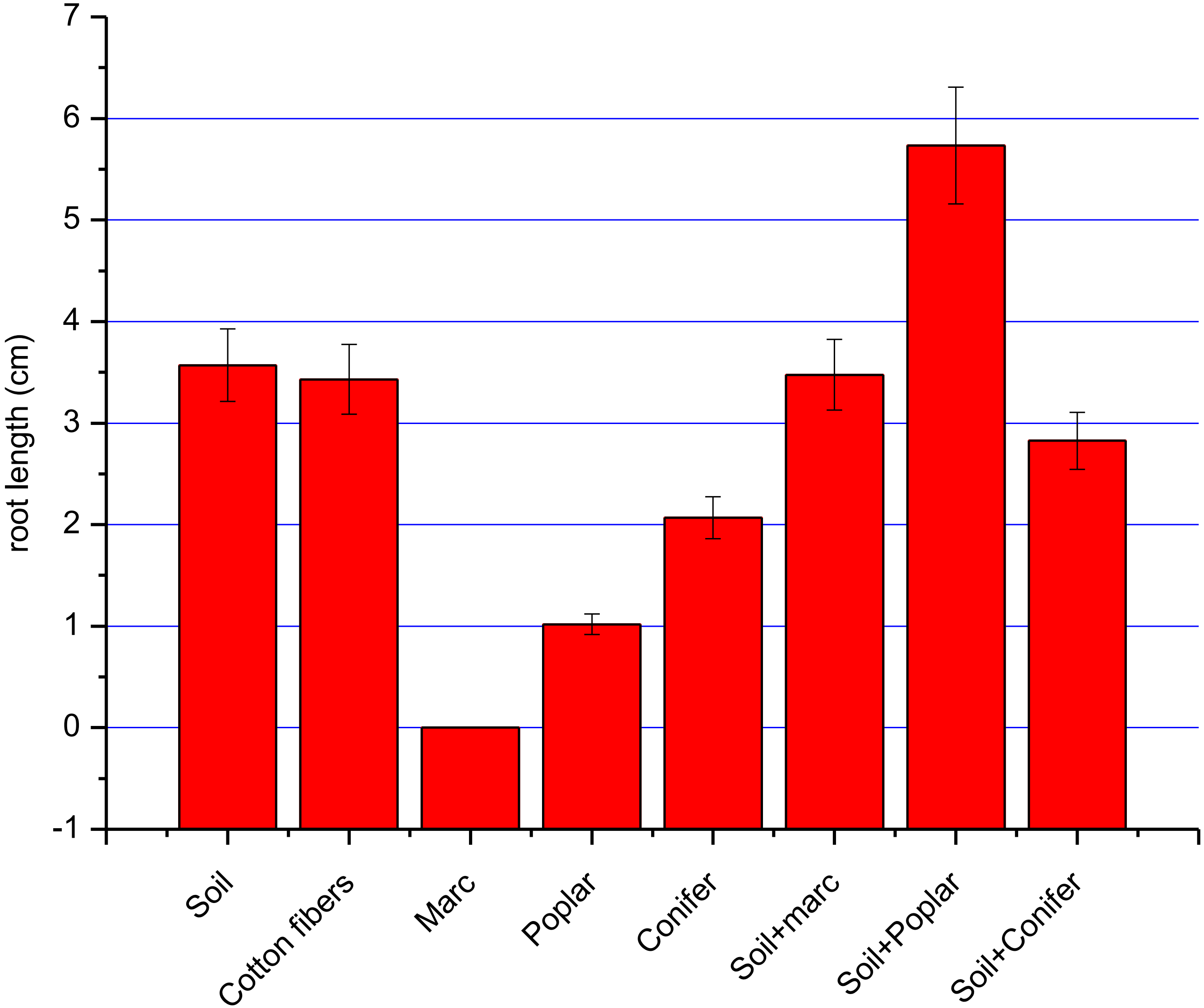
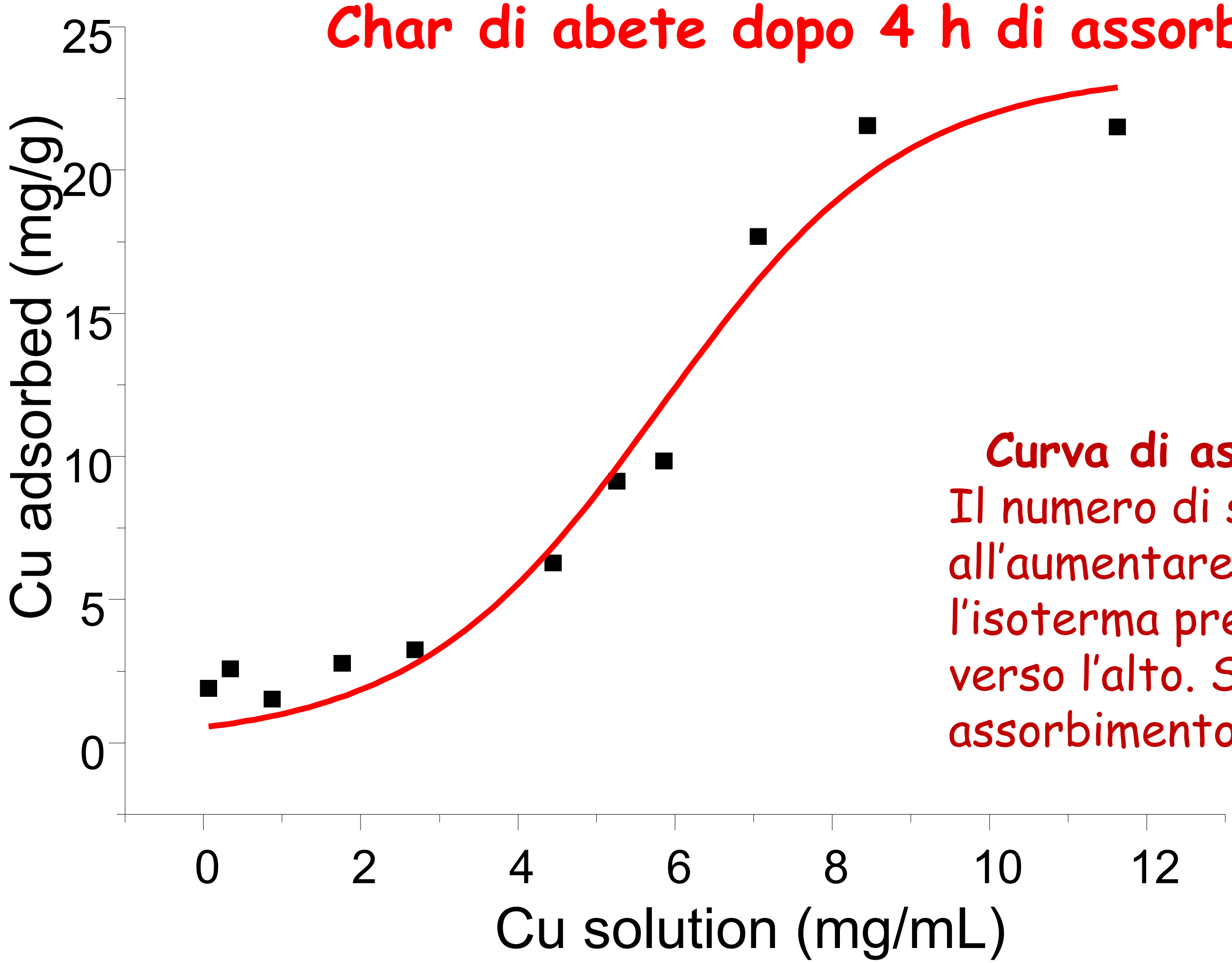


