

# The influence of soil charcoal on the adsorption of organic molecules

Ron Smernik<sup>1,2</sup>

*<sup>1</sup>Soil and Land Systems, School of Earth and Environmental  
Sciences, The University of Adelaide, Waite Campus,  
Urrbrae, SA 5064, Australia*

*<sup>2</sup>Research Institute for Climate Change and Sustainability,  
The University of Adelaide, SA 5005, Australia*

# Sorption of organic molecules to soil

In soil, molecular species (e.g. molecule A), exist in equilibrium between solution and sorbed states



This equilibrium is described by the equilibrium constant  $K_d$

$$K_d = \frac{[A_{\text{sorbed}}]}{[A_{\text{solution}}]}$$

$K_d$  is usually normalised to organic C content (or fraction,  $f_{\text{OC}}$ )

$$K_{\text{OC}} = K_d / f_{\text{OC}}$$

**Take home message:  $K_{\text{OC}}$  is a measure of an organic material's affinity for a given molecule**

## Role of BC (black carbon) in sorption

Black carbon (BC) or char has been widely suggested as a strongly sorbing organic matter domain

“Pure” BC materials have high sorption affinities ~10-1000 times the affinity of other types of organic present in soils

The variability of  $K_{OC}$  for BC is attributed to differences in its structure, in particular the “degree of aromatic condensation”

**Take home message: charcoal has a high affinity for organic molecules, but this affinity varies considerably**

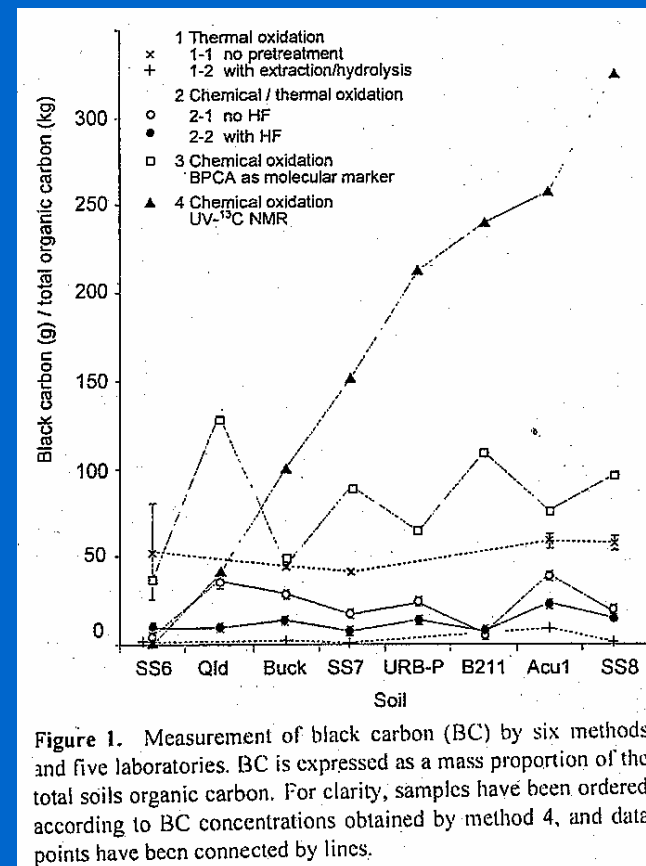
# How much charcoal is there in soils?

Charcoal may represent >10% of organic C in many soils, in which case it may be the dominant sorbing phase (if it has >10 times the sorption affinity)

Quantifying the contribution of BC to total soil carbon has proven difficult. Two reasons:

- Different techniques measure different sections of the “BC spectrum”
- There is a lot that can go wrong
- The “BC ring trial” is an attempt to sort out these problems

<http://www.geo.unizh.ch/phys/bc/>



Schmidt et al, 2001, Global Biogeochemical Cycles, 15, 163-167.

