RISK eLearning
Nanotechnology – Applications and Implications for Superfund

August 16, 2007
Session 6:
“Nanotechnology Fate and Transport of Engineered Nanomaterials”
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Factors Influencing Fate and Transport of Selected Nanomaterials in Water and Land

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Nanomaterials Have Exciting Benefits...

Novel Nanomaterial Strips Contaminants from Waste Streams
Oct. 27, 2004, *Environmental Science and Technology Online* — A unique chemically modified nanoporous ceramic can remove contaminants from all types of waste streams faster and at a significantly lower cost than conventional technologies.

Nanotechnology to Revolutionise Drug Delivery
Mar. 7, 2005, *In-Pharma* — The emergence of nanotechnology is likely to have a significant impact on drug delivery sector, affecting just about every route of administration from oral to injectable.

Color Coded Pathogens Offer Safer Food Formulation
Jun. 15, 2005, *Food Navigator* — New technology could soon make it cheap and easy to identify food pathogens by tagging them with color-coded probes made out of synthetic tree-shaped DNA. These tiny “nanobarcodes” fluoresce under ultraviolet light in a combination of colors that can then be read by a computer scanner.
Nanomaterials Can Be “Terrifying…”
Lipid Peroxidation of Brain, Gill and Liver After 40-Hour Exposure to 1ppm nC$_{60}$

E. Oberdörster, 2004
Examples of Four Types of Nanomaterials

(1) Carbon-based materials: Spherical fullerenes (buckyballs); cylindrical fullerenes (nanotubes). (Smalley, Curl and Kroto, Nobel Prize 1996)

(2) Metal-based materials: Nano-iron and -metal oxides such as TiO₂ for remediation; Quantum dots

(3) Dendrimers: Nano-sized polymers built from branched units.

(4) Composites: Combine nanoparticles with other nanoparticles or with larger, bulk type materials.
Applications and Implications of Environmental Nanomaterials Research

Applications address existing environmental problems, or prevent future problems.

Implications address the interactions of nanomaterials with the environment, and any possible risks that may be posed by nanotechnology, e.g. fate/transport.
Applications: Biosensors

Nanowires (or carbon nanotubes) coated with antibodies bind with proteins that change conductivity (e.g. James Heath, Charles Lieber, Hongjie Dai, Rick Colton)

Basis for new selective, sensitive sensing of microorganisms
Applications: Biosensors

✓ Microorganism identification
  - Virulent (Pathogens)
  - Microbial ecological function-
    e.g. in carbon and nutrient cycling

✓ Nanoscale devices for improvements in current biosensing instruments
Key Research Recommendations of White Paper

The Agency should undertake, collaborate on, and catalyze research to better understand and apply information regarding nanomaterials:

- chemical identification and characterization,
- environmental fate and transport,
- environmental detection and analysis,
- potential releases and human exposures,
- human health effects assessment,
- ecological effects assessment,
- environmental technology applications.
Potential Fate and Transport of Nanomaterials in Water and Air
Oberdörster, Oberdörster and Oberdörster, 2005

[Diagram showing potential fate and transport of nanomaterials in water and air.]
Fullerenes and Carbon Nanotubes

Fullerenes

$C_{60}$

$C_{70}$

Fullerene derivatives

PCBM

$C_{60}F_{15}(C_{6}H_{5})_{2}$

Carbon Nanotubes

Multi-walled Nanotube
Agglomeration

NP → xNP → (NP)x

Sorption/Complexation

NP ↔ NP

Natural organic matter ↔ Sediments
Appearance and Absorption Spectra of Dissolved and Colloidal C₆₀ in Organic Solvents and Water

Fortner et al, 2005
Effects of pH on Particle Size Distribution and Absorption Spectra of C$_{60}$ in Water

Fortner et al., 2005
Impact of C$_{60}$ on Aerobic Respiration of Gram-negative Escherichia coli (A) and Gram-positive Bacillus subtilis (B)

