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

J.J. Pignatello

Department of Soil and Water, Connecticut Agricultural Experiment Station, New Haven
and
Environmental Engineering Program, Yale University, New Haven

Properties of freshly-prepared biomass chars

- 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?

- 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.

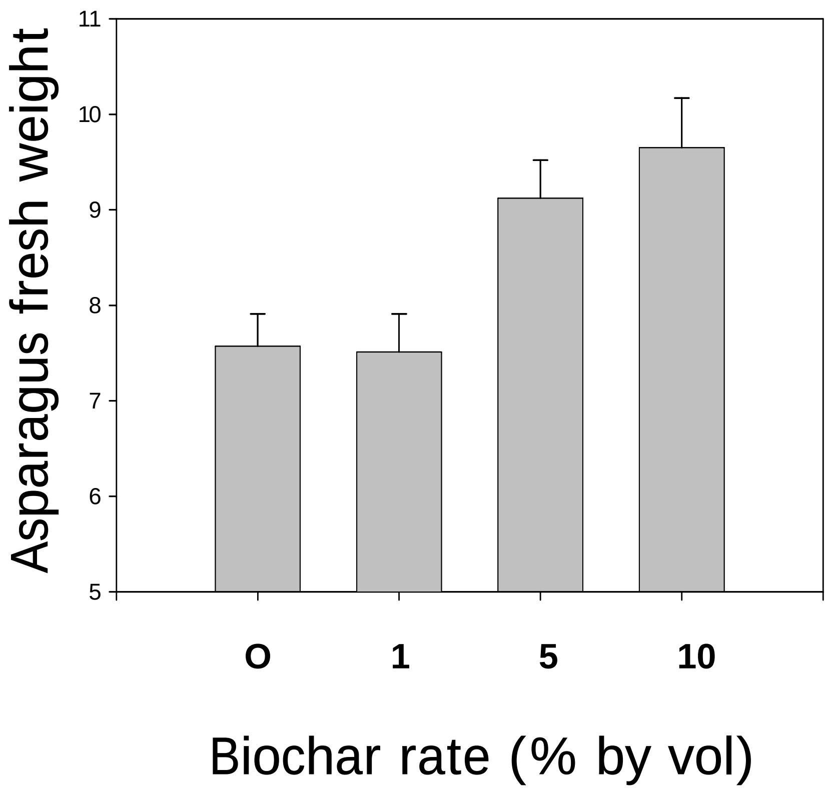
What are the implications for agriculture of adding a strong adsorbent to soil?

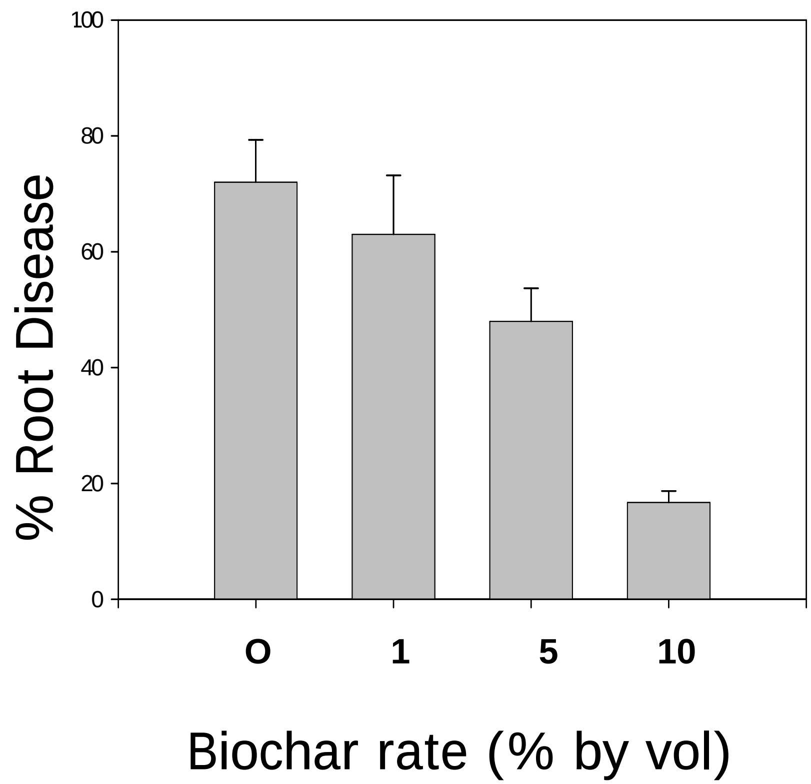
- HOWEVER, humic substances are capable of adsorbing to black carbon;
- Humic substances known to suppress sorption on activated carbon.

