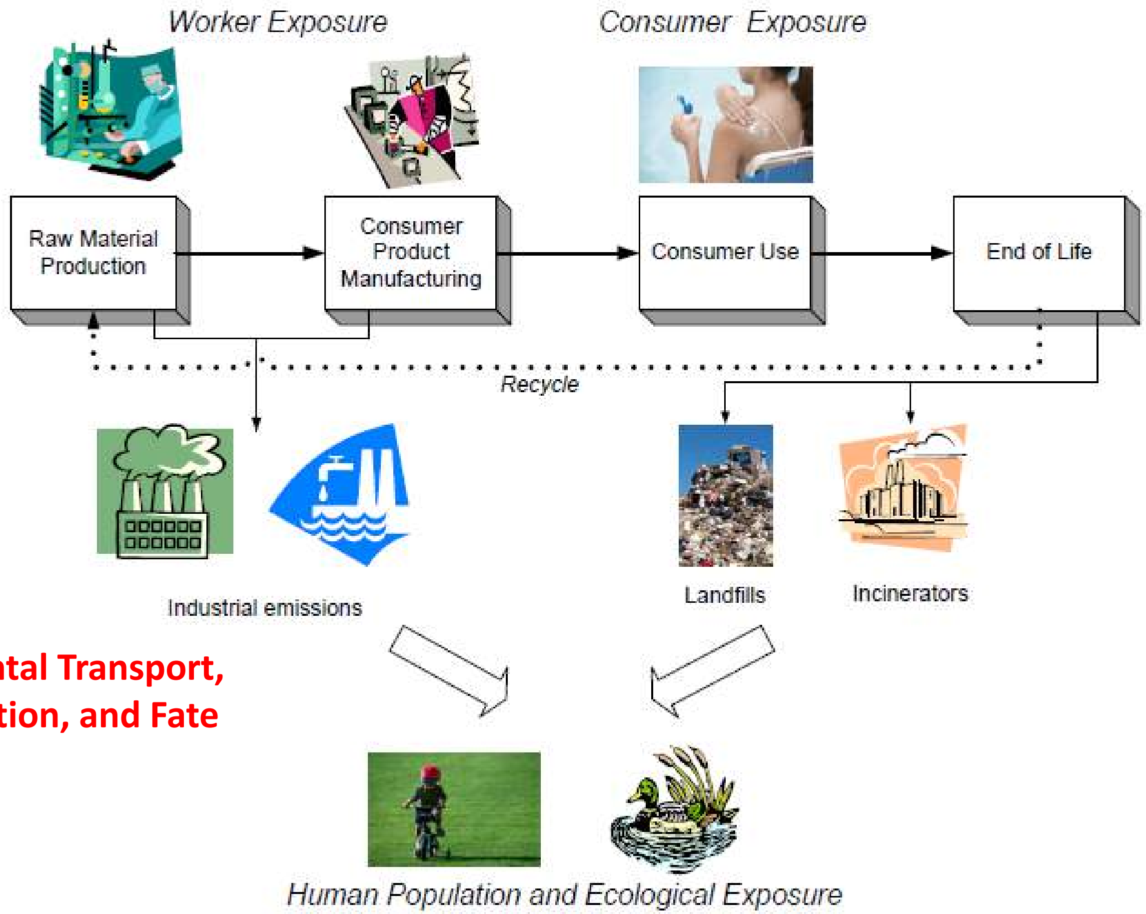
Nanoparticles in the Environment

- W. Ball: Very (!) brief introduction to Engineered Nanoparticles (ENPs)
- W. Ball presentation of M. Wiesner* slides on "Nanoparticle Behavior in Complex Environments"

* Center for the Environmental Implications of NanoTechnology (CEINT)

