# Correlating nanoparticle surface coating properties with reactivity, transport, and potential for exposure


Gregory V. Lowry

Associate Professor of Environmental Engineering
Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA

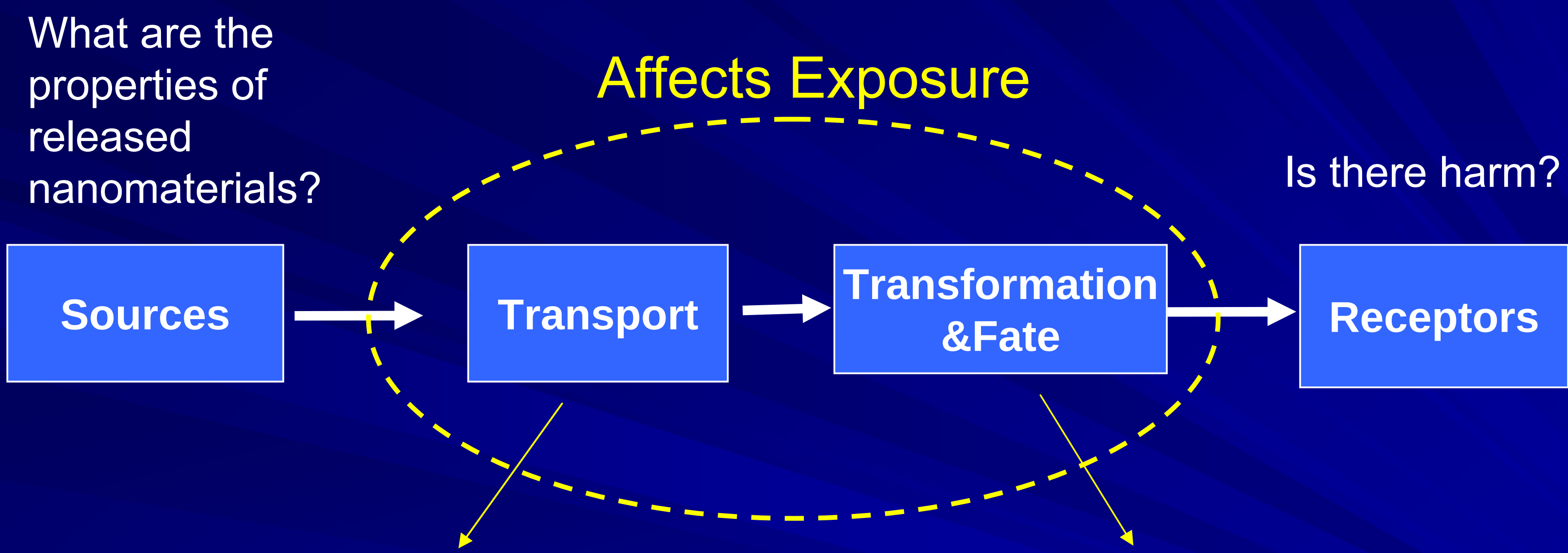

2007 Nanoscale Science and Technology Grantee Conference
National Science Foundation
December 6, 2007


This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R830898


CNXT

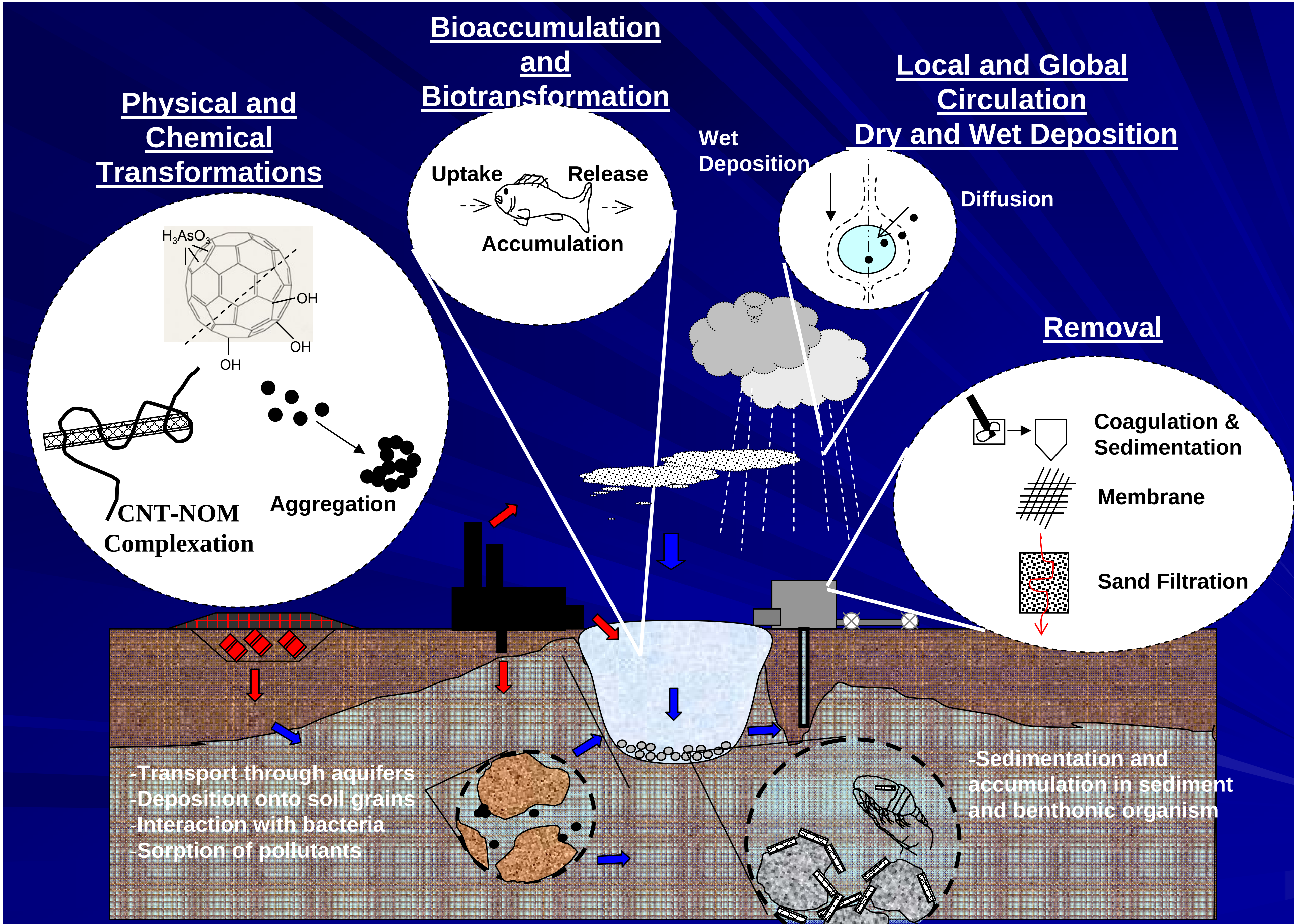
Civil and Environmental ENGINEERING
Carnegie Mellon

# Environmental Cycling and Potential Risks of Nanomaterials




- ✓How do they travel?
- ✓What factors affect mobility and distribution?

- ✓How are they transformed?
- ✓What do they become?
- ✓What 'compartments' do they reside
- ✓Do they bioaccumulate?

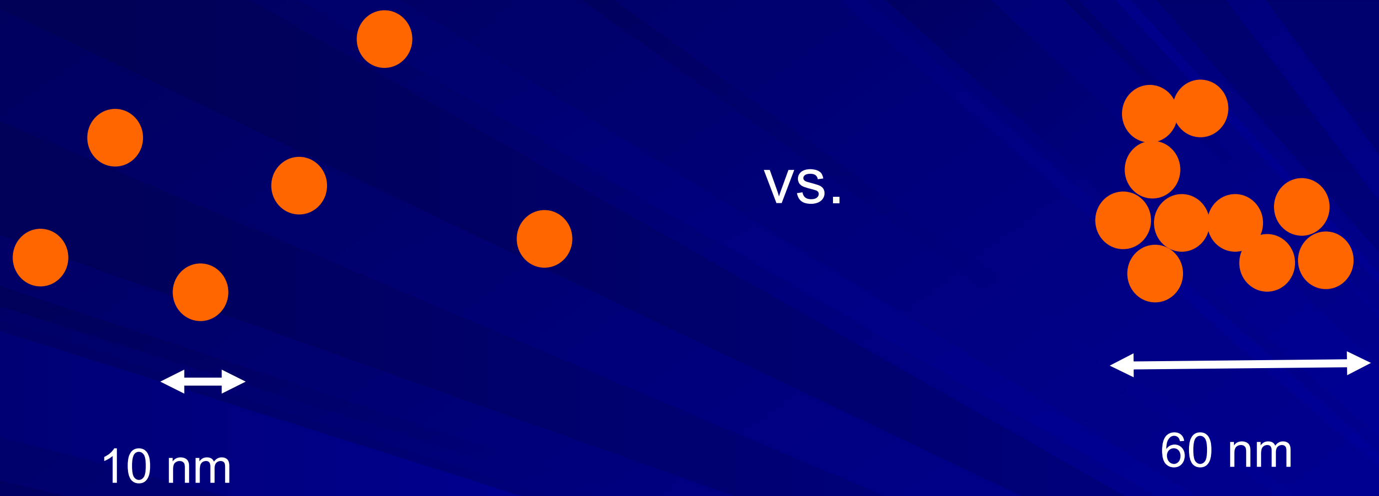



Lowry and Wiesner, in Nanotoxicology (Taylor and Francis)

# Fundamental Processes Affecting Transport and Exposure

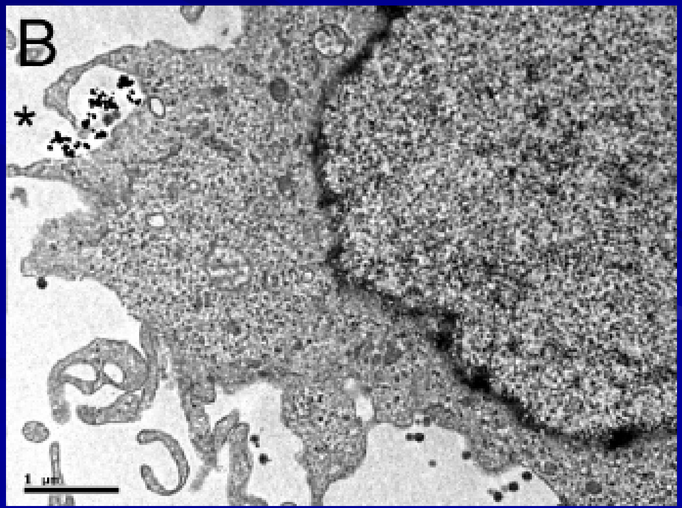
- Aggregation and Deposition
- Transformations
  - Biotransformations
    - Microbial-mediated redox transformations
  - Abiotic Transformations
    - Photolysis, hydrolysis, dissolution

