NIEHS National Institute of Environmental Health Sciences

RISK*e*Learning

Nanotechnology – Applications and Implications for Superfund

sbrp Superfund Basic Research Program — Balancing Scientific Excellence with Research Relevance

August 16, 2007
Session 6:
"Nanotechnology Fate and Transport of Engineered Nanomaterials"
Richard Zepp, US EPA NERL
Paul Westerhoff, Arizona State University

SBRP/NIEHS
William Suk
Heather Henry
Claudia Thompson
Beth Anderson
Kathy Ahlmark
David Balshaw

EPA
Michael Gill
Jayne Michaud
Warren Layne
Marian Olsen
Charles Maurice
Nora Savage
Barbara Walton
Randall Wentsel
Mitch Lasat
Martha Otto

MDB
Maureen Avakian
Larry Whitson
Larry Reed

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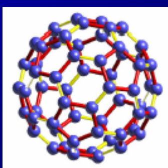
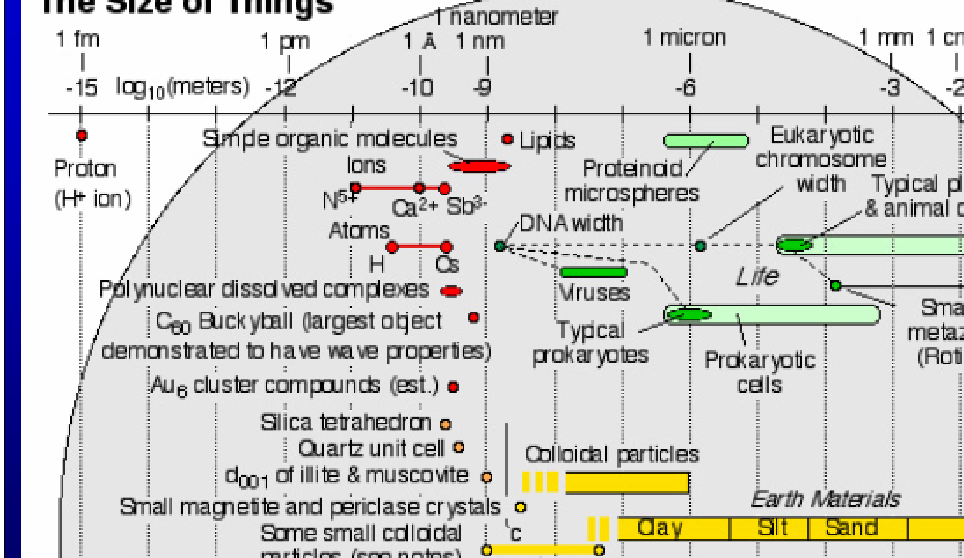
Factors Influencing Fate and Transport of Selected Nanomaterials in Water and Land



C_{60}

Richard Zepp
US EPA
National Exposure Research Laboratory
Ecosystems Research Division
Athens, GA

The Size of Things



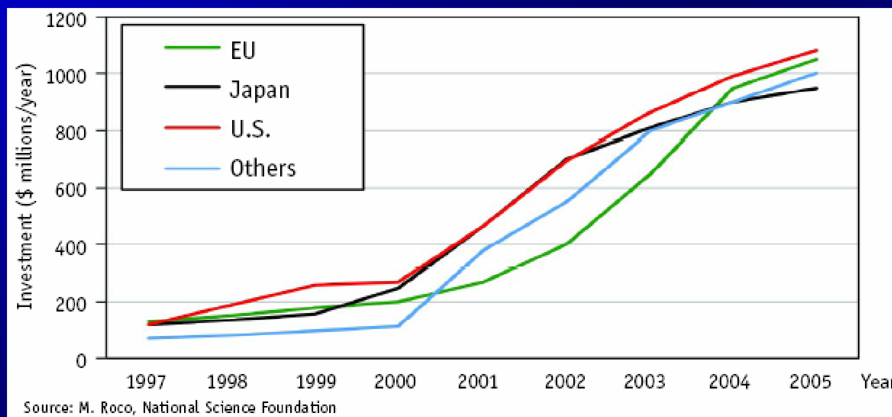
Nanomaterials Have Exciting Benefits...

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.

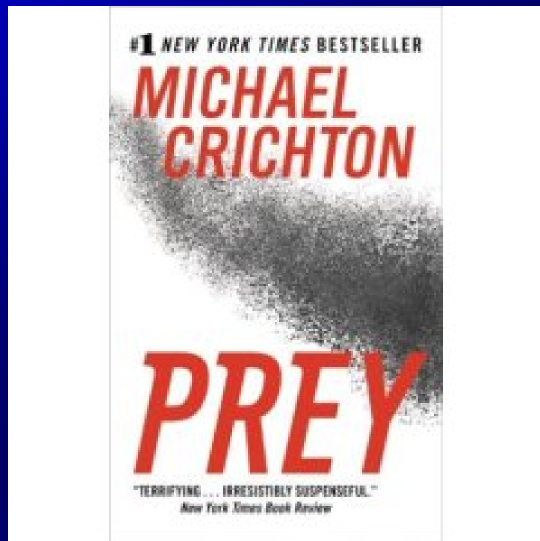
Color Coded Pathogens Offer Safer Food Formulation
Jun. 15, 2005, *Food Navigator* — New technology could soon make it cheap and easy to identify food pathogens by tagging them with color-coded probes made out of synthetic tree-shaped DNA. These tiny “nanobarcodes" fluoresce under ultraviolet light in a combination of colors that can then be read by a computer scanner

Government Investments in Nanotechnology



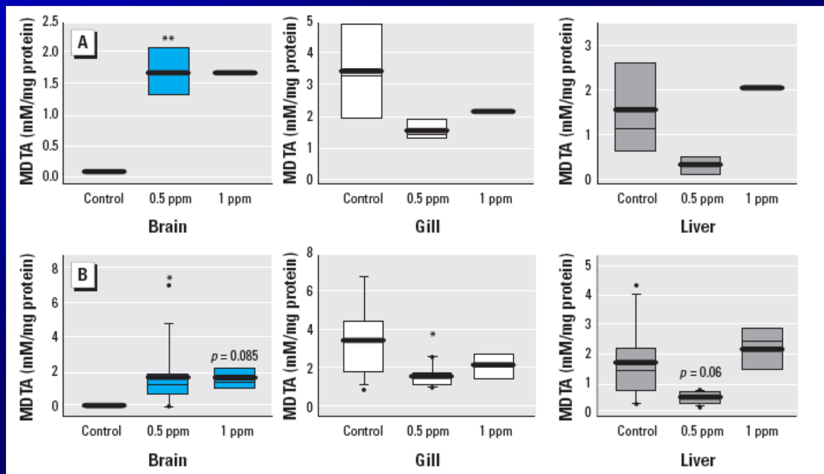
PCAST: NNI at Five Years, 2005

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 TiO_2 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