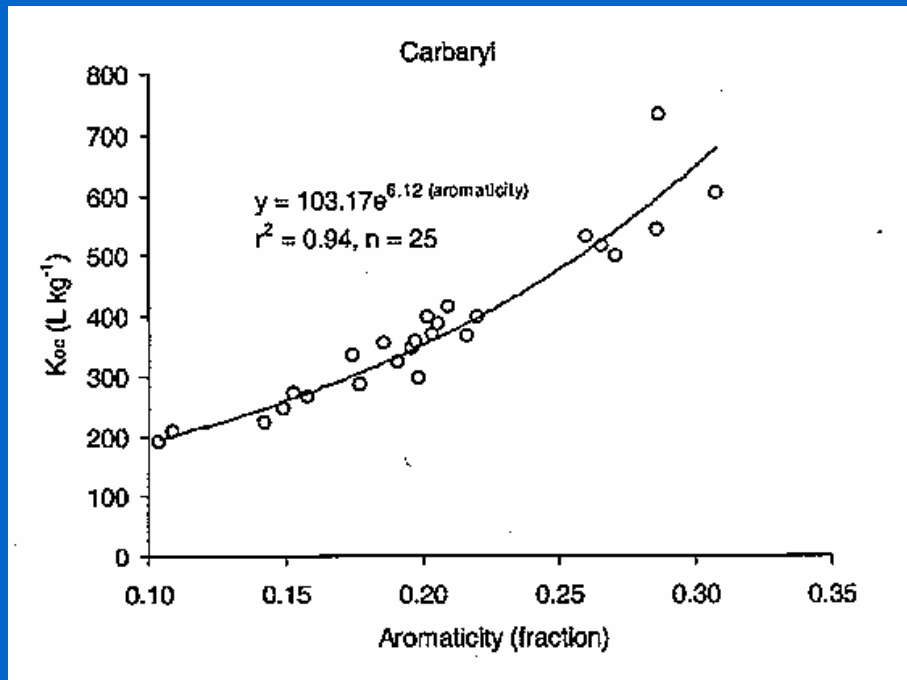
**Take home message: there's lots of charcoal in many soils (but just how much is a moot point) and it may dominate sorption**

# Does charcoal dominate sorption in soils?

Charcoal is highly aromatic. Therefore if charcoal dominates sorption, you'd expect a correlation between aromaticity and  $K_{OC}$

Do we see this?

Sometimes yes .....



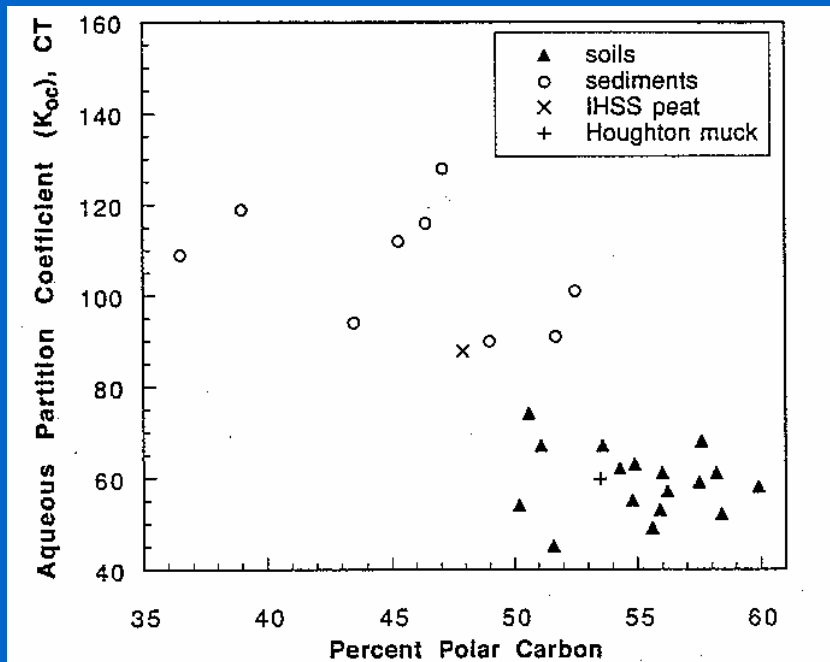
- Ahmad et al, ES&T 35, 878, 2001
- Positive correlation with aryl C
- Soils from Australia UK and Pakistan

# Does charcoal dominate sorption in soils?

Charcoal is highly aromatic. Therefore if charcoal dominates sorption, you'd expect a correlation between aromaticity and  $K_{OC}$

Do we see this?

.... and sometimes no



- Kile et al, ES&T 33, 2053, 1999
- Negative correlation with “polar C” (O-alkyl + carbonyl)
- No correlation with aromatic C

Take home message: expected relationship between aromaticity and  $K_{OC}$  the exception rather than the rule

# What's going wrong? Some possibilities

Lots of aromatic C isn't charcoal

Yes, but can correct for this

There are other highly sorptive phases

True in the case of model materials, but are these quantitatively important in soils?

