A simple method for determining biochar condensation

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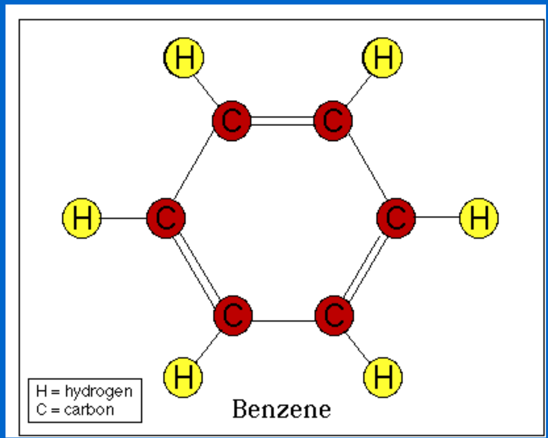
What does “biochar condensation” mean?

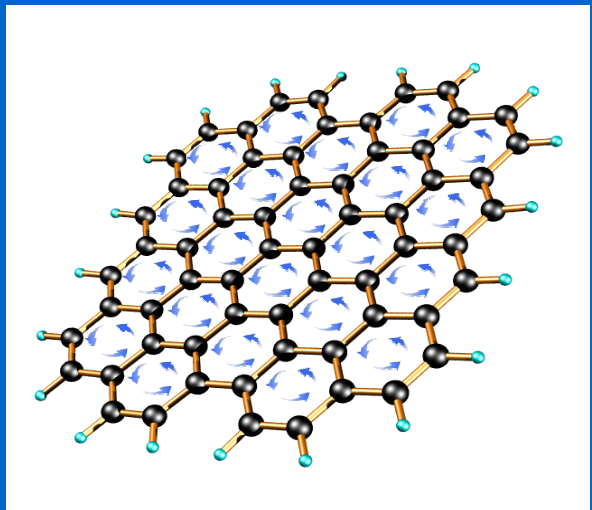
The chemical structure of biochar is very distinctive

Consists predominantly of fused aromatic rings



Basic unit is benzene – the simplest aromatic molecule

- Planar
- Chemically stable
- Clear colourless liquid



In biochar, “many” of these benzene rings are fused together

- Planar
- Stable (to chemical and biological breakdown)
- Black solid

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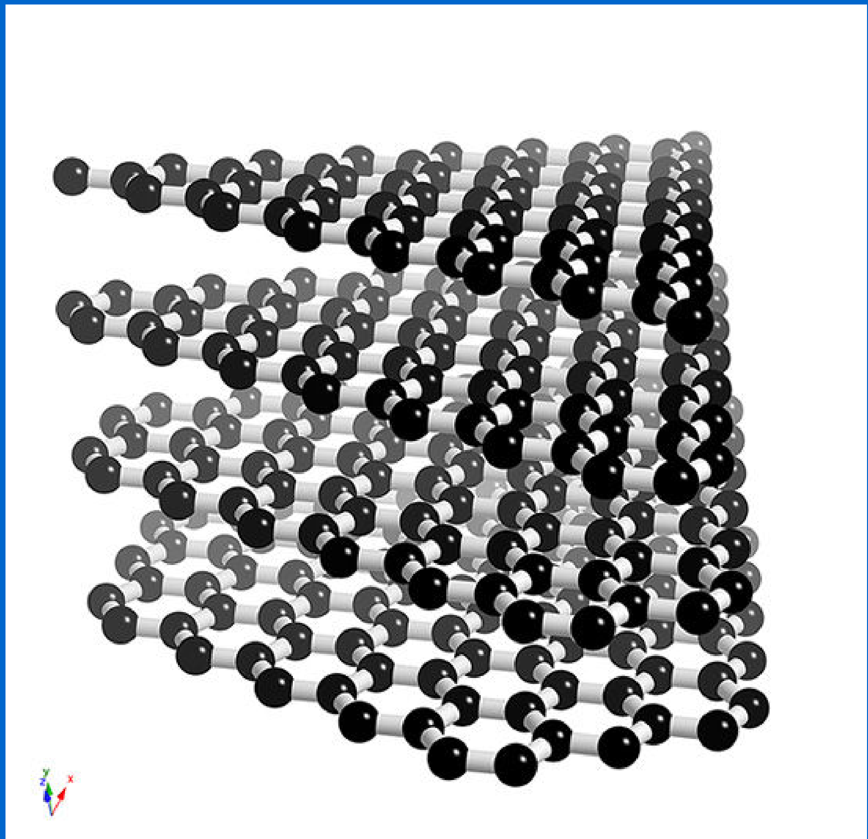


Graphite is the ultimate in fused aromatic structures

- Essentially infinite planar 2D sheets
- Stacked in 3rd dimension
  Chemically very stable
- Black solid (metallic sheen)

What does “biochar condensation” mean?