# Aggregation/Agglomeration



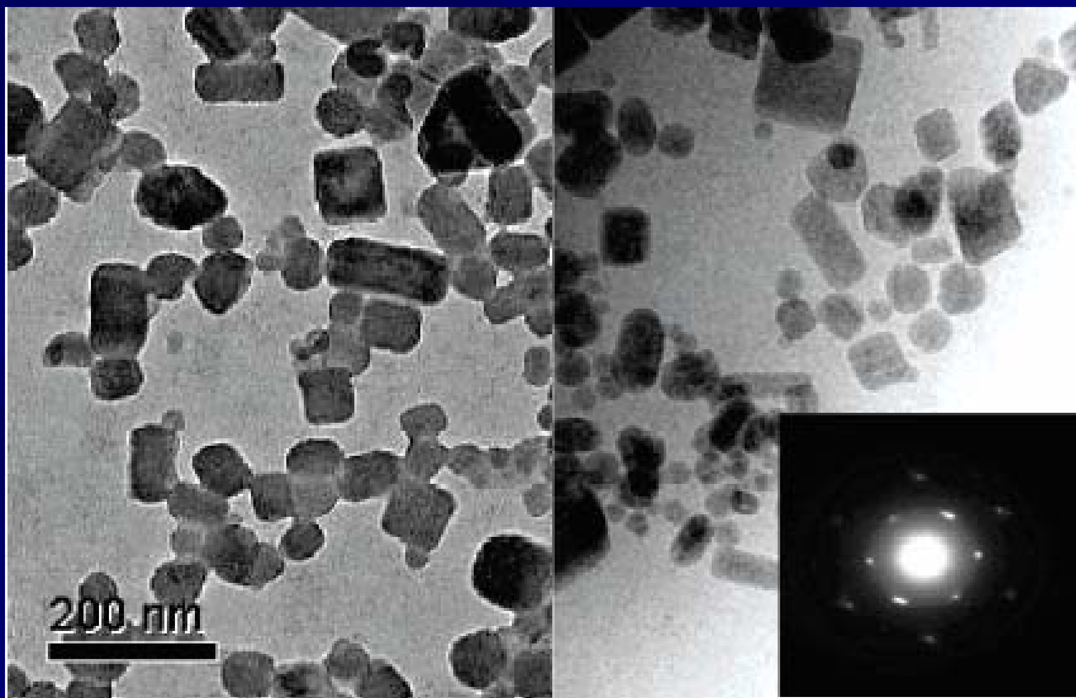

Affects:
- Transport-porous media, membranes, …
- Phagocytosis
- Transformation/degradation
- Reactivity-e.g. ROS
- Toxicity

SIZE MATTERS!




Long et al., 2006 *EST* 41 (14) 4346

# Fullerene Aggregation in Water




✓Cluster dimensions ranged from 25-500 nm

✓Stable suspensions ≤ 50 mM (NaCl)

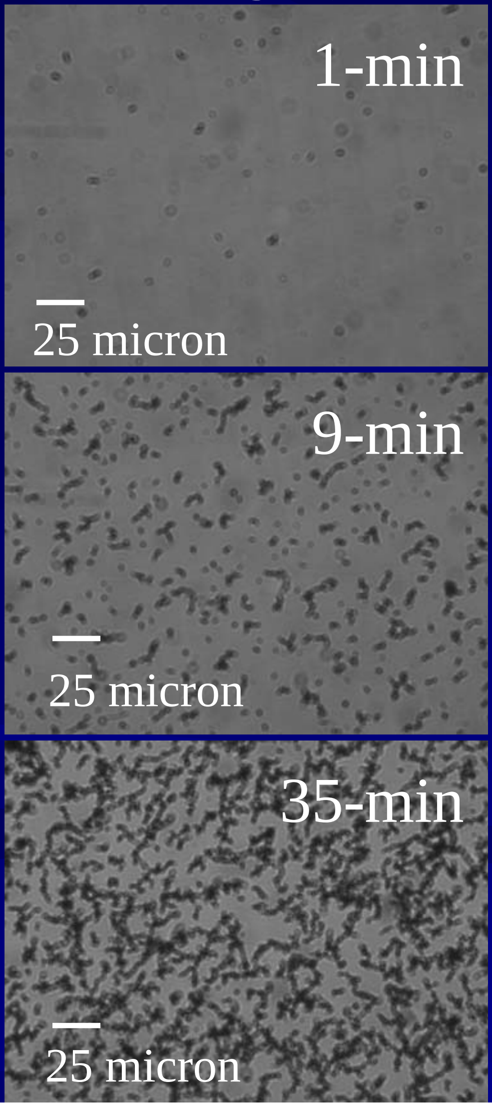
✓No surface coatings

✓Stabilization mechanism unclear

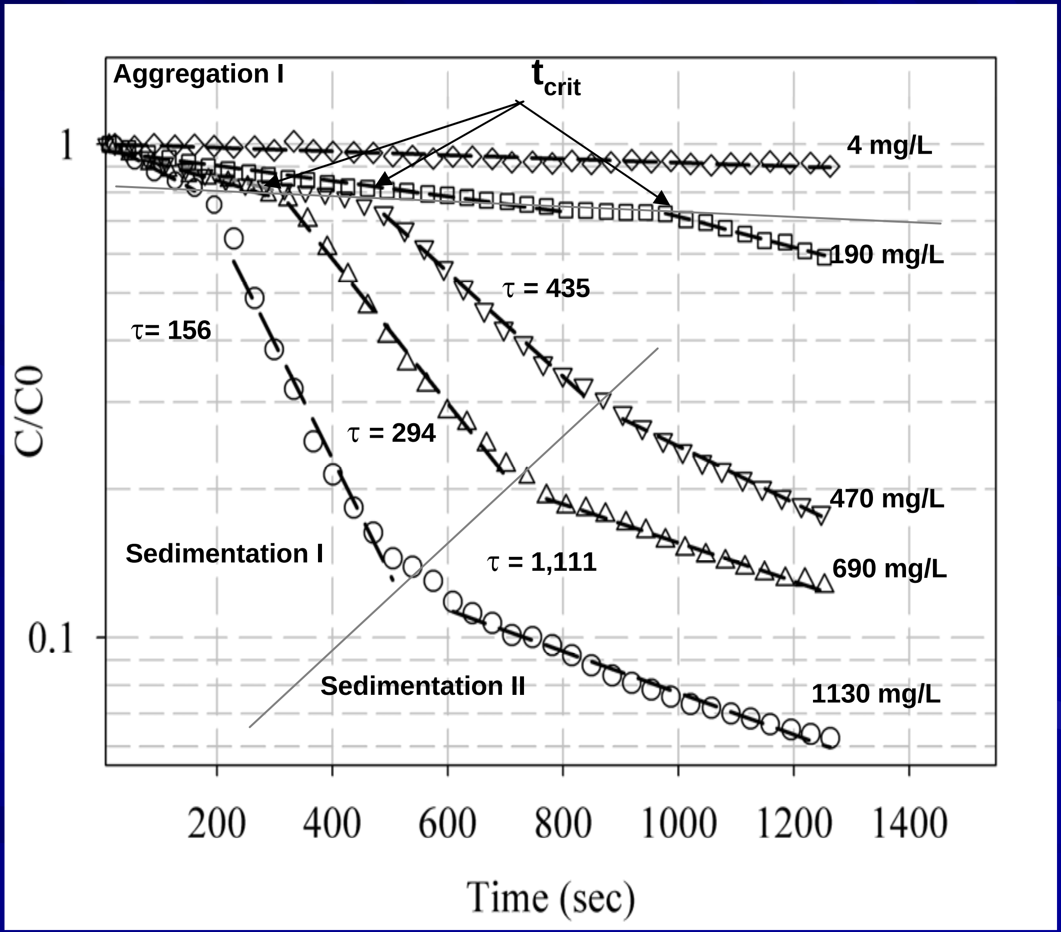
Fortner, et al. (2005). C60 in Water: Nanocrystal Formation and Microbial Response. *Environ. Sci. Technol.* 39(11); 4307-4316.

# Bare NZVI Aggregation & Sedimentation

$\Phi=10^{-5}$
(~80 mg/L)




**Nanoiron sedimentation in 1 mM NaCl**



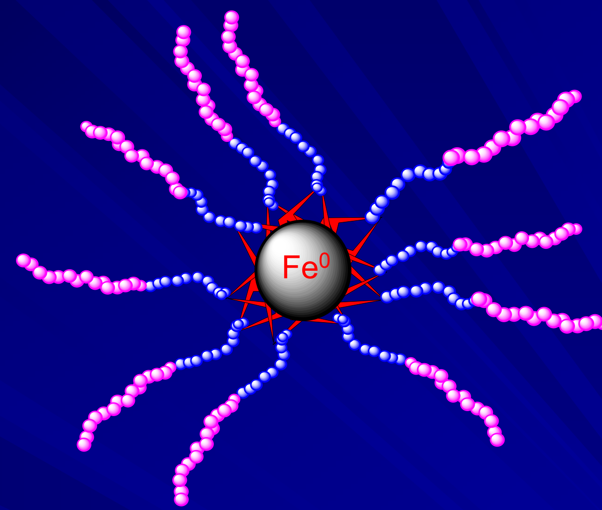

$d_p$~45 μm

$d_p$~120 μm

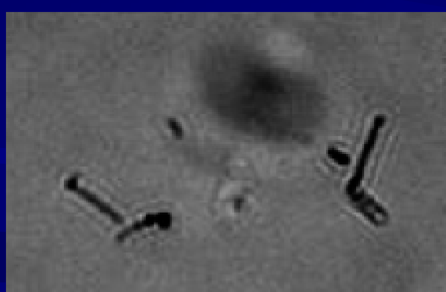
Phenrat T. et al., (2007) *ES&T* 41, 284.

# Coatings on Nanomaterials

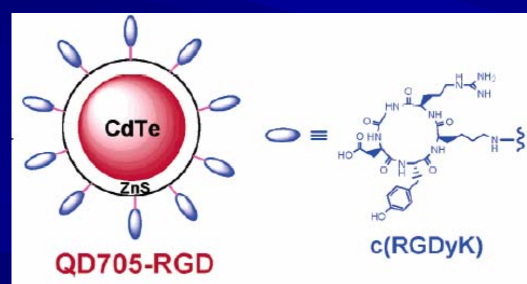
- Coatings provide…
  - Dispersion stability
  - Functionality
  - Targeting capabilities
  - Biocompatibility



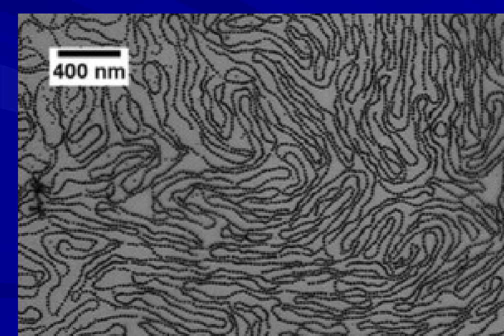

Saleh, et al. (2005) *Nano Lett.* 5 (12) 2489-2494.