Environmental applications

Curve di assorbimento
Char di abete dopo 4 h di assorbimento



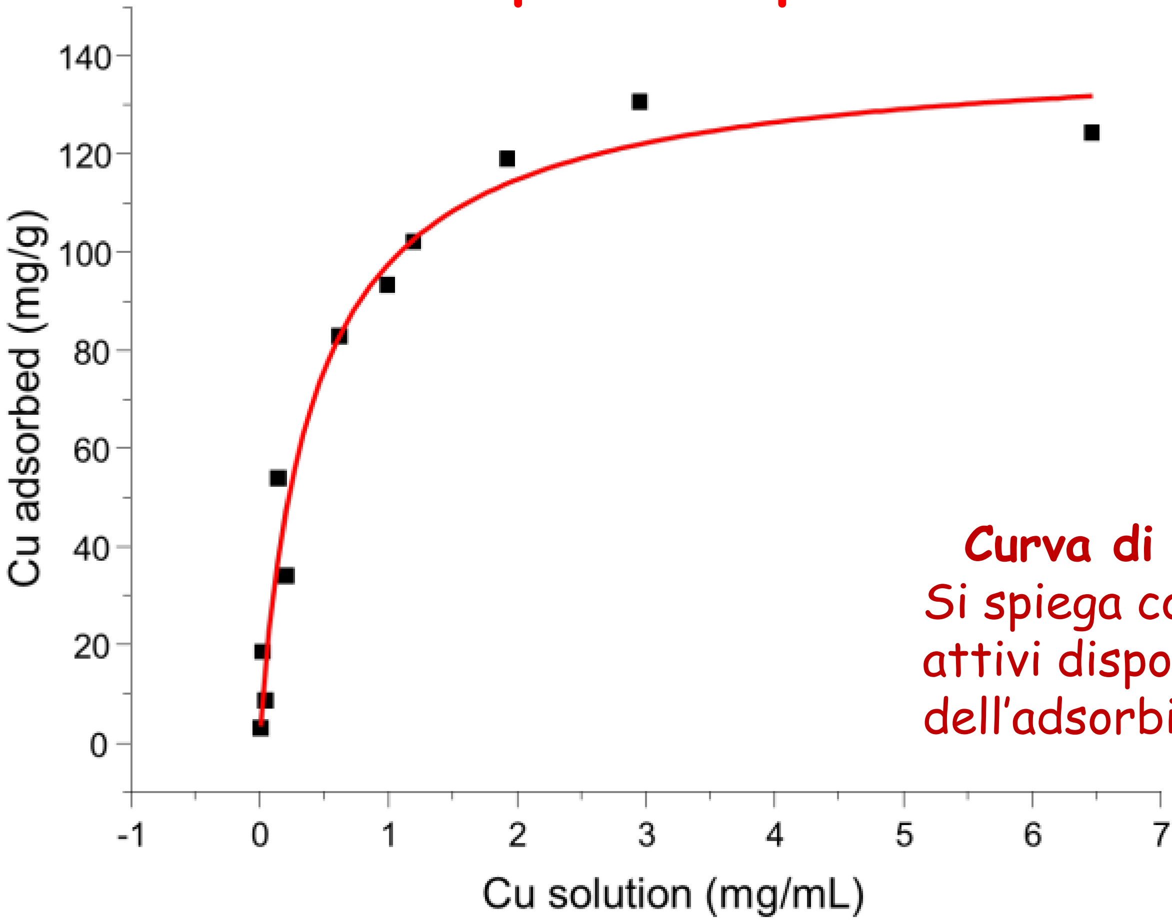
Curva di assorbimento di tipo S

Il numero di siti attivi aumenta all'aumentare dell'adsorbimento e l'isoterma presenta una curvatura verso l'alto. Si tratta di assorbimento cooperativo.

Environmental applications

Curve di assorbimento

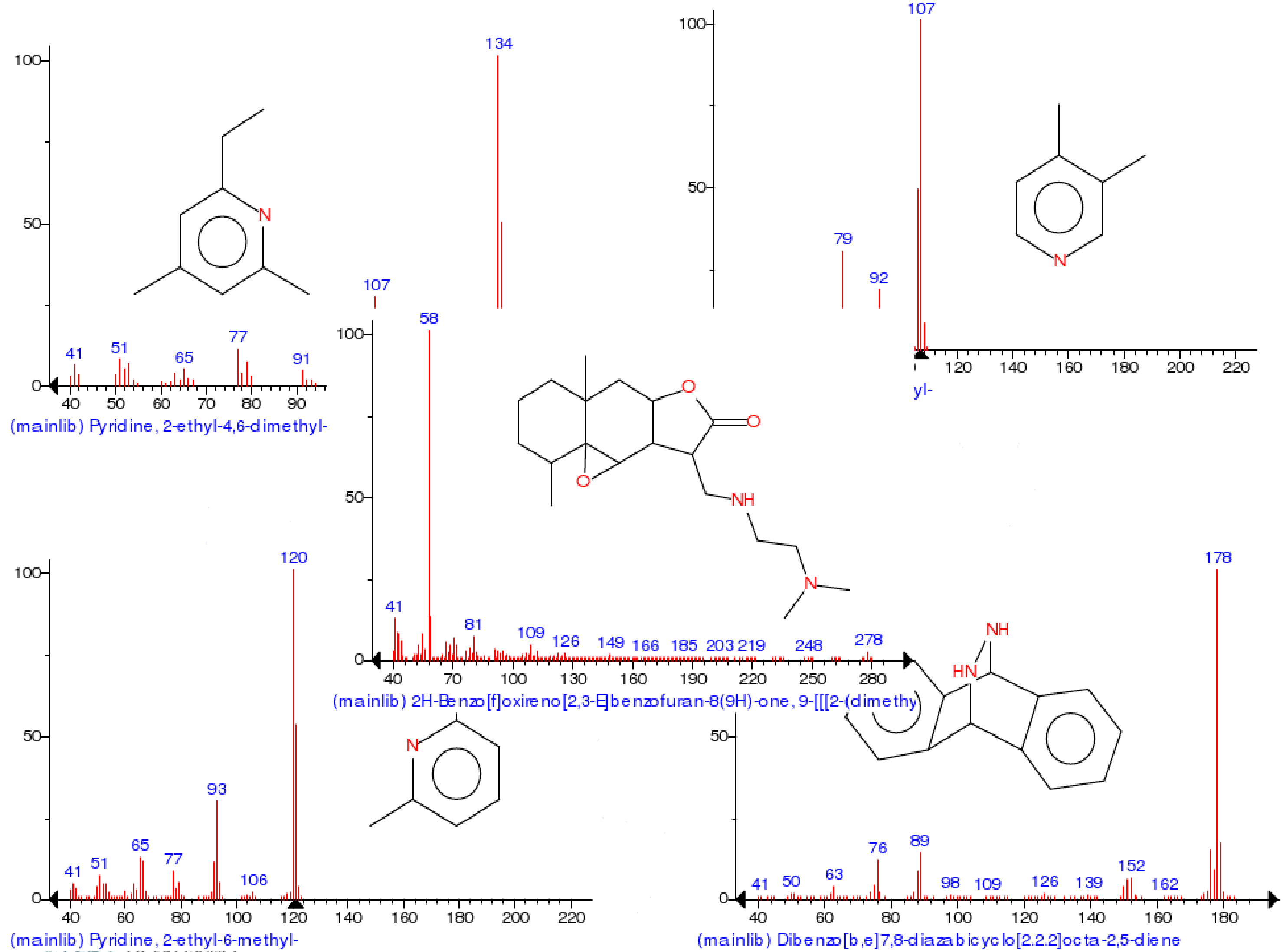
Char di pollina dopo 4 h di assorbimento



Curva di assorbimento di tipo L

Si spiega con la diminuzione dei siti attivi disponibili all'aumentare dell'adsorbimento