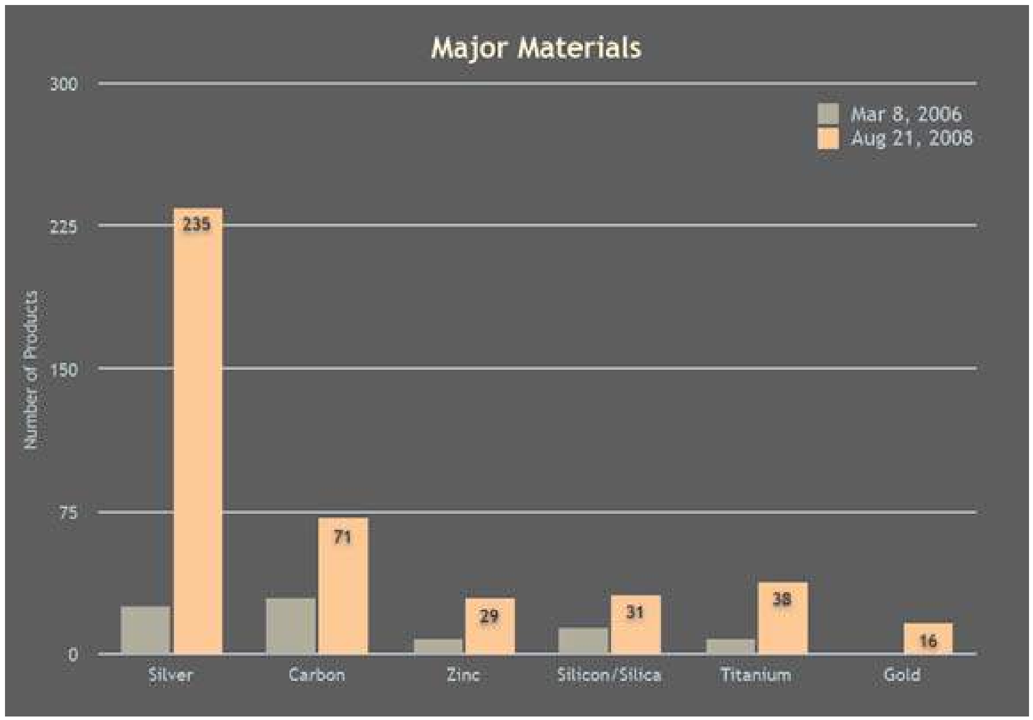


Environmental Transport, Transformation, and Fate

. **Life Cycle Perspective to Risk Assessment**

Consumer Goods and Technologies Containing Nanomaterials

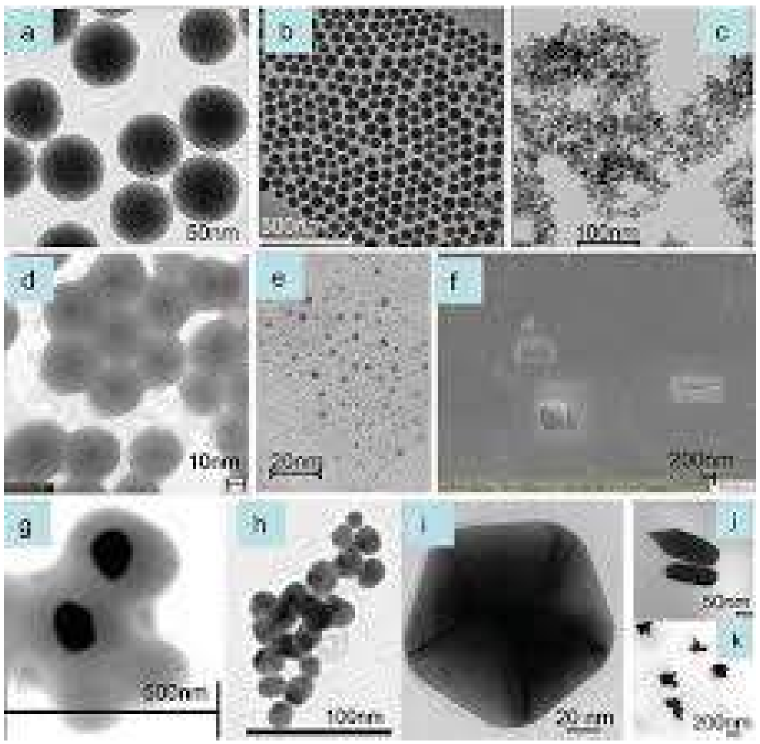
Thousands of manufacturer-identified nanotechnology-based consumer products currently on the market



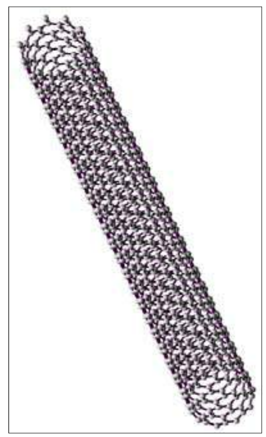
Woodrow Wilson International Center for Scholars
http://www.nanotechproject.org/

Engineered Nanoparticles

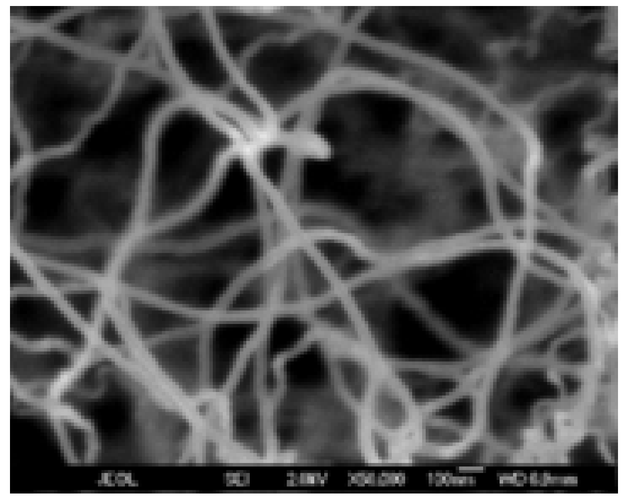
Inorganic ENPs



Carbon Nanotubes

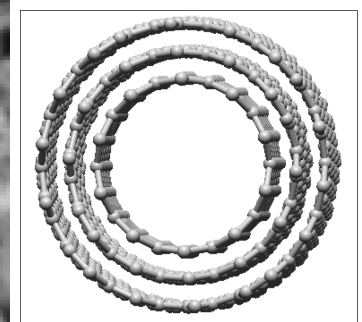


Single Walled Carbon Nanotube (SWCNT)



