

The Chemistry of Sorption by Black Carbon: The Important Role of Surface Oxides

William P. Ball

Dept. of Geography and Environmental Engineering (DoGEE)
Johns Hopkins University

Co-Authors:

Dr. Hyun Hee Cho (DoGEE)

T. Helen Nguyen (DoGEE)

Billy A. Smith, Kevin A. Wepasnick (Chemistry)

Prof. D. Howard Fairbrother (Chemistry)

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Black Carbon from the Perspective of an Environmental Engineer

Years	Black Carbon in Environmental Engineering	WPB's Professional Interests
~1500 BC to 1900	Adsorption of toxins and color from water by char	none!
~1900-1970	Granular Activated Carbon (GAC) production; Water & wastewater treatment	none!
1970's	Water & wastewater treatment; Refinements in GAC production	GAC in water and wastewater treatment
1980's	All of the above plus: Subsurface remediation; Soot as an air pollutant	GAC in ground water treatment GAC in wastewater reuse
1990's	All of the above plus: Environmental function of BC	Impacts of environmental BC on SOC sorption and diffusion
2000's	BC "sequestration" of toxins; Environmental impacts of carbonaceous nanomaterials	SOC sorption by chars and soots; SOC and heavy metal adsorption by carbon nanotubes (CNTs)

Chemistry of Sorption by Black Carbon

Some General Remarks (take-home messages?)

- Generalizations are difficult; probe studies are important: Sorption is strongly dependent on the *specific* chemical properties of the sorbate and sorbent.
- “BC” sorbents vary widely in their properties: Surface properties and morphology are *strongly* influenced by (1) starting material, (2) formation conditions, and (3) post-formation treatment
- Sorption/desorption rate is important to understand: Diffusion is usually the dominant concern. For small BC particles in sediments, diffusion rates will depend more upon the matrix in which the BC is found than the BC itself

Chemistry of Sorption by Black Carbon

Some Conclusions from Past Work

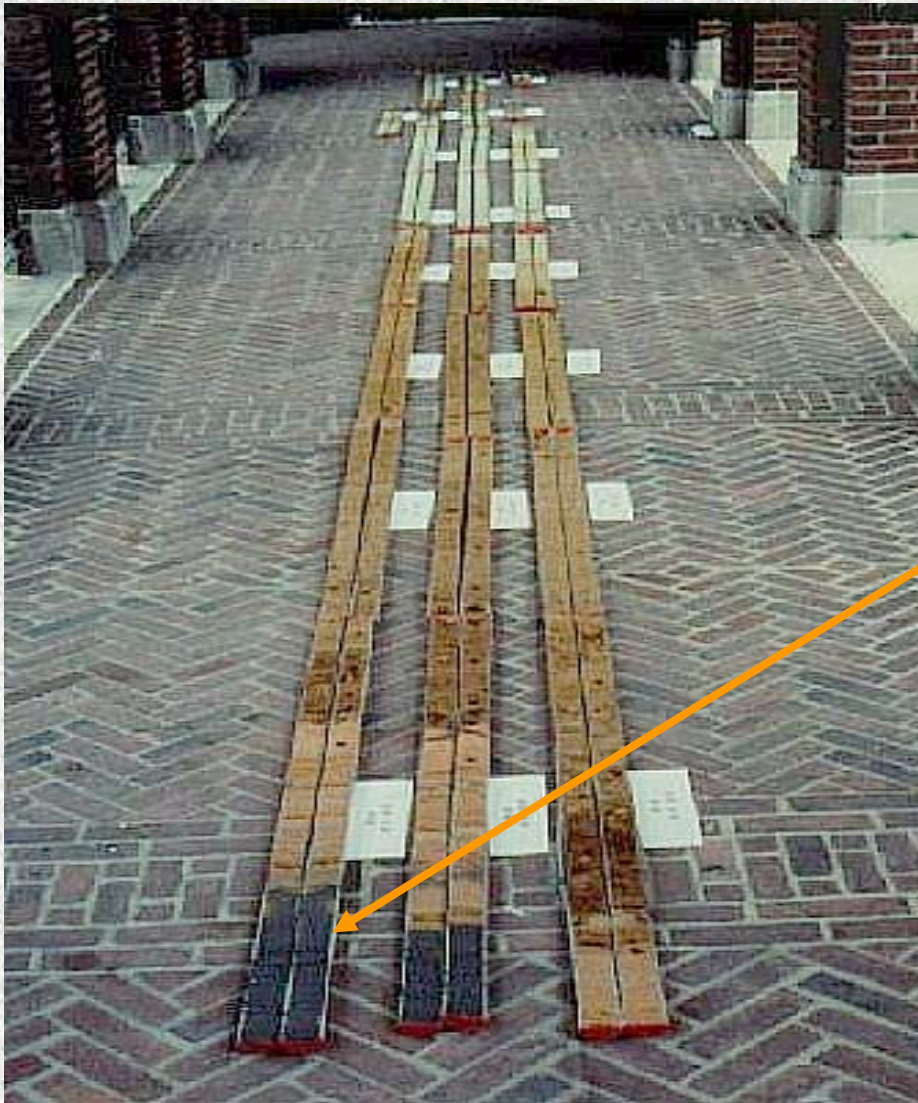
- BC contributions to sorption in sediments/soils are often substantial and sometimes dominant.
- The sorption of SOCs to BC is strong and nonlinear, even for apolar, nonionic compounds: In soils and sediments with BC, we need combined adsorption/absorption models:
 - $q_e = q_{e,ab} + q_{e,ad} = "K_d"C_e$ but $K_d \neq \text{constant}$ (nonlinear)
 $K_d = K_{abs} + K_{ads}$, where K_{ads} = function (concentration, competition)
- Extractable organic phases in soots and char can both inhibit adsorption and foster absorption.
- In many *in situ* soil/sediment matrices, sorption and desorption rates are well described by diffusion models based on the concept of *sorption-retarded aqueous diffusion* - i.e., rates inversely proportional to sorption K_d .

Chemistry of Sorption by Black Carbon

Some Conclusions from Recent Work

- The sorption of aqueous solutes by BC will be strongly influenced by the level of BC surface oxidation:
 - surface oxygen functional groups cause reduced affinity and capacity for apolar HOCs (e.g., naphthalene, phenanthrene, trichlorobenzene)
 - some surface oxide functional groups (notably COOH) cause increased affinity and capacity for cationic heavy metals (e.g. Zn^{2+} , Cd^{2+})
- New methods of surface characterization provide new means of quantifying and understanding these effects
- Studies with well characterized carbonaceous surfaces (e.g. CNTs) are beginning to provide new insights

"BC contributions to sorption in sediments/soils
are often substantial and sometimes dominant"
Example: Dover AFB aquitard material



Sub-sampling of cores was used to obtain total in-situ concentrations of TCE and PCE.
(immediately after splitting, from saran-covered core half) and preserved in methanol for subsequent extraction and analysis)

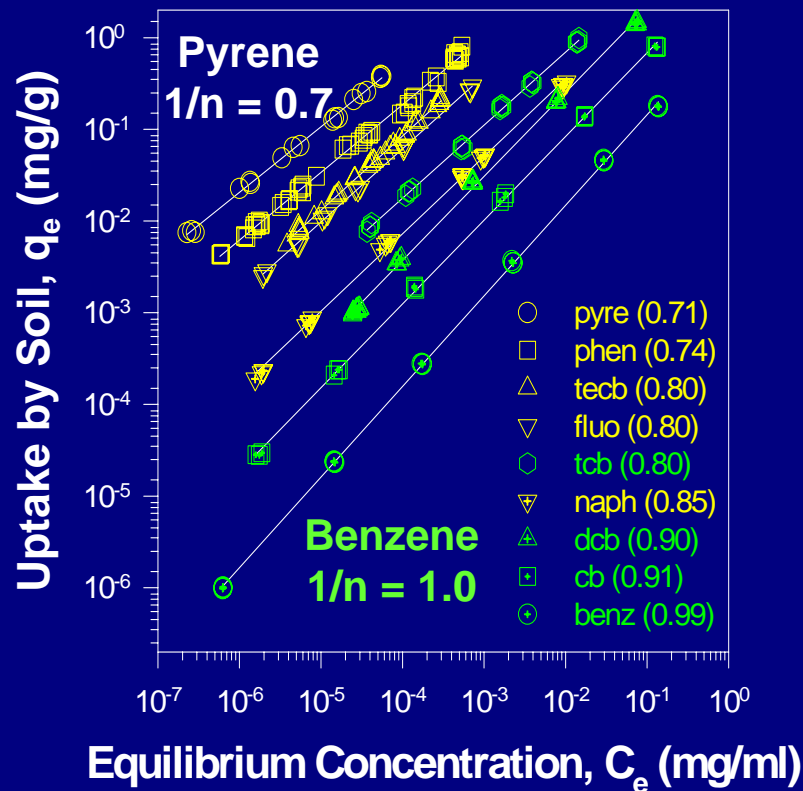
Samples of the aquitard material were taken and used for sorption isotherm studies

Xia et al., *GWMR*, 1997)

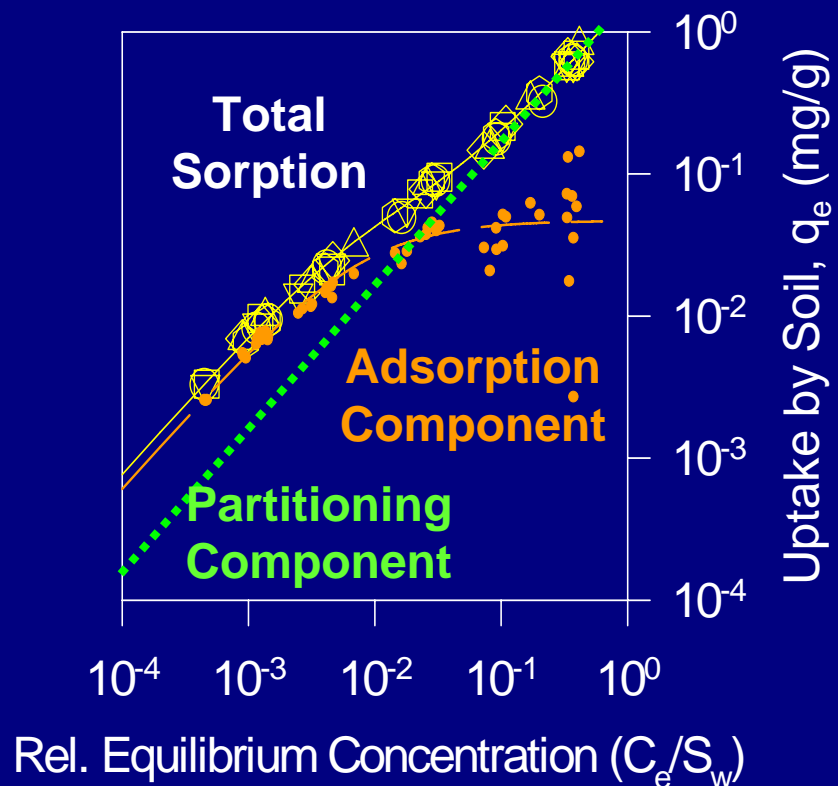
BC contributions to sorption in sediments/soils

Example: Dover AFB aquitard material

Freundlich Isotherms:



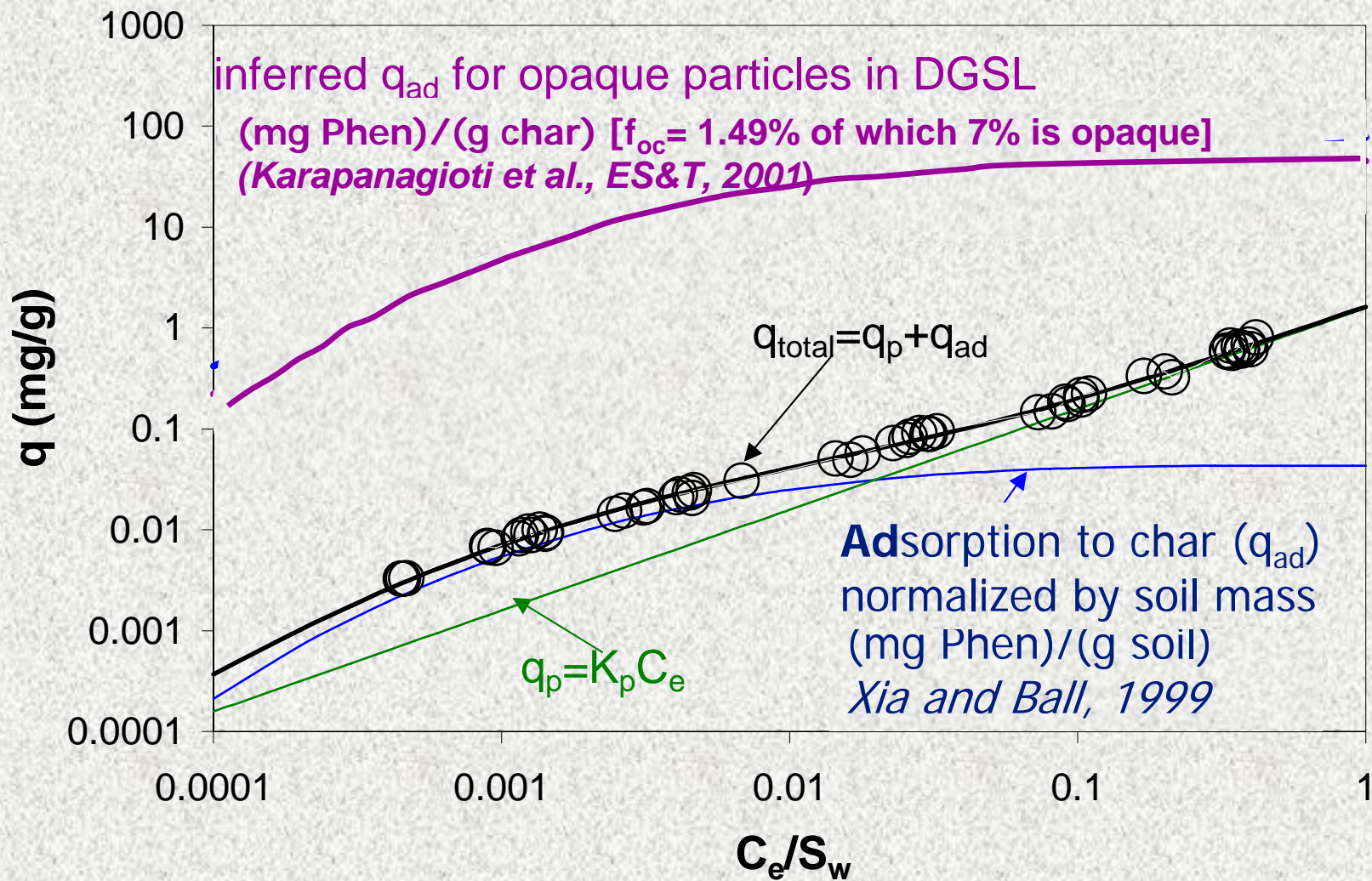
Adsorption + Partitioning (Polanyi-based model; PAHs)



