Oxytetracycline at Environmental Interfaces Studied by Second Harmonic Generation

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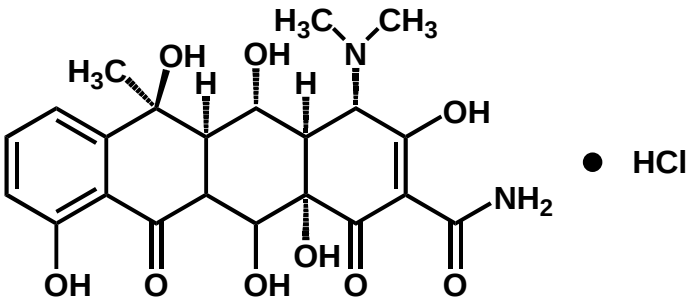
WMRC Symposium on PPCPs in the Illinois Environment -- April 25, 2008

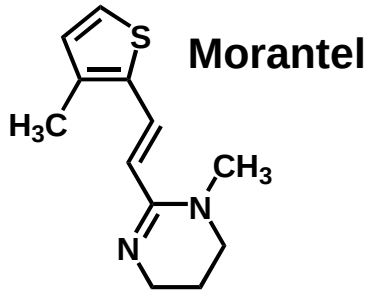
Oxytetracycline

Oxytetracycline (OTC)



Mifflin et al. *J. Phys. Chem. B* **2006,** *110,* 22577.
Hayes et al. *J. Phys. Chem. C* **2007,** *111,* 8796.

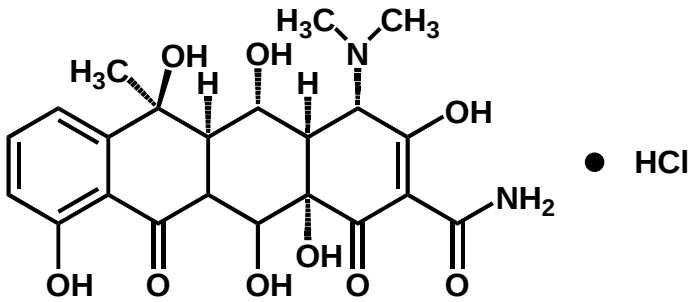
Morantel



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

Oxytetracycline

Oxytetracycline (OTC)



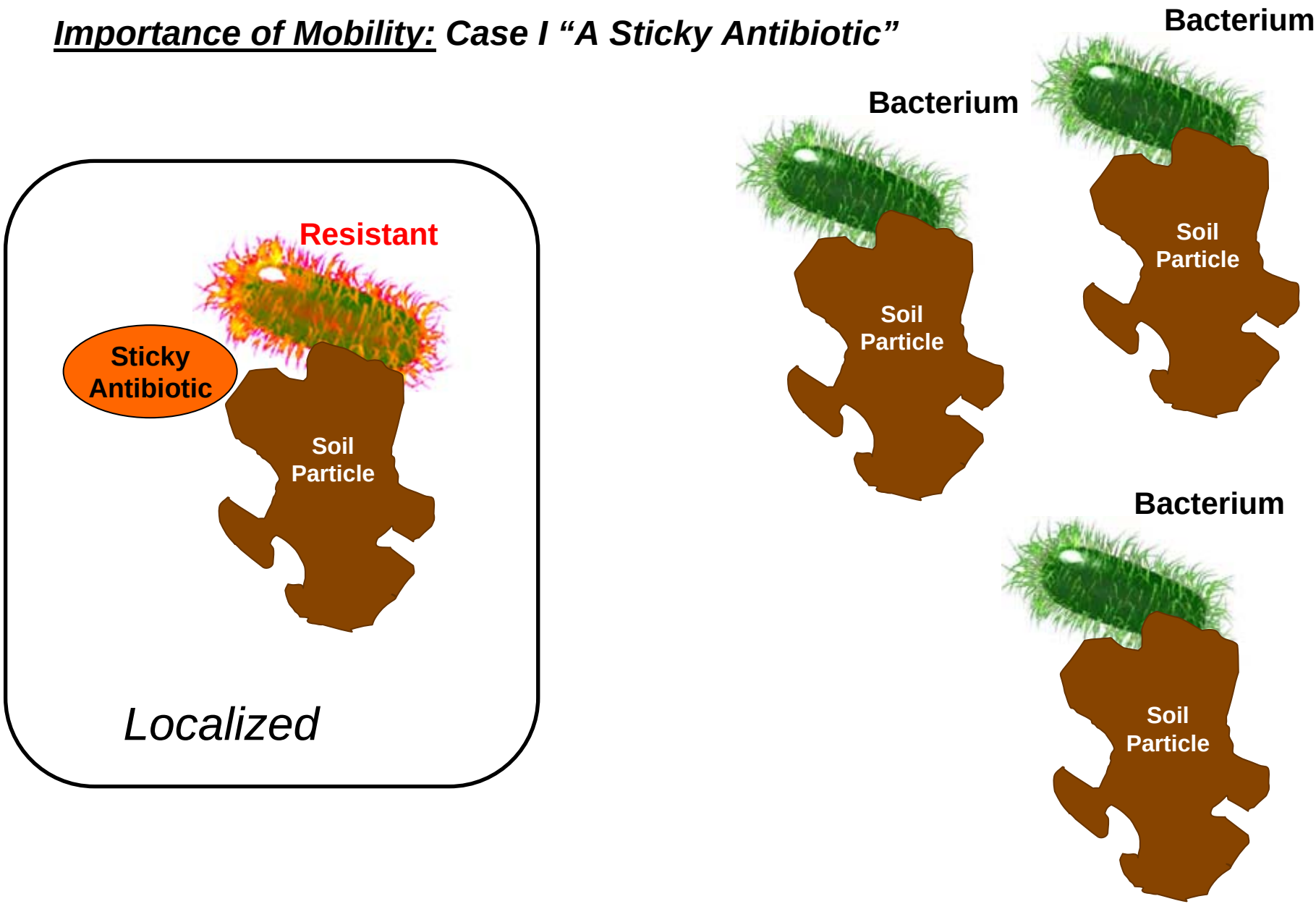
● HCl

- ***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.