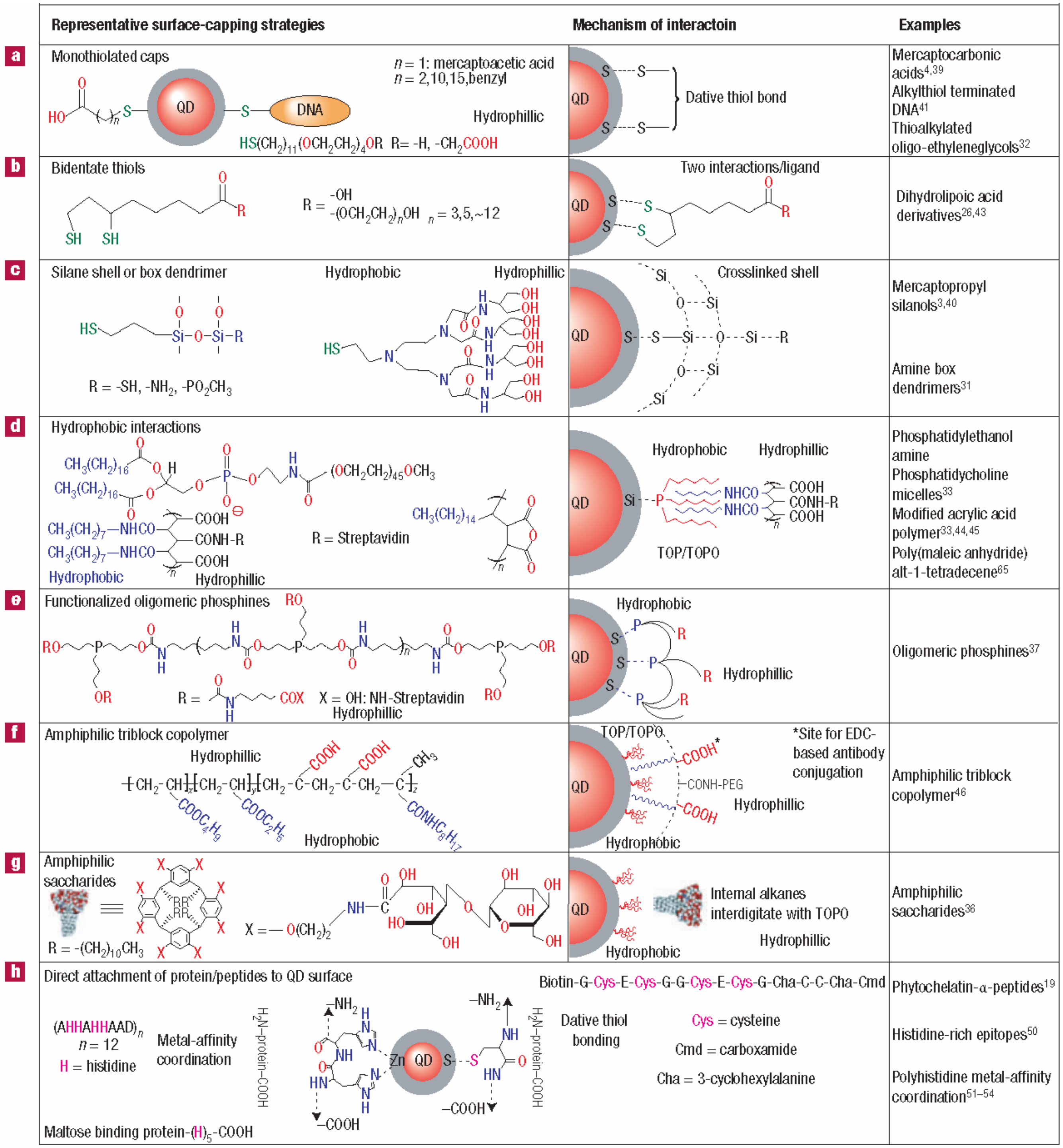
Hyung, et al. *EST* 41(1); 179-184




Cai et al., 2006 *Nanoletters* 6 (4) 669-676



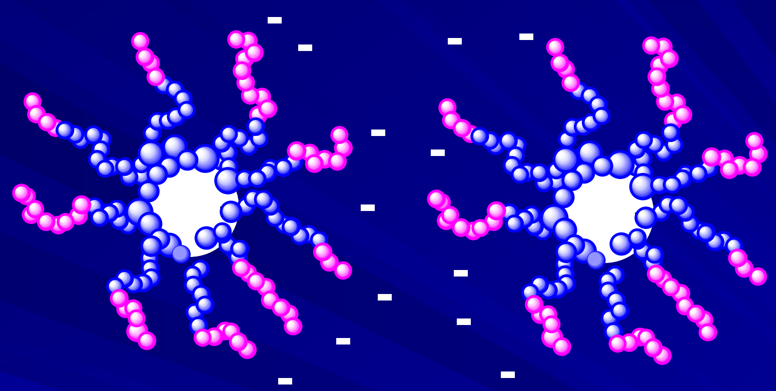

Keng et al. 2007 *ACS Nano*



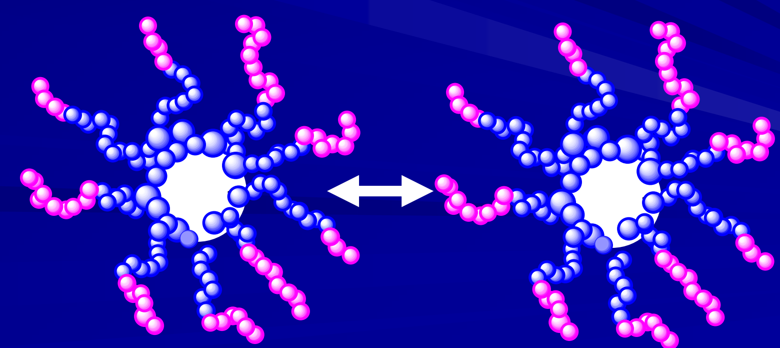

Medintz et al. (2005)

# Nanoparticle Stabilization

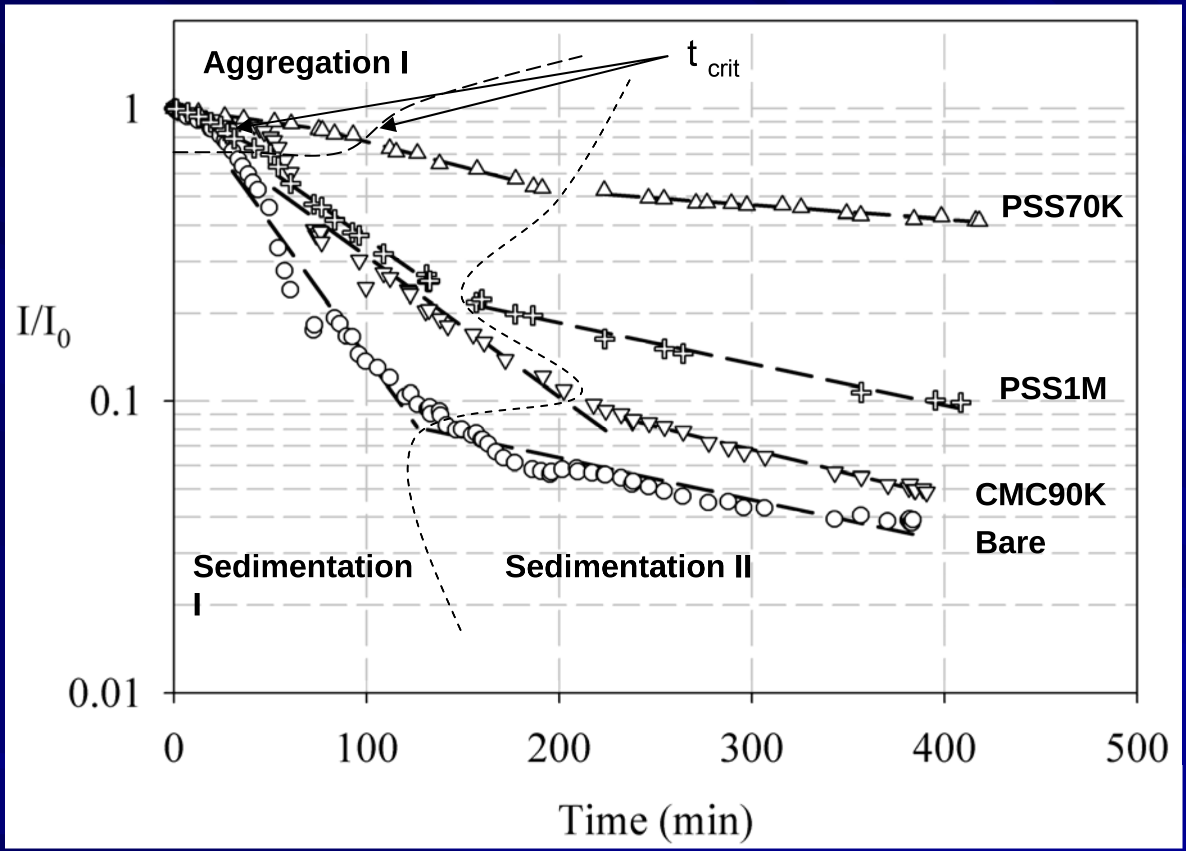
- Electrostatic Stabilization



- Steric Stabilization



# Modifiers Inhibit Agg/Sed




**Polymers inhibit aggregation and agglomeration and provide a stable fraction**

**No apparent trend with MW**

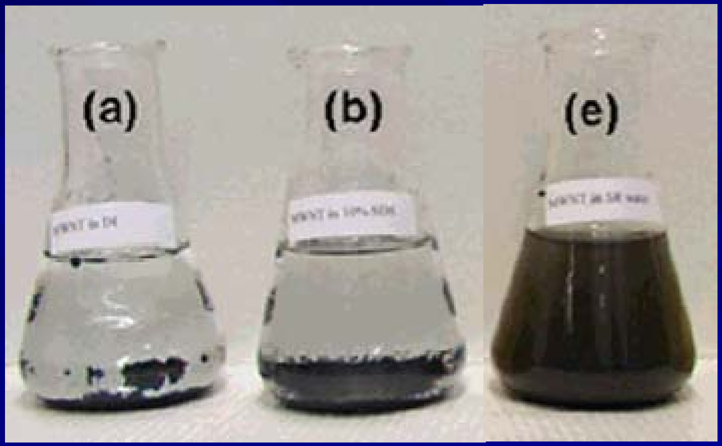
Saleh, N. et al. **(2005)**. “*Nano Lett.* 5 (12) 2489-2494.

Saleh, N. et al., (**2007**) *Environ. Eng. Sci.* 24 (1) p.45-57.

