Environmental Transport and Fate of Nanomaterials

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Nanomaterials

- Most active area of nanotechnology research
- Current or near term applications:
  - nano-engineered TiO_2 for sunscreens and paints
  - carbon nanotube composites in tires
  - silica nanoparticles as solid lubricants
  - reagents for groundwater remediation
  - protein-based nanomaterials in soaps, shampoos, and detergents.

M. R. Wiesner, G. V. Lowry, P. Alvarez, D. Dionysiou, and P. Biswas. *Environ. Sci. Technol.* (in press)

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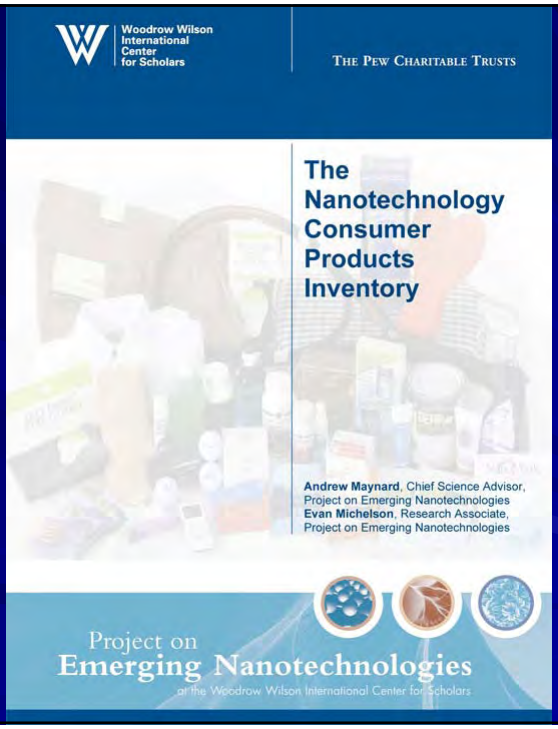

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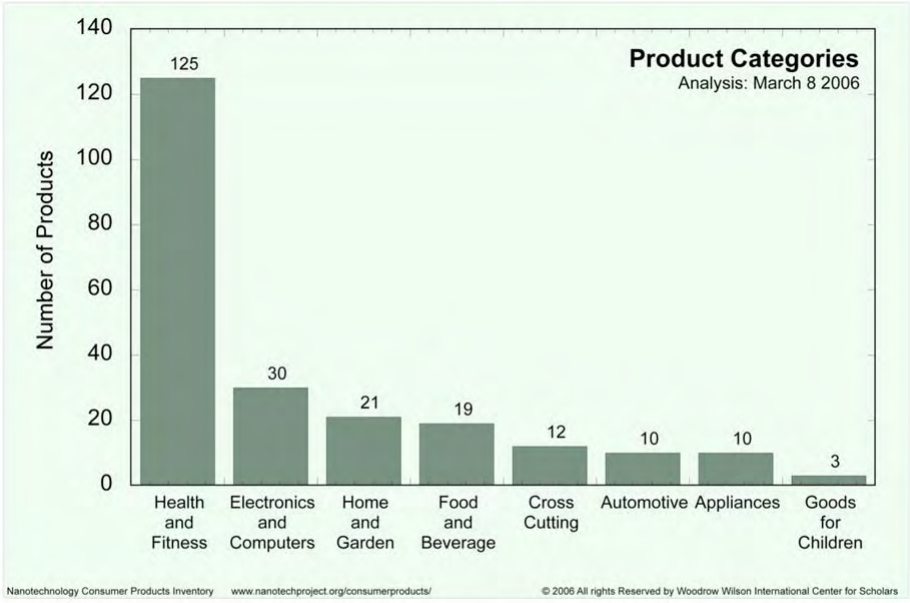

Figure 1. Number of products, according to category. Because some products are grouped into multiple categories, the total number of products in this chart exceeds 212.

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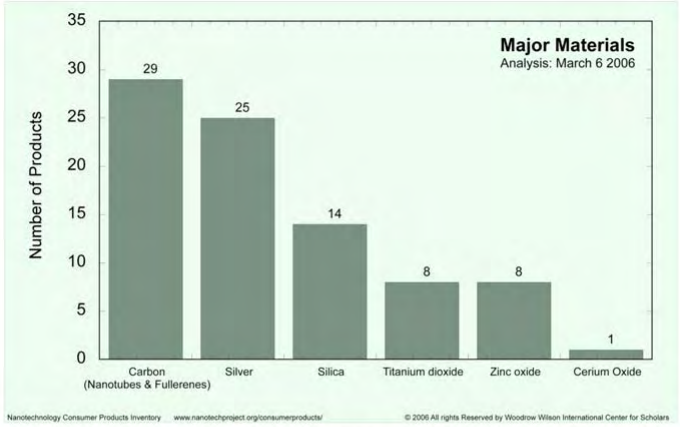

Figure 4. Numbers of products associated with specific materials.

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Potential Risks

- Nanotechnology risks are largely unknown
- Risk is a function of both <u>exposure</u> *and* <u>toxicity</u>
- Need to monitor
  - Exposure pathways
  - Fate and transport in the environment
  - Toxicity

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Environmental Cycling of Nanomaterials

What are source management alternatives?

Is there harm? Bioaccumulation or biomagnification?

Sources → Transport → Fate → Receptors

✓How do they travel?
✓What factors affect mobility?

