Environmental Transport and Fate of Nanomaterials

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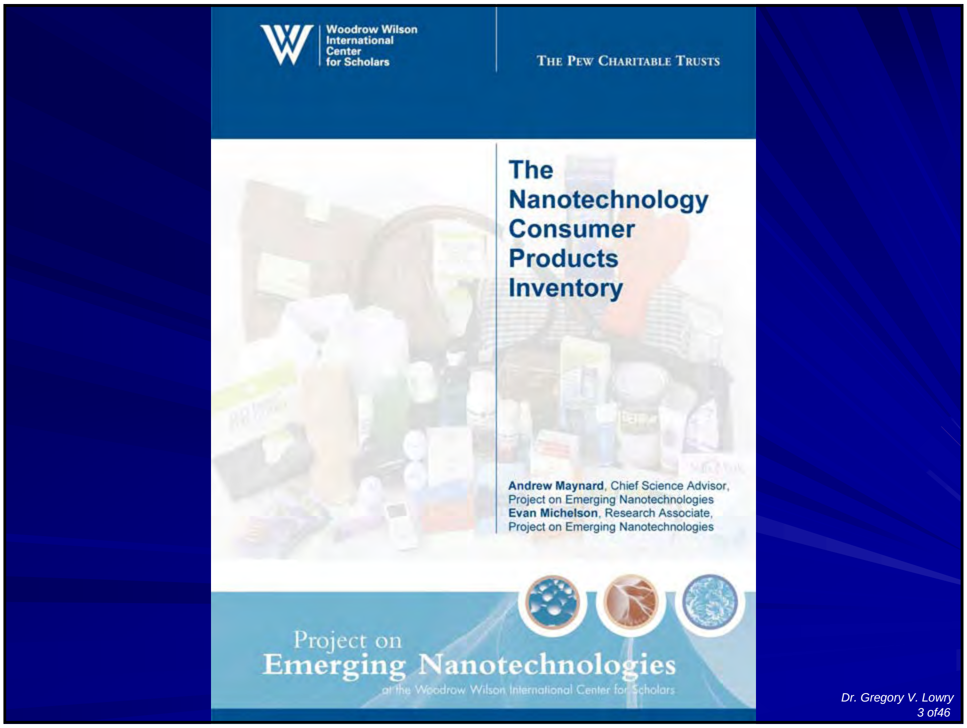
Nanomaterials

- 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)


Woodrow Wilson International Center for Scholars
The Pew Charitable Trusts
The Nanotechnology Consumer Products Inventory
Andrew Maynard, Chief Science Advisor, Project on Emerging Nanotechnologies
Evan Michelson, Research Associate, Project on Emerging Nanotechnologies
Project on Emerging Nanotechnologies
at the Woodrow Wilson International Center for Scholars
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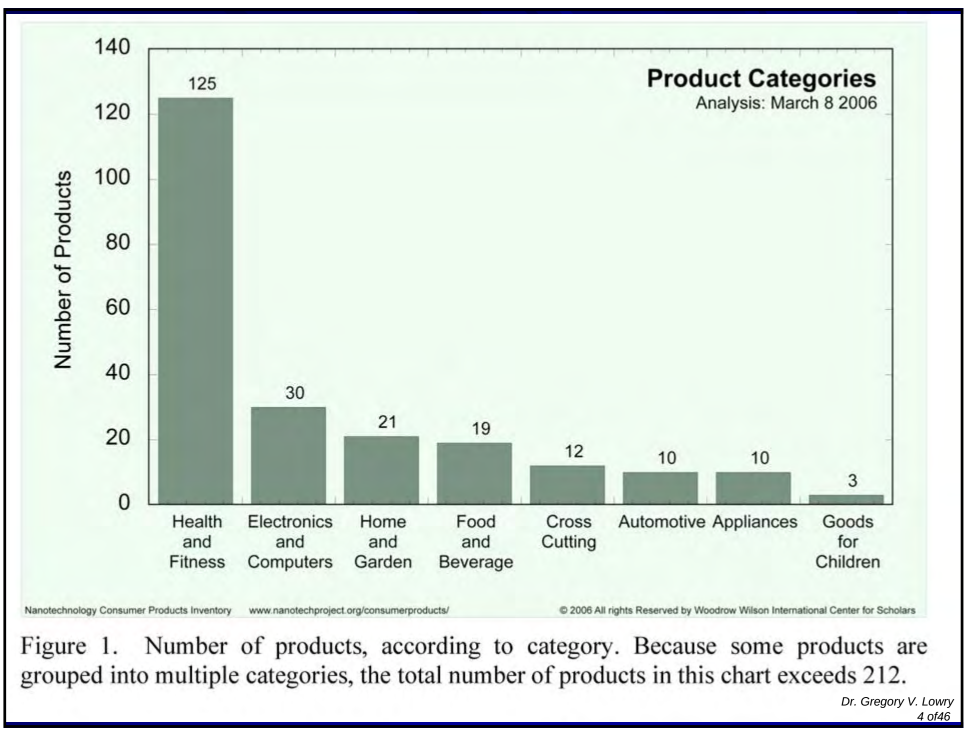
3 of46


Product Categories
Analysis: March 8 2006
Number of Products
0
20
40
60
80
100
120
140
125
30
21
19
12
10
10
3
Health and Fitness
Electronics and Computers
Home and Garden
Food and Beverage
Cross Cutting
Automotive
Appliances
Goods for Children
Nanotechnology Consumer Products Inventory www.nanotechproject.org/consumerproducts/ © 2006 All rights Reserved by Woodrow Wilson International Center for Scholars
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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4 of46

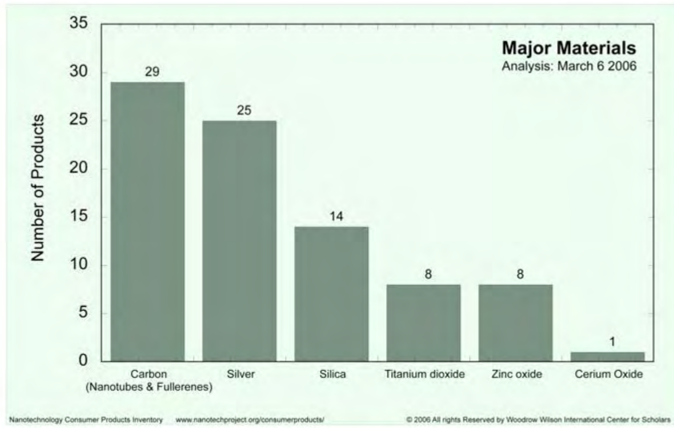

Figure 4. Numbers of products associated with specific materials.