Char di pollina: caratterizzazione via GC-MS



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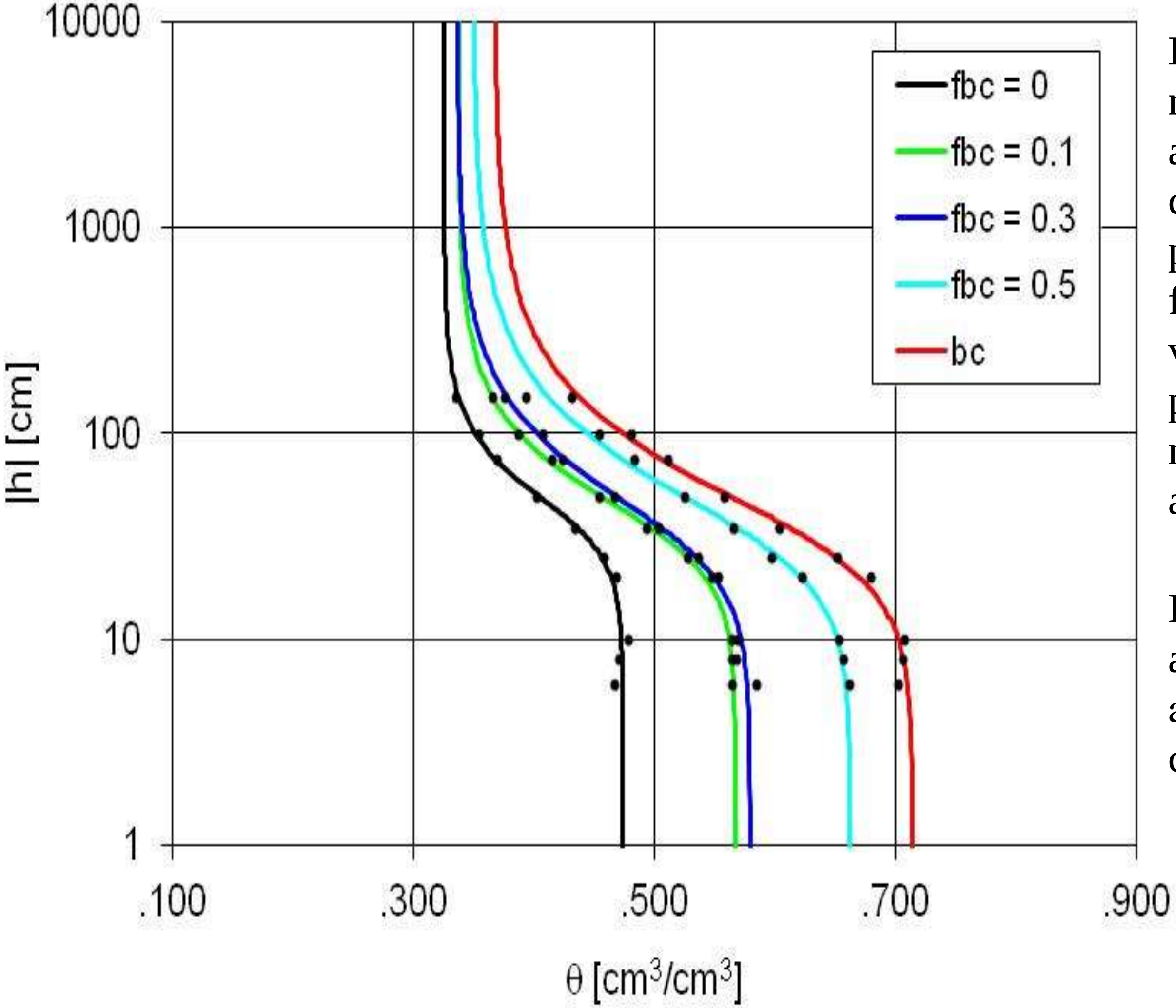
Applicazione di carbone di pioppo al suolo

Curva di ritenzione dell'acqua e indice strutturale del suolo

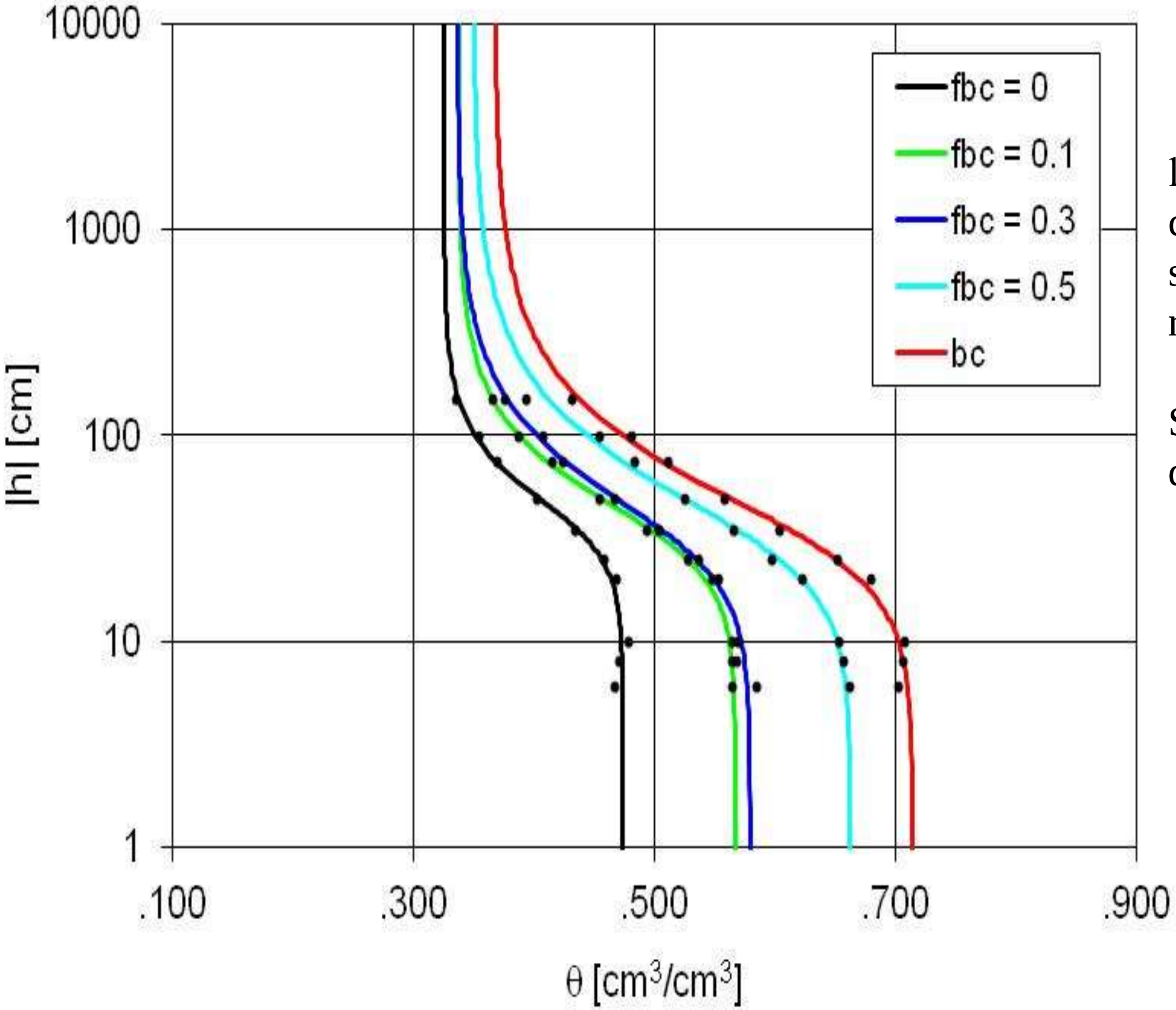


La figura mostra le curve di ritenzione idrica di un suolo ammendato con quantità crescenti di carbone vegetale (biochar) ottenuto per gassificazione di biomassa forestale (pioppeto). θ è il contenuto volumetrico di acqua e h è il potenziale di matrice (la forza che è necessaria per estrarre l'acqua legata alla matrice porosa).

