US EPA ARCHIVE DOCUMENT

Nanotechnology and the Environment

OSWER Conference
July 12-13, Washington DC

Center for Biological and Environmental Nanotechnology

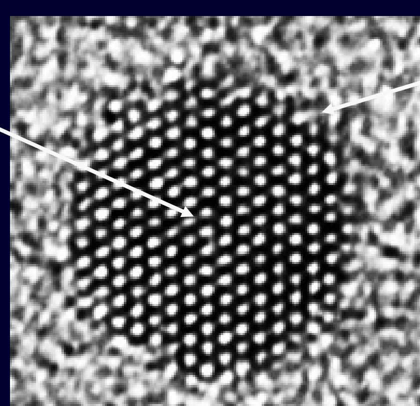
Dr. Vicki Colvin
Director, CBEN
Professor of Chemistry
Rice University

Small is Beautiful

Highly crystalline

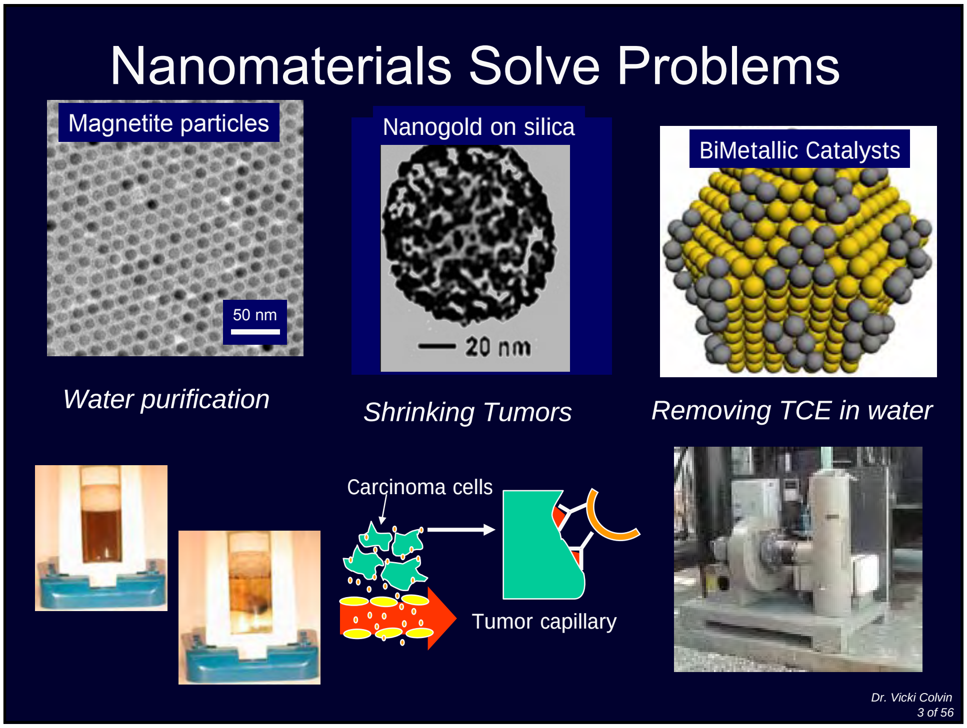
Huge surface areas

C-sixty
1nm



Cadmium Selenide nanocrystal
6 nm

Lysozyme
3 nm


Nanomaterials Solve Problems
Magnetite particles
50 nm
Nanogold on silica
20 nm
BiMetallic Catalysts
Water purification
Shrinking Tumors
Removing TCE in water
Carcinoma cells
Tumor capillary
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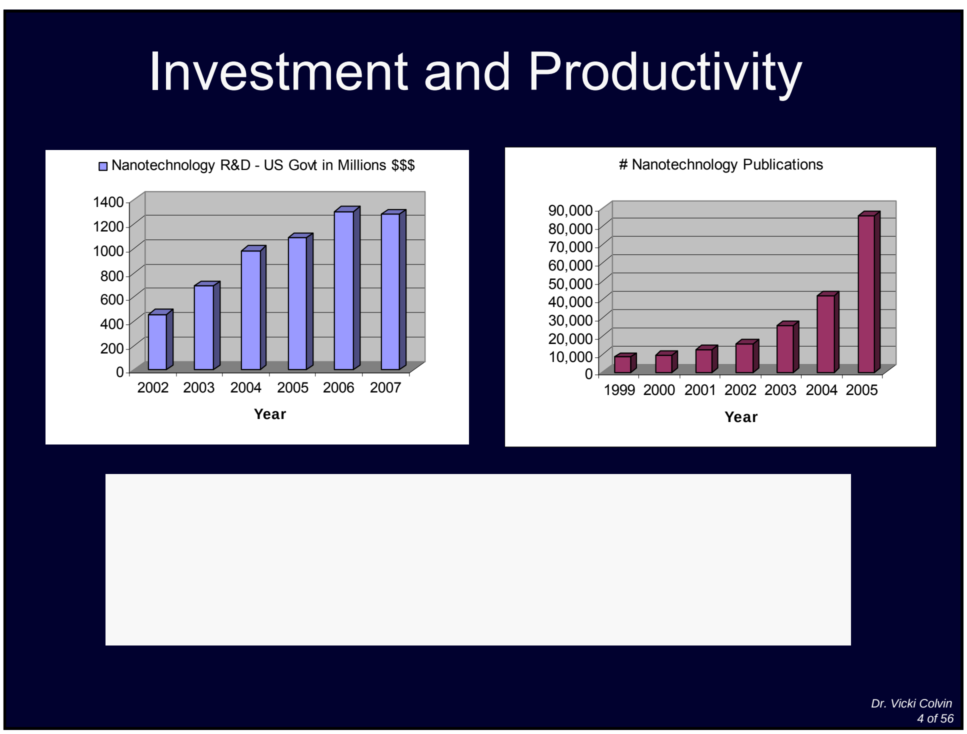
Investment and Productivity
Nanotechnology R&D - US Govt in Millions $$$
1400
1200
1000
800
600
400
200
0
2002 2003 2004 2005 2006 2007
Year
Nanotechnology Publications
90,000
80,000
70,000
60,000
50,000
40,000
30,000
20,000
10,000
0
1999 2000 2001 2002 2003 2004 2005
Year
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Nanotechnology: It's Here

Product	"Nano Inside"	Value Added
	Active Ingredient: Nanoscopic TiO_2/ZnO	Transparency
	Lined with Ceramic Nanoparticles	Gas Impermeability
	Embedded with "Nano Whiskers"	Stain- and Wrinkle-Resistance

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From "Wow" to "Yuck"?

- DDT cured malaria → Endangered birds
- Pesticides improved crop yields → Toxic to animals
- Refrigerants made houses cool → Lead to ozone hole
- Asbestos improved insulation → Liability expenses

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Today's Talk

Benefits

Risks

1. Applications of nanomaterials in water treatment
   Example: Nanosized magnetite for arsenic removal

2. Is size dangerous? Implications of nanotechnology

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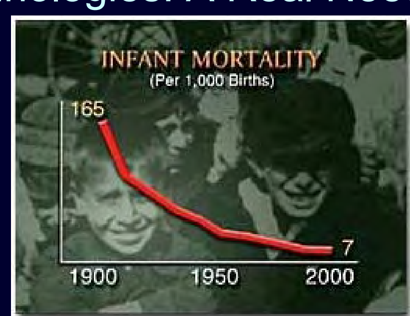
Water Treatment Technologies: A Real Need



- Waterborne illnesses major cause of death
- Increasing contamination in water
- Population growth increasing demand

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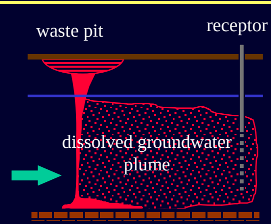
Nanomaterials in Water Treatment



J. Zhang, LeHigh University

Small size provides reactive surface

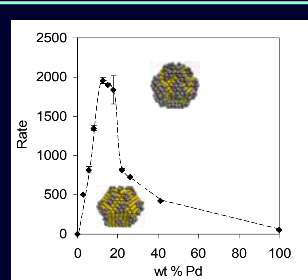
↓

100-fold improvement in TCE removal

Small size provides high surface area

↓

In-situ remediation of contaminated wells



M. Wong, Rice University

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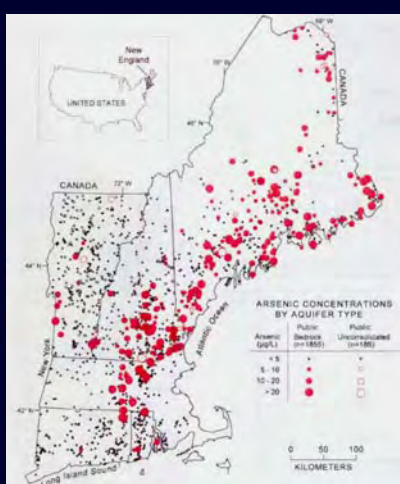
Arsenic in Drinking Water



Ayotte et al, Envi. Sci. Tech. 2003 37, p.2075

- Arsenic in water linked to cancer
- EPA standards: 50 ug/L to 10 ug/L
- Natural and anthropogenic sources
- Enormous interest in removal
  - Plants (phytofiltration)
  - Muds and sediments
  - Zero valent iron – in-situ
  - Mine tailings (e.g. iron oxides)

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Existing Sorbents for Arsenic Removal

" Our two year study showed that none of the (18) Arsenic Removal Plants could maintain arsenic in … water … below the WHO guidelines …."
- Hossain *et al* in ES&T 2005, p. 4300

