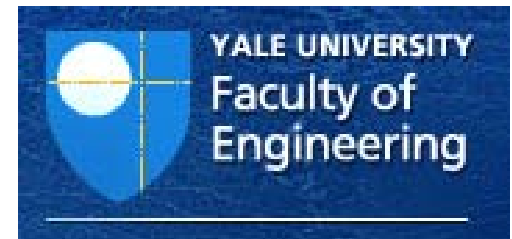


# Biochar as Soil Amendment: What Effect Will It Have on Chemical Availability?

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# Properties of freshly-prepared biomass chars

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- large surface area;
- high microporosity and mesoporosity;
- predominantly hydrophobic surface;
- strong adsorbent of organic compounds.



## What are the implications for agriculture of adding a strong adsorbent to soil?

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- Biochar may reduce the physical and biological availability of agriculturally important chemicals in soil:
  - pesticides
  - incidental soil contaminants
  - allelochemicals in soil.
- This reduction of availability may have positive or negative consequences.



## What are the implications for agriculture of adding a strong adsorbent to soil?

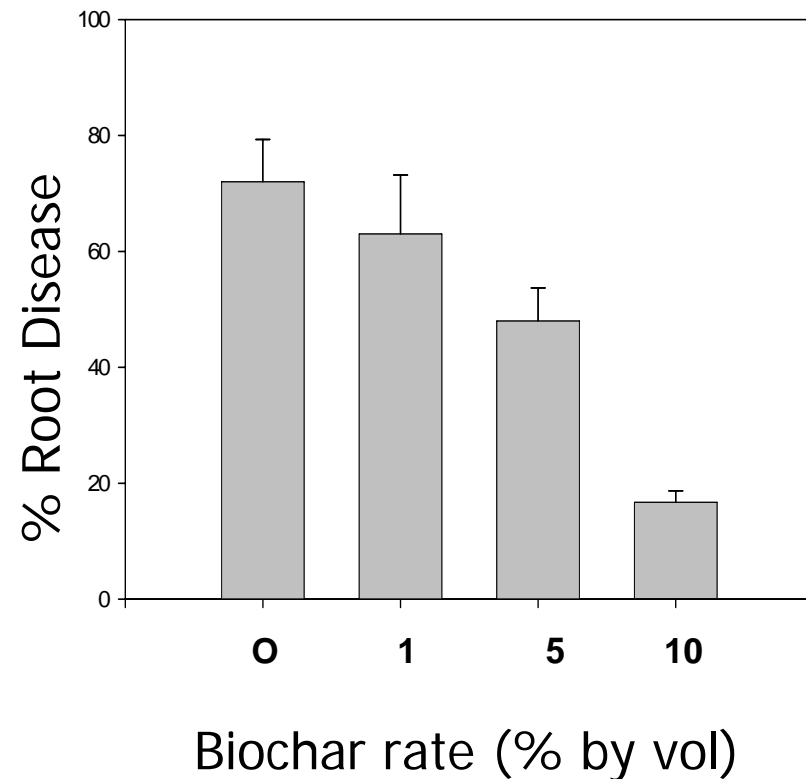
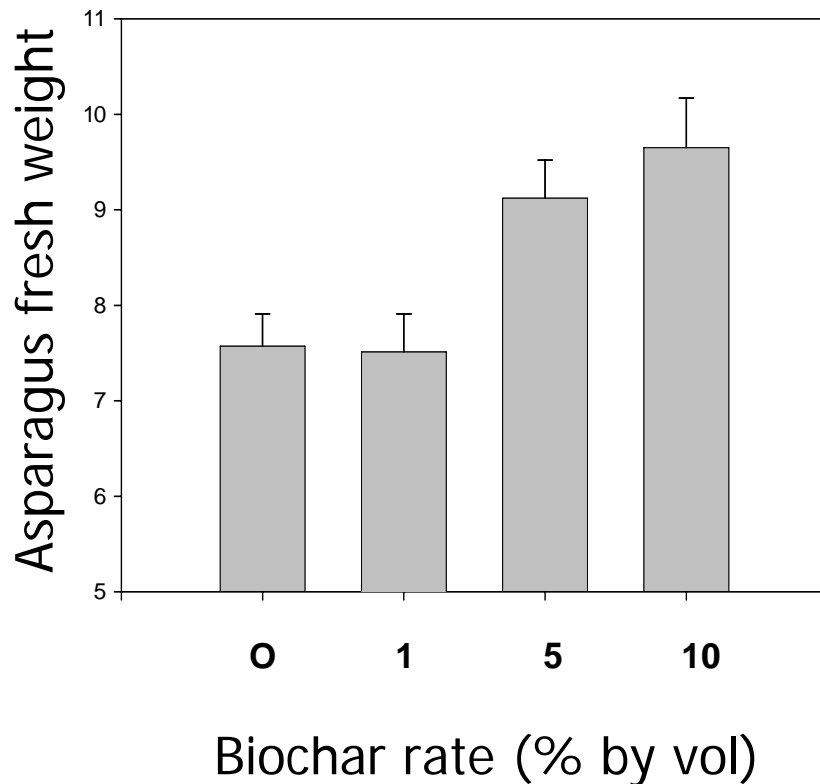
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- HOWEVER, humic substances are capable of adsorbing to black carbon;
- Humic substances known to suppress sorption on activated carbon.