Materials Properties

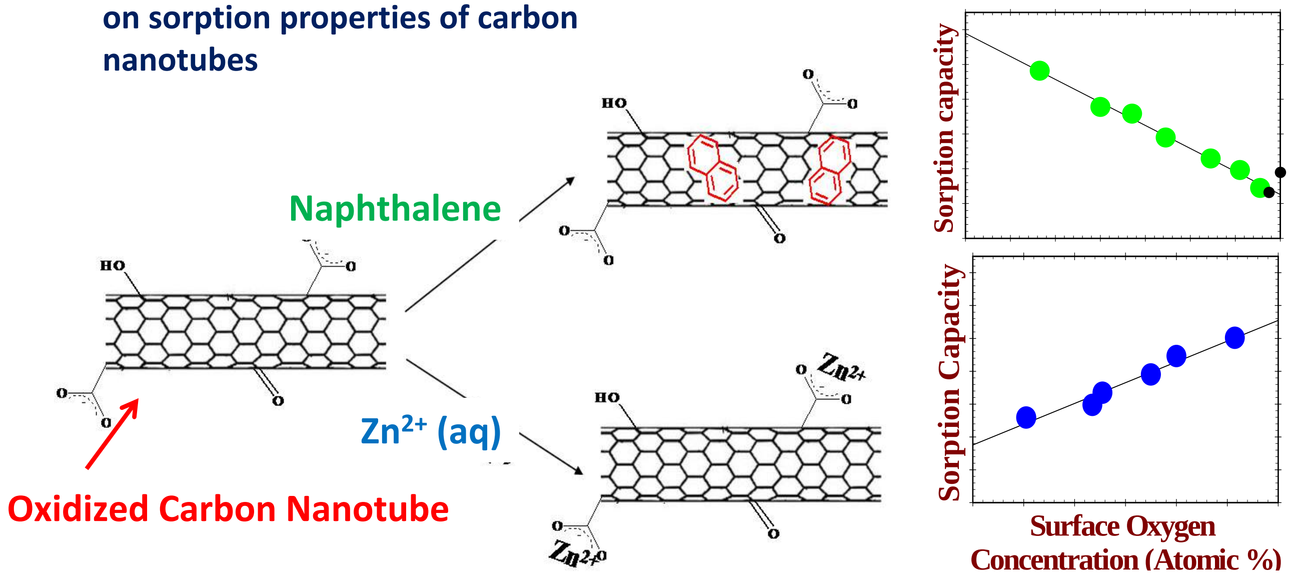
- **Mechanical Strength**
- **Electrical Conductivity**
- **High Aspect Ratio**



Multi Walled Carbon Nanotubes (MWCNT)

Rational development of “safe-by-design” nanomaterials will require knowledge of how intrinsic nanoparticles properties (size, shape, surface chemistry) impact environmentally relevant properties (colloidal stability, sorption properties)

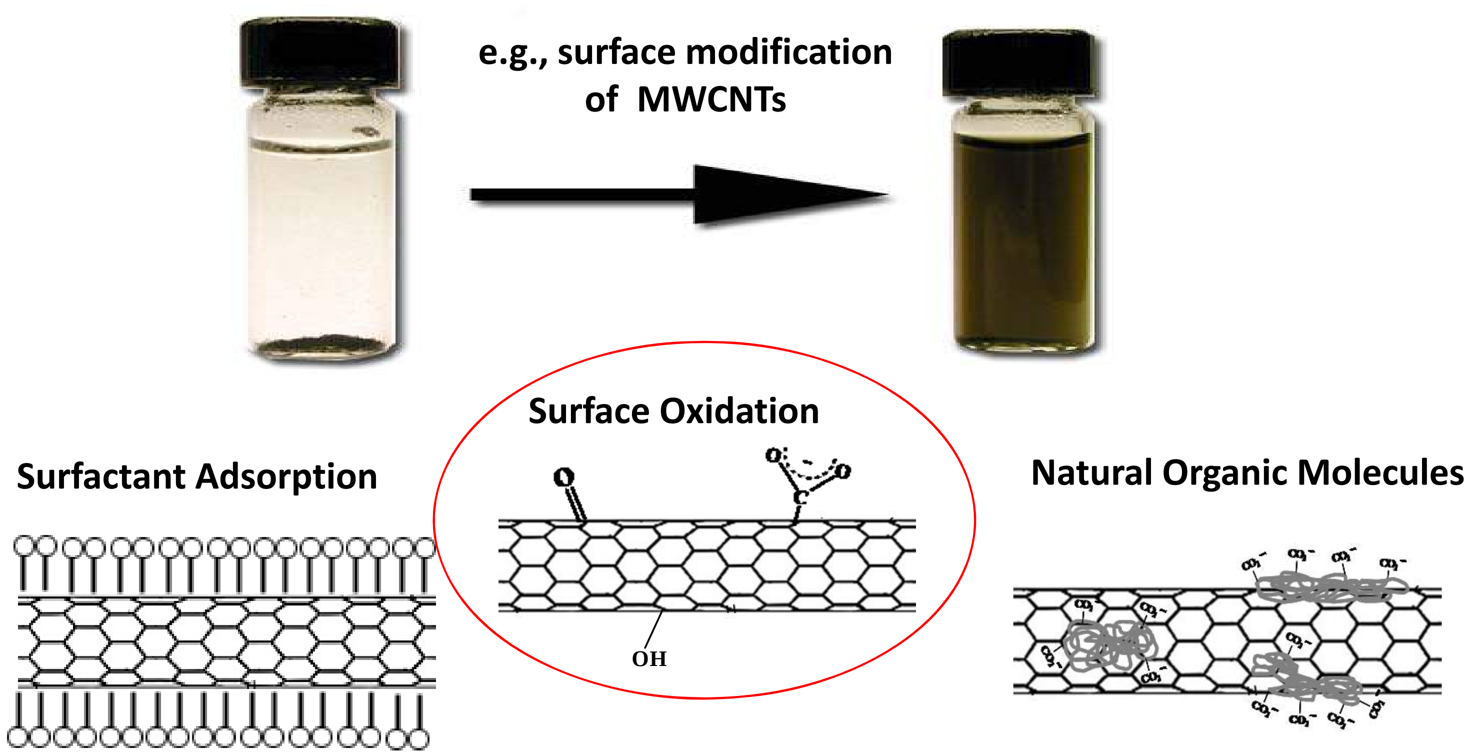
E.g. Impact of Surface Chemistry on sorption properties of carbon nanotubes



