

Oxytetracycline at Environmental Interfaces Studied by Second Harmonic Generation

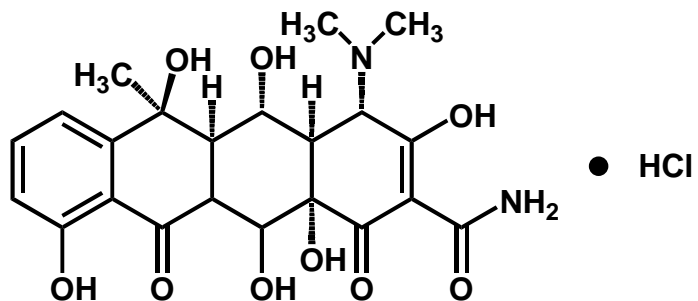


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WMRC Symposium on PPCPs in the Illinois Environment -- April 25, 2008

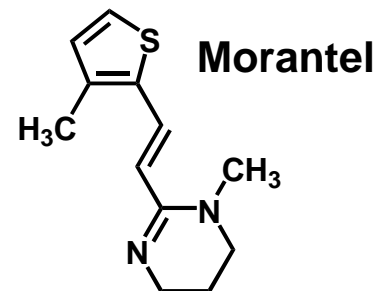
Oxytetracycline

Oxytetracycline (OTC)



Mifflin et al. *J. Phys. Chem. B* **2006**, *110*, 22577.

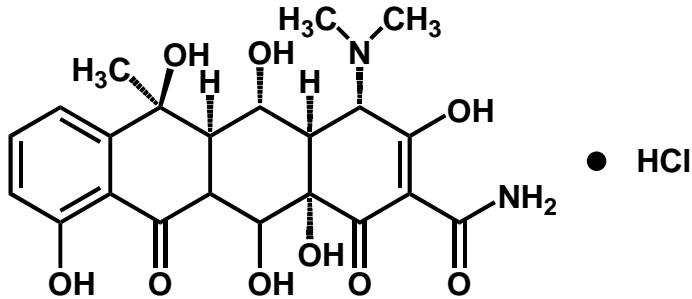
Hayes et al. *J. Phys. Chem. C* **2007**, *111*, 8796.



Konek et al. *J. Am. Chem. Soc.* **2005**, *127*, 15771.

Oxytetracycline

Oxytetracycline (OTC)



• **Tetracyclines are used in humans and cattle/poultry/swine**

• **Estimated 3 million pounds of tetracyclines used annually for growth stimulation in livestock!**

• **25-75% of tetracyclines administered to animals are excreted in the active form.**



Hileman, B. "Resistance is on the Rise" *Chem. Eng. News* **2001**, February 19, 47.

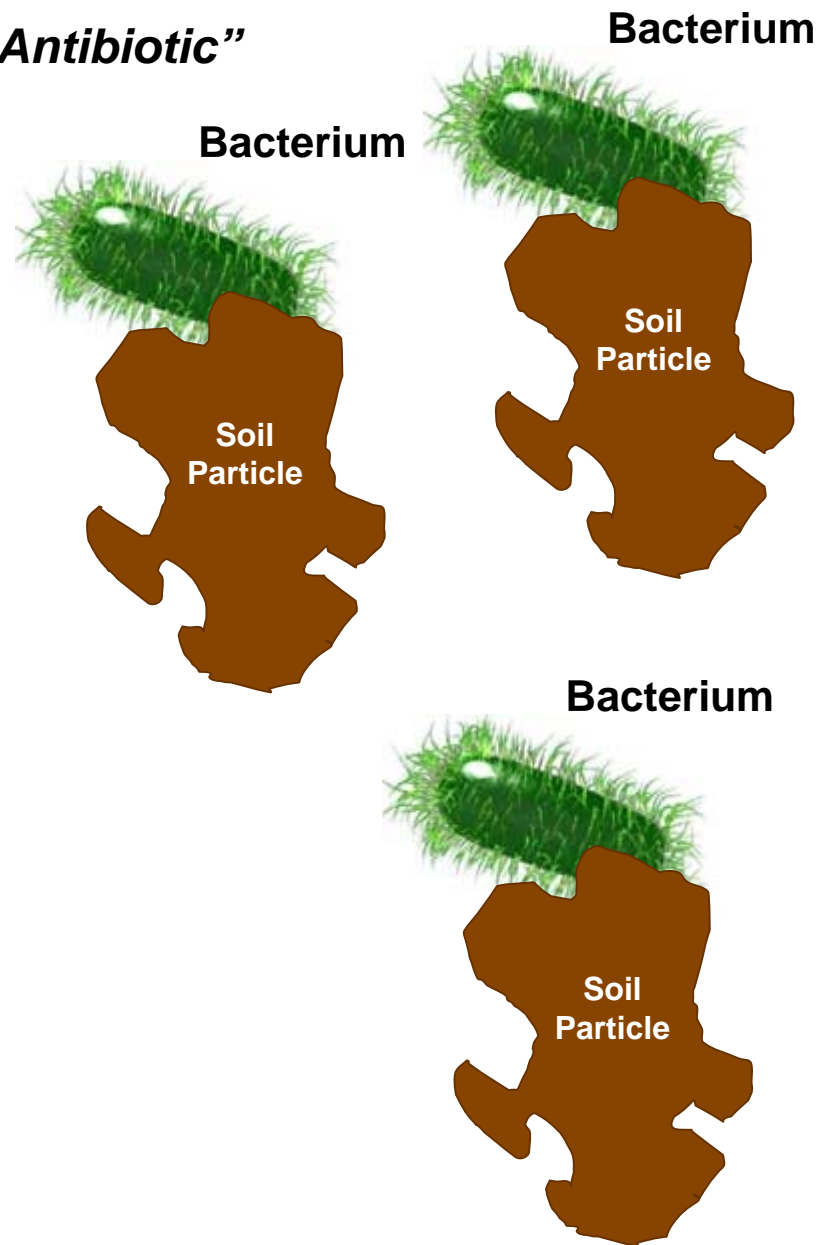
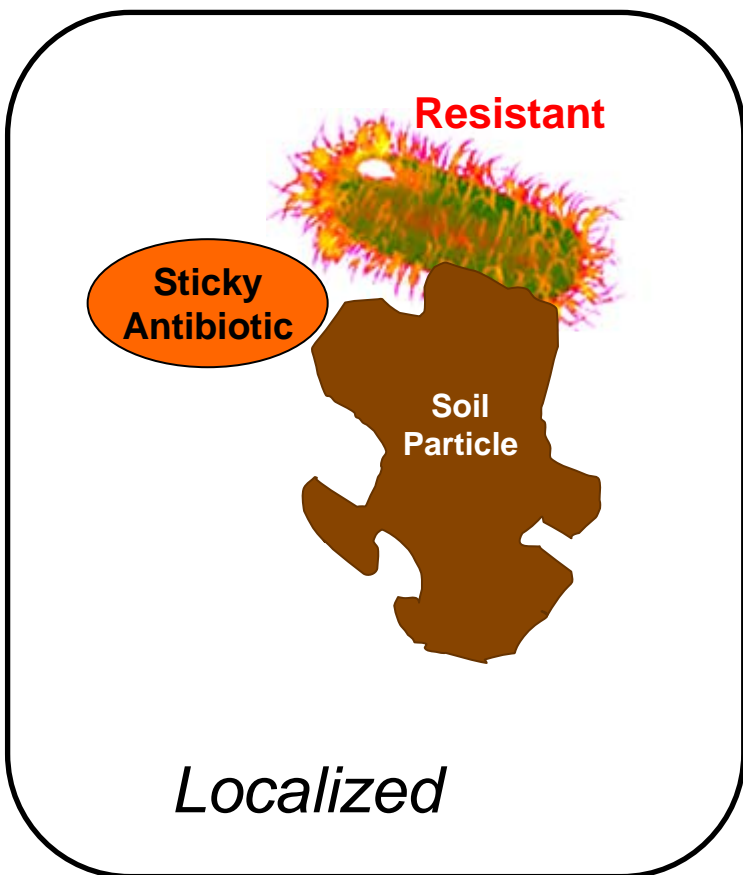
Kulshrestha, P.; Giese, R. F. Aga, D.S. *Environ. Sci. Technol.* **2004**, 38, 4097.