✓Can they be transformed?
✓What do they become?
✓Do transformations affect toxicity?
✓What 'compartment' do they reside

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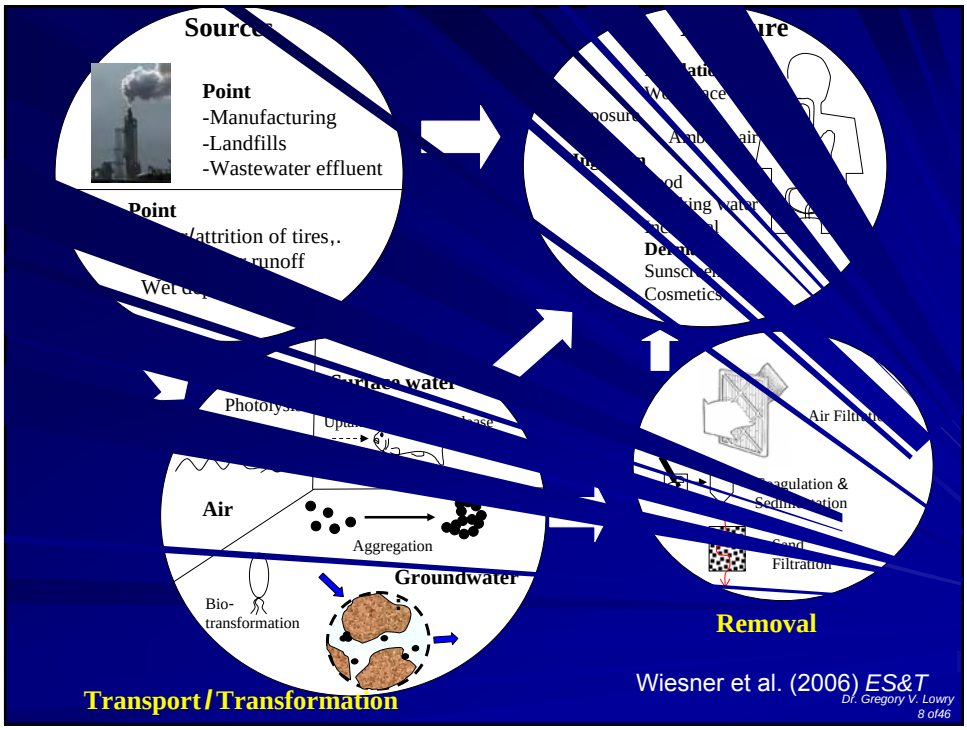

Wiesner et al. (2006) *ES&T*

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Outline

- Fate processes affecting the mobility of nanomaterials in the environment
  - Aggregation
  - Attachment/filtration
- Transformations
  - Abiotic (redox transformations, photolysis)
  - Biotransformation
- Mobility in the environment
  - Groundwater
  - Surface water

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Nanoparticle Aggregation

- Particles aggregate in water:
  - High Hamaker constant-i.e. attractive van der Waals forces
    - [illegible]mical bonding
    - Hydro[illegible]
    - [illegible] attractive
- Small particles have high diffusion coefficients and many collisions between particles

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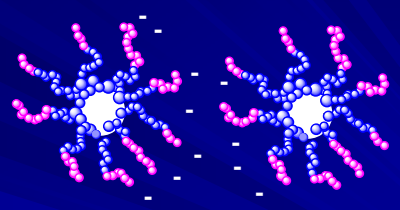
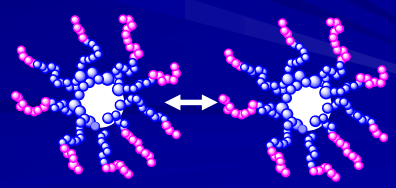
Nanoparticle Stabilization

- Charge Stabilization



- Steric Stabilization



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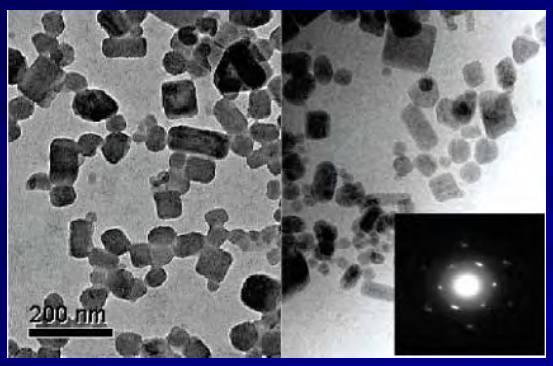
Fullerene Aggregation in Water



✓Cluster dimensions ranged from 25-500 nm

✓Stable suspensions ≤ 0.05M (NaCl)

✓No surface coatings

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

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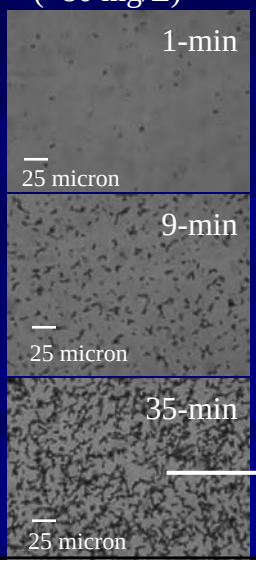
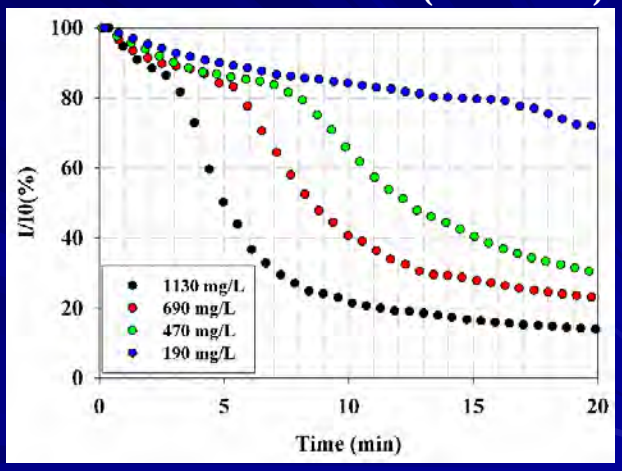
Nanoiron (Fe^0) Aggregation