Cho et al., *Env. Sci. Technol.* 43: 2899 (2008)

Cho et al., *Langmuir*, 26:967 (2010)

Probing the Influence of Surface Chemistry on Engineered Nanoparticle Behavior, Fate and Effects in Aquatic Environments

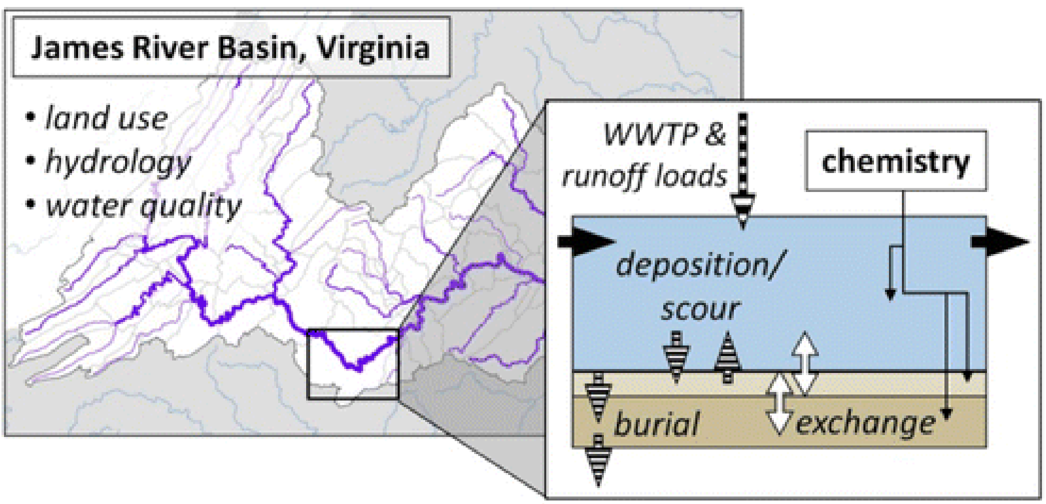


after Smith et al. *Environ. Sci.* 43: 819(2009).

Stream Dynamics and Chemical Transformations Control the Environmental Fate of Silver and Zinc Oxide Nanoparticles in a Watershed-Scale Model

Amy L. Dale †‡, Gregory V. Lowry ‡, and Elizabeth A. Casman *†

† Engineering and Public Policy, Carnegie Mellon University
‡ Civil and Environmental Engineering, Carnegie Mellon University
Environ. Sci. Technol., Article ASAP (2015)
DOI: 10.1021/acs.est.5b01205



Nanomaterial behavior in complex environments

Mark R. Wiesner

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A little more bio information…..

Education

B.A. Mathematics/Biology, Coe College, Cedar Rapids, Iowa, 1978

M.S. Civil and Environmental Engineering,
University of Iowa, Iowa City, Iowa, 1980
(Thesis advisor, J.L. Schnoor)

Ph.D. Environmental Engineering,
The Johns Hopkins University, Baltimore, Maryland, 1985
(Doctoral advisors, C.R. O'Melia and J.L. Cohon)

Post-Doctoral Studies
Chemical Engineering Sciences Laboratory,
Ecole Nationale Superieure des Industries Chimiques,
(ENSIC) Nancy, France 1986-87

Some take home points:

(WPB addition, based on summary comments from MRW)

- Nanoparticles (whether engineered [“ENPs”] or natural):
  can be taken up by plants and animals;
- NPs are subject to trophic transfer- in some cases with biomagnification, in some with dilution;
- Attachment efficiencies appear to be a promising way of predicting NP behavior.
- The toxicity issue is secondary.
  Most important -- growing awareness of:
  - Complexity of nanometric phases in their interactions with living systems; and
  - Potentially important roles of NPs in uptake of chemicals, nutrient cycling, transport of other species, etc.