Material	Sorbent (kg) / month	1 gram treats ____ L water	Waste to dispose of kg (1 yr)	Backwash frequency (day)
Alumina + Metal Oxide	0.24	3.8	2.88	14
Red Mud [As(III)]	360.7	0.002	4328.1	Periodic
Ion Exchange	No Removal of Toxic As(III)			~ 3

For a family of four, using 900 L water/month, at 500 ppb As levels (7.9 pH)

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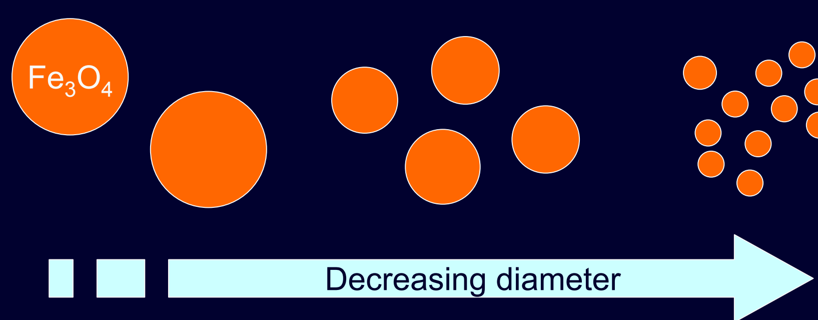
Nanomagnets: Two Advantages



1. Increased surface area for arsenic sorption

2. Enhanced magnetic susceptibilities improve separations

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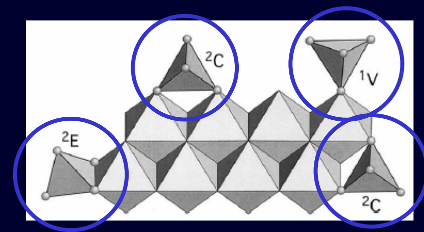
Arsenic sorption onto iron oxides

- *Strong and specific sorption*
- *Chemical transformation*
- *Subjected to interferences*
  - *Silicate and phosphates*
  - *Humic acids*



Models for surface interactions*

Are Nanoscale iron oxides are good candidates for sorbents?

MASON TOMSON, AMY KAN, SUJIN YEAN

* D. M. Sherman, S. R. Randall Geochimica et Cosmochimica v. 67 no. 22 p. 4223

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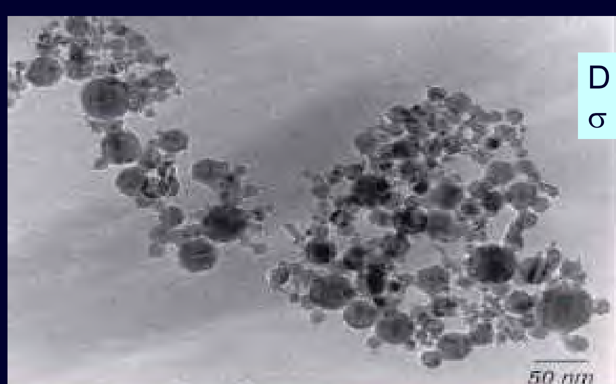
Commercial nanoscale iron oxides



D = 25 nm
σ ~ 35%

http://www.kemcointernational.com/IronOxide.htm

As particle size gets smaller sorptive area increases with R^2

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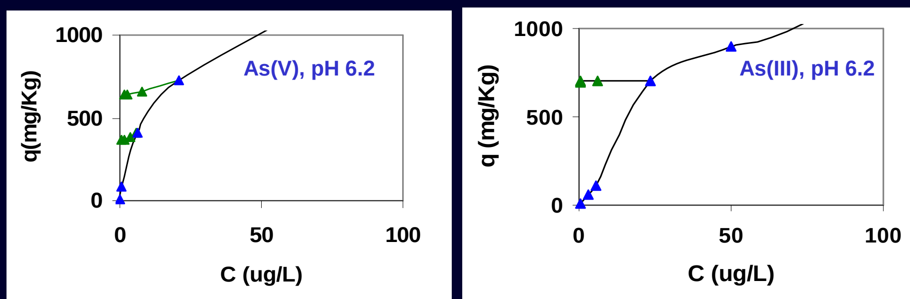
Sorption of Arsenic Onto Magnetite



- 20 nm Magnetite can sorb both As(V) and As(III)
- Sorption capacities (▲) of .1 % (w/w)
- Arsenic is irreversibly sorbed (▲) stable in storage

MASON TOMSON, AMY KAN – Rice University

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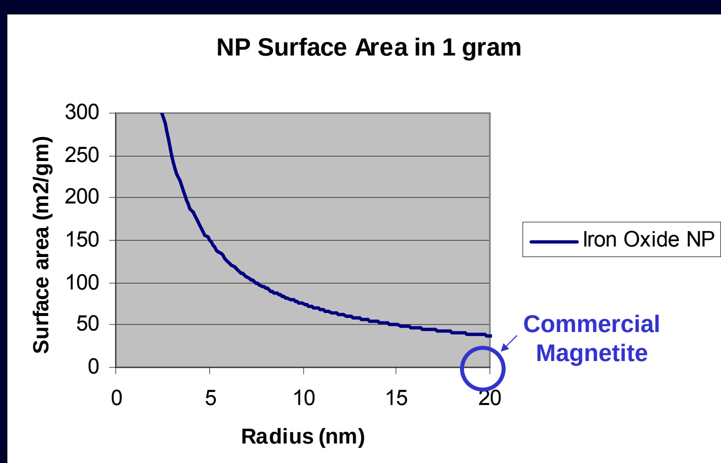
Size dependence: Surface Area



Surface area in 1 gram ~ $4 \pi r^2 / (4/3 \pi r^3 \cdot \text{density})$

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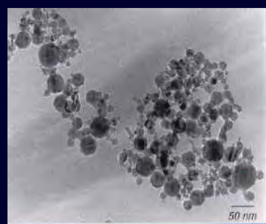
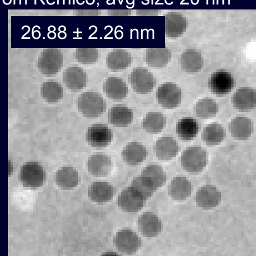
Synthesis of monodisperse nano-Fe_3O_4

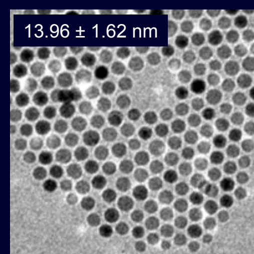


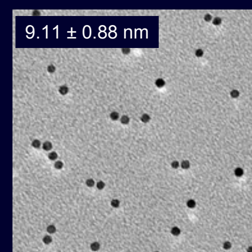
From Kemico, avg size 20 nm

Commercial nano-oxides have problems

- Agglomerated → poor magnetic separation
- Larger nanoparticles → lower sorption
- Bad size distribution → no optimization







W. Yu, V. L. Colvin, Chem. Comm. (2004)

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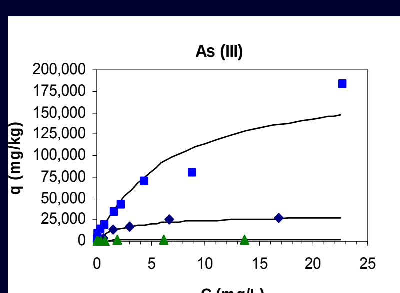
Nanomagnets: Large Sorption Capacity

Volume of water treatable by 1 Kg magnetite



Particle Size (nm)		Volume of Water (L)
12	As(III)	2,283
20	As(III)	594
300	As(III)	21
12	As(V)	1,435
20	As(V)	1,145
300	As(V)	150