In biochar fused aromatic ring systems are of finite size and contain impurities (other atoms e.g. O, N, functional groups, radicals, holes)

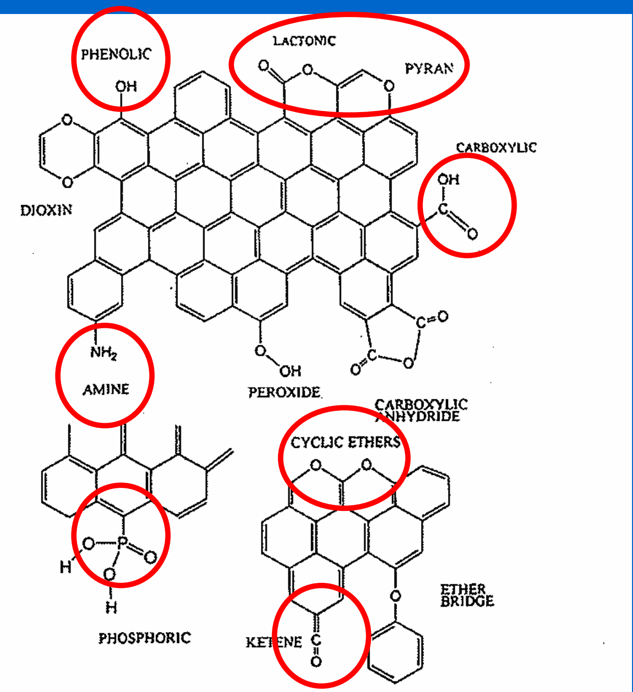
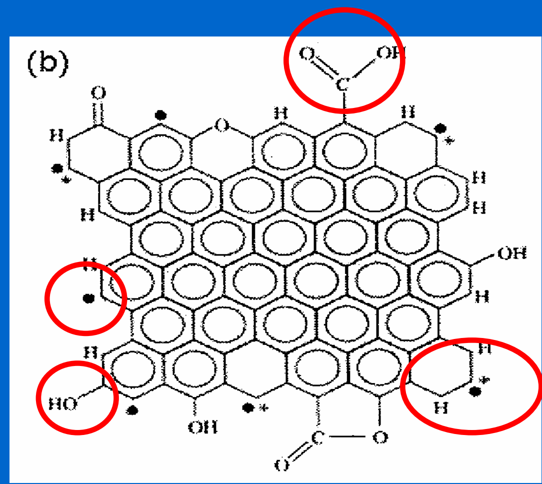
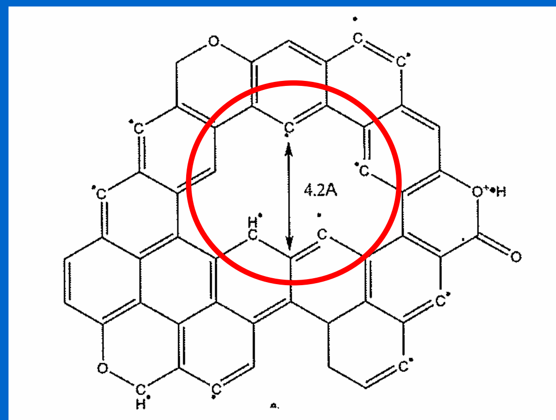


Figure 3.10 *Heteroatoms and functional groups commonly found in activated carbons*

Source: reprinted from Brennan et al (2001) with permission from Elsevier





How large and pure (condensed) are the fused aromatic structures in biochar?

We don't really know!