RESEARCH & DEVELOPMENT

Building a scientific foundation for sound environmental decisions

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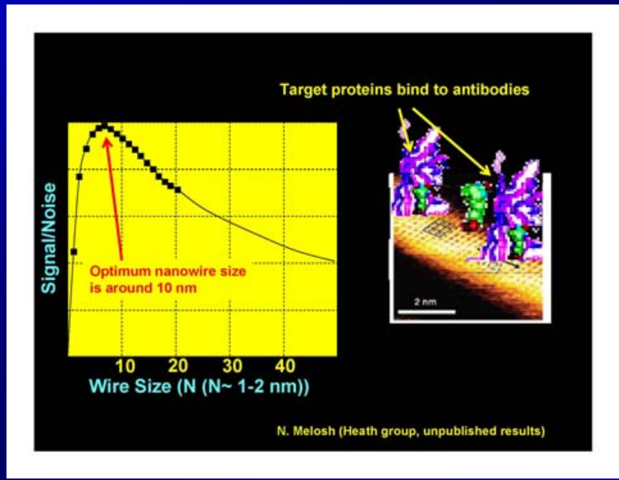
Applications: Biosensors



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

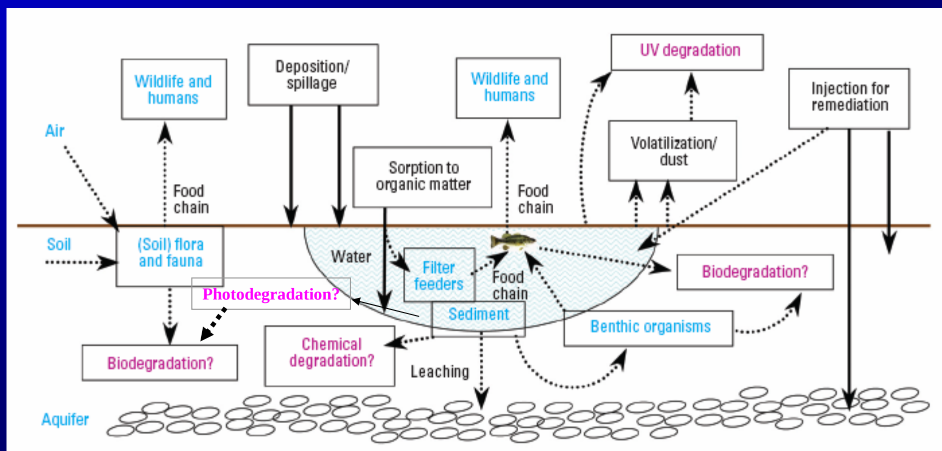
Key Research Recommendations of White Paper

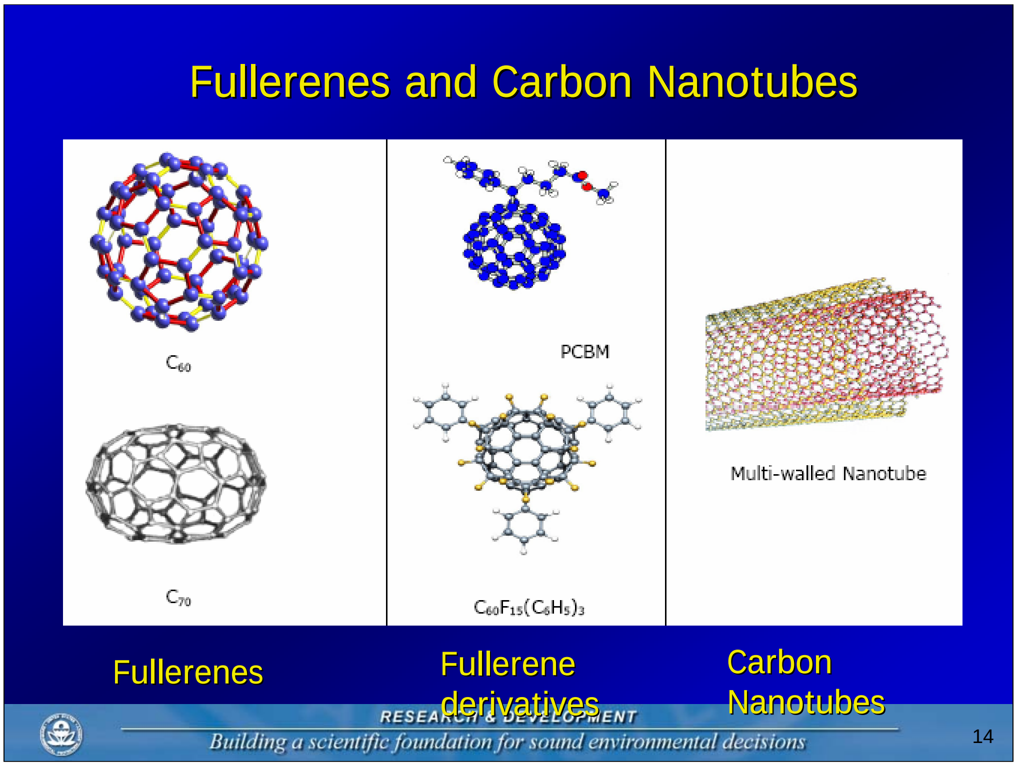
The Agency should undertake, collaborate on, and catalyze research to better understand and apply information regarding nanomaterials:

o chemical identification and characterization,
o environmental fate and transport,
o environmental detection and analysis,
o potential releases and human exposures,
o human health effects assessment,
o ecological effects assessment, and
o environmental technology applications.