Remaining Challenge: Nanoparticles are difficult to remove

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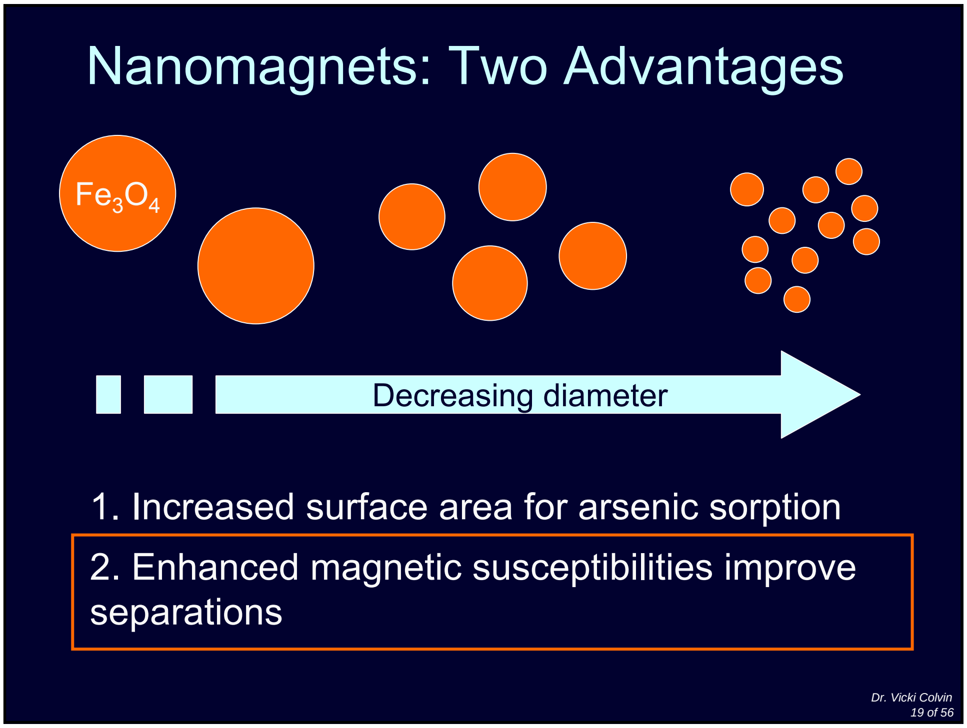
Nanomagnets: Two Advantages
Fe3O4
Decreasing diameter
1. Increased surface area for arsenic sorption
2. Enhanced magnetic susceptibilities improve separations
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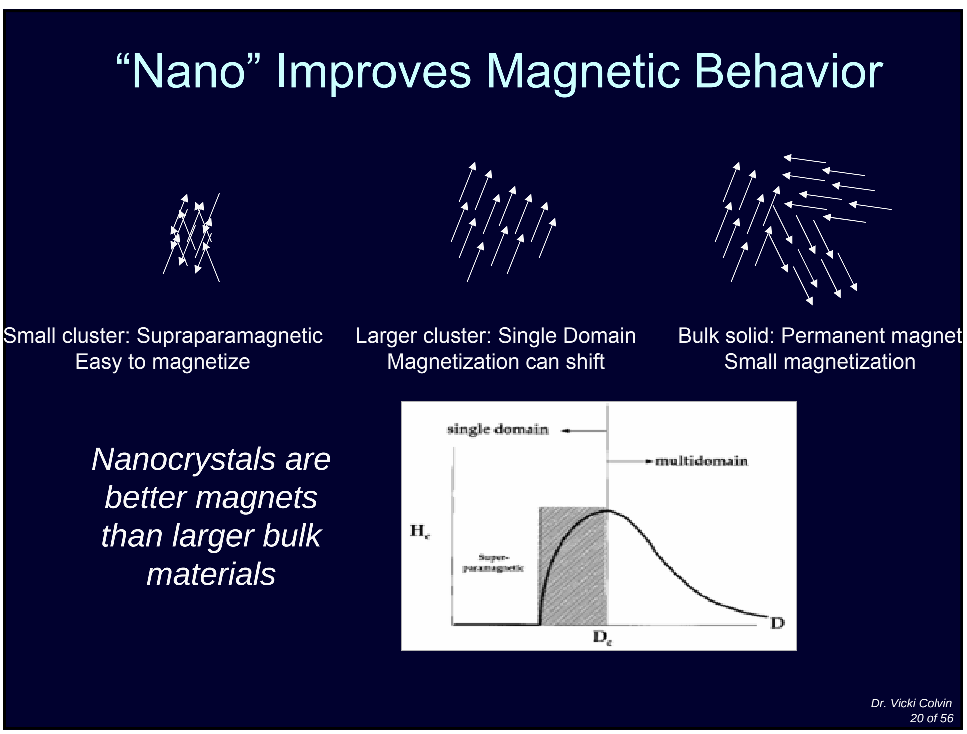
"Nano" Improves Magnetic Behavior
Small cluster: Supraparamagnetic
Easy to magnetize
Larger cluster: Single Domain
Magnetization can shift
Bulk solid: Permanent magnet
Small magnetization
Nanocrystals are better magnets than larger bulk materials
single domain
multidomain
Hc
Super-paramagnetic
Dc
D
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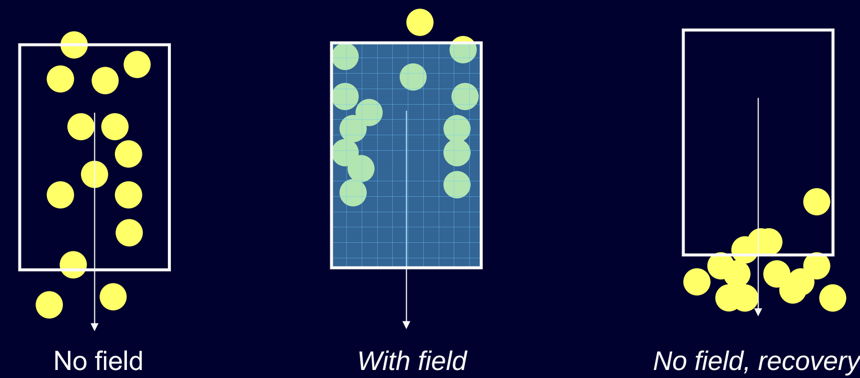
Magnetic Filtration for Nanosorbents



- Requires no pressure gradients
- No fouling of separation system

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Magnetic Separations in Water Treatment

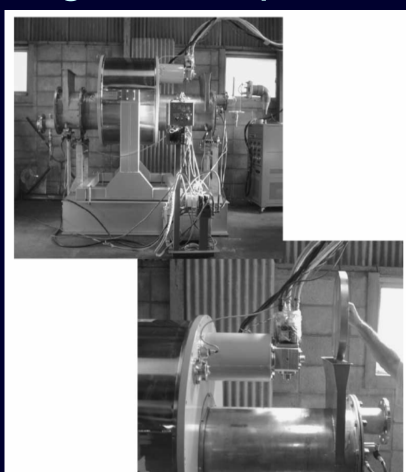

Fig. 4. Superconductive magnet used in the 500 tons/day plant.

- Gravitational settling
- Filtration
- Induced coagulation
- Magnetic Separations

External fields >> 1- 2 Tesla
Particle sizes >> 50 nm

Kakihara, Y., T. Fukunishi, et al. (2004). "Superconducting high gradient magnetic separation for purification of wastewater from paper factory." Ieee Transactions on Applied Superconductivity **14**(2): 1565-1567.

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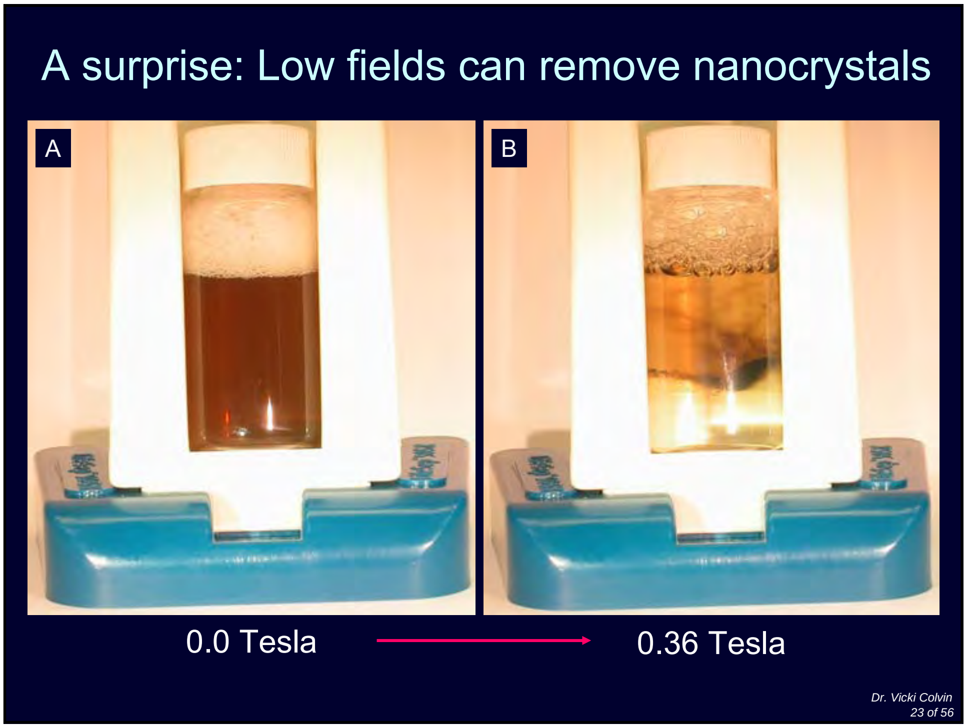
A surprise: Low fields can remove nanocrystals
A
B
0.0 Tesla
0.36 Tesla
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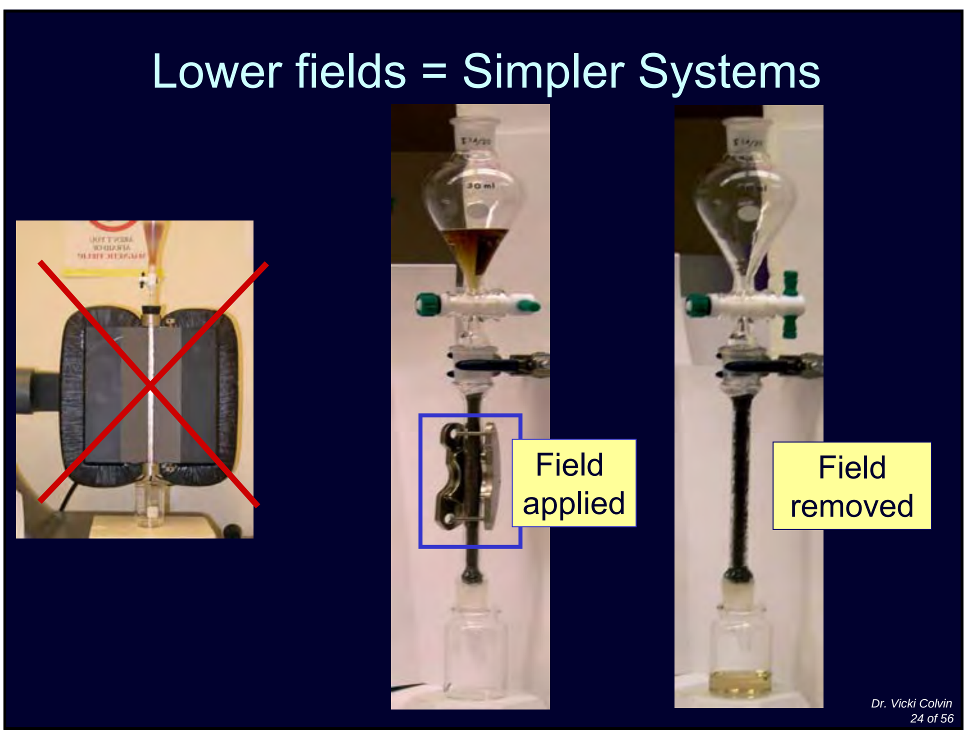
Lower fields = Simpler Systems
Field applied
Field removed
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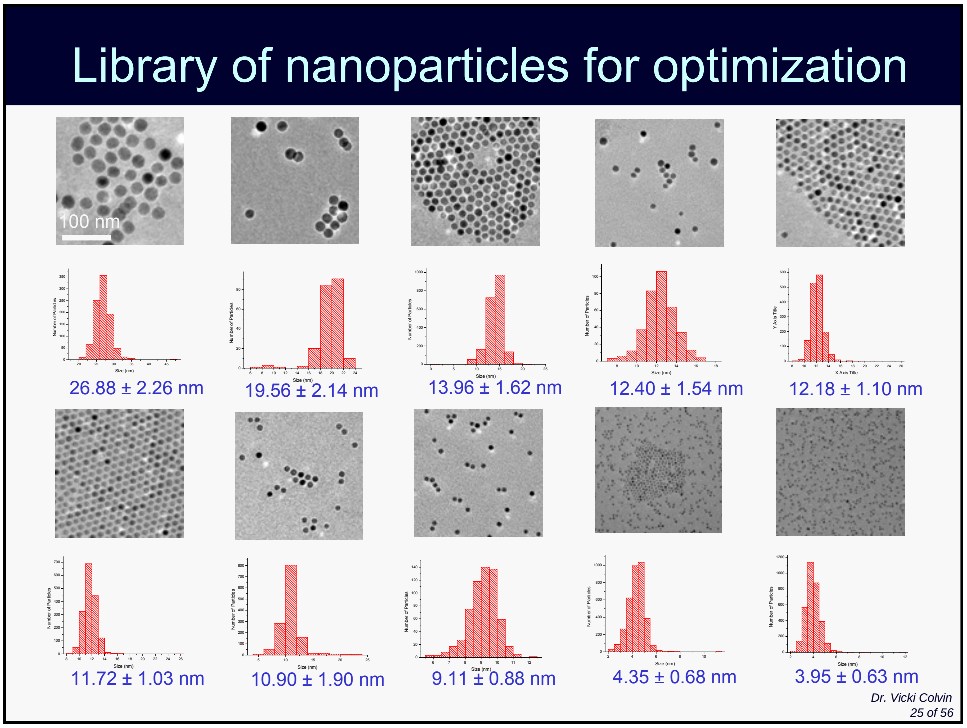