La figura mostra come la quantità di acqua legata al suolo aumenti all'aumentare della quantità di carbone aggiunto.

Applicazione di carbone di pioppo al suolo

Curva di ritenzione dell'acqua e indice strutturale del suolo



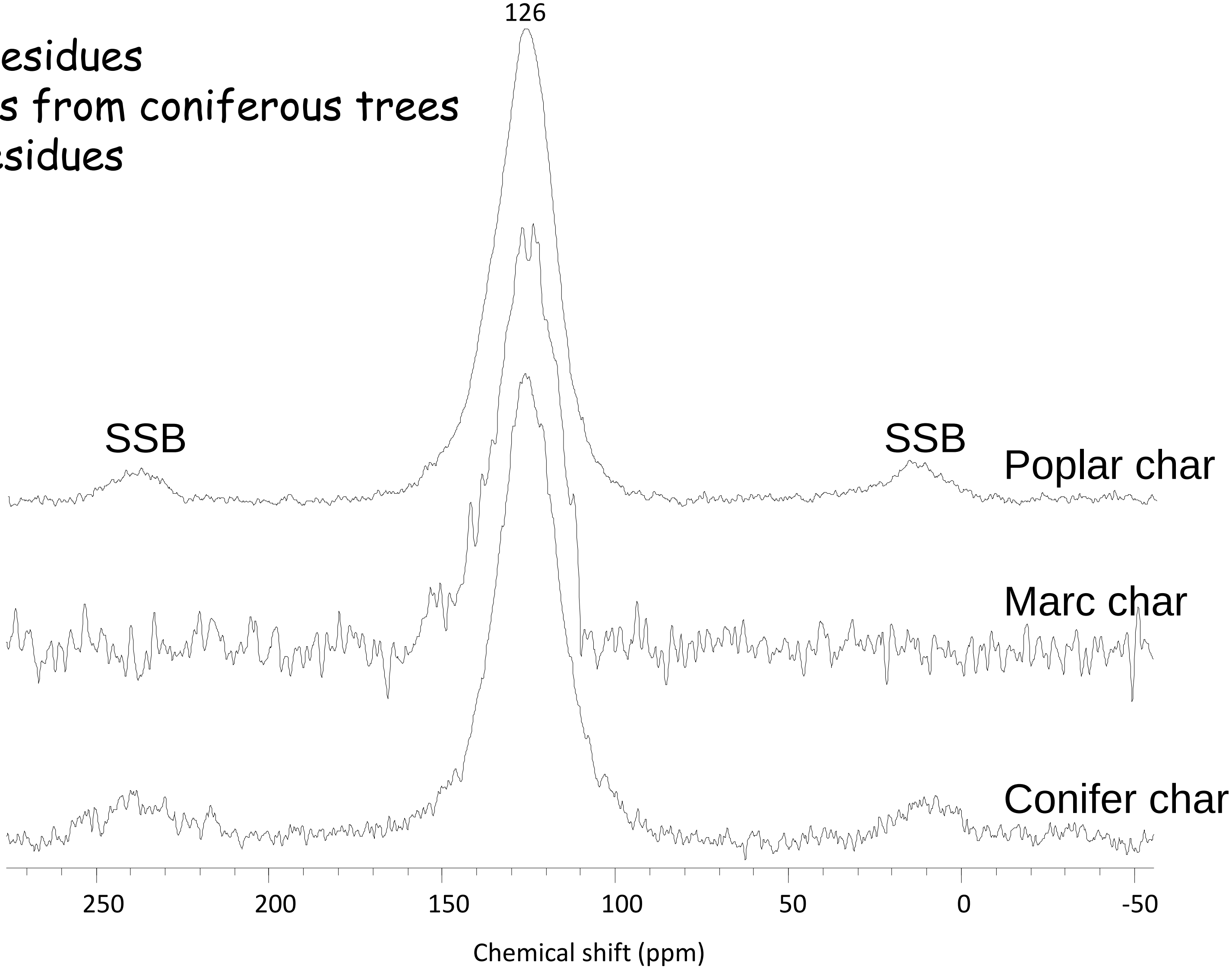
Conseguenze:

l'aumento di ritenzione idrica comporta una migliore struttura del suolo e, di conseguenza, una migliore resistenza all'erosione.