Potential Fate and Transport of Nanomaterials in Water and Air

Oberdörster, Oberdörster and Oberdörster, 2005




Fullerenes and Carbon Nanotubes
C_{60}
C_{70}
PCBM
$C_{60}F_{15}(C_6H_5)_3$
Multi-walled Nanotube
Fullerenes
Fullerene derivatives
Carbon Nanotubes
RESEARCH & DEVELOPMENT
Building a scientific foundation for sound environmental decisions
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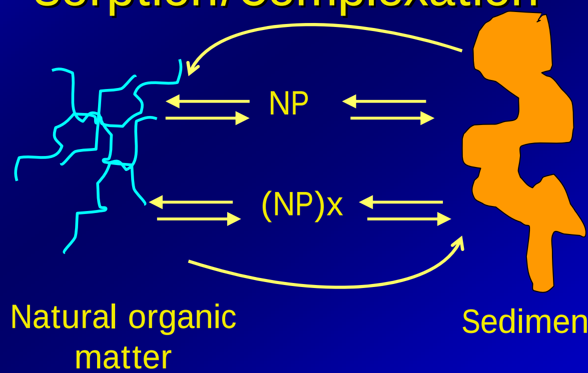
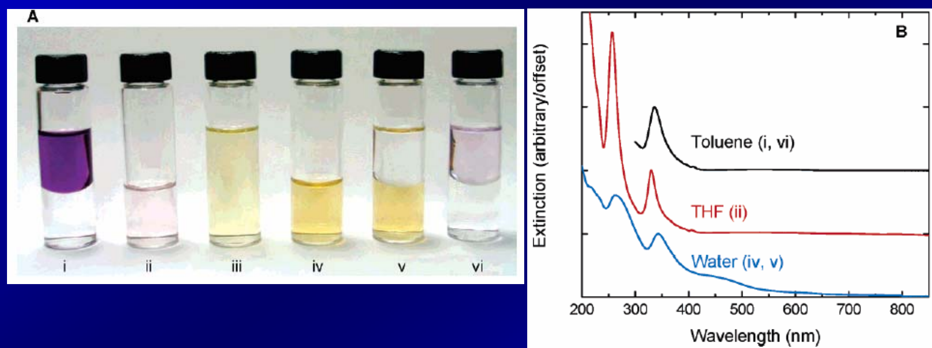
Agglomeration

$$NP \xrightarrow{xNP} (NP)x$$

Sorption/Complexation

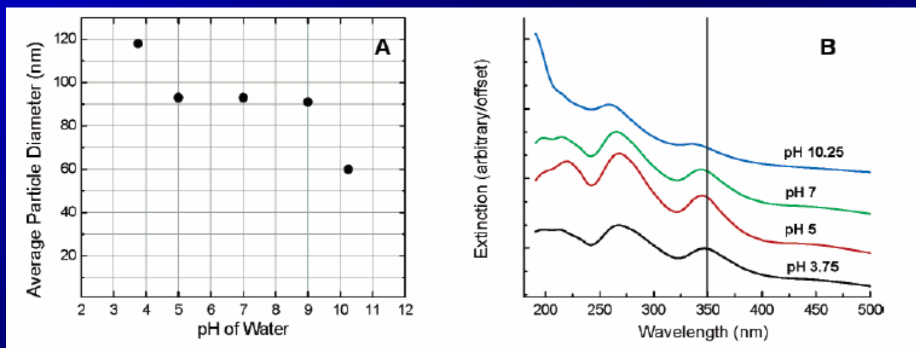


Appearance and Absorption Spectra of Dissolved and Colloidal C_{60} in Organic Solvents and Water



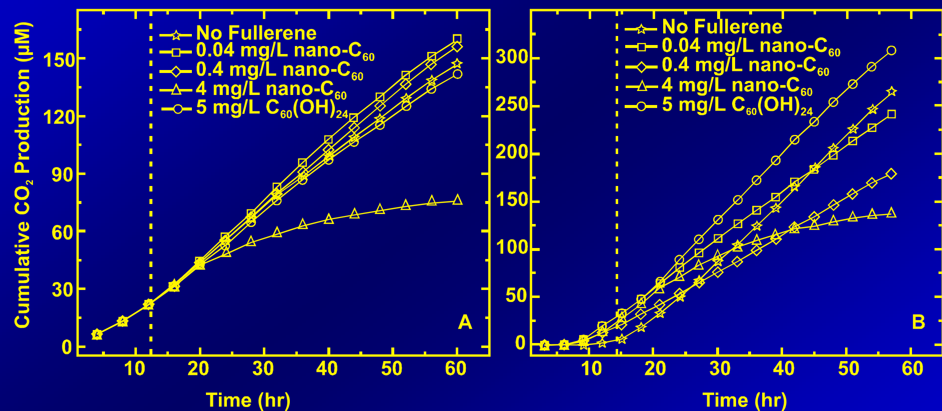
Fortner et al, 2005

Effects of pH on Particle Size Distribution and Absorption Spectra of C_{60} in Water



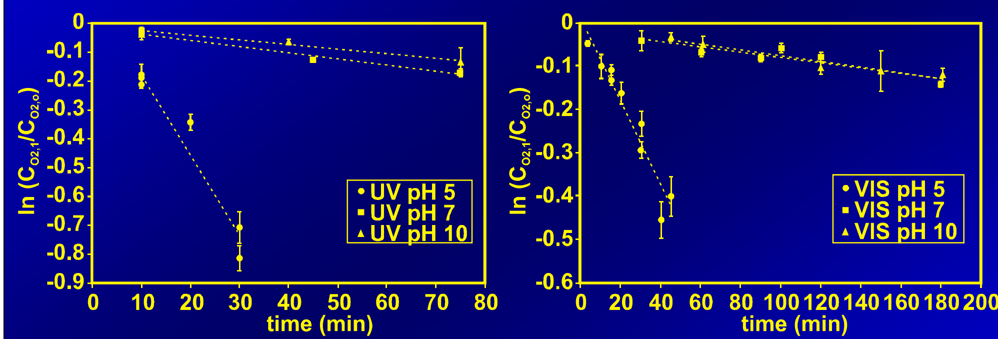
Fortner et al, 2005

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



$$\text{Fullerol} + O_2 \xrightarrow{\text{light}} {}^1O_2$$

$${}^1O_2 + \text{FFA} \longrightarrow \text{oxygenated products}$$

Pickering and Wiesner, 2005

Potential Mechanisms for Photoproduction of Reactive Oxygen Species From Fullerenes