Soil charcoal isn't the "high affinity type"

Probably not the highest affinity type, but still pretty good

Something happens to charcoal in soil that makes it less sorptive

This is where my money is

# We need some new tools!

Correlations between  $K_{OC}$  and % aromatic C are very crude because:

- There is aromatic C that is not charcoal
- There may be varying amounts of highly sorptive material that is neither aromatic nor charcoal

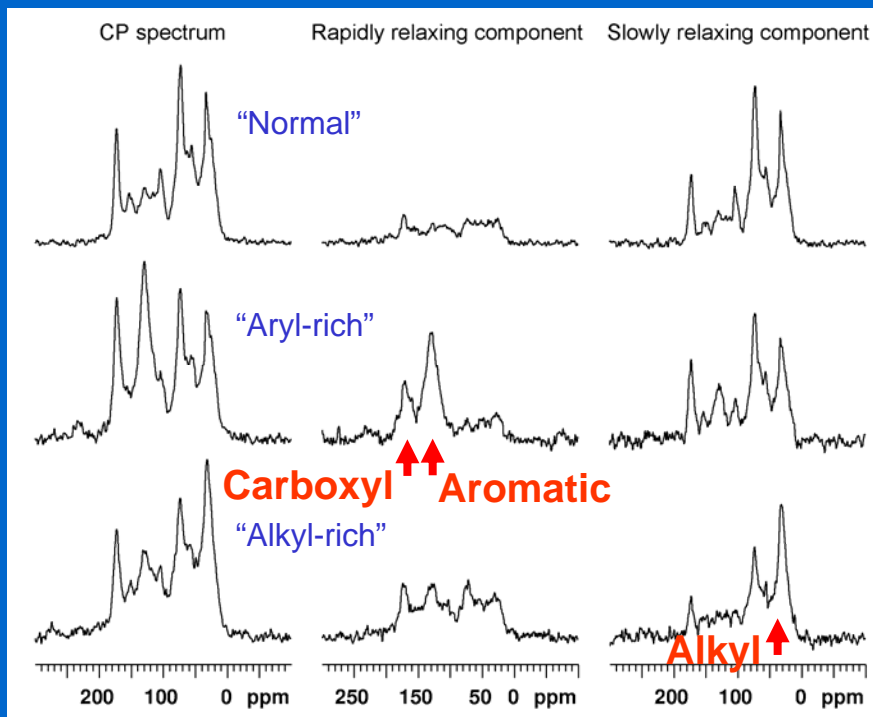
Need more detailed information on where sorbed molecules are

# PSRE – proton spin relaxation editing

Fancy solid-state NMR technique and I won't bore you with how it works

NMR = nuclear magnetic resonance (spectroscopy)

Identifies, quantifies and characterizes organic matter domains at submicron scale