Library of nanoparticles for optimization
100 nm
26.88 ± 2.26 nm
19.56 ± 2.14 nm
13.96 ± 1.62 nm
12.40 ± 1.54 nm
12.18 ± 1.10 nm
11.72 ± 1.03 nm
10.90 ± 1.90 nm
9.11 ± 0.88 nm
4.35 ± 0.68 nm
3.95 ± 0.63 nm
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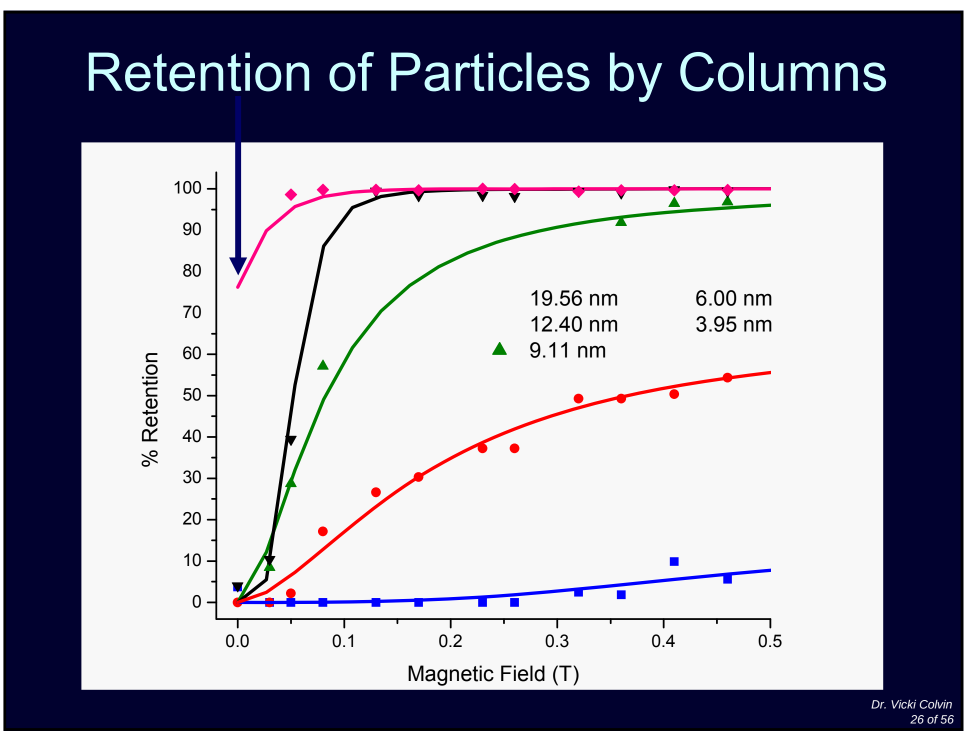

Retention of Particles by Columns
% Retention
Magnetic Field (T)
19.56 nm
12.40 nm
9.11 nm
6.00 nm
3.95 nm
100
90
80
70
60
50
40
30
20
10
0
0.0
0.1
0.2
0.3
0.4
0.5
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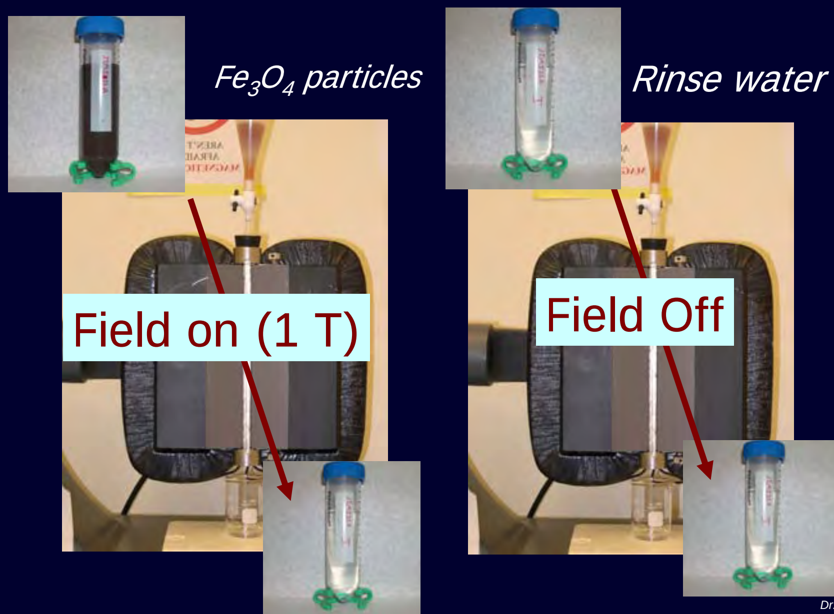
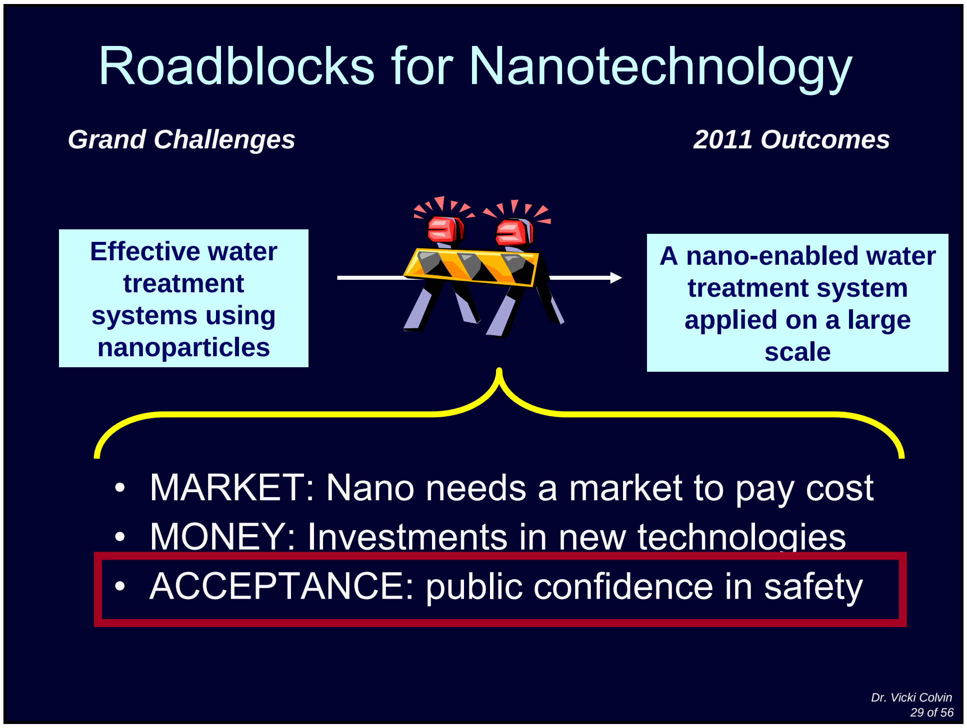
Nanocrystals must be supraparamagnetic