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



Nanoiron sedimentation curves (1 mM NaCl)



→ ~40-140 micron diameter (D_F=1.8)

Phenrat et al. ES&T (submitted)

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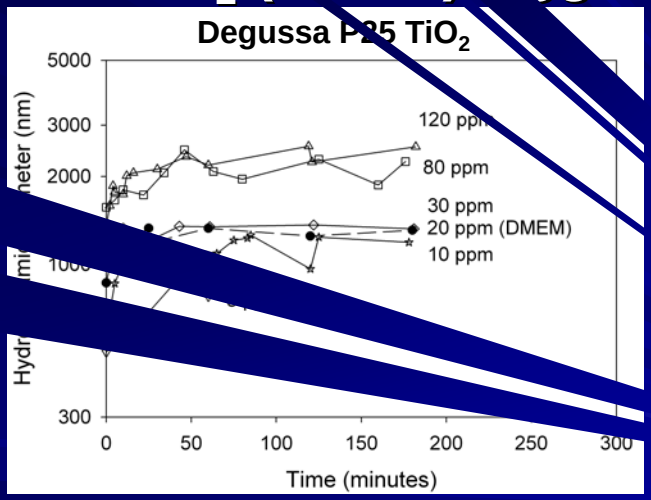
TiO_2 (30 nm) Aggregation



↑ Increasing Conc.

Aggregate size is a function of time and concentration

Long et al. (2006). Titanium Dioxide (P25) Produces Oxidative Stress in Immortalized Brain Microglia (BV2): Implication of Nanoparticle Neurotoxicity. *ES&T* (in press)

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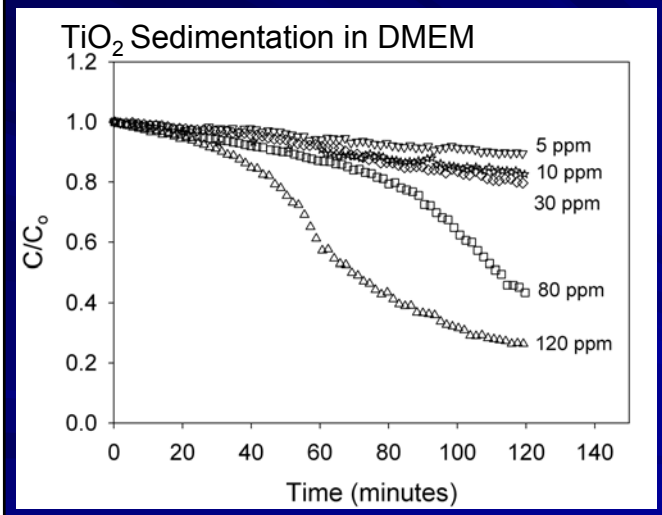
Nanoparticle Size and Sedimentation



Particle concentration affects:

1. Size of aggregates formed
2. Stability of suspensions
3. Fate of the particles

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Attachment to Surfaces

- Attachment is an important fate process
  - Limits mobility in porous media
    May affect bioavailability
  - [illegible] transformation/degradation
- [illegible] (Hamaker Constant) and its surface properties
  - Differences between NPs

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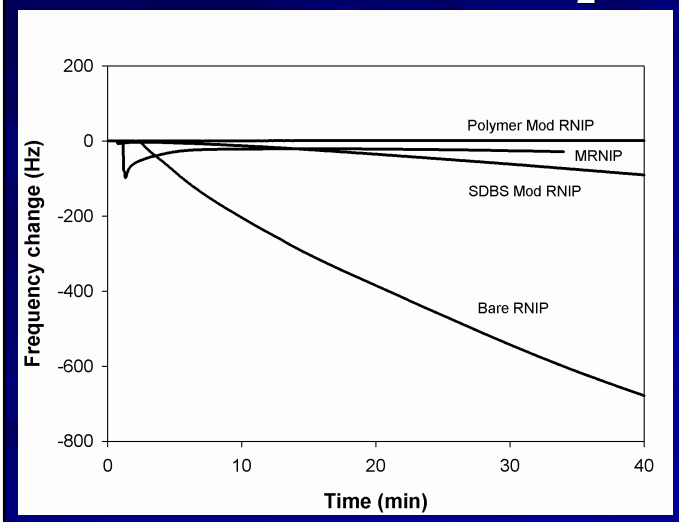
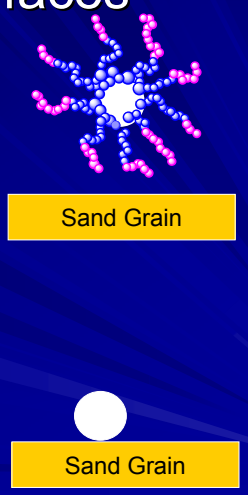
QCM Monitors Nanomaterial Attachment to SiO_2 Surfaces





Saleh et al. EES (in press)