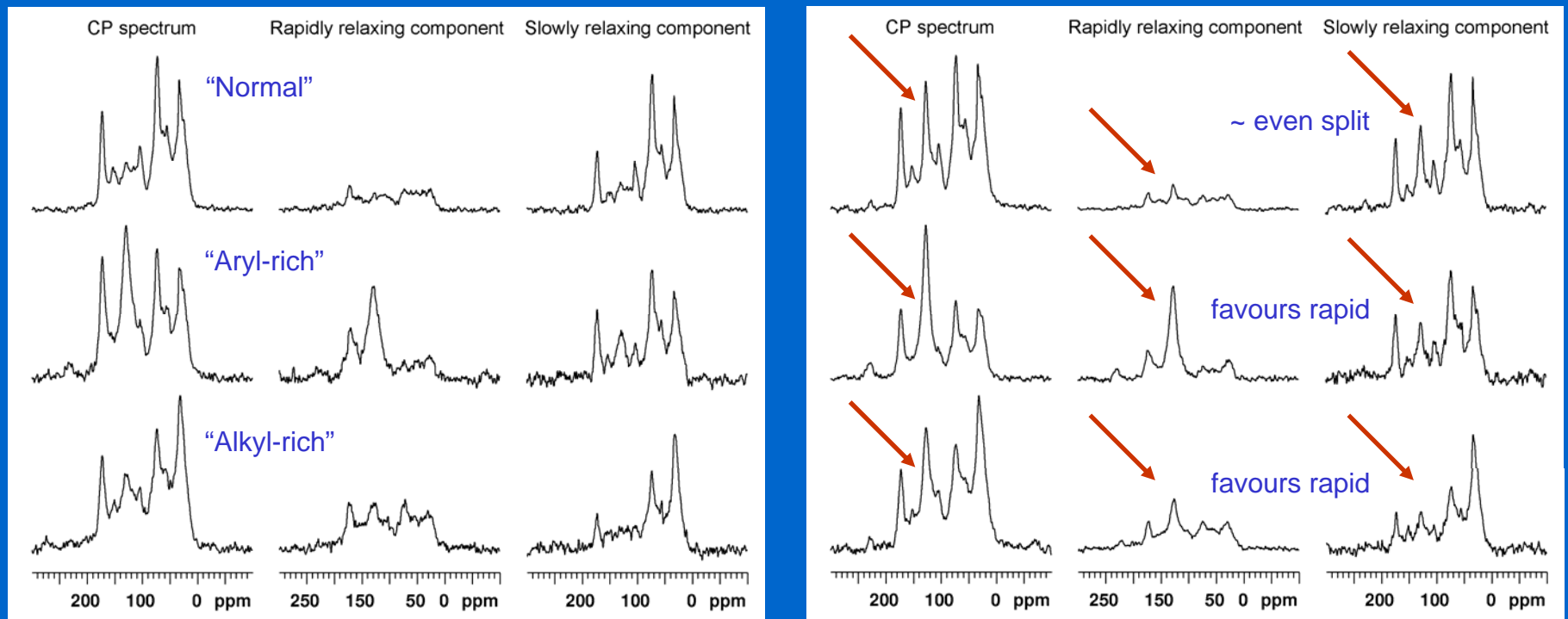
Small amount of “DOC-like” component

Large amount of “char-like” component (but note the large amount of carboxyl C)

Large amount of “alkyl-rich component”

# PSRE – proton spin relaxation editing

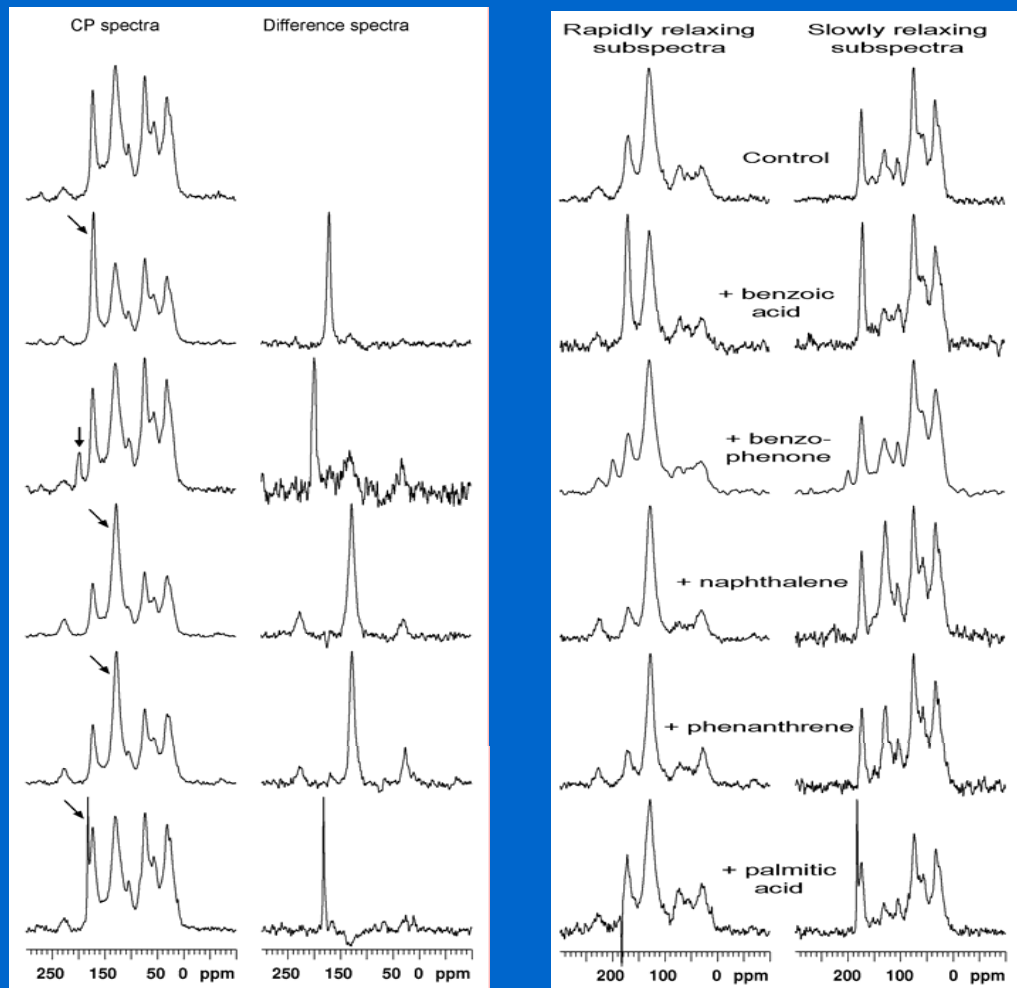
If you add a  $^{13}\text{C}$ -labelled compound, PSRE tells you where it is!