Phenrat, Tilton, and Lowry, *J Nanopart. Res.* (in press)

# NOM Stabilized Carbon MWNTs

- Natural Fulvic Acids in Suwannee River stabilize MWNTs (500 mg/L)



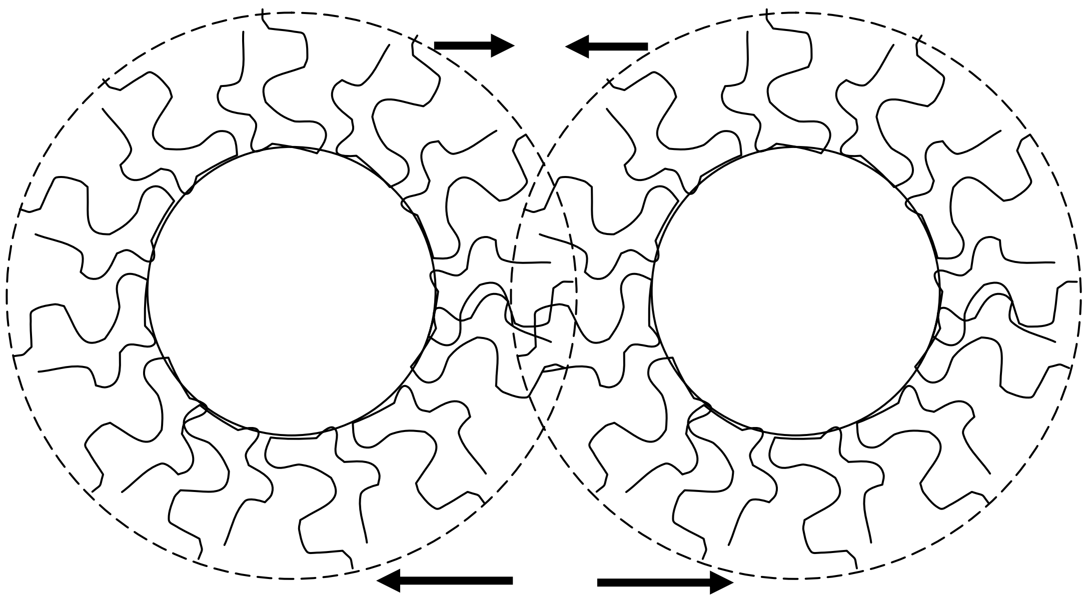

DI 1% SDS Suwannee River Water

After mixing and 4-days settling

Hyung, et al. *Environ. Sci. Technol*. 2006 41(1); 179-184

# Forces Affecting Agglomeration (and Deposition)

Attraction due to $V_{vdw}$+$\boldsymbol{V_M}$

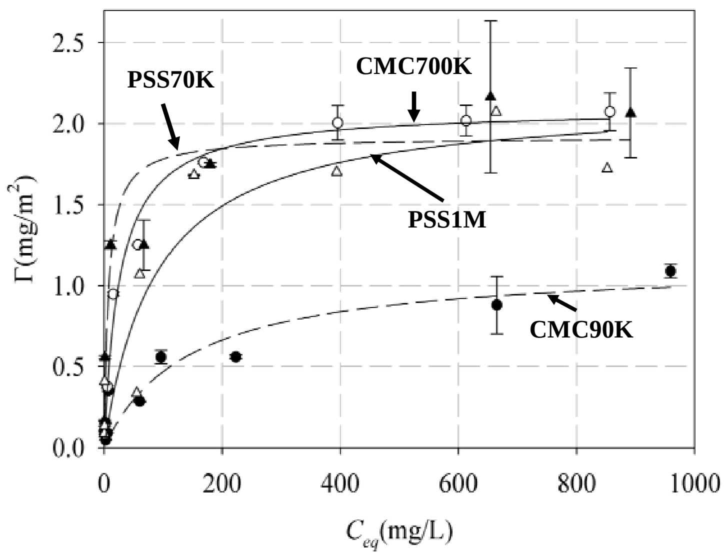


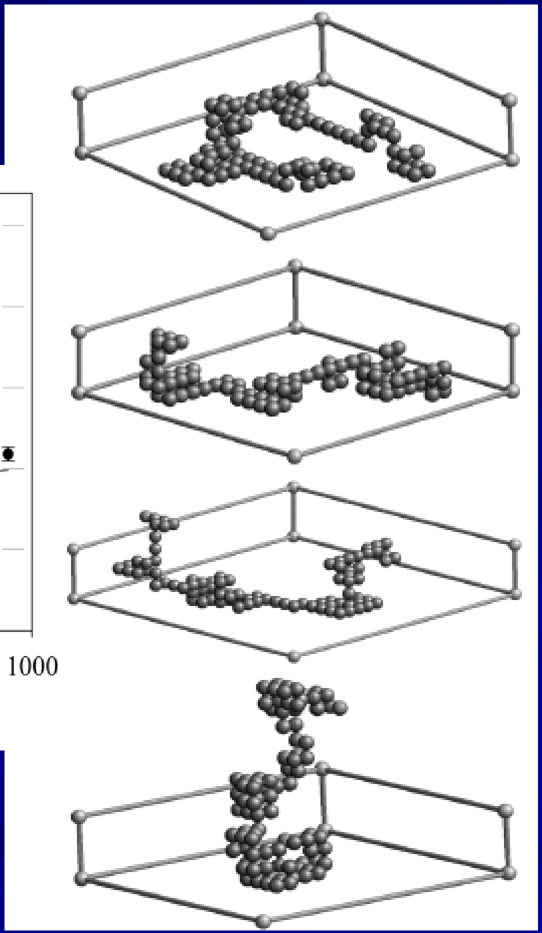
Repulsion due to $V_{ES}$+$\boldsymbol{V_{osm}}$ + $\boldsymbol{V_{elas}}$

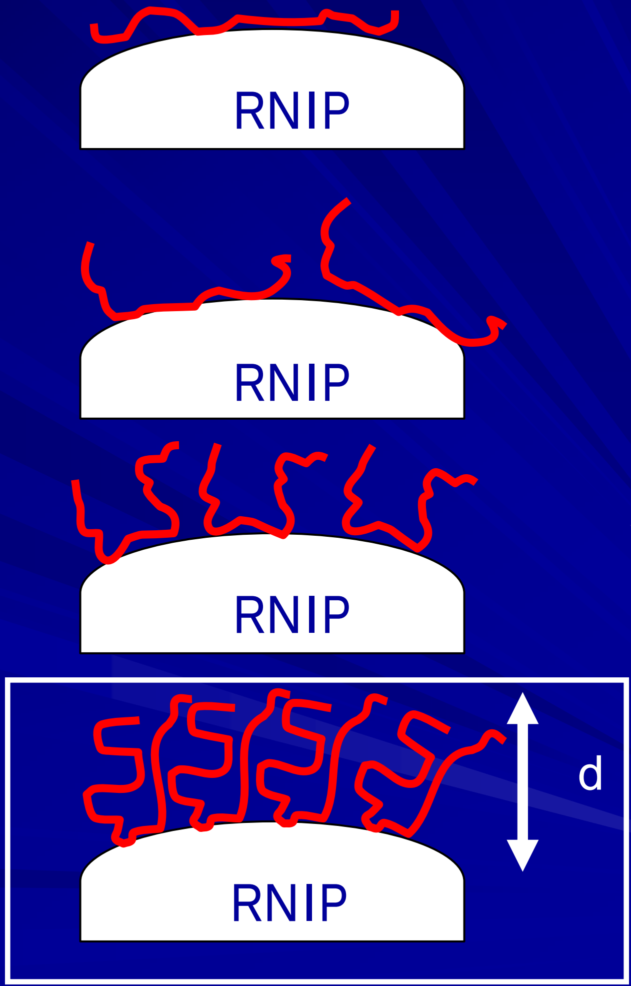
Also: polar interactions, acid base, surface roughness

# Configuration of Adsorbed Homopolymer

Adsorption Isotherm






**Important parameters: Adsorbed mass and layer thickness (d)**

# Ohshima’s Model

$$u_e = \frac{\varepsilon}{\eta}\frac{\psi_0/\kappa_m + \psi_{DON}/\lambda}{1/\kappa_m + 1/\lambda} f\left(\frac{d}{a}\right) + \frac{ZeN}{\eta\lambda^2} + \frac{8\varepsilon k_B T}{\eta\lambda ze}.\tanh\frac{ze\zeta}{4k_B T}.\frac{e^{-\lambda d}/\lambda - e^{-\kappa_m d}/\kappa_m}{1/\lambda^2 - 1/\kappa_m^{\ 2}}$$

$$\psi_{DON} = \frac{k_B T}{ze}\sinh^{-1}\left(\frac{ZN}{2zn}\right)$$

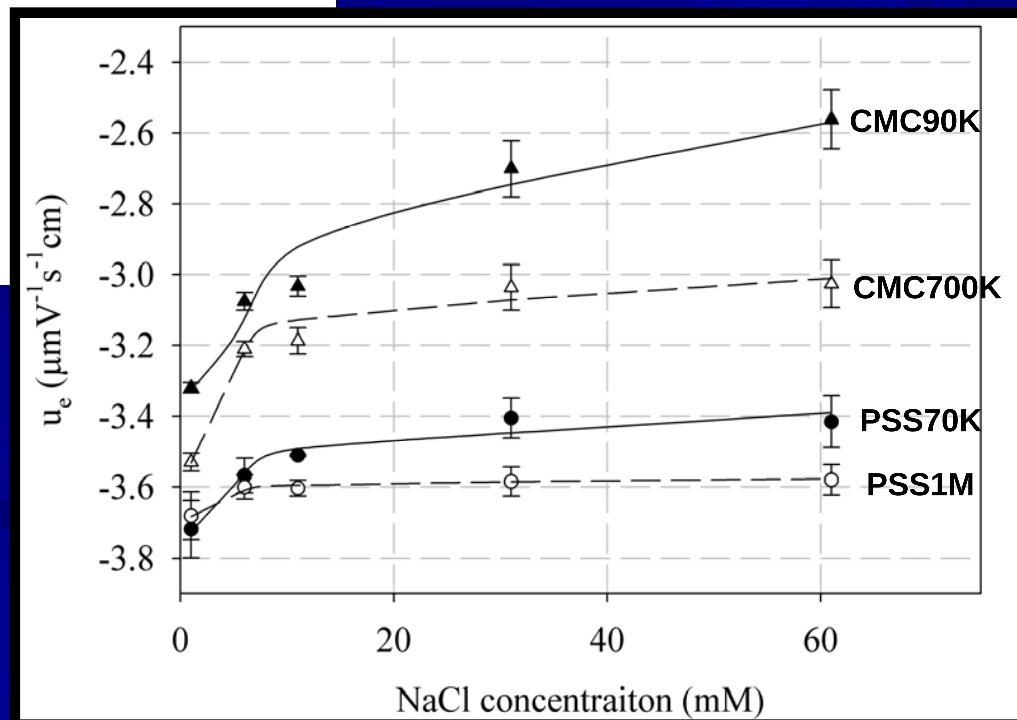
$$\psi_0 = \psi_{DON} - \frac{k_B T}{ze}\tanh\left(\frac{ze\,\psi_{DON}}{2k_B T}\right) + \frac{4k_B T}{ze}.e^{-\kappa_m d}\tanh\frac{ze\,\zeta}{4k_B T}$$

$$f\left(\frac{d}{a}\right) = \frac{2}{3}\left[1 + \frac{1}{2(1+d/a)^3}\right]$$

$$\kappa_m = \kappa\left[\cosh\left(\frac{ze\psi_{DON}}{k_B T}\right)\right]^{1/2}$$

Parameters:
d-layer thickness
N-charge density in layer
$1/\lambda$–debye length

H. Ohshima, M. Nakamura and T. Kondo, *Colloid Polym. Sci. 270* (1992) 873-877.




Phenrat, Tilton, and Lowry, *J Nanopart. Res.* (in press)