Xia and Ball, *ES&T* 33:262 (1999)

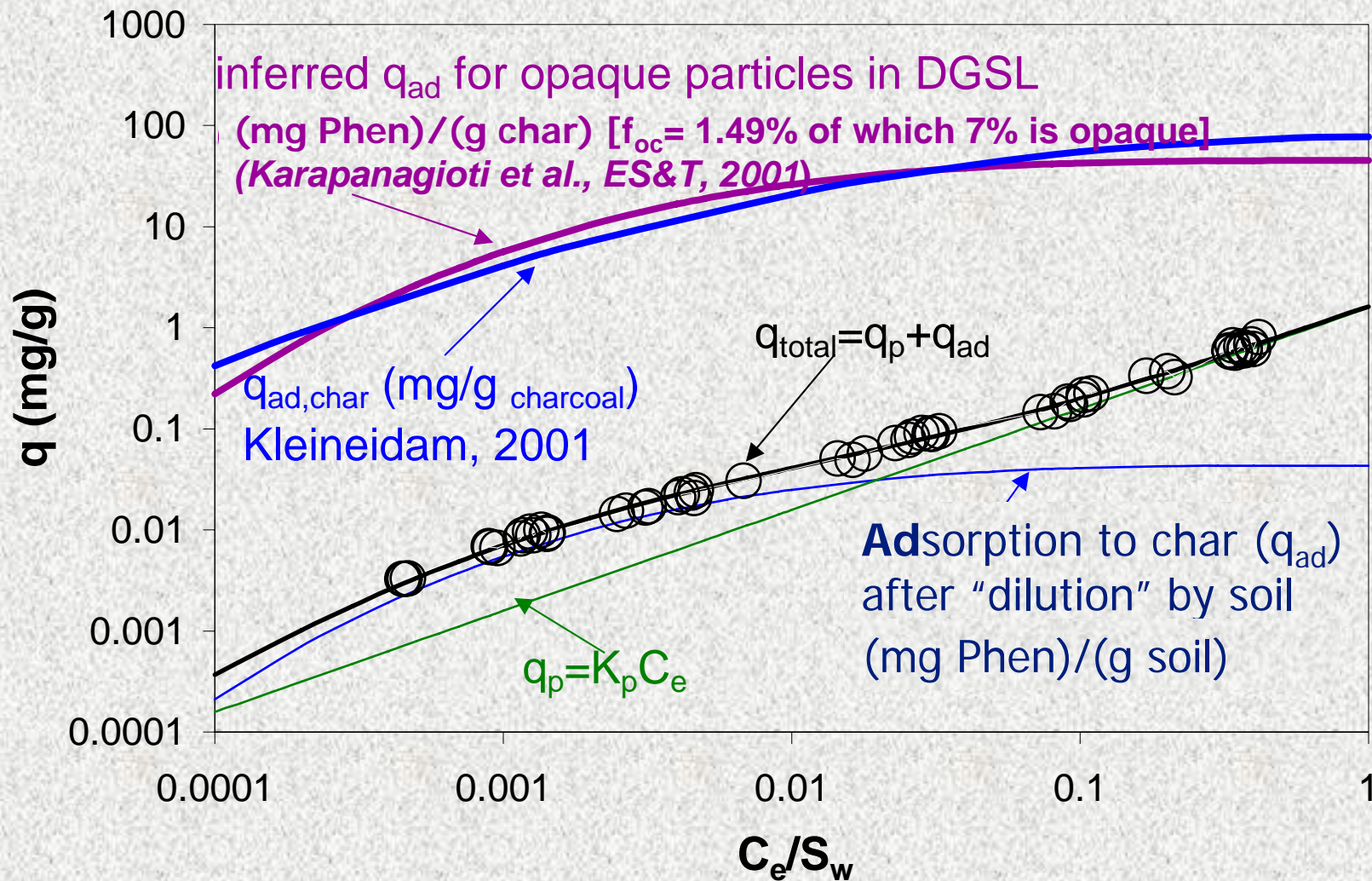
"In soils and sediments with BC, we need combined adsorption/absorption models" ($q_e = q_{e,ab} + q_{e,ad}$)
Example: Dover AFB aquitard material

(Xia and Ball, *ES&T*, 1998; Allen-King et al., *Adv. Water Res.*, 2002)

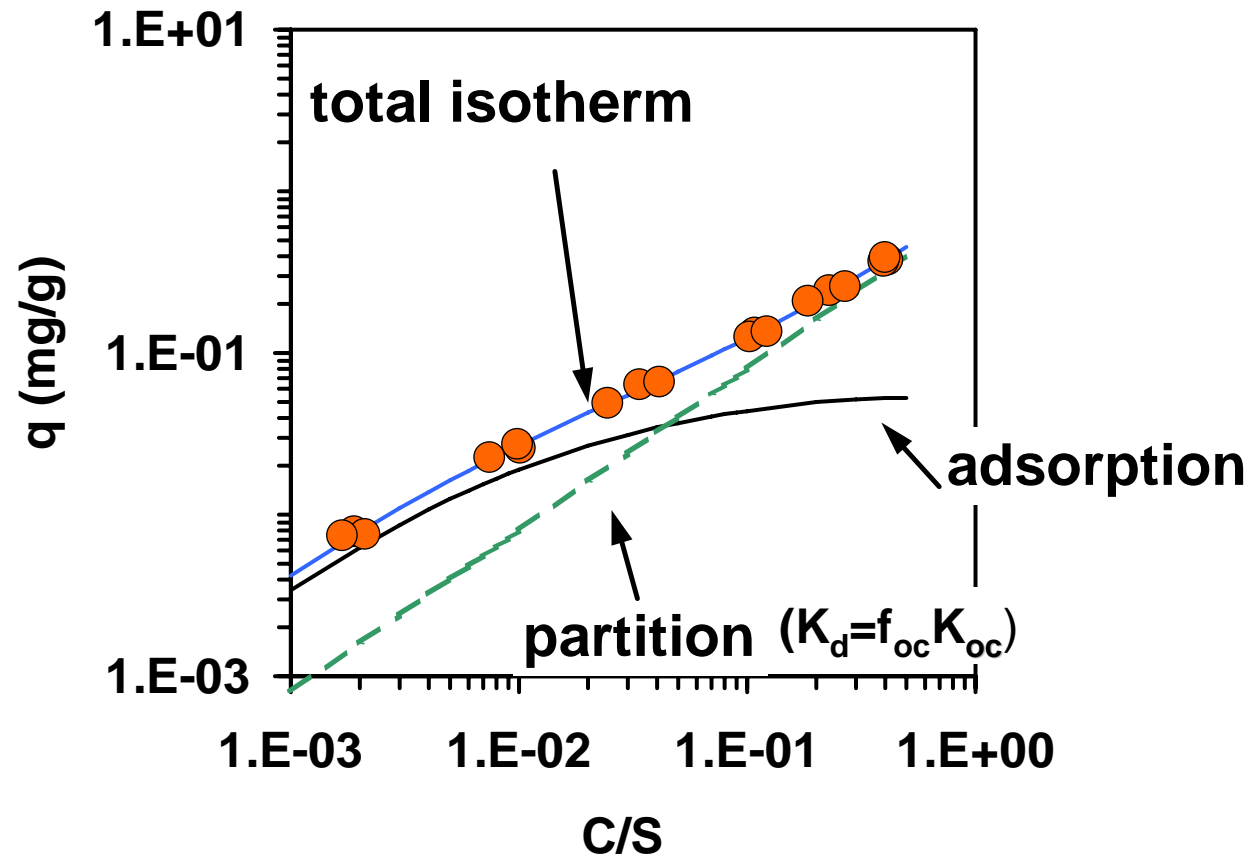


“In soils and sediments with BC, we need combined adsorption/absorption models” ($q_e = q_{e,ab} + q_{e,ad}$)
 Example: Dover AFB aquitard material

(Xia and Ball, *ES&T*, 1998; Allen-King et al., *Adv. Water Res.*, 2002)



"In soils and sediments with BC, we need combined adsorption/absorption models" ($q_e = q_{e,ab} + q_{e,ad}$)
Example: Dover AFB aquitard material



Model prediction for pyrene sorption using parameters scaled from phenanthrene isotherm modeling

Environmentally Occurring Black Carbon



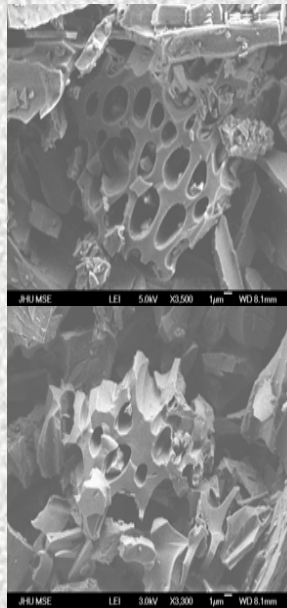
K. Soper photo, www.wildfire.com



www.ars.usda.gov/is/AR/archive/apr98/weed0498.htm

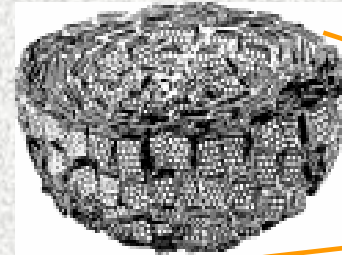


NC1 = natural char from pitch pine (*Pinus rigida*) collected after a prescribed burn in the Lebanon State Forest of the New Jersey Pinelands.



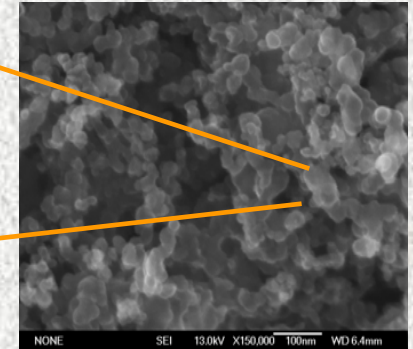
(Nguyen et al., *ES&T*, 41:1212, 2007)

~20 nm



soot structure; Heidenreich et al., *J. Applied Crystall.*, 1968

~1 µm



SRM 2975 diesel soot

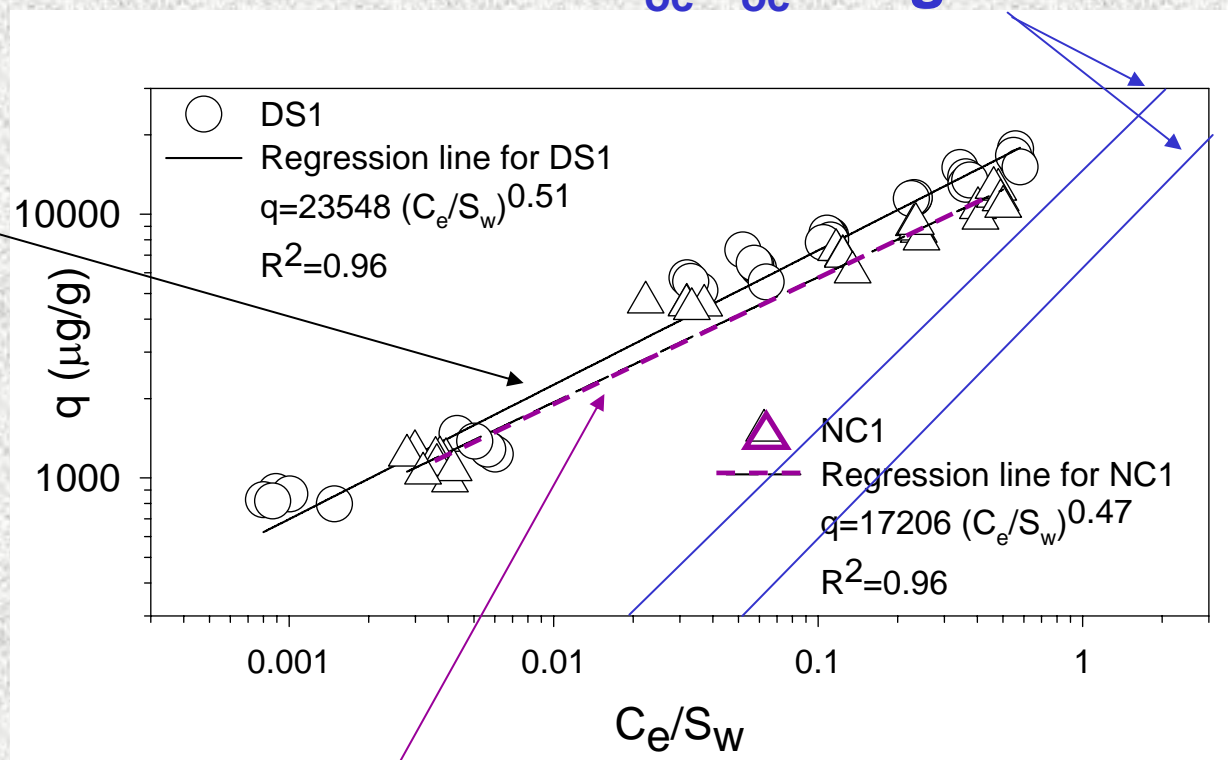
(Nguyen et al., *ES&T*, 38:3595, 2004)

“The sorption of SOCs to BC is strong and nonlinear,
even for apolar, nonionic compounds”

Example: Phenanthrene Adsorption by Wood Char and Diesel Soot
(Nguyen et al., *ES&T*, 2004, 2006, 2007)

$f_{oc} K_{oc}$ range

**DS1 = Diesel soot
SRM 2975
(SA = 127 m²/g)**



**NC1 = Natural Wood Char
(SA = 8.8 m²/g, but SA = 310 m²/g after 10 hrs at 450°C under N₂)**

“Extractable organic phases in soots and char can both inhibit adsorption and foster absorption”

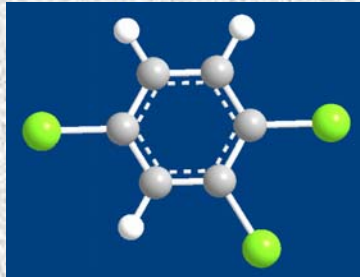
(Nguyen et al., *ES&T*, 2006, 2007)