$$C_{60}(OH)_{24} \xrightarrow{\hbar v} C_{60}(OH)_{24}^{+}$$

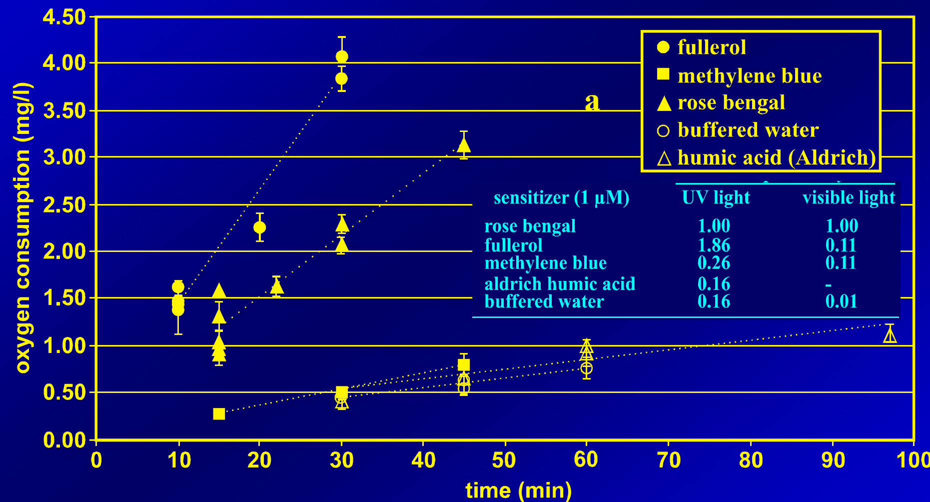
$$C_{60}(OH)_{24}^{+} + O_2 \rightarrow C_{60}(OH)_{24} + {}^{1}O_2$$

$$C_{60}(OH)_{24} + e^{-}_{aq} \rightarrow C_{60}(OH)_{24}^{+-}$$

$$C_{60}(OH)_{24}^{+-} + O_2 \rightarrow C_{60}(OH)_{24} + O_2^{+-}$$

Pickering and Wiesner, 2005

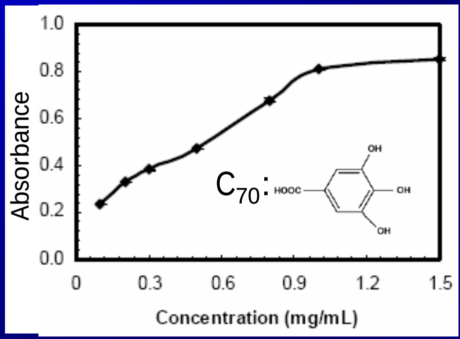
Rates of Oxygen Consumption Photosensitized by Fullerol and Other Colored Organic Compounds

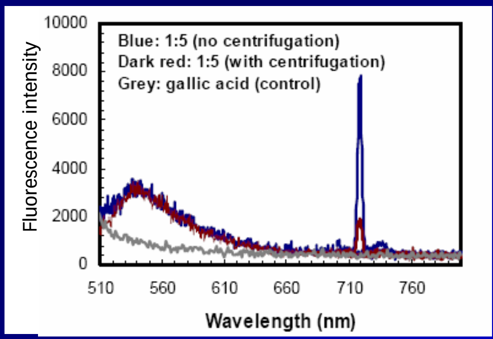


sensitizer (1 µM)	UV light	visible light
rose bengal	1.00	1.00
fullerol	1.86	0.11
methylene blue	0.26	0.11
aldrich humic acid	0.16	-
buffered water	0.16	0.01

Pickering and Wiesner, 2005

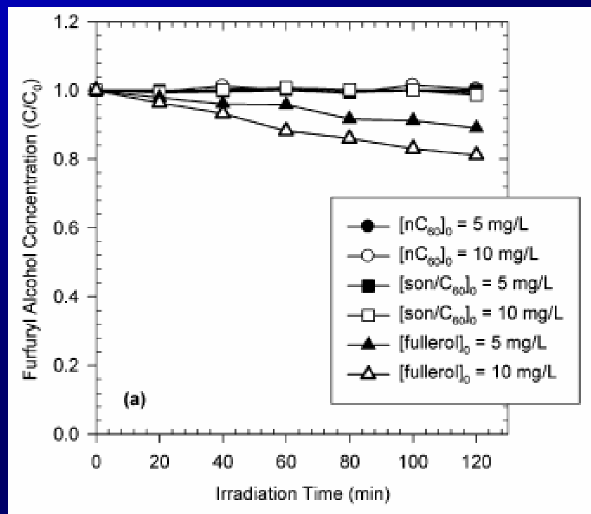
Humic Constituent, Gallic Acid, Enhances Solubility and Fluorescence of C_{70} in Water





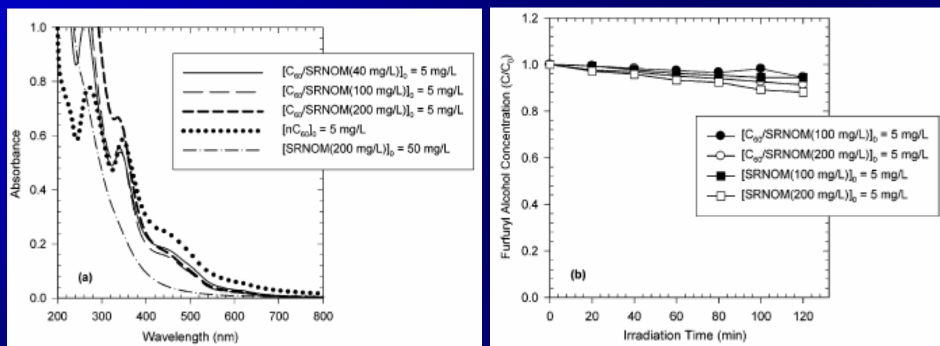
Lin et al, 2006

C_{60} Aggregates Exhibit Lower Photosensitizing Efficiency than Non-aggregated C_{60} Derivative