Boxall, A. B. A. *EMBO Reports* **2004**, 5, 1110.

Simon, N. S. *Environ. Sci. Technol.* **2005**, 39, 3480.

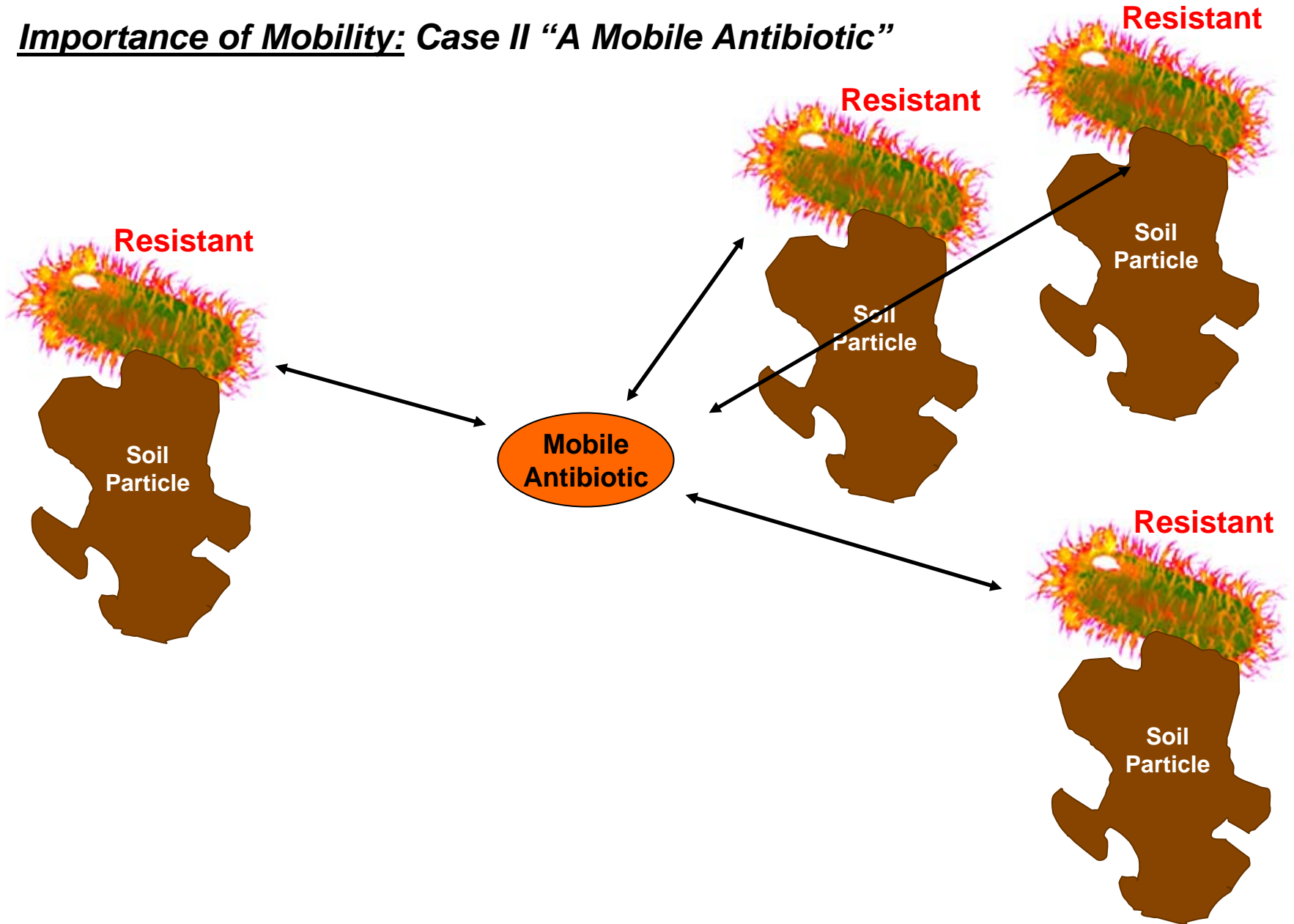
Antibiotic Resistance in Soil Bacteria

Importance of Mobility: Case I “A Sticky Antibiotic”

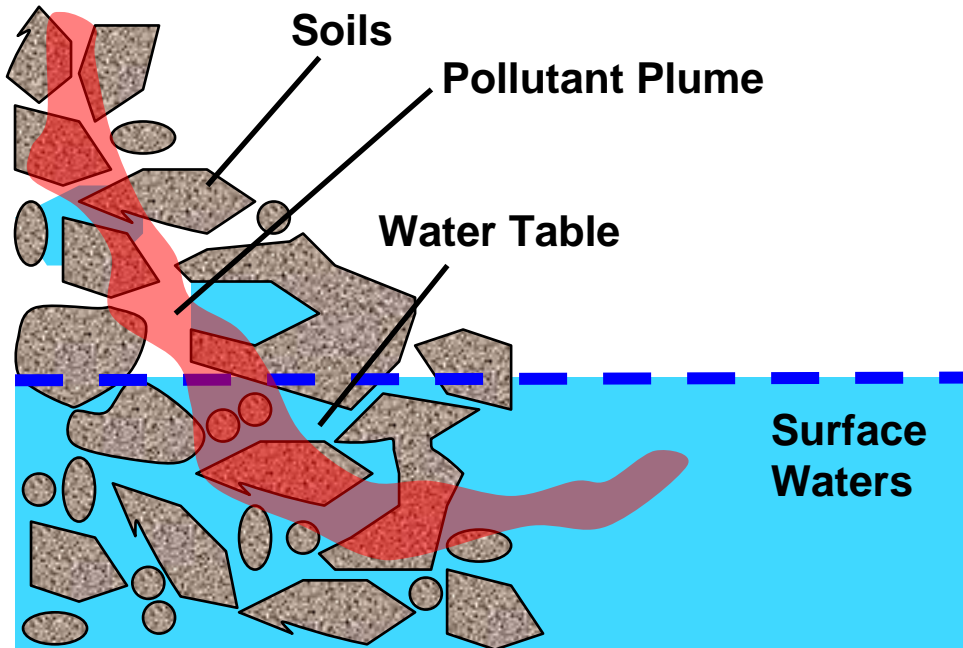


Antibiotic Resistance in Soil Bacteria

Importance of Mobility: Case II "A Mobile Antibiotic"