*Hypothesis: the high surface activity of raw char is attenuated by interaction with soil substances.*

# Biochar mitigates damage to **asparagus** in soils containing allelochemicals (phenolic acids) that inhibit growth and promote disease

(Biochar source, Dynamotive)

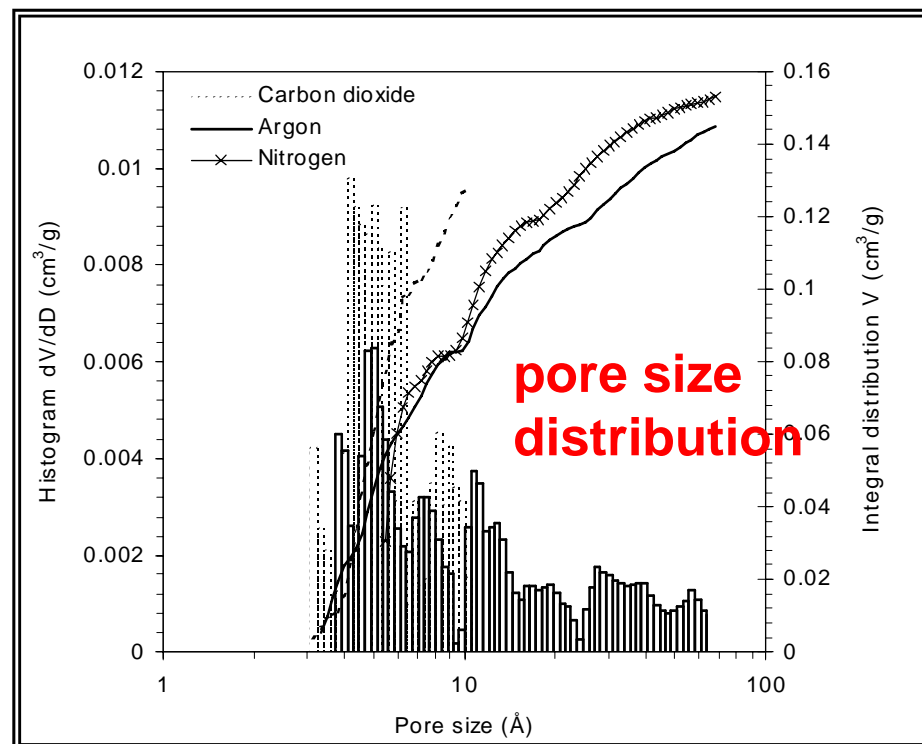
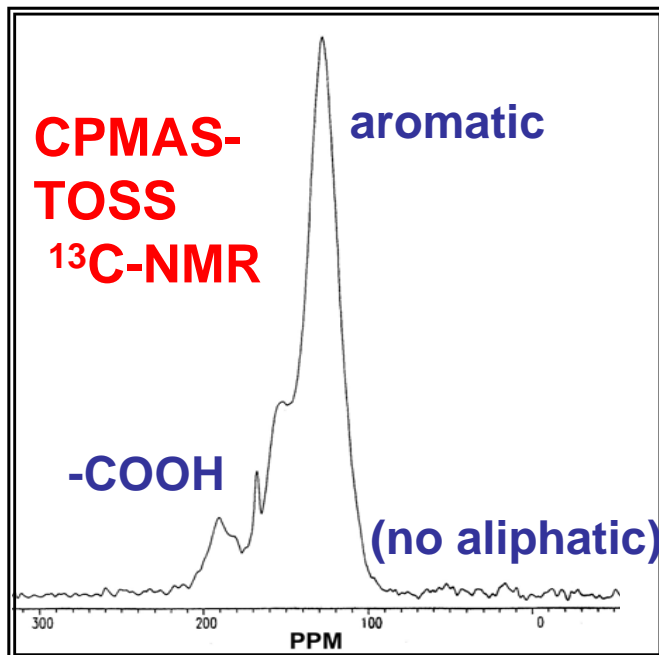


# Properties and composition of maple wood char (400 °C, 2 h, limited oxygen)

% C	71.97
% H	2.83
% N	0.51
% ash	2.03
atomic C/H	2.13
atomic C/N	165
atomic C/O	~4.2

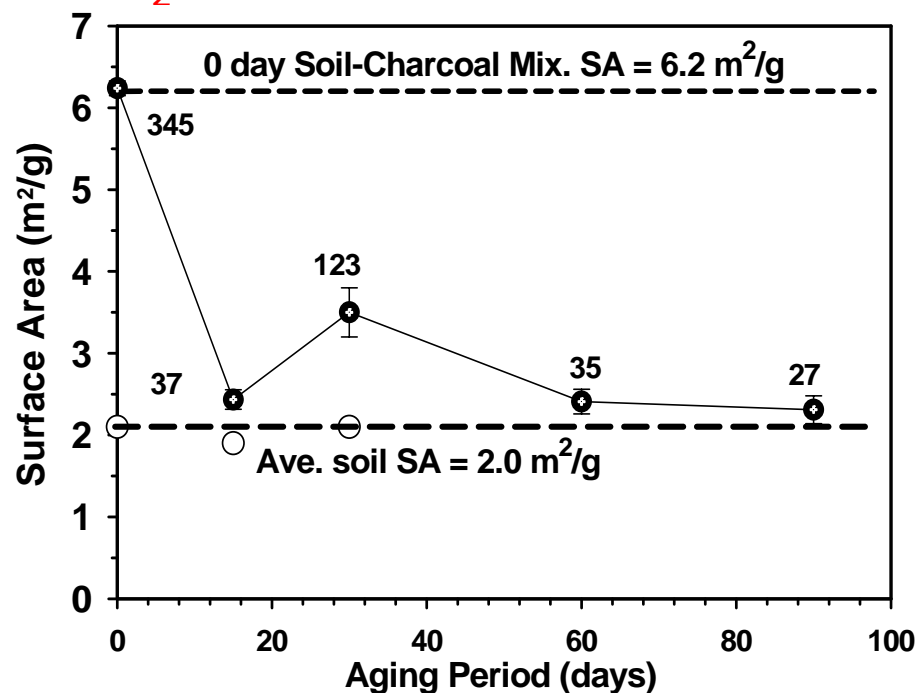
## Pore characterization (N<sub>2</sub>, Ar, CO<sub>2</sub>; NLDFT, MC):