Varies with production conditions

- Heat treatment temperature

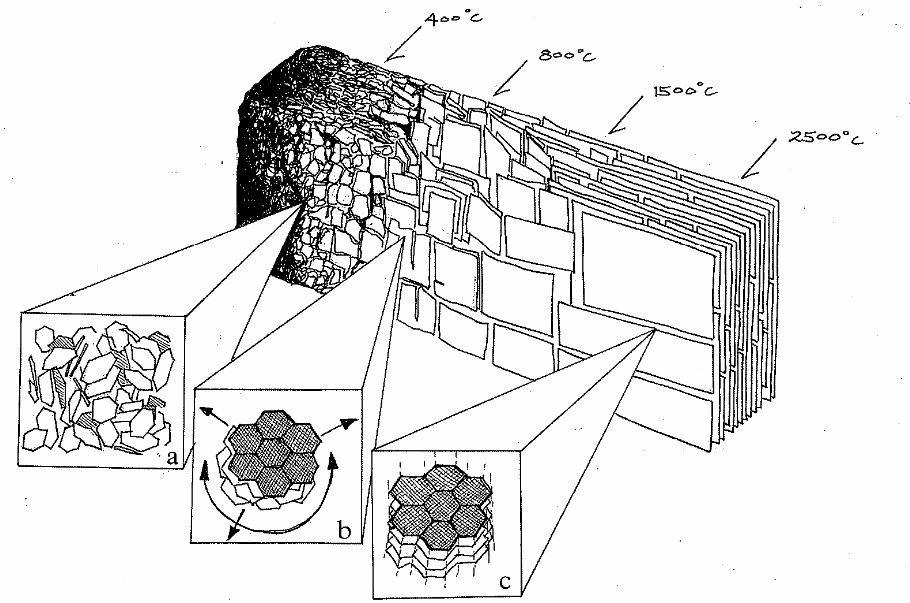


Figure 2.1 *Ideal biochar structure development with highest treatment temperature (HTT): (a) increased proportion of aromatic C, highly disordered in amorphous mass; (b) growing sheets of conjugated aromatic carbon, turbostratically arranged; (c) structure becomes graphitic with order in the third dimension*

How large and pure (condensed) are the fused aromatic structures in biochar?

We don’t really know!

Varies with production conditions

- Heat treatment temperature
- Heating time
- Starting material (wood, manure etc.)

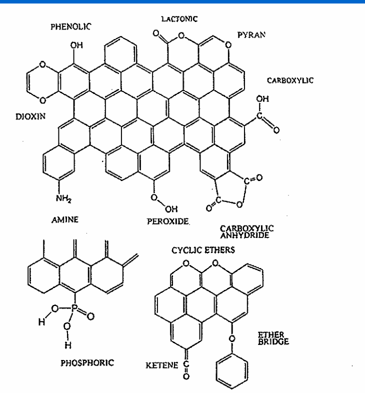


Figure 3.10 *Heteroatoms and functional groups commonly found in activated carbons*

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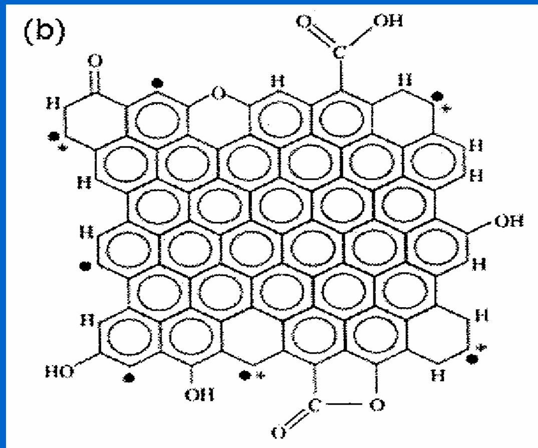
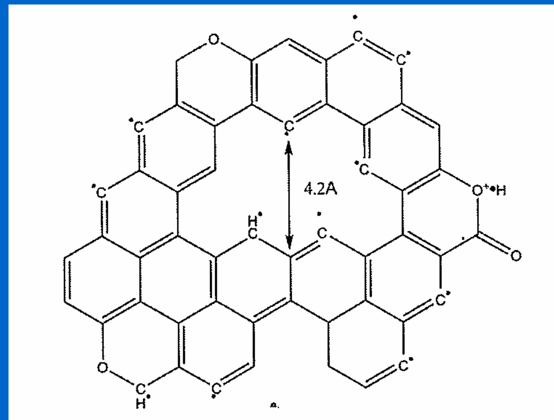




These are only “representative structures” (best guesses)

Why is biochar condensation important?