Nanomaterial behavior in complex environments

Mark R. Wiesner

Director

Center for the Environmental Implications of NanoTechnology

Duke University

CEINT
Center for the Environmental Implications of NanoTechnology

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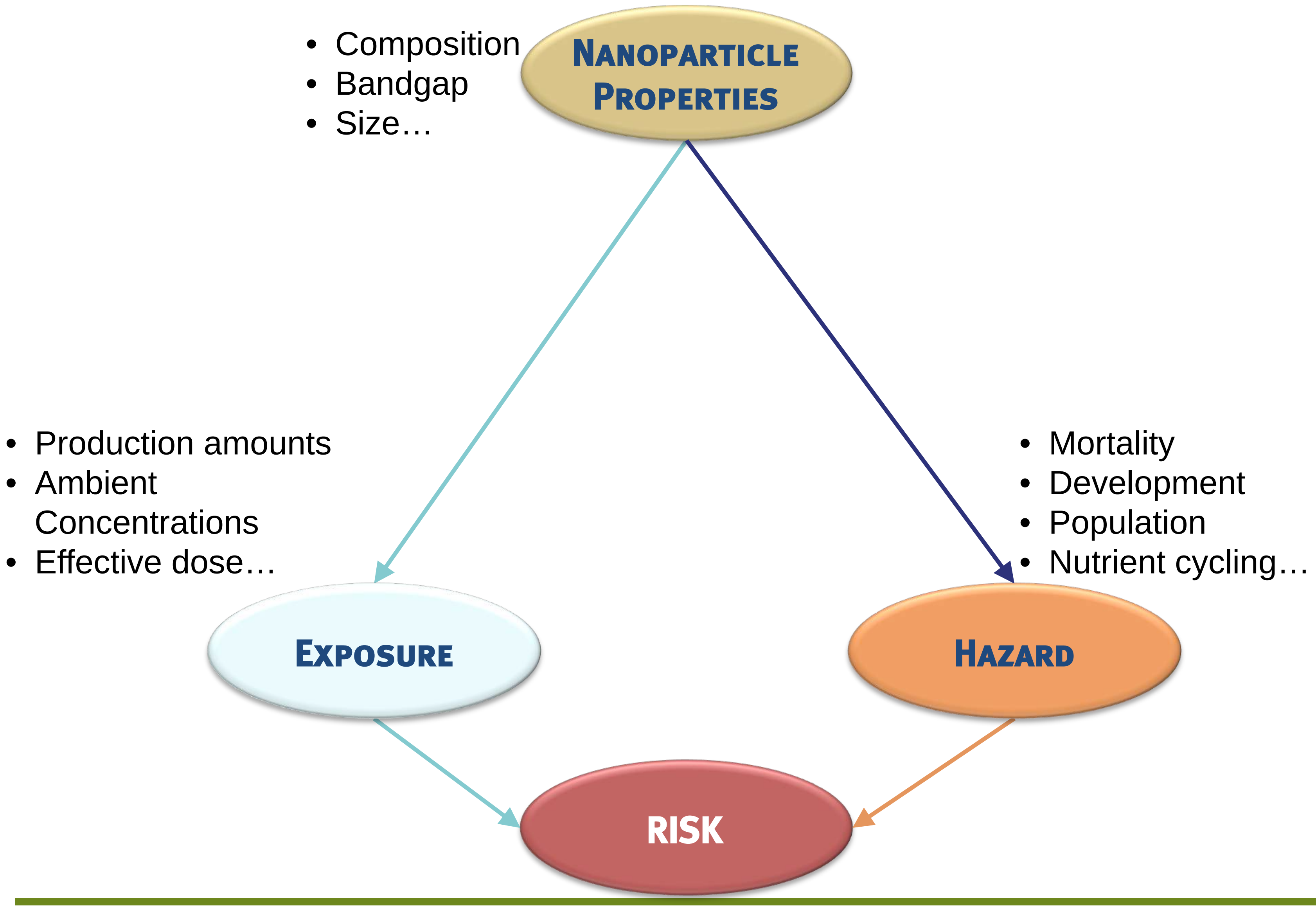
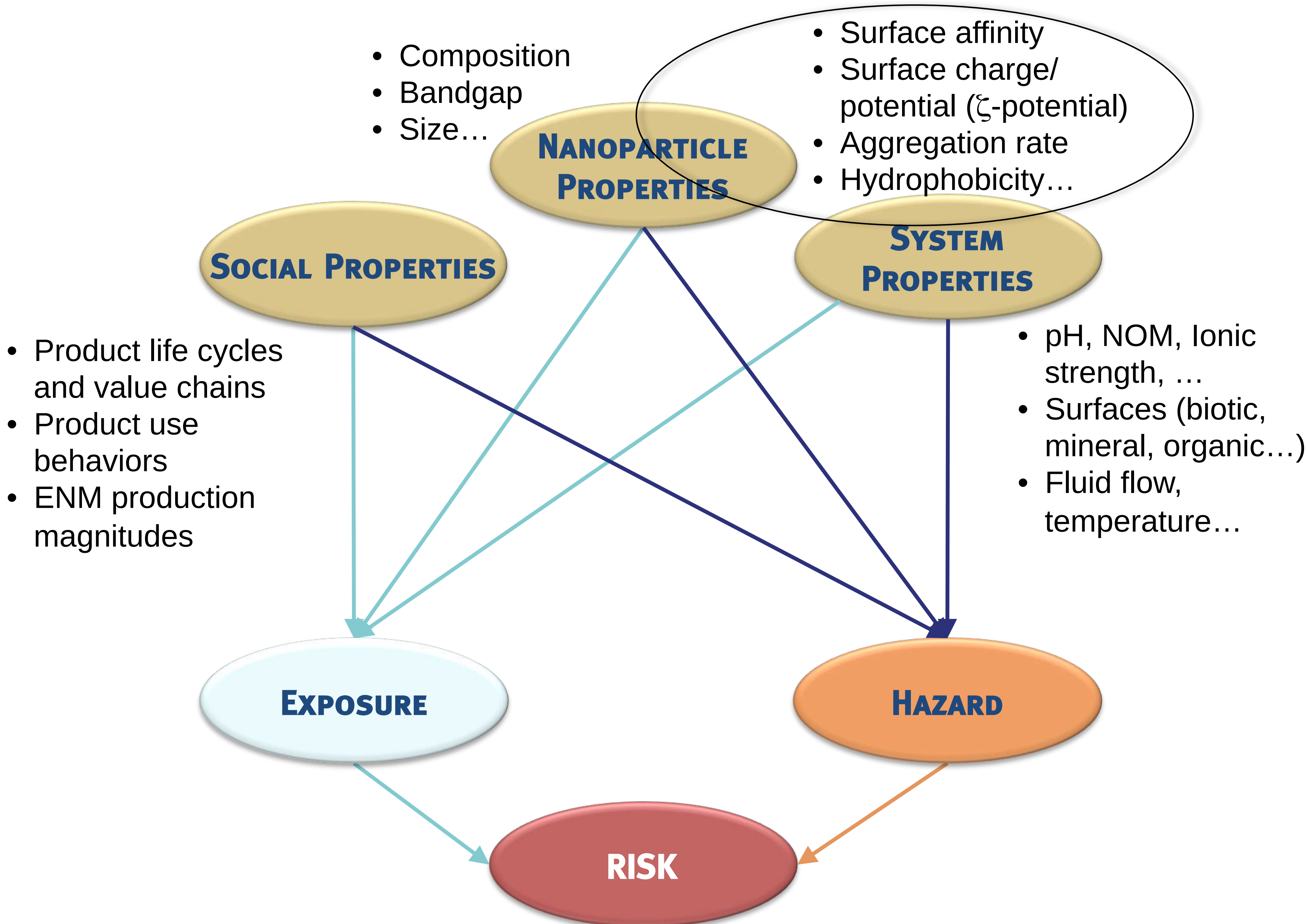
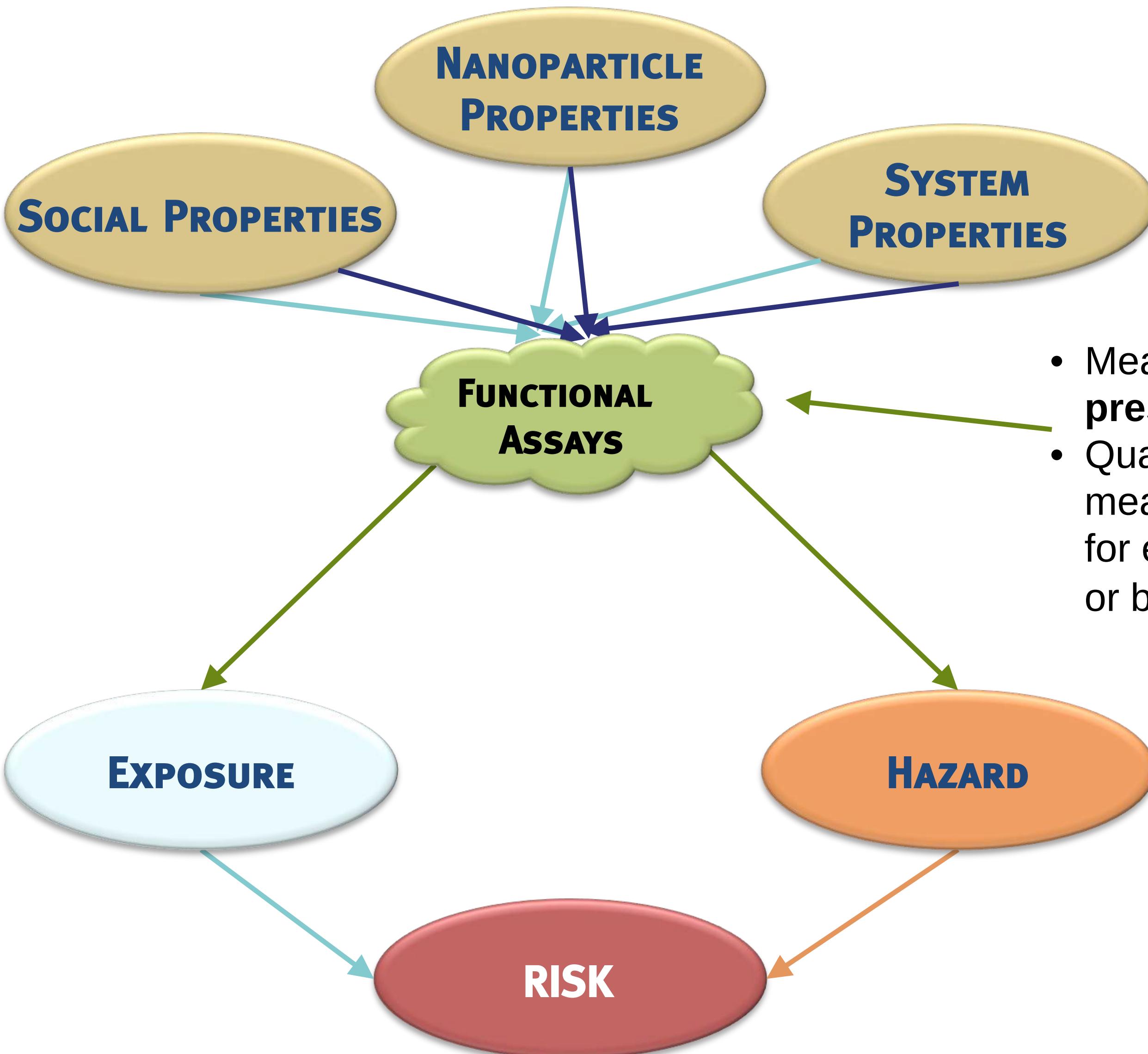