Si inibiscono i processi di desertificazione

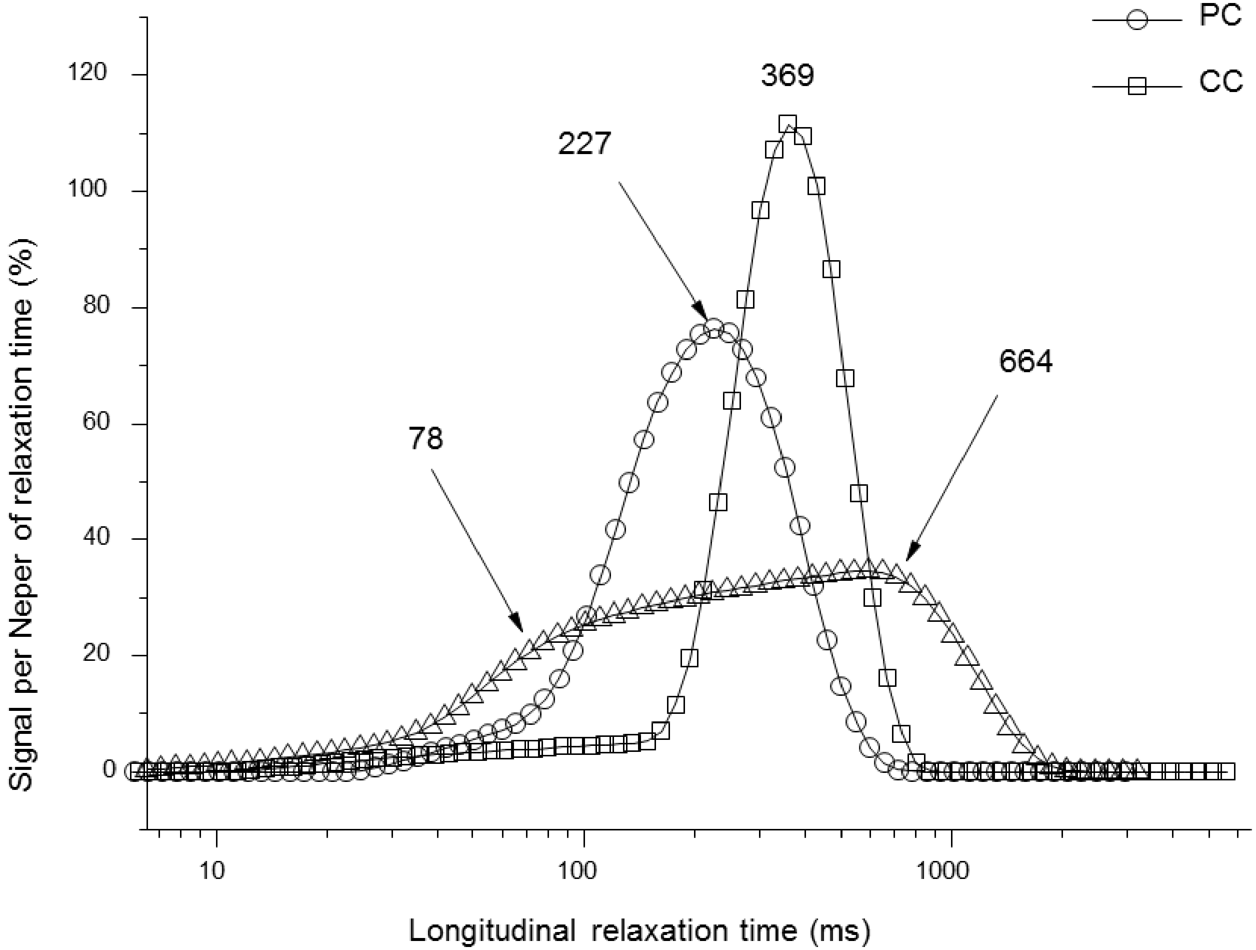
Biochar produced from gasification of

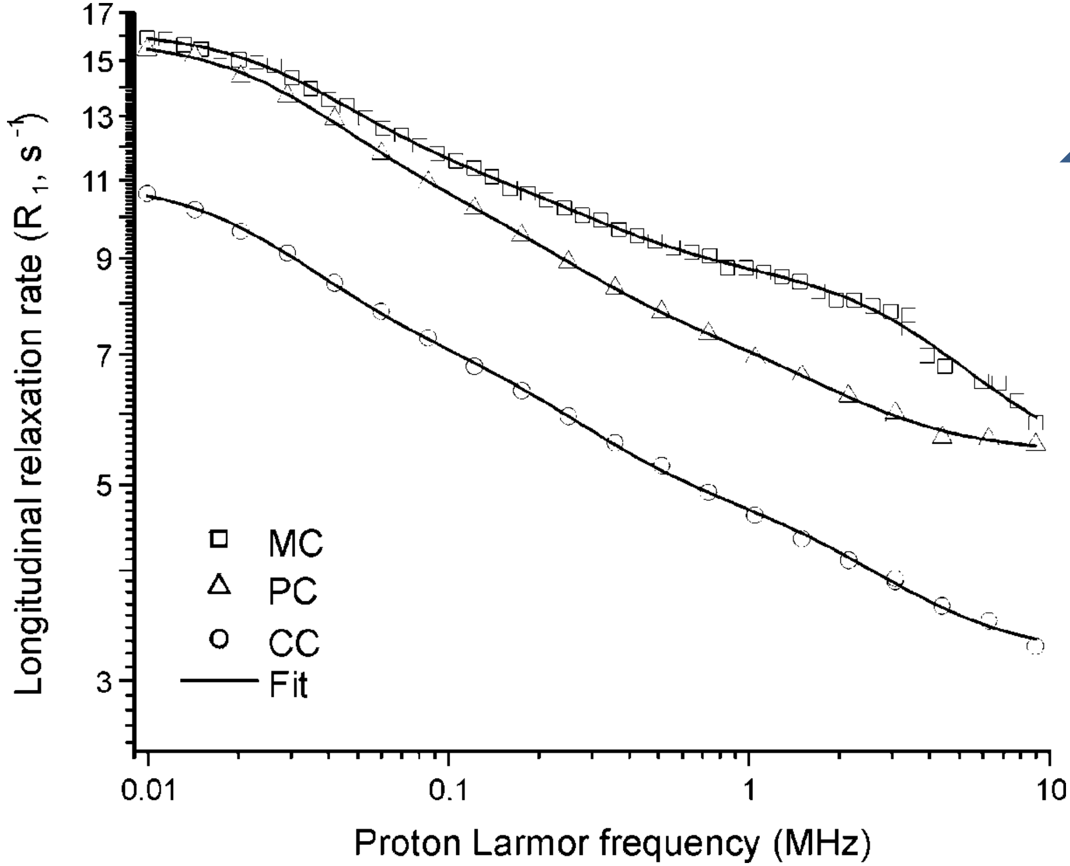
1. Poplar residues
2. Residues from coniferous trees
3. Marc residues



poplar char is richer in small sized pores, whereas large pore sizes appear to be characteristic for the conifer char.

Samples	**Surface area ($m^2 \cdot g^{-1}$)**
Marc char	42±4
Poplar char	98±6
Conifer char	66±5





Relaxation rate increase

Increase in relaxation rate is related to the different pore sizes. The smaller the pore size, the stronger are the dipolar interactions thereby leading to faster R_1 values

Biochar – hydrophobic
Water – hydrophilic
Do they chemically interact?

What do we expect?

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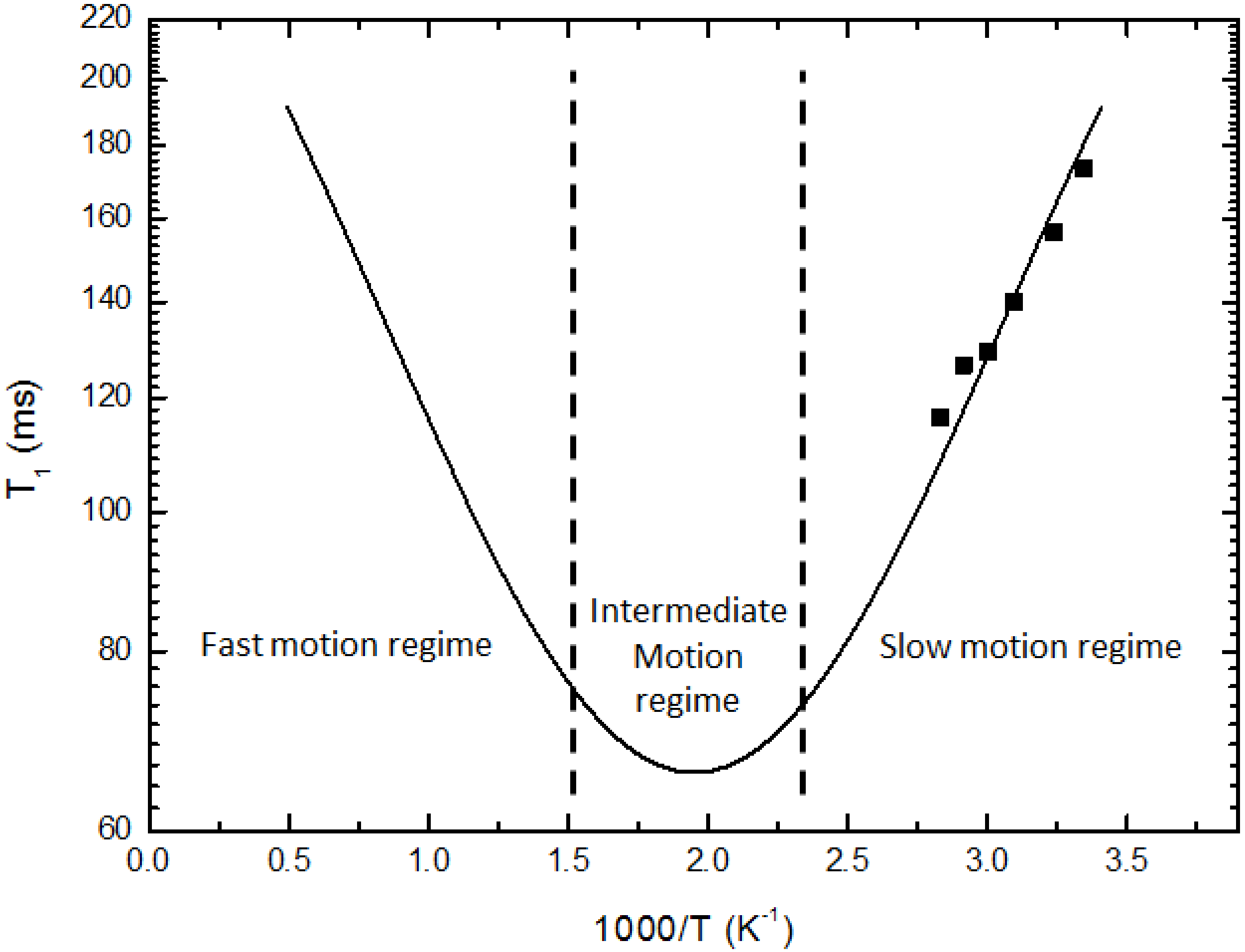
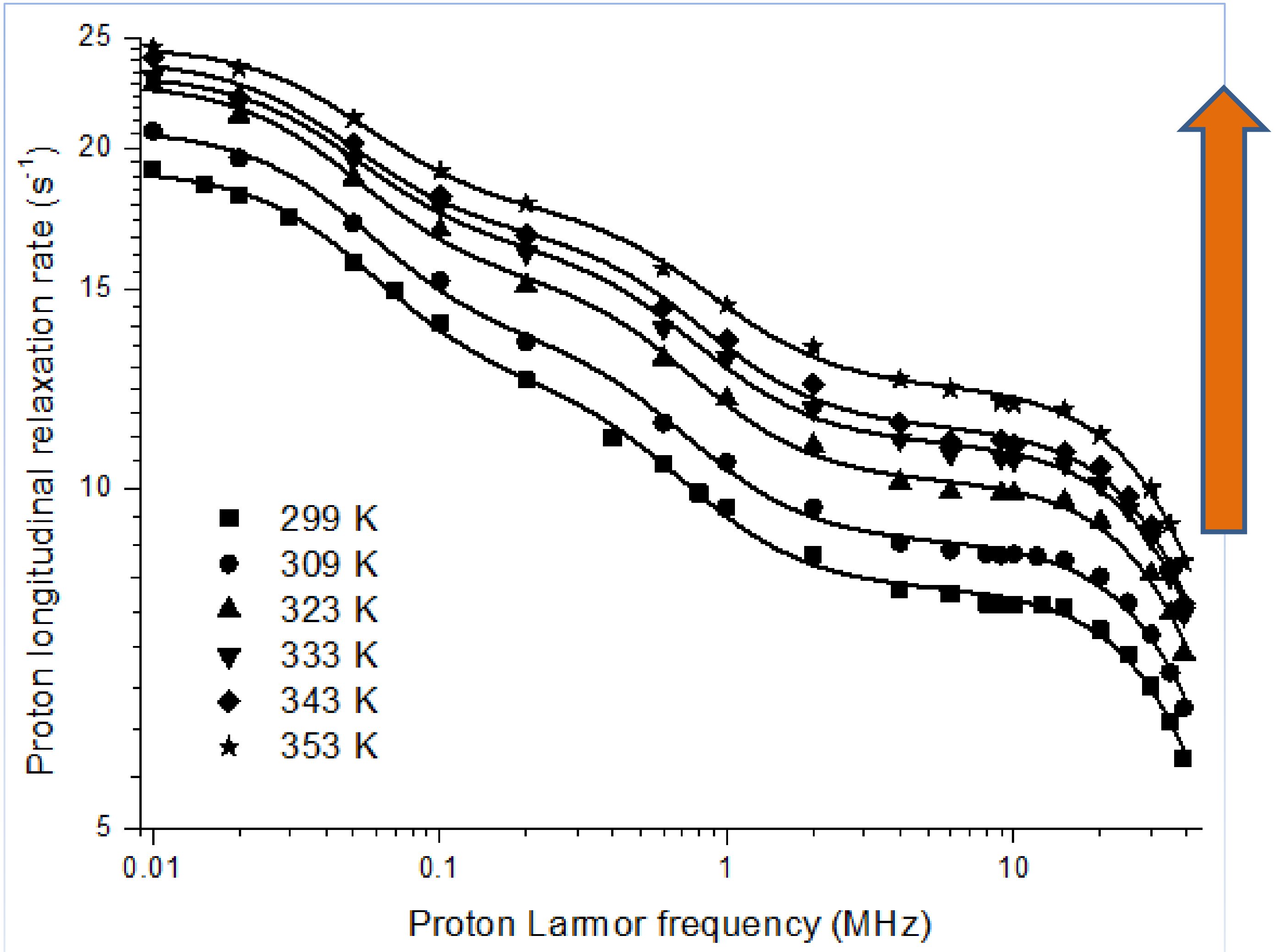
Surface properties of poplar biochar