# Measured Layer Properties

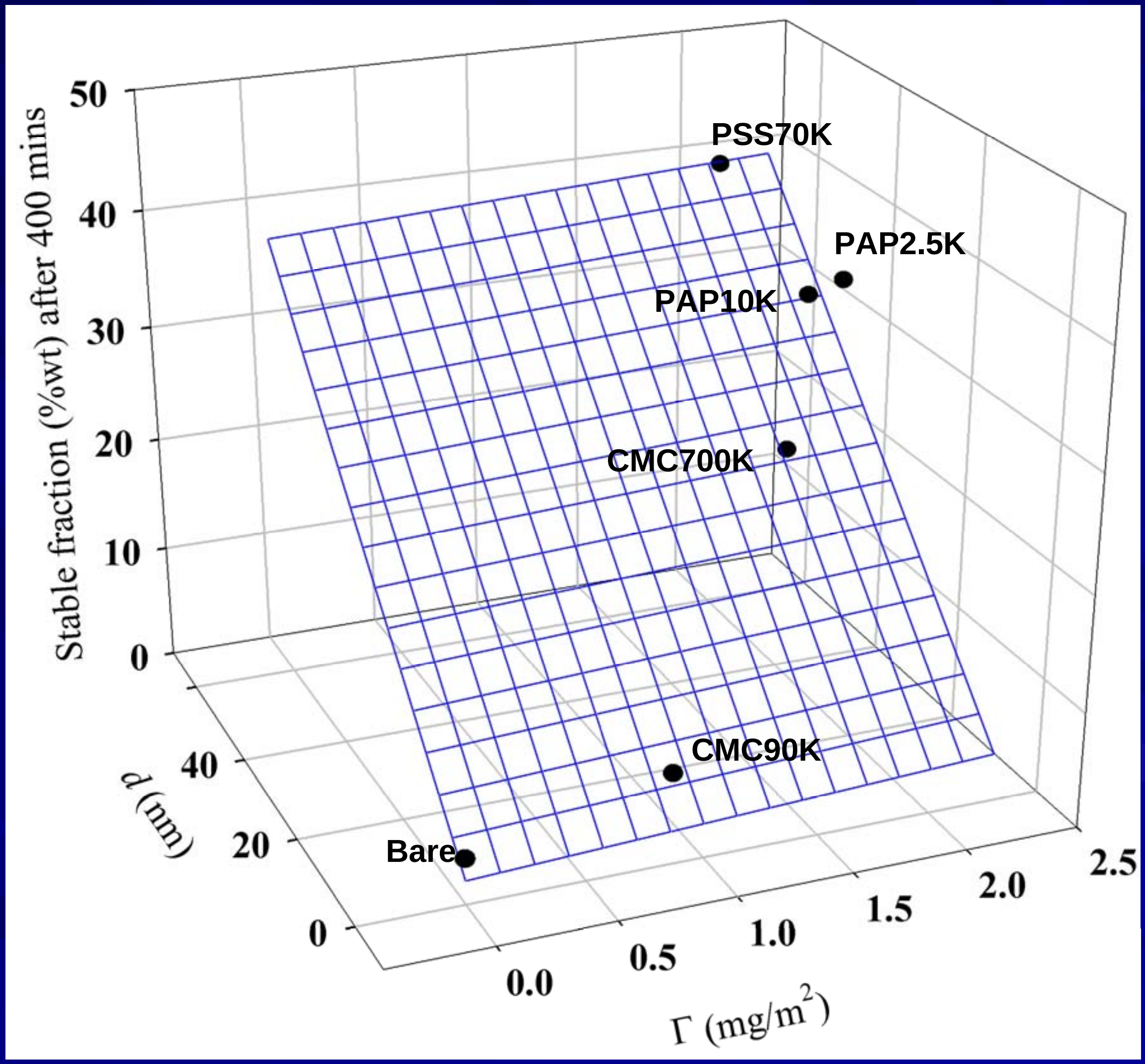
| Modifier | $M_w$ (kg/mole) | $D_P$ (--) | $\Gamma$ (mg/m$^2$) | $d$ (nm) | $1/\lambda$ (nm) | $\|\psi_{DON}\|^*$ (mV) | $\|\psi_0\|^*$ (mV) |
|---|---|---|---|---|---|---|---|
| PSS 70k | 70 | 340 | 2.1±0.3 | 67±7 | 37±1 | 2.1±0.2 | 1.1±0.1 |
| PSS1M | 1,000 | 4,850 | 1.9±0.2 | 198±30 | 49±1 | 1.7±0.1 | 0.85±0.0 |
| CMC90K | 90 | 342 | 0.9±0.2 | 7.2±3.2 | 9±0.1 | 3.8±0.2 | 19.7±1.5 |
| CMC 700K | 700 | 2661 | 2.0±0.1 | 40±6.5 | 24±1 | 4.2±0.2 | 2.7±0.1 |
| PAP2.5K | 2-3 | 16 | 2.3±0.2 | 40±12 | 24±1 | 5.1±0.1 | 3.0±0.2 |
| PAP 10k | 10 | 64 | 2.2±0.3 | 44±13 | 26±1 | 4.5±0.2 | 2.6±0.2 |

Steric Repulsions

ES Repulsion

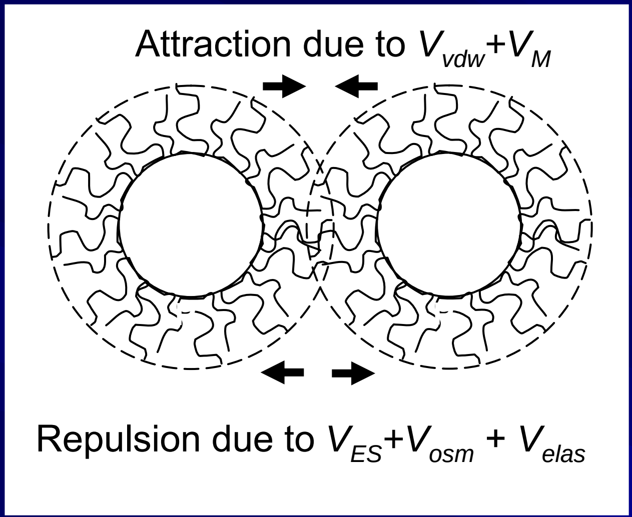
Phenrat, Tilton, and Lowry, *J Nanopart. Res.* (in press)

# Surface Excess and Layer Thickness correlate with ability to Stabilize NZVI



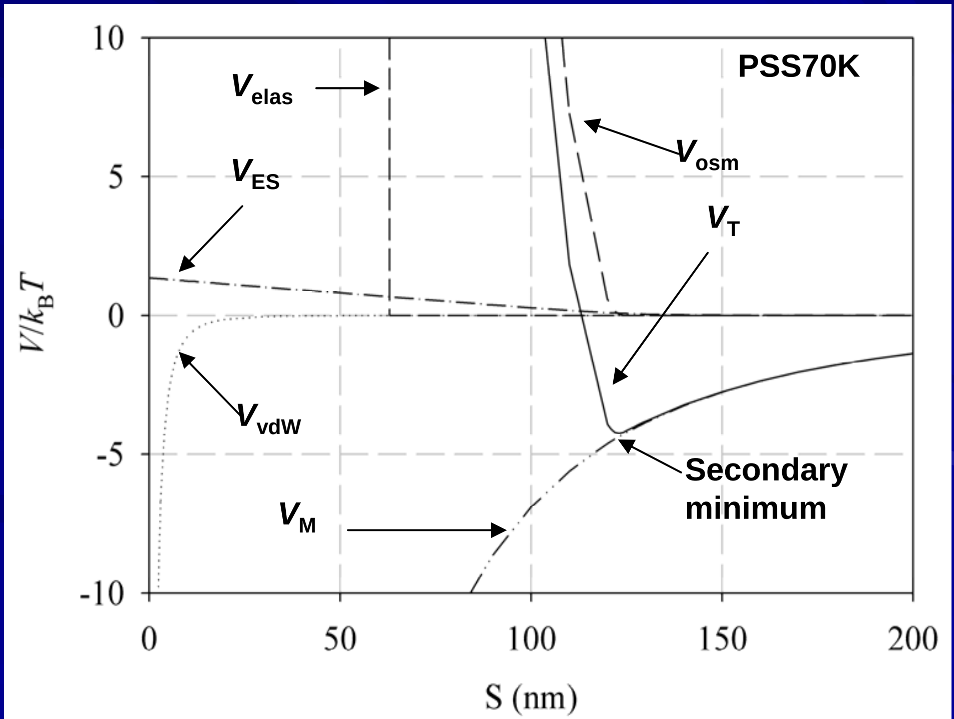

Phenrat, et al., *J Nanopart. Res.* (in press)