Studied soots

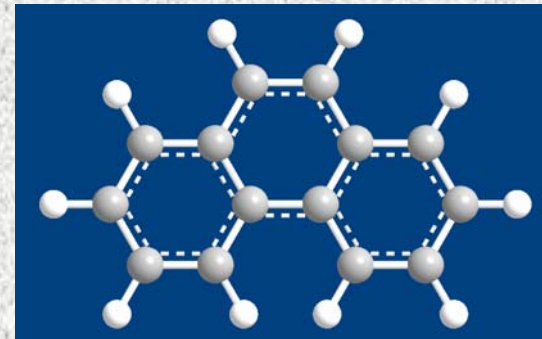
- Diesel soot SRM 1650b (extractable f_{op} = 20%)
- Diesel soot SRM 2975 & hexane soot (extractable f_{op} = 2%)
- Natural char NC1
- NC1 after Soxhlet extraction (f_{op} removal; CHCl_2 at 140°C for 48 hrs)

Studied chemicals

1,2,4-trichlorobenzene (TCB)

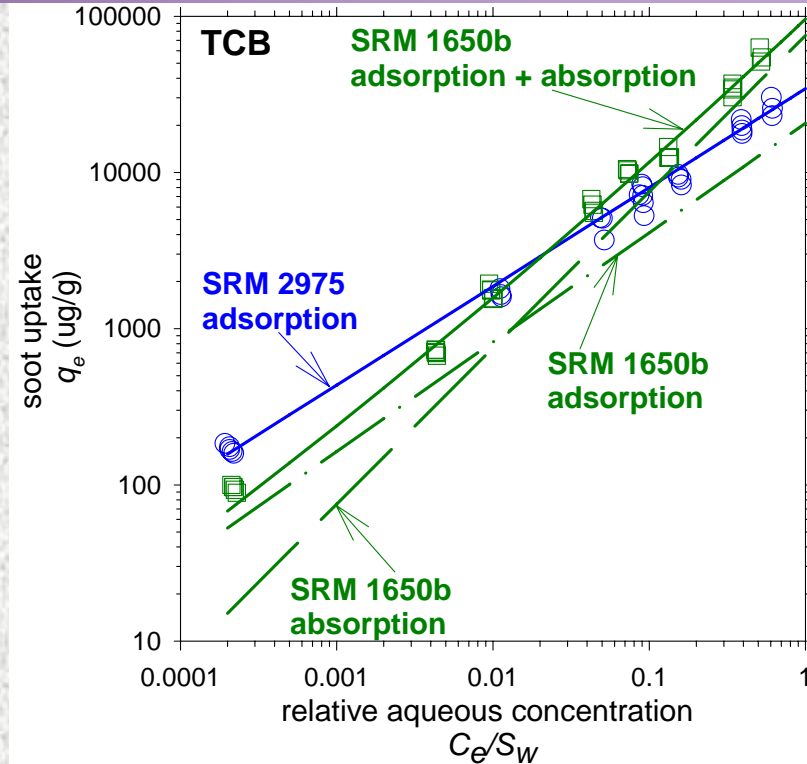
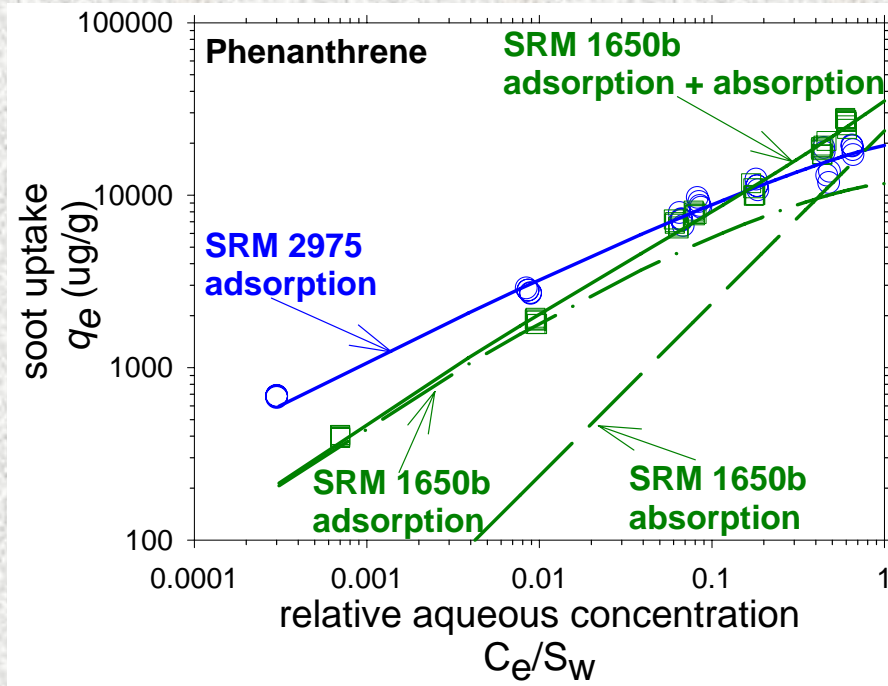


Phenanthrene



“Extractable organic phases in soots and char can both inhibit adsorption and foster absorption”

(Nguyen et al., *ES&T*, 2004, 2006)



Modeling partition with the extractable organic phase of SRM 1650b:

with $\gamma_{op}=1$ for phenanthrene in the f_{op} , we find $MW_{op} = 316$ g/mol
(vs. 200-300 g/mol from experimental data; Apicella *et al.*, 2004)

with $MW_{op} = 316$, we find $\gamma_{op}=1.52$ for TCB

(vs. 1.27 for substituted benzene in coal tar; Peters *et al.*, 1999)

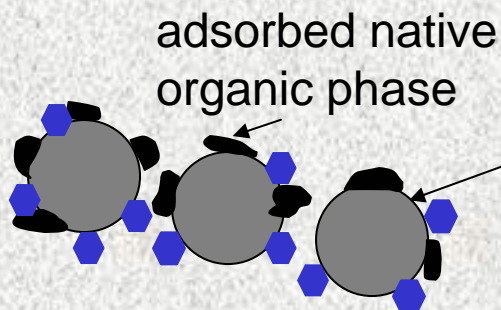
“Extractable organic phases in soots and char can both inhibit adsorption and foster absorption”

(Nguyen et al., *ES&T*, 40:2958, 2006)

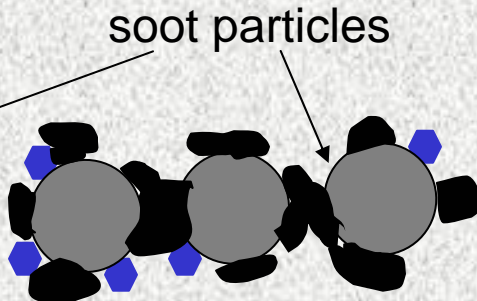
- **SRM 2975 (NIST Ref Mat'l)**
(Nguyen et al., *ES&T*, 2006)
- **Hexane soot**
(Nguyen et al., *ES&T*, 2006)
- **Lampblacks CA-2 & CA-5**
(Hong et al., *ES&T*, 2003)

SRM 1650b (NIST Ref Mat'l)
(Nguyen et al., *ES&T*, 2006)

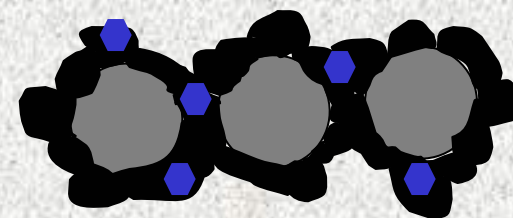
**Lampblacks CA-10,
CA-17 & CA-18**
(Hong et al., *ES&T*, 2003)



ADsorption to graphenic surfaces dominates sorption at all concentrations



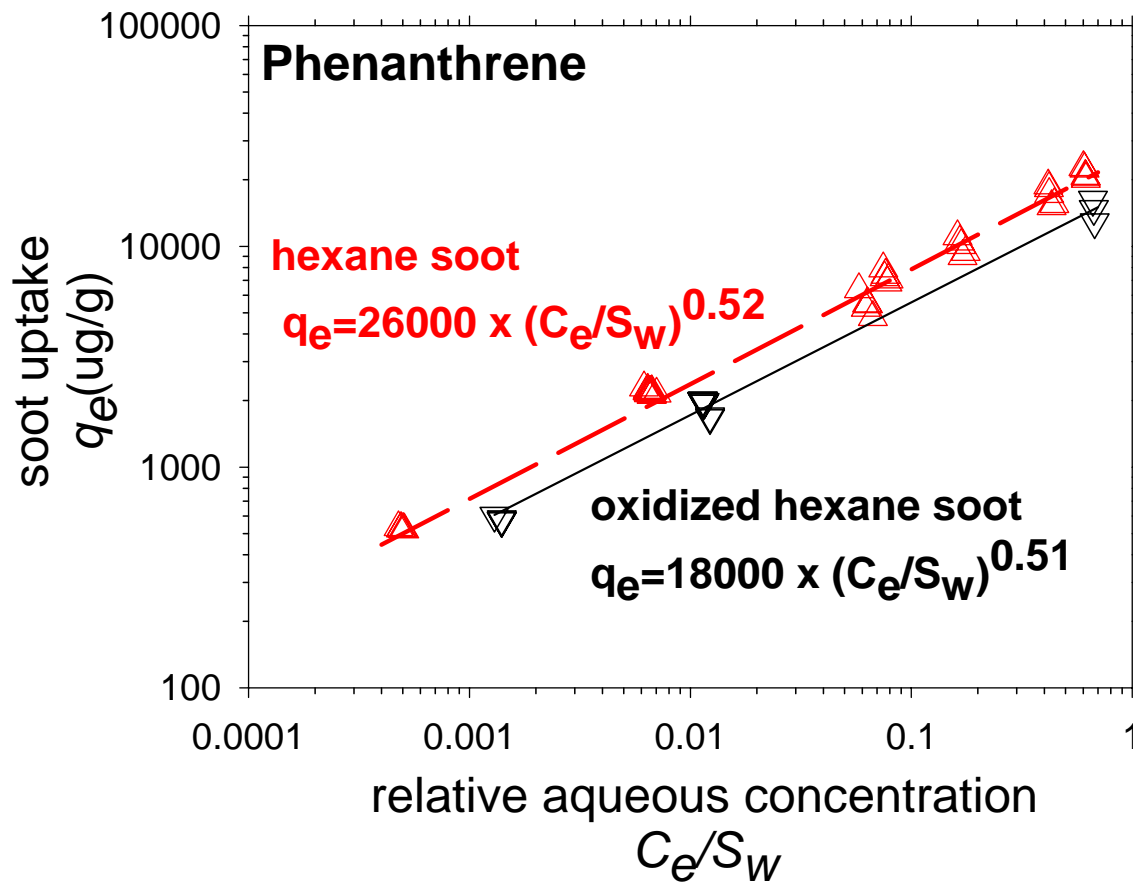
ADsorption and **AB**sorption both play roles. Adsorption dominates only at the lowest relative concentrations.



ABsorption to the native organic phase is significant at all concentrations.

“The sorption of aqueous solutes by BC will be strongly influenced by the level of BC surface oxidation”

(Nguyen et al., *ES&T*, 40:2958, 2006)



O/C Results based on X-ray photoelectron spectroscopy (XPS):

hexane soot:

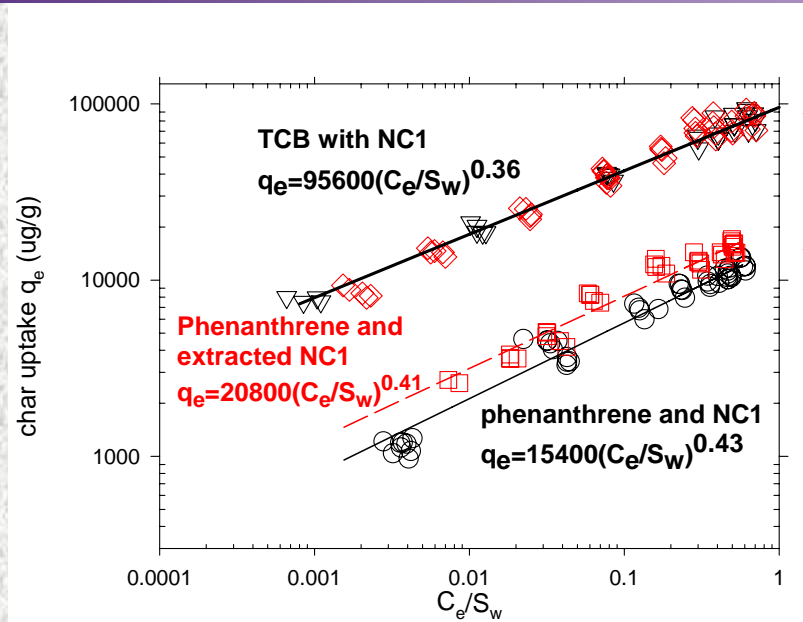
O/C = 0.10

oxidized hexane soot:

O/C = 0.20

"Extractable organic phases in soots and char can both inhibit adsorption and foster absorption"

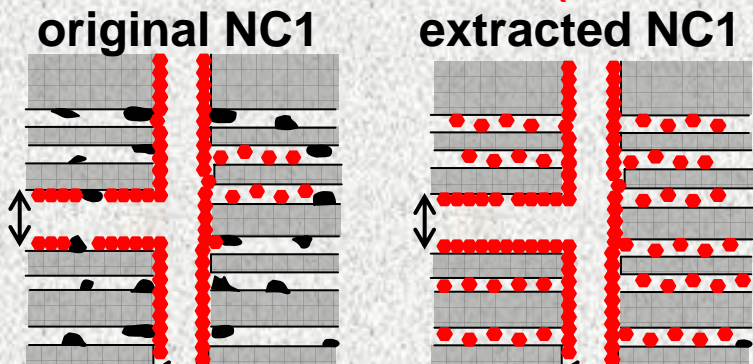
(Nguyen et al., *ES&T*, 41:1212 2007)



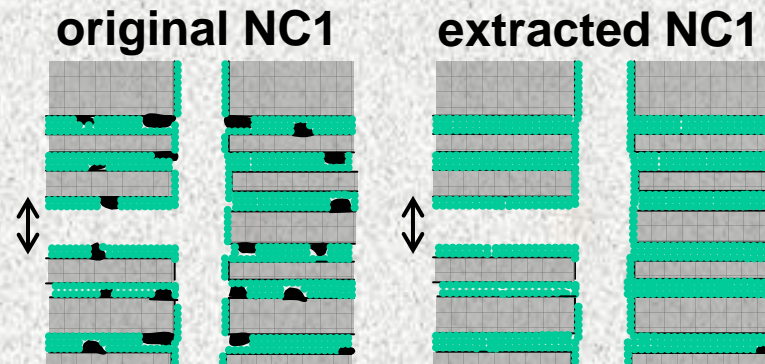
← Trichlorobenzene

← Phenanthrene

Phenanthrene sorption as with NC1 and with extracted NC1 (as solid?)