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5 of46

Potential Risks

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

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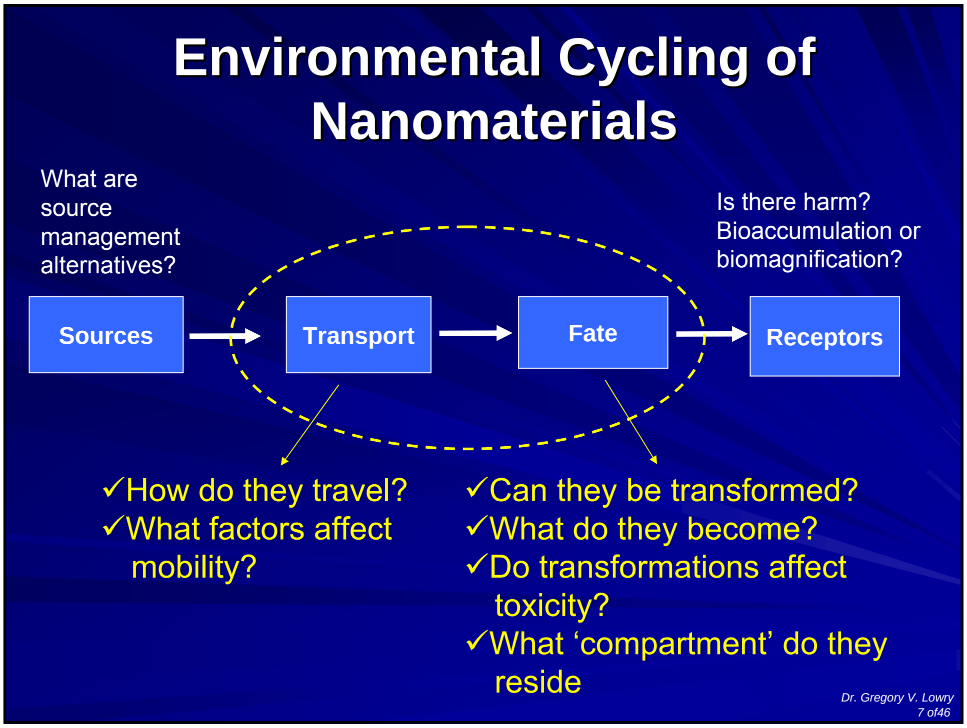
6 of46


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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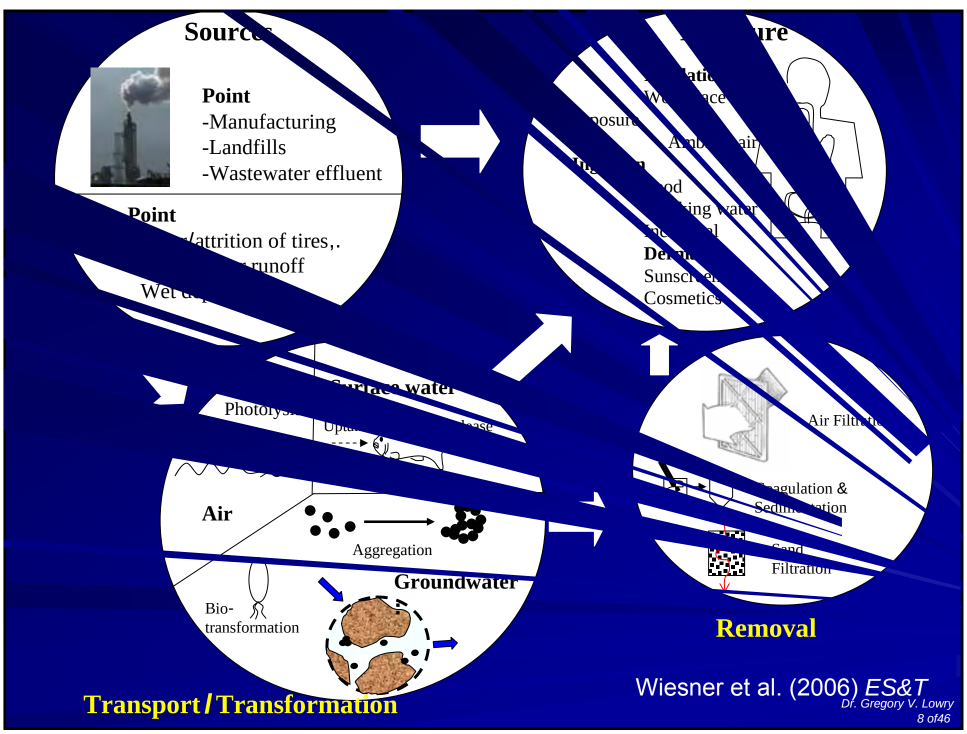
7 of46


Point
-Manufacturing
-Landfills
-Wastewater effluent
Surface water
Air
Aggregation
Groundwater
Bio-
transformation
Transport / Transformation
Sunscreen
Cosmetics
Air Filtration
Sand
Filtration
Removal
Wiesner et al. (2006) ES&T
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8 of46

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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9 of46

Nanoparticle Aggregation

- Particles aggregate in water:
  - High Hamaker constant-i.e. attractive van der Waals forces
  - Chemical bonding
  - Hydrophobicity
  - Magnetic attraction
- Small particles have high diffusion coefficients and many collisions between particles

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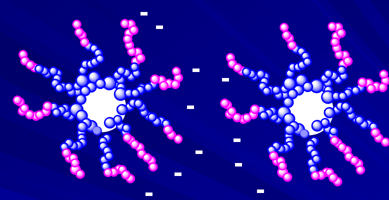
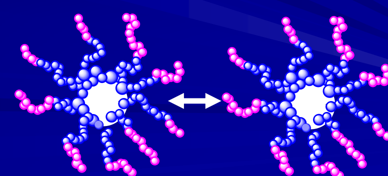
10 of46

Nanoparticle Stabilization

- Charge Stabilization



- Steric Stabilization



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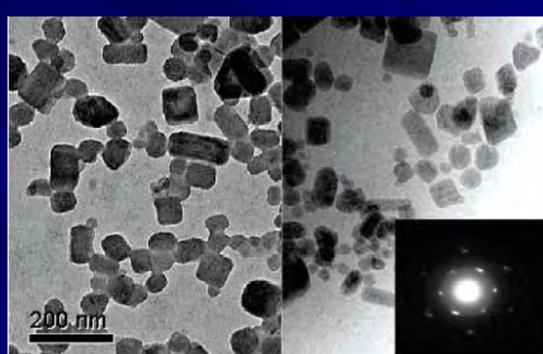
11 of46