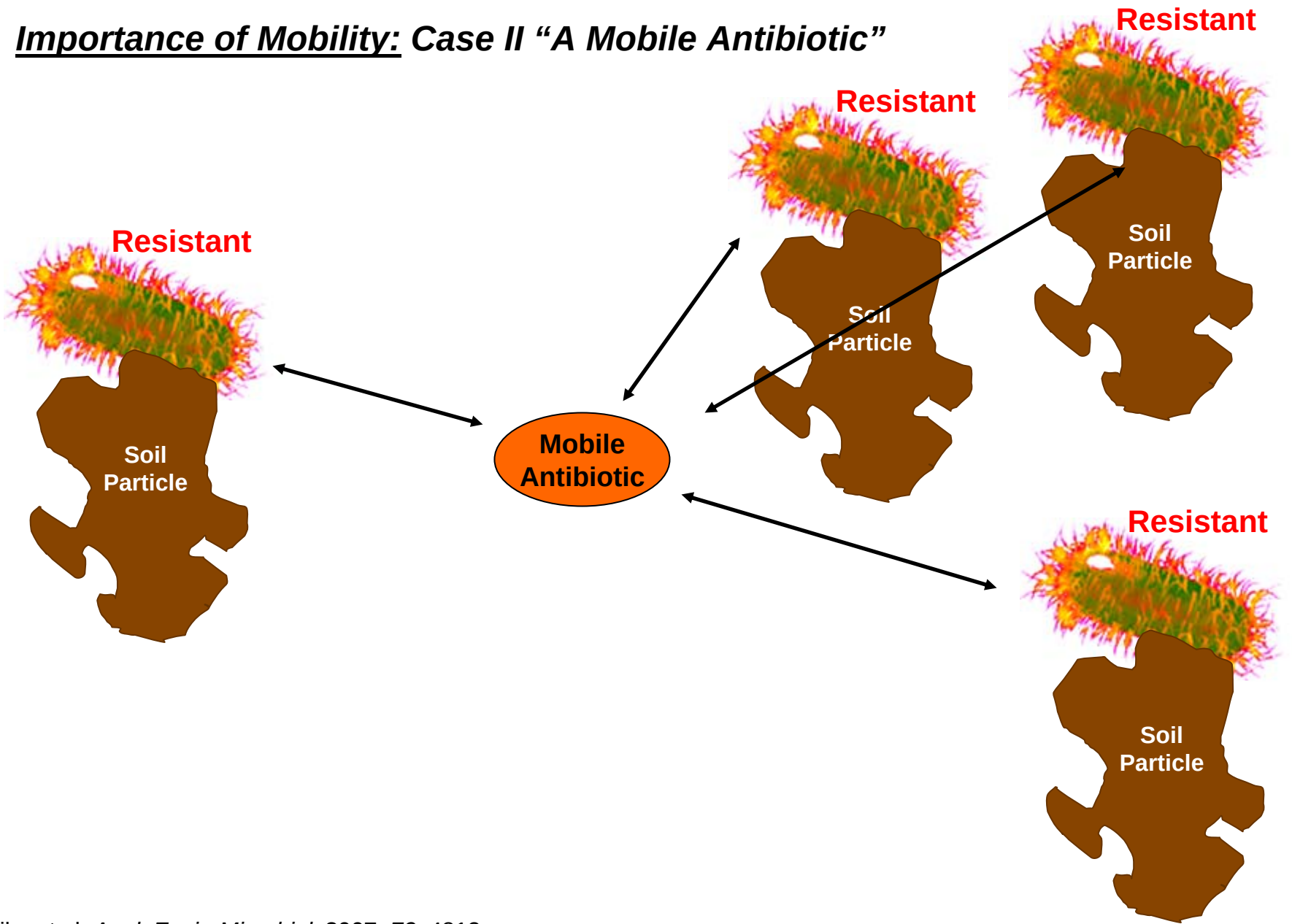
Antibiotic Resistance in Soil Bacteria

<u>Importance of Mobility:</u> Case I "A Sticky Antibiotic"



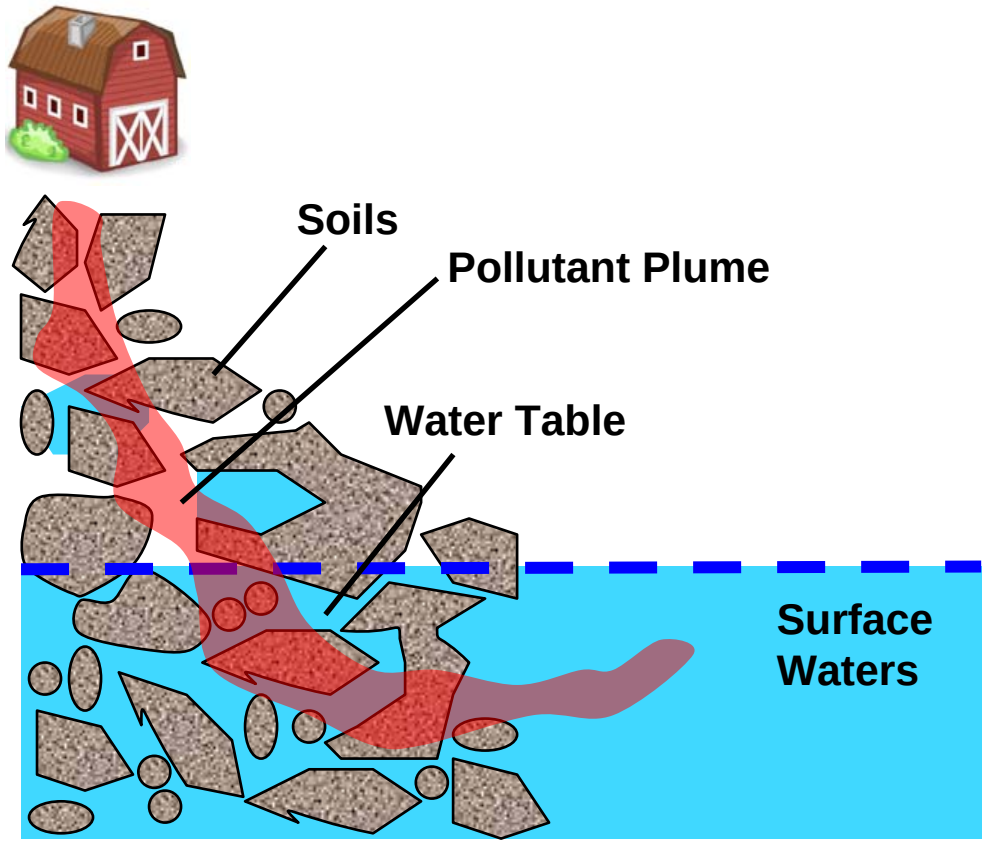
Antibiotic Resistance in Soil Bacteria

***Importance of Mobility:* Case II "A Mobile Antibiotic"**



Koike et al. *Appl. Envir. Microbiol.* **2007,** *73,* 4813.