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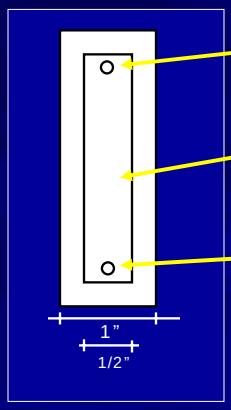
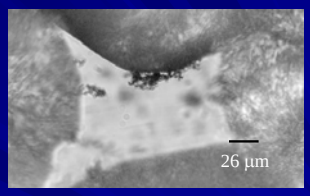
Attachment Limits Mobility



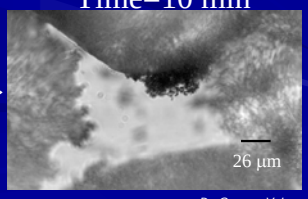
Micro-fluidic PDMS cell

Time=1 min



Nanoiron aggregates are filtered

Time=10 min



Saleh et al. EES (in press)

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Nanomaterial Transformations

- Fundamental Questions
  - How long do the particles last?
  - What do they become?
- Abiotic transformations
  - Redox reactions
  - Photolysis (not in groundwater)
- Biotransformations
  - Aerobic oxidations
  - Anaerobic reductions

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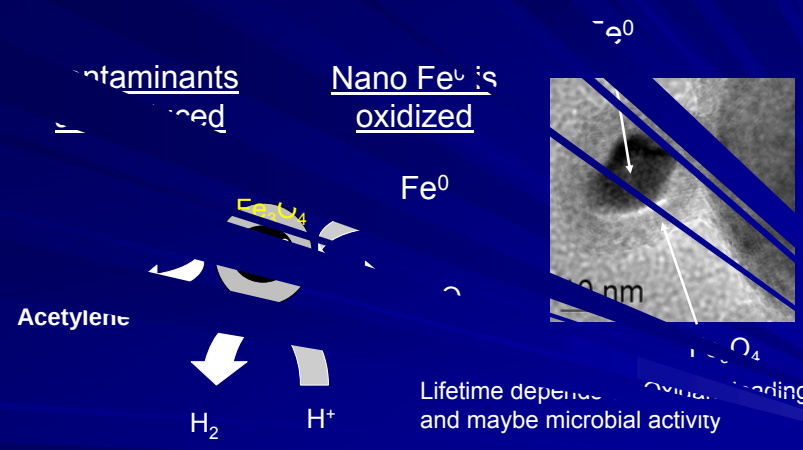
Reactive Fe^0 Nanoparticles



Lifetime depends on oxidant loading, pH, and maybe microbial activity

Liu et al, (2005) *ES&T 39*, 1338

Liu and Lowry, (2006) *ES&T (submitted)*

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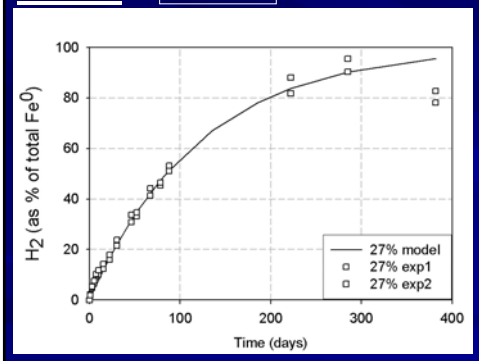
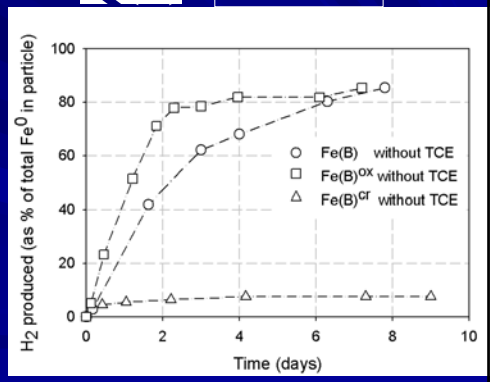
Fe^0 Lifetime Depends on Particle Type

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow$$

RNIP ~1 year



Fe(B) ~1-2 weeks



Liu and Lowry (2006) *ES&T* (in revision)

Liu et al., (2005) *Chem Mat.* *17*, 5315.

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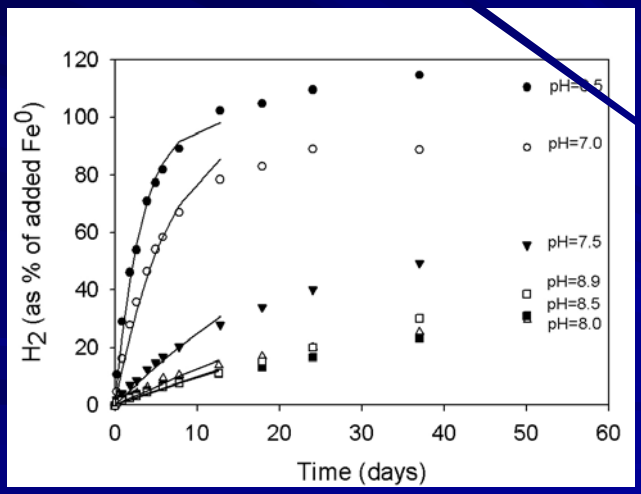
Fe^0 Lifetime Depends on pH

RNIP



~2 weeks
pH=6.5

~1 year
pH=8.9

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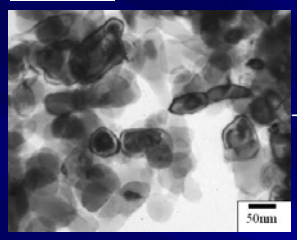
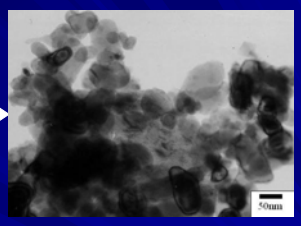
Nanoparticle Fate: Reaction with TCE in Water