Fortner et al, 2005
Oxygen Consumption in Fullerol/Furfuryl Alcohol Solution Under Visible Light and Ultraviolet Light

Fullerol + O₂ → ¹O₂ + FFA → oxygenated products

Pickering and Wiesner, 2005
Potential Mechanisms for Photoproduction of Reactive Oxygen Species From Fullerenes

\[ C_{60}(OH)_{24}^+ \xrightarrow{h\nu} C_{60}(OH)_{24}^+ \]
\[ C_{60}(OH)_{24}^+ + O_2 \rightarrow C_{60}(OH)_{24}^+ + ^1O_2 \]
\[ C_{60}(OH)_{24} + e^-_{aq} \rightarrow C_{60}(OH)_{24}^+ \]
\[ C_{60}(OH)_{24}^+ + O_2 \rightarrow C_{60}(OH)_{24}^+ + O_2^+ \]

Pickering and Wiesner, 2005
Rates of Oxygen Consumption Photosensitized by Fullerol and Other Colored Organic Compounds

Pickering and Wiesner, 2005
Humic Constituent, Gallic Acid, Enhances Solubility and Fluorescence of C$_{70}$ in Water

Lin et al, 2006
C$_{60}$ Aggregates Exhibit Lower Photosensitizing Efficiency than Non-aggregated C$_{60}$ Derivative

Lee et al., ES&T, 2007
Absorption Spectra and Photosensitizing Capacity of C₆₀ With Humic Substances Present

Lee et al., ES&T, 2007

Reduction in photosensitization rate: due to altered nature of C₆₀ or reaction of ¹O₂ within humic aggregate?
Laser Flash Studies Demonstrate That Metal Oxides (TiO$_2$, ZnO) Photoreact With Humic Substances

Vinodgopal and Kamat, 1994
UV-Induced Production of Reactive Oxygen Species From Humic Substances

ROS = reactive oxygen species

\[ \text{CDOM} \xrightarrow{\text{hv}} \text{CDOM} \xrightarrow{\text{heat}} \text{CDOM} \]

\[ \text{CDOM} + \text{OCDOM} \rightarrow \text{RO}_2 \]

\[ \text{RO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

\[ \text{e}^- + \text{CDOM} \rightarrow \text{RO}_2^- \]

\[ \text{O}_2 \rightarrow \text{O}_2^- \]
Can photoreactions enhance biodegradation of refractory fullerenes?
Conclusions

• Sorption, complexation, aggregation
• Fullerenes are light sensitive, esp. to UV
• Nano-sized particles generally more reactive
• Natural organic matter can strongly affect environmental transformations and transport of nanomaterials in water
Acknowledgements

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- Paul Gilman

This presentation has been approved by the US EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.
Nanoparticle Interactions during wastewater and water treatment

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Arizona State University (Tempe, AZ)

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Outline for presentation

- Nanoparticles as emerging contaminants for water and wastewater systems
- Fate of Nanoparticles in aqueous engineered systems
- Conclusions
Nanoparticles as emerging contaminants

- Nanoparticles are likely to occur in aquatic systems.
- Evidence suggests potential adverse effects from nanoparticles to aquatic ecosystems and mammals. Dose-response relationships are not well developed yet.
- New nanoparticles come into existence weekly.
- Behavior of engineered nanoparticles in water and fate of nanoparticles in natural or engineered systems are being defined.
- Routes of exposure for nanoparticles will be influenced by fate in natural and engineered systems.
Fate of Nanoparticles in Engineered Systems

- Society
- Wastewater Treatment plant
- Land Application of Biosolids
- River or Lake
Fate of Nanoparticles in Engineered Systems

Not Everyone Lives Upstream
Release of Nanoparticles in Sewage Water

- Example: Nano-Ag release from socks
  - Measure silver content of sock
  - Determine how much silver leaches during cleaning
  - Attempt to differentiate silver ions from silver nanoparticles in sock and in wash water

- Sock washing protocol:
  - Socks placed in DI water for 24 hours on orbital mixer (first wash)
  - Socks removed and dried
  - Repeated for subsequent washings