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)





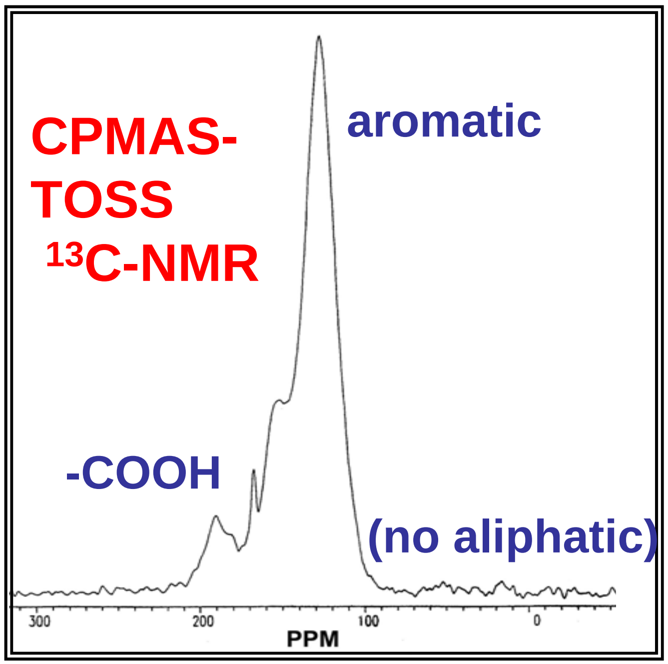
Wade Elmer, Connecticut Agricultural Experiment Station, unpublished

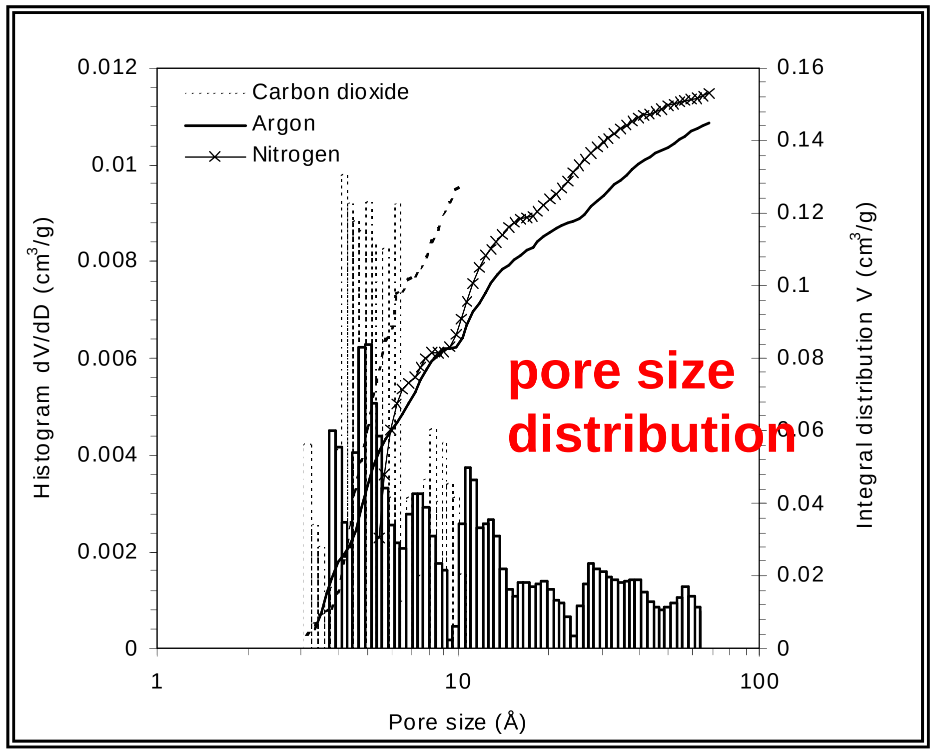
Properties and composition of maple wood char (400 ^{o}C, 2 h, limited oxygen)

% 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_2, Ar, CO_2; NLDFT, MC):

- **Specific Surface Area, 400 m^2/g (N_2)**
- **pore volume, 0.15 cm^3/g**
- **>60% of porosity lies in pores between 4 and 10 Å**
- **>80% of porosity lies in pores between 4 and 20 Å**