RNIP (Fe^0/Fe_3O_4)

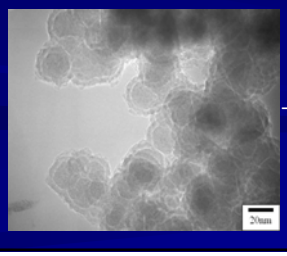


+ TCE/H_2O

(Fe_3O_4/Fe_2O_3)

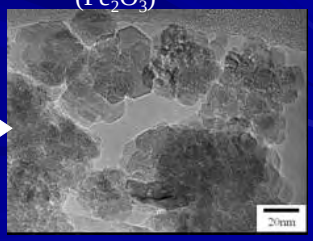


Fe(B) ($Fe^0/FeB_x/Na_2B_4O_7$)



+ TCE/H_2O

(Fe_2O_3)



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Other transformations that could affect particle toxicity or mobility

- Surface functionalization
  - E.g. hydroxylation of fullerene to fullerol
  - Sorption of DOM or alginates
- Oxidation of NPs in the atmospheric
  - E.g. oxidation of diesel soot
- Loss of surface coatings on NP
  - Biodegradation of coatings
  - Desorption of coatings
- Biotransformations
  - Microbially induced redox transformations
    - Direct or indirect through release of reactive oxygen species or reductants (e.g. Fe^{2+})

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

Wiesner et al. (2006) *ES&T*

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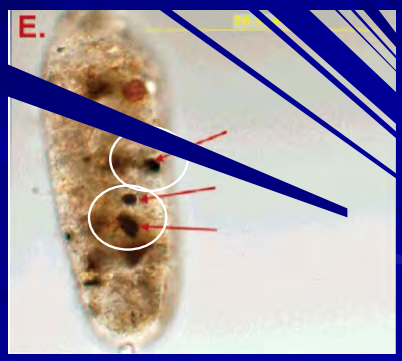
SWNT ingested by benthic Copepods

Aggregates of SWNTs moving through the gut



SWNTs in Copepod Feces

Templeton, et al. (2006) *Environ. Sci. Technol.* ASAP

Note: SWNT were hydroxylated and carboxylated

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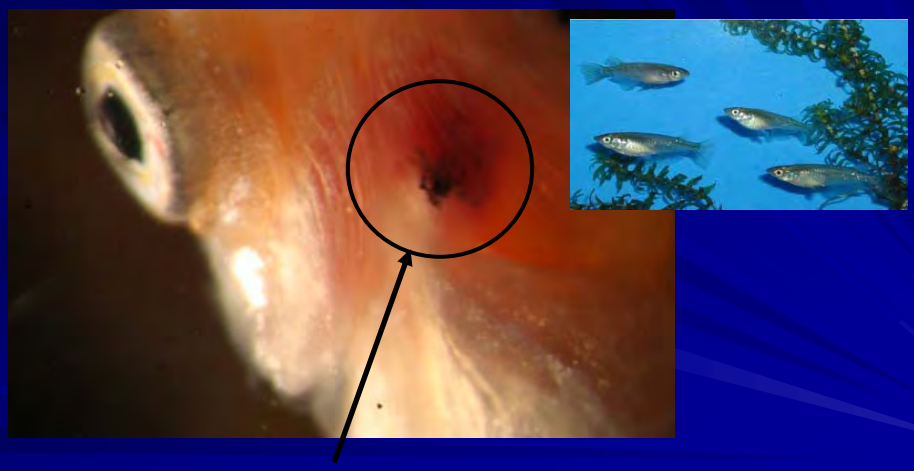
Nanoiron on Medaka Fish Gils



Nanoiron aggregates accumulate on Medaka fish gills-(Richard Winn UGA)

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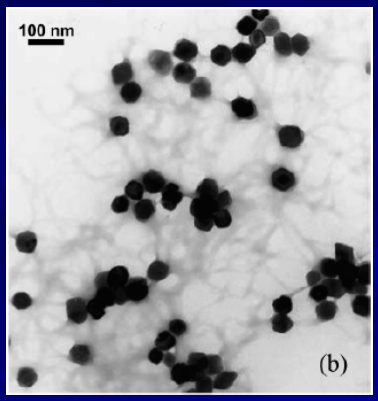
Nanoparticle Functionalization in Natural Waters (Sorption of DOM)



Hematite-Alginate Aggregates
10^9 particles/mL; 784 μg/L alginate

- Alginates- biopolymers produced by brown seaweed
- Natural Organic Matter

Chen et al., 2006 *ES&T* 40 1516-1523

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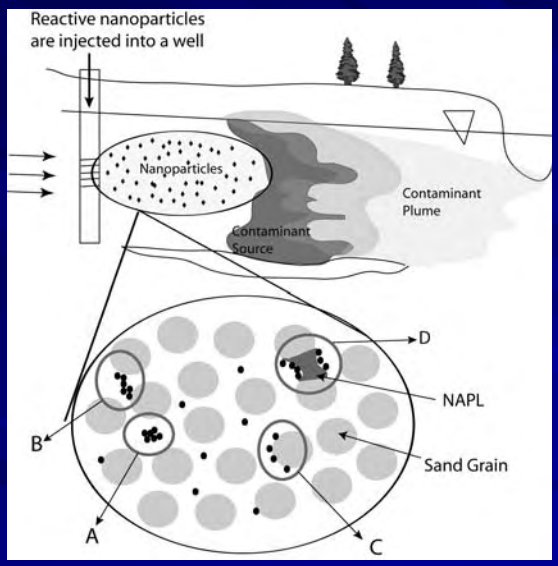
Nanomaterial Mobility in Porous Media



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

Lowry, *Env. Nanotech.* (in press).