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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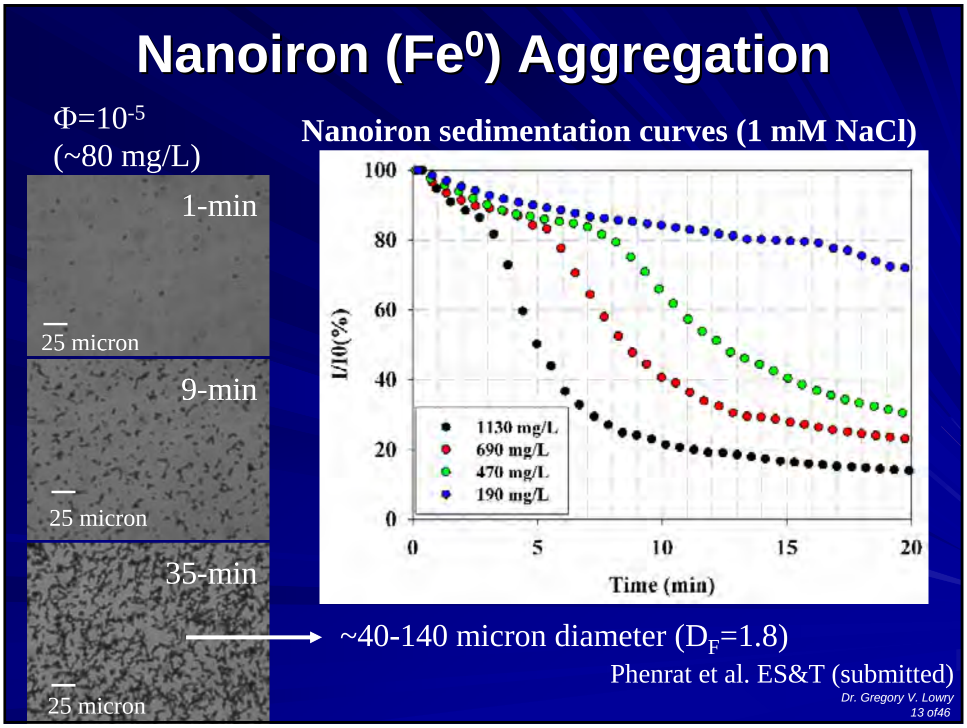
12 of46


Nanoiron (Fe0) Aggregation
Φ=10-5
(~80 mg/L)
1-min
25 micron
9-min
25 micron
35-min
25 micron
Nanoiron sedimentation curves (1 mM NaCl)
I/I0(%)
Time (min)
1130 mg/L
690 mg/L
470 mg/L
190 mg/L
~40-140 micron diameter (DF=1.8)
Phenrat et al. ES&T (submitted)
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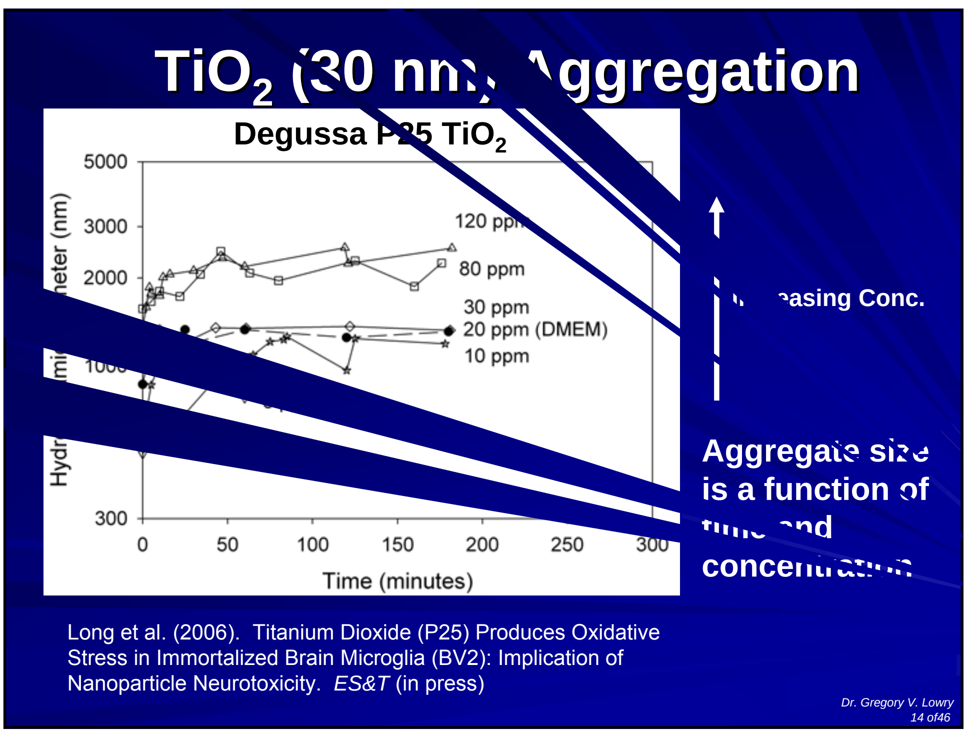
13 of46


Degussa P25 TiO2
120 ppm
80 ppm
30 ppm
20 ppm (DMEM)
10 ppm
Time (minutes)
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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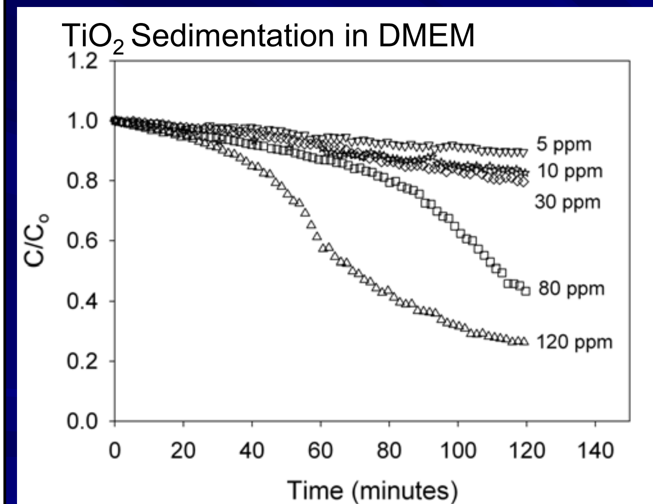
14 of46

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
  - transformation/degradation
- (Hamaker Constant) and its surface properties
  - Differences between NPs

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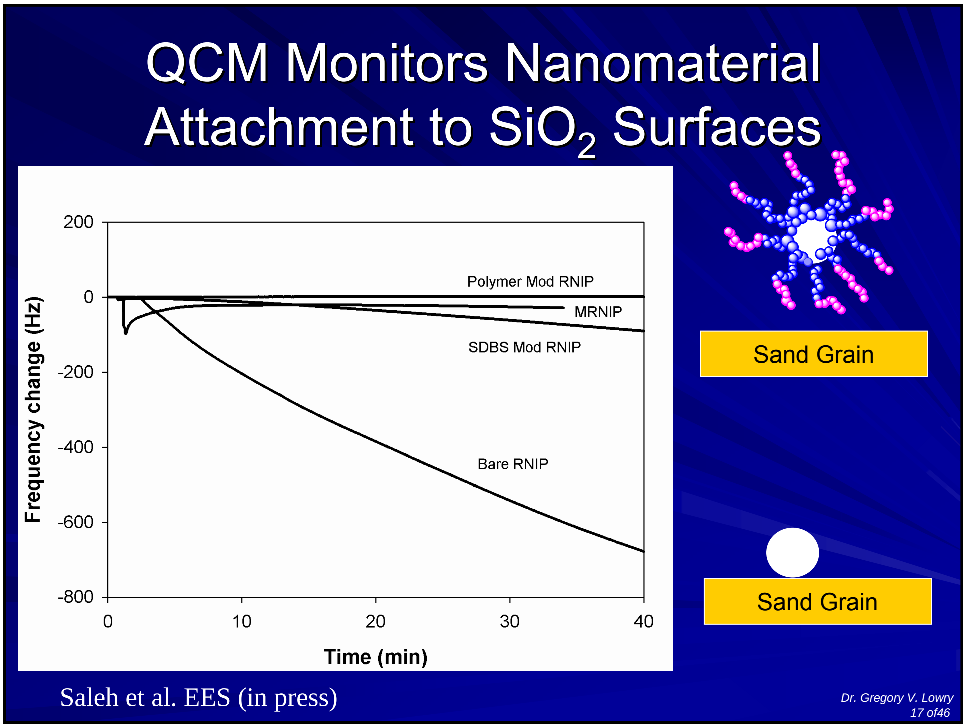
16 of46