+  $^{13}\text{C}$ -labelled phenanthrene

Take home message: PSRE enables the sorption affinity of charcoal within soil to be determined directly

# PSRE – “char-rich” soil + range of compounds

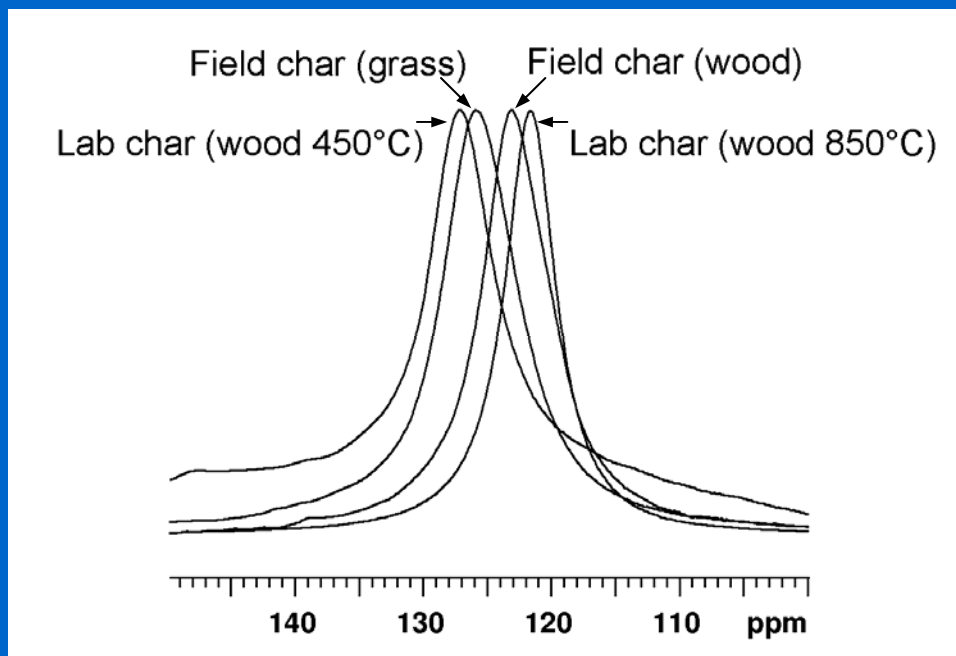


	$K_{ow}$	$K_{oc}$ "fast" / $K_{oc}$ "slow"
Benzoic acid	75	2.1
Benzophenone	1500	2.2
Naphthalene	2000	5.5
Phenanthrene	29000	9.4
Palmitic acid	1500000	-

Take home message: soil char has 2-10 times higher affinity for organic compounds (not 10-1000 times)

## Another new tool – ring-current shifts

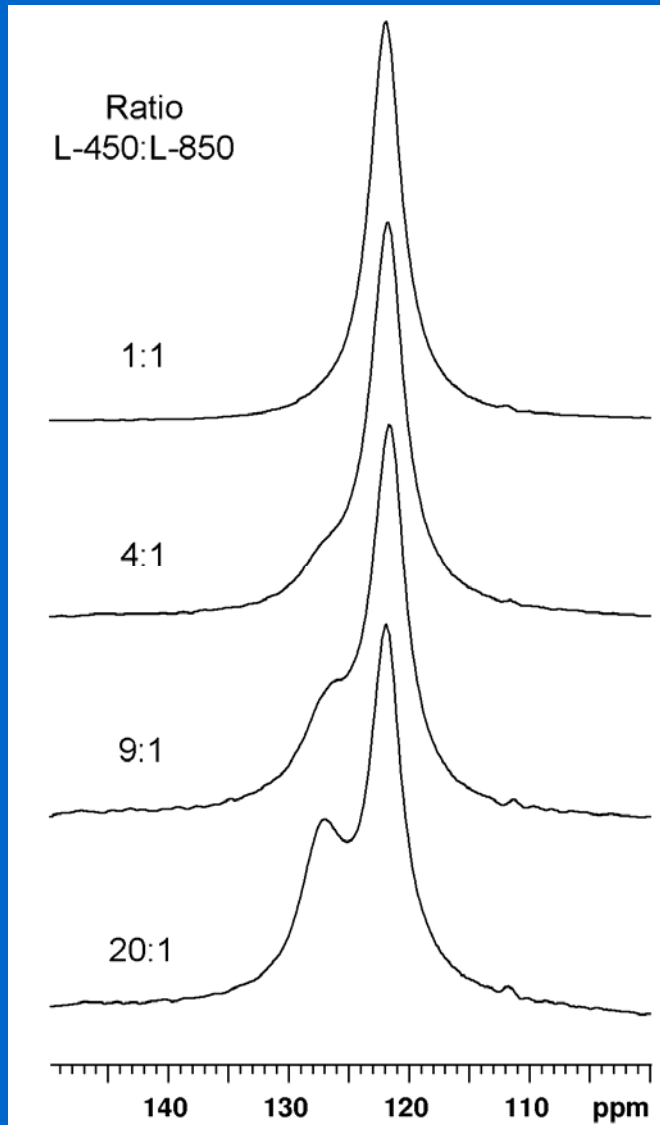
A strange thing happened when I ran spectra of  $^{13}\text{C}$ -benzene sorbed to a range of charcoals – their chemical shift varied (considerably!)