Environmental Interfaces Control Transport, Reactivity, Bioavailability

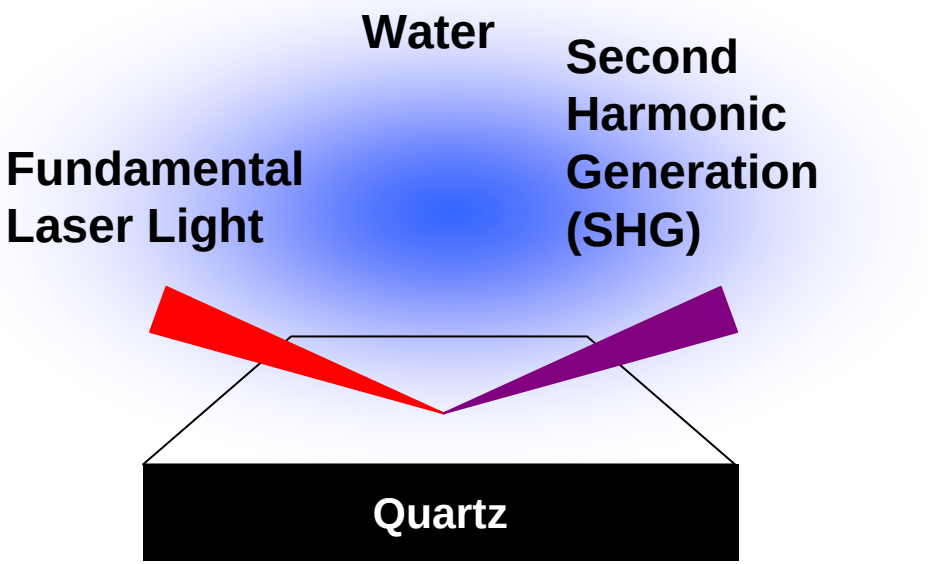


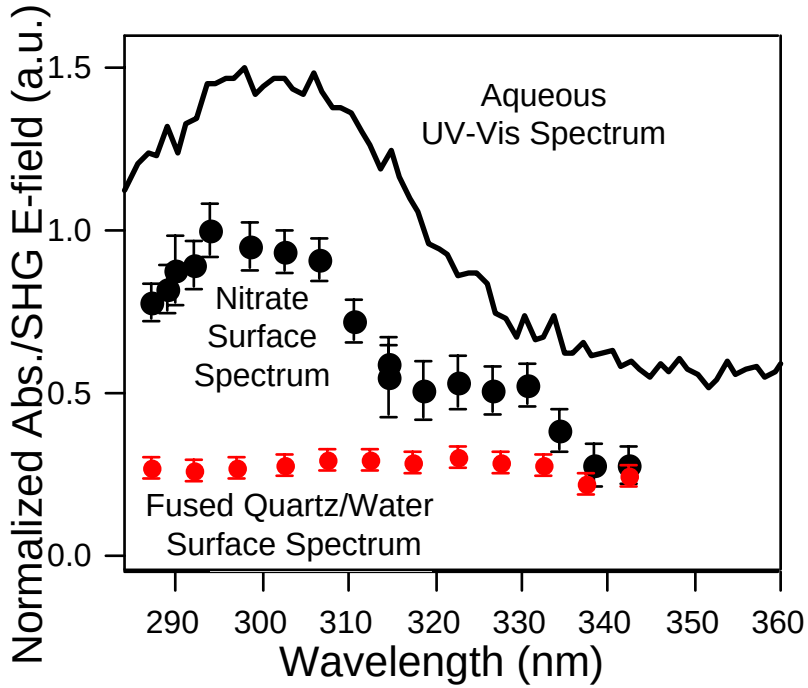
Challenges:

- **Complexity**
- **Separating Bulk from Surface**
- **Sensitivity**

Second Harmonic Generation

Second Harmonic Generation (SHG)





<u>Advantages</u>:

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

"Measurable" is $E_{SHG} \propto N_{ads}$

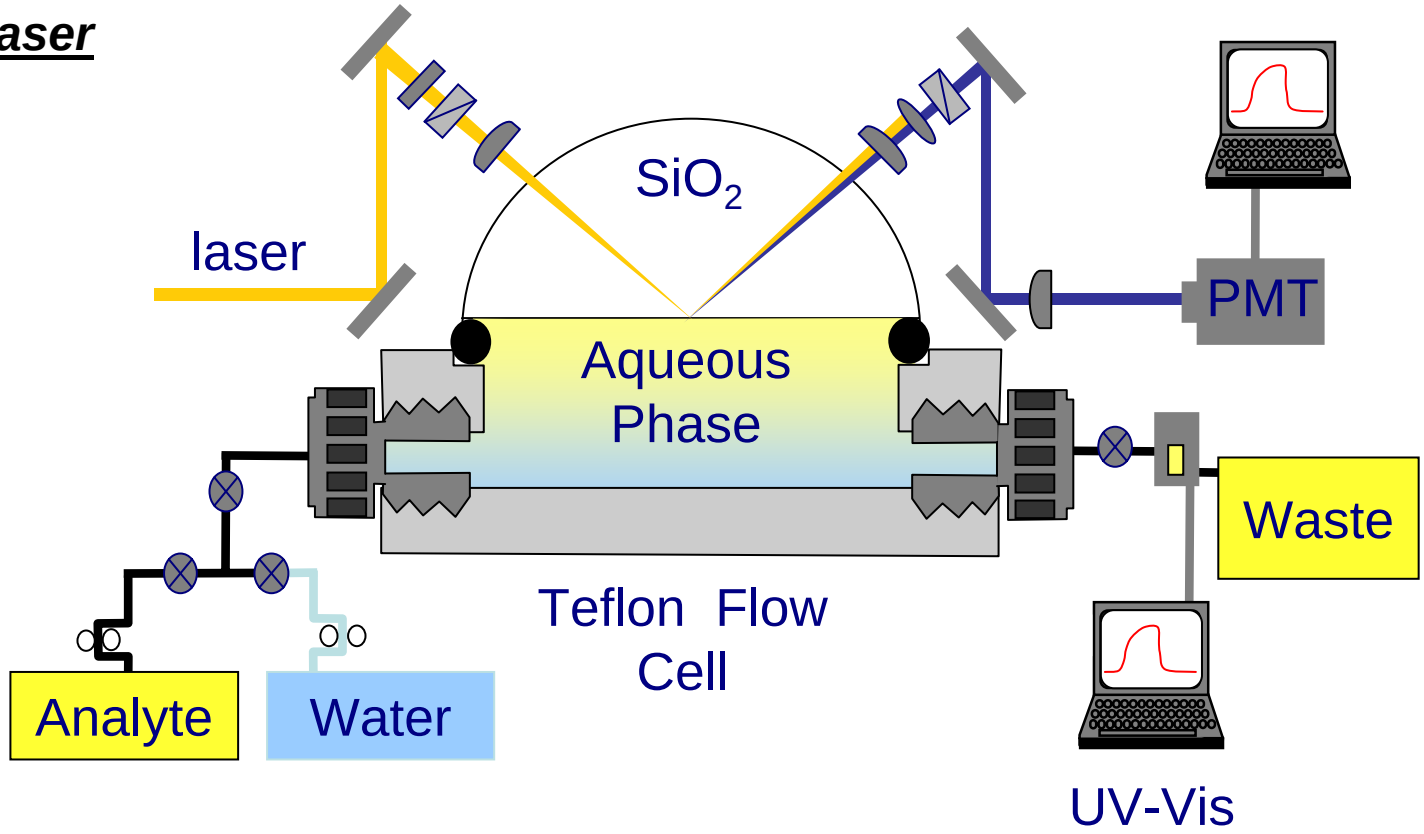
Eisenthal, K. B. *Chem. Rev.* **1996,** *96,* 1343.