# Agglomeration (and deposition) is in a Secondary Minimum

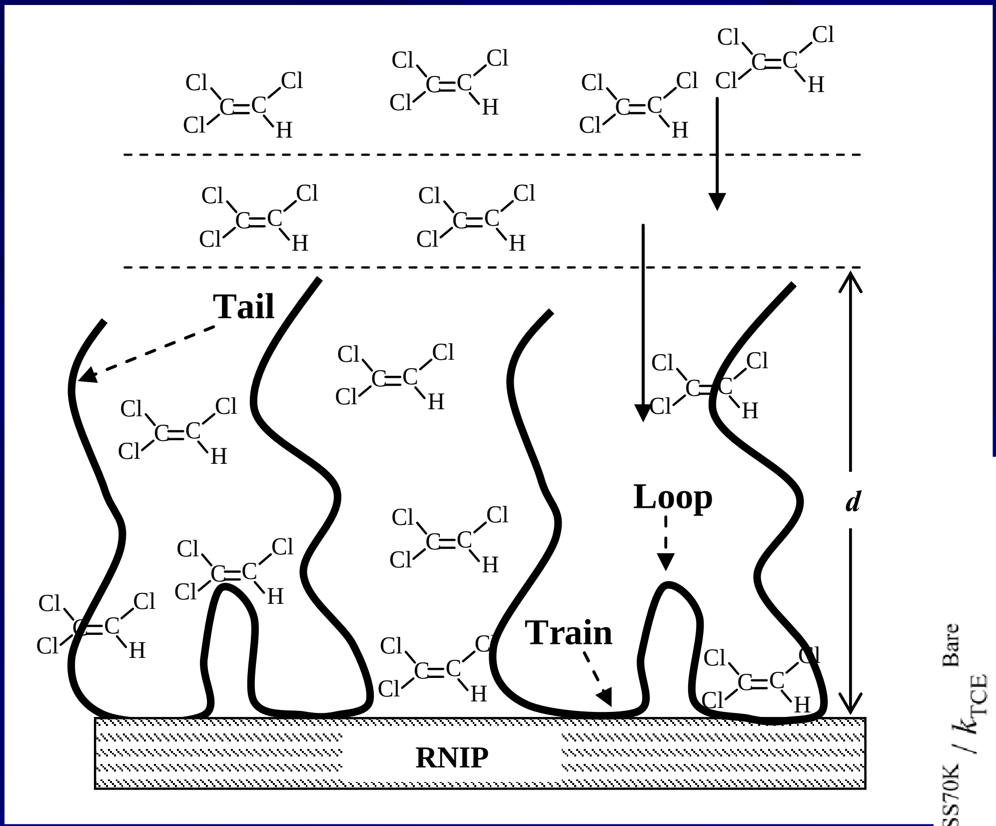



$V_{osm}$ is strong repulsive force and results in secondary minimum

Need to consider:
$V_{elas}$, $V_{osm}$
due to polyelectrolyte

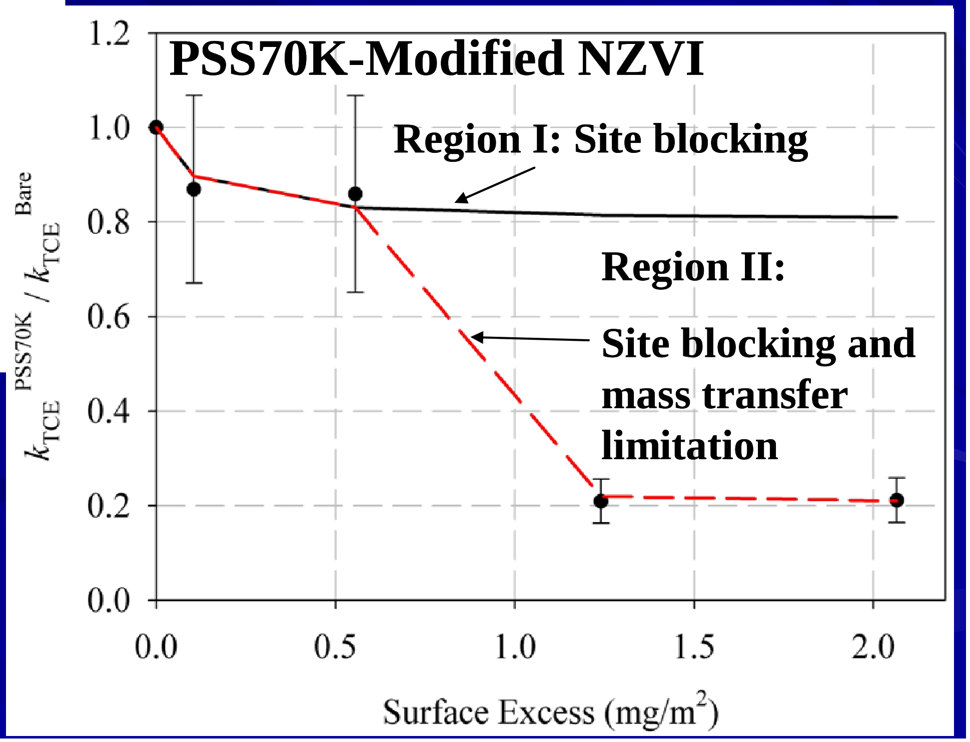


# Coatings also Affect Reactivity



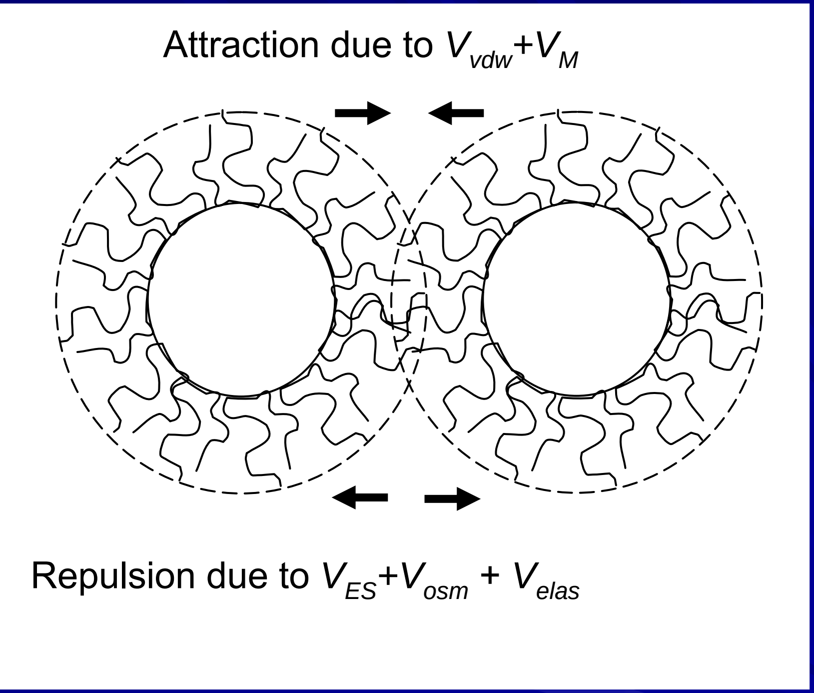

Reactive site blocking by trains

Mass transfer resistance by loops and tails



# But……

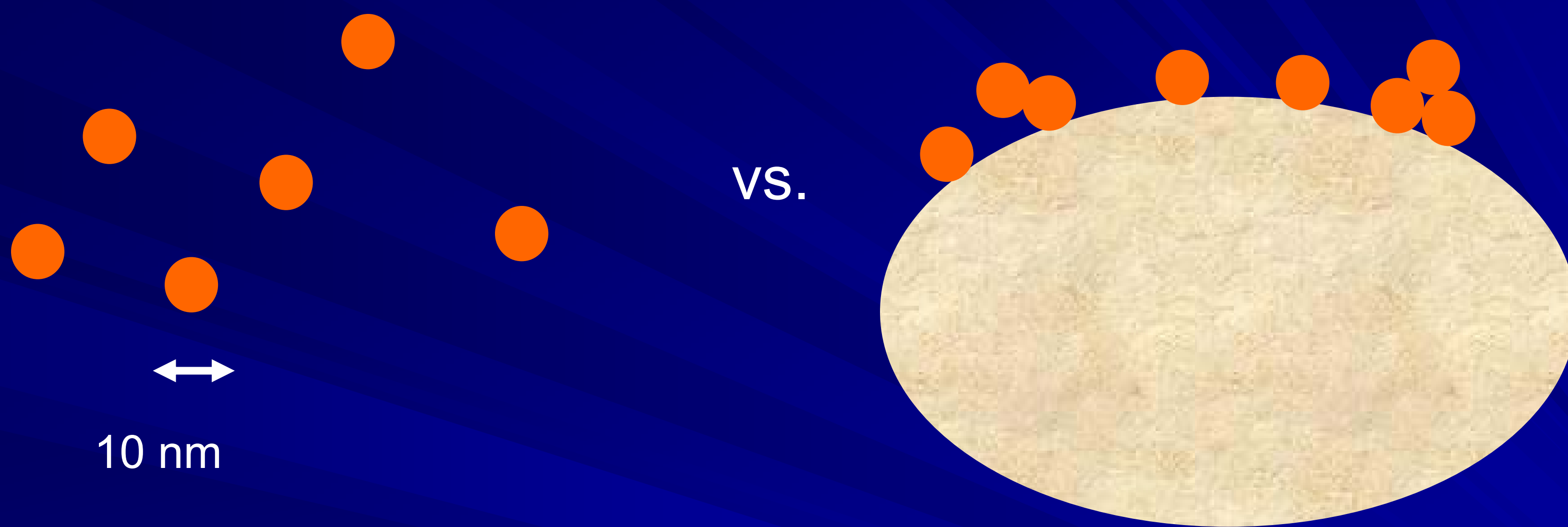
- $V_{osm}$ and $V_{elas}$ depends on:
  - Coating properties
  - Fluid properties
  - Temperature
  - Particle size?




Rich area for research-

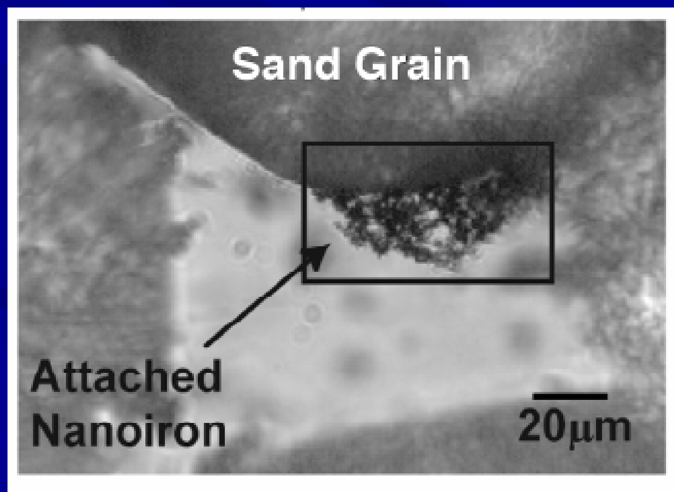
How is conformation of adsorbed macromolecules, affected by solution properties?

# Deposition

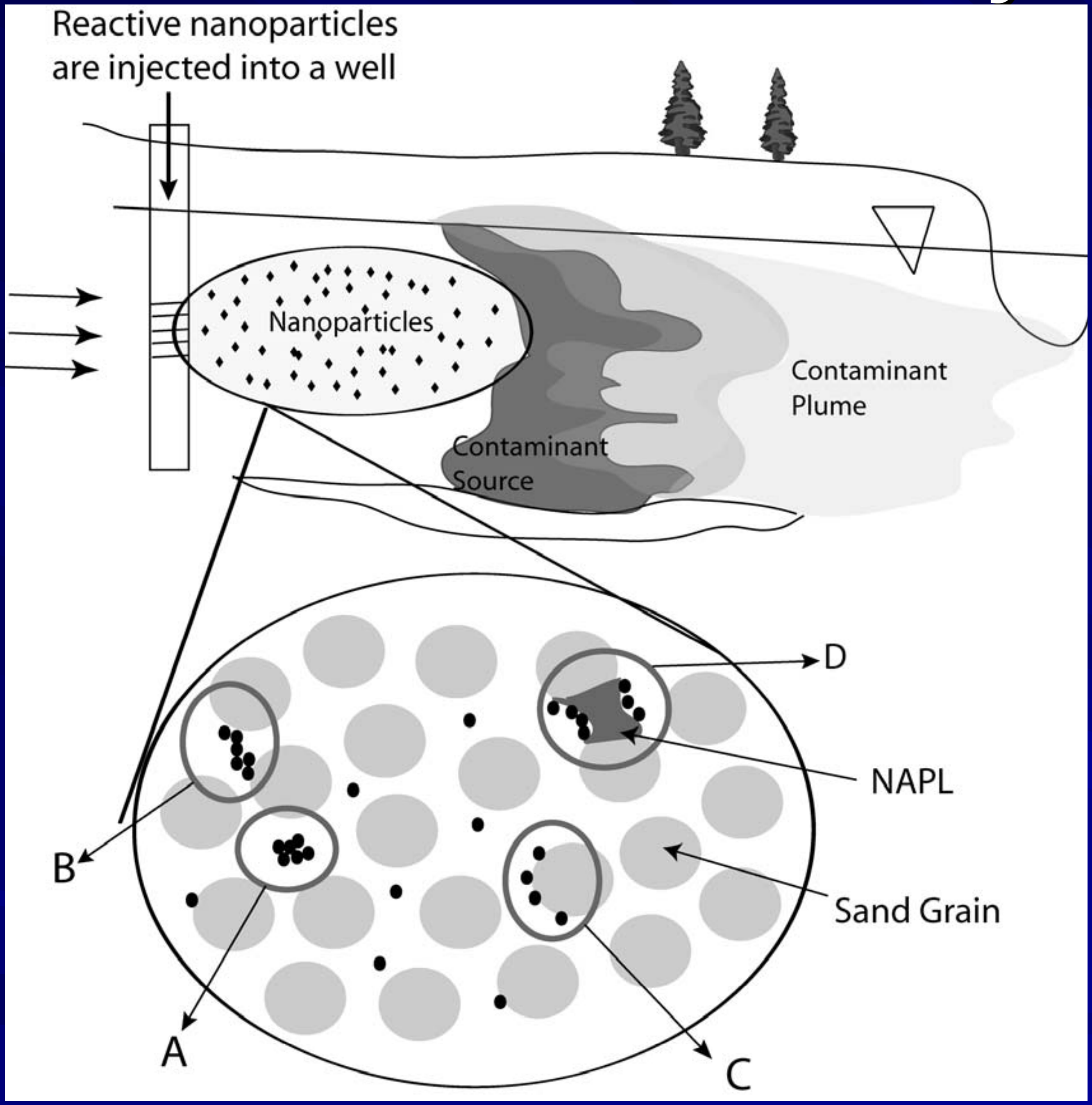



Affects important transport processes:
- Transport-porous media, surface water
- Reactivity-e.g. ROS
- Bioavailability
- Degradation

Saleh et al. 2007 EES 24 (1) 45.