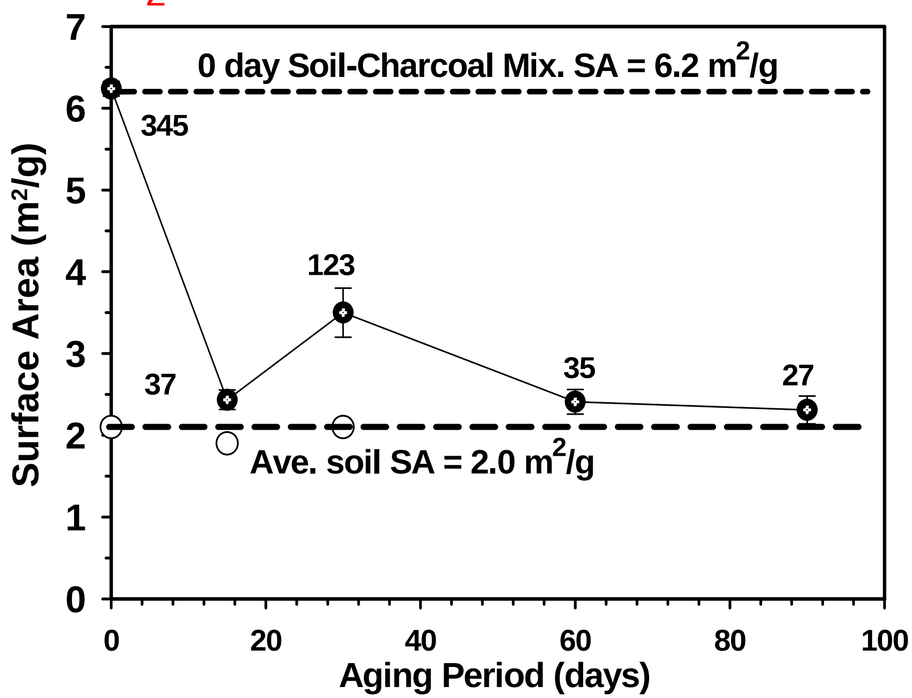




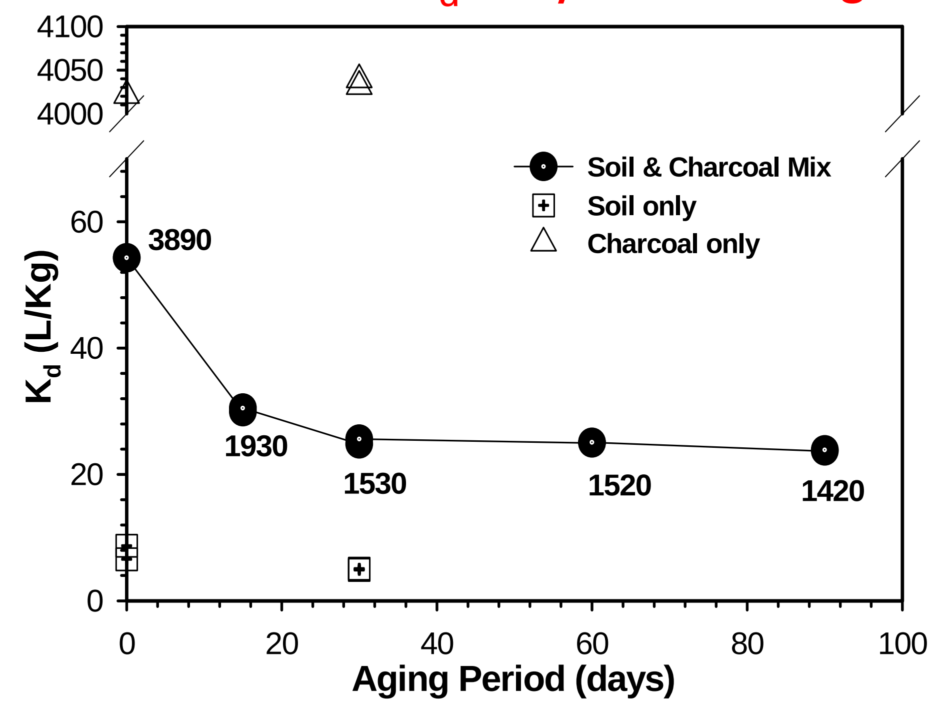
Braida et al. *ES&T, 37*, 409 (2003)

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



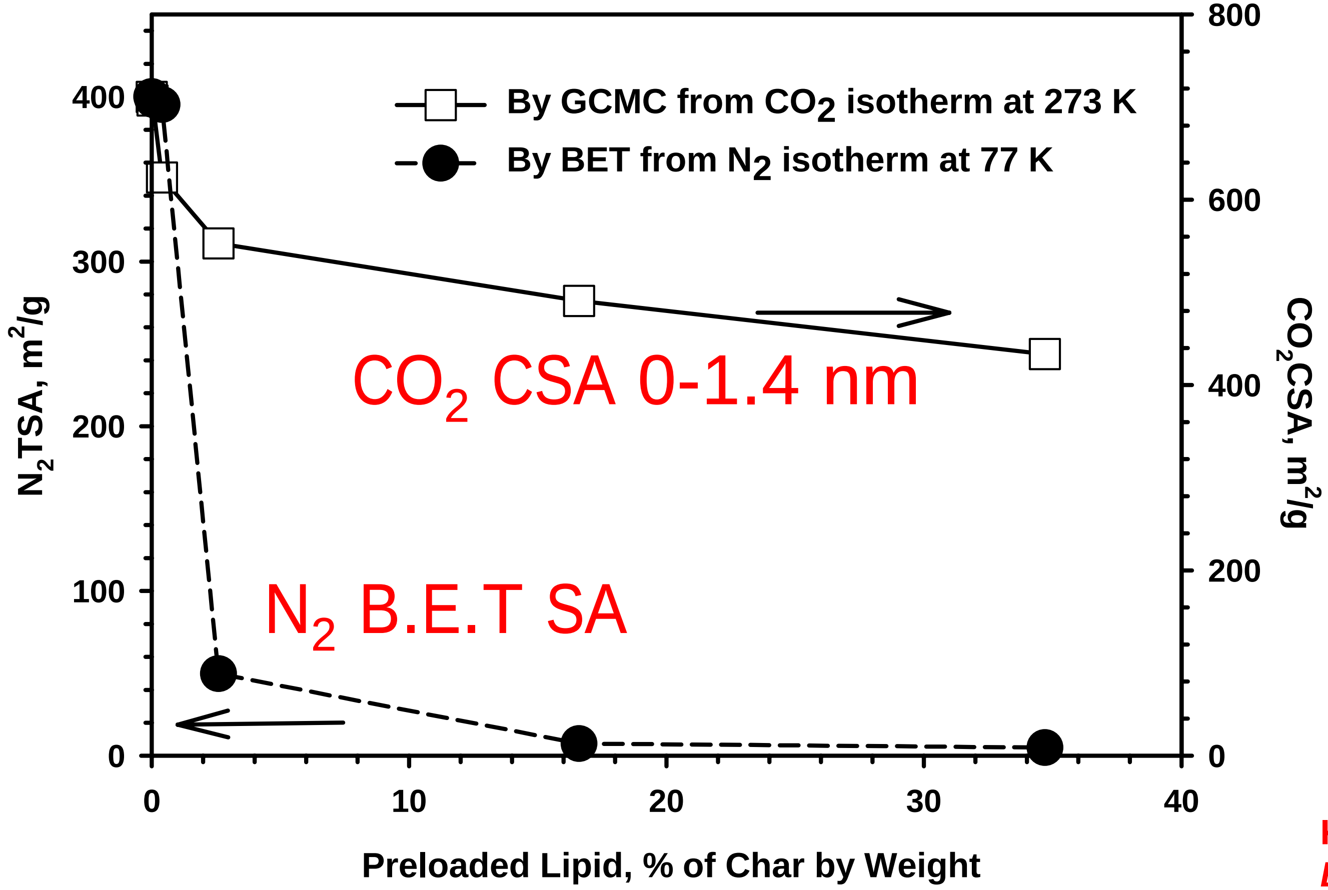
* char-C/OC ratio = 0.05; 45 °C; soil: Terric Haplosaprist, 18.9% OC.