Shen, Y. R. "*The Principles of Nonlinear Optics*" John Wiley & Sons: New York, 2003.

Experimental Setup

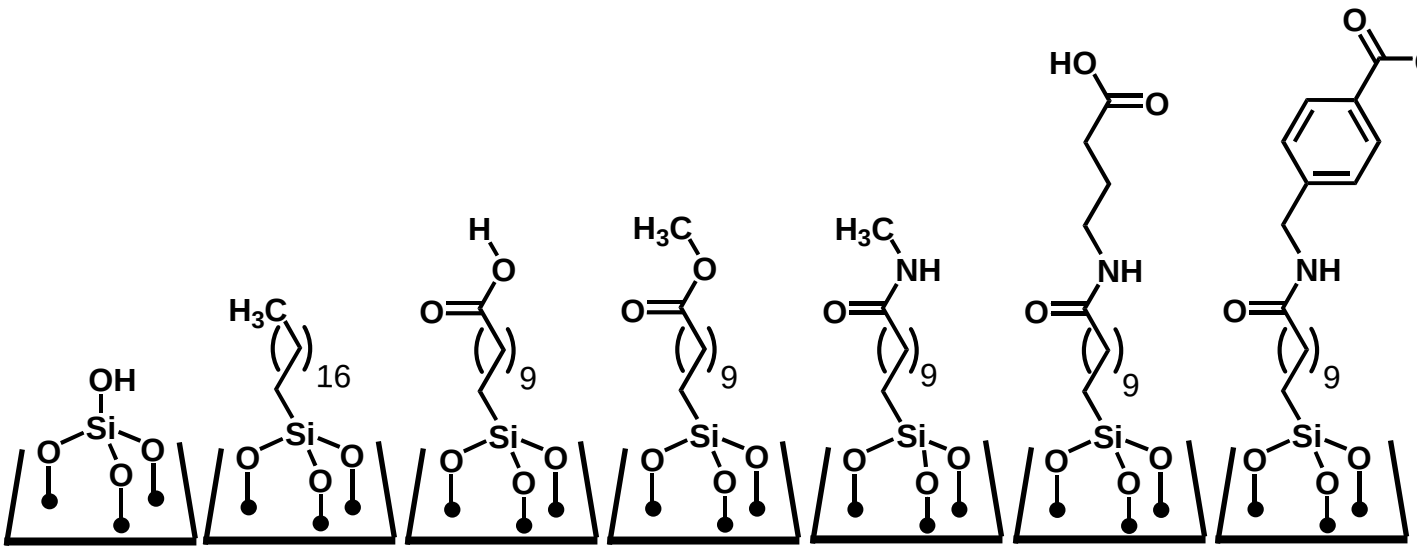
Spectra-Physics Lasers & Photonics

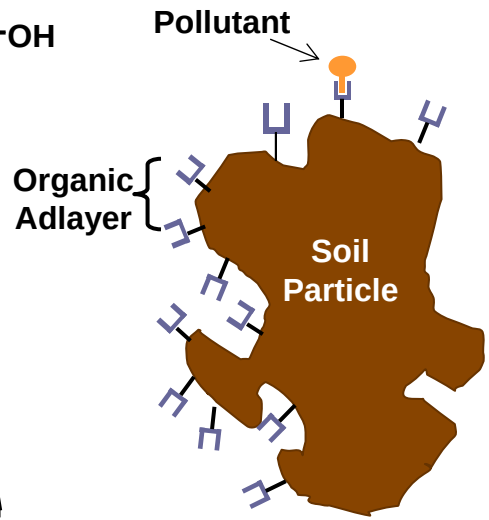
Pulsed & Tunable Laser



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





Increasing Complexity

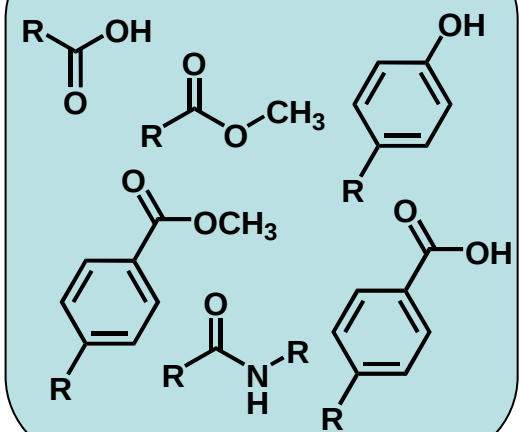
Our Strategy:

Use synthetic chemistry to:

(1) Isolate and study individual functional groups.

(2) Build more complex model interfaces.