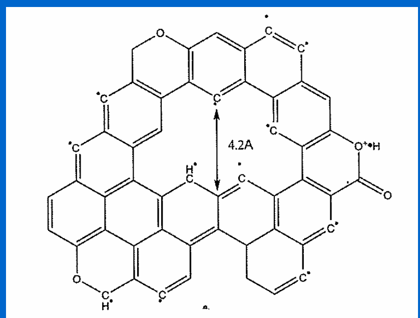
The unique properties of biochar relate to its chemical structure

The expectation is that more condensed (graphitic) biochars:

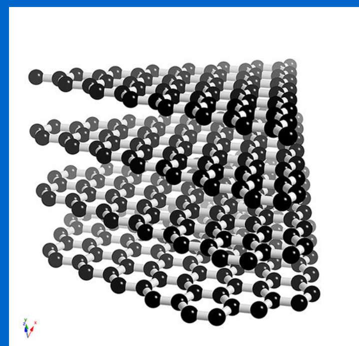
- are more inert (better C storage)
- are more slowly functionalized (take longer to develop Terra Preta properties)

We need to be able to measure biochar condensation to:

- classify biochars
- predict the lifetime of C in soil for different biochars
- predict long-term fertility benefits of different biochars
- follow changes that occur to charcoal chemistry over time



Where on this continuum does a given biochar lie, and how will that change over time?



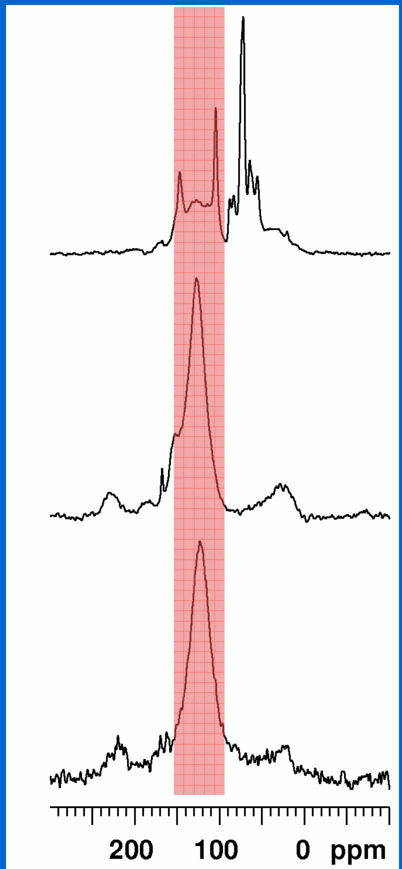
Measuring biochar condensation

Many techniques have been used to characterize biochar – none provide a direct measure of condensation

We have developed such a method – it uses NMR spectroscopy and is based on “ring currents” that are produced in condensed aromatic structures