Environmental Interfaces Control Transport, Reactivity, Bioavailability



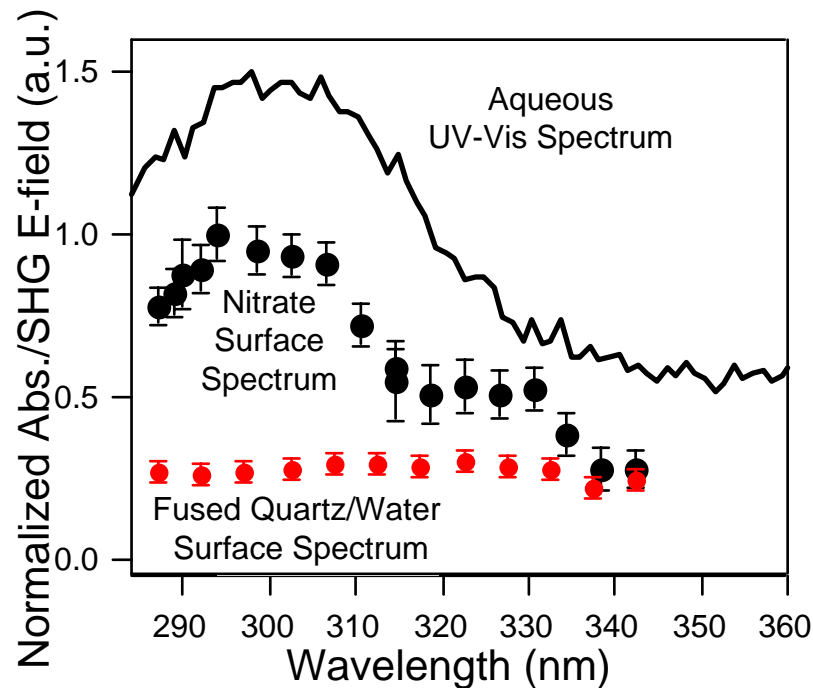
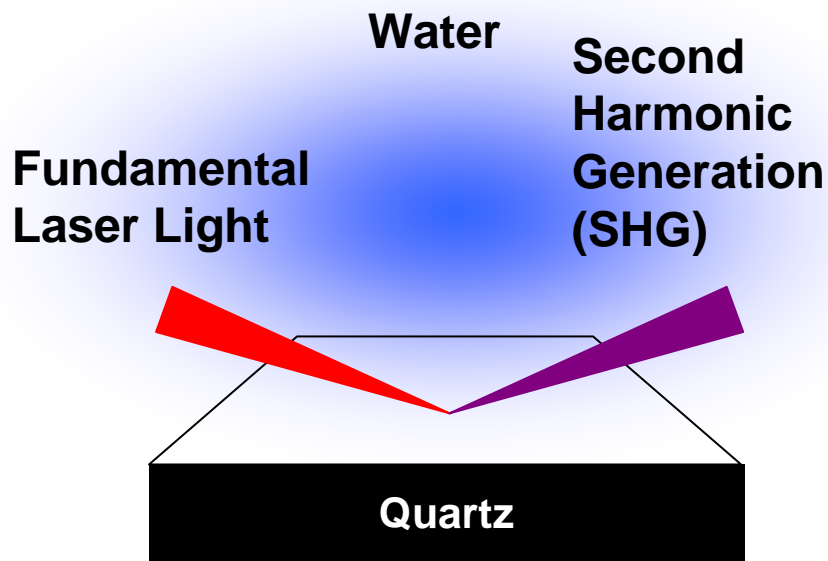
Challenges:

- Complexity
- Separating Bulk from Surface
- Sensitivity



Second Harmonic Generation

Second Harmonic Generation (SHG)



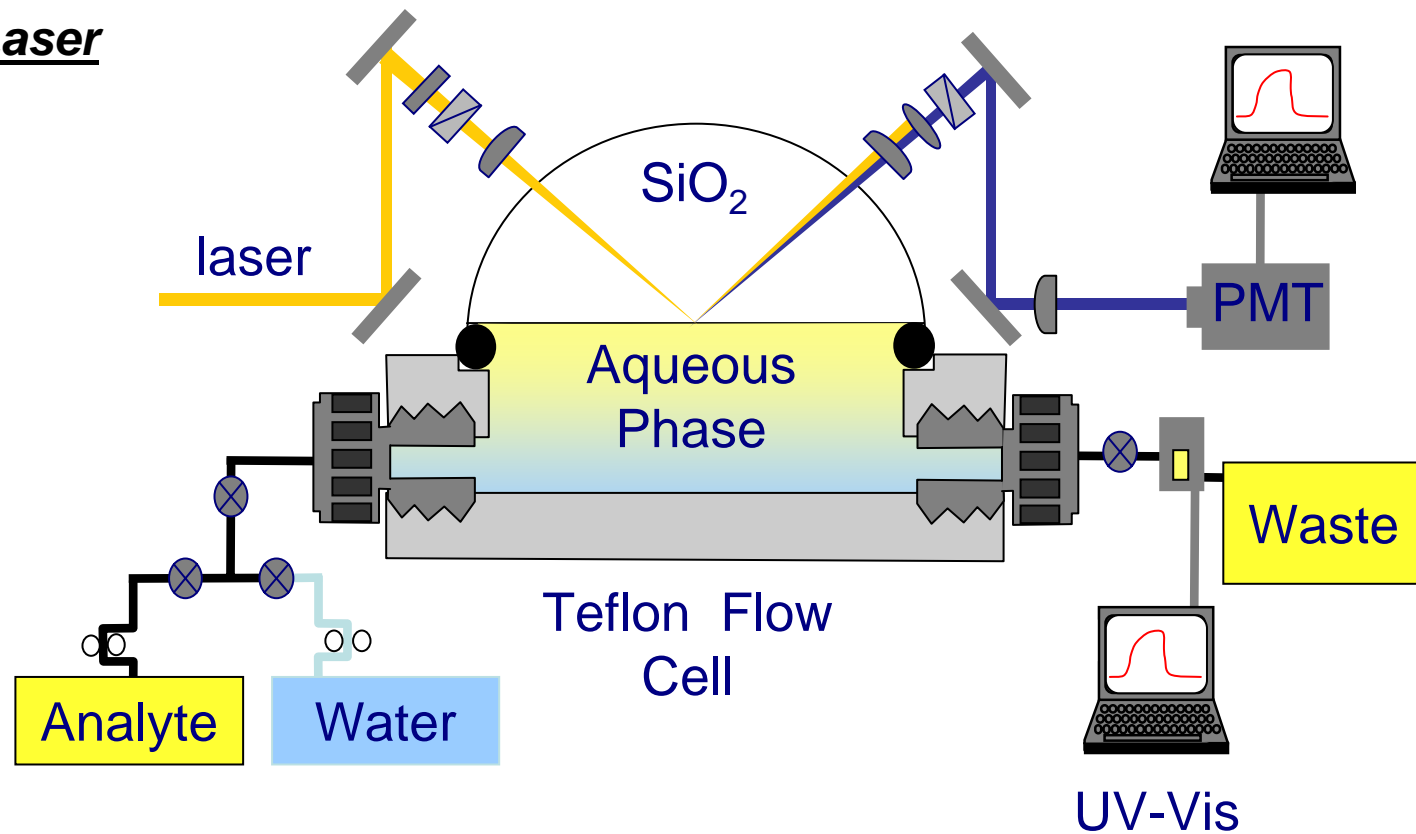
Advantages:

- Surface-Specific
- Sensitivity Allows for Real-time Monitoring of Adsorption
- Experiments Run Under Flow Conditions

“Measurable” is $E_{\text{SHG}} \propto N_{\text{ads}}$

Experimental Setup

Pulsed & Tunable Laser



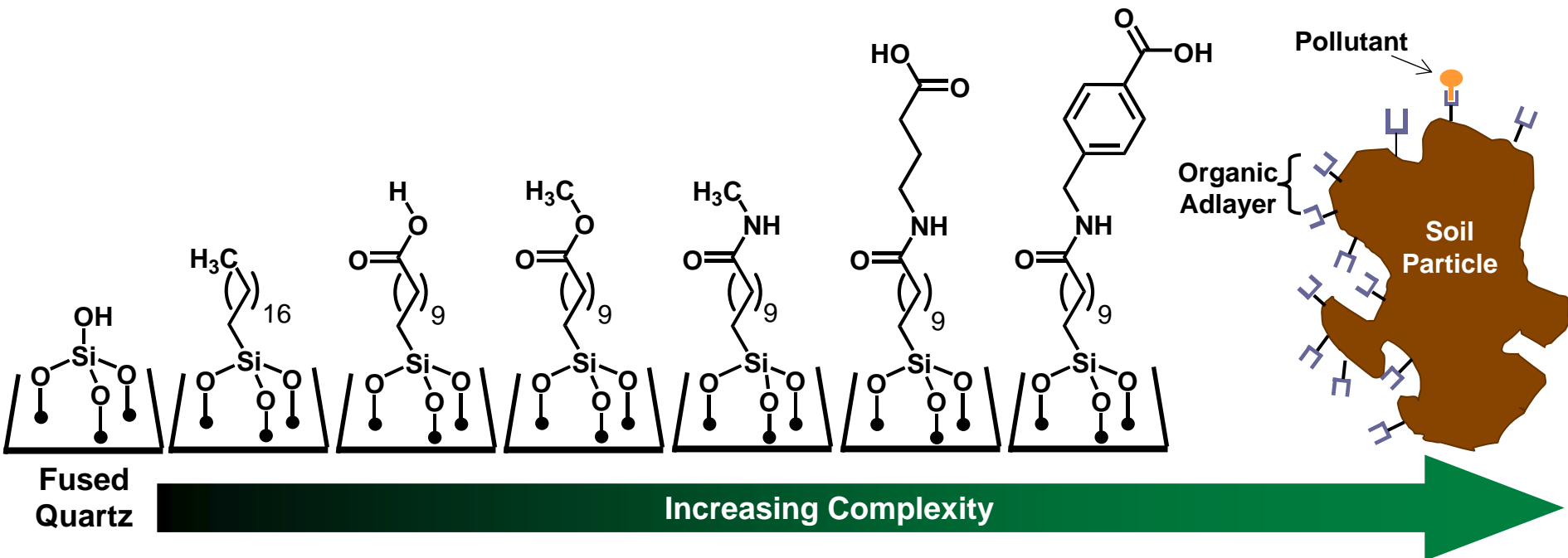
Mifflin, A.L.; Gerth, K.A.; Weiss, B.M. Geiger, F.M. *J. Phys. Chem. A* **2003**, *107*, 6212.

Mifflin, A.L.; Gerth, K.A.; Geiger, F.M. *J. Phys. Chem. A* **2003**, *107*, 9620.

Mifflin, A.L.; Musorrafiti, M.J.; Konek, C.T.; Geiger, F.M. *J. Phys. Chem. B* **2005**, *109*, 24386.

Hayes et al. *J. Phys. Chem. C* **2007**, *111*, 8796.

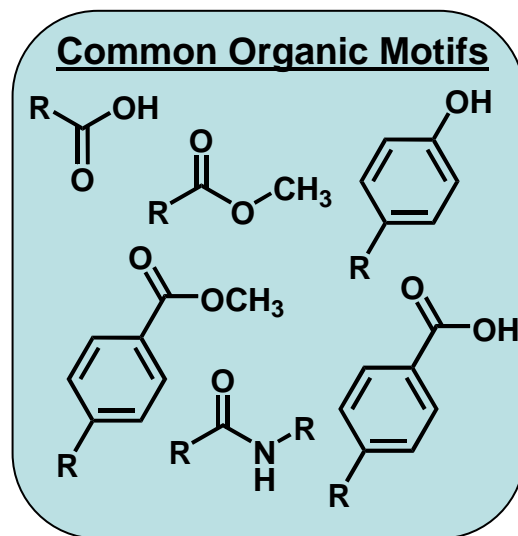
Model Environmental Interfaces



Our Strategy:

Use synthetic chemistry to:

- (1) Isolate and study individual functional groups.
- (2) Build more complex model interfaces.