- Specific Surface Area, 400 m<sup>2</sup>/g (N<sub>2</sub>)
- pore volume, 0.15 cm<sup>3</sup>/g
- >60% of porosity lies in pores between 4 and 10 Å
- >80% of porosity lies in pores between 4 and 20 Å

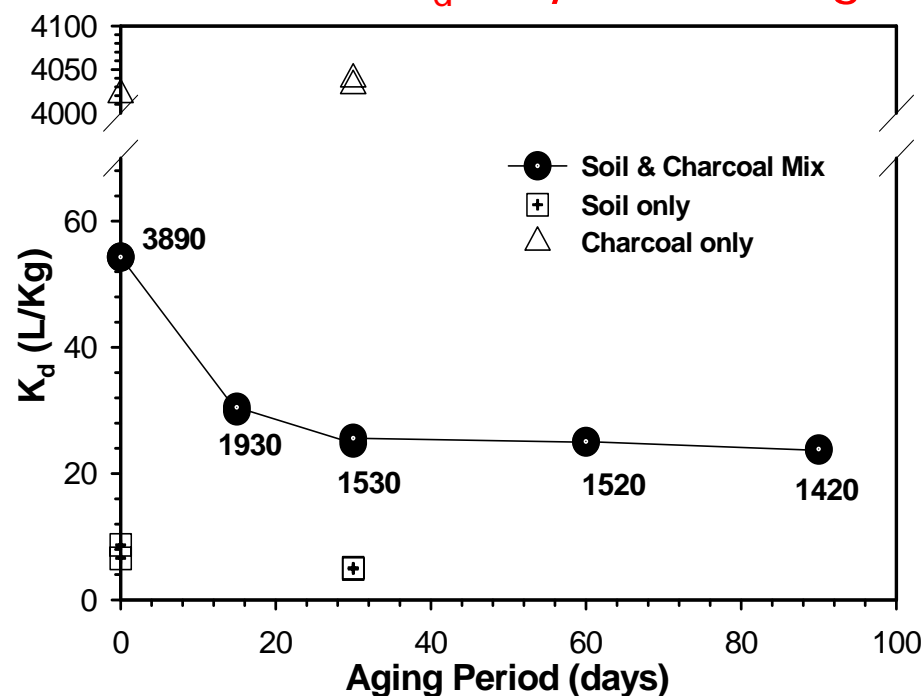


# Reduction of char surface activity after "weathering" in a soil-water suspension\*

$N_2$ -B.E.T. surface area



equilibrium benzene distribution coefficient  $K_d = q/C$  @ 1 mg/L

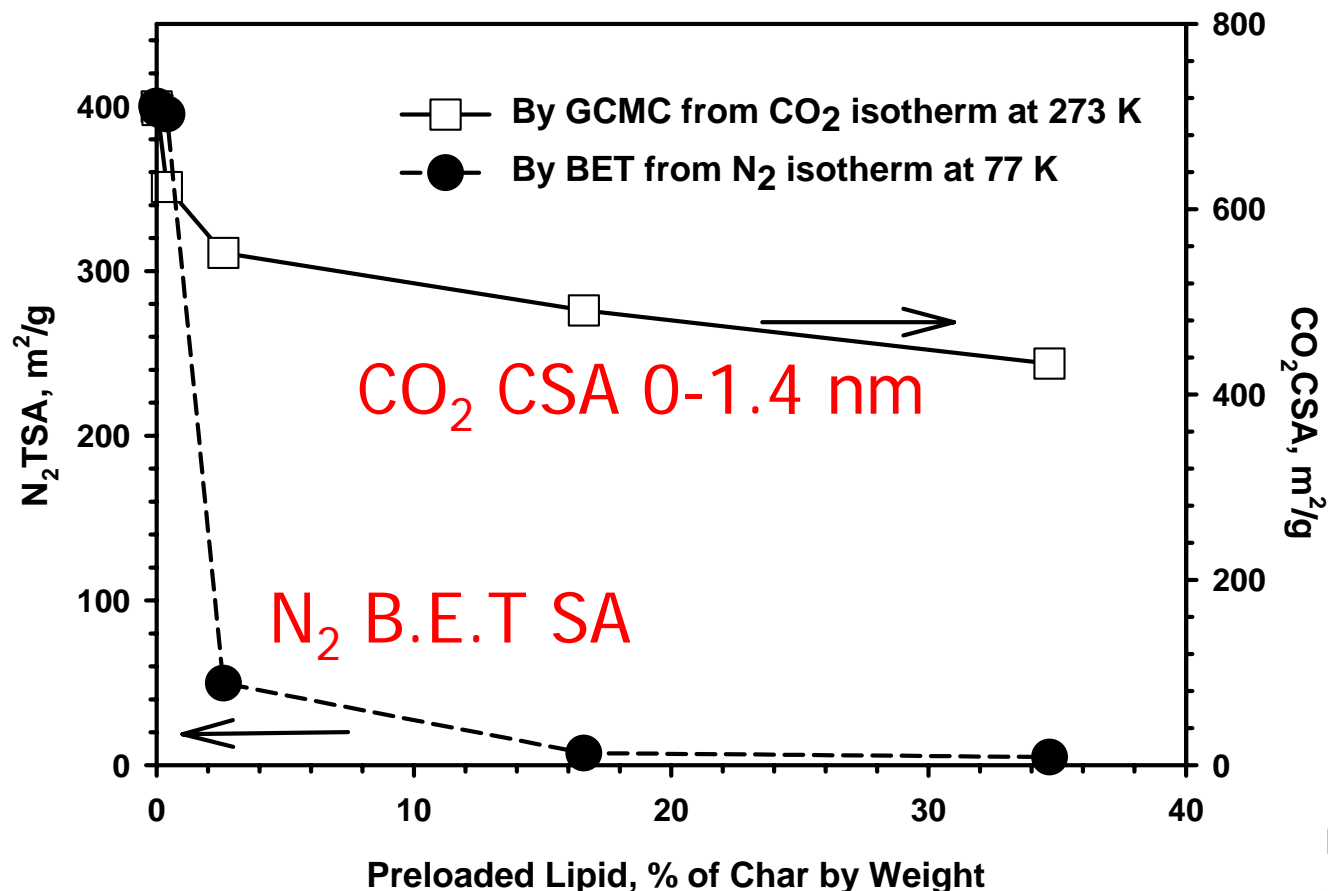


\* char-C/OC ratio = 0.05; 45 °C; soil: Terric Haplosaprist, 18.9% OC.

(number next to points is calculated value attributing all changes to char)

# Surface properties of char after uptake of natural organic substances

humic lipid substances (modeled by triacylglycerides in soybean oil)