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Factor Affecting Nanomaterial Mobility in the Environment

Schrick et al., 2004 *Chem Mat* 16 2187-2193

Nanoiron aggregates on top of sand

Modified nanoiron flows through sand

- ✓ **Chemical**
  - *(pH, I, particle surface chemistry)*
- ✓ **Physical**
  - *(Particle size and concentration, collector grain size, flow velocity, heterogeneity)*

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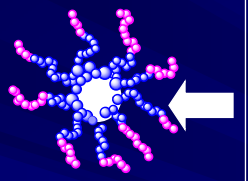
Surface Modifiers Increase Mobility



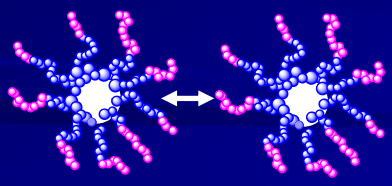
1. Potential Surface Coatings

Polyelectrolyte (electrosteric)
- ✓ **Triblock copolymers**
- ✓ **Polyaspartic acid**

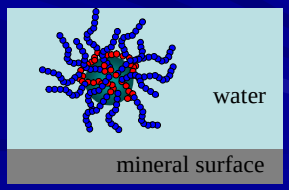
Surfactants (electrostatic)
- ✓ **SDBS**

Polymers (steric)
- **Cellulose/polysaccharides**
- **PEG**

Inhibits Aggregation



Inhibits Particle-Media Interactions



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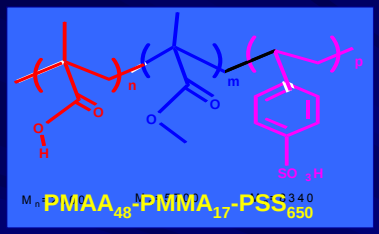
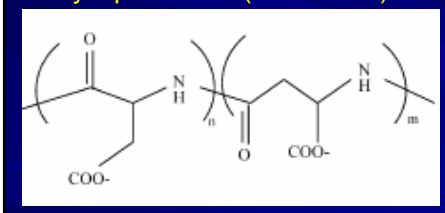
Modifiers Evaluated

Copolymer (MW=40k to 60k)



$PMAA_{48}$-$PMMA_{17}$-PSS_{650}

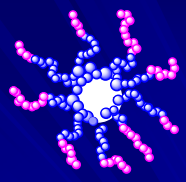
Polyaspartic acid (MW=2k-3k)



SDBS (MW=350)

$C_{12}H_{25}(C_6H_4)SO_3^-$

Increasing MW



Polyelectrolytes

Surfactant

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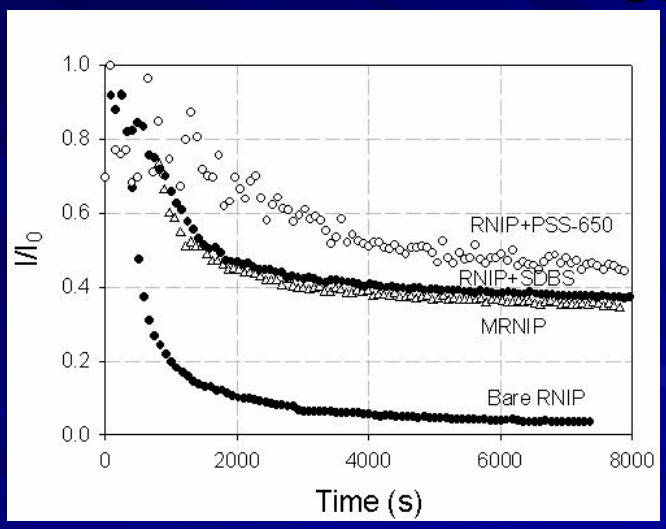
Modifiers Inhibit Agg/Sed



Largest Polymer
Least aggregation

No Polymer
Most aggregation

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

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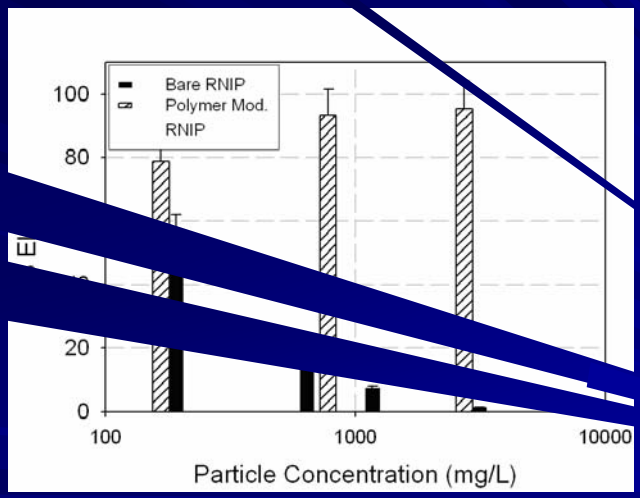
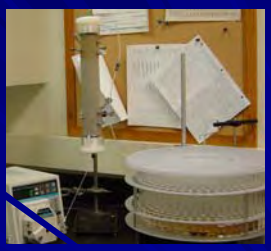
Coatings Enhance Mobility