QCM Monitors Nanomaterial Attachment to SiO2 Surfaces
Frequency change (Hz)
Time (min)
Polymer Mod RNIP
MRNIP
SDBS Mod RNIP
Bare RNIP
Sand Grain
Sand Grain
Saleh et al. EES (in press)
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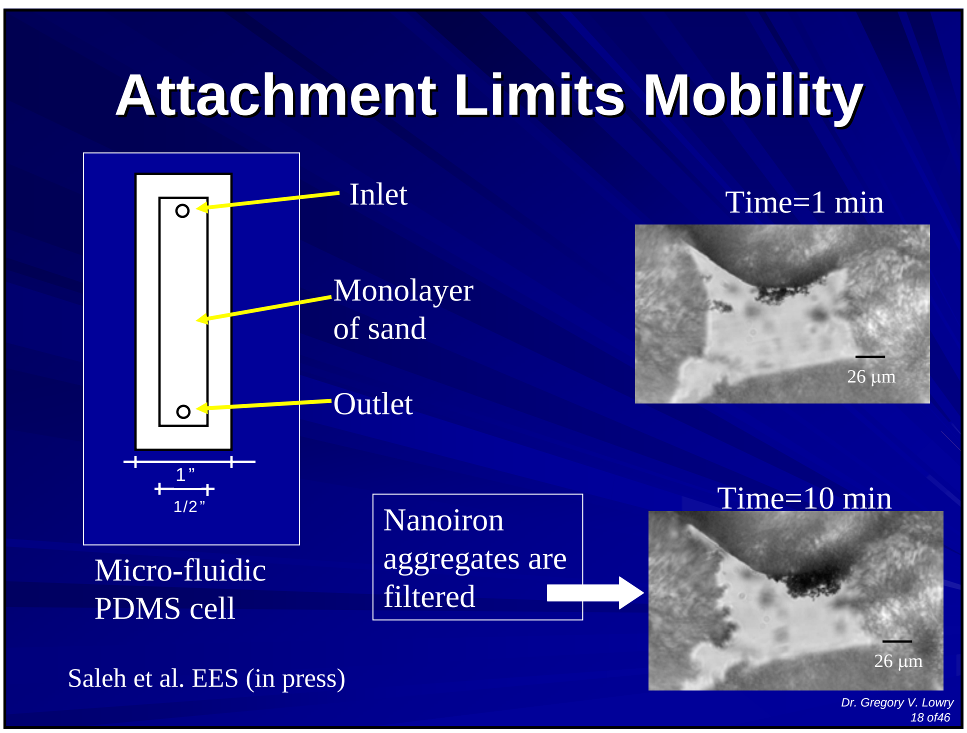
17 of46


Attachment Limits Mobility
Inlet
Monolayer of sand
Outlet
1"
1/2"
Micro-fluidic PDMS cell
Time=1 min
26 µm
Time=10 min
26 µm
Nanoiron aggregates are filtered
Saleh et al. EES (in press)
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18 of46

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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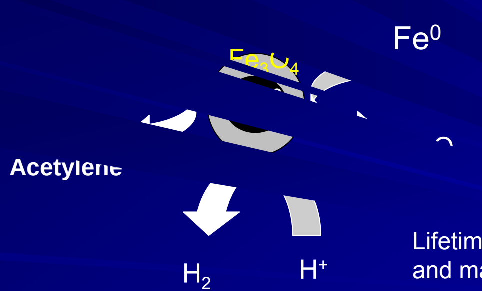
19 of46

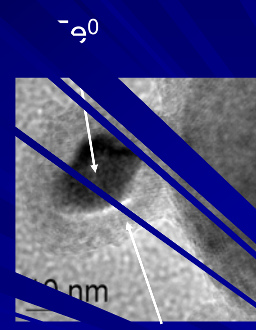
Reactive Fe^0 N...oparticles

...ntaminants ...ced

Nano Fe^0 is oxidized



H+ is reduced



Lifetime depen... ...ding, pH, and maybe microbial activity

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

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

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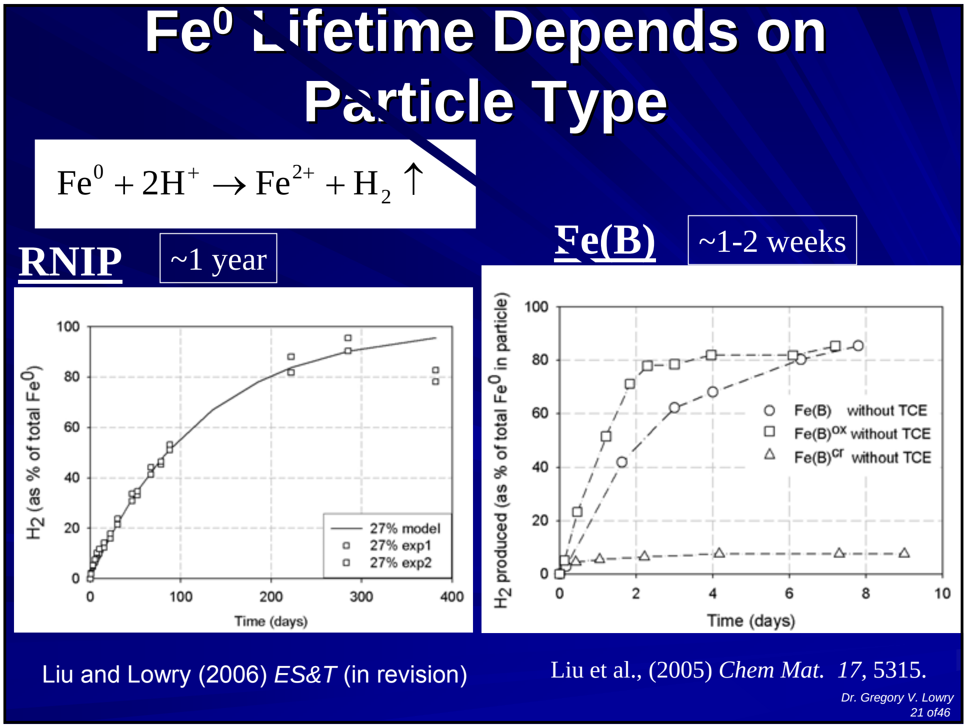
20 of46