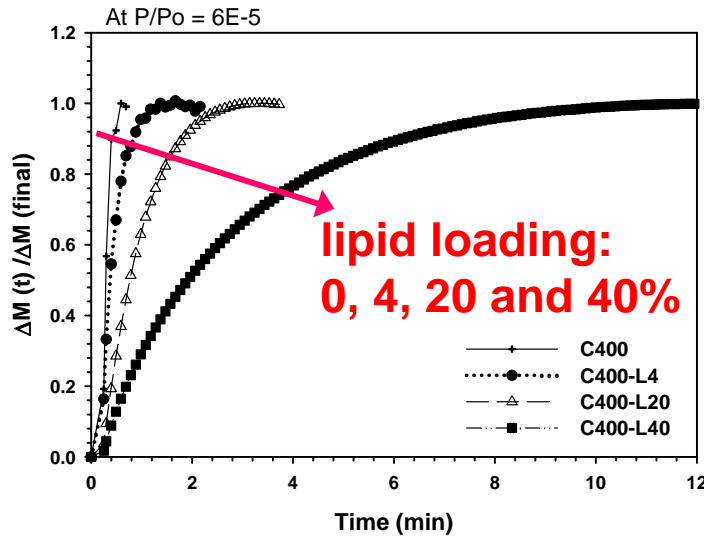
## soil humic and fulvic acids

% OM by wt	N <sub>2</sub> -B.E.T. TSA, m <sup>2</sup> /g		CO <sub>2</sub> CSA, m <sup>2</sup> /g	
	sample	char component only (calc)	sample	char component only (calc)
char alone →	0	400	698	698
char filtered from 1000 mg/L DOC soln.	trace	379	651	651
	trace (FA)	276	586	586
char-HA solution evaporated to dryness	1.5	18	250	253
	7.0	16	237	253
	23	14	176	220
	43	6.3	131	207
	60	1.4	99	202
	75	0.7	1.1	77
HA alone →	100	0.6	30	--

CSA is cumulative surface area up to 14 Å (273 K; DFT-MC)

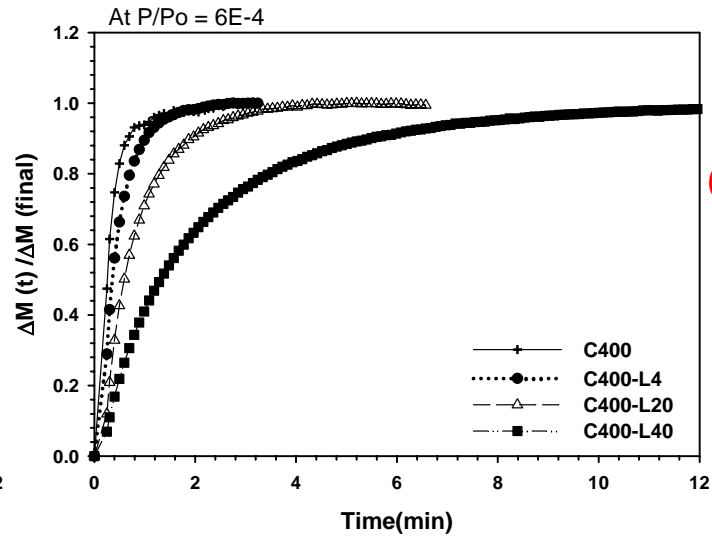
# Rate of normalized uptake of CO<sub>2</sub> by char and lipid-loaded chars at different pressures (273 K)

