Adsorption/Desorption of Pollutants to Nanoparticles

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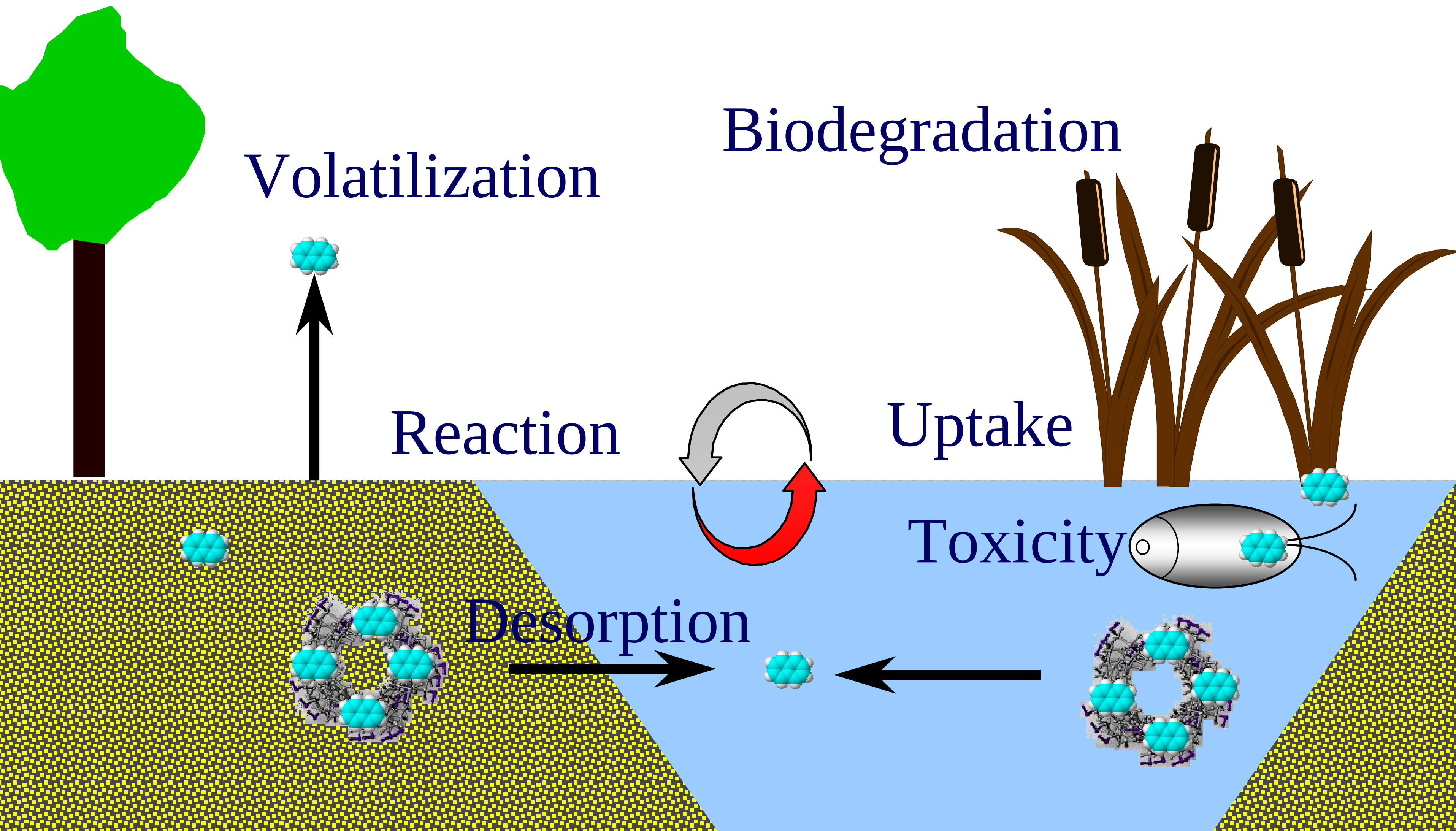
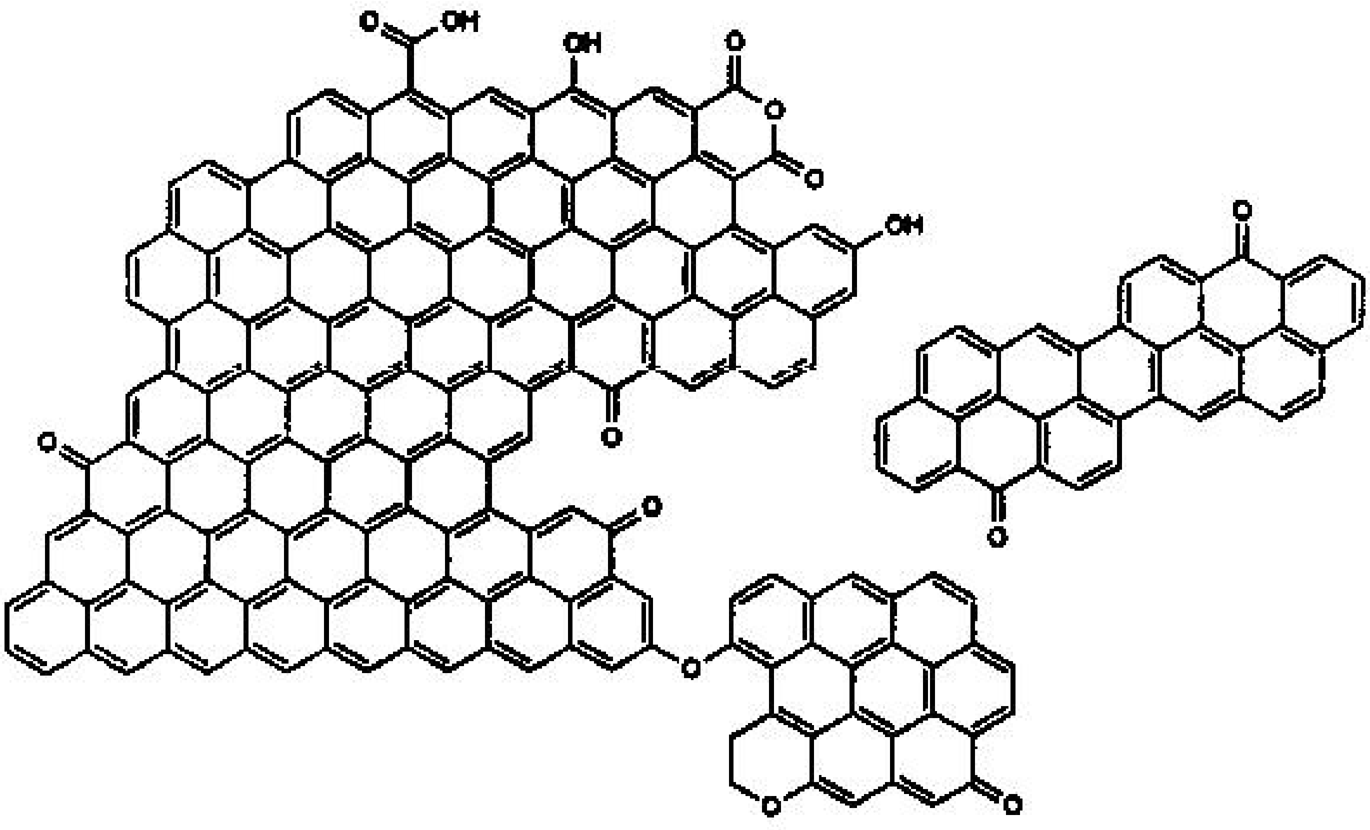
September 15, 2003