Existing Sorbents for Arsenic Removal

Material	Sorbent (kg)/ month	1 gram treats ____ L water	Annual waste to dispose kg [3]	Backwash Frequency (day)	Efficiency[1]
Alumina + Metal Oxide	0.24	3.8	2.88[3]	14	0.003
Red Mud [As(III)]	360.7	0.002	4328.1[3]	Periodic	~0.003
Ion Exchange	No Removal of Toxic As(III)			~ 3	0.014
Nanoscale Iron Oxides	**0.09**	**10**	**1.1**	**0**	**~7.5 to 75 [2]**

1. "Efficiency" as defined by NAE in the "Granger Challenge, June, 2005" The object is to maximize the efficiency.
2. 12 nm magnetite cost estimated as a synthesized chemical at $2.00/lb and a multiplication factor of cost by 3x to 30x for estimated conditioning chemicals and packaging.
3. The amount (kg) + the backwash frequency


Roadblocks for Nanotechnology
Grand Challenges
2011 Outcomes
Effective water treatment systems using nanoparticles
A nano-enabled water treatment system applied on a large scale
• MARKET: Nano needs a market to pay cost
• MONEY: Investments in new technologies
• ACCEPTANCE: public confidence in safety
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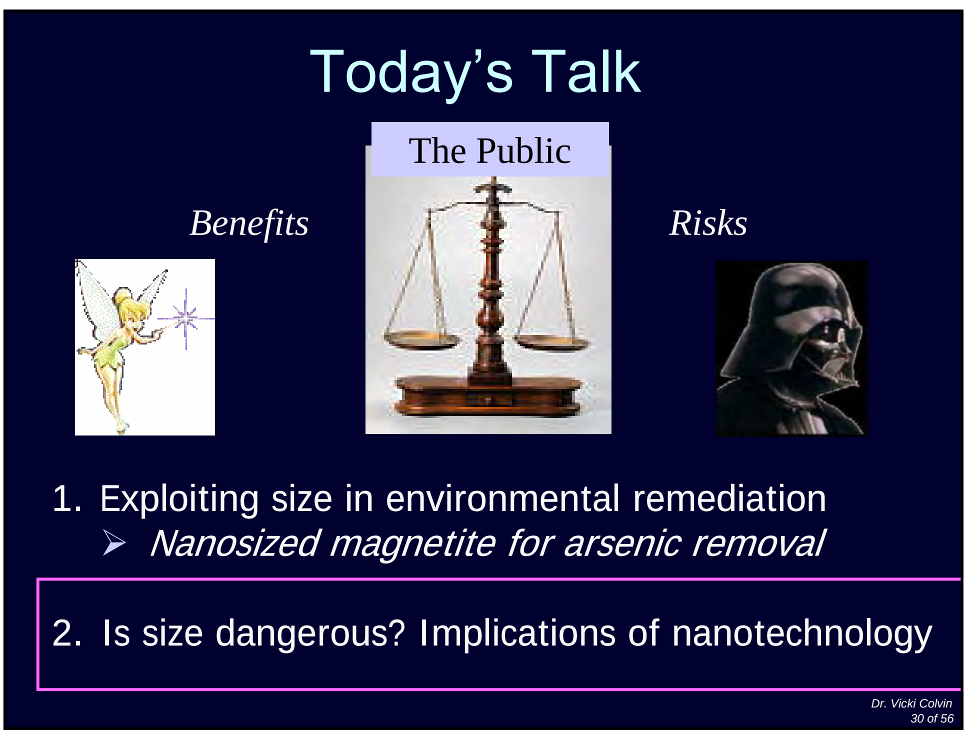
Today's Talk
The Public
Benefits
Risks
1. Exploiting size in environmental remediation
➢ Nanosized magnetite for arsenic removal
2. Is size dangerous? Implications of nanotechnology
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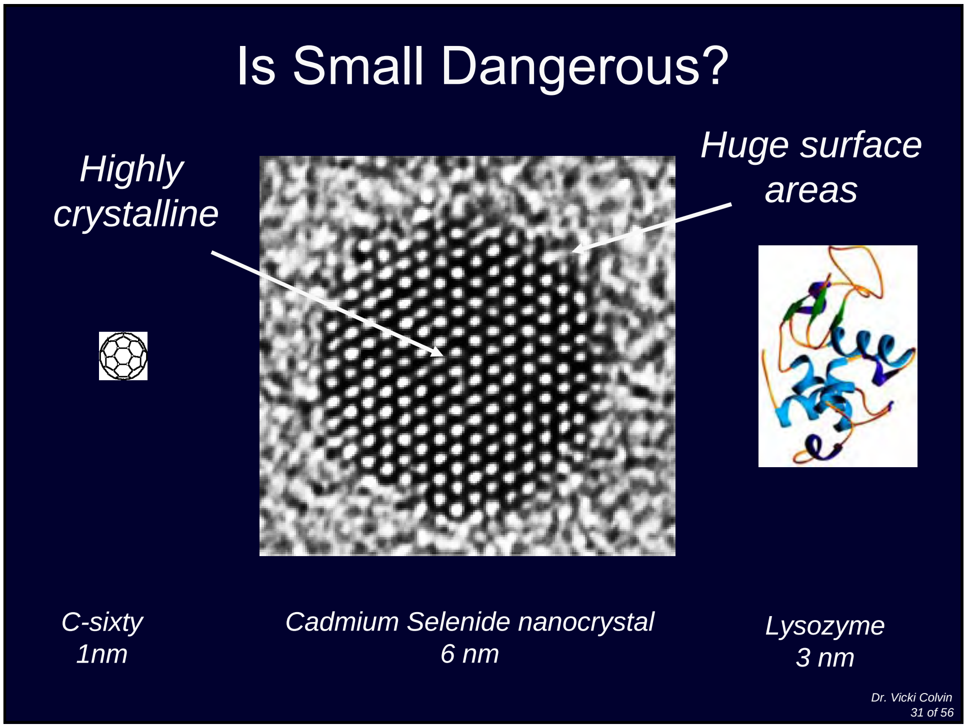
Is Small Dangerous?
Highly crystalline
Huge surface areas
C-sixty
1nm
Cadmium Selenide nanocrystal
6 nm
Lysozyme
3 nm
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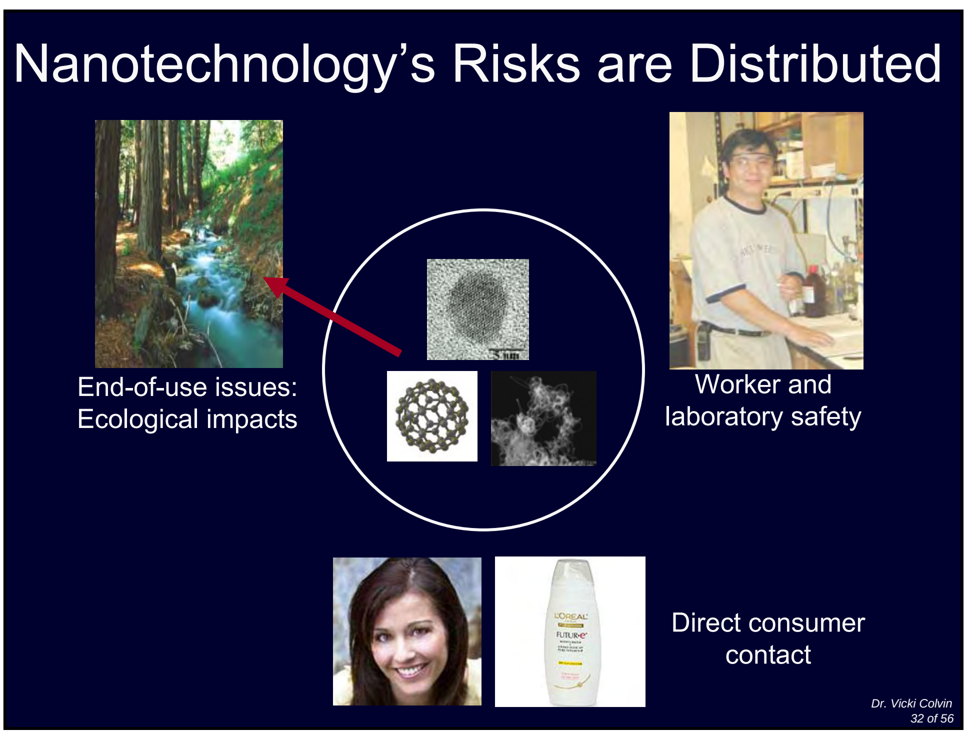
Nanotechnology's Risks are Distributed
End-of-use issues:
Ecological impacts
Worker and
laboratory safety
Direct consumer
contact
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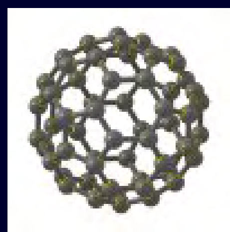
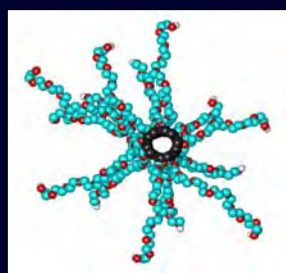
Carbon nanostructures: Model Systems



C-sixty or C_{60}
- Factory production (Frontier Carbon)
- Highly controlled "molecular" species
- Fuel cells, face creams, medical treatments
- Extremely hydrophobic in pristine state



Single-walled Carbon Nanotubes (SWNT)
- Factory production (CNI, NEC, Samsung)
- Complex mixtures, distributions of types
- Flat panel displays, composites
- Extremely hydrophobic in pristine state

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Risk : From Source to Receptor