Trichlorobenzene sorption with NC1 and with extracted NC1 (as liquid?)

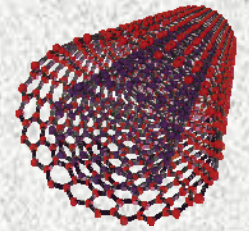


Studies with carbon nanotubes

WHY?

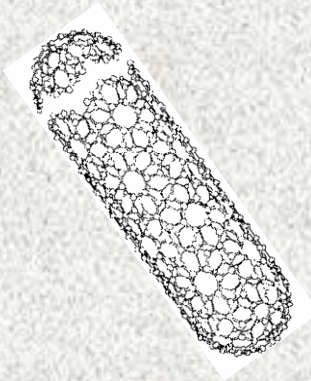
- Emerging contaminants
(can be stable in water with surface modification);
- Possible facilitated transport of sorbed contaminants
("Trojan Horse effect")
- Potential for environmental application
(disinfectant properties; membranes; sorbents)
- Surface structure can be reproducibly modified and readily characterized for the study of solute adsorption by BC materials

Carbon nanotubes (CNTs) consist of one or more graphene sheets rolled into a long, thin, and hollow cylinder.

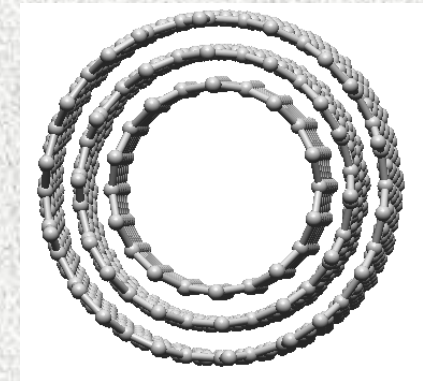


Material Properties

- ✓ Small Size
- ✓ Large Surface Area
- ✓ High Mechanical Strength
- ✓ High Electrical Conductivity



Single-Walled Carbon Nanotube (SWCNT)

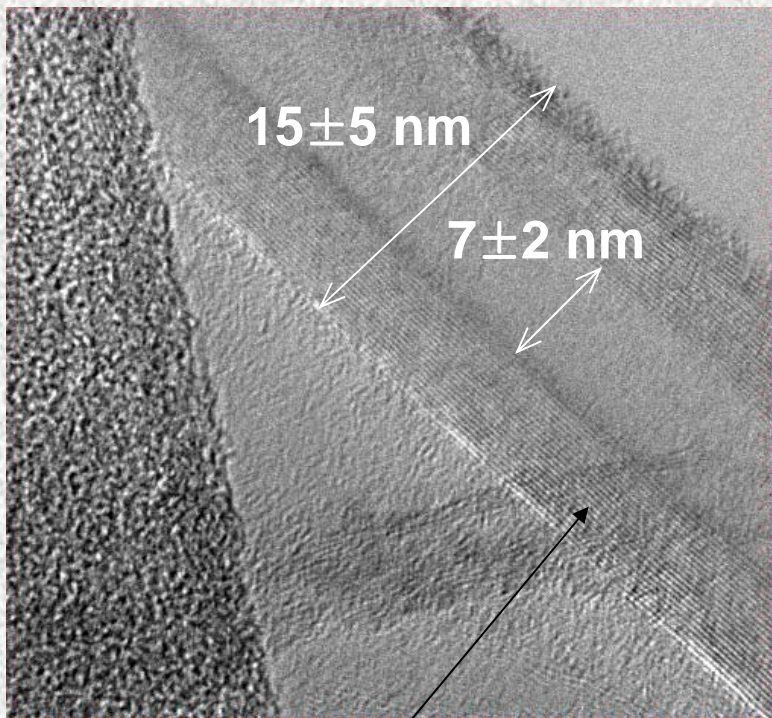


Multi-Walled Carbon Nanotubes (MWCNT)

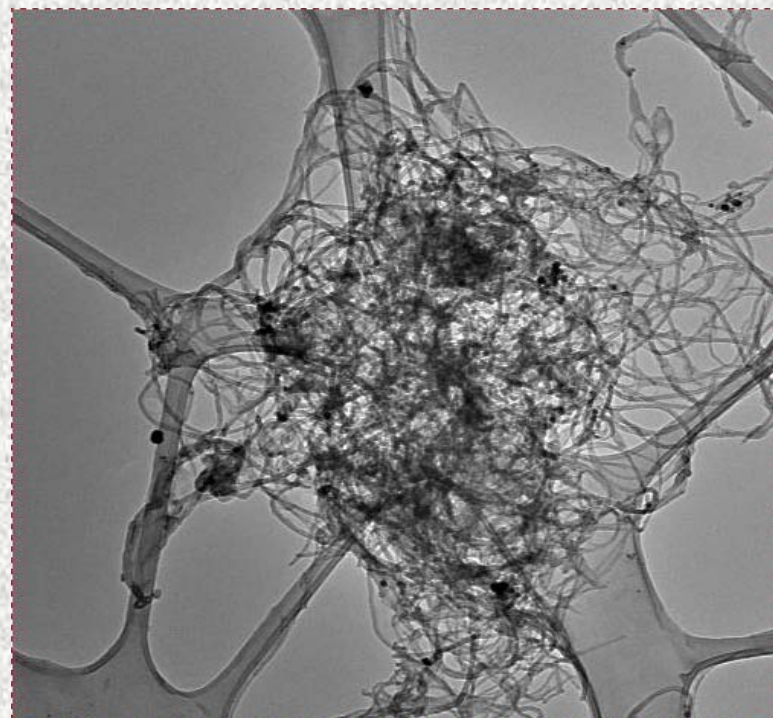
Annual production rate: MWCNTs > SWCNTs

The global annual production of multi-walled CNTs was 100 tons in 2004 and is expected to soon exceed 250 tons.

TEM images of MWCNTs used in our study



Multiwall CNTs



CNTs aggregates

Selected Structural Properties of Carbonaceous Materials

	5MWCNT	20MWCNT	NC1	F400
Outer DI (nm)	15±5	15±5	-	-
Inner DI (nm)	7±2	7±2	-	-
Length (μm)	1-5	5-20	-	-
Purity (%)	95+	95+	-	-
Surface oxides (%)	3.3	2.1	23 ^a	8 ^a
C (%)	98.9	98.9	79 ^b	89 ^c
Surface Area (m ² /g)	283	270	46 ^b	1,004

↓
few capped

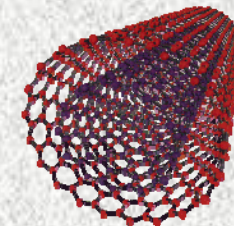
↓
most capped

^a from Langley et al., 2006

^b from Nguyen et al., 2007

^c from Chingombe et al., 2006

Surface Oxidation of Carbon Nanotubes



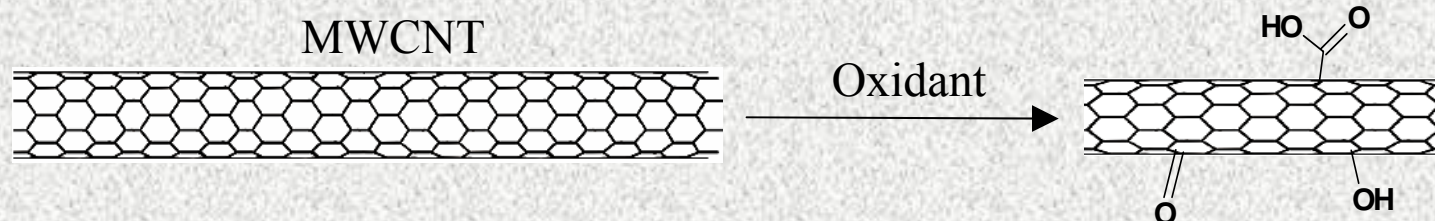
Results from:

- Deliberate oxidative treatment for
 - Surface functionalization
 - Purification (e.g. removal of metals and amorphous C)
- Incidental environmental exposure to oxidants
 - Photolysis
 - Ozonation

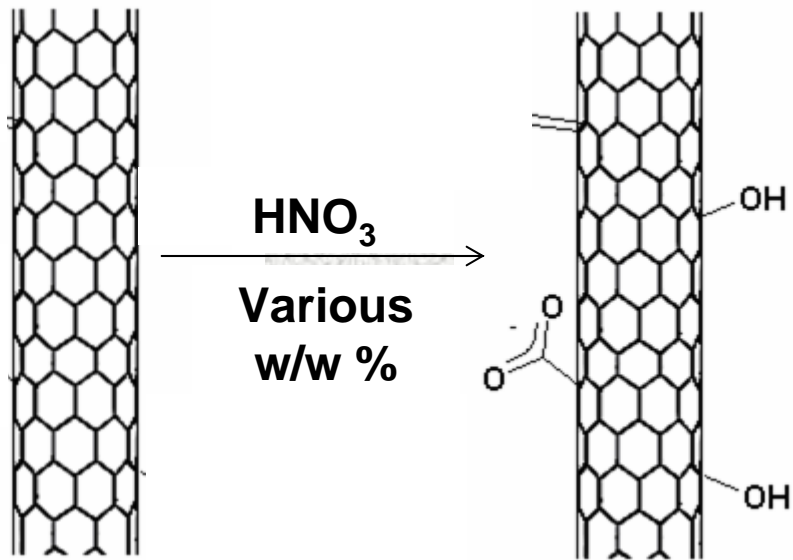
Oxidants

- KMnO_4 • H_2O_2 • H_2SO_4
- **HNO_3** • O_3 • $\text{H}_2\text{SO}_4/\text{HNO}_3$

↑
Prevalent Oxidative Method



Influence of Oxidizing Conditions

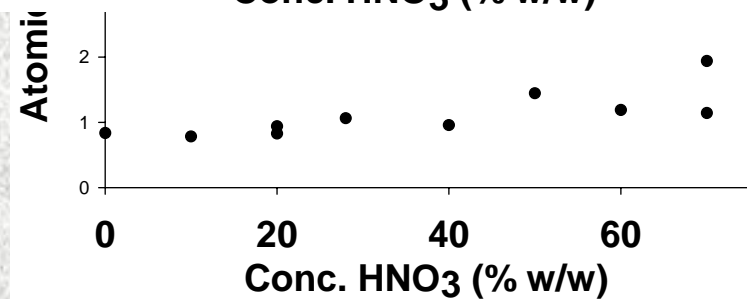
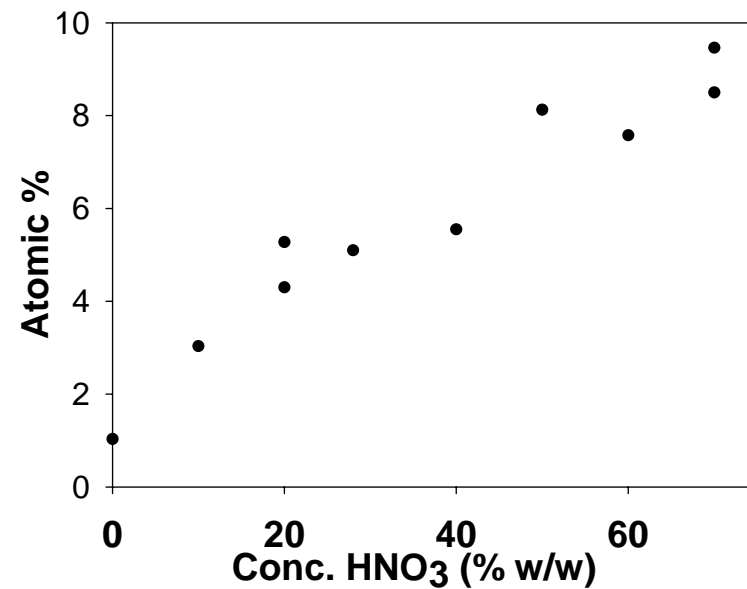


Fairbrother et al., in *Nanoscience and Nanotechnology*, J. Wiley & Sons, 2008.

Functional Groups



Total Oxygen



Comparison of CNT sorption isotherms with other carbonaceous materials (naphthalene)

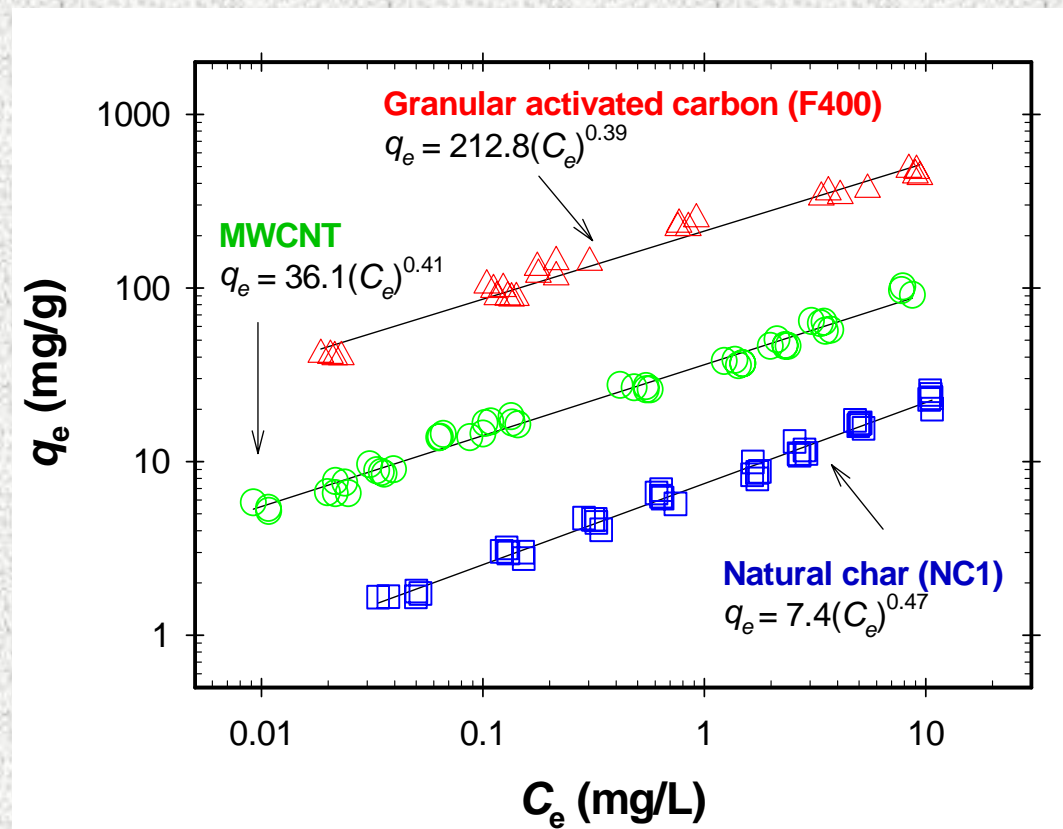
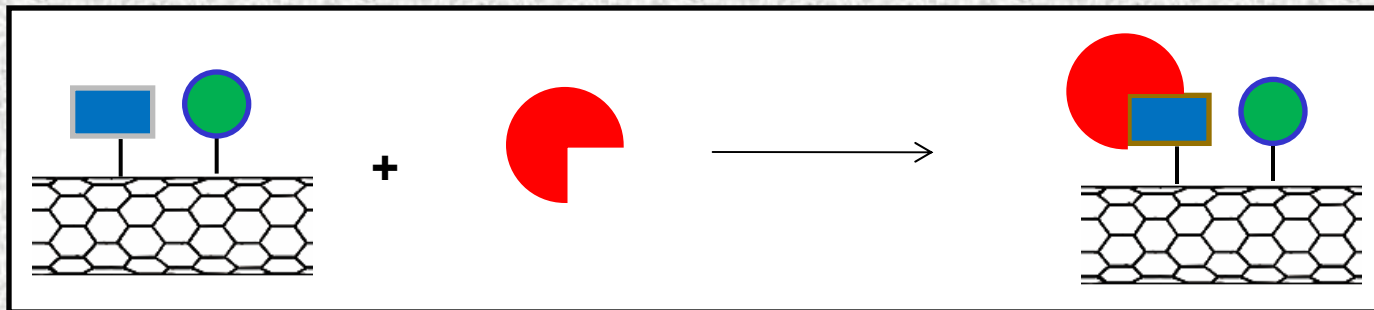


Figure 3. Sorption isotherms for pristine MWCNT, natural char (NC1), and granular activated carbon (F400) with naphthalene.