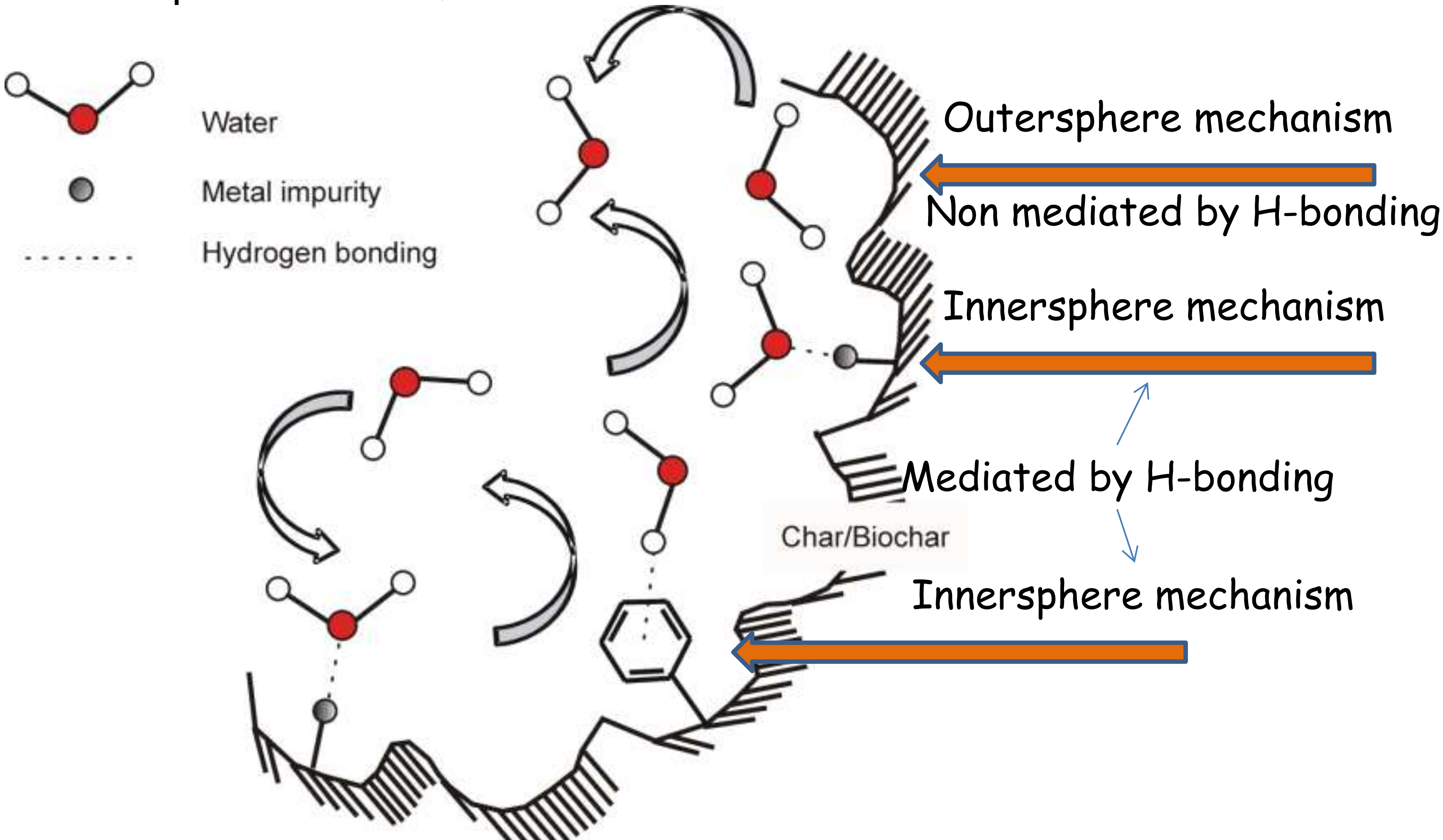
Temperature variation of T_1 values at 39 MHz





R_1 increases as temperature is enhanced

Relaxation rate (R_1) is given by the combination of the outersphere and the innersphere contributions