2. TRANSPORT

1. CHEMISTRY

3. TOXICITY

Risk = Exposure • Effect

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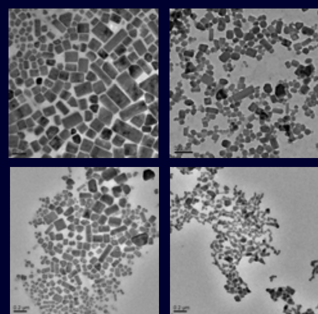
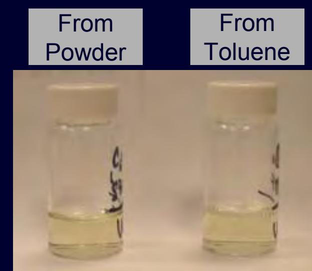
Environmental Chemistry of Fullerenes





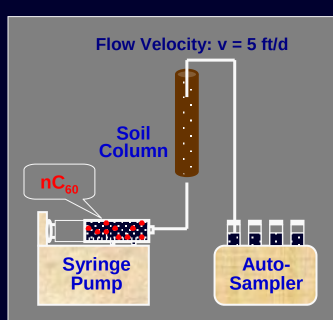
Yellow suspensions

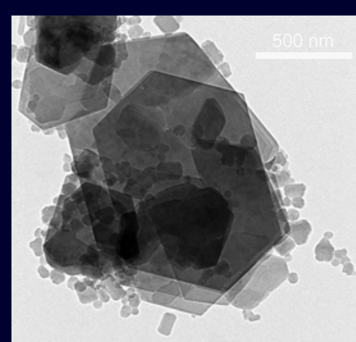
Hydrophobic fullerenes CLUSTER when they sit in water

Preparation conditions affect CLUSTERING and BEHAVIOR

Dirt and other residues stick to CLUSTERS in groundwater

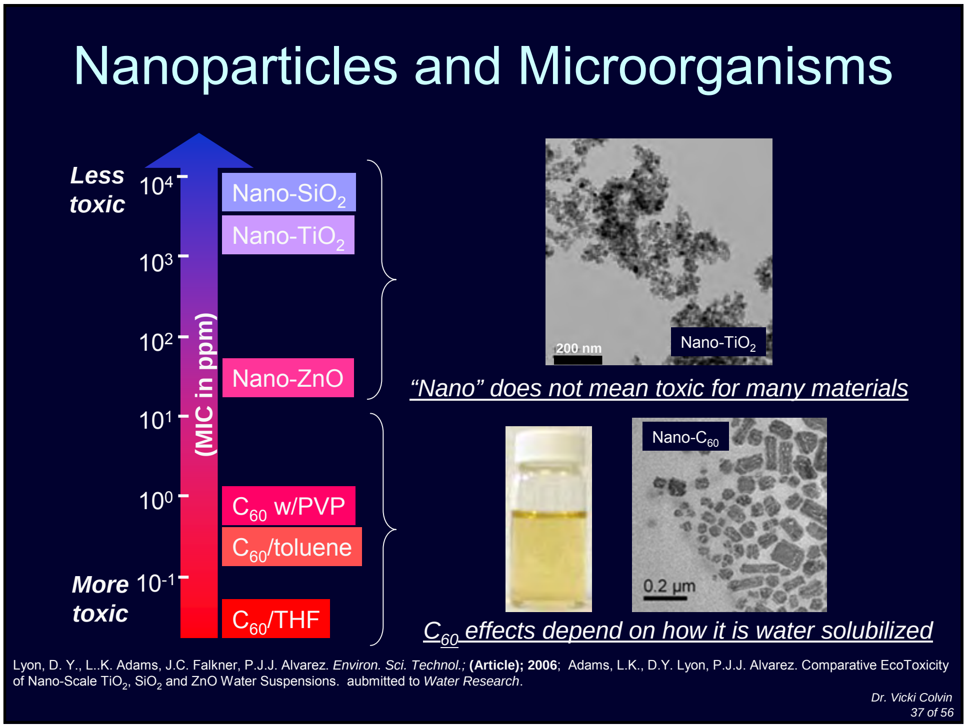
Movement of Nanoparticles in Soils





- SMALL ≠ MOBILE (nanoparticles are sticky)
- MODELS too predict distribution in soil/water

Wiesner (Duke); Hughes (GaTech)



Nanoparticles and Microorganisms
Less toxic
More toxic
10^4
10^3
10^2
10^1
10^0
10^{-1}
(MIC in ppm)
Nano-SiO_2
Nano-TiO_2
Nano-ZnO
C_{60} w/PVP
C_{60}/toluene
C_{60}/THF
200 nm
Nano-TiO_2
"Nano" does not mean toxic for many materials
Nano-C_{60}
0.2 µm
C_{60} effects depend on how it is water solubilized
Lyon, D. Y., L..K. Adams, J.C. Falkner, P.J.J. Alvarez. Environ. Sci. Technol.; (Article); 2006; Adams, L.K., D.Y. Lyon, P.J.J. Alvarez. Comparative EcoToxicity of Nano-Scale TiO_2, SiO_2 and ZnO Water Suspensions. aubmitted to Water Research.
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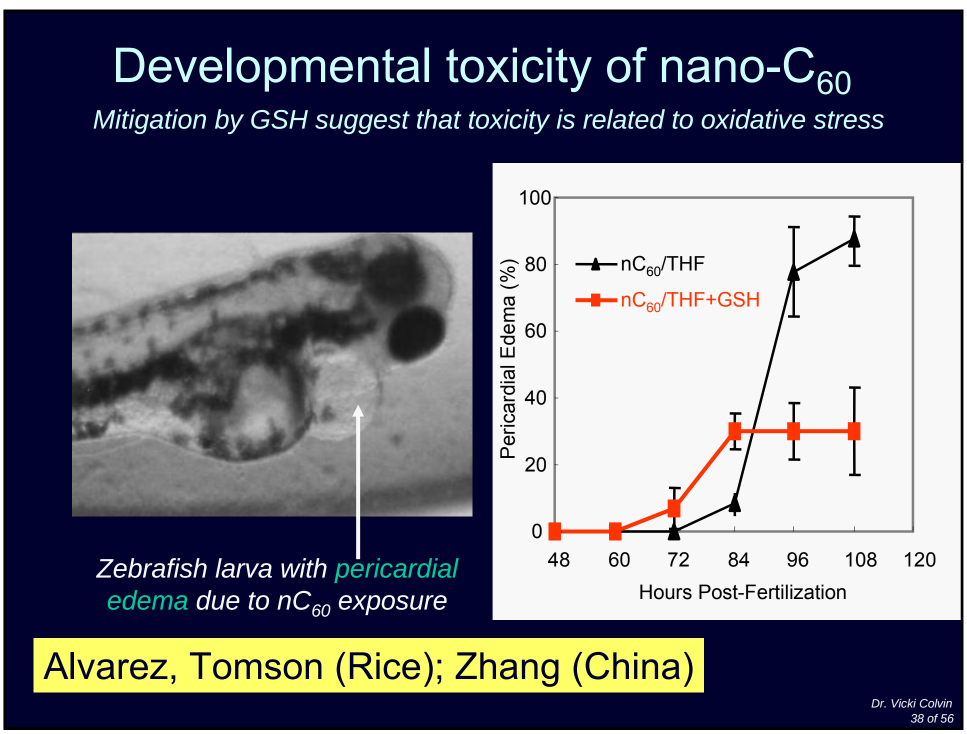