What is Chemical Derivatization?

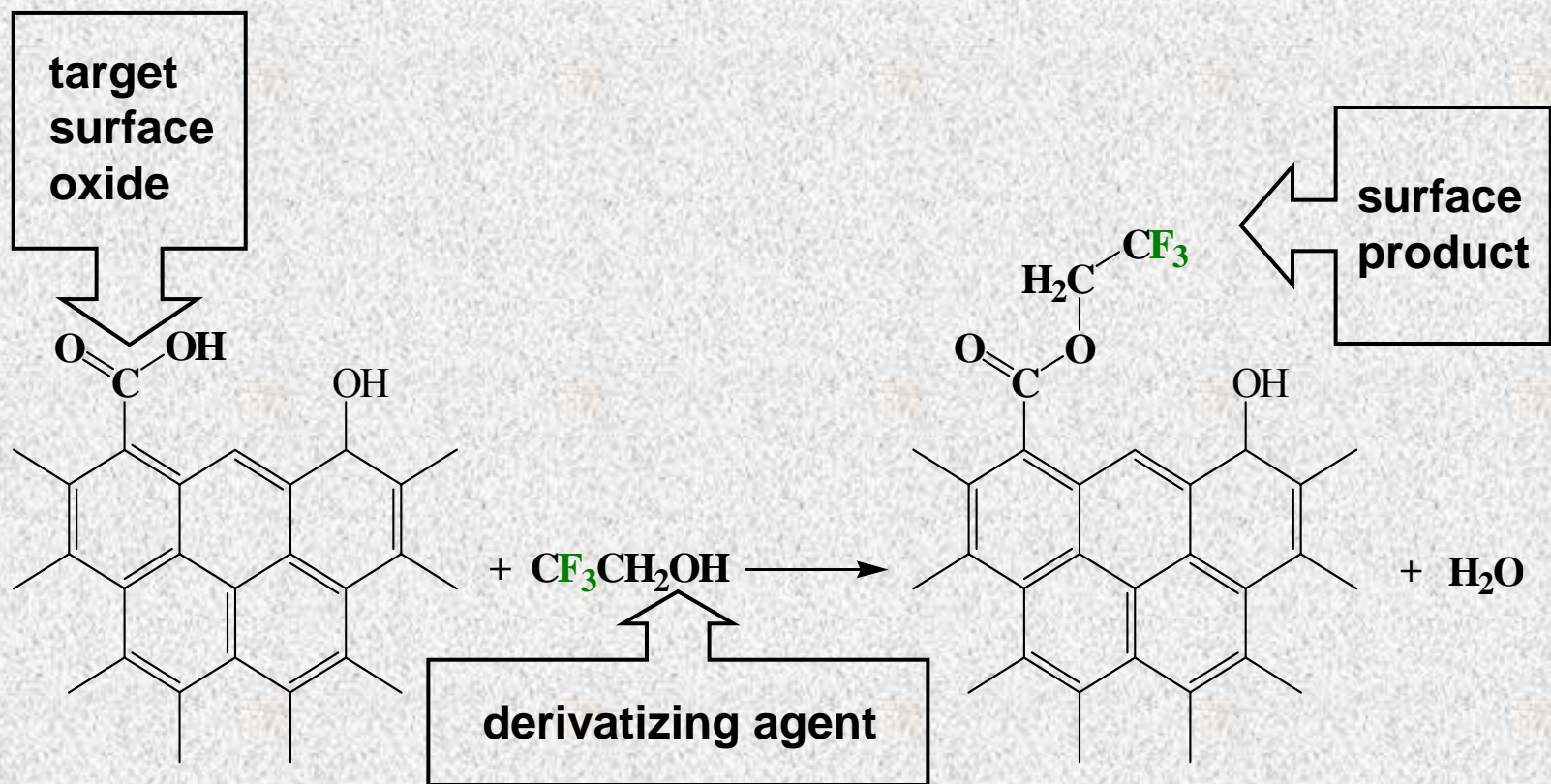
- Reagent selectively reacts with specific functional groups
- Reagent contains a CF₃ tag.
- Vapor phase chemical process
- Label chemical quantified by XPS



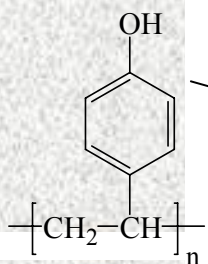
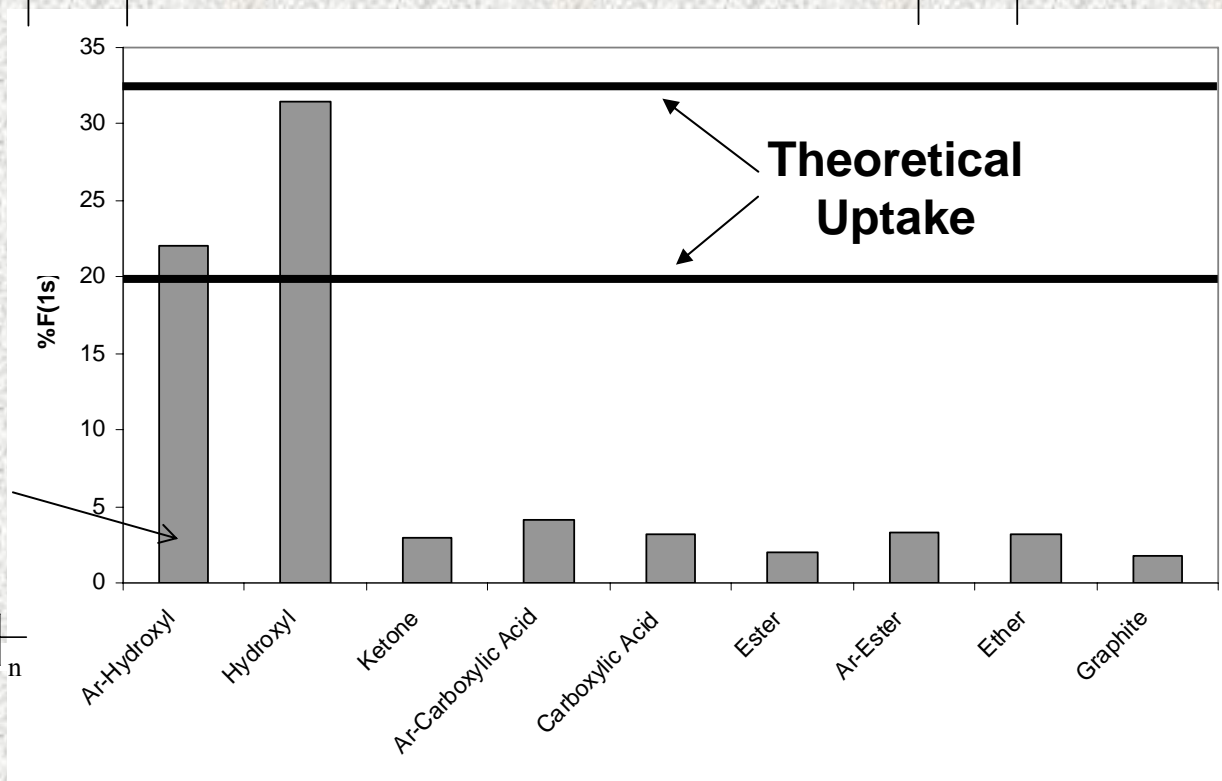
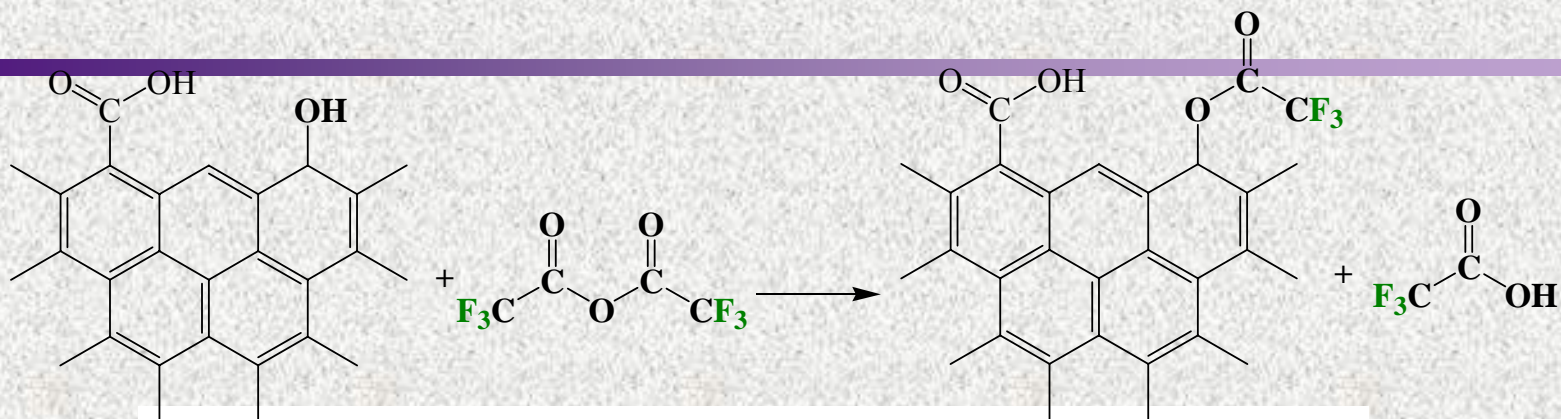
Fairbrother et al., in *Nanoscience and Nanotechnology*, J. Wiley & Sons, 2008.

Chemical Derivatization XPS

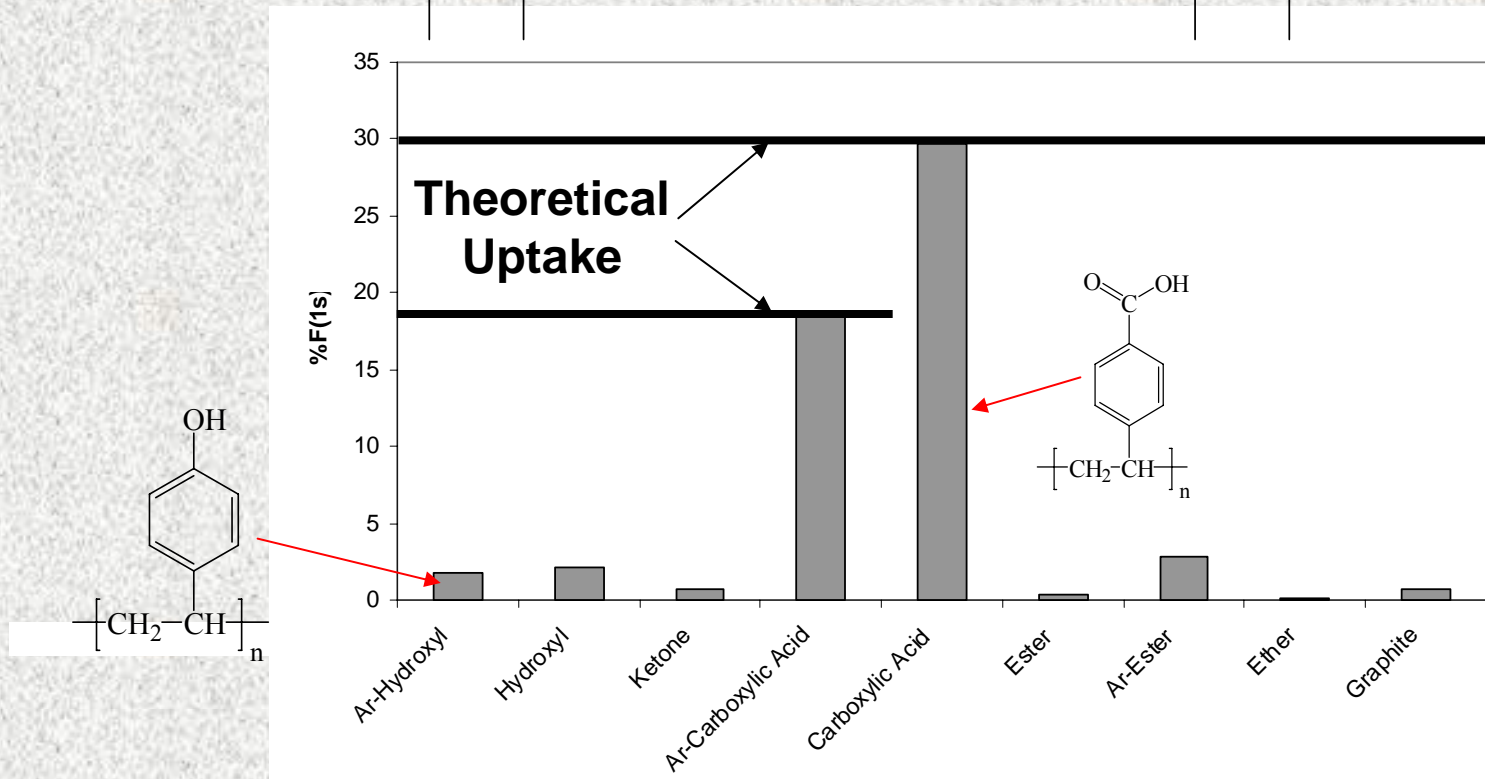
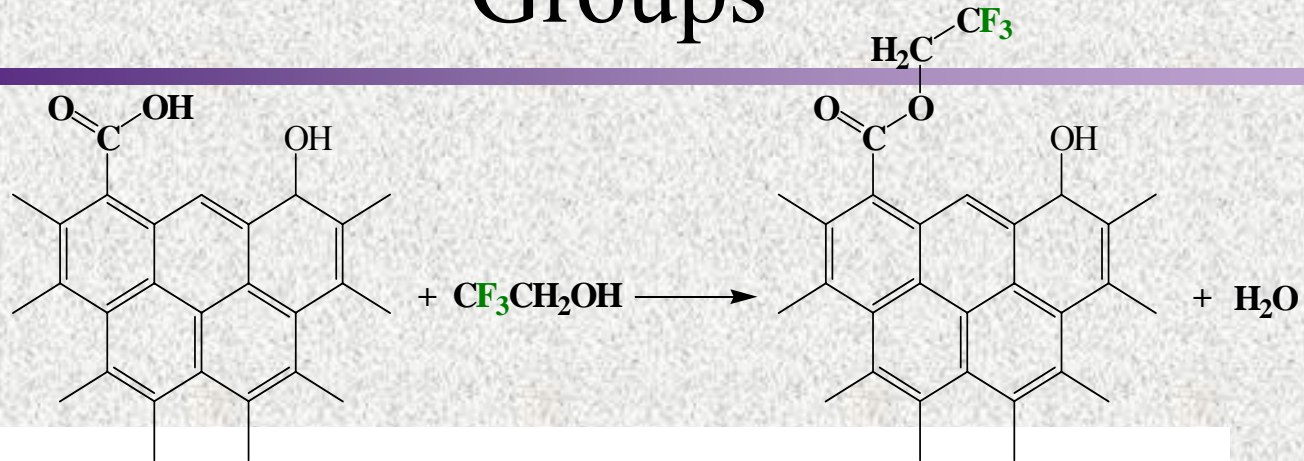
- Technique exploiting a reaction that selectively targets one surface functionality with a **derivatizing agent**, containing an easily detectable chemical **tag (fluorine)**