- All four easily differentiated
- Variation in chemical shift ~5.5ppm
- Chemical shift decreases with increasing degree of condensation
- Caused by “ring currents” in condensed aromatic structures

$^{13}\text{C}$  signal of the  $^{13}\text{C}$ -benzene

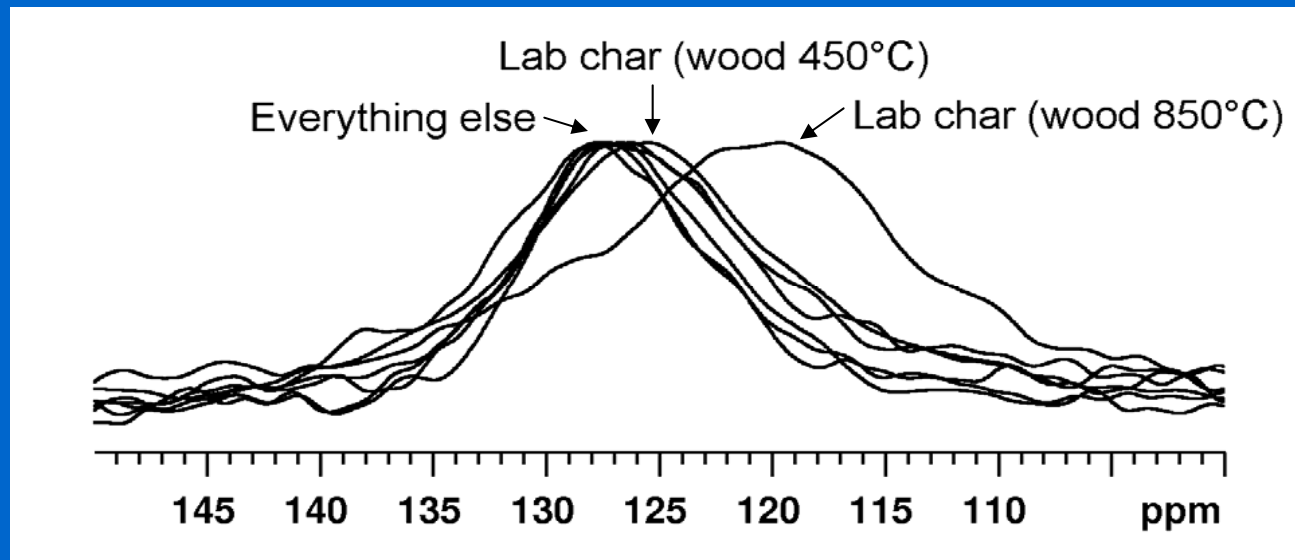
# Another new tool – ring-current shifts



- The effect is local – only <sup>13</sup>C-benzene molecules sorbed to the charcoal are affected (not the whole sample)
- Here <sup>13</sup>C-benzene was added to mixes of the wood chars produced at 450°C and 850°C – separate signals are produced
- Enables quantification of <sup>13</sup>C-benzene sorbed to each (L-850 has ~20 times the affinity)
- Works with other (any) sorbate molecules
- Should enable direct identification and quantification of species sorbed in char in soils

# Another new tool – ring-current shifts

- Should – but doesn't! – results for  $^{13}\text{C}$ -phenanthrene
- Still get differentiation of 450°C and 850°C chars
- Little or no differentiation for “everything else” – low char soil, high-char soil, “urban dust” (high char), harbour sediment (high char)
- Either sorbed molecules are not on char or char is not that aromatic



Take home message: molecules sorbed to soils containing char do not “see” char surfaces