Developmental toxicity of nano-C_{60}
Mitigation by GSH suggest that toxicity is related to oxidative stress
Zebrafish larva with pericardial edema due to nC_{60} exposure
Pericardial Edema (%)
0
20
40
60
80
100
nC_{60}/THF
nC_{60}/THF+GSH
48
60
72
84
96
108
120
Hours Post-Fertilization
Alvarez, Tomson (Rice); Zhang (China)
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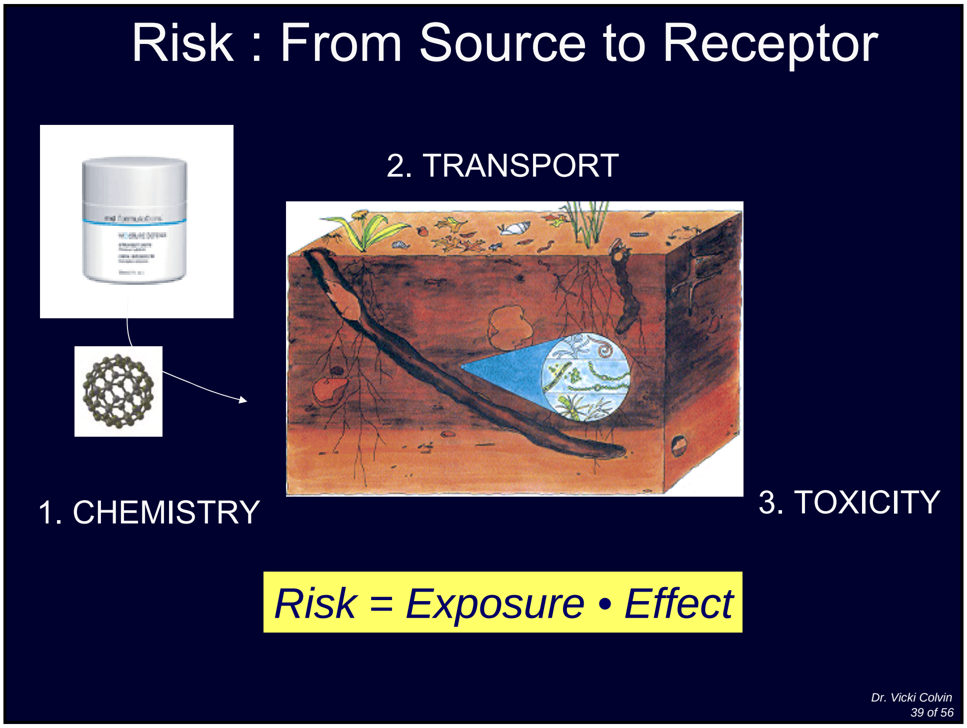
Risk : From Source to Receptor
2. TRANSPORT
1. CHEMISTRY
3. TOXICITY
Risk = Exposure • Effect
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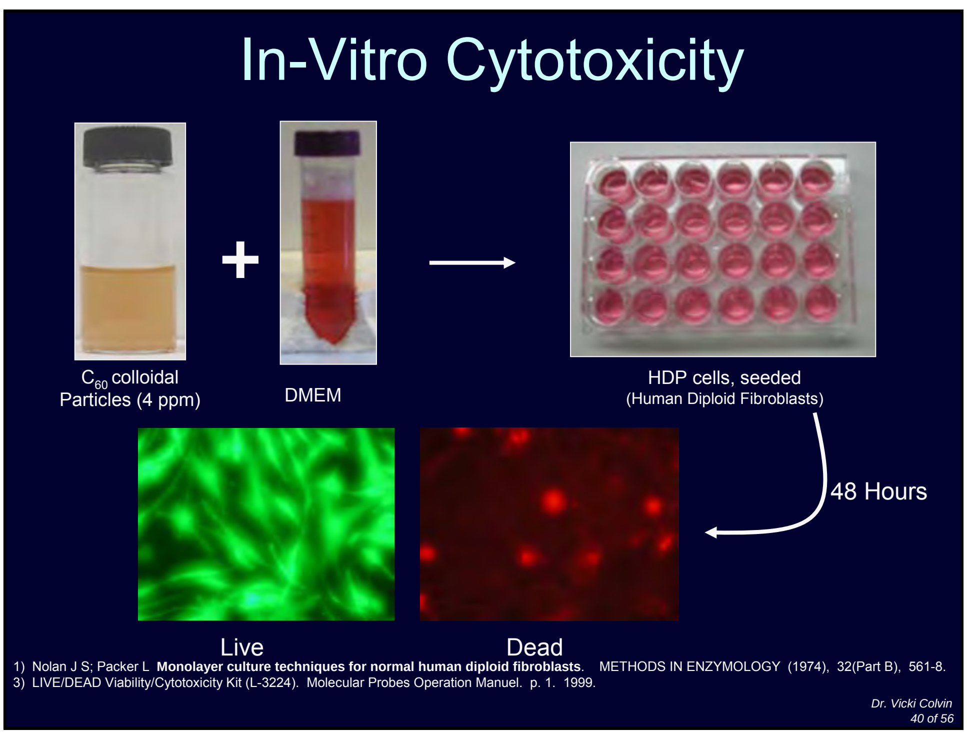
In-Vitro Cytotoxicity
+
C60 colloidal
Particles (4 ppm)
DMEM
HDP cells, seeded
(Human Diploid Fibroblasts)
48 Hours
Live
Dead
1) Nolan J S; Packer L Monolayer culture techniques for normal human diploid fibroblasts. METHODS IN ENZYMOLOGY (1974), 32(Part B), 561-8.
3) LIVE/DEAD Viability/Cytotoxicity Kit (L-3224). Molecular Probes Operation Manuel. p. 1. 1999.
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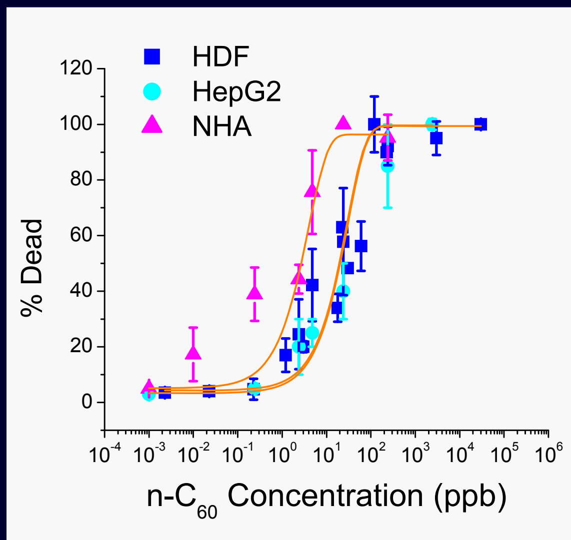
Dose Response Curve for n-C_{60}



Human Cell Line	LC_{50} (ppm)
HepG2	0.05
HDF	0.02
NHA	0.002

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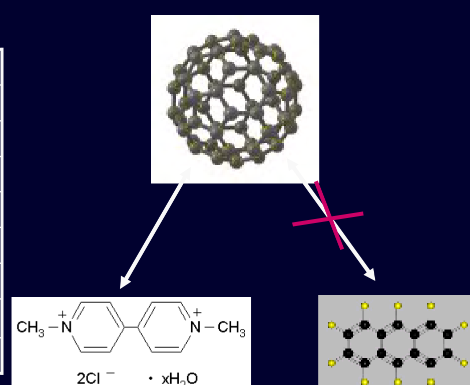
n-C_{60} Relative Cytotoxicity

Toxin	LC50, mg/kg
C_{60}-$(OH)_x$	> 100,000
Ethyl Alcohol*	17,000
THF	11,000
Toluene	1,600
Paraquat	100
Benzo[a]pyrene*	10
n-C_{60}	**0.02**
Dioxin*	0.001



* National Institute of Health, Registry of Cytotoxicity Data (ZEBET)

Aggregated C-sixty is a very toxic substance in cell culture

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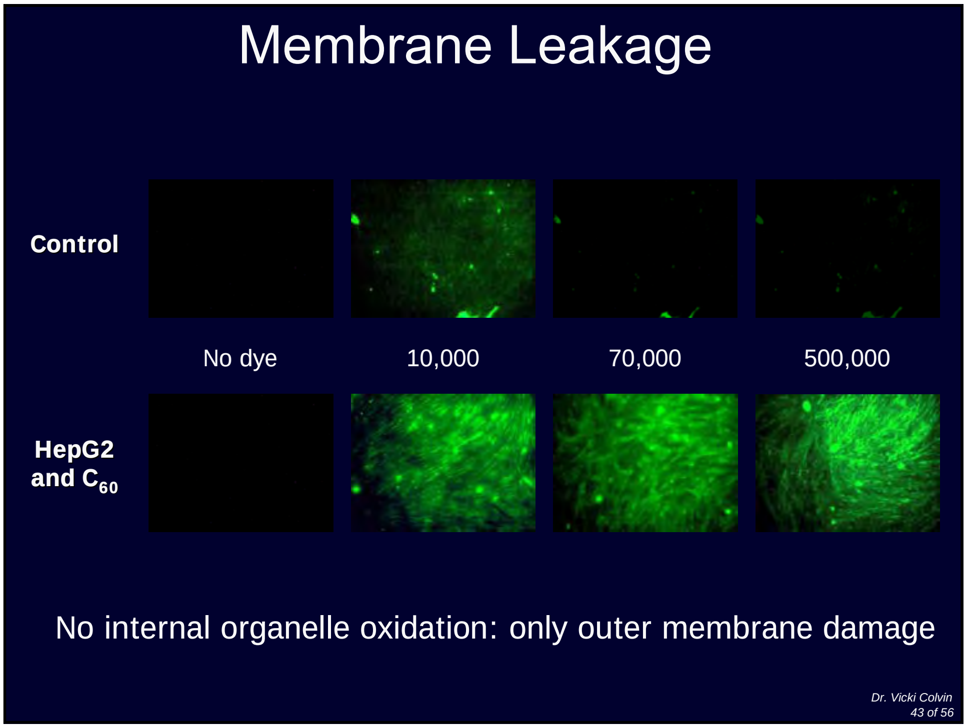
Membrane Leakage
Control
No dye
10,000
70,000
500,000
HepG2 and C_{60}
No internal organelle oxidation: only outer membrane damage
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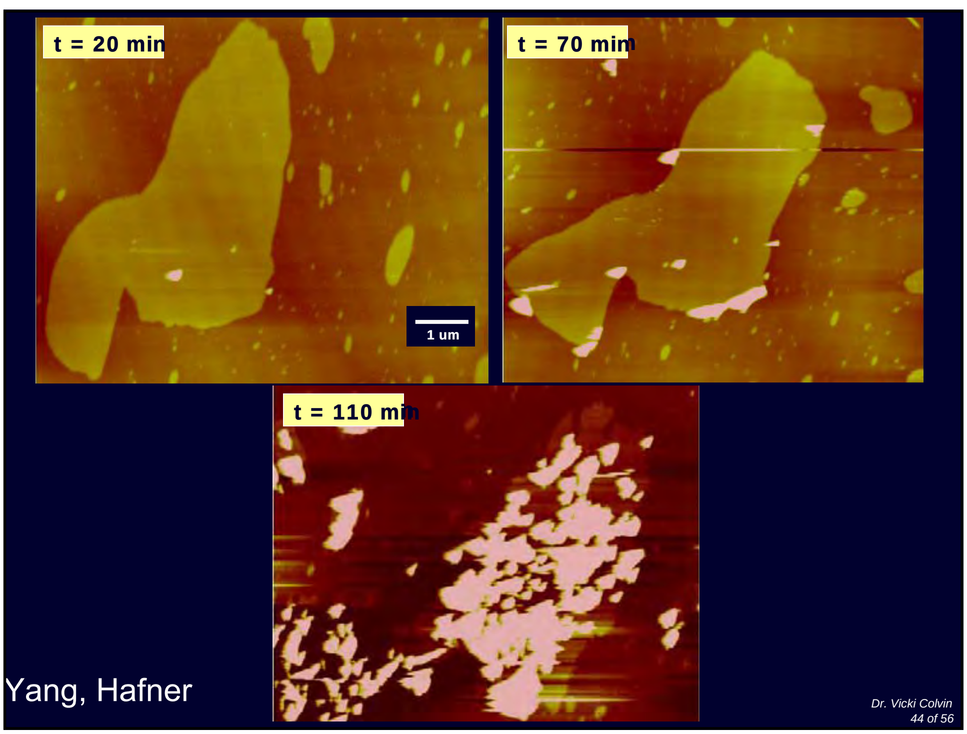
t = 20 min
t = 70 min
1 um
t = 110 min
Yang, Hafner
Dr. Vicki Colvin
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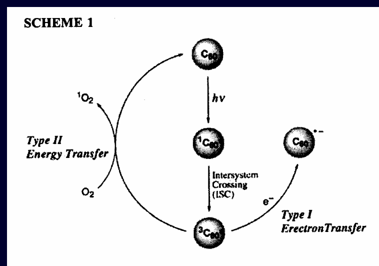
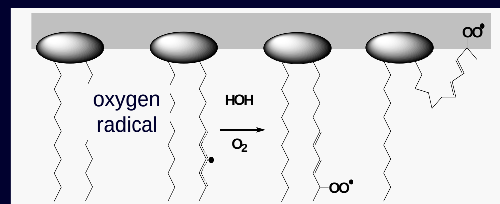
Origins of fullerenes bioactivity