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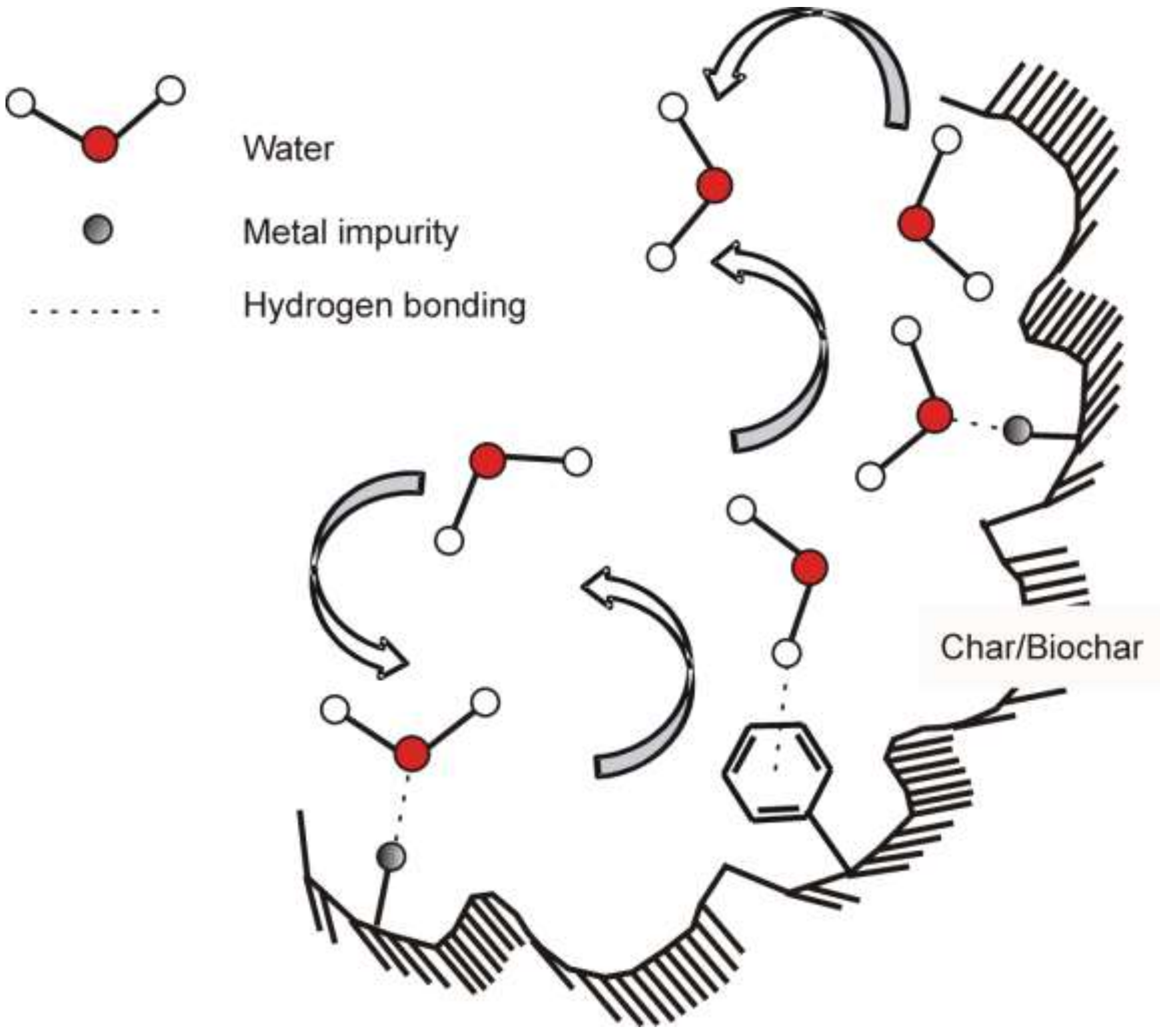


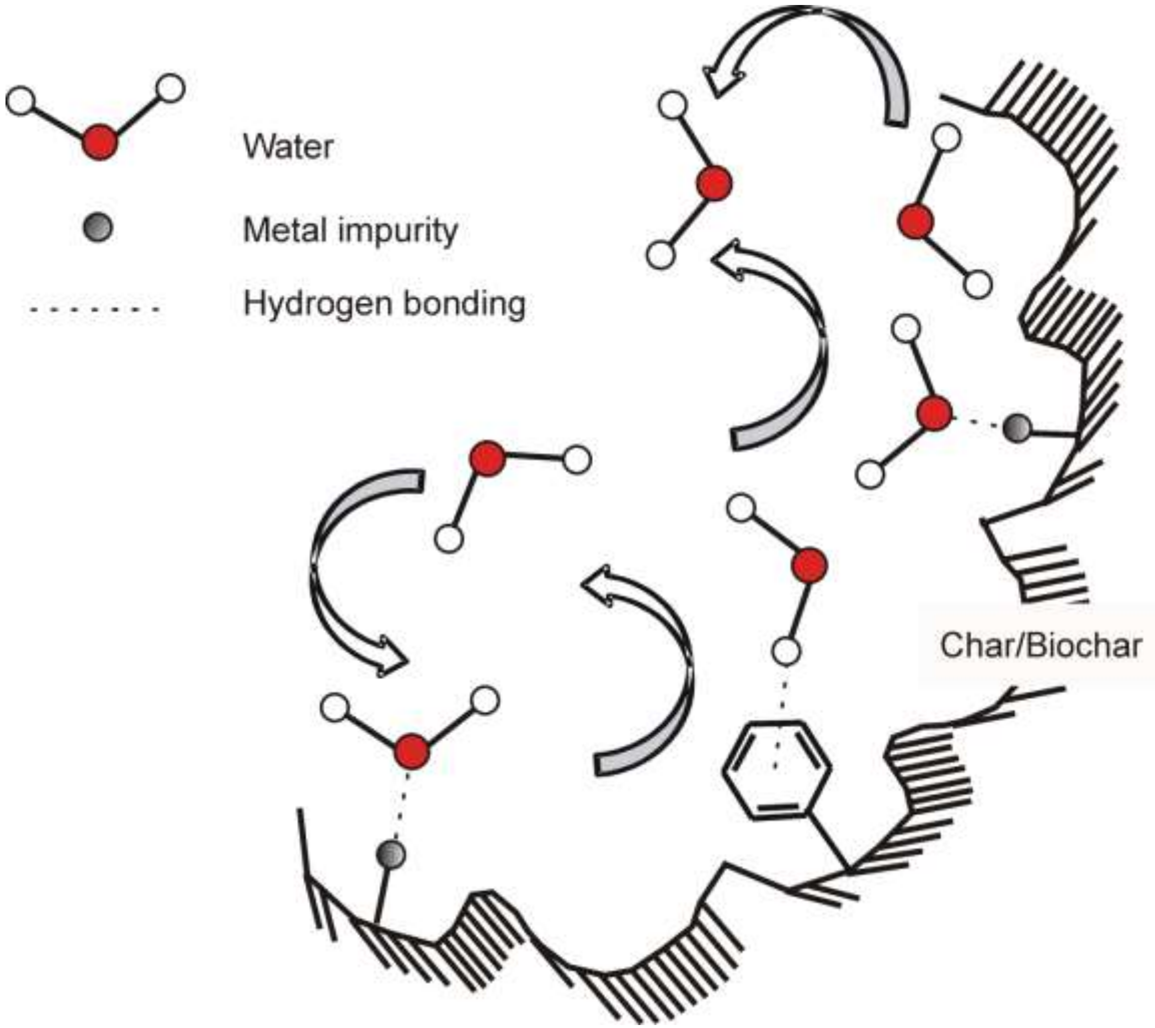
Outersphere mechanism

$$\tau_D \propto \frac{\eta d^2}{kT}$$

Correlation time measures the time needed for the molecular reorientation. The higher the temperature, the shorter is the time needed for a molecule to reorientate.

The outersphere mechanism does not explain the NMRD profiles.