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

Kwon and Pignatello, *ES&T* 39, 7932-7939 (2005)

Surface properties of char after uptake of natural organic substances

humic lipid substances (modeled by triacylglycerides in soybean oil)



Kwon and Pignatello,
ES&T 39, 7932-7939 (2005)

soil humic and fulvic acids

	N_2-B.E.T. TSA, m^2/g		CO_2 CSA, m^2/g	
% OM by wt	sample	char component only (calc)	sample	char component only (calc)
0	400	400	698	698
trace	379	379	651	651
trace (FA)	276	276	586	586
1.5	18	18	250	253
7.0	16	17	237	253
23	14	18	176	220
43	6.3	11	131	207
60	1.4	2.7	99	202
75	0.7	1.1	77	215
100	0.6	--	30	--

char alone → (0)

char filtered from 1000 mg/L DOC soln. (trace, trace (FA))

char-HA solution evaporated to dryness (1.5 – 75)

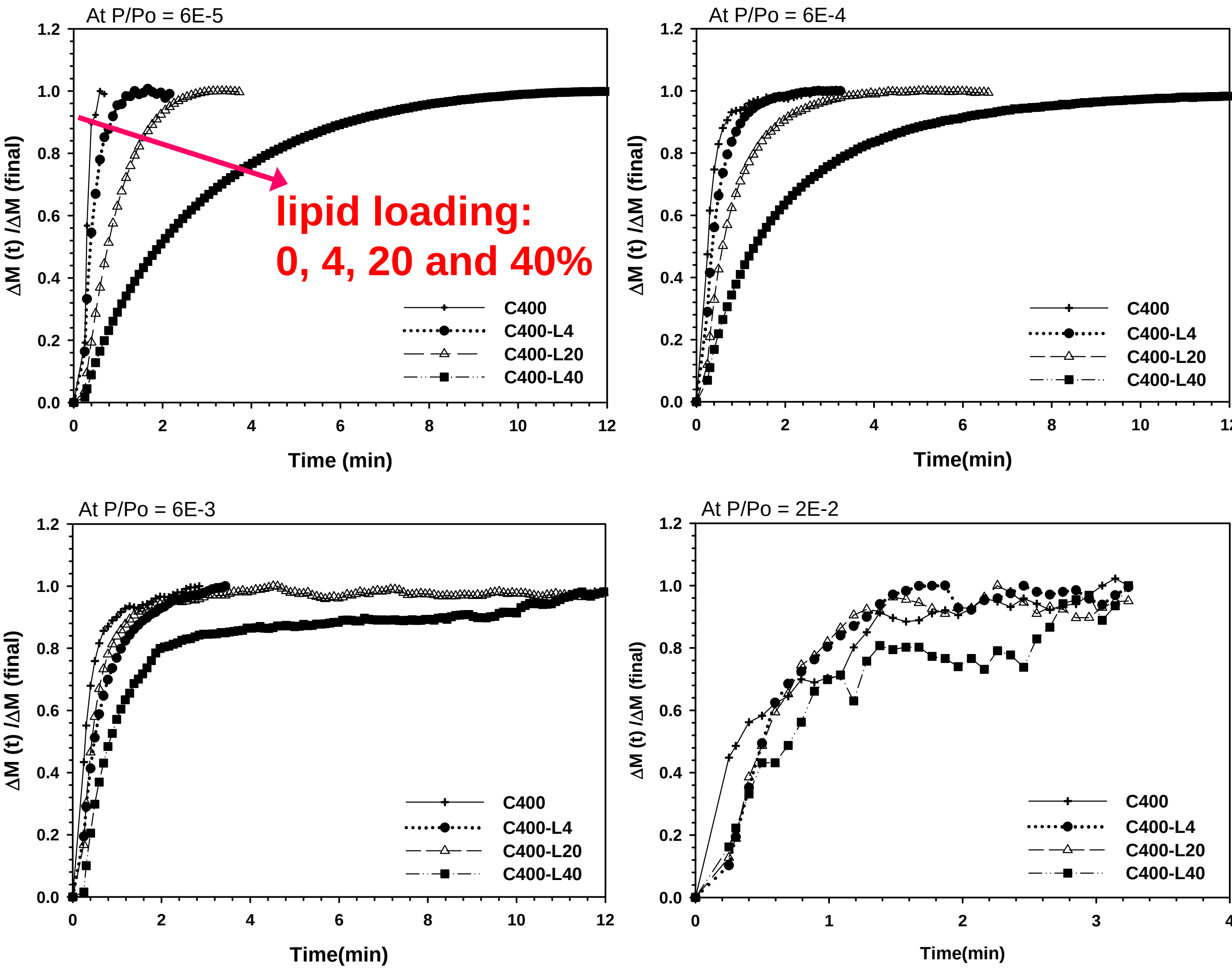
HA alone → (100)