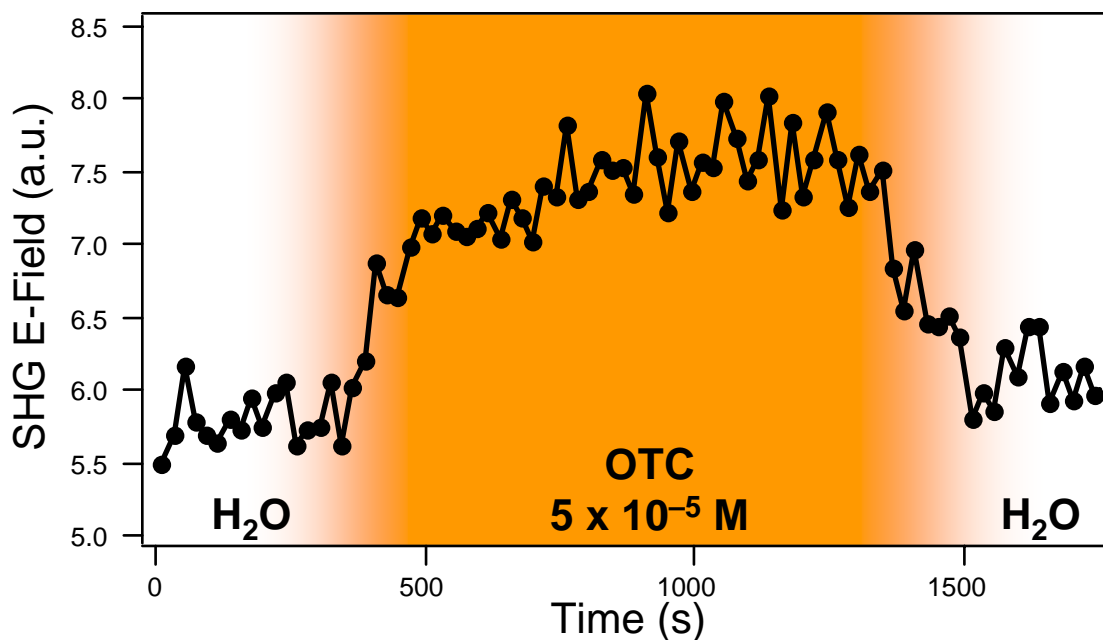
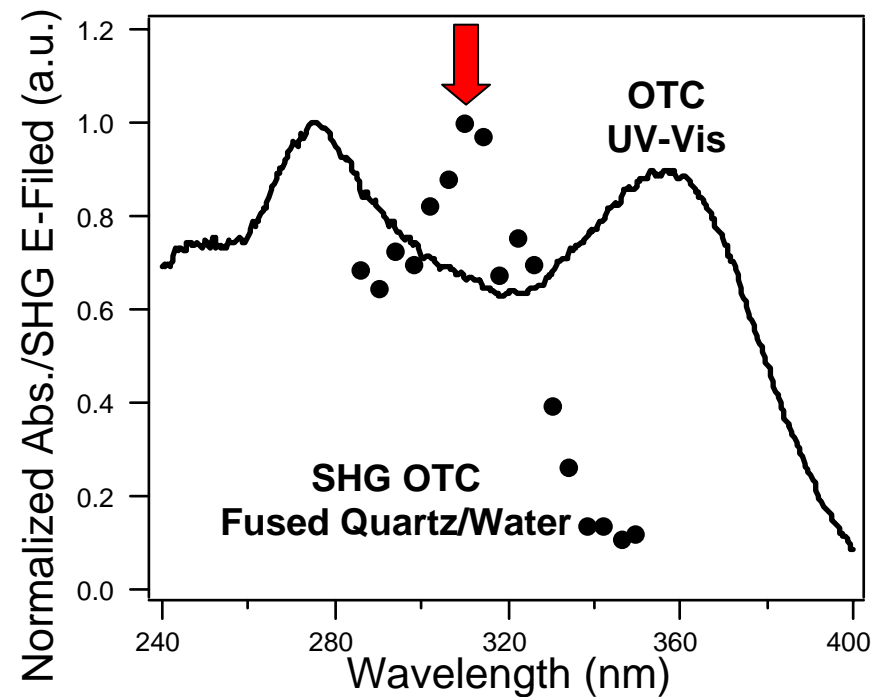
Sutton, R.; Sposito, G. *Environ. Sci. Technol.* **2005**, 39, 9009.

Al-Abadleh et al. *J. Am. Chem. Soc.* **2004**, 126, 11126.

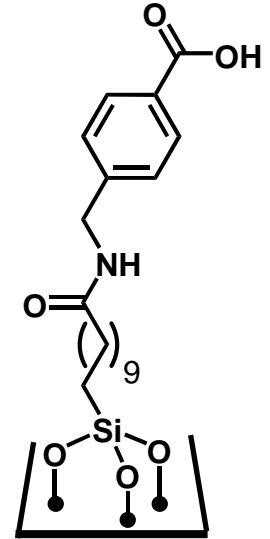
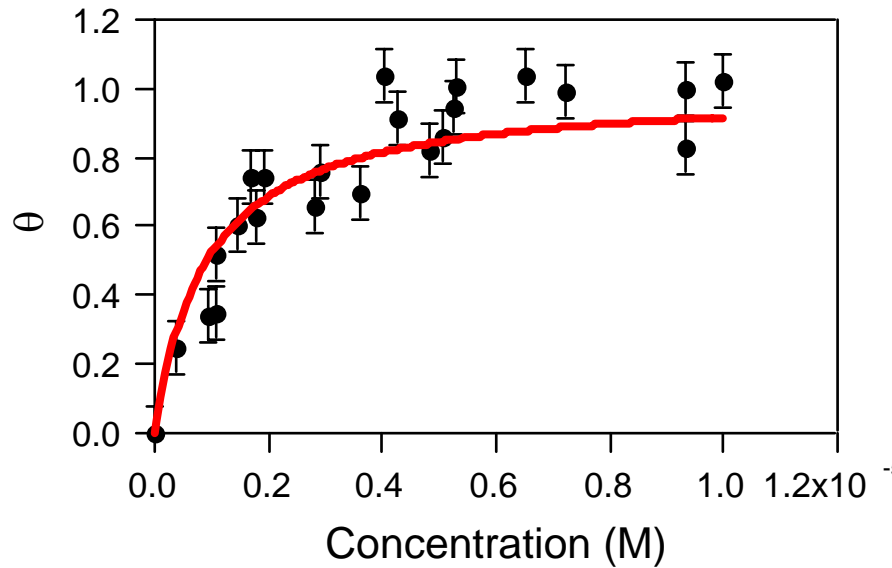
Gibbs-Davis, J.M.; Hayes, P.L.; Scheidt K. A.; Geiger F.M. *J. Am. Chem. Soc.* **2007**, 129, 7175.

Hayes et al. *J. Phys. Chem. C* **2007**, 111, 8796.