From left to right: 1) Lounge (Sharper Image) 2) Athletic (Sharper Image) 3) XStatic (Fox River) 4) E47 (Arctic Shield) 5) Zensah
## Silver Content of Socks

<table>
<thead>
<tr>
<th>Sock ID</th>
<th>Complete Sock Mass (g)</th>
<th>Silver in Sock (µg Ag)</th>
<th>Silver in Sock (µg Ag / g Sock)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.3</td>
<td>755</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>28.6</td>
<td>61</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>23.0</td>
<td>31,000</td>
<td>1360</td>
</tr>
<tr>
<td>4</td>
<td>58.6</td>
<td>2100</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>24.2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Silver in Sock appears as nanoparticles by SEM (Sock 1)

Pure silver nanoparticles present
Is silver present in wash water from “washing the sock”?

<table>
<thead>
<tr>
<th>Sock ID</th>
<th>Silver in sequential washings (ug Ag in 500 mL wash water)</th>
<th>Total silver leached (ug)</th>
<th>Percent of silver leached from Sock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
<td>#2</td>
<td>#3</td>
</tr>
<tr>
<td>1</td>
<td>150</td>
<td>600</td>
<td>75</td>
</tr>
<tr>
<td>2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3 *</td>
<td>17</td>
<td>34</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

* Highest Silver content (31 mg Ag / 23 g sock)
Is released silver ionic form or nanoparticles?

- Still tough to determine
- Sequential filtration (0.45 / 0.10 / 0.02 um membranes) indicate
  - 60% is less than 0.02 um for Sock #3
  - 40% is clearly non-ionic and aggregated silver nanoparticles
  - For sock #1 only ~20% passes 0.02 um, so >80% is aggregated nano-Ag
  - Control tests with silver ion (Ag+) had 100% passage through 0.02 um
  - These values change over time, suggesting that nano-Ag may slowly be dissolving into ionic Ag+
- SEM confirms nano-Ag presence in wash waters
- We are now using a silver ion selective electrode to differentiate Ag⁺ from nano-Ag
What about release of other engineered Nanoparticles?

Nano ZnO “transparent” sunscreen

Fullerene in “revitalizing” night creams

Nano-silver in Bandages & socks

Nano-sized “additives”

Nano-Aluminum in cosmetics
Fate of Sewage-Nanoparticles during Wastewater Treatment

Common Wastewater Processes:
- Sedimentation
- Activated sludge (biological treatment of organics and nitrogen species)
- Disinfection
Typical process-flow diagram
Will Nanoparticles be present in liquid effluent of biosolids?

- We initiated sampling with the USGS of effluents and biosolids (results by winter hopefully)
- In absence of data, we attempt to simulate where nanoparticles should reside
- Use mass balance relationships on nanoparticles within activated sludge systems
Mass balance on nanoparticles in a WWTP operating at steady state

- Assume sorption to biological matter dominates over biodegradation or volatilization for engineered nanoparticles.
- Mass Balance Equation (mass NPs per time) at steady state:

\[
QC_0 - QC - \left( \frac{KC_e^{1/n}}{\Theta} \right)XV = 0
\]

- Terms are common WWTP parameters: Q = water flowrate, \( C_0 \) & \( C_e \) are inlet and effluent nanoparticle concentrations, \( X \) is biomass concentration, \( \Theta \) is sludge retention time, \( V \) is reactor volume, \( K \) and \( 1/n \) are Freundlich isotherm parameters.
- Estimate \( K \) and \( 1/n \) from batch isotherms.
Let’s consider a different nanoparticle (instead of nano-Ag)

- Fullerenes are in increasing use in many products and could enter sewage systems.
- We solubilized fullerenes into water using sonication, forming quasi-stable aggregates (n-C60).
- N-C60 measured by UV/Vis spectroscopy at >0.1 mg/L, and we developed a LC/MS method for down to 0.1 ug/L.
Batch Sorption Procedure

- nC60 concentration same for all samples
- Vary water quality
- Vary biomass source and dosage