Sand
L=10 cm
porosity=0.33
velocity 10^{-3} m/s
I=1 mM (NaCl)
pH=7.4

$PMAA_{48}$-$PMMA_{17}$-PSS_{462}

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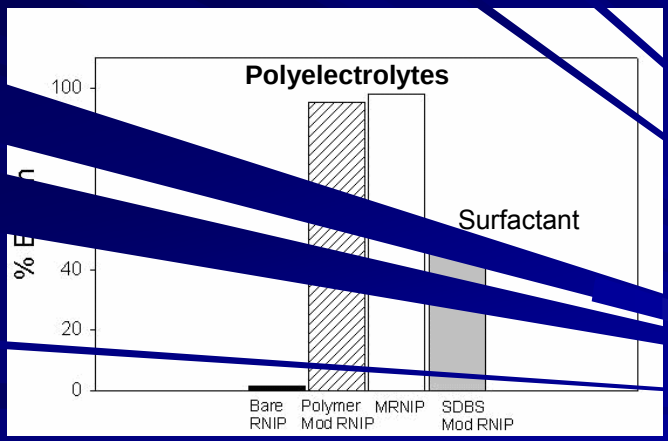
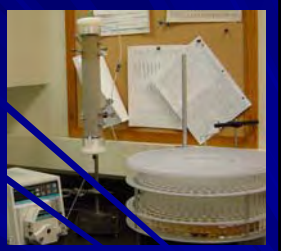
Enhancement Depends on Coating Type





Sand
L=10 cm
porosity=0.33
velocity 10^{-3} m/s
I=1 mM (NaCl)
3g/L particles

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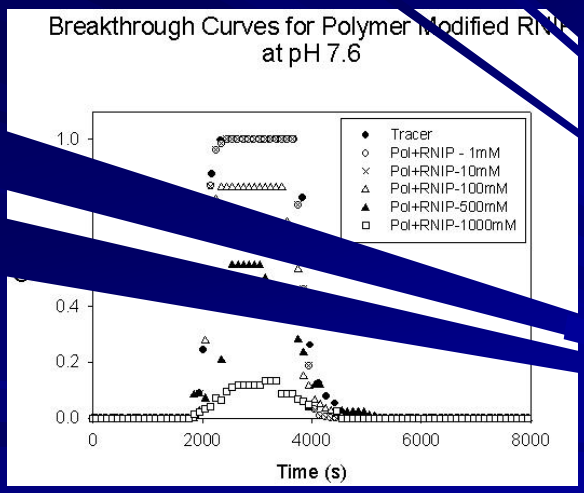
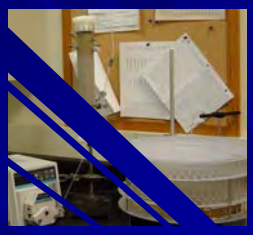
Mobility Depends on Ionic Strength and Composition





Sand
L=61 cm
porosity=0.33
[illegible]ity 3.2[illegible]-2 cm/s
I=1 [illegible]
Na^+ or Ca^{2+}
30 mg/L particles

Saleh et al. ES&T (in prep)

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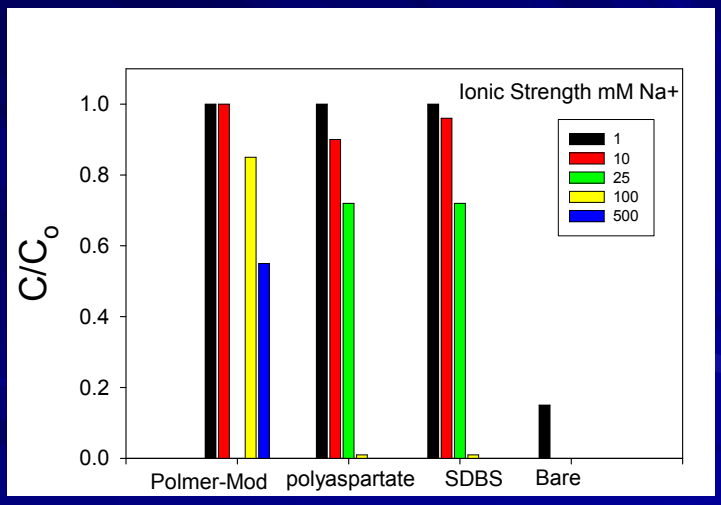
Elution of Modified Nanoiron at Different Ionic Strength (Na^+)



Modified particles immobile at I>100mM except high MW polymer

Bare NPs immobile

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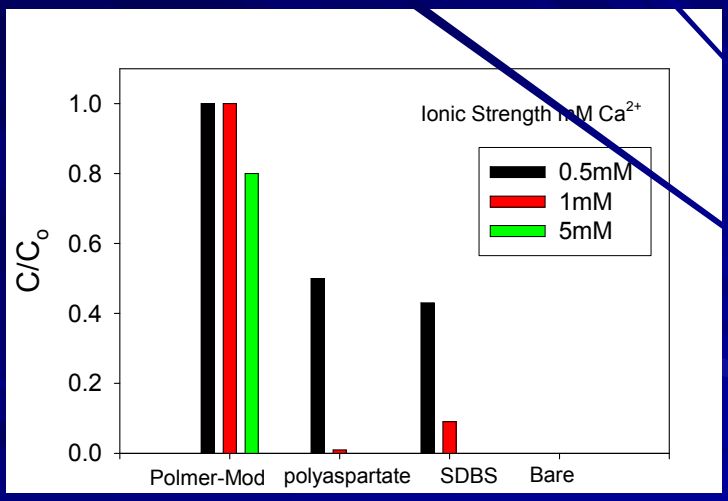
Elution of Modified Nanoiron at Different Ionic Strength (Ca^{2+})