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

Rate of normalized uptake of CO_2 by char and lipid-loaded chars at different pressures (273 K)

@ P/P_0 = 6×10^{-5}

@ P/P_0 = 6×10^{-4}



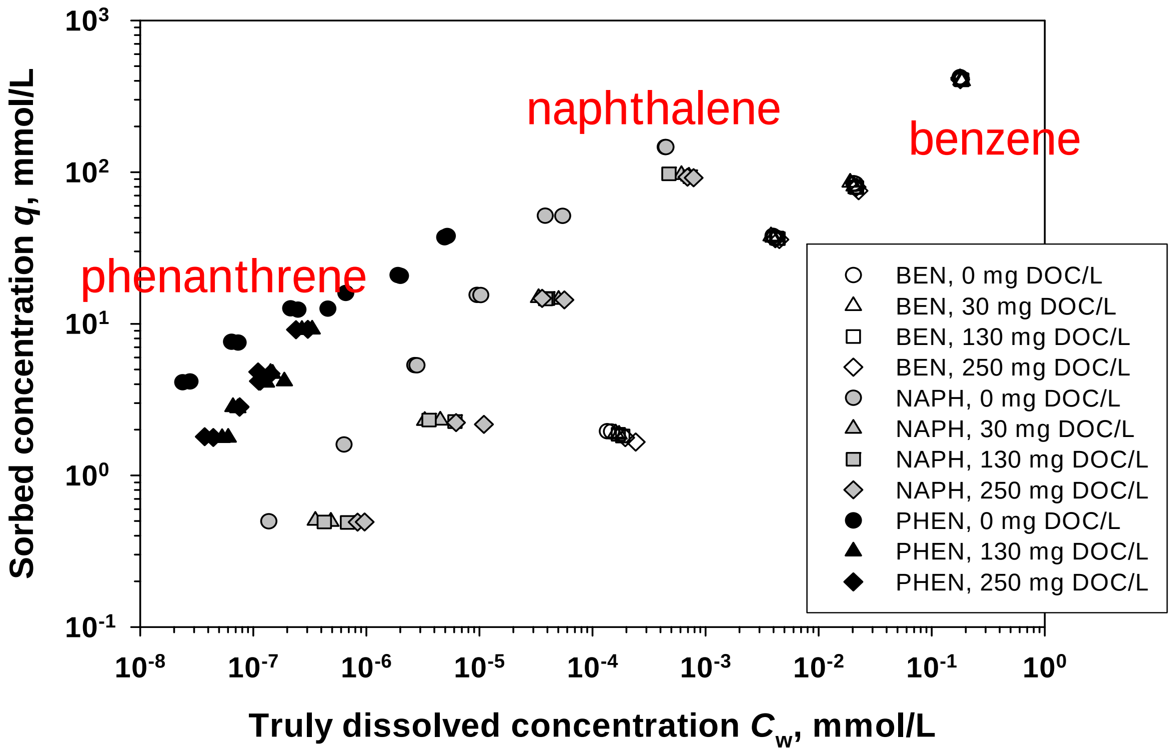
@ P/P_0 = 0.006

@ P/P_0 = 0.02

Kwon and Pignatello, *ES&T* 39, 7932-7939 (2005)

Suppression of adsorption to char by dissolved humic acid

DOC, 0 - 250 mg/L



(adsorption corrected for partitioning to DOC)