Lee et al., ES&T, 2007

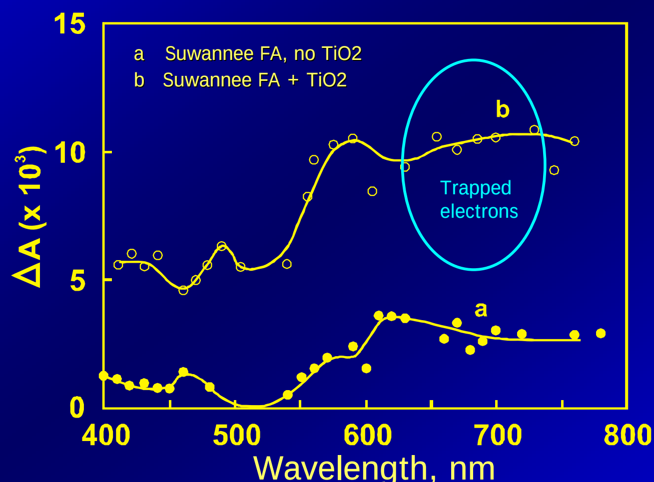
Absorption Spectra and Photosensitizing Capacity of C_{60} With Humic Substances Present



Lee et al., ES&T, 2007

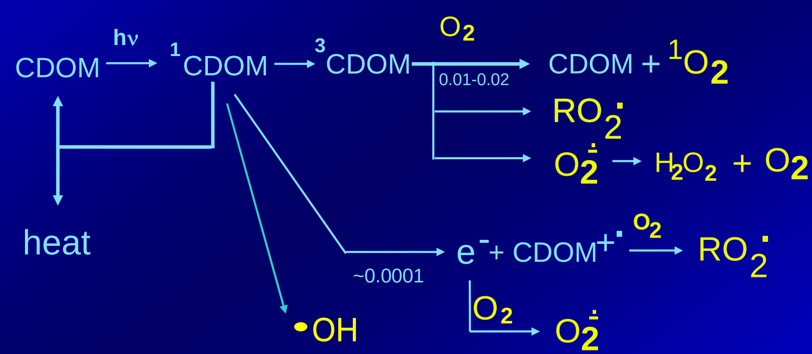
Reduction in photosensitization rate: due to altered nature Of C60 or reaction of $^1O_2$ within humic aggregate?

Laser Flash Studies Demonstrate That Metal Oxides (TiO2,ZnO) Photoreact With Humic Substances



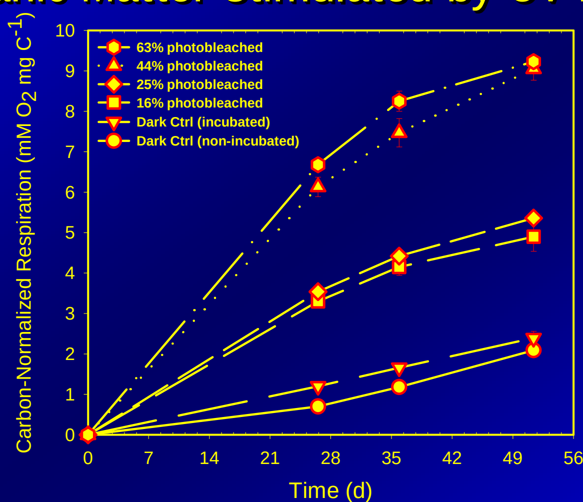
Vinodgopal and Kamat, 1994

UV-Induced Production of Reactive Oxygen Species From Humic Substances



ROS = reactive oxygen species

Microbial Availability (BR) of Refractory Natural Organic Matter Stimulated by UV Exposure



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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- ✓ Barb Walton
- ✓ 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

Paul Westerhoff
Professor
Department of Civil and Environmental Engineering
Arizona State University (Tempe, AZ)

Contributors to this presentation: Troy Benn, Ayla Kiser, Yang Zhang, John Crittenden, Yongsheng Chen

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Outline for presentation

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

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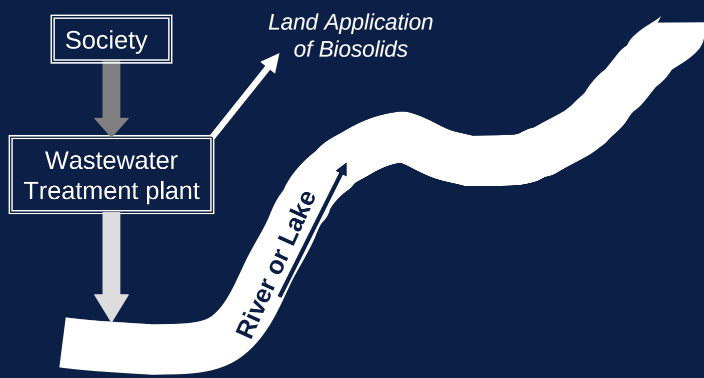
Nanoparticles as emerging contaminants

- 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



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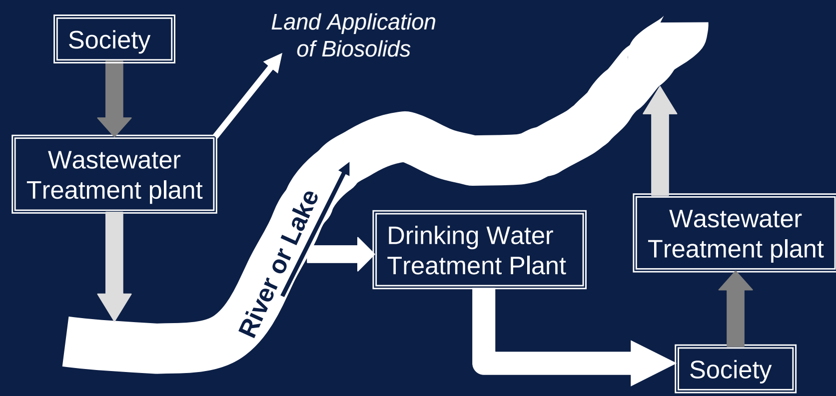
Fate of Nanoparticles in Engineered Systems



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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

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Silver Content of Socks

Sock ID	Complete Sock Mass (g)	Silver in Sock (ug Ag)	Silver in Sock (ug Ag / g Sock)
1	29.3	755	26
2	28.6	61	2.0
3	23.0	31,000	1360
4	58.6	2100	36
5	24.2	0	0