Fe0 Lifetime Depends on Particle Type
$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow$
RNIP
~1 year
Fe(B)
~1-2 weeks
H2 (as % of total Fe0)
Time (days)
27% model
27% exp1
27% exp2
H2 produced (as % of total Fe0 in particle)
Fe(B) without TCE
Fe(B)ox without TCE
Fe(B)cr without TCE
Liu and Lowry (2006) ES&T (in revision)
Liu et al., (2005) Chem Mat. 17, 5315.
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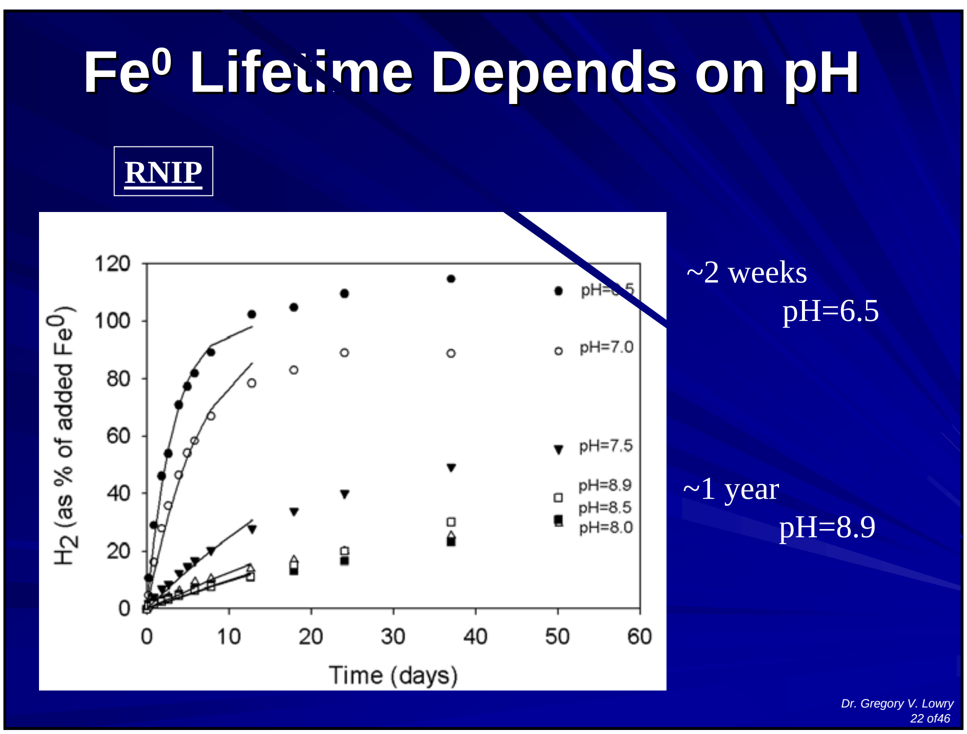
21 of46


Fe0 Lifetime Depends on pH
RNIP
H2 (as % of added Fe0)
Time (days)
pH=7.0
pH=7.5
pH=8.9
pH=8.5
pH=8.0
~2 weeks
pH=6.5
~1 year
pH=8.9
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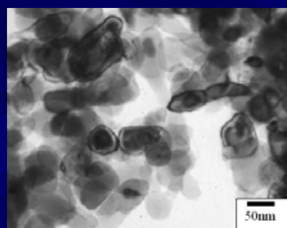
22 of46

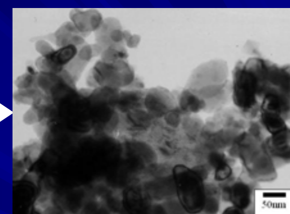
Nanoparticle Fate: Reaction with TCE in Water

RNIP (Fe^0/Fe_3O_4)

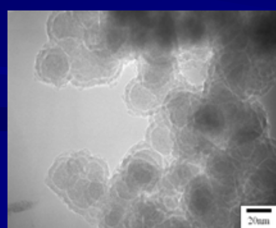


+ TCE/H_2O →

(Fe_3O_4/Fe_2O_3)

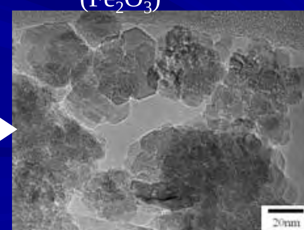


Fe(B) ($Fe^0/FeB_x/Na_2B_4O_7$)



+ TCE/H_2O →

(Fe_2O_3)



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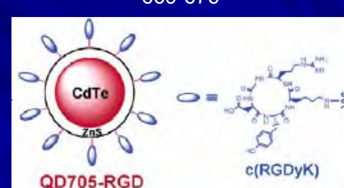
23 of46

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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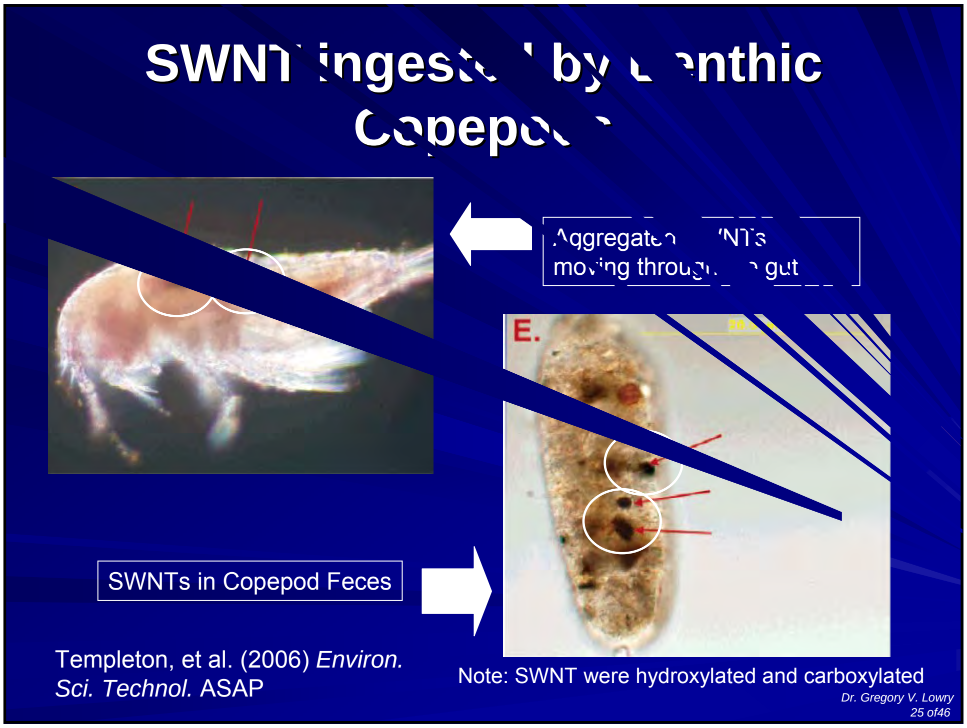
24 of46