# Nanomaterial Mobility in Porous Media




- A---Aggregation
- B---Straining
- C---Deposition
- D---NAPL Targeting

Depends on:

Chemical factors

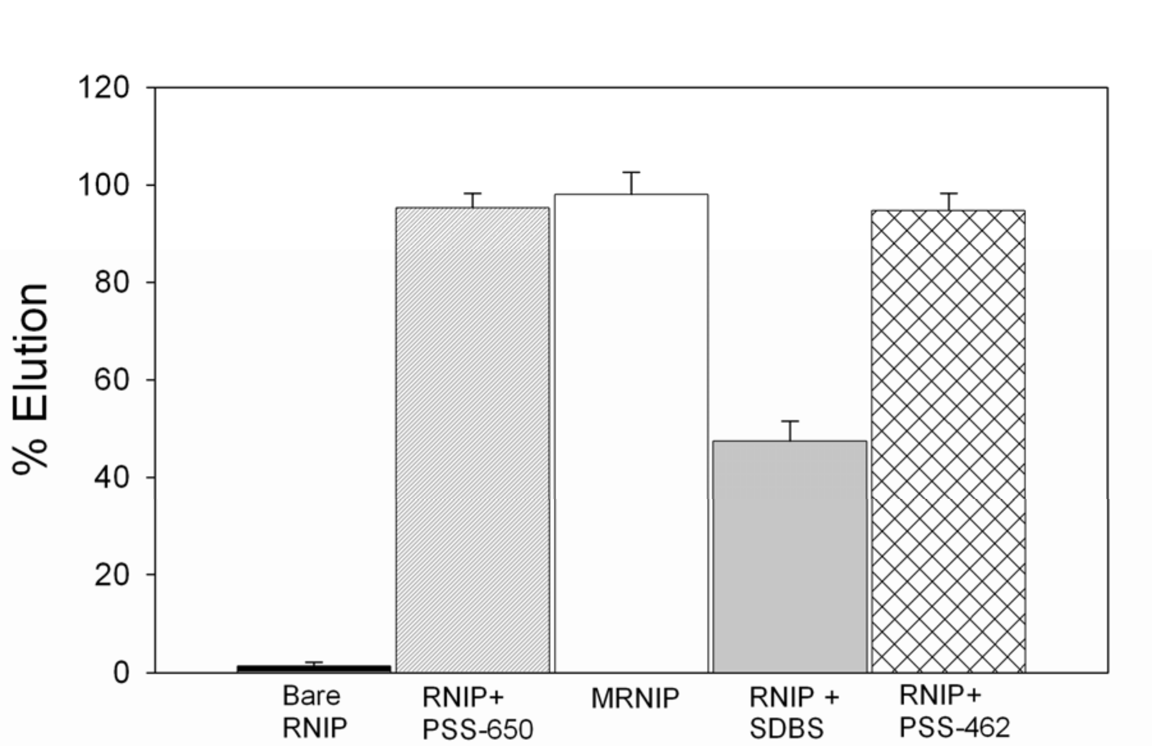
pH, ionic strength, ionic composition, surface chemistry

Physical factors

flow velocity, particle/aggregate size, heterogeneity


Lowry, G. V. (**2007**). Groundwater Remediation Using Nanoparticles. In *Environmental Nanotechnology: Applications and Impacts of Nanomaterials*. Eds. M. Wiesner and F. Bottero, McGraw-Hill, New York, NY, 2007 p.297-333.

# RNIP with Adsorbed Polymer Mobile in Saturated Sand columns

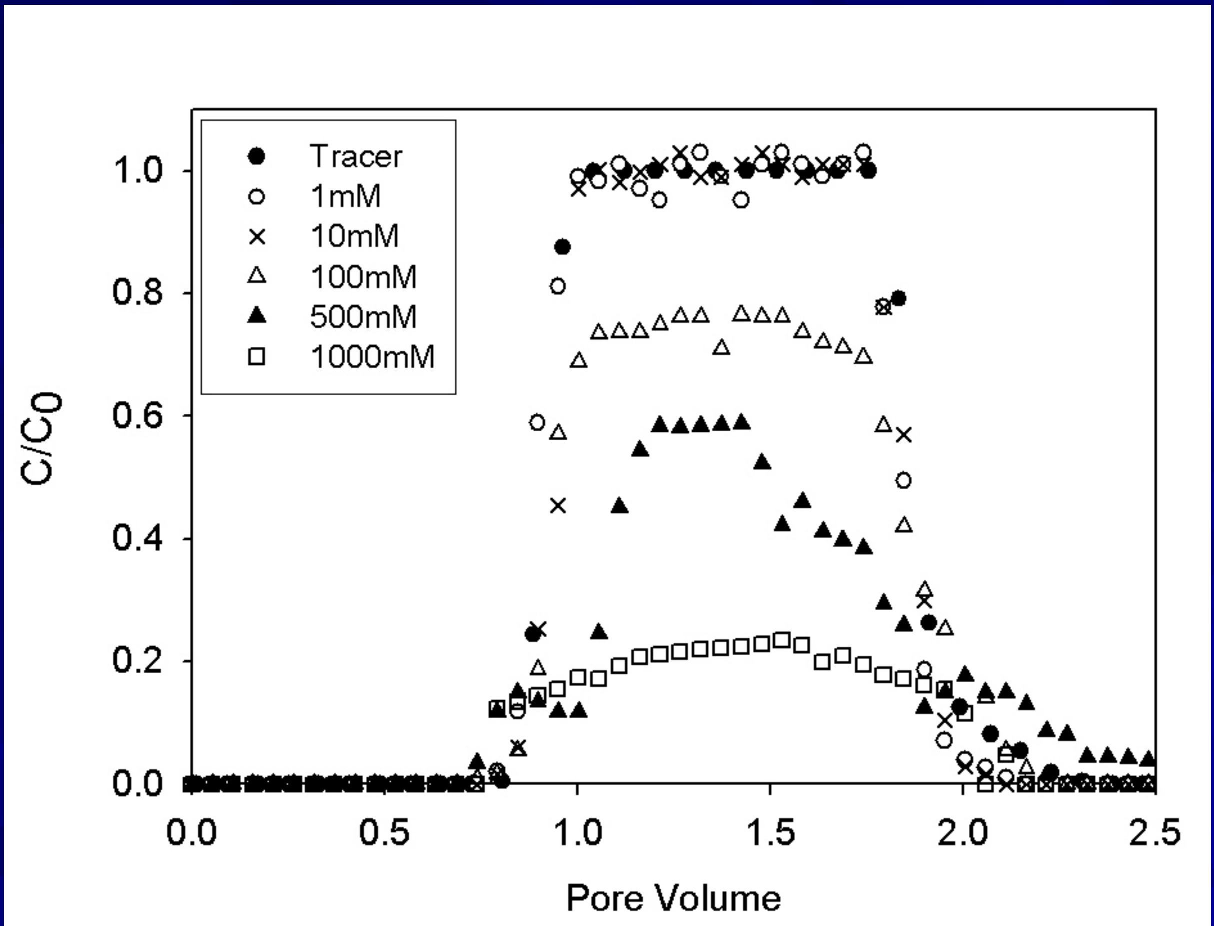



L=12.5-cm silica sand column with porosity of 0.33. Particle concentration is 3 g/L and I=1mM. Modifying agents were added at 2g/L concentration in each case. MRNIP was supplied by Toda Kogyo, Inc. The approach velocity was 93 m/d.

- ✓ **All modifiers enhance mobility relative to bare RNIP**
- ✓ **Variation between polymers and surfactants implies potential to select a transport distance**

**Saleh et al., 2007 EES 24(1) 45-57.**

# Mobility Depends on Ionic Strength and Composition




**Sand**
**L=61 cm**
**porosity=0.33**
**Velocity $3.2x10^{-2}$ cm/s**
**I=1-1000 mM**
**$Na^{+}$ or $Ca^{2+}$**
**<u>30 mg/L</u> particles**

Saleh, N. et al. ES&T (in revision)

# Mobility Depends on Coating Type and Geochemistry (30 mg/L particles)

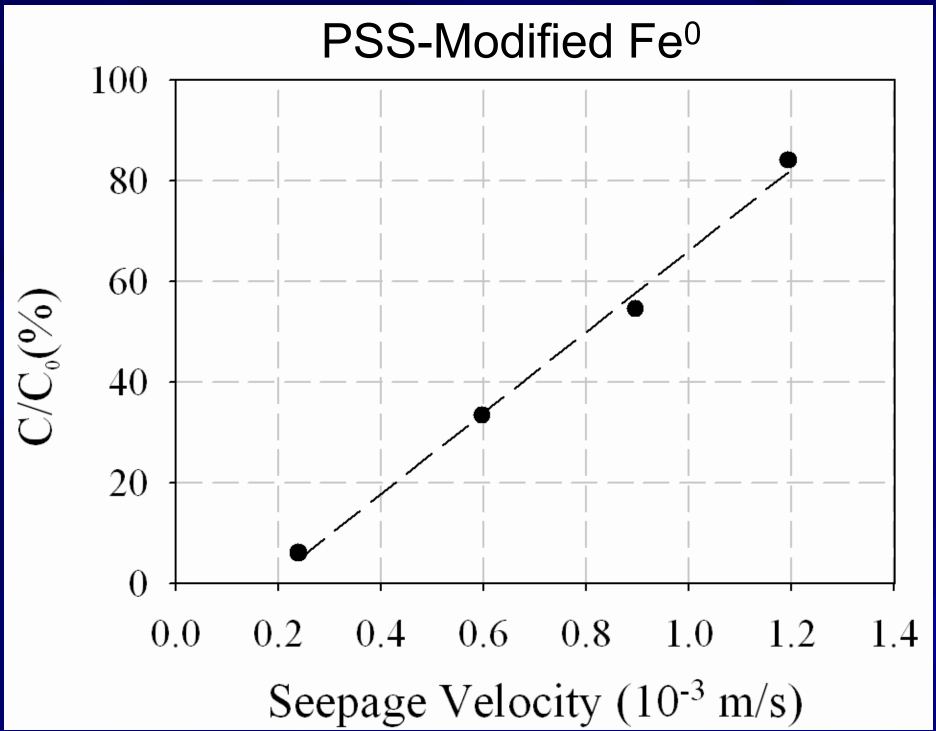
Applying a simple filtration model yields the predicted transport distance needed for 99% removal

| Modifier | $Na^+$ (mM) | Log α (--) | Dist. (m) | $Ca^{2+}$ (mM) | Log α (--) | Dist. (m) |
|---|---|---|---|---|---|---|
| **Polymer** | 10 | -- | -- | 0.5 | -- | -- |
| (MW=125k) | 100 | -2 | 33 | 5 | -1.89 | 25 |
| **Aspartate** | 10 | -2.5 | 45 | 0.5 | -1.77 | 8 |
| (MW=3k) | 100 | -0.96 | 1.2 | 1 | -0.96 | 1.2 |
| **SDBS** | 10 | -2.7 | 150 | 0.5 | -1.33 | 6.6 |
| (MW=350) | 100 | -0.6 | 1.2 | 1 | -0.89 | 2.4 |

| Site | $K^+ + Na^+$ mM | $Ca^{2+} + Mg^{2+}$ mM |
|---|---|---|
| Alameda Point, CA | 197 | 2.4 |
| Paris Island, SC | 6.1 | 1.3 |
| Mancelona, MI | 0.14 | 1.9 |