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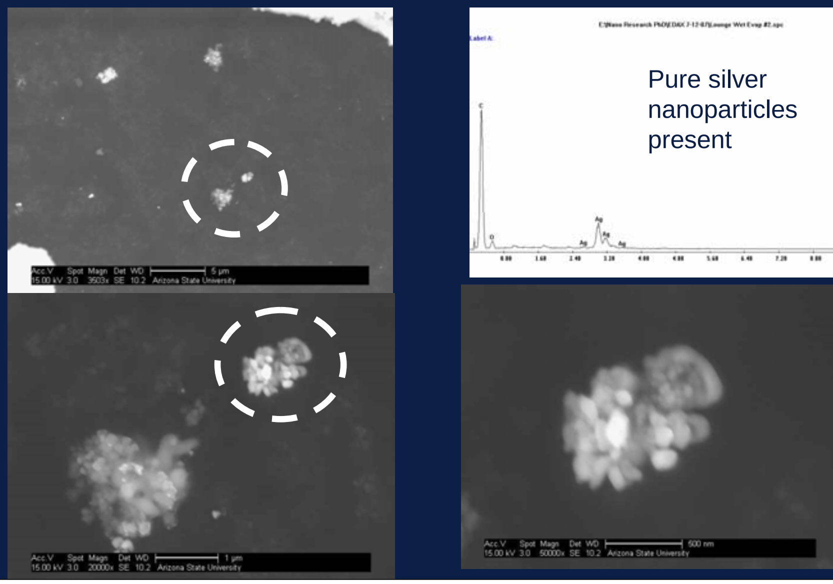
Silver in Sock appears as nanoparticles by SEM (Sock 1)



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

Sock ID	Silver in sequential washings (ug Ag in 500 mL wash water)				Total silver leached (ug)	Percent of silver leached from Sock
	#1	#2	#3	#4		
1	150	600	75	11	836	~100%
2	<1	<1	<1	<1	<1	~0%
3 *	17	34	49	65	165	0.5%
4	<1	<1	<1	<1	<1	~0%
5	<1	<1	<1	<1	<1	~0%

** Highest Silver content (31 mg Ag / 23 g sock)*

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Is released silver ionic form or nanoparticles?

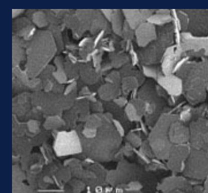
- Still tough to determine
- Sequential filtration (0.45 / 0.10 / 0.02 um membranes) indicate
  - 60% is less than 0.02 um for Sock #3
  - 40% is clearly non-ionic and aggregated silver nanoparticles
  - For sock #1 only ~20% passes 0.02 um, so >80% is aggregated nano-Ag
  - Control tests with silver 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-Aluminum in cosmetics

Nano-sized "additives"

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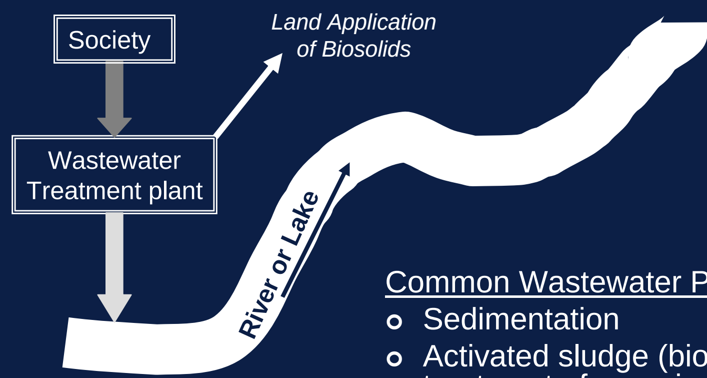
Fate of Sewage-Nanoparticles during Wastewater Treatment



Common Wastewater Processes:

- Sedimentation
- Activated sludge (biological treatment of organics and nitrogen species)
- Disinfection

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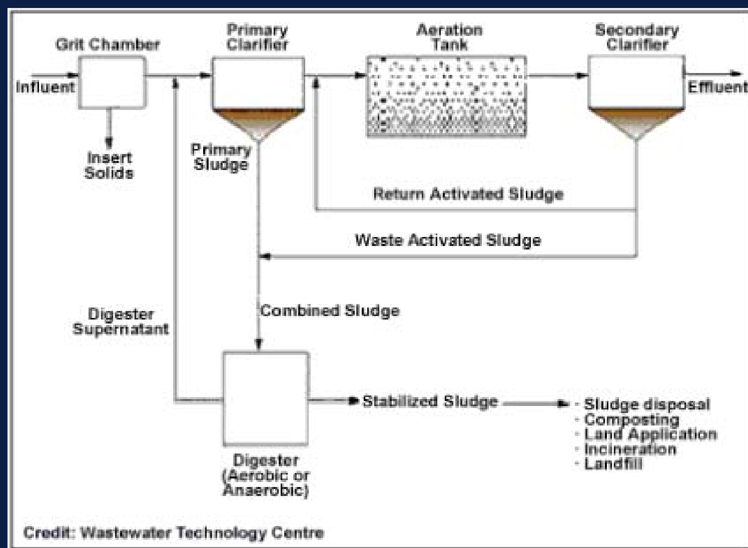
Typical process-flow diagram



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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

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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:

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

- Terms are common WWTP parameters: Q = water flowrate, C_0 & C_e are inlet and effluent nanoparticle concentrations, X is biomass concentration, θ is sludge retention time, V is reactor volume, K and 1/n are Freundlich isotherm parameters
- Estimate K and 1/n from batch isotherms

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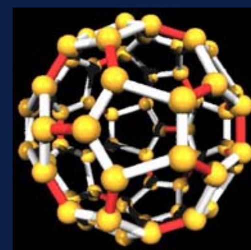
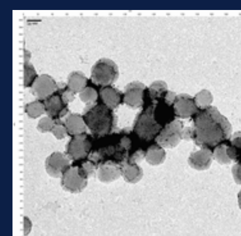
Let’s consider a different nanoparticle (instead of nano-Ag)