Relaxation rate (R_1) is given by the combination of the outersphere and the innersphere contributions



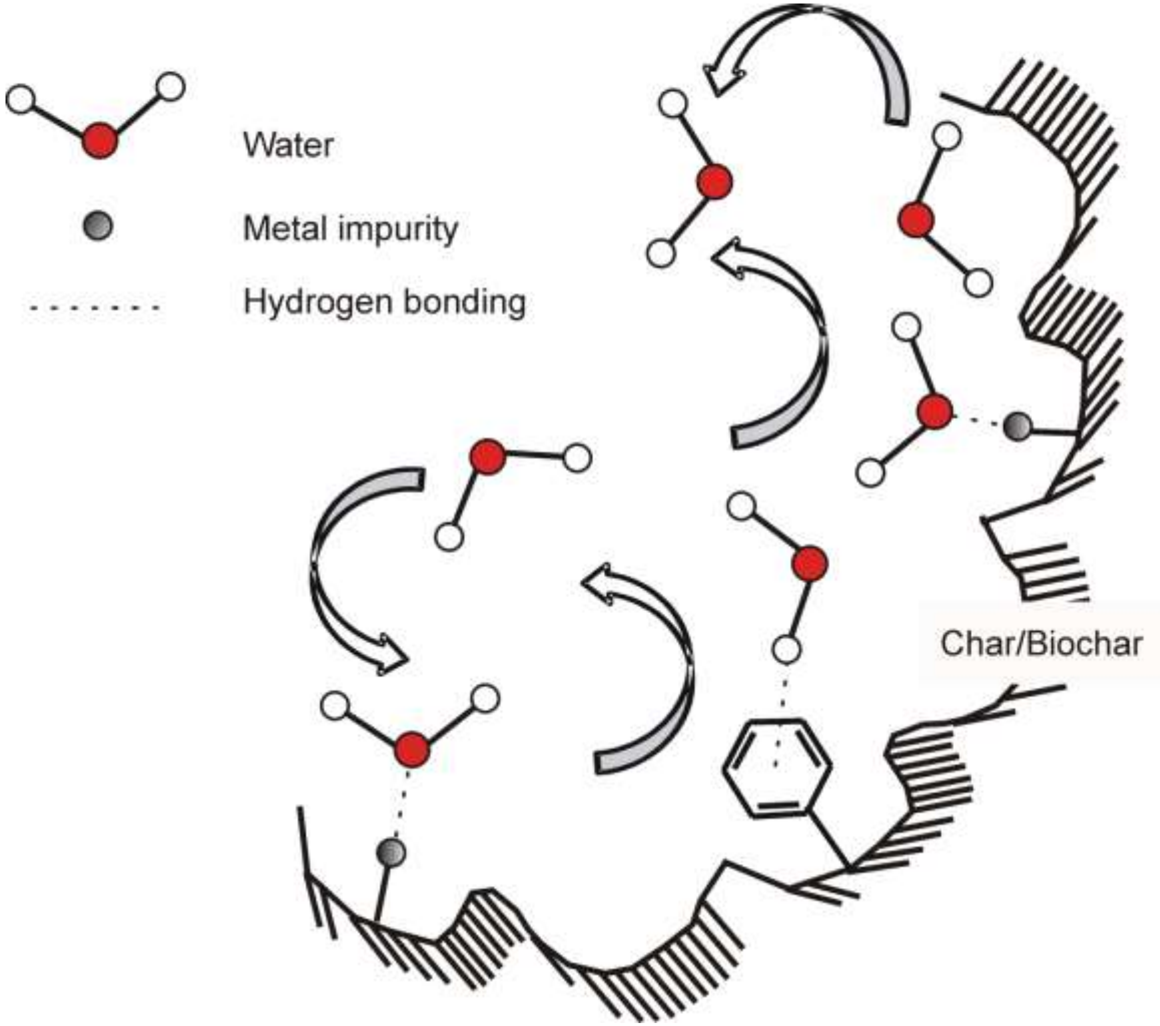
Innersphere mechanism

$$R_{1inn} = \frac{f_M}{T_{1M} + \tau_M}$$

If $T_{1M} >> t_M$ fast motion regime occurs; temperature increase is associated to R_1 decrease

If $T_{1M} << t_M$ slow motion regime occurs; temperature increase is associated to R_1 increase

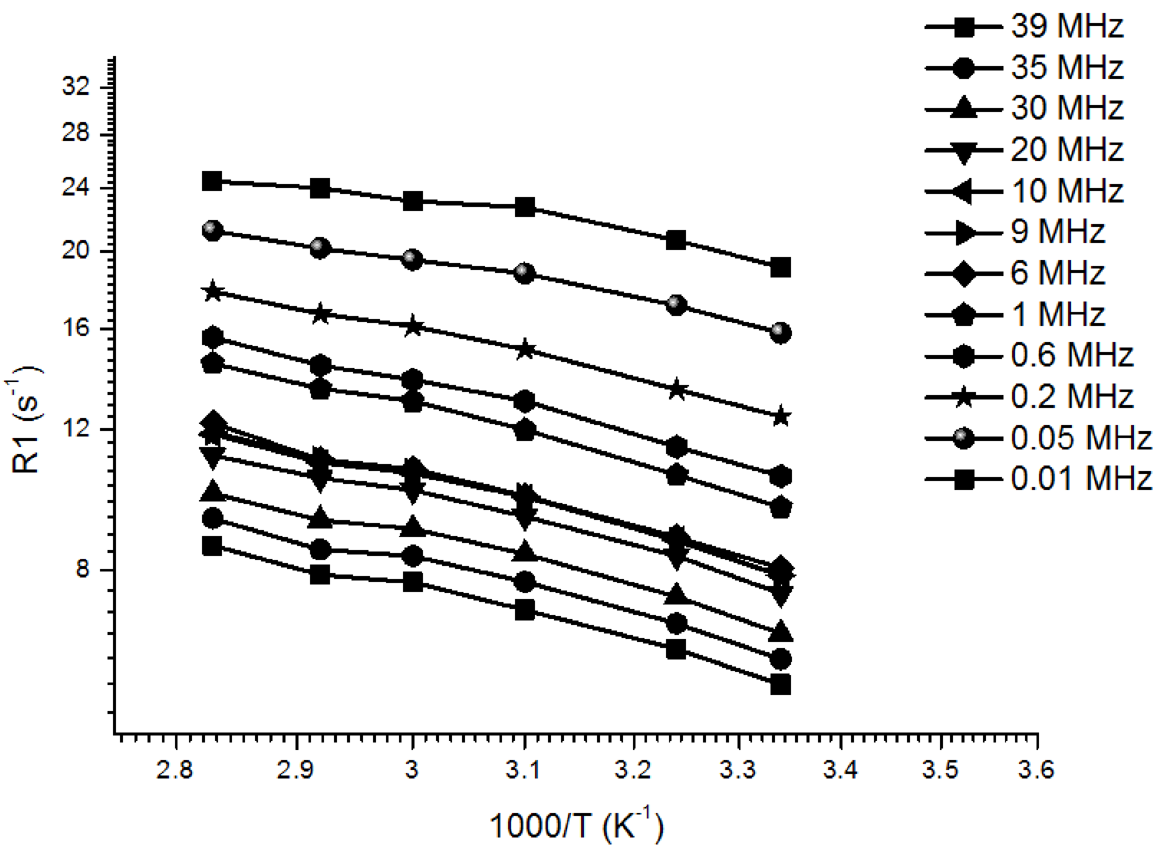
Relaxation rate (R_1) is given by the combination of the outersphere and the innersphere contributions



The innersphere mechanism is predominant.

Weak non conventional hydrogen bonds occurr between metal impurities, aromatic biochar centers and water molecules

Attempt to measure H-bond strength



Arrhenius graphs reporting the temperature variations of the relaxation rate values.

Activation energy of **6 kJ/mol**

This activation energy value is consistent with H-bonds between water molecules and p-systems in aromatic molecules

Thank you