@  $P/P_0 = 6 \times 10^{-5}$

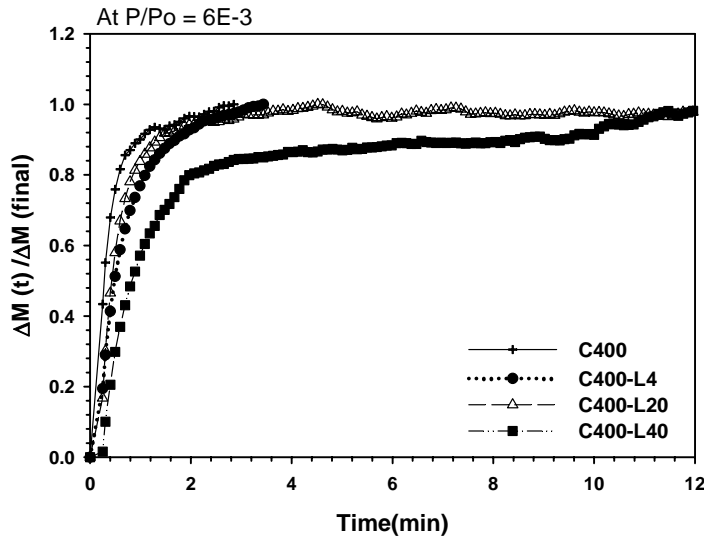


lipid loading:  
0, 4, 20 and 40%

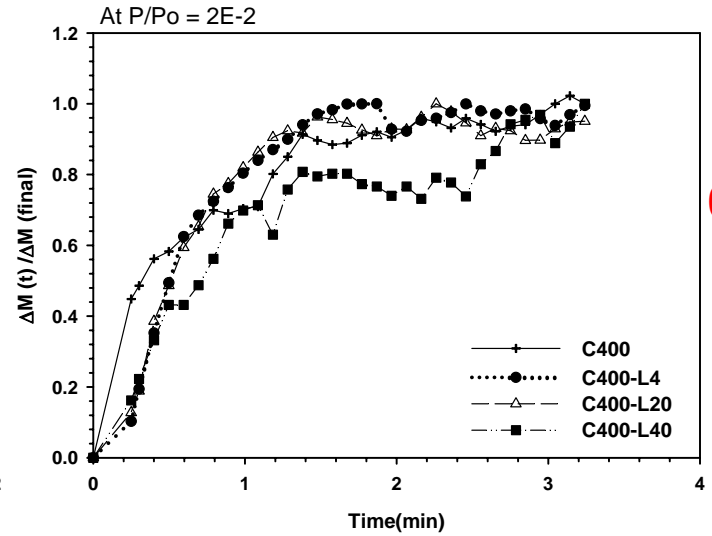
@  $P/P_0 = 6 \times 10^{-4}$



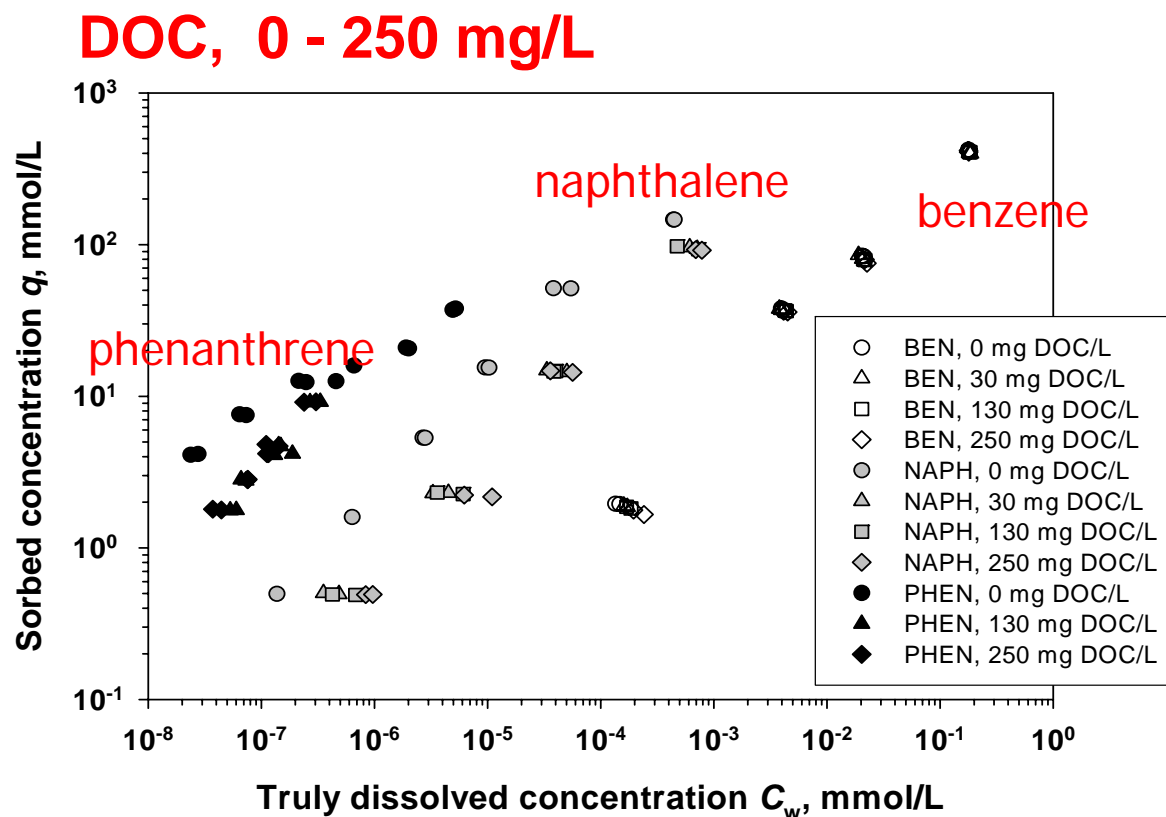
@  $P/P_0 = 0.006$



@  $P/P_0 = 0.02$



# Suppression of adsorption to char by dissolved humic acid



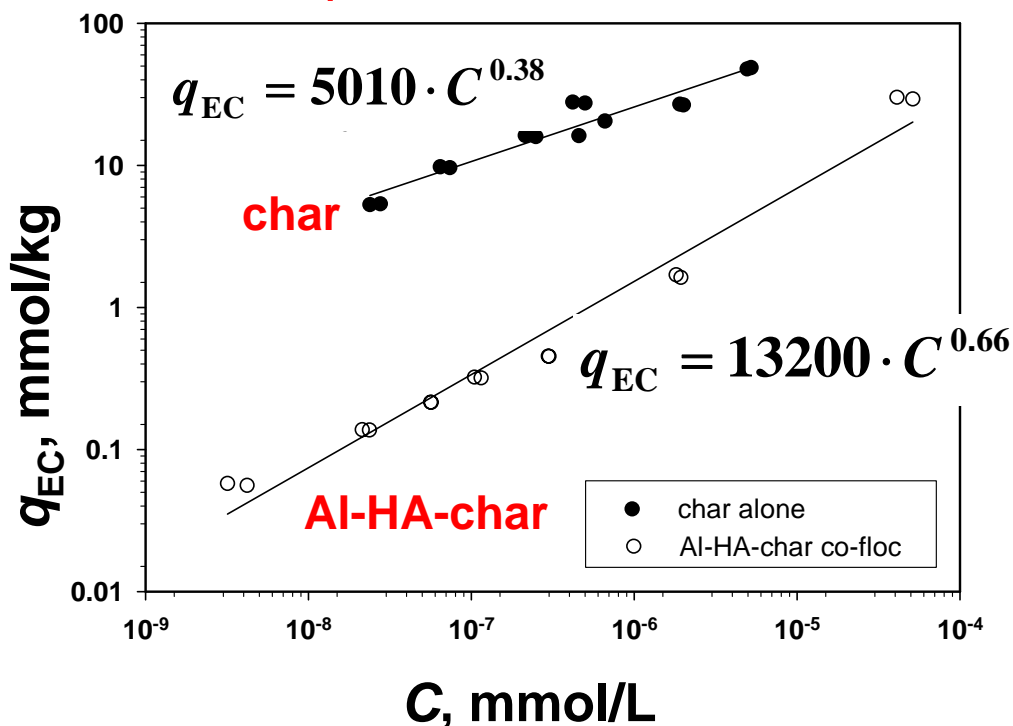