- 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





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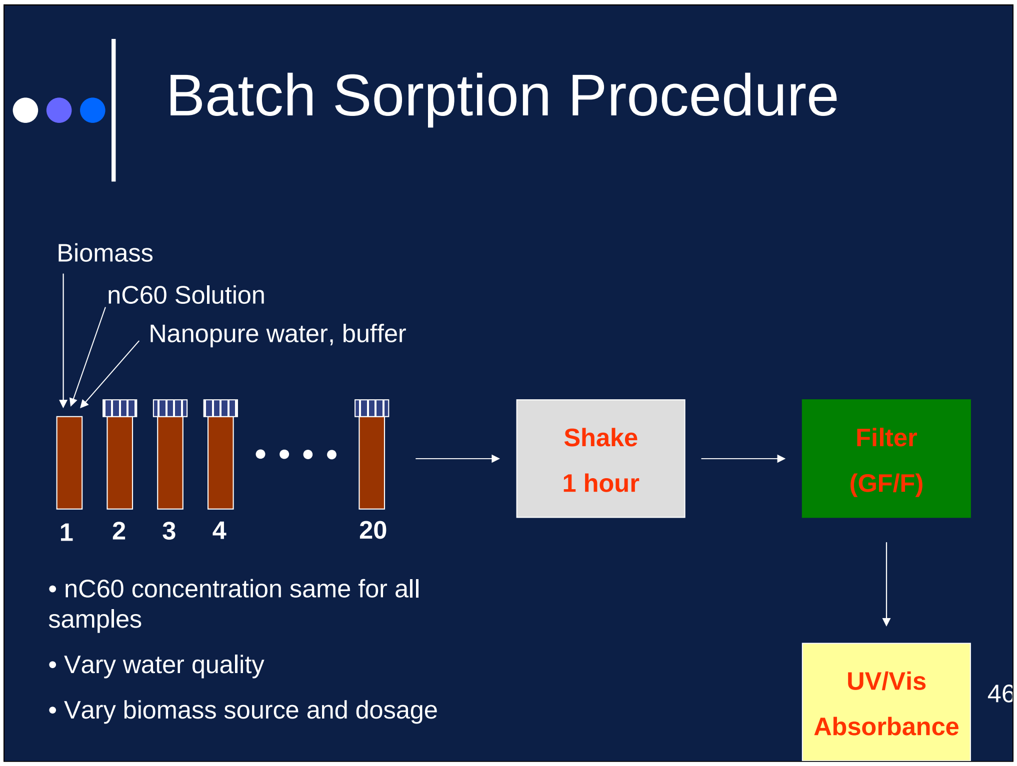
Batch Sorption Procedure
Biomass
nC60 Solution
Nanopure water, buffer
1
2
3
4
20
Shake
1 hour
Filter
(GF/F)
UV/Vis
Absorbance
• nC60 concentration same for all samples
• Vary water quality
• Vary biomass source and dosage
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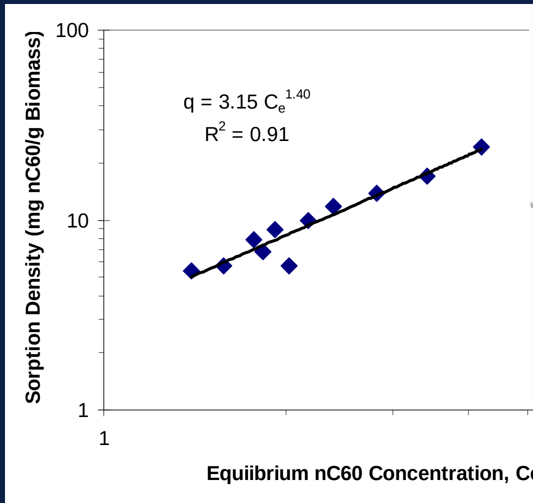
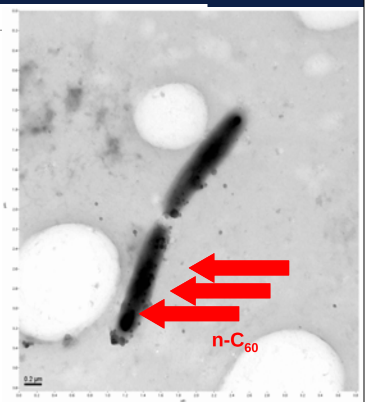
Representative Data at nC60 initial concentration of 6 mg/L





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Mass balance modeling at WWTP on nC60

<u>Input Parameters</u>

- Q = 2.3 mgd
- HRT = 2.3 hours
- θ = 5 days
- C_0 = 6 mg/L
- K = 3.1
- 1/n = 1.4

<u>Results</u>

- 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

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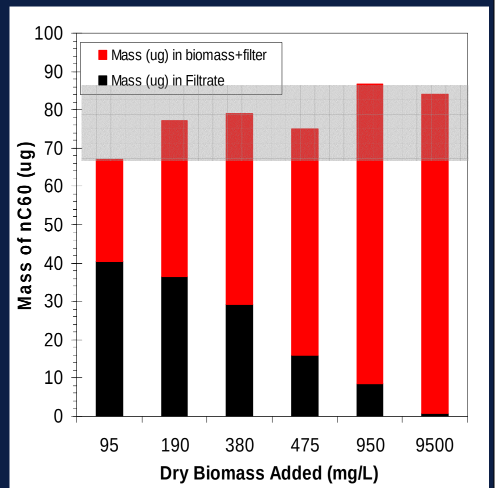
Can you measure nC60 in biosolids?

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



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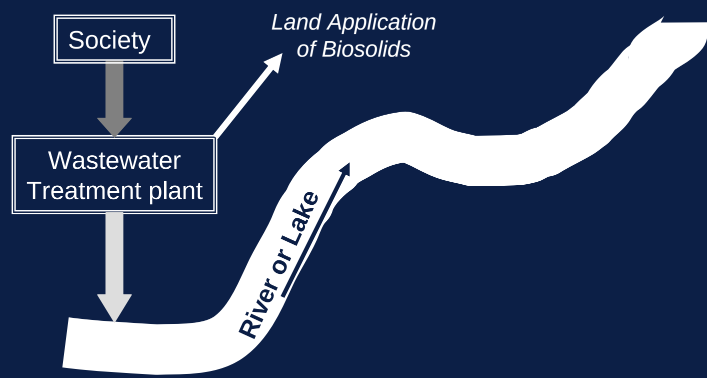
Let’s continue looking downstream



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Natural nanoparticles already exist in our waters

Particle size distributions in fresh waters and sediments

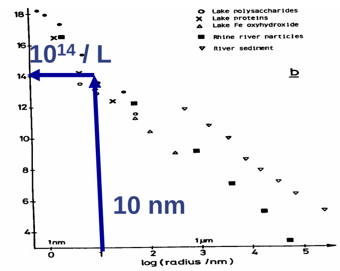

Figure 2. Example of size distributions of important aquatic particles. a–Size distribution, based on particle mass, of the Rhine river particles in Netherlands (same data as ■ in Figure b-) b–Size distributions of various types of particles, based on particle number. Results based on fractionation by filtration; particle numbers and proportions of particle mass are values obtained for each filtration fractions.