C_{60} can form superoxide anion, and singlet oxygen

C_{60} is also a highly lipophilic substance

Cytotoxic substance which destroys lipid membranes

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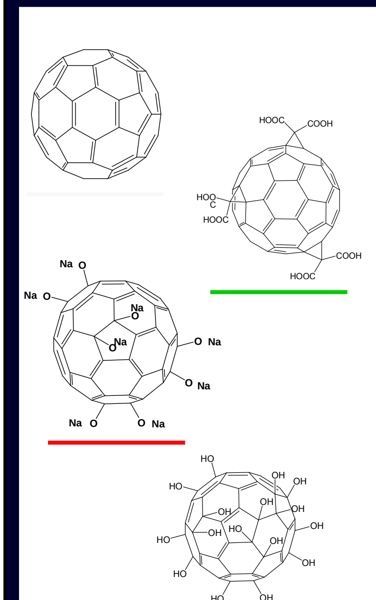
Systematic Variation of Surface Chemistry



Increasing derivatization lowers photoinduced singlet oxygen generation

More polar functionality creates higher water solubility in materials

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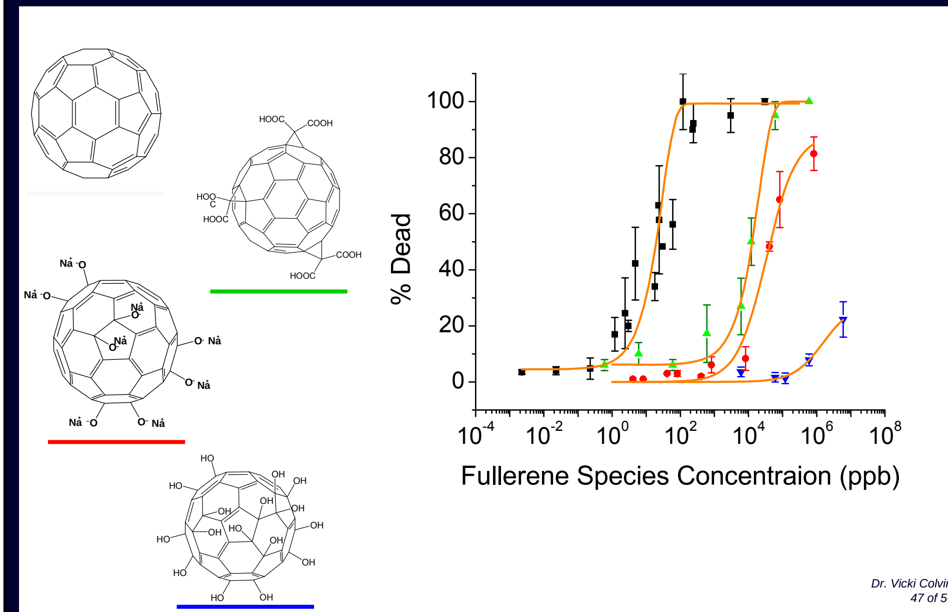
Structure/Activity Relationship Revealed



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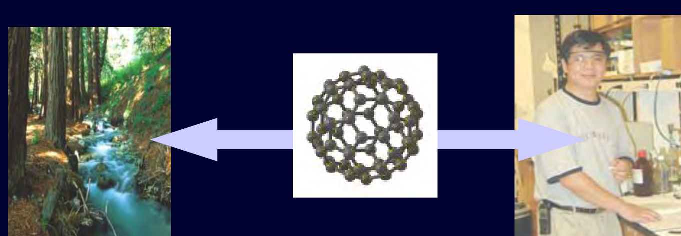
Information Supports Risk Management



- Development of pre-treatment schemes for waste
  - Mild oxidation for fullerenes
  - Thermal treatments for titania
- Simple ex-vivo screens for nanoparticle formulators
- Foundation for testing structure-function hypotheses

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Framing a new question

Are engineered nanoparticles dangerous?

↓

How can we engineer safe nanoparticles?

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Today's Talk

Benefits

Risks

1. Nanocrystalline magnetite irreversibly sorbs Arsenic
2. "Nano" makes magnetic separations practical
    1. *Higher removal at lower fields*
    2. *Very high surface areas increase capacity*
3. Ongoing implications work improves technology

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Acknowledgements

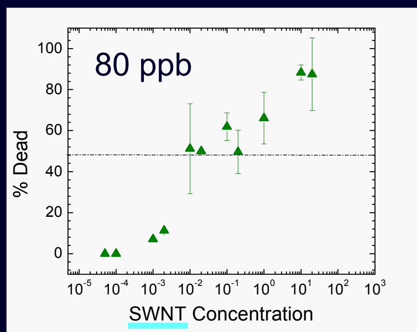
- **Dr. Christie Sayes**
- **John Fortner**
- Dr. Joe Hughes
- Dr. Jennifer West
- Joe Mendez
- Delina Lyon
- Adina Boyd
- Andre Gobin
- Yi Yang
- Raj Wahi
- Dr. David Warheit (DuPont)
- Dr. Wenh Guo
- Dr. Yitzhi Jane Tao
- Dr. Mason Tomson
- Dr. Kevin Ausman
- Dr. Jane Grande-Allen
- Dr. Lon Wilson
- Dr. Jason Hafner

Want to learn more? Do more?

- Copies of presentation: colvin@rice.edu
- Center web page: http://cben.rice.edu//
- Check-out
  - ICON: http://icon.rice.edu/. Multi-stakeholder group devoted to minimizing risks of nanotechnology
  - Standards activities: http://www.astm.org. (E56) Help write standards on nanotechnology and risk assessment, management.

NanoX: Not Toxicology As Usual

Are single-walled carbon nanotubes toxic?



- 20 major types of SWNT
- 4 manufacturing types (trace impurities)
- Lengths ranging from 5 – 300 nm
- 5 methods of purification
- 10 possible surface coatings

> 50,000 SWNT samples

Basic structure-function relationships for nanomaterials and biological impacts are necessary

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Acknowledgements

- **Professor Mason Tomson**
- **Dr. Amy Kan**
- **Sunjun Yean**
- **Cafer Yavuz**
- **J. T. Mayo**
- **Arjun Prakash**
- **Dr. William Yu**
- **Yi Hua**
- **Josh Falkner**

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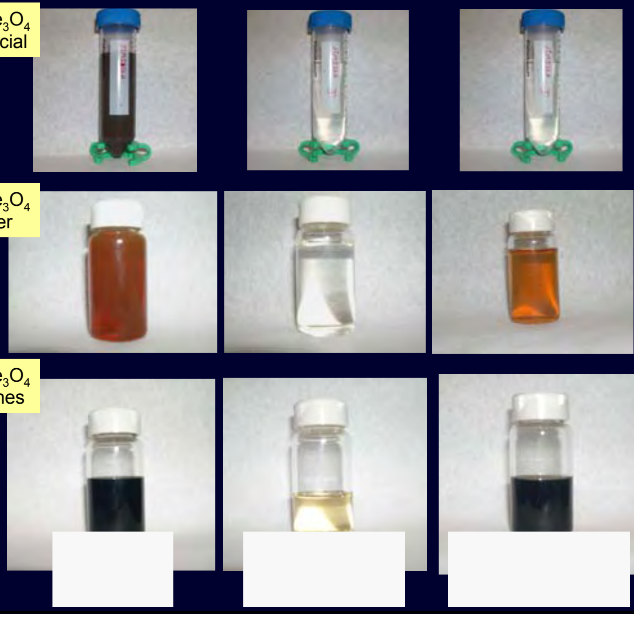
Magnetic Separations Optimized

30 nm Fe_3O_4 commercial

10 nm Fe_3O_4 in water

22 nm Fe_3O_4 in hexanes



No recovery

1 Tesla Magnetic fields

.1 Tesla Magnetic fields

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Arsenic Removal, with Magnetic Field

Particle Size (nm)	As(V) or As(III)	Initial As Concentration (mg/L)	Residual As Concentration (mg/L)	% Removal
12	As (III)	500	3.9	99.2
20	As (III)	500	45.3	90.9
300	As (III)	500	375.7	24.9
12	As (V)	500	7.8	98.4
20	As (V)	500	17.3	96.5
300	As (V)	500	354.1	29.2

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