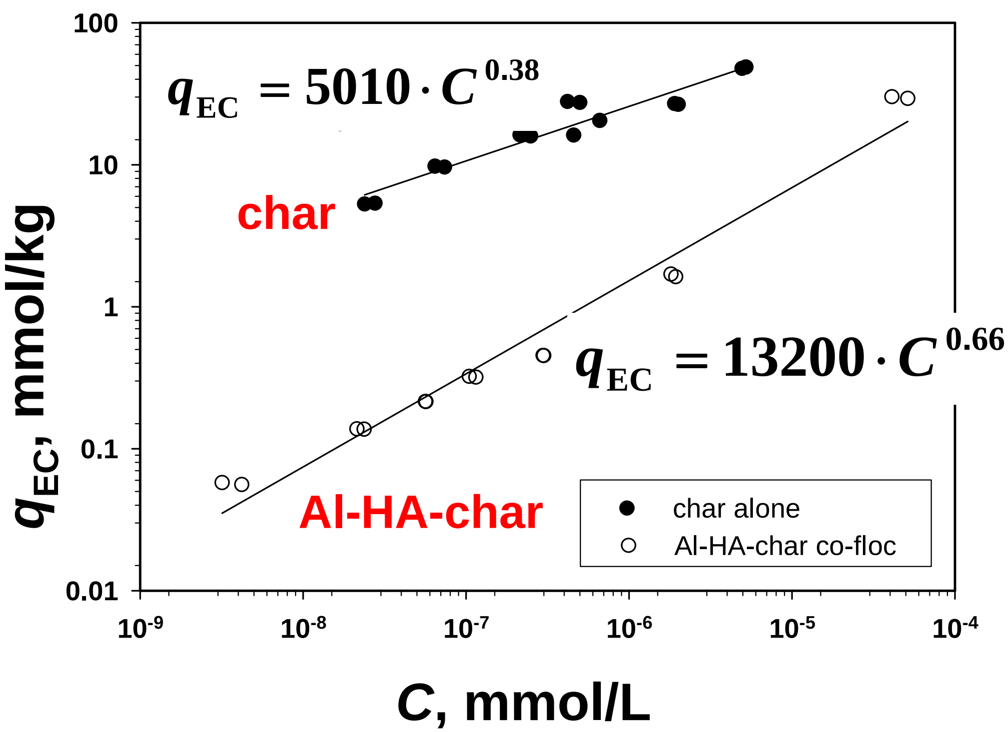
Suppression increases with [DOC] and follows order in solute molecular size (BEN < NAPH < PHEN)

Pignatello, Kwon and Lu, ES&T, 40: 7757 (2006).

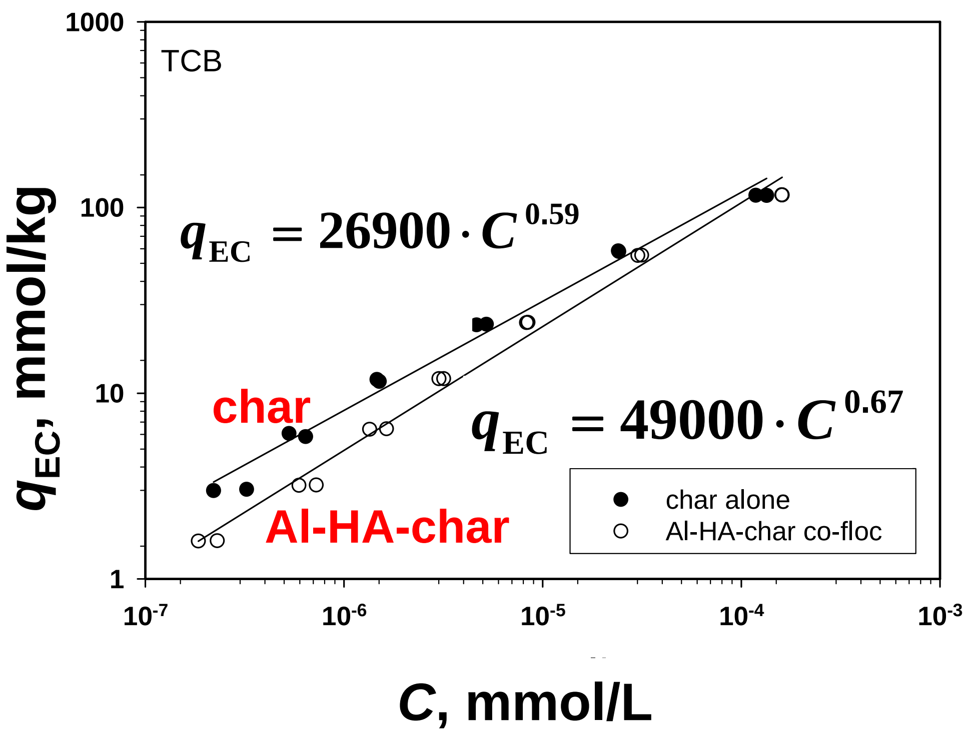
Suppression of adsorption to char by humic acid coatings (as Al^{3+}-HA floc)