SWNT ingest by enthic
Copepo
Aggregate NTs
moving throug gut
E.
SWNTs in Copepod Feces
Templeton, et al. (2006) *Environ. Sci. Technol.* ASAP
Note: SWNT were hydroxylated and carboxylated
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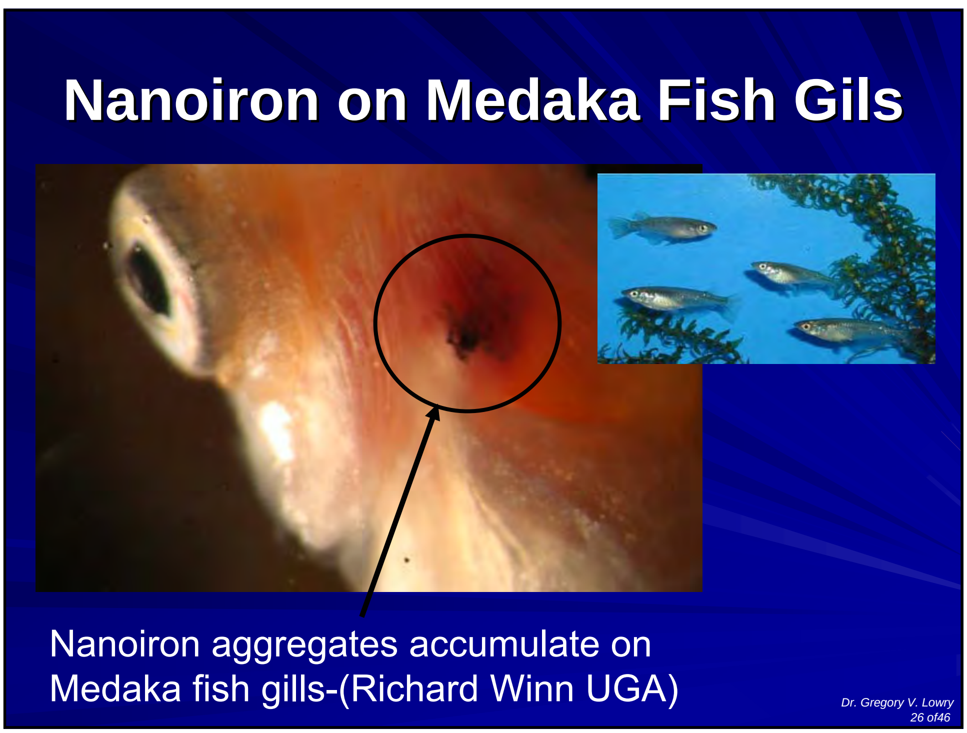
25 of46


Nanoiron on Medaka Fish Gils
Nanoiron aggregates accumulate on
Medaka fish gills-(Richard Winn UGA)
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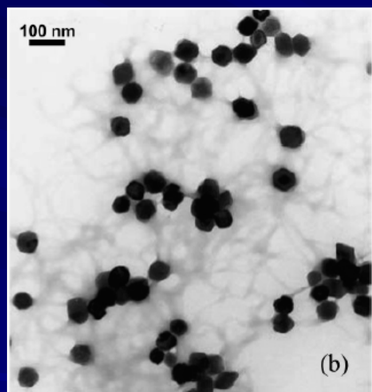
26 of46

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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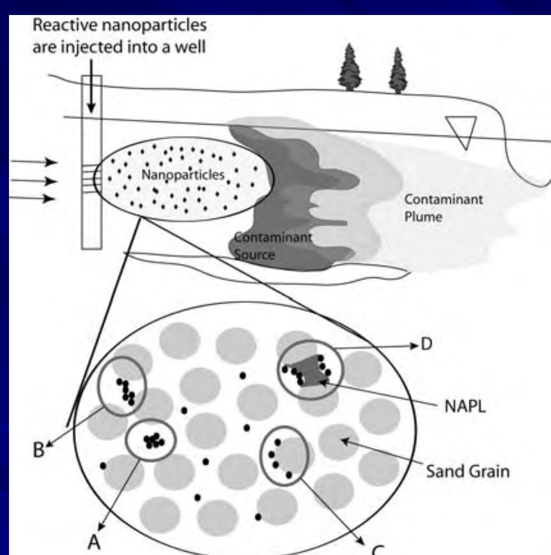
27 of46

Nanomaterial Mobility in Porous Media



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

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

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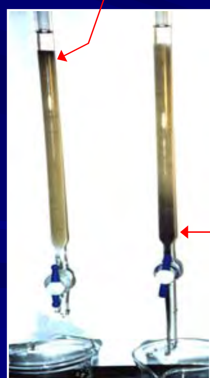
28 of46

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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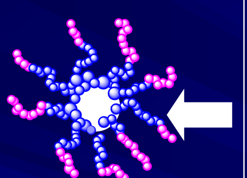
29 of46

Surface Modifiers Increase Mobility



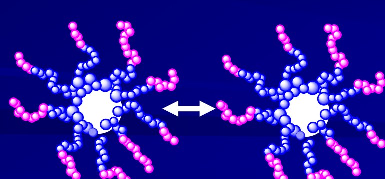
1. Potential Surface Coatings

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

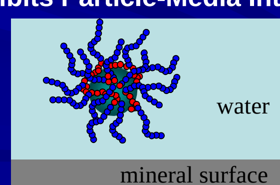
Surfactants (electrostatic)
- ✓ **SDBS**