Derivatization of Hydroxyl Groups

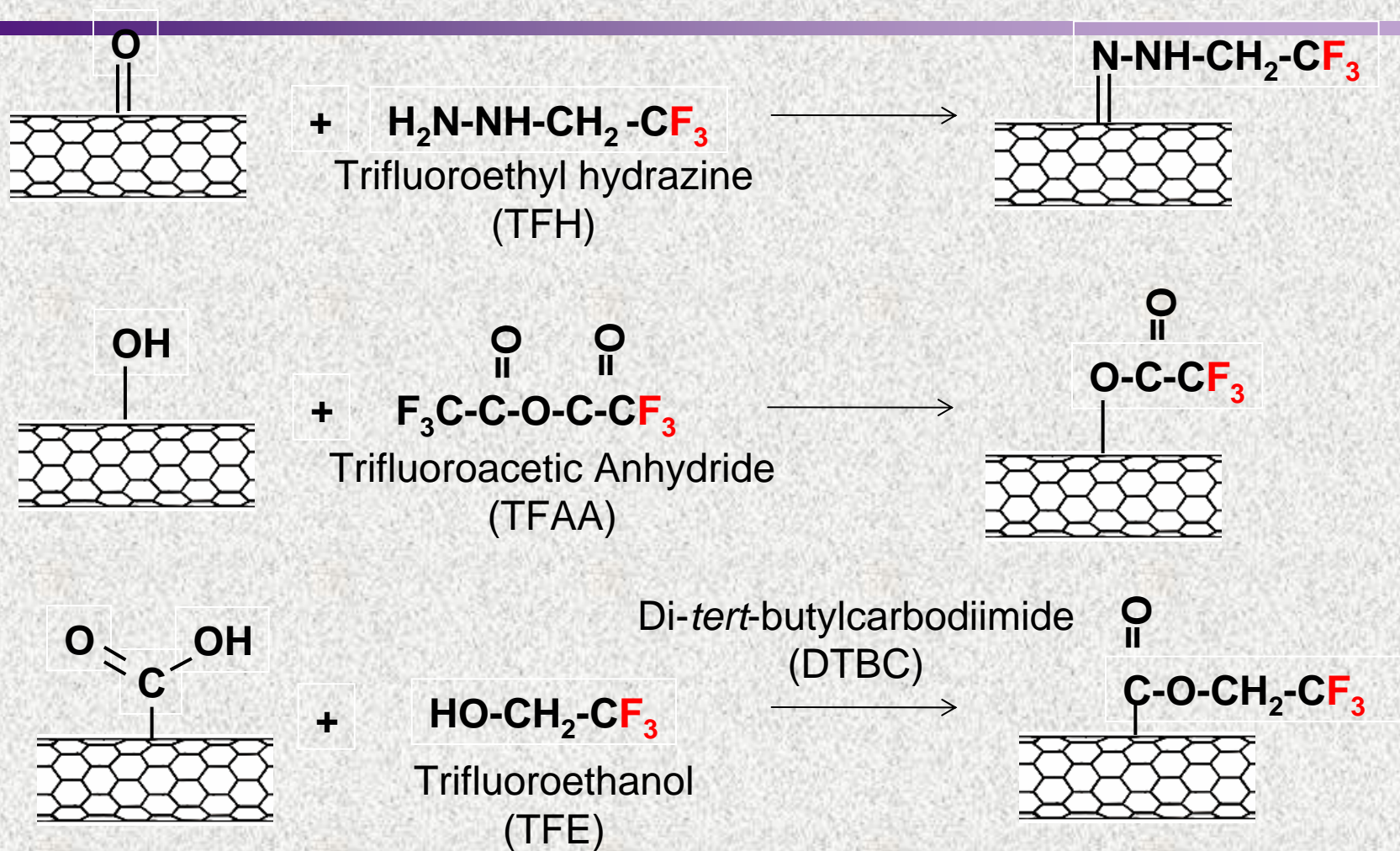


Derivatization of Carboxylic Acid Groups



Labeling Reaction Schemes

Fairbrother et al., in *Nanoscience and Nanotechnology*, J. Wiley & Sons, 2008.



Naphthalene sorption with MWCNTs

(H-H Cho *et al.*, 2009. *Environ. Sci Technol.*, 42: 2899)

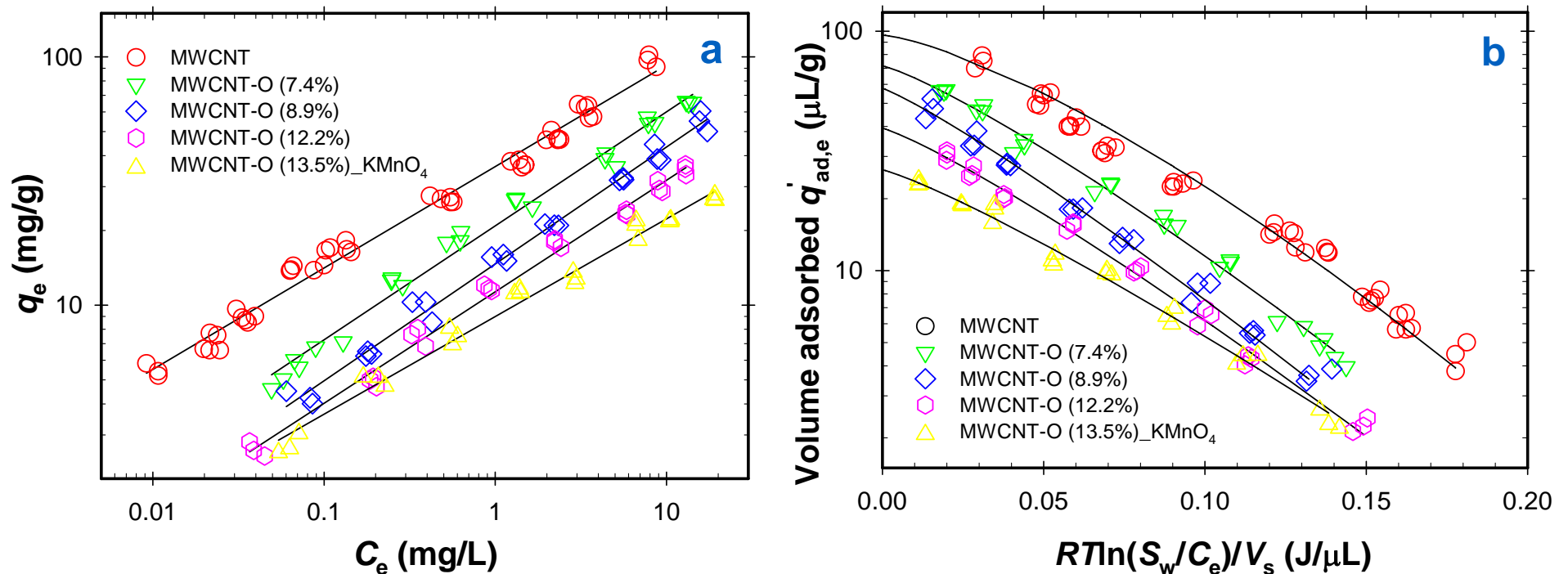


Figure 2. Sorption isotherms for naphthalene with MWCNT and oxidized MWCNTs. Lines through the data in Figures 2(a) and 2(b) are based on fits obtained using the Freundlich adsorption model and the Polanyi-based Dubinin-Astikov (DA) adsorption model, respectively.

Naphthalene sorption with MWCNTs

(H-H Cho *et al.*, 2009. *Environ. Sci Technol.*, 42: 2899)

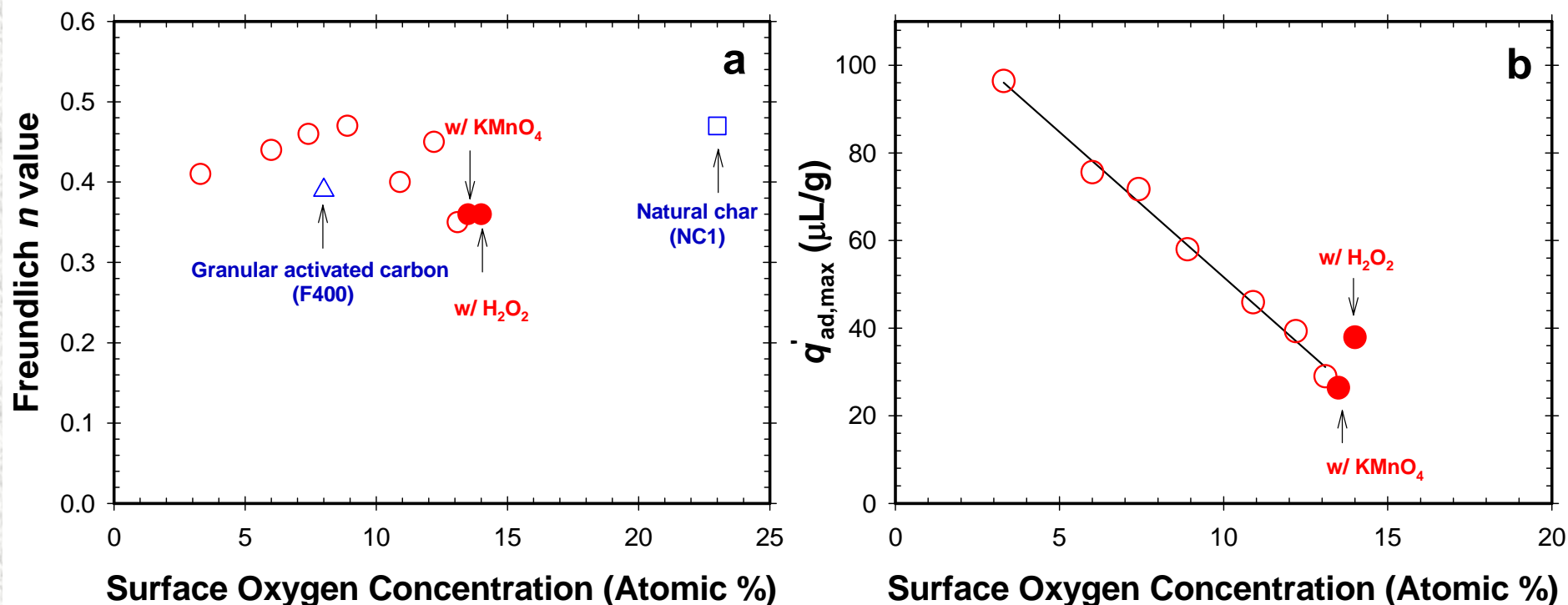
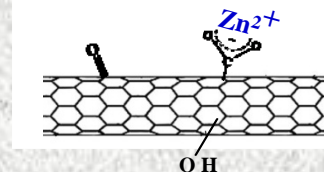


Figure 4. (a) Freundlich n -values for naphthalene adsorption plotted against surface oxygen concentration for MWCNTs, natural char (NC1), and granular activated carbon (F400). (b) Maximum adsorption capacity ($q'_{ad,max}$) for naphthalene from the Polanyi-based Dubinin-Astikov adsorption model plotted against surface oxygen concentration.