Adsorption/Desorption Hysteresis



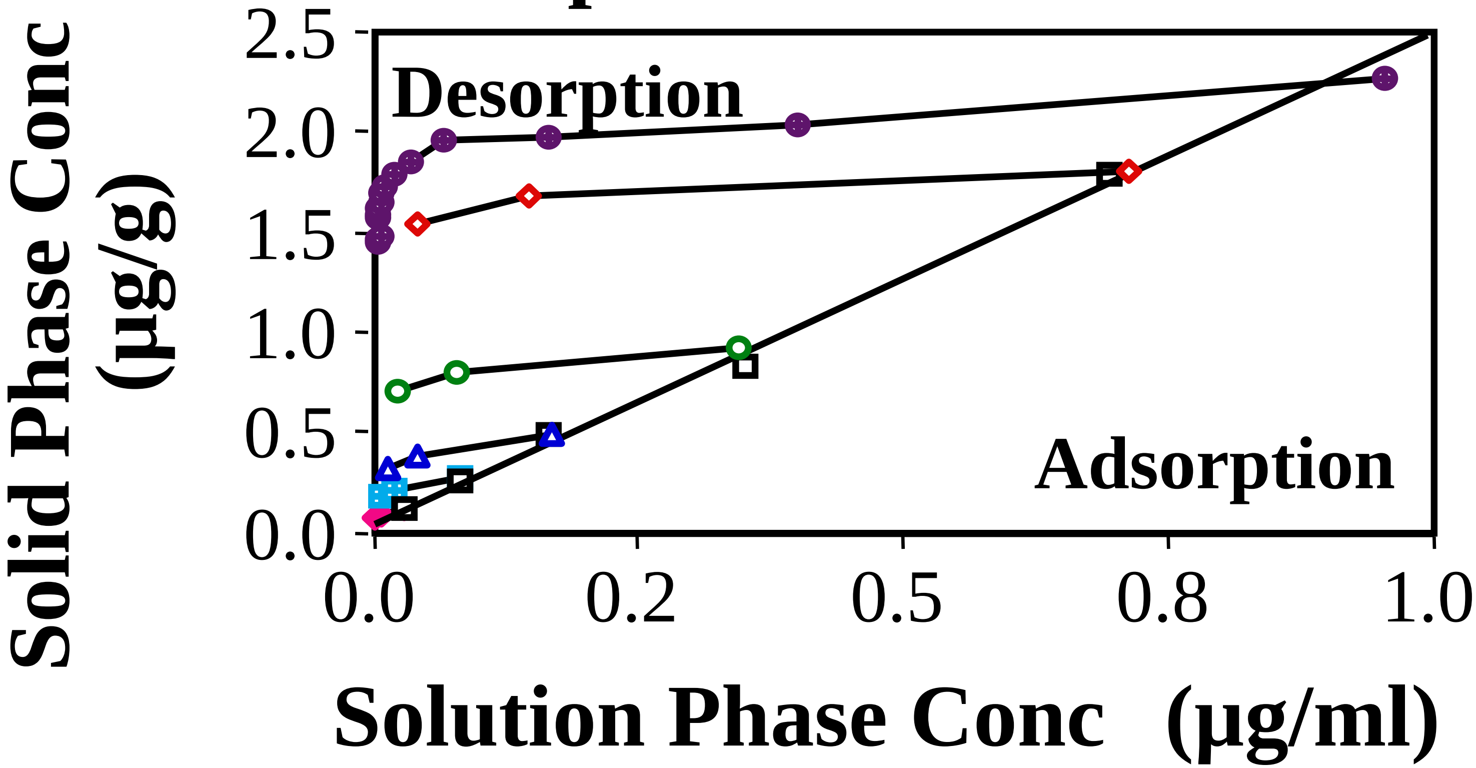
Black Carbon



Sorption/Desorption Hysteresis

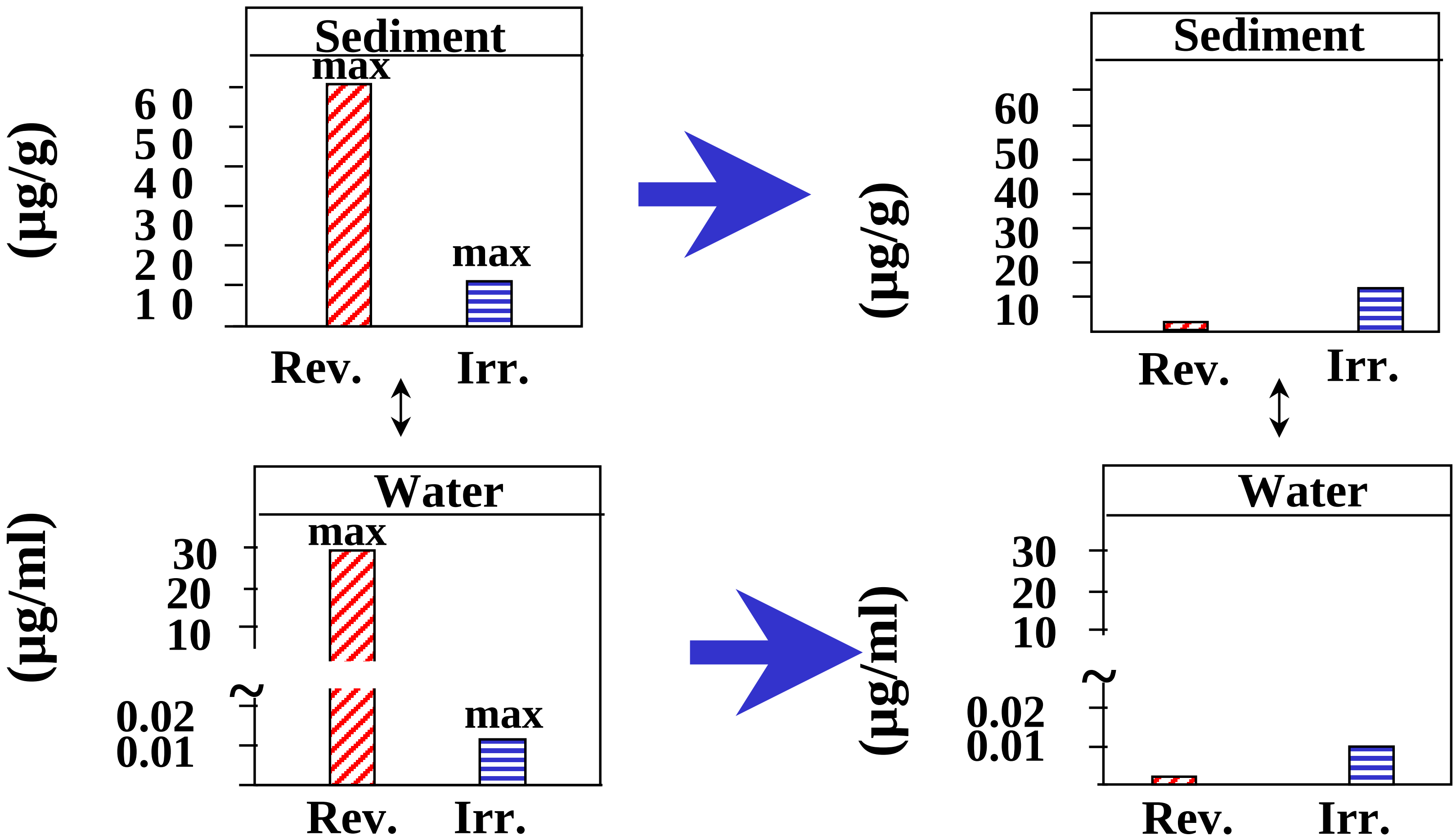
$$K_p^{des} > K_p^{ads}$$

Naphthalene/Lula

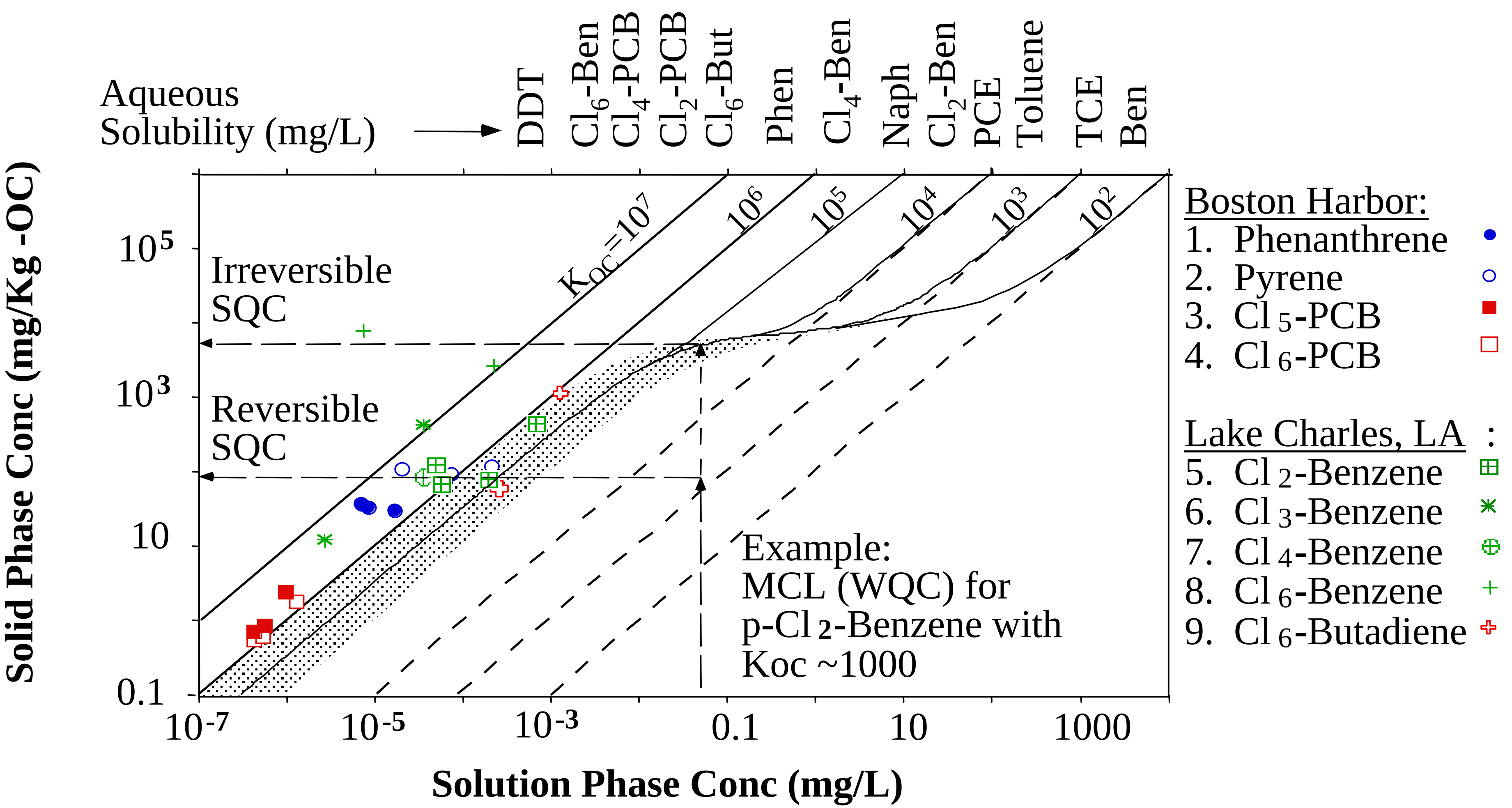


"**Unweathered**, non-remediated, or freshly contaminated"

"**Weathered**, remediated, or aged"



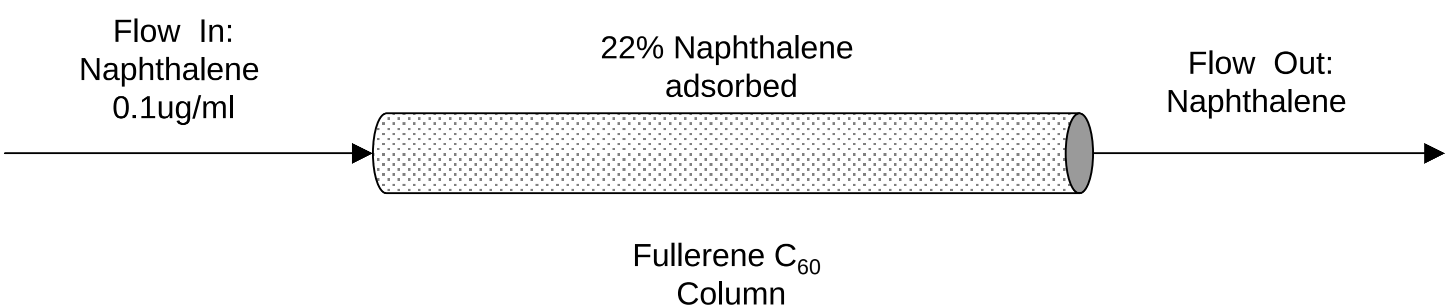
Adsorption/Desorption Hysteresis



Naphthalene Adsorption onto Original C_{60} Particles

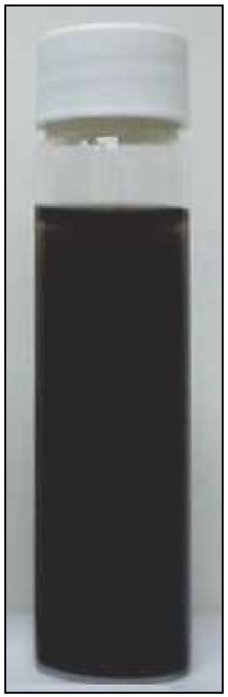
E. Ballesteros et al. 2000 J. Chromatography A —

Little adsorption from naphthalene aqueous solution onto fullerene C_{60} particles was found...



$K_p \sim 10$

Carbon Nano-Particle Transport



C_{60} small aggregates

Toluene extraction

C_{60} colloidal particles

Toluene No extraction

C-18 Sep-Pak® No adsorption

Adsorption of Organic Contaminants from Solution to C_{60} Fullerene

Batch Adsorption/Desorption Study:

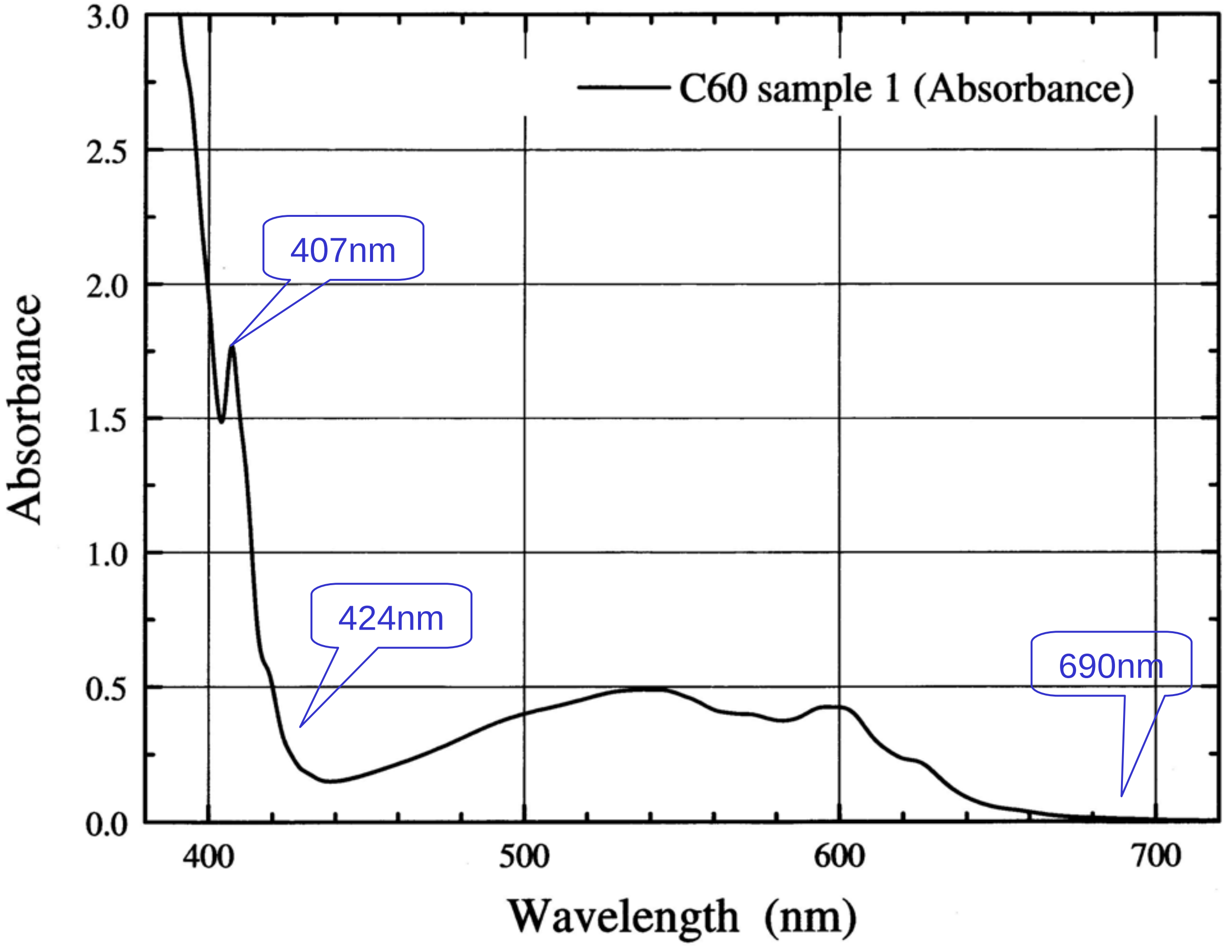
C_{60} large aggregates

C_{60} small aggregates

C_{60} colloidal particles

UV/Vis Spectrum of C_{60} in Toluene

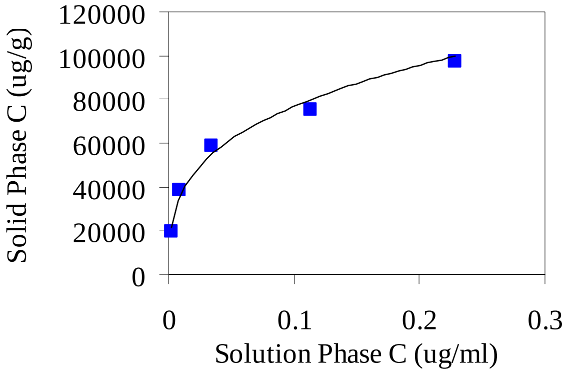
Sampled from small aggregates



Naphthalene-Carbon Adsorption Isotherms

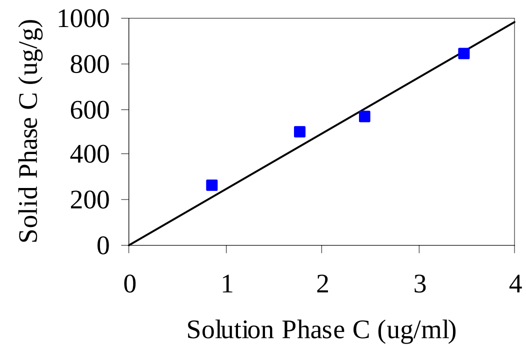
(1) Activated carbon

$$q=10^{5.20}C^{0.31}$$



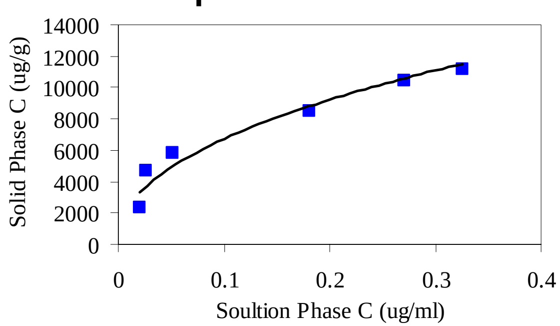
(2) Large aggregates

$$q=10^{2.39}C$$



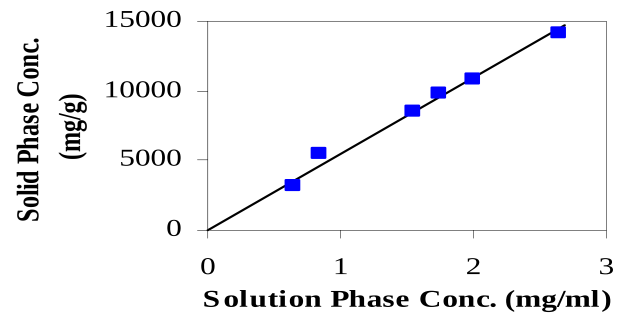