OTC Spectroscopy and Adsorption/Desorption Trace at Fused Quartz/Water Interface (pH 8)



OTC Isotherm & The K_d Model (pH 8)



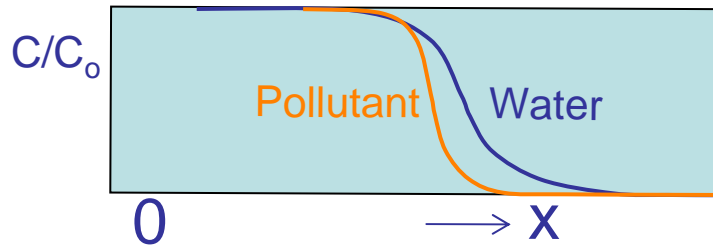
Retardation Factor:

$$R = 1 + (\rho/n) \cdot K_d$$

$$K_d = 0.11 \text{ mL/g}$$

$$\text{Taking: } (\rho/n) = 4 - 10 \text{ g/cm}^3$$

$$R_f = 1.44 - 2.1$$



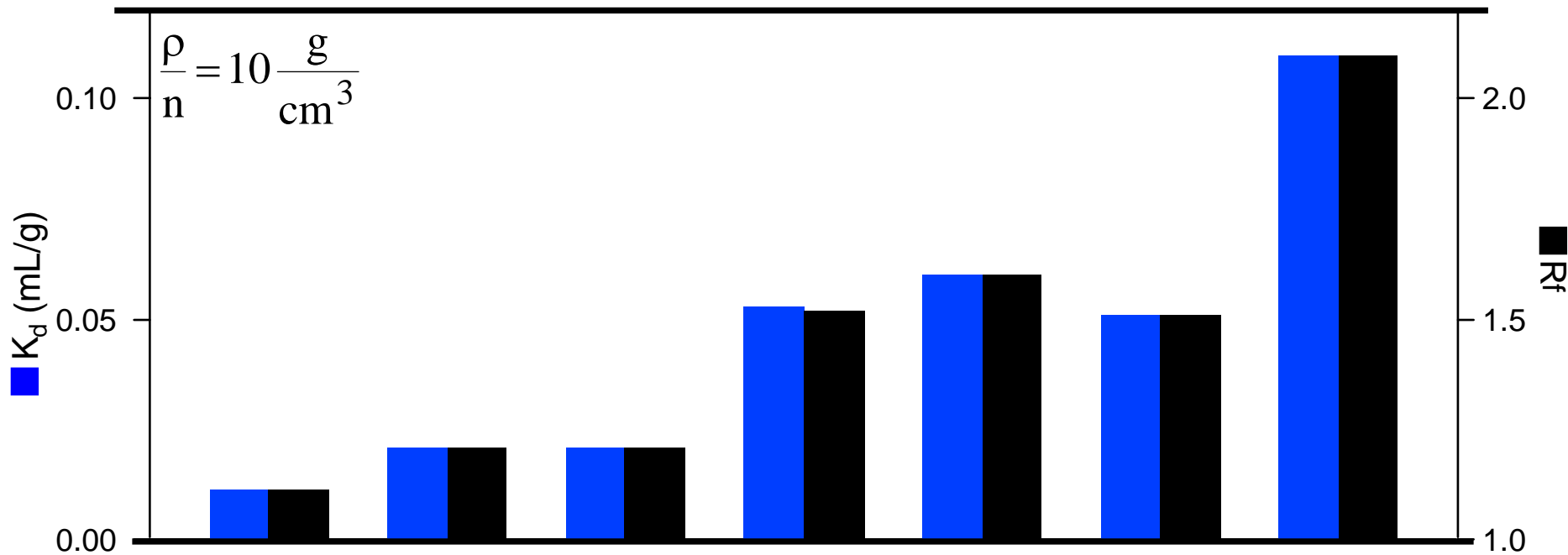
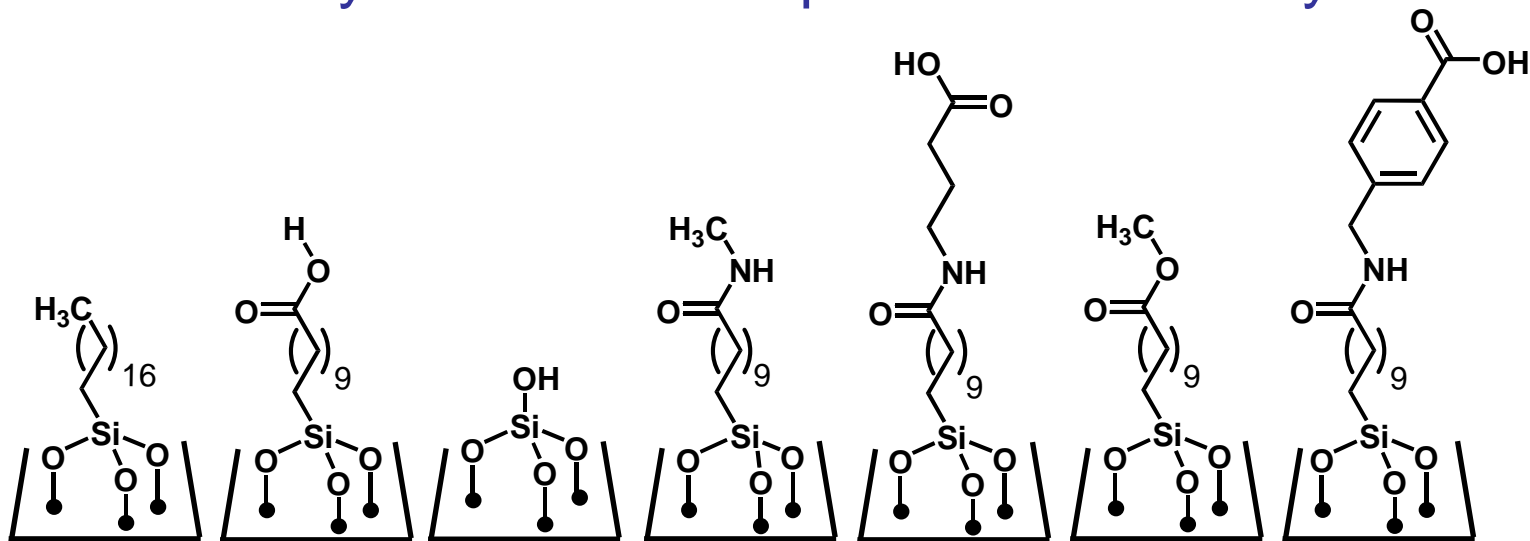
→ $R_f = 2$, corresponds to 50% reduction in OTC mobility relative to water.

Langmuir, D. *Aqueous Environmental Geochemistry*; Prentice Hall, Inc: New Jersey, 1997.

Hayes et al. *J. Phys. Chem. C* **2007**, 111, 8796.

Mifflin et al. *J. Phys. Chem. B* **2006**, 110, 22577.