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

Inhibits Aggregation



Inhibits Particle-Media Interactions



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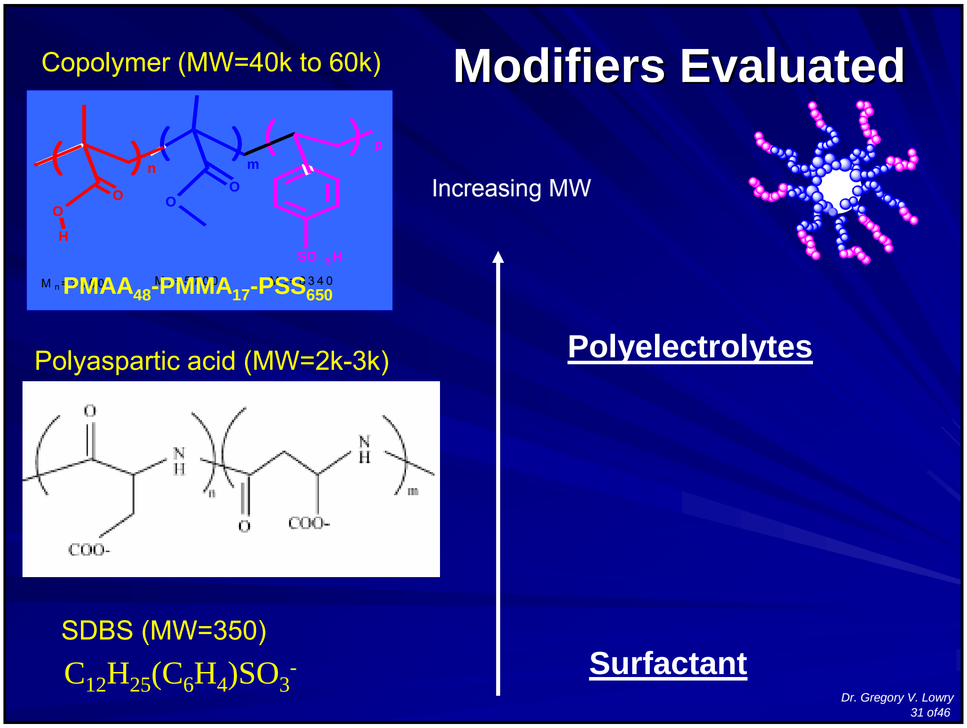
30 of46


Modifiers Evaluated
Copolymer (MW=40k to 60k)
PMAA48-PMMA17-PSS650
Polyaspartic acid (MW=2k-3k)
SDBS (MW=350)
C12H25(C6H4)SO3-
Increasing MW
Polyelectrolytes
Surfactant
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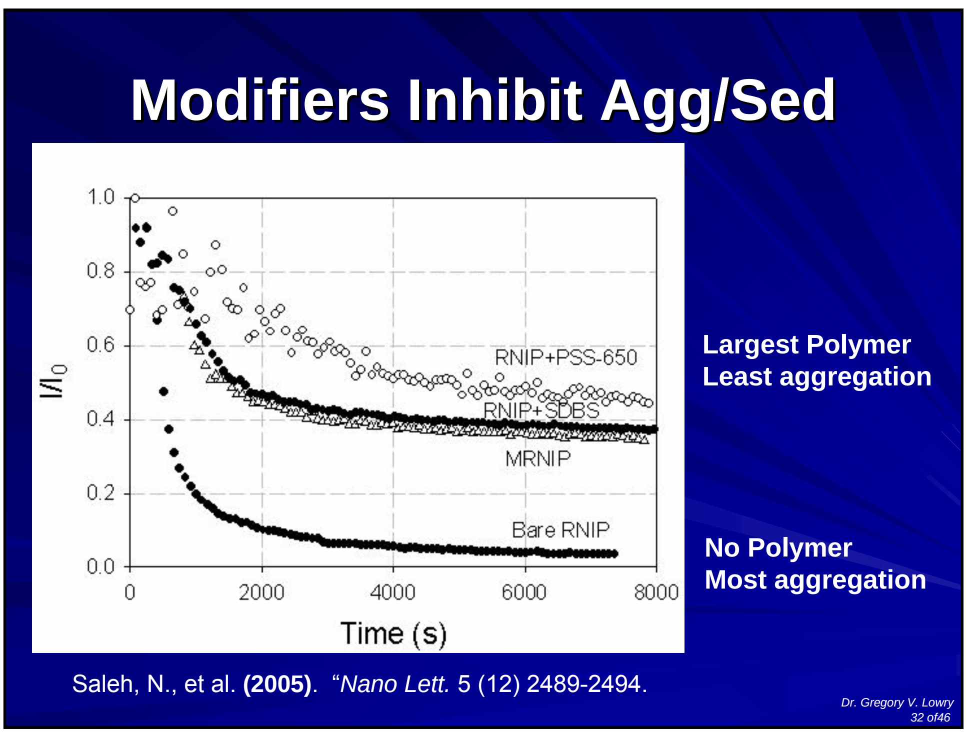
31 of46


Modifiers Inhibit Agg/Sed
I/I0
Time (s)
RNIP+PSS-650
RNIP+SDBS
MRNIP
Bare RNIP
Largest Polymer
Least aggregation
No Polymer
Most aggregation
Saleh, N., et al. (2005). "Nano Lett. 5 (12) 2489-2494.
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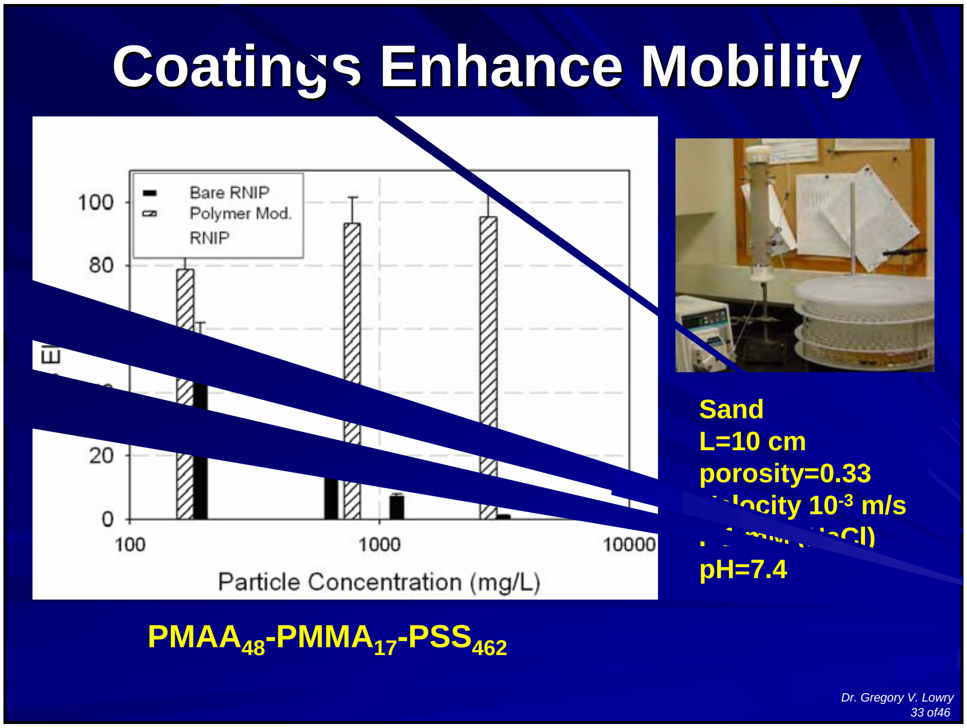
32 of46