(3) Small aggregates

$$q=10^{4.27}C^{0.44}$$

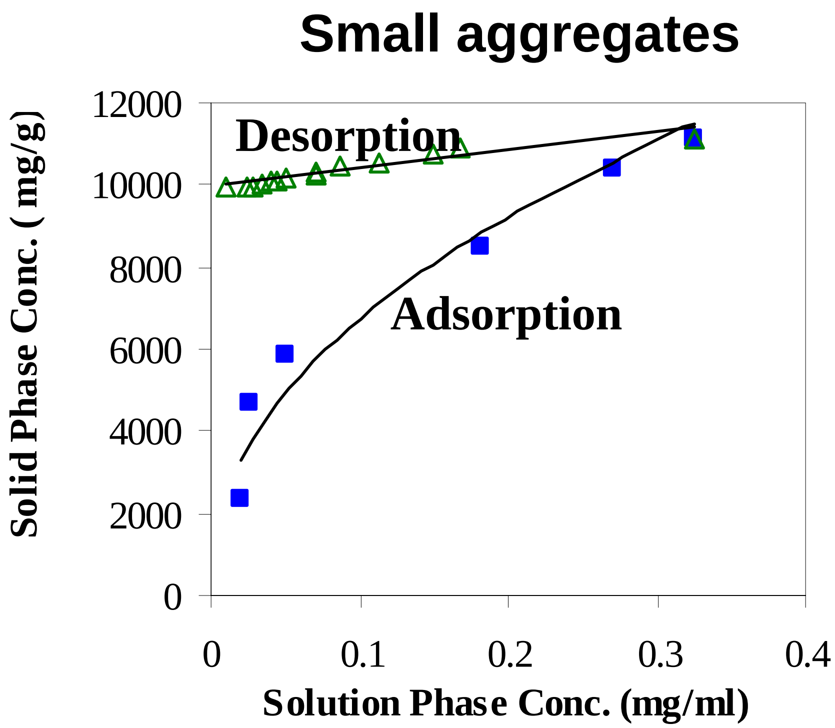


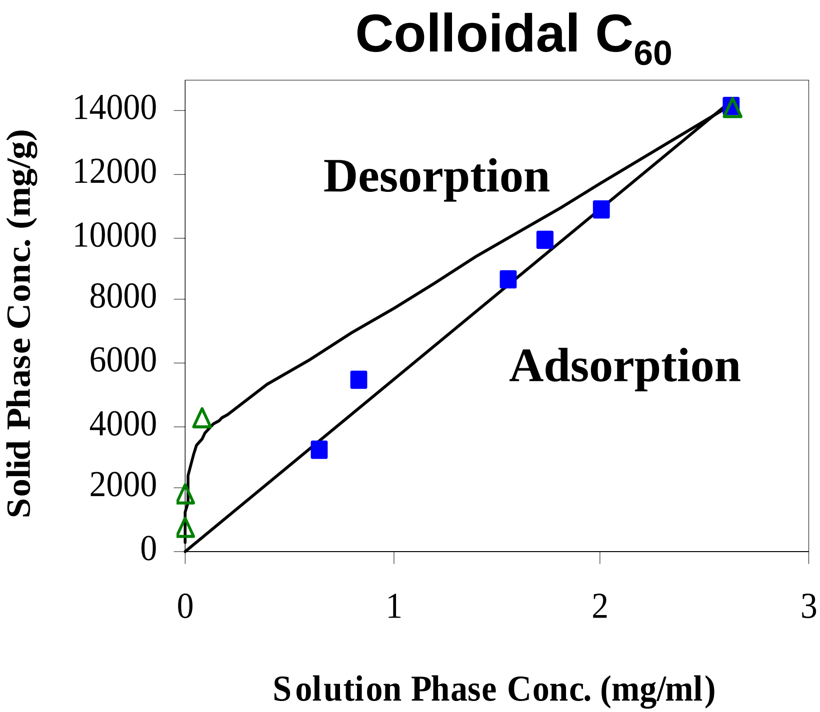
(3) Colloidal C_{60}

$$q=10^{3.75}C$$

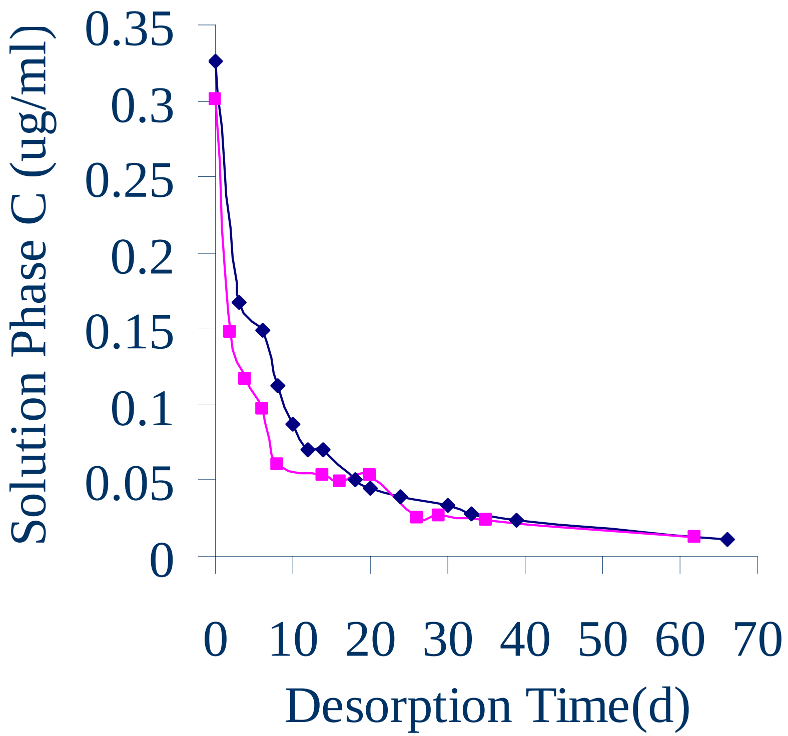


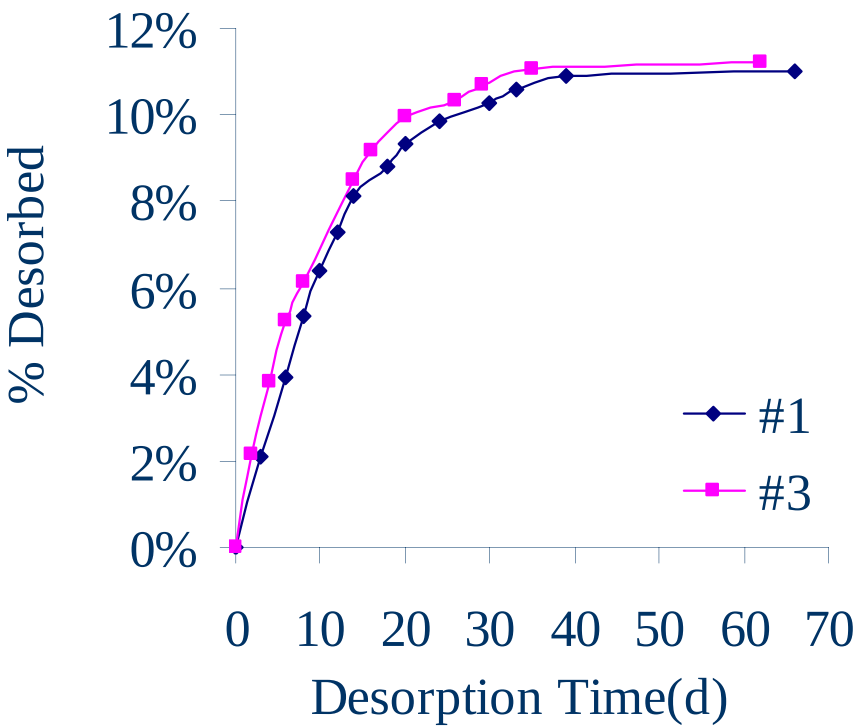
Adsorption/Desorption of Naphthalene
(Small Aggregated and Colloidal C_{60} Particles)





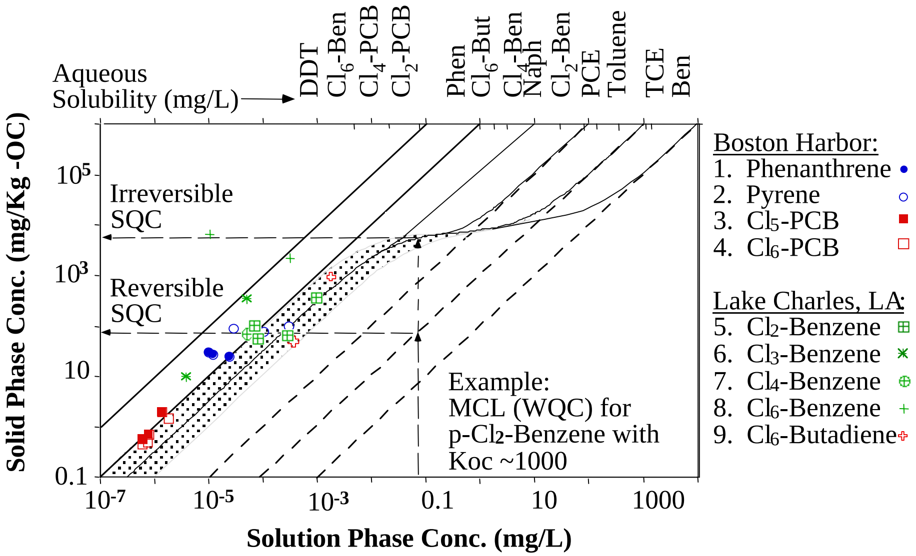
Adsorption/Desorption of Naphthalene to Small Aggregated C_{60} Particles