Common Organic Motifs



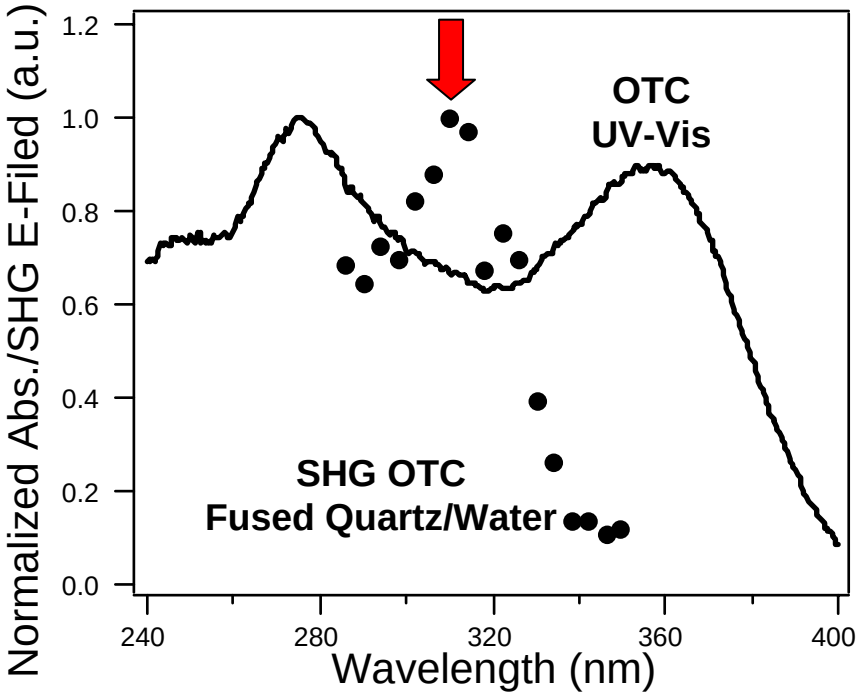
Sutton, R.; Sposito, G. *Environ. Sci. Technol.* **2005,** *39,* 9009.

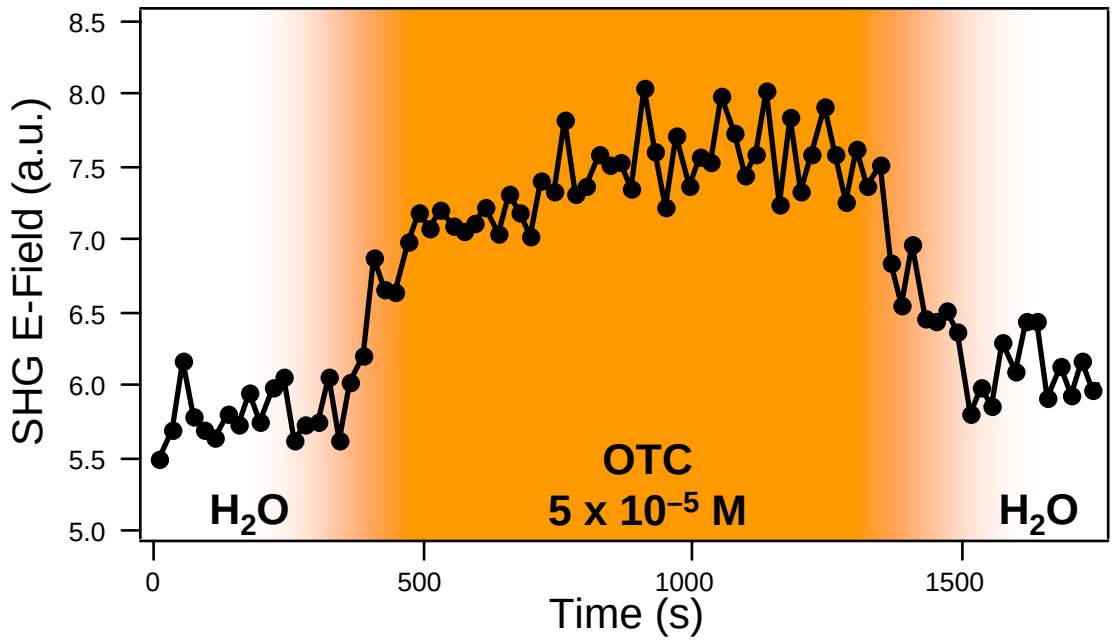
Al-Abadleh et al. *J. Am. Chem. Soc.* **2004,** *126,* 11126.

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.

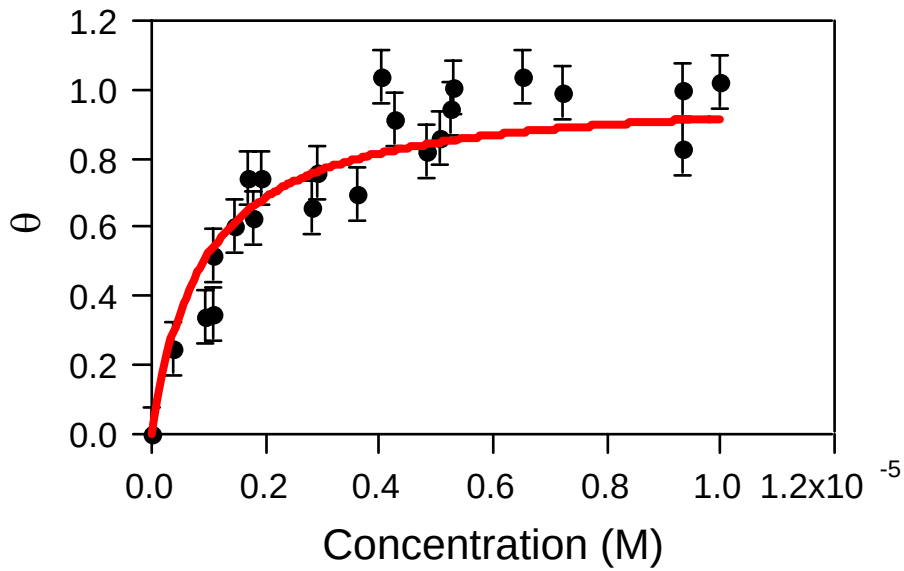
OTC Spectroscopy and Adsorption/Desorption Trace at Fused Quartz/Water Interface (pH 8)

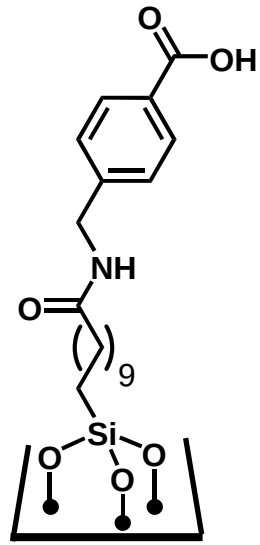




Mifflin et al. *J. Phys. Chem. B* **2006,** *110,* 22577.