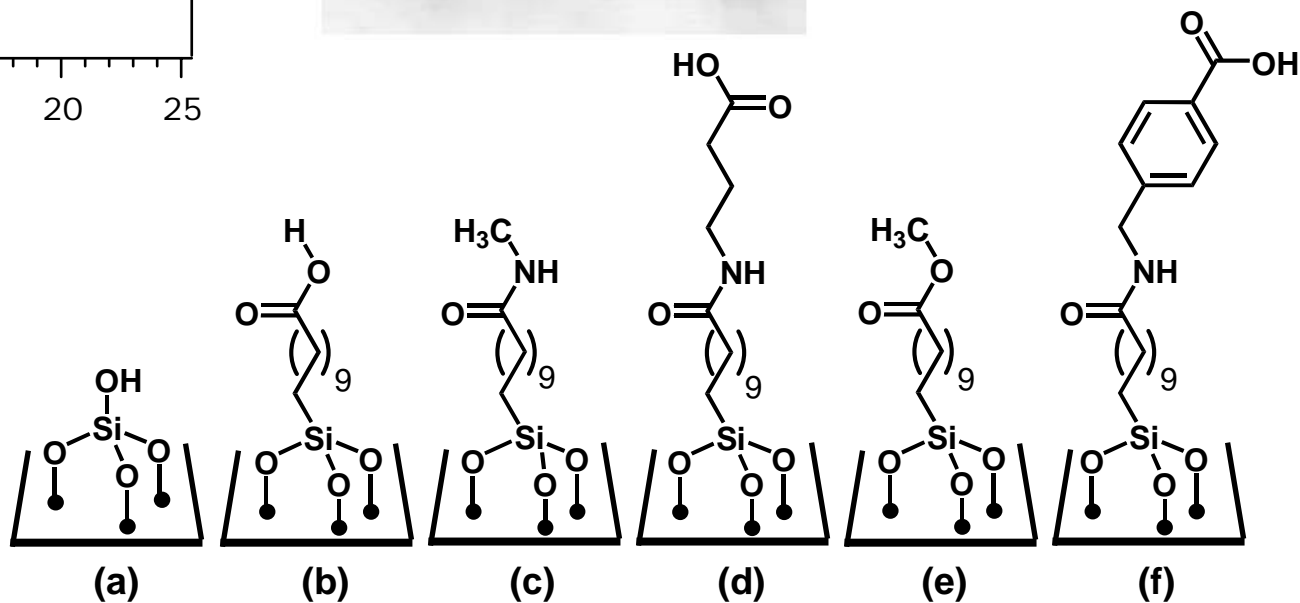
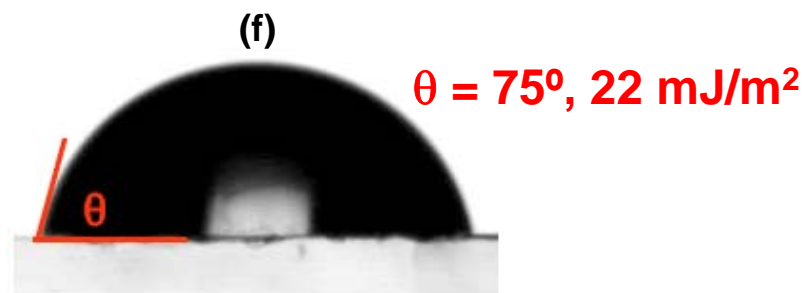
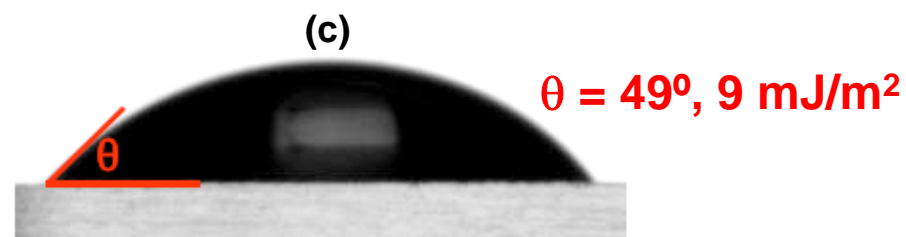
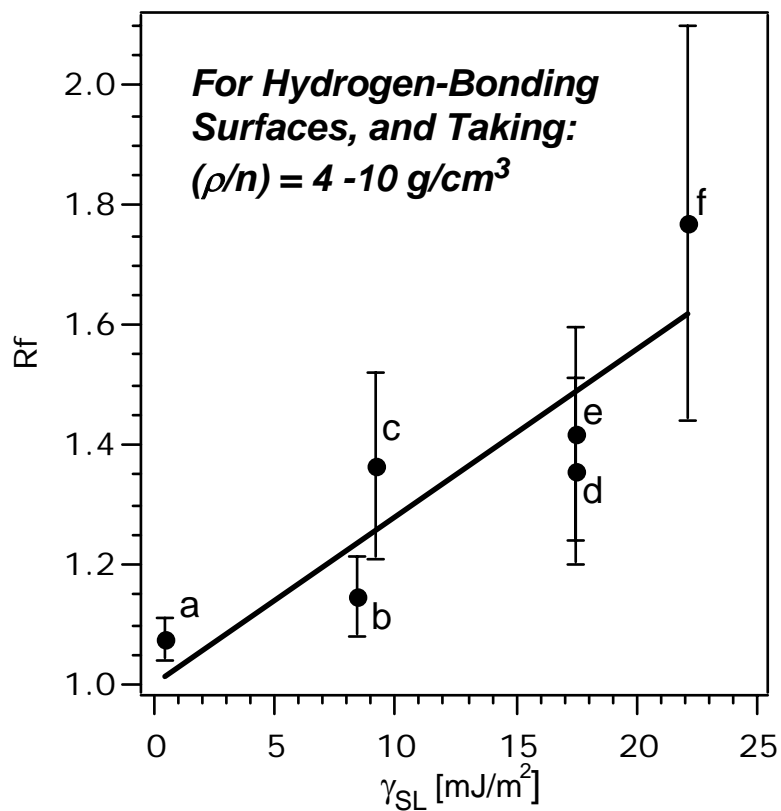
Summary of Isotherm Experiments: Mobility



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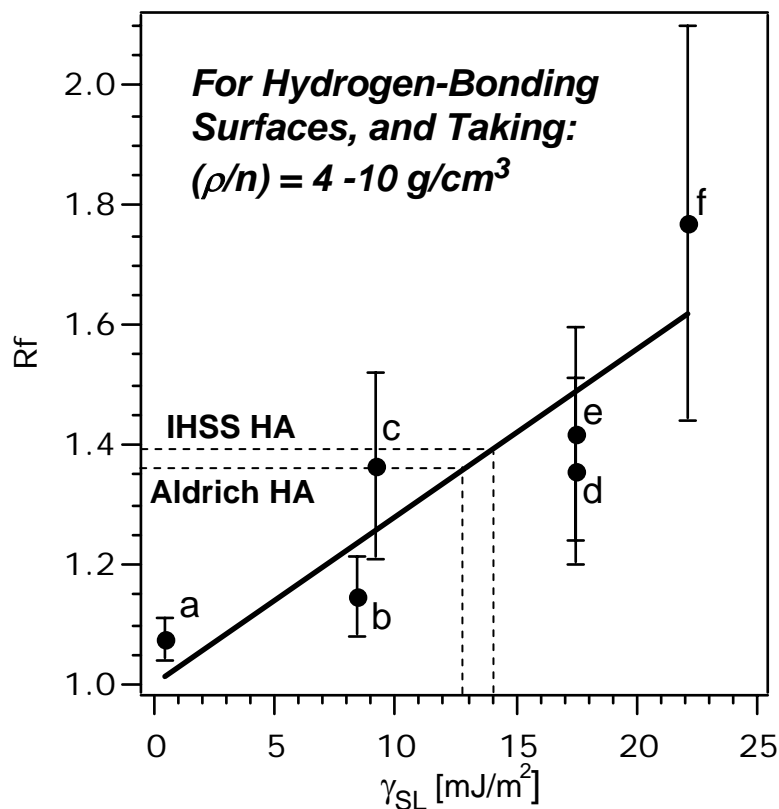
Predicting OTC Mobility: Surface Energy and OTC Retardation