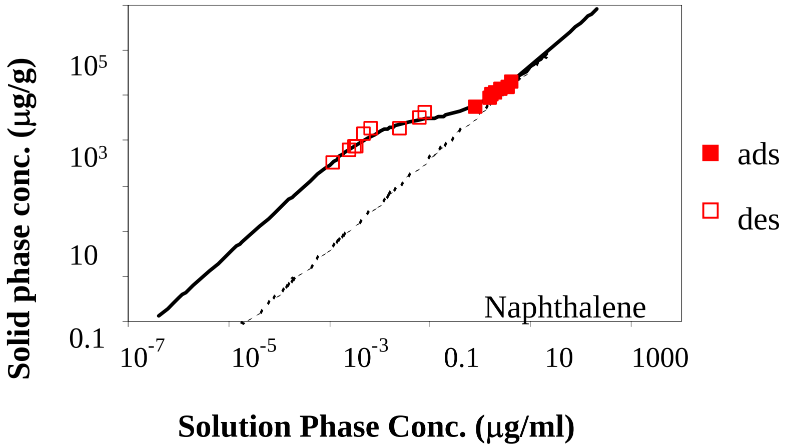


Adsorption and Desorption of Organic Contaminants

Naturally occurring soil organic carbon

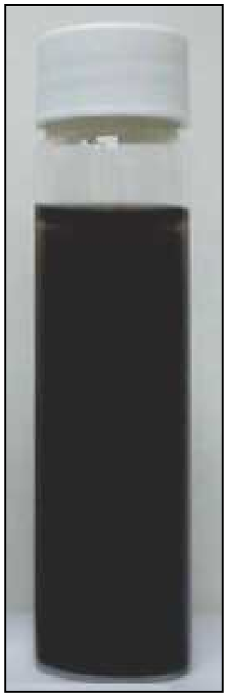


C_{60} Fullerene



<u>Solid Lines Represent the Rice University Dual Equilibrium Model</u>

Carbon Nano-Particle Transport



C_{60} small aggregates

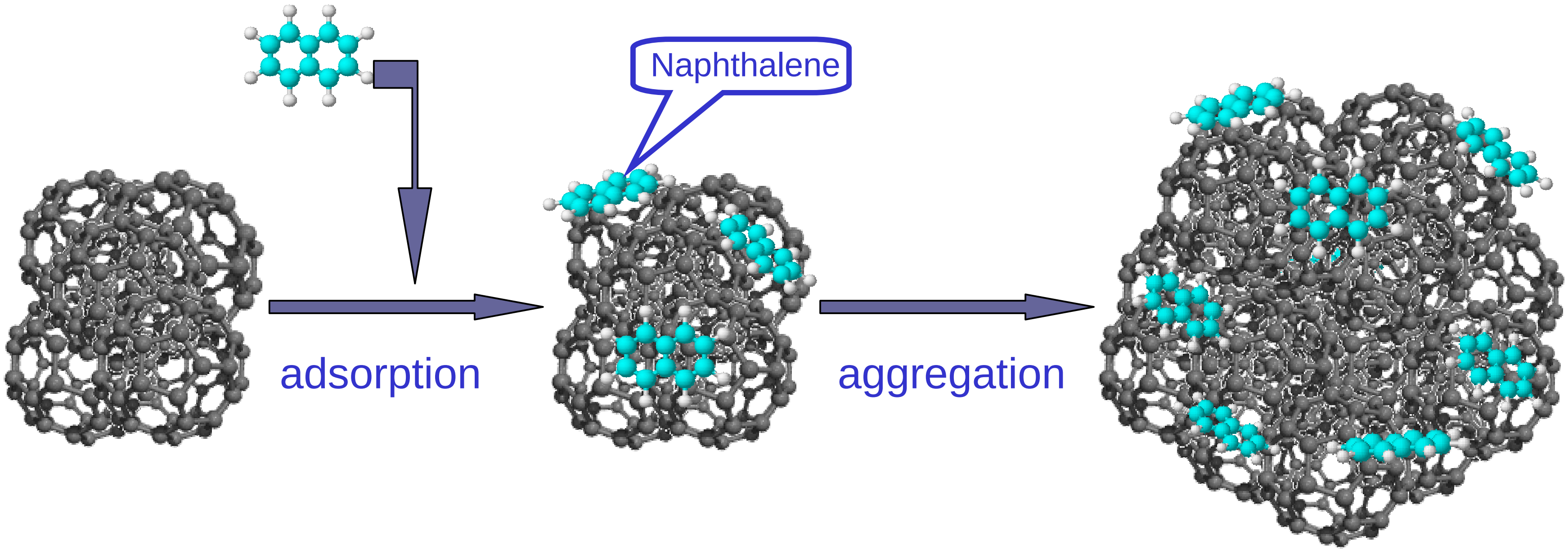
Toluene extraction

C_{60} colloidal particles

Toluene No extraction

C-18 Sep-Pak® No adsorption

What Happened During Adsorption?

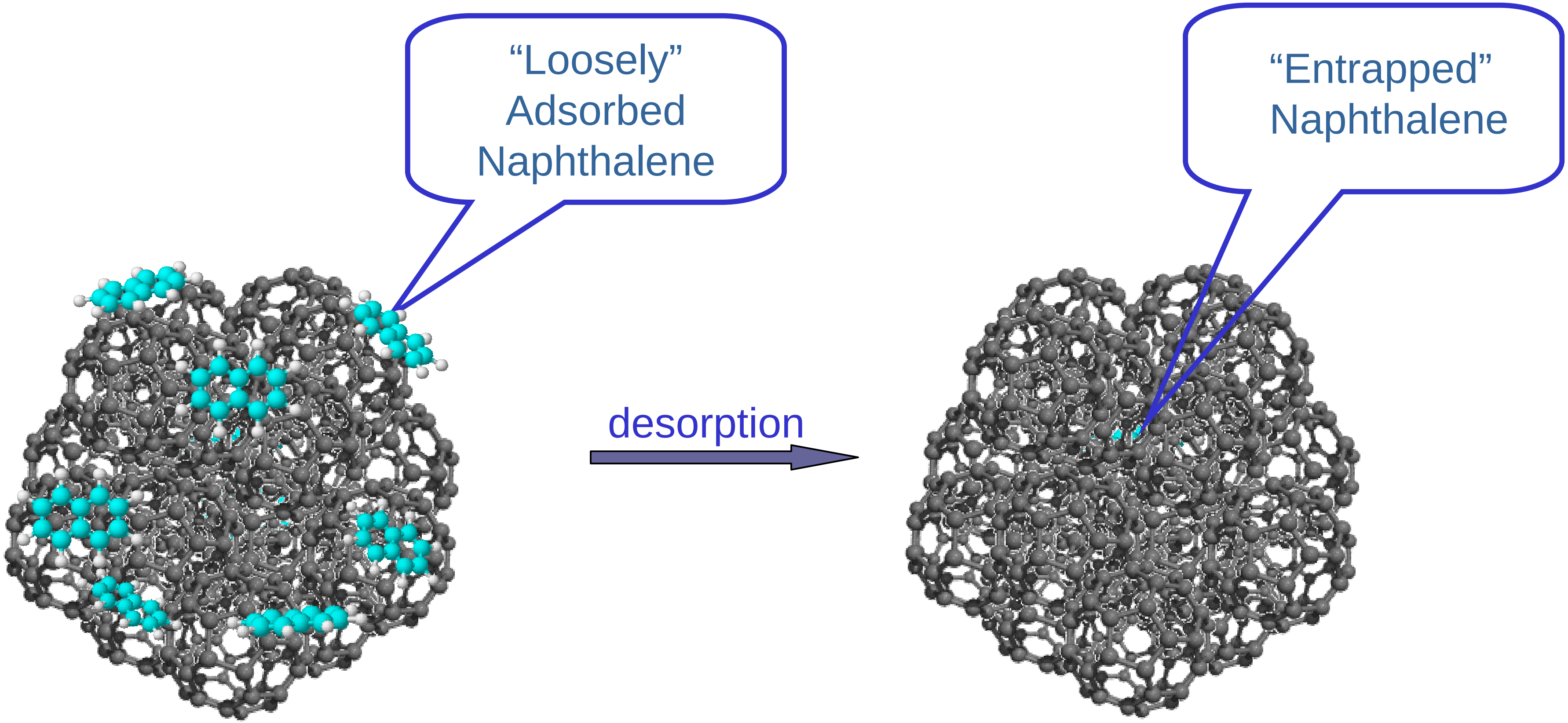


Small Fullerene Aggregates

Naphthalene Adsorption

Clusters Aggregation & Naph. Entrapment

What Happened During Desorption?



Possible Explanations

- Two parts of adsorption/desorption:

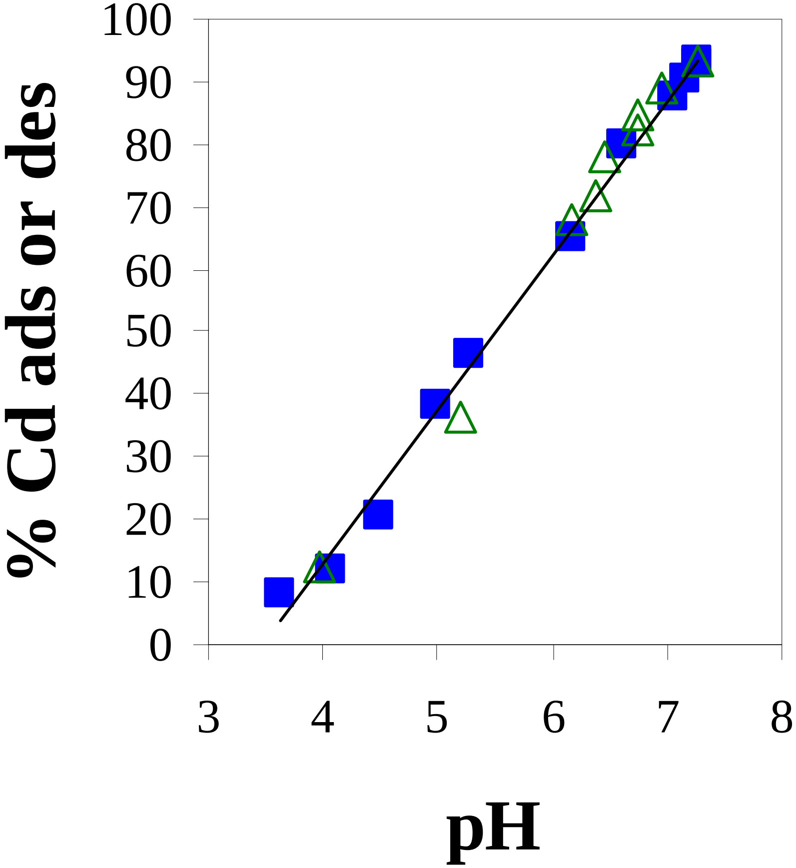
  q_1: adsorption onto surfaces

  q_2: entrapment in clusters
- q_1 account for ≈ 11% adsorption;
- q_2 account for ≈ 89% adsorption
- Possibility of adsorption/desorption hysteresis
- Adsorption/desorption hysteresis needs further study