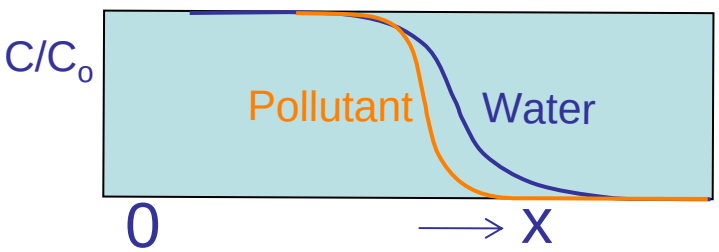
OTC Isotherm & The K_d Model (pH 8)





Retardation Factor:

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



K_d = 0.11 mL/g

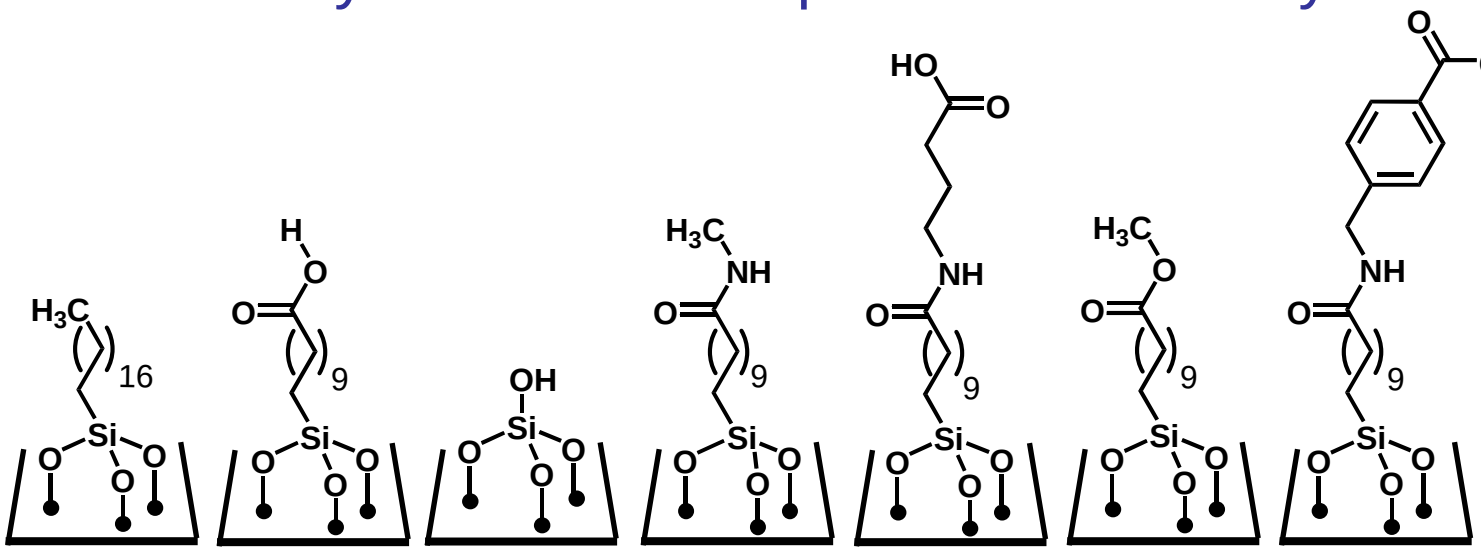
Taking: (ρ/n) = 4 – 10 g/cm^3

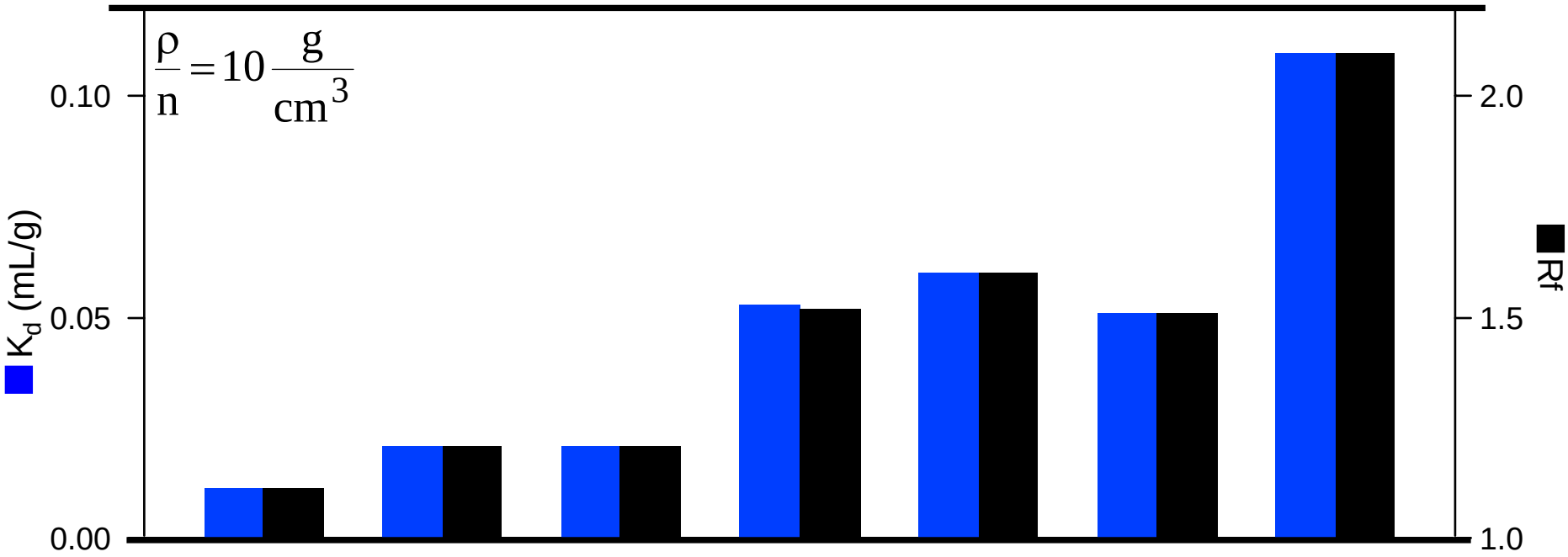
R_f = 1.44 - 2.1

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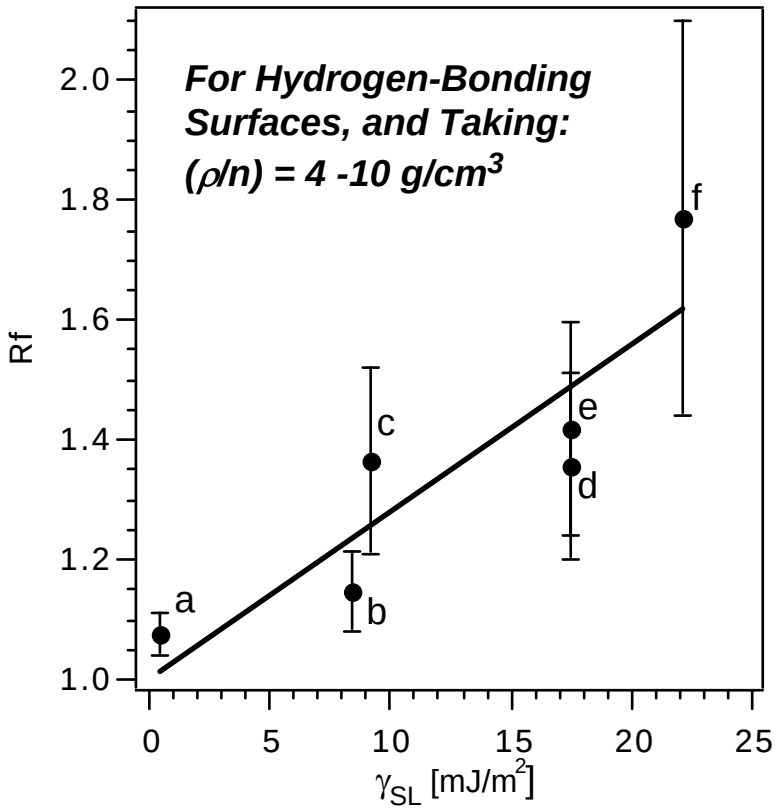