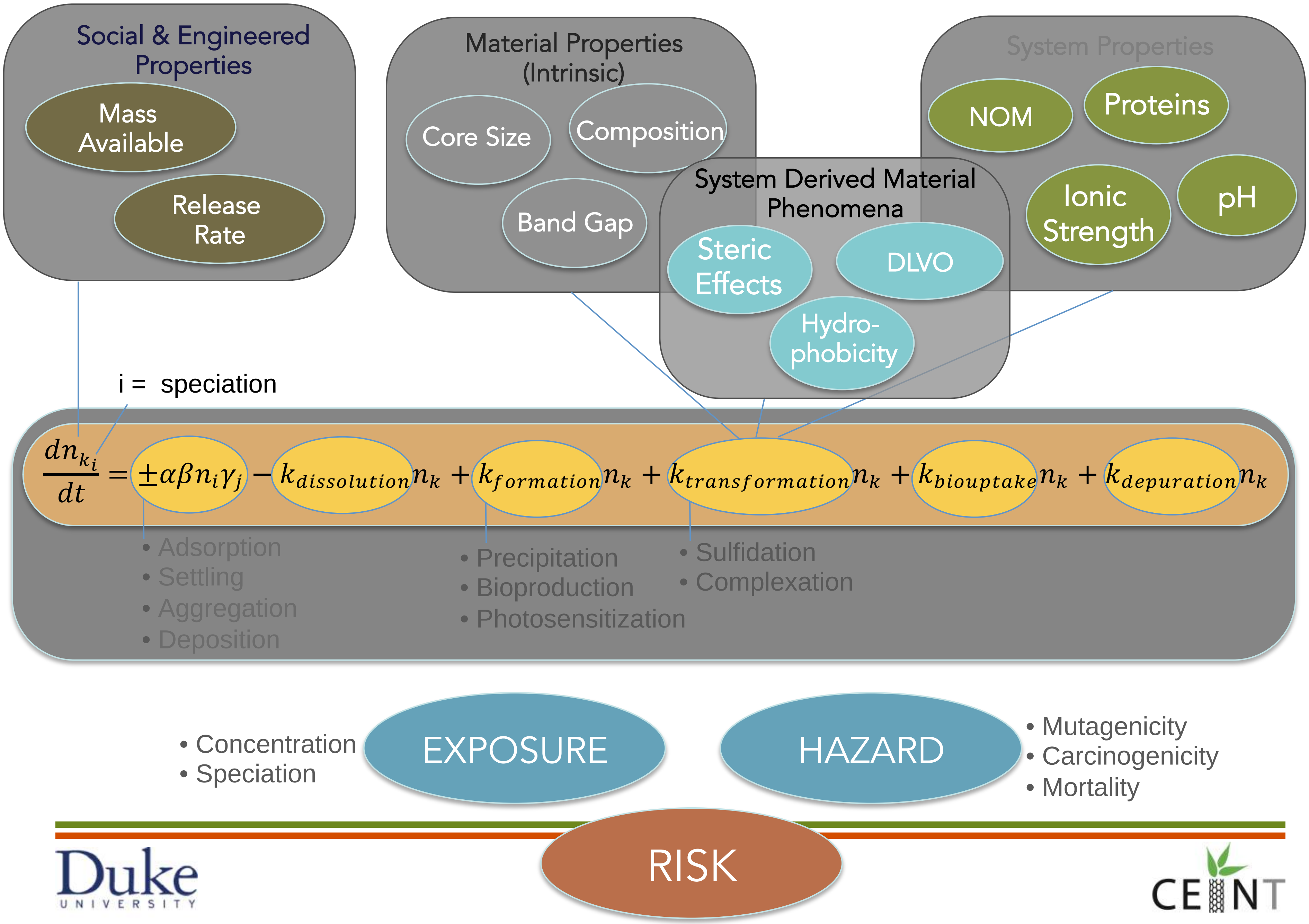
- Composition
- Bandgap
- Size…
NANOPARTICLE PROPERTIES
- Production amounts
- Ambient Concentrations
- Effective dose…
- Mortality
- Development
- Population
- Nutrient cycling…
EXPOSURE
HAZARD
RISK