**(adsorption corrected for partitioning to DOC)**

Suppression increases with [DOC] and follows order in solute molecular size (BEN < NAPH < PHEN)

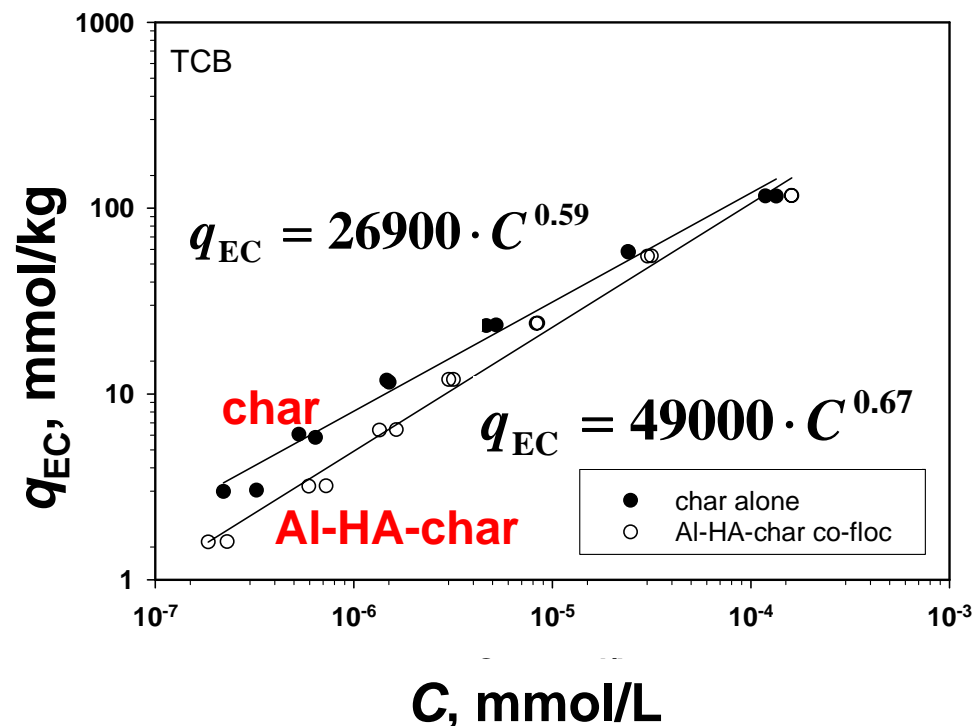
# Suppression of adsorption to char by humic acid coatings (as Al<sup>3+</sup>-HA floc)