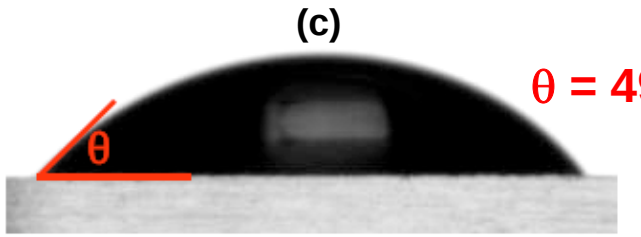
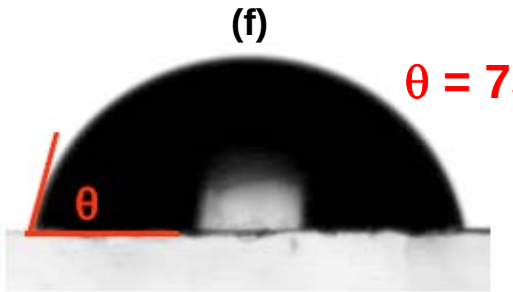
Hayes et al. *J. Phys. Chem. C* **2007,** *111,* 8796.

Predicting OTC Mobility: Surface Energy and OTC Retardation

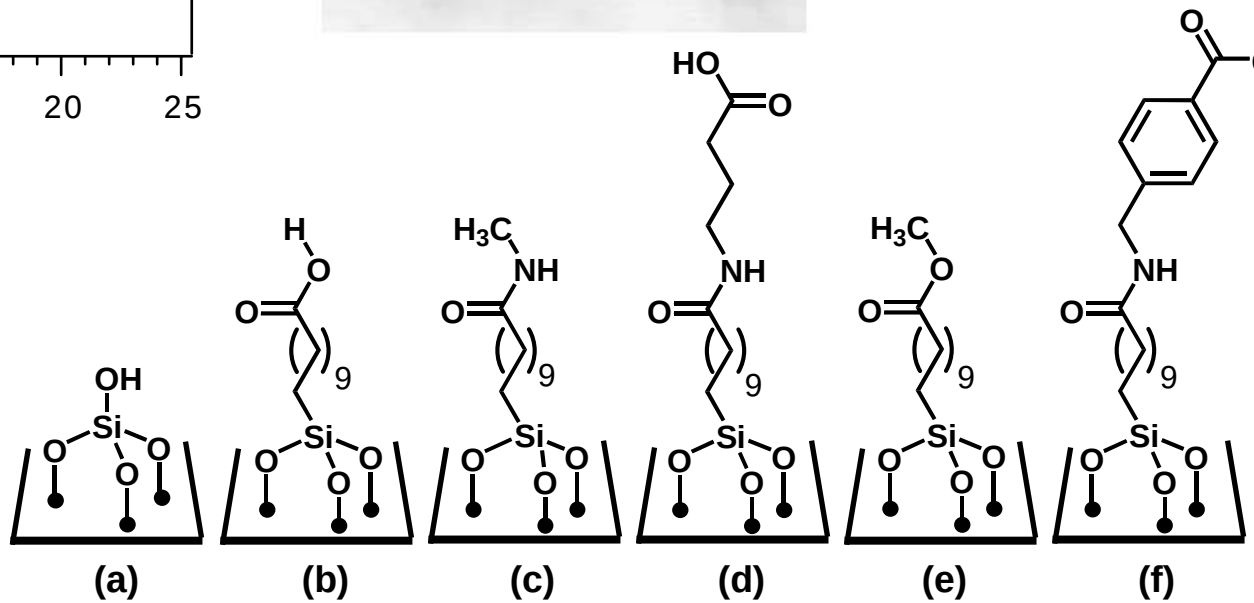




θ = 49°, 9 mJ/m²



θ = 75°, 22 mJ/m²



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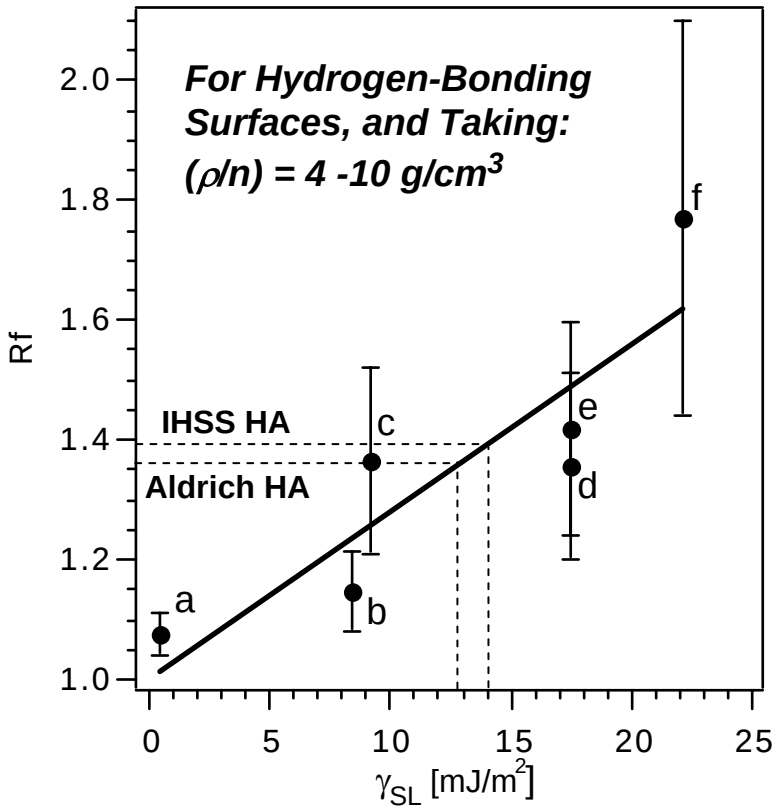
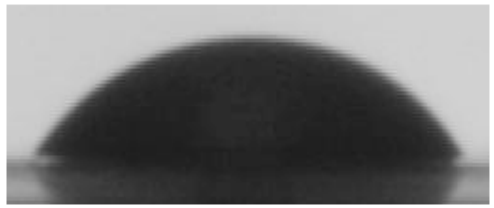