Coatings Enhance Mobility
Bare RNIP
Polymer Mod. RNIP
100
80
20
0
100
1000
10000
Particle Concentration (mg/L)
Sand
L=10 cm
porosity=0.33
pH=7.4
PMAA48-PMMA17-PSS462
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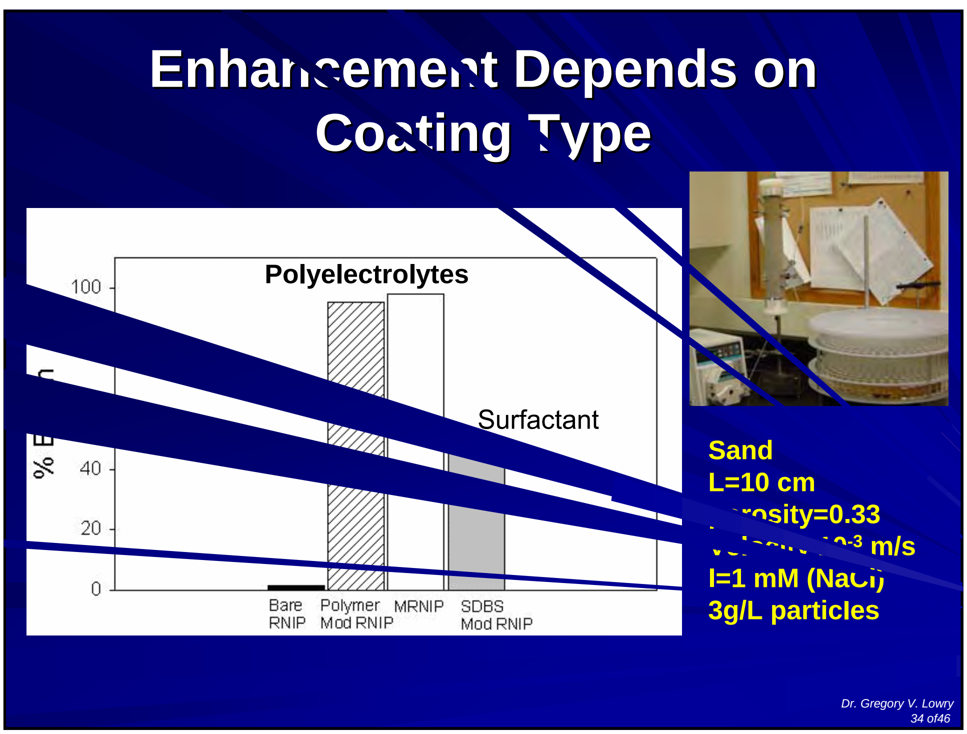
33 of46


Enhancement Depends on Coating Type
Polyelectrolytes
Surfactant
100
40
20
0
Bare RNIP
Polymer Mod RNIP
MRNIP
SDBS Mod RNIP
Sand
L=10 cm
3g/L particles
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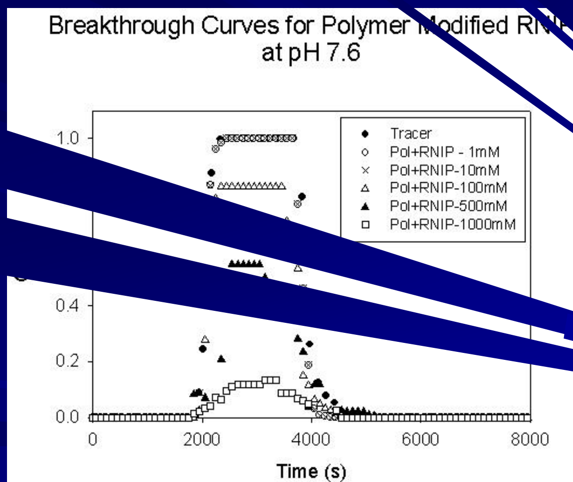
34 of46

Mobility Depends on Ionic Strength and Composition



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

Saleh et al. ES&T (in prep)

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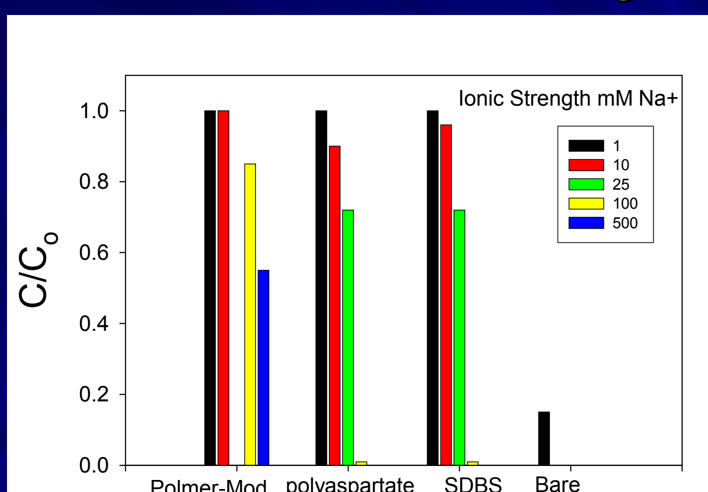
35 of46

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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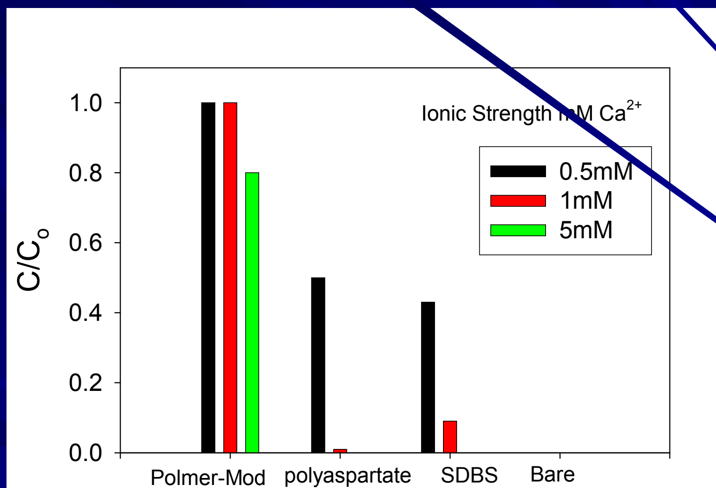
36 of46

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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37 of46

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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38 of46

Estimated Transport Distance for (C/C_o=0.01)

Mod	Na^+ (mM)	Log α (--)	Dist. (m)	Ca^{2+} (mM)	Log α (--)	Dist. (m)
Polymer	10	--	--	0.5	--	--
(MW=60k)	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

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39 of46

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.

Dr. Gregory V. Lowry
40 of46

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

Dr. Gregory V. Lowry
41 of46

Mobility in Surface Waters

- Mobility in surface waters is unknown
  - [illegible] in receiving waters may li[illegible] aggrega[illegible] or promote disaggregation
  - [illegible] surface c[illegible]ings in surface waters is not known
  - Attachm[illegible] other suspended solids is possible and my result in sedimentation and partitioning to solids
  - Photolysis in surface waters is possible

Dr. Gregory V. Lowry
42 of46

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)

Dr. Gregory V. Lowry
43 of46

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

Dr. Gregory V. Lowry
44 of46

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?

Dr. Gregory V. Lowry
45 of46

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Dr. Gregory V. Lowry
46 of46