“Standard” NMR spectroscopy

NMR spectroscopy is widely used to determine the aromatic C content of biochars



250°C biochar

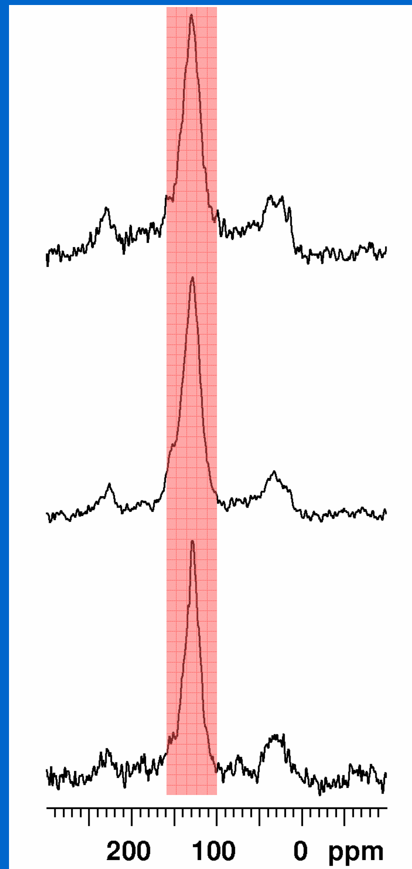
Very Little aromatic C

450°C biochar

Mostly aromatic C

850°C biochar

Virtually all aromatic C



Very little change once the majority of C is aromatic

Not sensitive to biochar condensation

Wood biochars – different temps

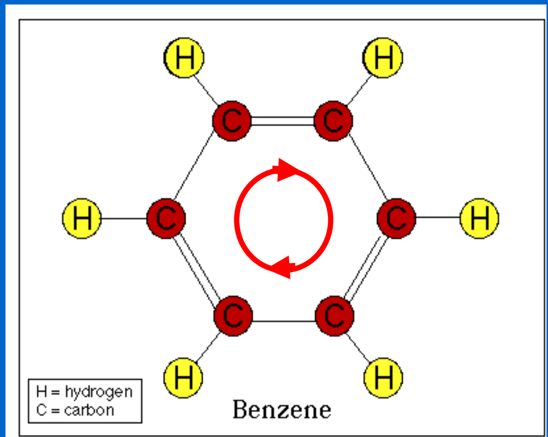
Different starting materials 500-600°C

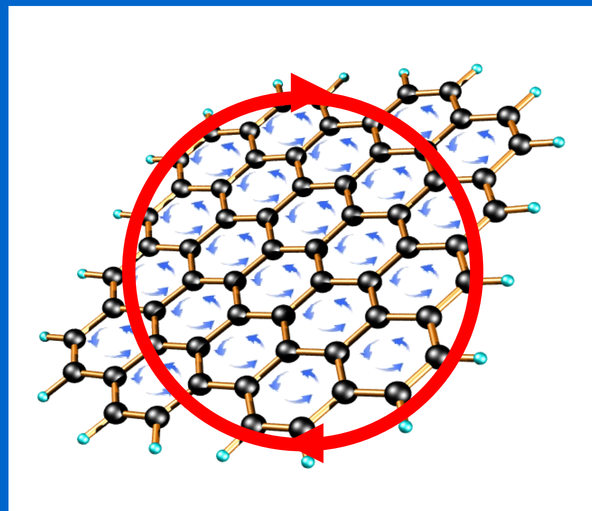
What is a ring current?

Electrons are free to move in aromatic rings

In the presence of an external magnetic field, they circulate, and this induces a localized, weak magnetic field near the ring

Larger and purer (more condensed) ring systems produce larger ring currents and stronger magnetic fields





NMR differentiates atoms based on slight differences in magnetic field due to “shielding” by electrons (chemical shift)