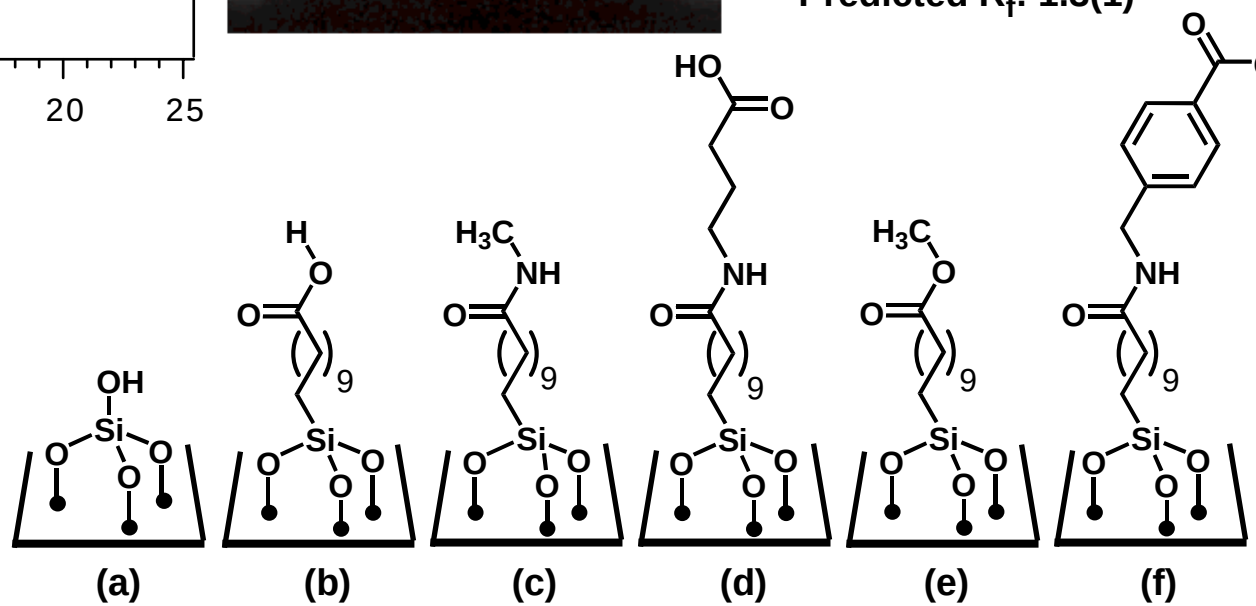
IHSS Humic Acid:



Contact Angle: 59(3)
Surface Energy: 14(1) mJ/m^2
Predicted R_f: 1.4(1)

Aldrich Humic Acid:

Contact Angle: 57(3)
Surface Energy: 13(1) mJ/m^2
Predicted R_f: 1.3(1)



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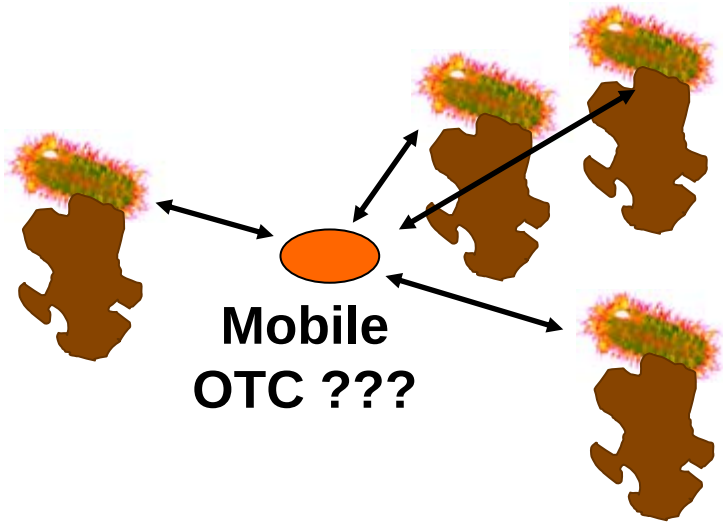
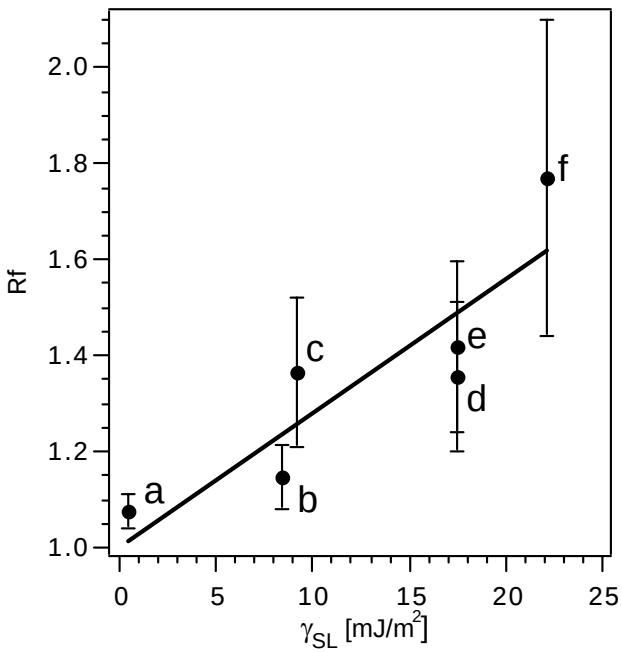
Hayes et al. *J. Phys. Chem. C* **2007,** *111,* 8796.

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

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