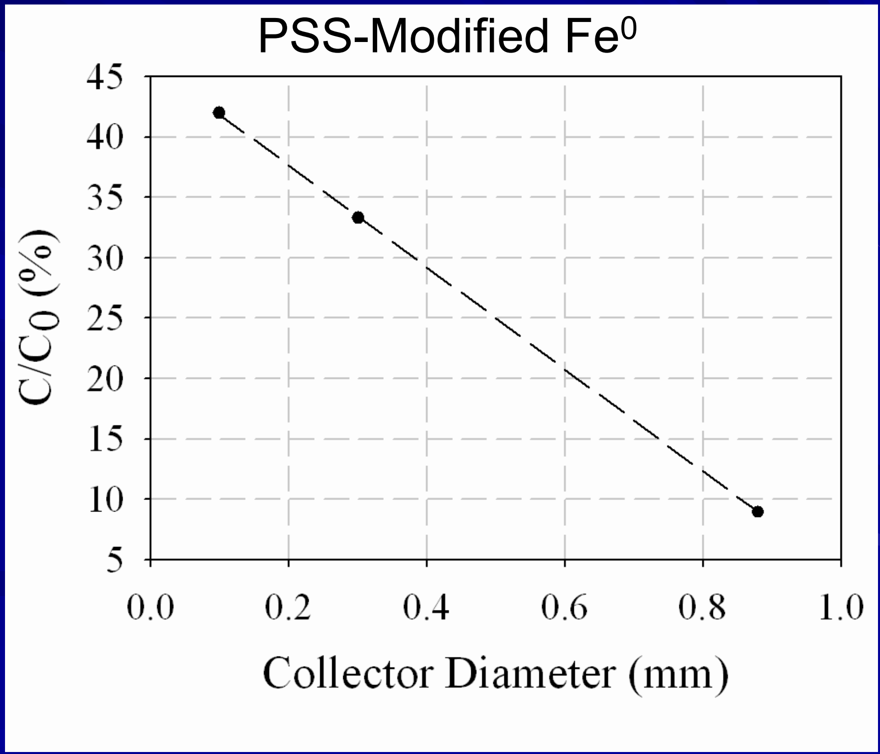
"Typical" concentrations of monovalent and divalent cations

# Effect of Fluid Velocity and Grain Size



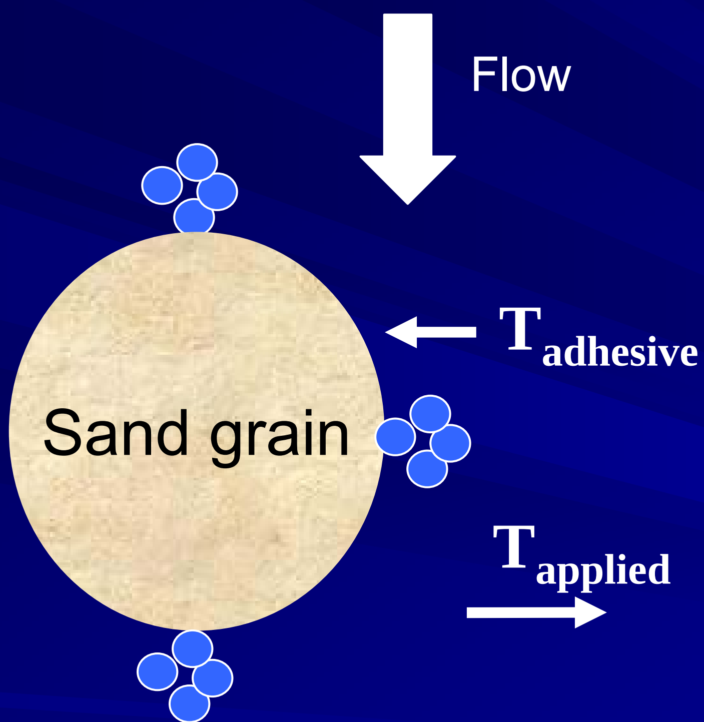

Greater mobility at higher velocity

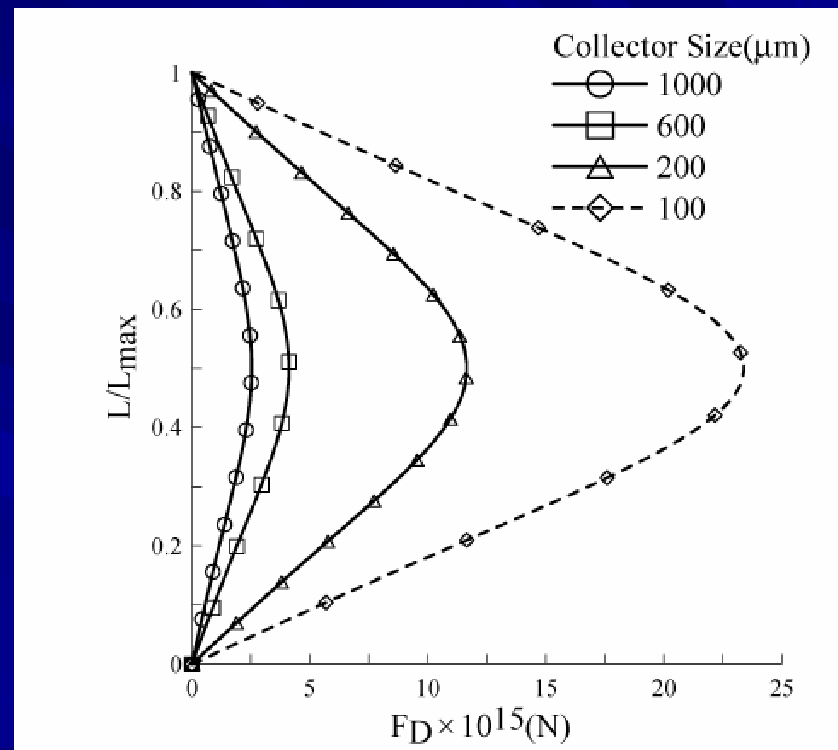
Lower mobility with larger sand grain size



# Effect of Hydrodynamics on Deposition and Detachment

Torkzaban et al. *Langmuir* 2007, 23, 9652-9660.




**$T_{applied}$ is proportional to velocity**

**$T_{applied}$ is inversely proportional to $d_c$ at a constant v**

# Factors Affecting Coating Lifetime

- Desorption
- Microbial degradation
- Biotransformations

# Desorption of Coatings

Polymer adsorption to RNIP is strong and effectively irreversible

Higher MW=stronger sorption

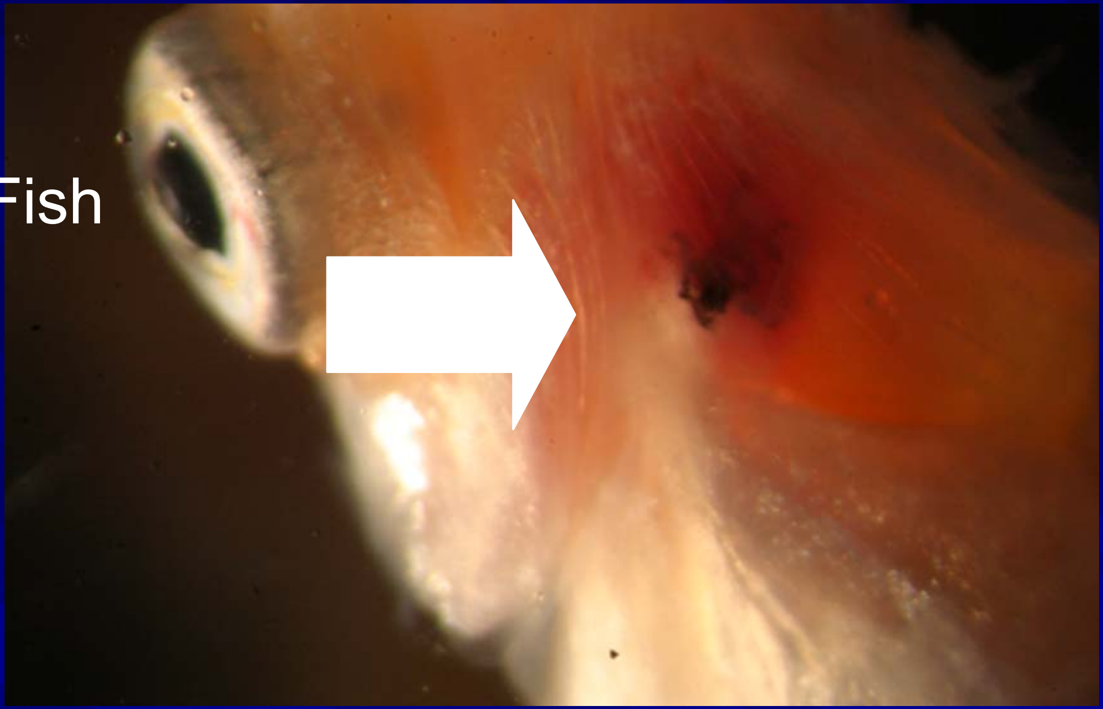
Mitigates concern of NAPL mobilization

| | | Percent Remaining Adsorbed | | |
|---|---|---|---|---|
| Modifier | Initial Adsorbed mass (mg/m²) | 2weeks | 4weeks | 8weeks |
| PAP 2.5K | 0.85±0.23 | 91 ± 3 | 86 ± 4.7 | 82 ± 5.5 |
| PAP 10K | 1.47±0.14 | 94 ± 4.1 | 91 ± 2.5 | 90 ± 2 |
| | | 2weeks | 5weeks | 8weeks |
| PSS 70K | 2.89±0.59 | 94 ± 0.5 | 93 ± 0.6 | 93 ± 0.6 |
| PSS 1M | 2.55±0.45 | 96 ± 4.1 | 95 ± 4.7 | 95 ± 4.7 |
| | | 2weeks | 6weeks | 8weeks |
| CMC 90K | 2.09±0.02 | 88 ± 2.1 | 83 ± 2.9 | 81 ± 3.1 |
| CMC 700K | 3.71±0.43 | 94 ± 0.4 | 91 ± 0.8 | 90 ± 0.9 |

Kim, H-J., Lowry, G.V. et al., (in prep)

# Biotransformations

Nano $Fe^0$ on Medaka Fish



Templeton, et al. (2006) *EST* 40(23), 7387-7393.


CNT ingestion and cycling

Roberts, et al. (2006) *EST* 41(8); 3025-3029.

# Summary

- Surface coatings must be considered in determining the fate of nanomaterials in the environment
  - Significant effects on aggregation and deposition
  - Determining the properties and fate of the coatings is important
- Agglomeration (and likely deposition) of coated nanomaterials occurs in a secondary minimum
  - Energy determined by coating and environment properties
  - Implies reversibility
  - Hydrodynamics need to be included in “filtration” models
- Nanomaterial-biota interactions are expected
  - Effects of these transformations on subsequent transport/exposure and toxicity are unknown

# Thank You

- Questions?