Location	*Number of Particles of ~ 10 nm*
surface waters	$10^{11}/cm^3$
groundwater	$10^{10}/cm^3$
ocean	$10^{9}/cm^3$

Buffle and van Leeuwen, Environmental Particles 1, 1992
Ideas first represented by O Melia (2007)

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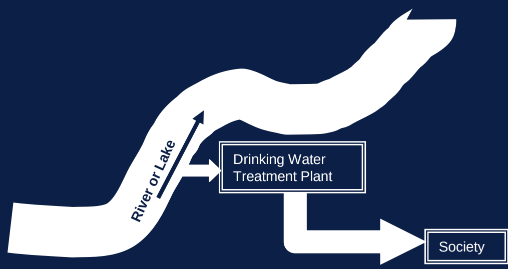
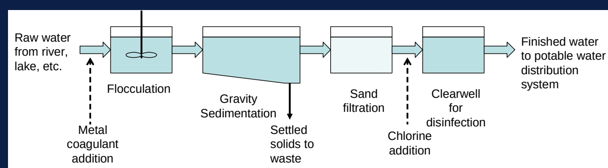
Moving further downstream: What factors affect nanoparticle removal in WTPs?





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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)

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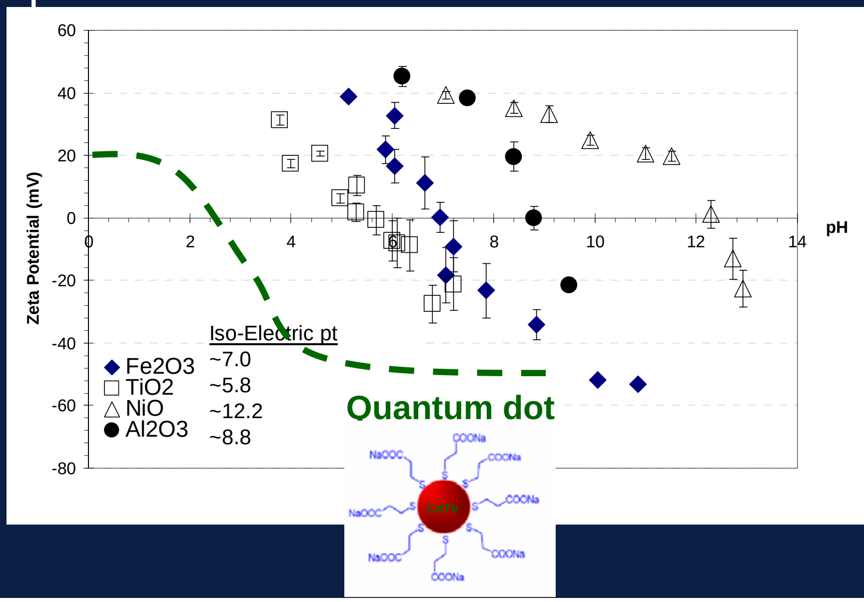
Nanoparticles have surface charge



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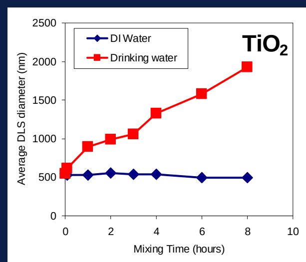
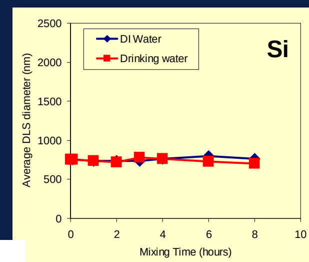
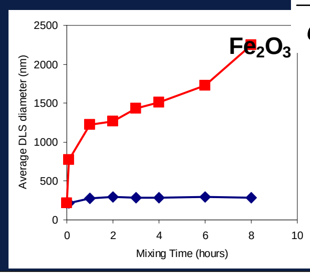
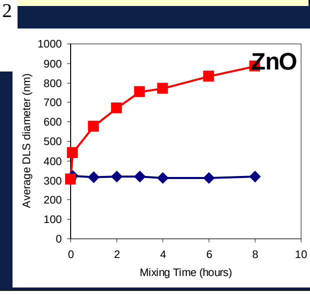
Example: Effects of salts on aggregation kinetics





$$\frac{dN}{dt} = -\alpha \frac{4kT}{3\mu} N^2$$





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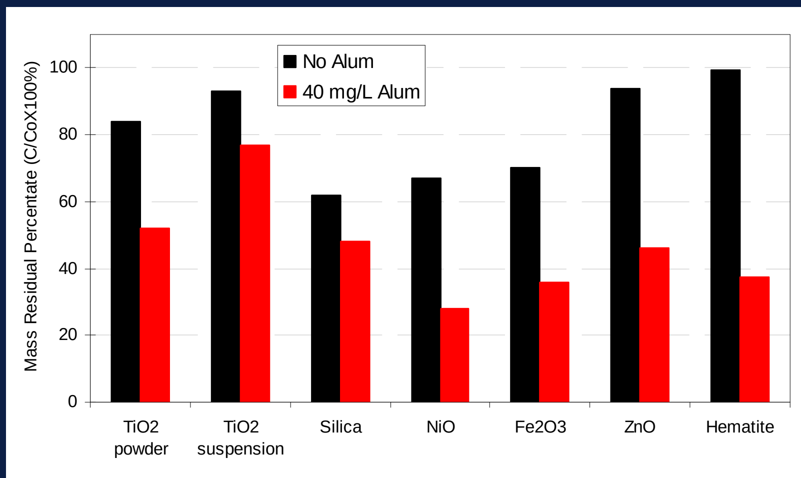
Example: Dissolved organic matter (DOM) limits hematite aggregation (1 hr mix)

Condition	Zeta Potential (mV)	DLS Average Size (nm)
Initial		100
DOM = 0	-20.5	500
DOM = 1 mg/L	-36.5	126
DOM = 4 mg/L	-34.5	118
DOM = 10 mg/L	-37.0	102

Example: Effect of Alum coagulant on nanoparticle removal (coag/floc/sedimentation)



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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 evaluated, standardized and characteristics determined
- Biosorption is probably key mechanism for nanoparticle removal in WWTPs
- Nanoparticles will aggregate in water due to the presence of salts, but NOM stabilizes nanoparticles, and affect 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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