Isotherms for sorption on <u>char carbon</u> (sorption to Al^{3+}-HA subtracted out)

phenanthrene



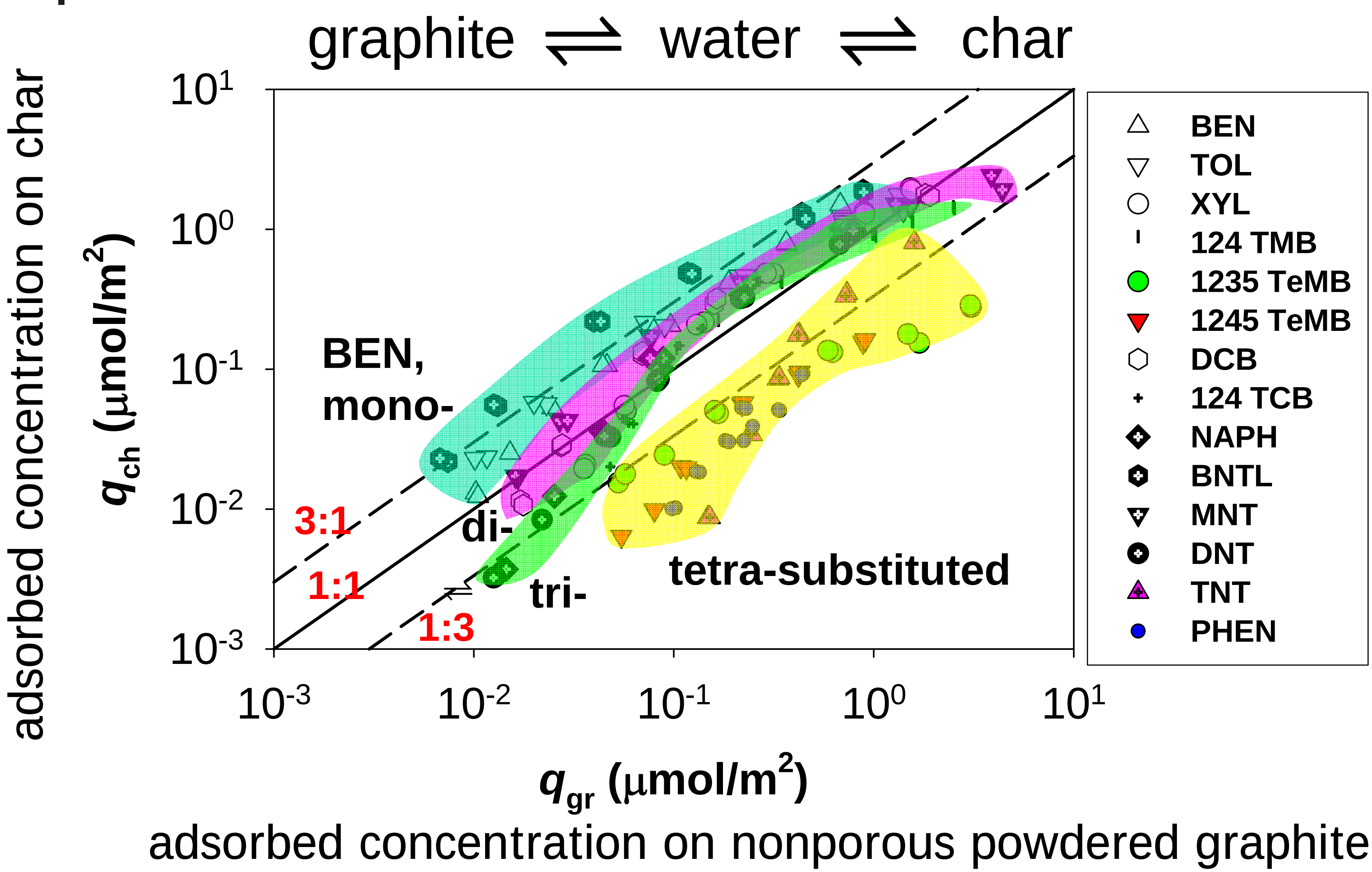
1,2,4-trichlorobenzene



Suppression follows order in molecular size TCB < PHEN

Pignatello, Kwon and Lu, ES&T, 40: 7757 (2006).