# State of play – soil char and sorption

- Charcoal has a high affinity for organic molecules
- Many soils contain a lot of charcoal
- This implies that soil charcoal should dominate the sorption properties of soils – on the whole it doesn't
- “Fancy” NMR techniques show that:
  - i. Soil charcoal contains a lot of carboxyl C
  - ii. Molecules sorbed to char-rich soils do not “see” the type of char surfaces found in “pure” charcoal
- This may be because:
  - i. Soil charcoal is “different” (e.g. oxidised)
  - ii. Soil char surfaces already have something else on them (clays or other organics)

# How is this relevant to Agrichar?

Two key properties of agrichar are:

development of cation exchange capacity (improves soil fertility)

resistance to degradation (carbon sink)

We need to know what happens to agrichar in the field and that means more than knowing just how much C is left

# How is this relevant to Agrichar?

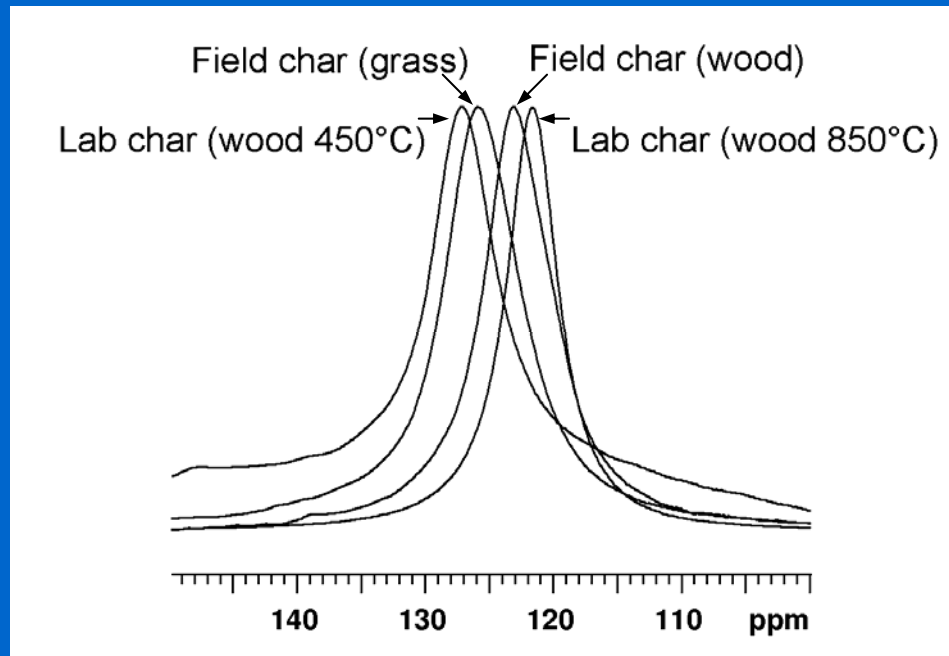
The techniques described here should enable:

- i. the degree of condensation of agrichar to be determined

# How is this relevant to Agrichar?

The techniques described here should enable:

- i. the degree of condensation of agrichar to be determined



# How is this relevant to Agrichar?

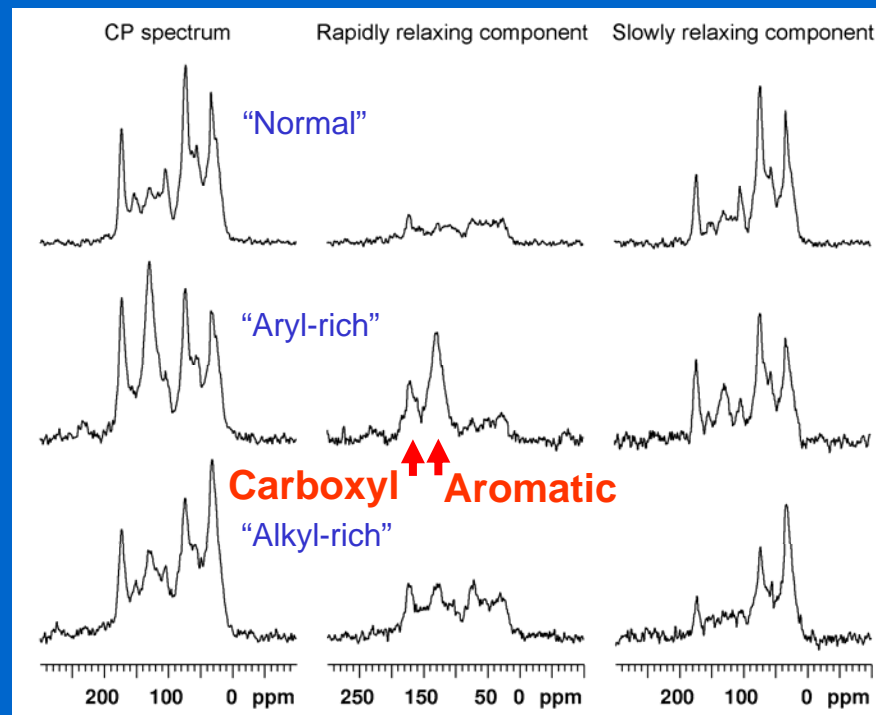
The techniques described here should enable:

- i. the degree of condensation of agrichar to be determined
- ii. the build-up of carboxyl functionality on the agrichar to be followed through time

# How is this relevant to Agrichar?

The techniques described here should enable:

- i. the degree of condensation of agrichar to be determined
- ii. the build-up of carboxyl functionality on the agrichar to be followed through time



# How is this relevant to Agrichar?

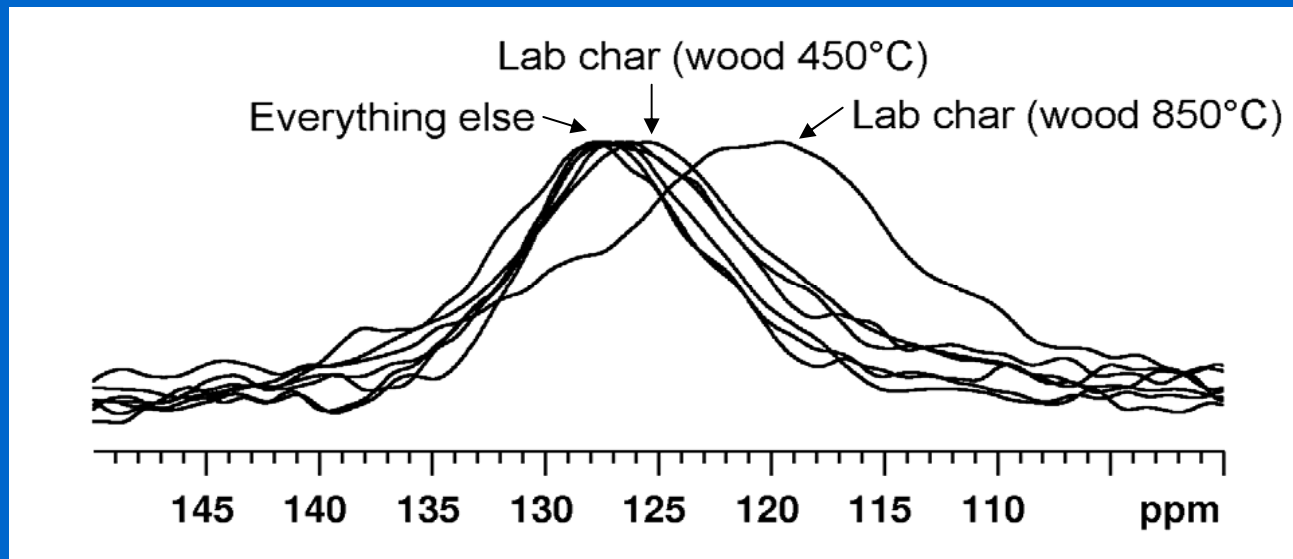
The techniques described here should enable:

- i. the degree of condensation of agrichar to be determined
- ii. the build-up of carboxyl functionality on the agrichar to be followed through time
- iii. changes in the accessibility of the char surfaces to be followed through time.

# How is this relevant to Agrichar?

The techniques described here should enable:

- i. the degree of condensation of agrichar to be determined
- ii. the build-up of carboxyl functionality on the agrichar to be followed through time
- iii. changes in the accessibility of the char surfaces to be followed through time.



# How is this relevant to Agrichar?

The techniques described here should enable:

- i. the degree of condensation of agrichar to be determined
- ii. the build-up of carboxyl functionality on the agrichar to be followed through time
- iii. changes in the accessibility of the char surfaces to be followed through time.

Together, this will provide a much better understanding of the processes that effect soil charcoal (both natural and added)

# Predictions (that I would love to test)

1. Agrichar itself has a high sorption affinity for neutral organics (the exact degree will depend mainly on the production temperature)
2. Addition of agrichar will substantially increase the sorption affinity of the soil
3. PSRE will be able to differentiate agrichar from other soil organic matter and be able to quantify the proportion of an added organic sorbed to agrichar
4. Sorption affinity of agrichar-amended soil will decrease over time due to:
  - Oxidation of the char
  - Interaction with clay minerals
  - Sorption of other organics present
5. The timing of this decrease and the effects of soxhelet and HF treatment on sorption affinity will provide very useful information about the processes affecting soil char