Isotherms for sorption on char carbon (sorption to Al<sup>3+</sup>-HA subtracted out)

phenanthrene

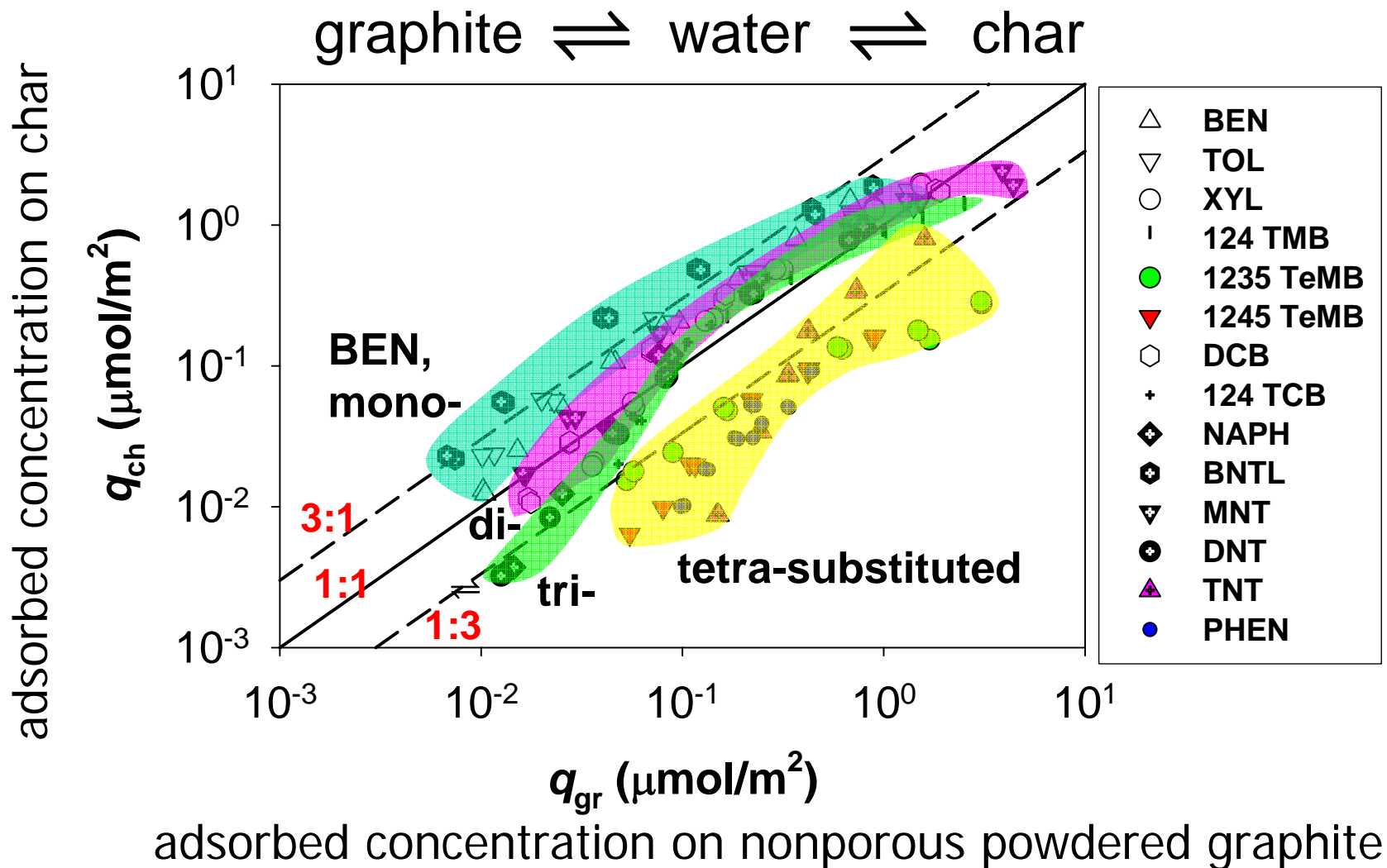


1,2,4-trichlorobenzene



Suppression follows order in molecular size TCB < PHEN

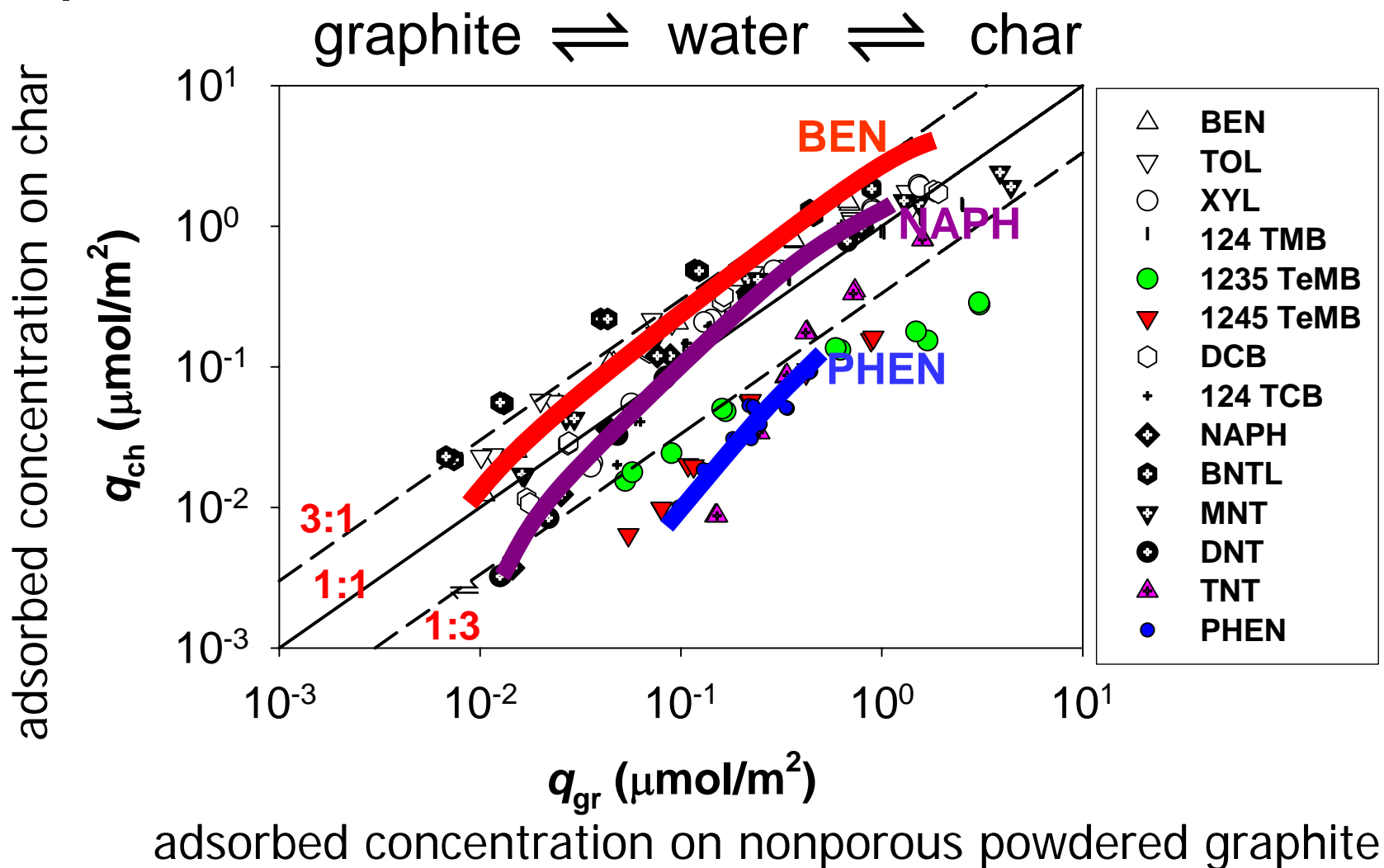
# Steric effects in adsorption by char



polar and nonpolar aromatic compounds

Zhu et al., *ES&T*, 39, 2033 (2005); Pignatello et al., *ES&T*, 40, 7757 (2006)

# Steric effects in adsorption by char



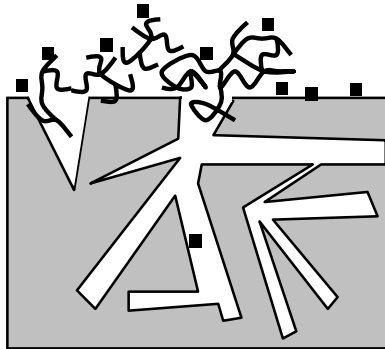
polar and nonpolar aromatic compounds

Zhu et al.,  
*ES&T*, 39,  
2033 (2005);  
Pignatello et  
al., *ES&T*, 40,  
7757 (2006)

# Mechanism for attenuation of char surface activity

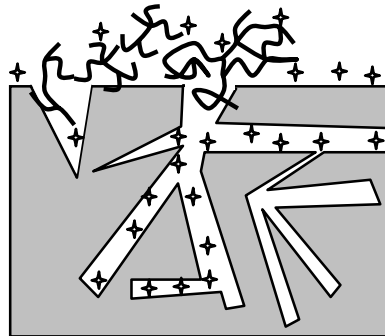
Premise: NOM molecules restricted to external surface and pore throats.

**N<sub>2</sub>, 77 K**



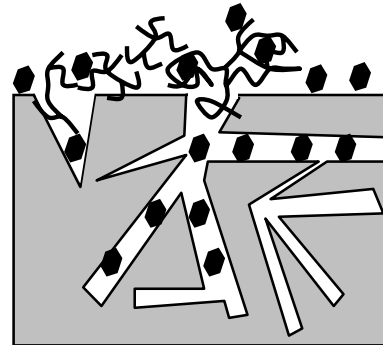
- NOM molecules are stiff; pore throats are blocked
- gives artificially low surface area.

**CO<sub>2</sub>, 273 K**

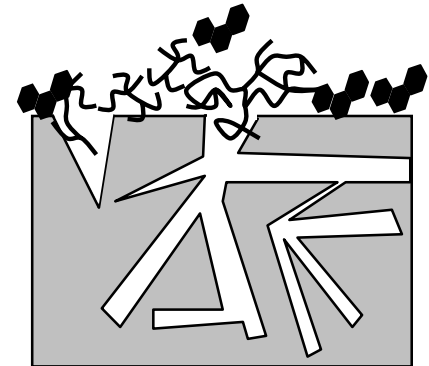


- NOM molecules are more flexible than at 77 K;
- interior pores are more accessible, although rate may be slowed;
- competition by NOM is less important;

**Small organics, 293 K**



**Large organics, 293 K**



- Solute has limited access to internal pores;
- competition by NOM is more important.



# Summary

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- Biochar may reduce the availability of agriculturally important chemicals;
- Humic substances attenuate the surface activity of char;
- Attenuation is likely caused by competitive adsorption & pore-blocking.



# Acknowledgments

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- Seokjoon Kwon
- Donqiang Zhu
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