Particles immobile at I>1 mM Ca^{2+}except high MW polymer

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Relative Mobility and Estimated Transport Distances

- Calculate the sticking coefficient from breakthrough data

Column Length **Breakthrough**

$$L_T = -\ln\left(\frac{C_L}{C_o}\right)\left(\frac{4a_c}{3(1-n)\alpha\eta_o}\right)$$

Travel Length **Tolerance level**

- Estimate Travel Distance for given tolerance (C/C_o)

a_c=media grain radius; n=porosity
η_o=single collector efficiency
α=sticking coefficient (function of I)

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Estimated Transport Distance for (C/C_o=0.01)

Mod	Na^+ (mM)	Log α (--)	Dist. (m)	Ca^{2+} (mM)	Log α (--)	Dist. (m)
Polymer (MW=60k)	10	--	--	0.5	--	--
	100	-2	33	5	-1.89	25
Aspartate (MW=3k)	10	-2.5	45	0.5	-1.77	8
	100	-0.96	1.2	1	-0.96	1.2
SDBS (MW=350)	10	-2.7	150	0.5	-1.33	6.6
	100	-0.6	1.2	1	-0.89	2.4

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Mobility of Carbon and Metal-oxide Nanomaterials

TABLE 1. Characteristics of Nanomaterials Used for Filtration Experiments and Calculated Particle Mobility in a System Resembling a Sandy Groundwater Aquifer[a]

nanomaterial	size (nm)	electrophoretic mobility (10^{-8} $m^2 s^{-1} V^{-1}$)	C/C_0 ± 2 SD	α ± 2 SD	log α	distance to reduce C/C_0 to 0.1% (m)[b]
fullerol	1.2, M	not detectable	0.99 ± 0.01	(0.0001 ± 0.0001)	−3.98	14
SWNT	0.7−1.1[c] × 80−200, P (d_h = 21 nm[d])	−3.98	0.94 ± 0.01	(0.001 ± 0.0004)	−2.89	10
silica	57, M	−1.95	0.97 ± 0.01	0.008 ± 0.003	−2.10	2.4
alumoxane	74, P	−2.45	0.85 ± 0.02	0.039 ± 0.001	−1.32	0.6
silica	135, M	−2.58	0.68 ± 0.01	0.169 ± 0.004	−0.77	0.2
n-C_{60}	168, M	−1.99	0.56 ± 0.06	0.298 ± 0.013	−0.52	0.1
anatase	198, P	−0.27	0.56 ± 0.01	0.336 ± 0.005	−0.47	0.1
ferroxane	303, P	−0.43	0.30 ± 0.03	0.895 ± 0.023	−0.05	0.1

[a] M, monodisperse suspensions; P, polydisperse suspensions. [b] Conditions assumed for calculations: T = 15 °C, H = 10^{-20} J, Darcy velocity = 0.003 cm/s, porosity = 0.30, mean sand grain diameter = 350 μm. [c] According to the model cross-section of an individual fullerene nanotube encased in a close-packed cylindrical surfactant micelle (*16*), the outer diameter of this nanomaterial is close to 4 nm with a specific gravity of approximately 1.0. [d] Average hydrodynamic diameter.

I= 10 mM, pH=7, v=0.003 cm/s

Lecoanet, et al. (2004). Laboratory Assessment of the Mobility of Nanomaterials in Porous Media. *Environ. Sci. Technol.* 38(19); 5164-5169.

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Mobility of Nanomaterials from Landfills

- Mobility from landfills could be limited considering leachate properties*
  - Calcium 200-3000 mg/L (<5mM)
  - Magnesium 50-1500 mg/L
  - Sodium 100-200 mg/L
  - Clay liners and leachate collection

*Davis and Masten, *Principles of Environmental Engineering and Science*, McGraw Hill, 2004

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Mobility in Surface Waters

- Mobility in surface waters is unknown
  - [illegible]n in receiving waters may [illegible] aggrega[illegible] or promote disaggregati[illegible] [illegible] surface coatings in surface waters is not known
  - Attach[illegible] other suspended solids is possible and my result [illegible] sedimentation and partitioning to solids
  - Photolysis in surface waters is possible

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Conclusions

- Nanomaterials aggregate in the environment
  - Predominantly present as aggregates
  - Sizes range from 10's of nanometers to 10's of microns depending on ionic strength and composition
- Nanomaterial mobility in porous media is low under typical GW conditions
  - Surface modifcation enhances mobility
  - Mobility in/from landfills will likely be low
  - Mobility in surface water should be high, with sorption and sedimentation the likely sink (i.e. in sediments)

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Conclusions

- Redox transformations change the surface characteristics of the particles
  - Oxidation, hydroxylation
  - Sorption of organic matter
  - Biotransformations are likely but not demonstrated
- Nanomaterials appear to cycle with other particles in the environment
  - Copepods
  - Transformations during this process are not known

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Open Questions

- Fate and Transport
  - Will NMs bioaccumulate or facilitate the bioaccumulation of other contaminants?
  - How significant are biotransformations of NMs?
  - Is photolysis significant?
  - What role does heterogeneity play in particle mobility?
  - Is incineration effective at destroying NMs?
  - What is the fate of surface coatings on nanomaterials?
- Toxicity
  - What are "environmentally relevant" concentrations of NMs?
  - Despite aggregation, is the low population of single particles responsible for toxicity?
  - Do surface coatings enhance or mitigate the toxicity of the particles?

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