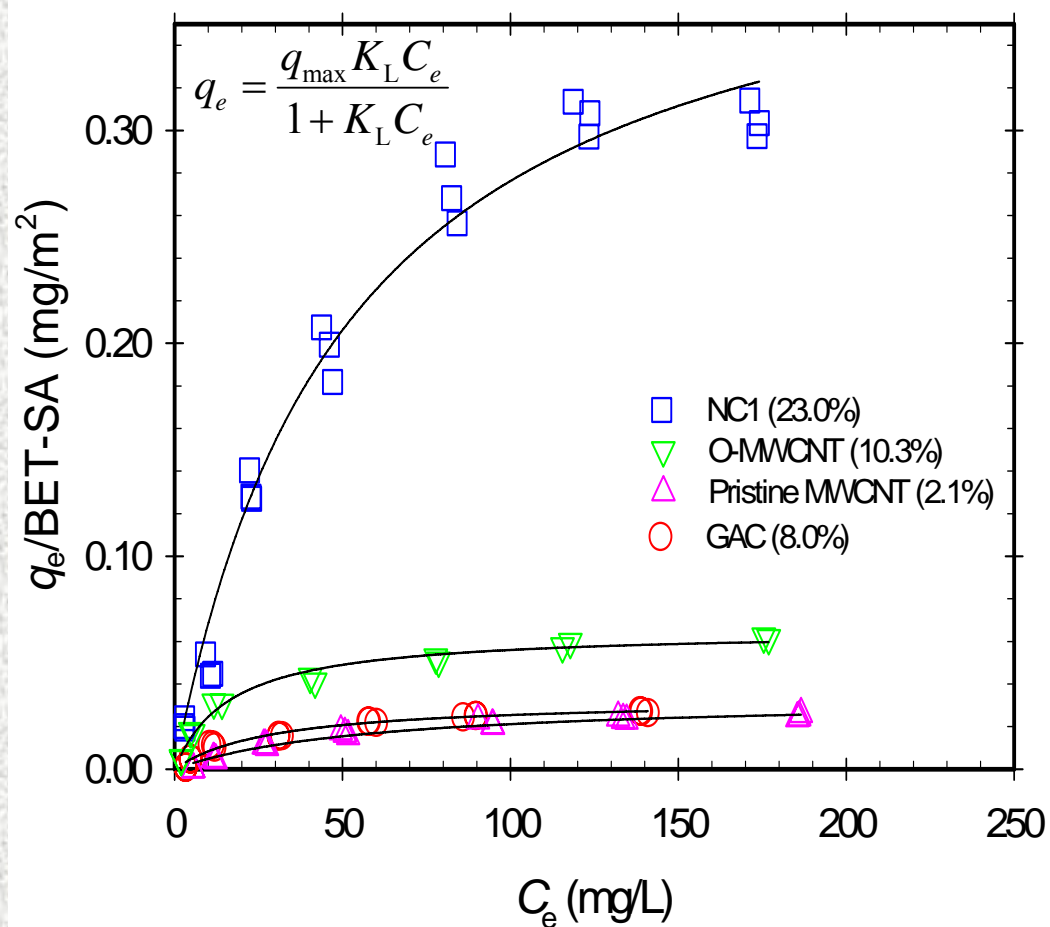
Zn(II) Sorption with MWCNTs and other Carbonaceous Materials



(H-H Cho *et al.* draft results; in prep. for submission to *Langmuir*, 2009)

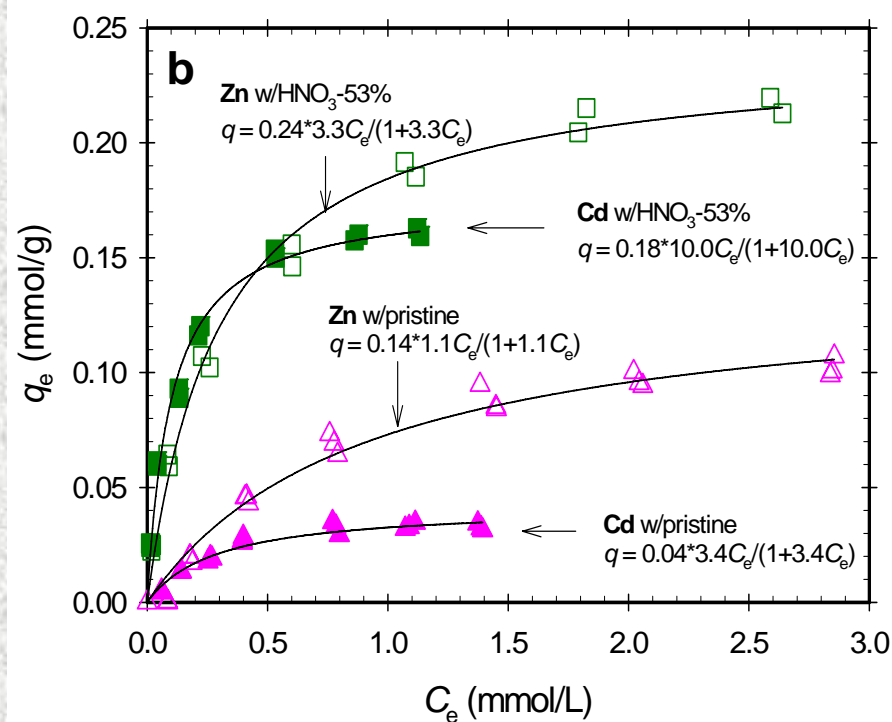
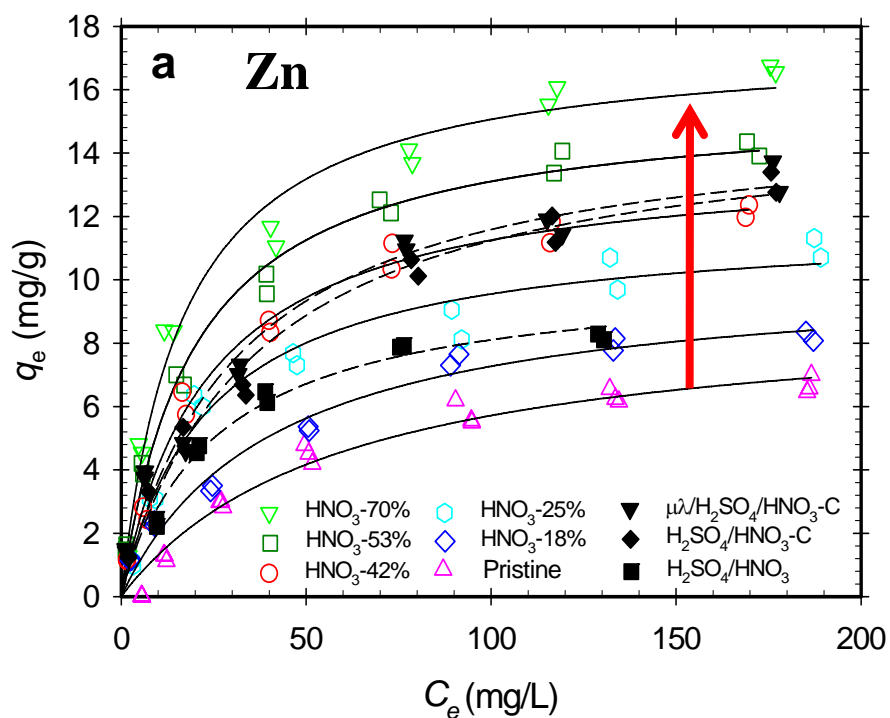
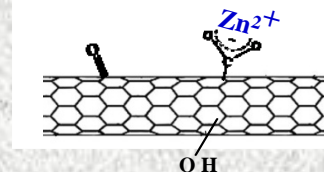
q_{\max} (mg/g)	SA	Oxid.
GAC (33.1)	High	Mod.
NC1 (20.5)	Low	High
O-MWCNT (17.6)	Mod.	Mod.
MWCNT (9.1)	Mod.	Low

q_{\max} / SA (mg/m ²)	SA	Oxid.
NC1 (0.42)	Low	High
O-MWCNT (0.065)	Mod.	Mod.
MWCNT (0.034)	Mod.	Low
GAC (0.033)	High	Mod.



Effect of Surface Oxidation:

Zn(II) and Cd(II) sorption isotherms

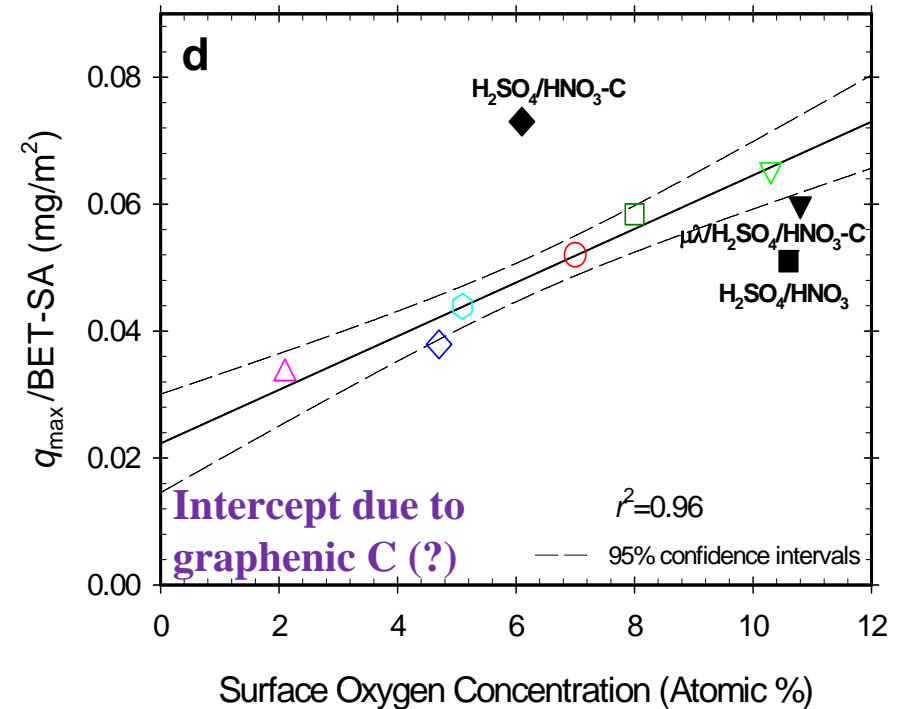
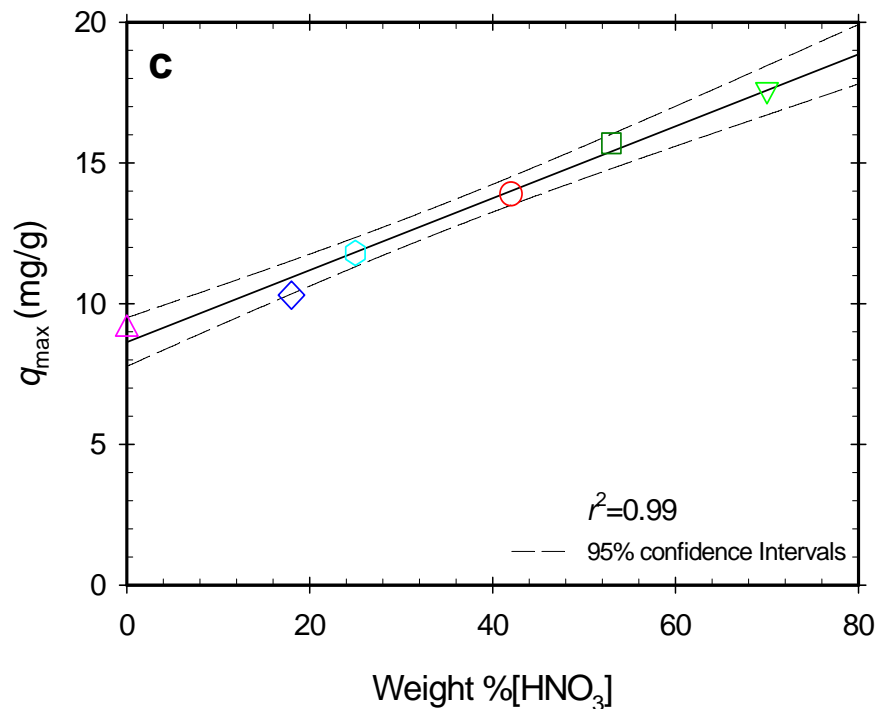
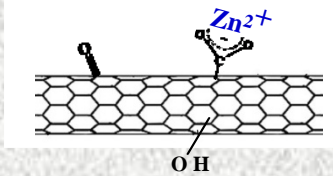


(H-H Cho *et al.* draft results; in prep. for submission to *Langmuir*, 2009)

Effect of Surface Oxidation:

Zn(II) sorption isotherms w/ MWCNTs

(H-H Cho *et al.* draft results; in prep. for submission to *Langmuir*, 2009)



Correlation is strong only for HNO₃-treated samples.

These have invariant functional group distribution –

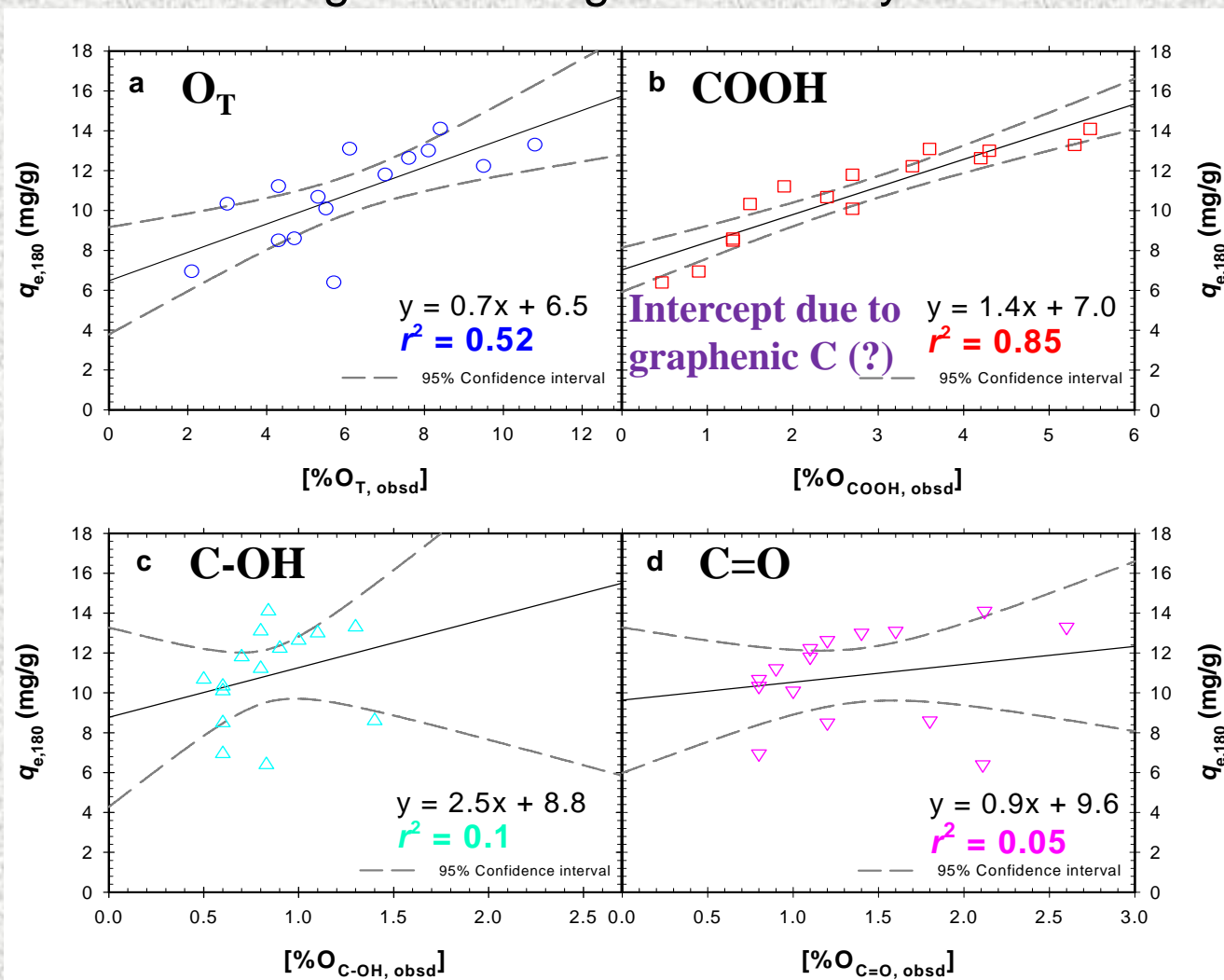
i.e., similar fractions of their total oxides are COOH.