Ring currents effects are superimposed on chemical shift effects

How to measure these ring currents

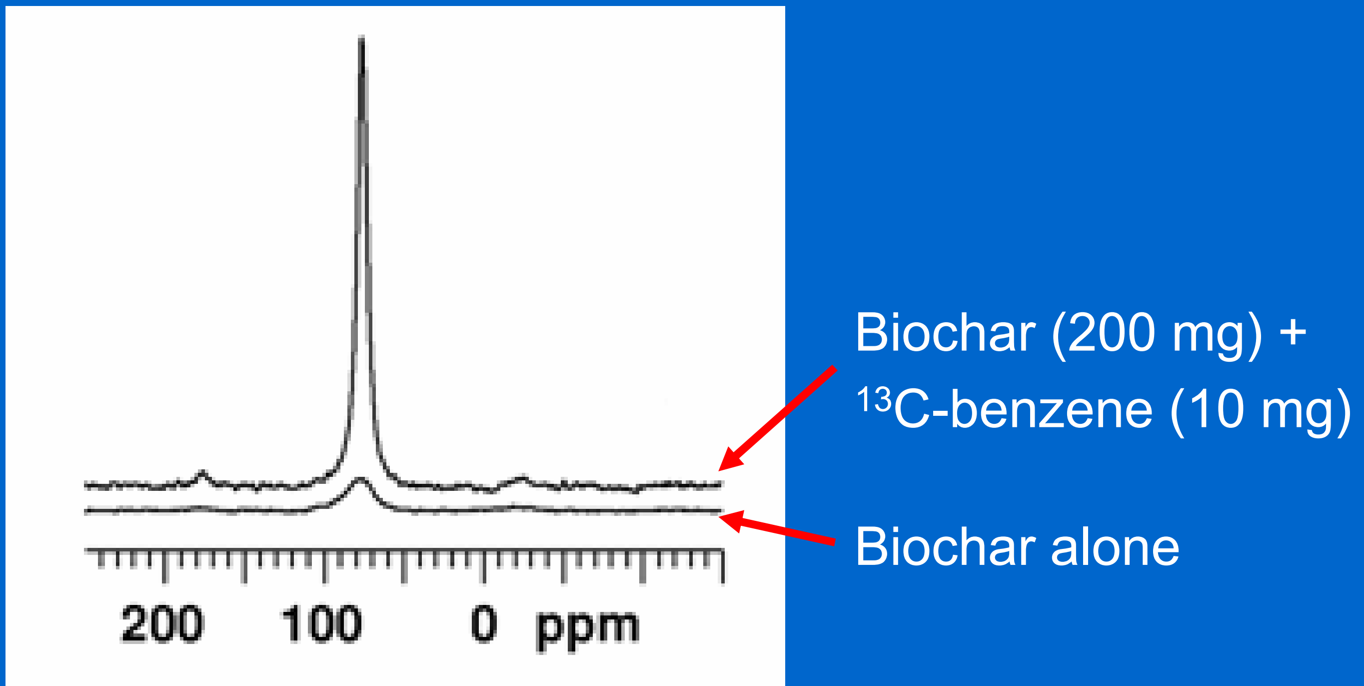
^{13}C-Benzene
δ=128.7 ppm

sample + probe molecule → solid-state ^{13}C NMR spectrometer

How to measure these ring currents

By using a ^{13}C-labelled probe molecule we ensure most NMR signal (which comes from only ^{13}C nuclei) is from the probe molecule

Only ~1% of carbon in the biochar is ^{13}C (natural abundance)

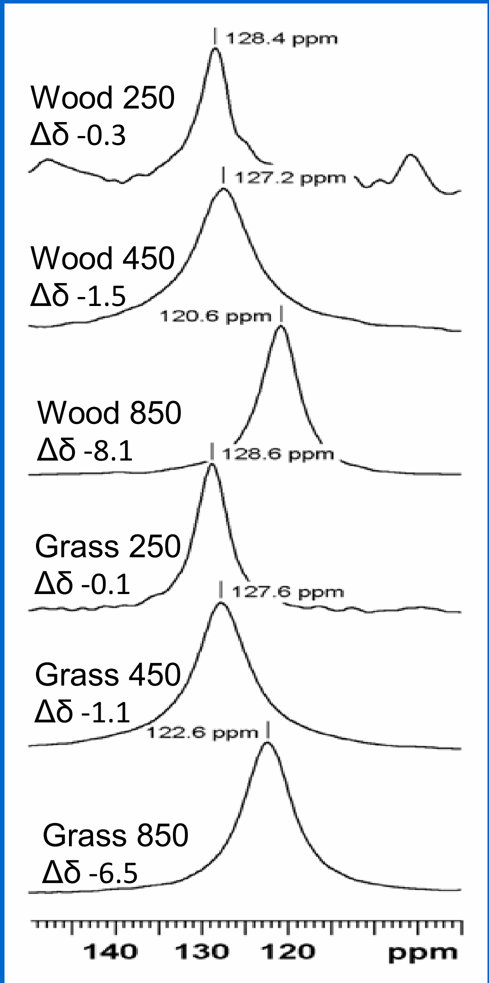


The output

In the absence of ring currents, ^{13}C-benzene gives a peak at 128.7 ppm.

Ring currents shift that peak to lower values when sorbed to biochar

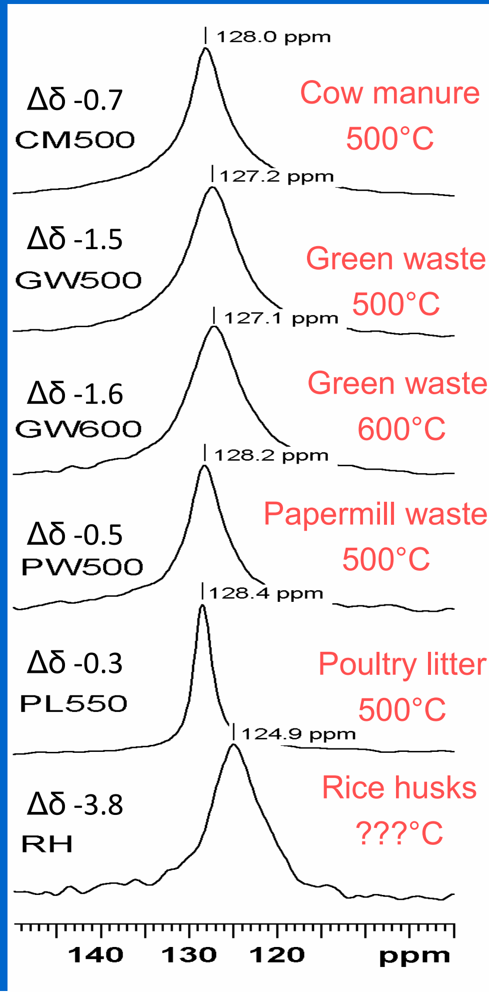
Expressed as Δδ – i.e. the difference from 128.7 ppm