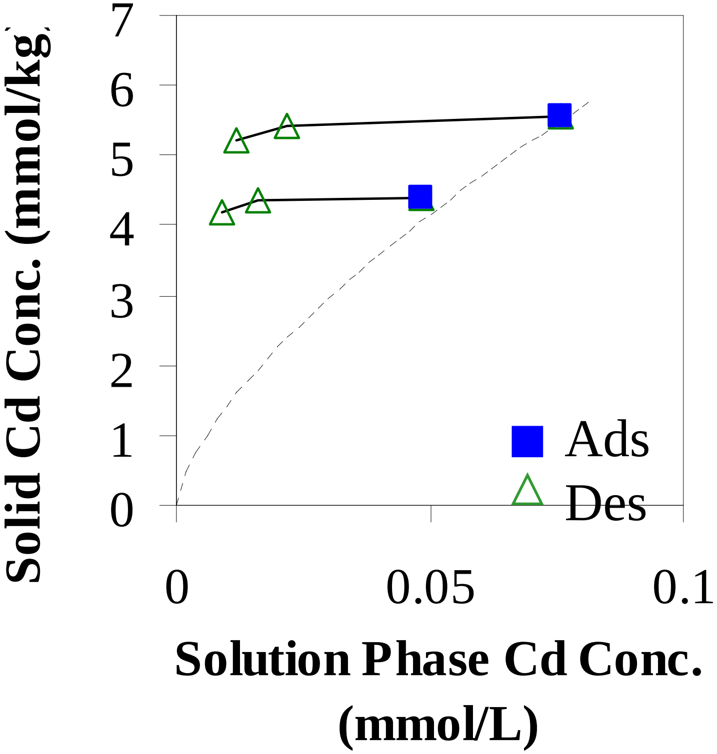
Adsorption of Cadmium to Anatase Nanoparticles

Adsorption/Desorption of Cd to Soil

Reversible



Irreversible

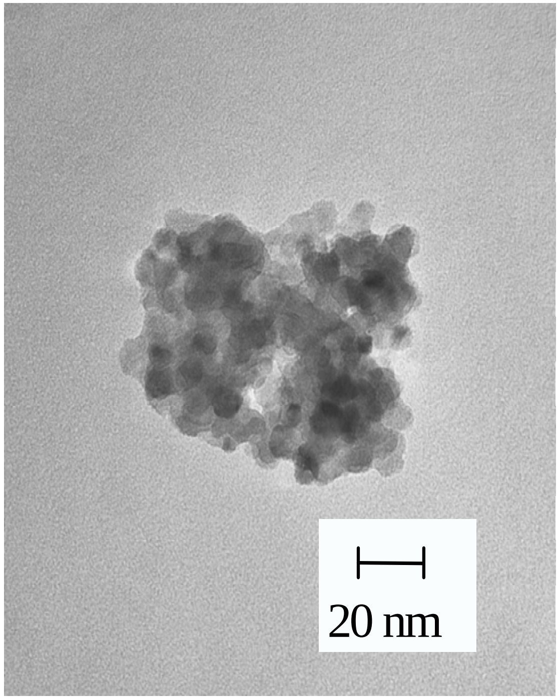


Physical Characteristics of Anatase

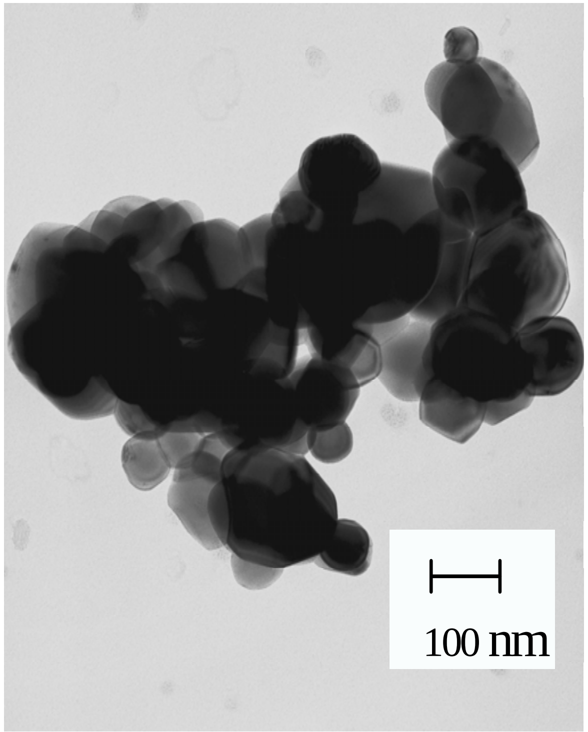
Sample	Crystalline Phases Detected by XRD	Specific Surface Area, (m^2/g)	Mean Particle Size (nm)	Amorphous TiO_2 Detected by TG/DTA
Sigma	Anatase	10.8	145	none
Alfa Aesar	Anatase	11.2	139.5	none
TiNano	Anatase	39.8	39.2	none
P-25	Anatase (80%), rutile (20%)	46.9	33.3	none
RHT 47	Anatase	75.1	20.8	none
RHT 24	Anatase	108.5	14.4	--
RHT 45	Anatase	--	9.45	--
RHT 43	Anatase	--	7.72	--
RHT 69	Anatase	195.3	8.0	none
RHT 127	Anatase	193.4	8.08	none

TEM Images of Anatase

Nanoparticles (RHT-69)

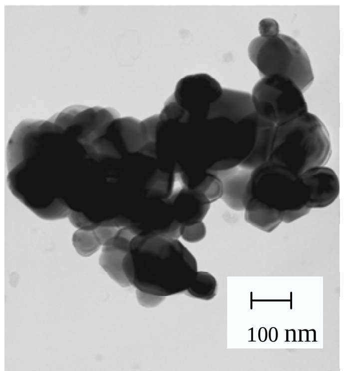


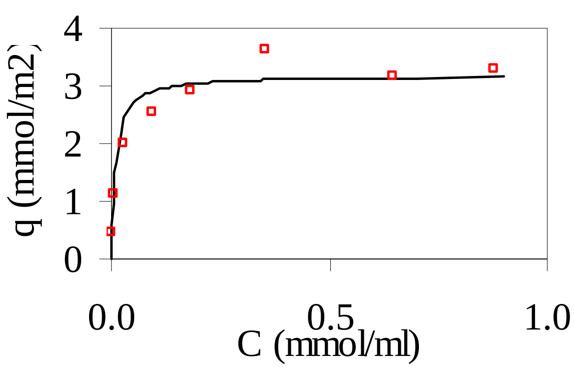
Large Crystals



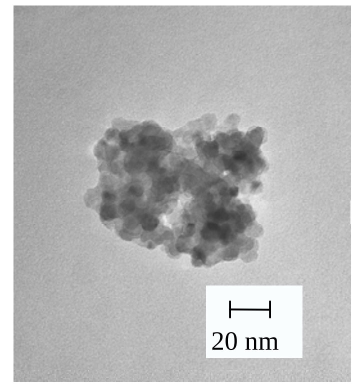
Adsorption of Cadmium to Large and Nano-Anatase