1. Biomass
2. nC60 Solution
3. Nanopure water, buffer
4. Shake 1 hour
5. Filter (GF/F)
6. UV/Vis Absorbance
Representative Data at nC60 initial concentration of 6 mg/L

\[ q = 3.15 \times C_e^{1.40} \]

\[ R^2 = 0.91 \]

Equilibrium nC60 Concentration, \( C_e \) (mg/L)
Mass balance modeling at WWTP on nC60

Input Parameters
- Q = 2.3 mgd
- HRT = 2.3 hours
- θ = 5 days
- C₀ = 6 mg/L
- K = 3.1
- 1/n = 1.4

Results
- Predicted effluent C₆₀ conc = 4.7 mg/L (78%)
- 22% of nC60 would go to biosolids
- Model estimates must be validated with lab and field measurements
Can you measure nC60 in biosolids?

- We developed a toluene extraction protocol that quantitatively recovers nC60 (78±7% recovery)
- Increasing biomass addition reduces concentration in filtrate
- Ongoing biosolids survey underway
Let’s continue looking downstream

Land Application of Biosolids

Society

Wastewater Treatment plant

River or Lake
Natural nanoparticles already exist in our waters

Particle size distributions in fresh waters and sediments

<table>
<thead>
<tr>
<th>Location</th>
<th>Number of Particles of ~10 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>surface waters</td>
<td>$10^{11}$/cm$^3$</td>
</tr>
<tr>
<td>groundwater</td>
<td>$10^{10}$/cm$^3$</td>
</tr>
<tr>
<td>ocean</td>
<td>$10^{9}$/cm$^3$</td>
</tr>
</tbody>
</table>

Buffle and van Leeuwen, Environmental Particles 1, 1992
Ideas first represented by O Melia (2007)
Moving further downstream:
What factors affect nanoparticle removal in WTPs?

River or Lake
Drinking Water Treatment Plant
Society

Raw water from river, lake, etc.
Flocculation
Gravity Sedimentation
Settled solids to waste
Sand filtration
Cleaned for disinfection
Chlorine addition
Finished water to potable water distribution system
What affects removal of Nanoparticles in WTPs?

- Surface charge affects interaction between particles
  - Aggregation of particles
  - Attachment in sand filters

- Size of particle, or size of aggregates
  - Affects mechanism of movement (Brownian vs Advective)
  - Affects rate of settling (Stokes-Einstein Law)
Nanoparticles have surface charge
Example: Effects of salts on aggregation kinetics

\[ \frac{dN}{dt} = -\alpha \frac{4kT}{3\mu} N^2 \]
Example: Dissolved organic matter (DOM) limits hematite aggregation (1 hr mix)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Zeta Potential (mV)</th>
<th>DLS Average Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>DOM = 0</td>
<td>-20.5</td>
<td>500</td>
</tr>
<tr>
<td>DOM = 1 mg/L</td>
<td>-36.5</td>
<td>126</td>
</tr>
<tr>
<td>DOM = 4 mg/L</td>
<td>-34.5</td>
<td>118</td>
</tr>
<tr>
<td>DOM = 10 mg/L</td>
<td>-37.0</td>
<td>102</td>
</tr>
</tbody>
</table>
Example: Effect of Alum coagulant on nanoparticle removal (coag/floc/sedimentation)

0.2 um membrane filtration removes another 20%-40% – but never 100% removal.
Conclusions

- Commercial nanoparticles will enter aquatic systems, where many incidental and natural nanoparticles exist.
- Release rates of nanoparticles from commercial products need to be evaluated, standardized, and characteristics determined.
- Biosorption is probably the key mechanism for nanoparticle removal in WWTPs.
- Nanoparticles will aggregate in water due to the presence of salts, but NOM stabilizes nanoparticles, and affects their removal during sedimentation and filtration.
- Polar (carboxylic functionalized quantum dots) or hydrophilic (silica) non-aggregated nanoparticles are most difficult to remove.
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- Support on two current USEPA projects
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