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Predicting OTC Mobility: Surface Energy and OTC Retardation



IHSS Humic Acid:

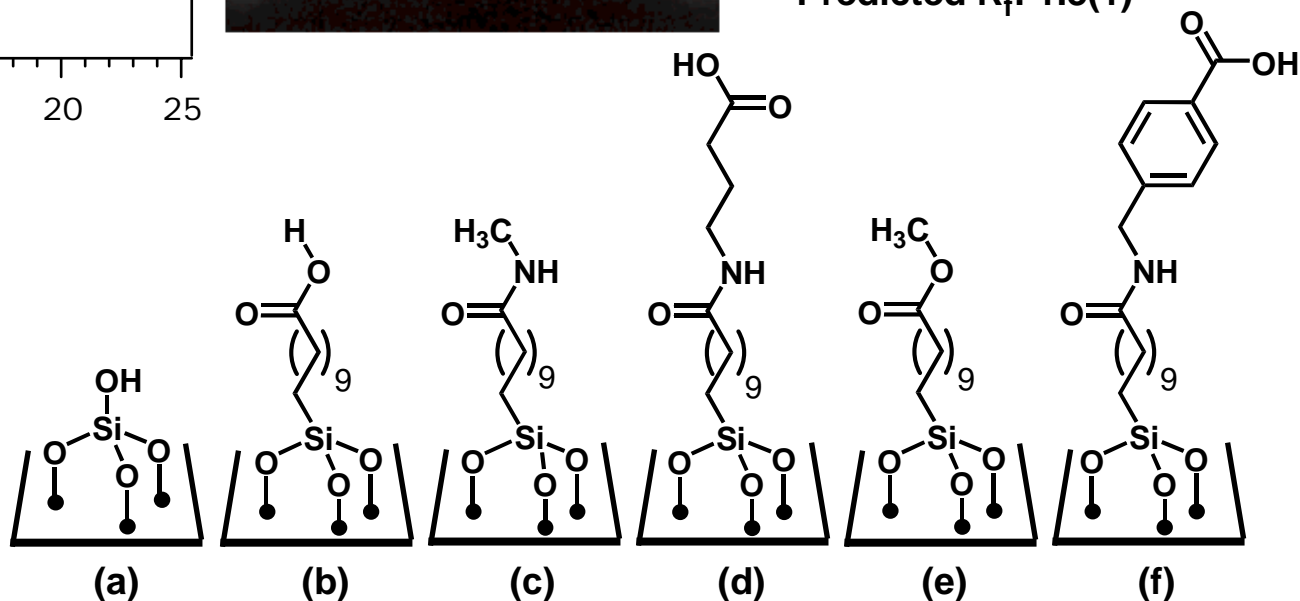


**Contact Angle: 59(3)
Surface Energy: 14(1) mJ/m²
Predicted R_f: 1.4(1)**

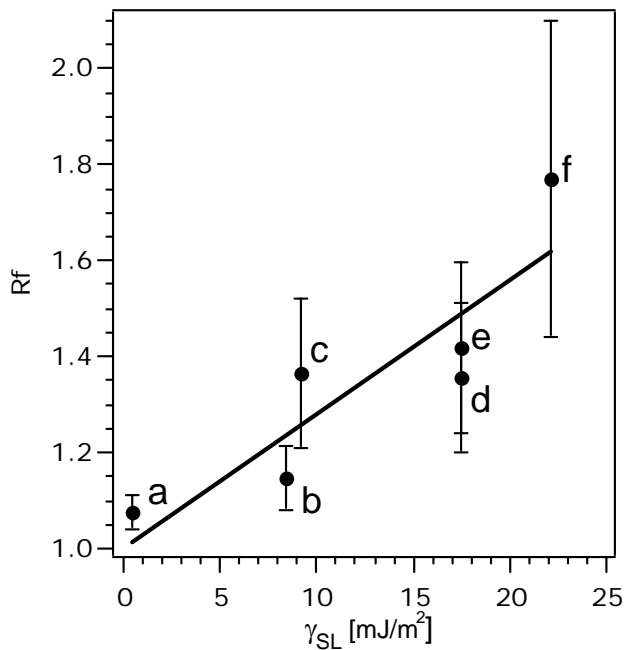
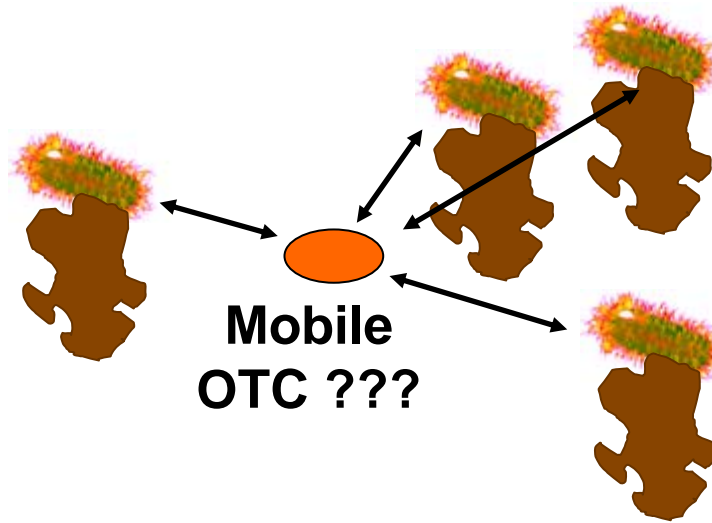
Aldrich Humic Acid:



**Contact Angle: 57(3)
Surface Energy: 13(1) mJ/m²
Predicted R_f: 1.3(1)**



Connections to Mobility



OTC will tend to be less mobile in silica-rich soils that:

- ***Contain natural organic matter with a large density of benzoic acid functional groups***
- ***Display high interfacial energy***

Acknowledgements



Geiger Group 2006

*Professor Franz M. Geiger
Dr. Amanda Mifflin (OTC)
Dr. Julianne Gibbs-Davis
Professor Karl A. Scheidt*

Funding:

Schlumberger