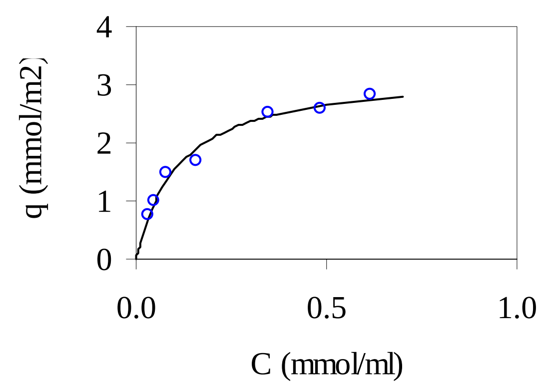
Large crystals





Nanoparticles

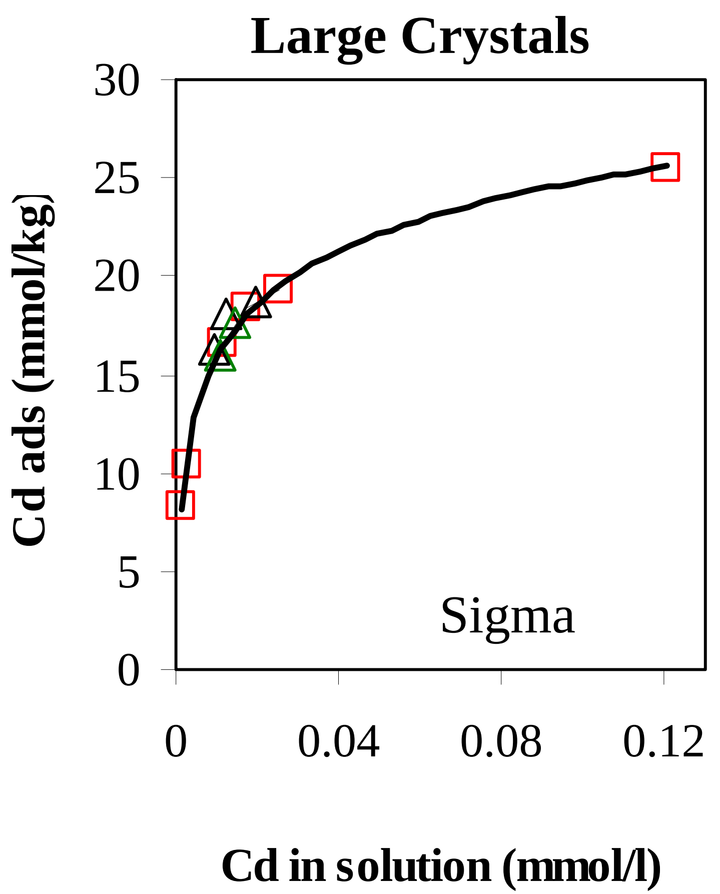


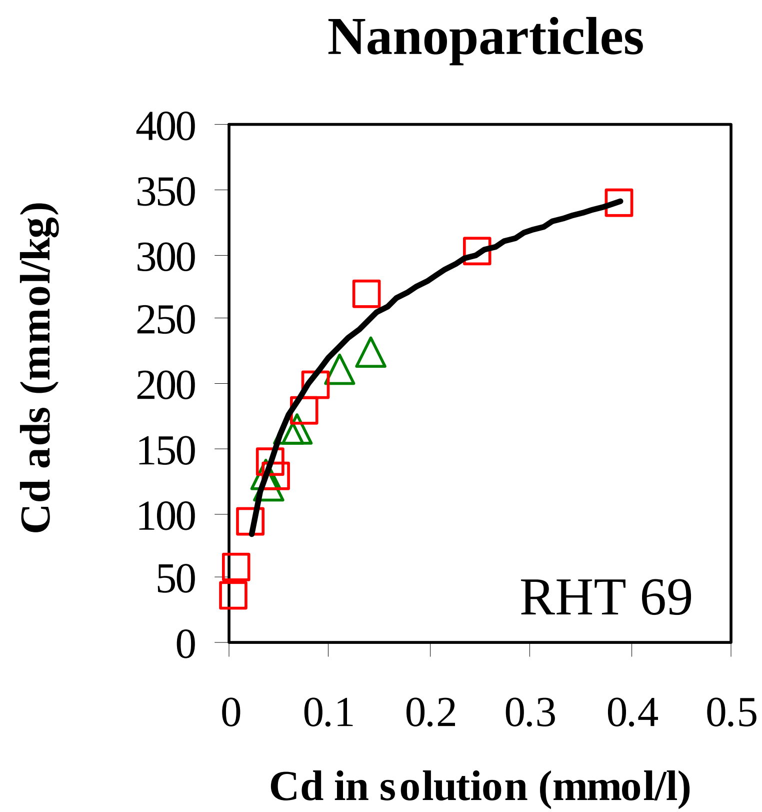


Langmuir Adsorption Isotherm Parameters

Solid	Q_{max} (μmol/m^2)	b (ml/μmol)	$Q_{max} \cdot b$ (ml/m^2)	σ_{Q^o}[c] (ml/m^2)	σ_b[c] (ml/μmol)	R[c]
Sigma and Alfa Aesar[a]	3.19	108.7	346.75	0.12	29.2	0.978
P-25 and TiNano[b]	3.50	3.70	12.94	0.10	0.40	0.985
RHT-47	3.25	8.94	29.02	0.15	1.33	0.991
RHT 69	2.55	7.71	19.7	0.12	1.06	0.991

Adsorption/Desorption Reversibility





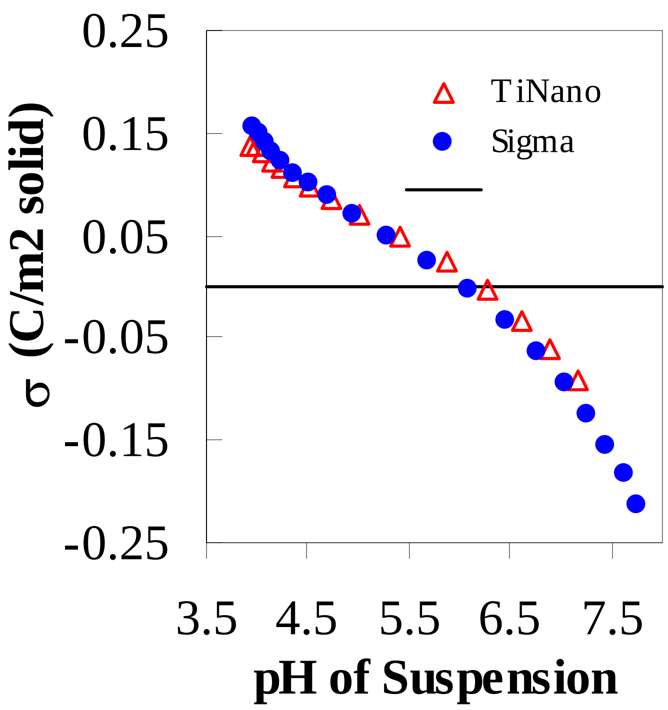
Electrochemical Properties

g of solid added	Initial pH	Final pH	$\frac{\Delta pH}{m^2}$
0.8g Sigma Anatase	7.50	6.59	0.105
0.2g Tinano 40	7.51	6.61	0.113
2.0g Sigma Anatase	7.30	6.37	0.043
0.5g Tinano 40	7.32	6.33	0.050
0.8g Sigma Anatase	6.03	5.99	0.002
0.2g Tinano 40	6.02	5.92	0.007
2.0g Sigma Anatase	6.01	5.97	0.005
0.5g Tinano 40	6.00	5.86	0.012

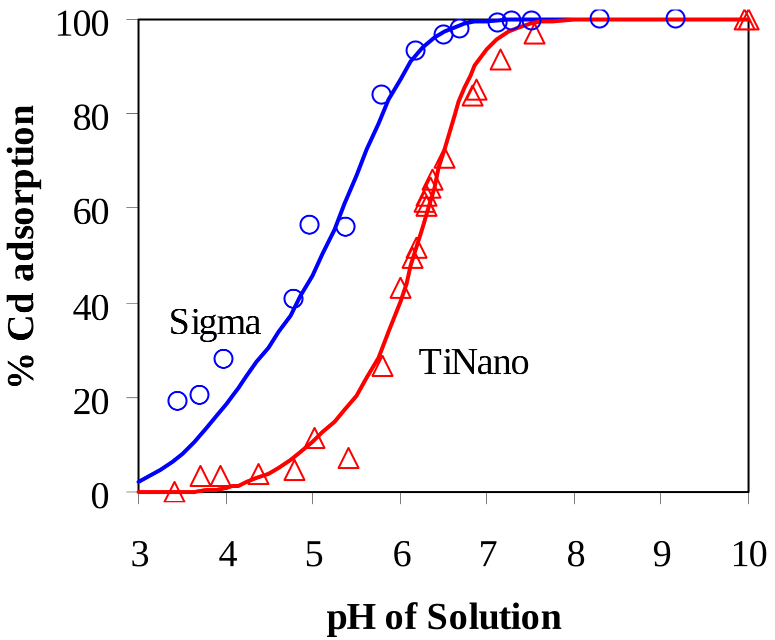
Reported pzc: 5.8 - 6.1 pH

Surface Charges and pH Adsorption Edge

Potential Titration
TiO_2 suspension



Cd adsorption vs. pH



Summary

- States of aggregation of nanoparticles may change in various aqueous environment
- Adsorption of contaminants to the surfaces of nanoparticles is very strong
- Adsorption/desorption of organic compounds to nanoparticles might be hysteretic
- Adsorption/desorption of heavy metals onto/from nanoparticles are predictable based on surface area normalized sorption isotherm
- Nanomaterials in natural aqueous environments may affect the fate and transport of contaminants substantially

Future

- Responsible Use
- Remediation