Note the intercept, presumably due to graphenic C (There is no nitrogen...)

Correlation of $q_{e,180}$ with Selected Surface Functional Groups

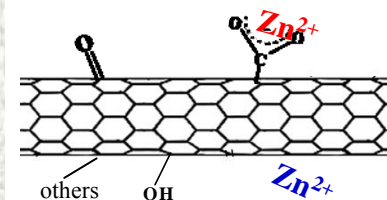
(Cho *et al.* in prep., 2009)

Single linear regression analysis



Correlation of $q_{e,180}$ with Multiple Surface Functional Groups:

Multiple-linear regression analysis



	$q_{e,180} = a[\%C_{\text{Graphene}}] + b[\%C_{\text{COOH}}] + \dots\dots$	F value	r^2
1	$0.08[\%C_{\text{Graphene}}] + 0.27[\%C_{\text{OT}}]$	4.45	0.20
2	$0.08[\%C_{\text{Graphene}}] + 0.94[\%C_{\text{COOH}}]$	1.04	0.83
3	$0.08[\%C_{\text{Graphene}}] + 0.91[\%C_{\text{COOH}}] + 0.03\{[\%C_{\text{C-OH}}] + [\%C_{\text{C=O}}] + [\%C_{\text{Other}}]\}$	1.12	0.85
4	$0.08[\%C_{\text{Graphene}}] + 0.98[\%C_{\text{COOH}}] + 0.23[\%C_{\text{C-OH}}] - 0.27[\%C_{\text{C=O}}] + 0.08[\%C_{\text{Other}}]$	1.03	0.89

(H-H Cho et al. draft results; in prep. for submission to *Langmuir*, 2009)

Langmuir Two-Site Model: Individual fits

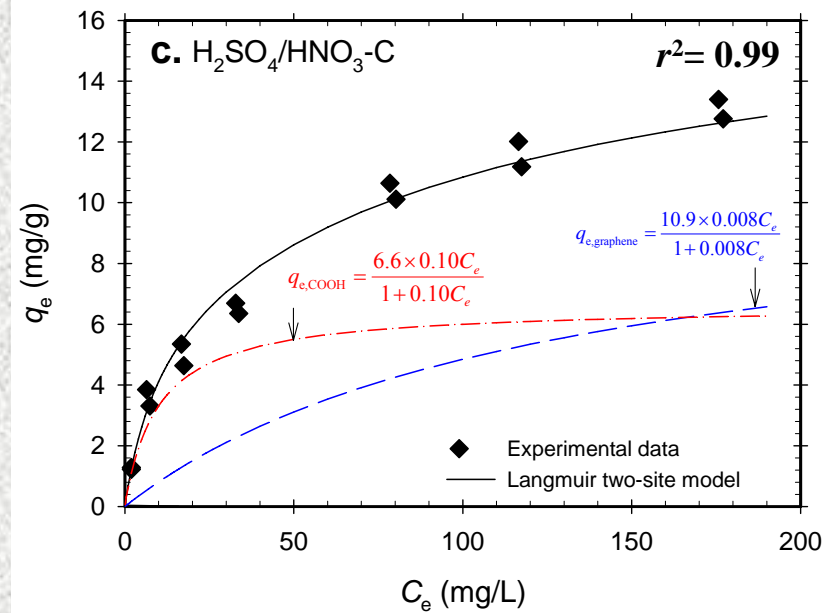
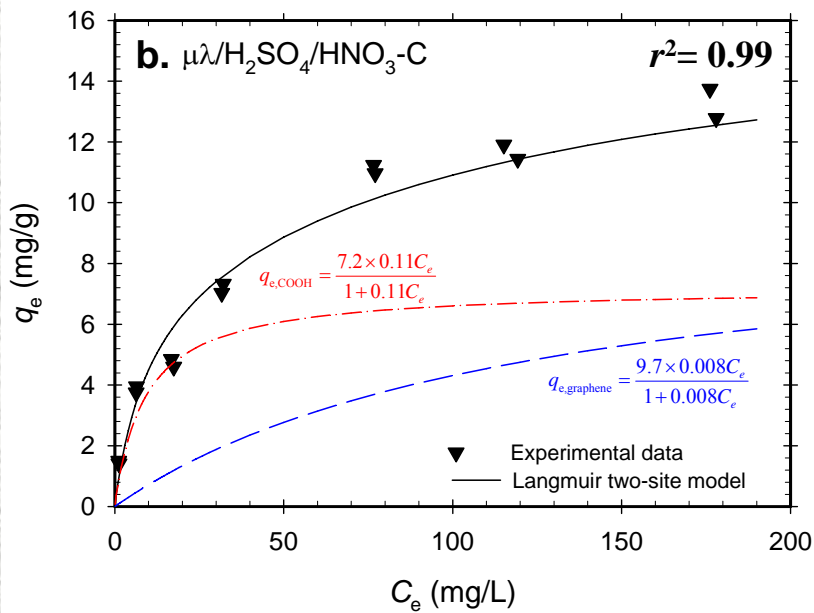
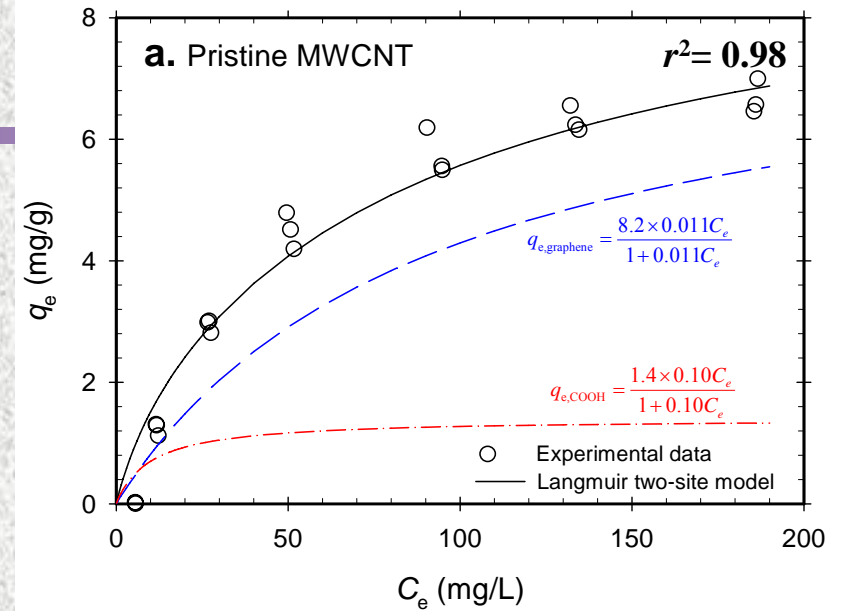
(Cho *et al.* in prep., 2009)

$$q_e = q_{e,\text{Graphene}} + q_{e,\text{COOH}}$$

$$= \frac{q_{\text{max,G}} K_{\text{L,G}} C_e}{1 + K_{\text{L,G}} C_e} + \frac{q_{\text{max,C}} K_{\text{L,C}} C_e}{1 + K_{\text{L,C}} C_e}$$

$$K_{\text{L,G}} = 0.008 \sim 0.010$$

$$K_{\text{L,C}} = 0.10 \sim 0.11$$



Langmuir Two-Site Model:

(Cho *et al.* in prep., 2009)

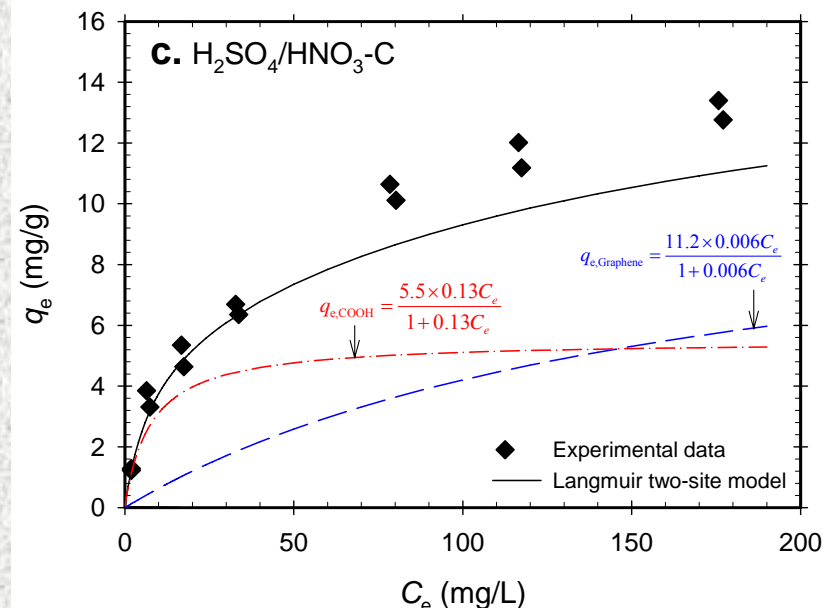
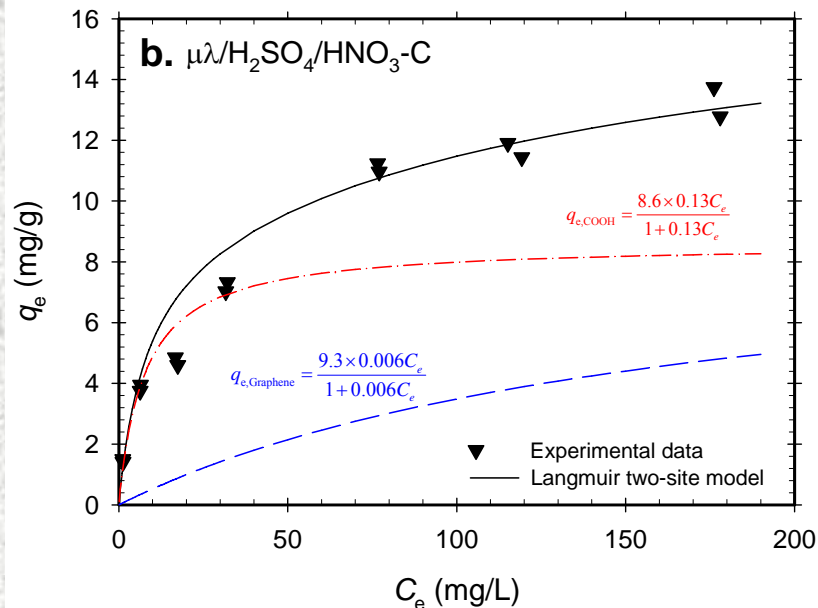
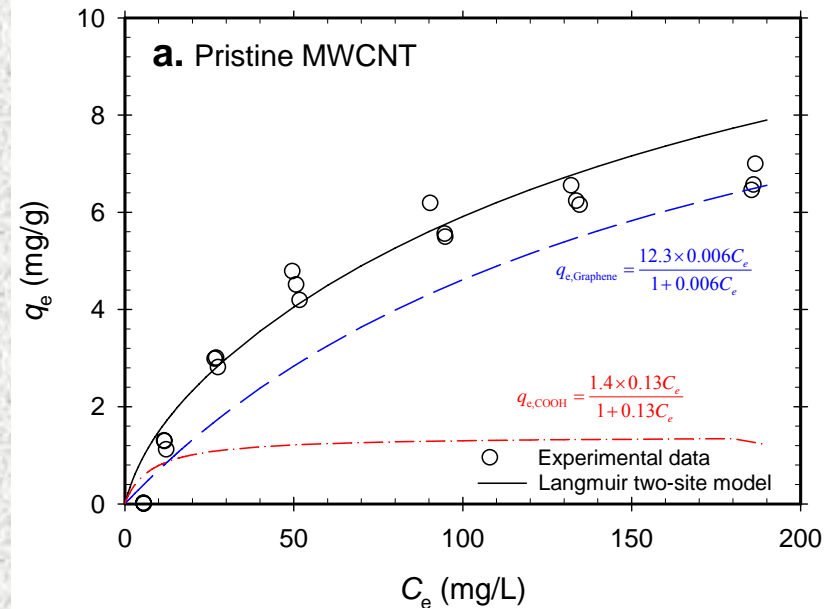
Common $K_{L,G}$, $K_{L,C}$, α , and β :

$$q_{e,180} = a[\%C_{\text{Graphene}}] + b[\%C_{\text{COOH}}]$$

$$q_e = \frac{q_{\max,G} K_{L,G} C_e}{1 + K_{L,G} C_e} + \frac{q_{\max,C} K_{L,C} C_e}{1 + K_{L,C} C_e}$$

if $C_e = \infty$, $\alpha = \frac{q_{\max,G}}{[\%C_{\text{Graphene}}]}$, $\beta = \frac{q_{\max,\text{COOH}}}{[\%C_{\text{COOH}}]}$

$K_{L,G} = 0.006$, $K_{L,C} = 0.13$, $\alpha = 0.13$, $\beta = 0.94$



Chemistry of Sorption by Black Carbon

Some Conclusions from Recent Work (take-home messages)

- The sorption of aqueous solutes by BC will be strongly influenced by the level of BC surface oxidation:
 - surface oxygen functional groups cause reduced affinity and capacity for apolar HOCs (e.g., naphthalene, trichlorobenzene)
 - some surface oxide functional groups (notably COOH) cause increased affinity and capacity for cationic heavy metals (e.g. Zn^{2+} , Cd^{2+})
- New methods of surface characterization provide new means of quantifying and understanding these effects
- Studies with well characterized carbonaceous surfaces (e.g. CNTs) are beginning to provide new insights