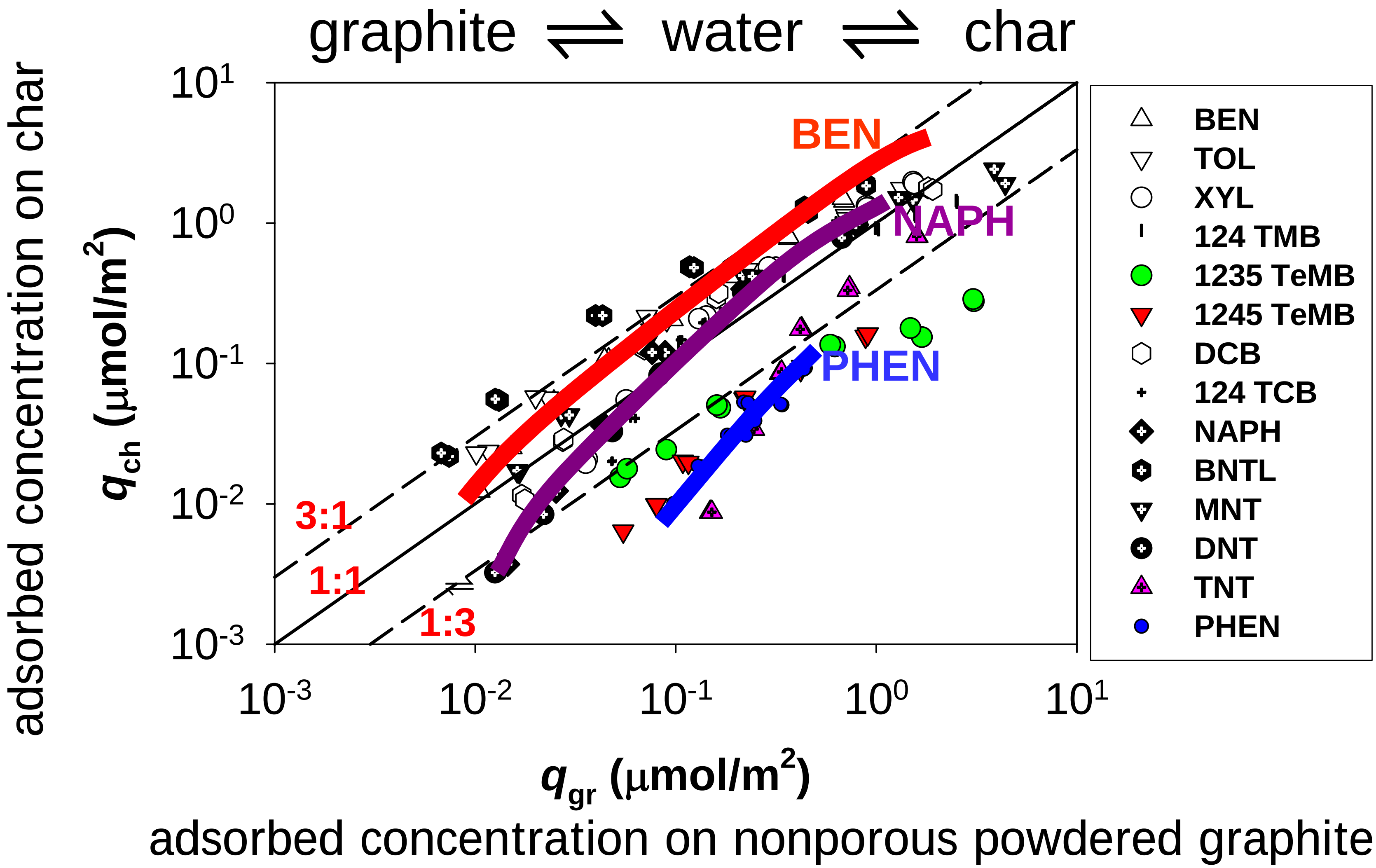
Steric effects in adsorption by char



polar and nonpolar aromatic compounds

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

Steric effects in adsorption by char



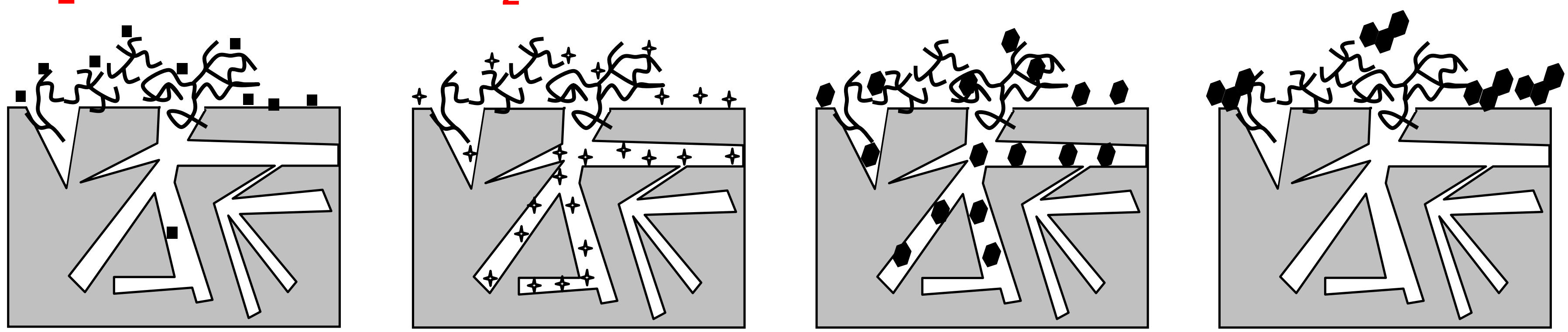
polar and nonpolar aromatic compounds

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_2, 77 K | **CO_2, 273 K** | **Small organics, 293 K** | **Large organics, 293 K**



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

- **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;**

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

Pignatello, Kwon and Lu, ES&T, 40: 7757 (2006).

Summary

- 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

- Seokjoon Kwon
- Donqiang Zhu
- Yeufeng Lu
- Washington Braida
- Wade Elmer
- Peter Ravikovitch
- Alex Neimark
- Baoshan Xing

- NSF