Lab-produced biochars – long heating times (~2h)

Clear effect of production temperature – more negative Δδ values for higher temps (more condensed)

Smaller effect of starting material – wood biochars more condensed than grass biochars



Fast pyrolysis biochars – shorter heating times

Generally less negative Δδ values for given temps

High ash biochars have lower condensation

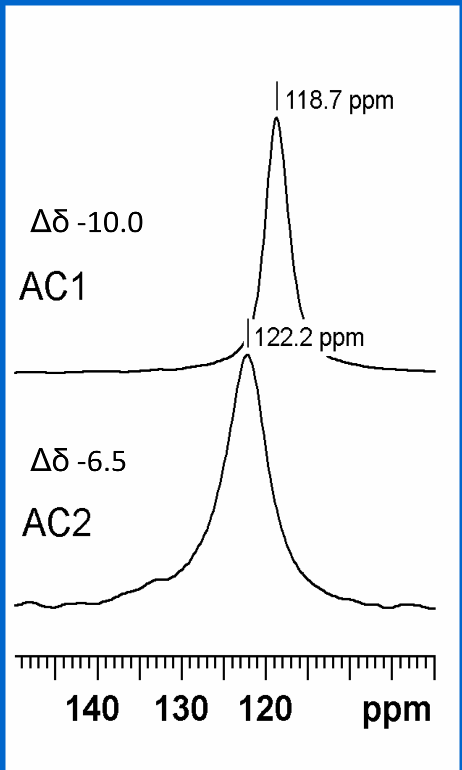
Rice husk char (production temp unknown) substantially more condensed

The output

In the absence of ring currents, ^{13}C-benzene gives a peak at 128.7 ppm.

Ring currents shift that peak to lower values when sorbed to biochar

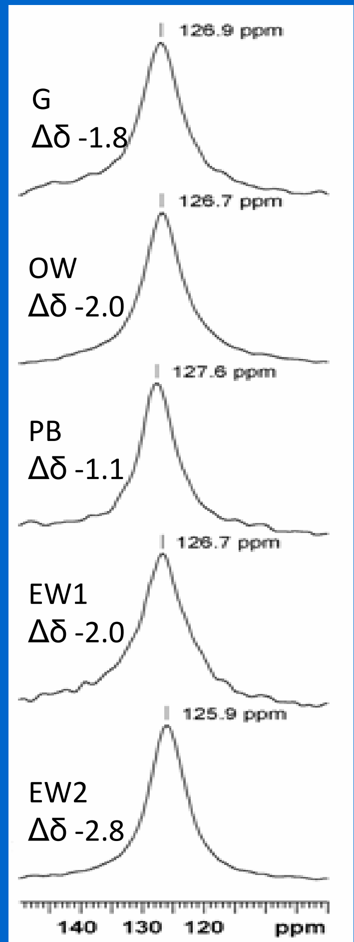
Expressed as Δδ – i.e. the difference from 128.7 ppm



Activated biochars

Highly condensed structures (very negative Δδ values)

Commercial activated carbon (AC1) more condensed than activated cow manure biochar (AC2)



Natural biochars – from a bushfire

Effect of starting material – wood biochars (OW, EW) more condensed than grass biochar (G) and bark biochar (PB)

“Apparent” production temperature ~500-600°C for wood biochars

Summary of findings so far

- Biochar condensation increases with production temp
- Influenced by starting material (woody materials give most condensed chars)
- Provides a measure for biochars produced at unknown temps

- Very old (Terra Preta type) biochar gives $\Delta\delta \sim 0$ – technique is sensitive to aging effects
- Minimal effects on aging in soil for ~ 1 year
- Soot has surprisingly low degree of condensation

Potential of the technique

- Decomposability index for fresh biochar
- Measure of production temp for natural chars
- Measure of changes to biochar surfaces on aging

Advantages

- No other technique provides such a direct measure of this parameter
- Simple procedure, no pre-treatment
- Relatively inexpensive (~$100 per sample)

Continuing research

- Detailed temperature scale
- Temperature – time matrix
- Effects of aging – lab, field incubation; old chars (decades-centuries)
- Mechanisms of decrease in $\Delta\delta$ (surface oxidation, interaction with minerals, organics)

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