Composition
Bandgap
Size…
Surface affinity
Surface charge/ potential (ζ-potential)
Aggregation rate
Hydrophobicity…
Nanoparticle Properties
Social Properties
System Properties
Product life cycles and value chains
Product use behaviors
ENM production magnitudes
pH, NOM, Ionic strength, …
Surfaces (biotic, mineral, organic…)
Fluid flow, temperature…
Exposure
Hazard
RISK

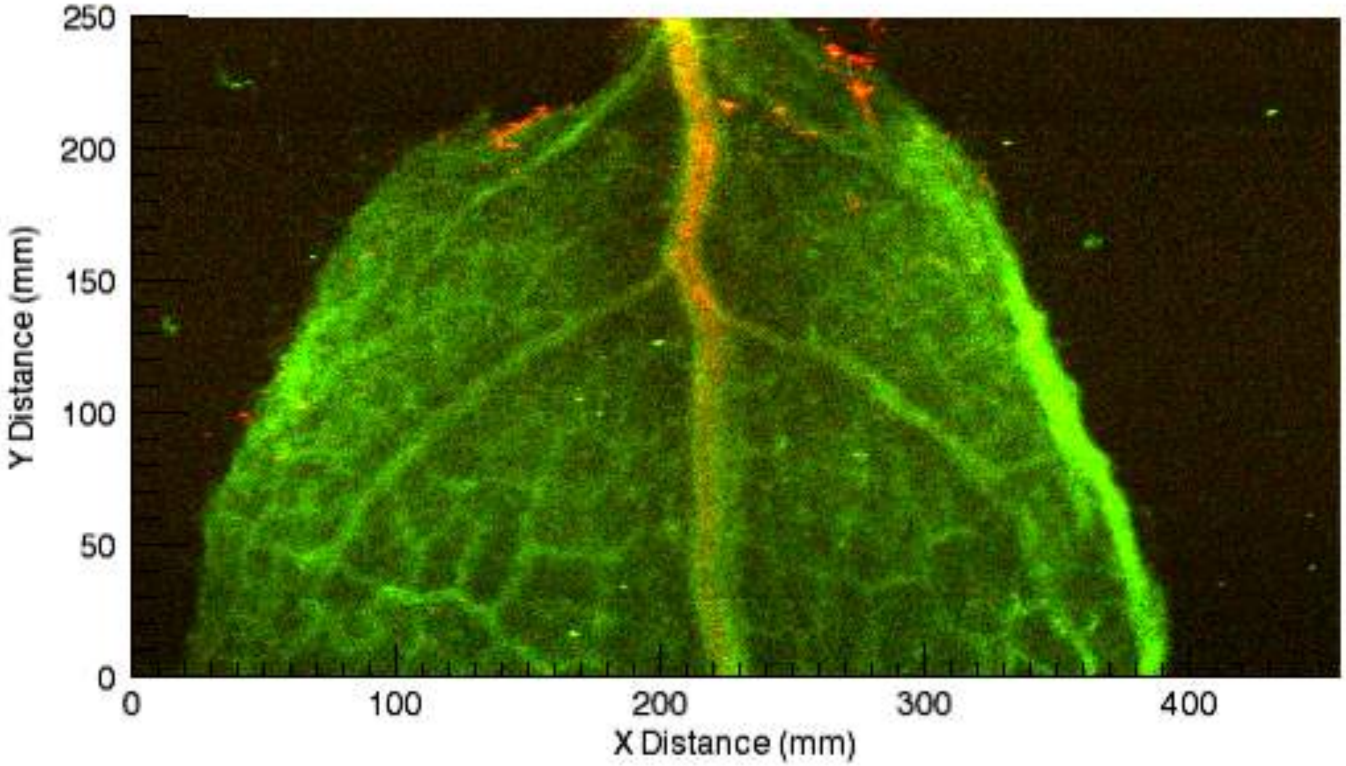


- Measurement in **prescribed system**
- Quantifies a meaningful process for exposure, hazard or both

Functional Assay Focus – Fate & Transport Example



Translocation of Au NPs in *Nicotiana xanthi*



30 nm Au-citrate NPs

Judy et al., ES&T 46:8647 2012

Effect of Particle Size and Shape on Reactivity

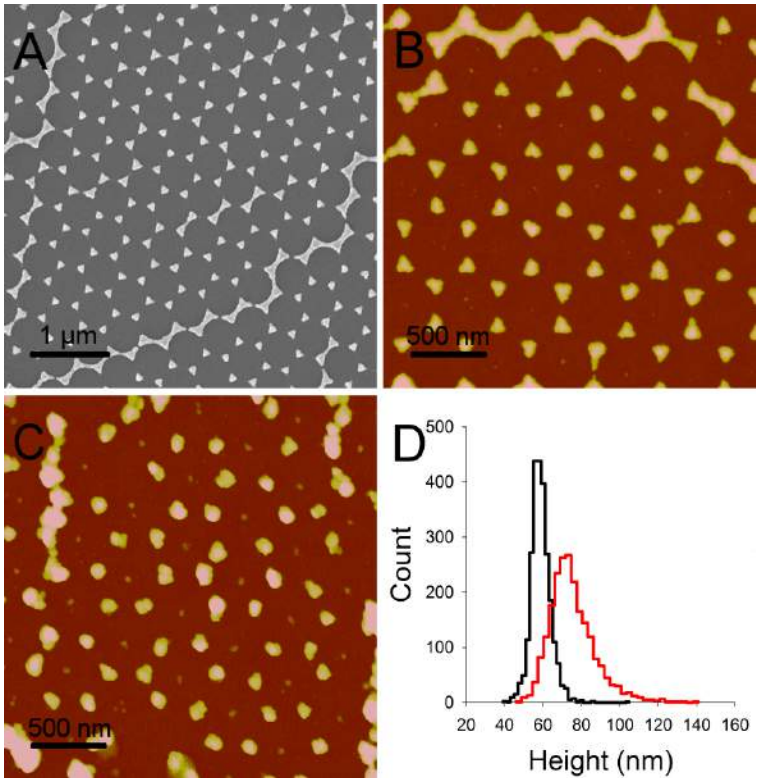


Figure 1. A) SEM and B) AFM images of unsulfidized AgNP arrays produced by NSL. C) AFM image of an AgNP array after a 2-d exposure to 10 µM Na_2S. D) AgNP height distributions before (black) and after (red) the exposure.

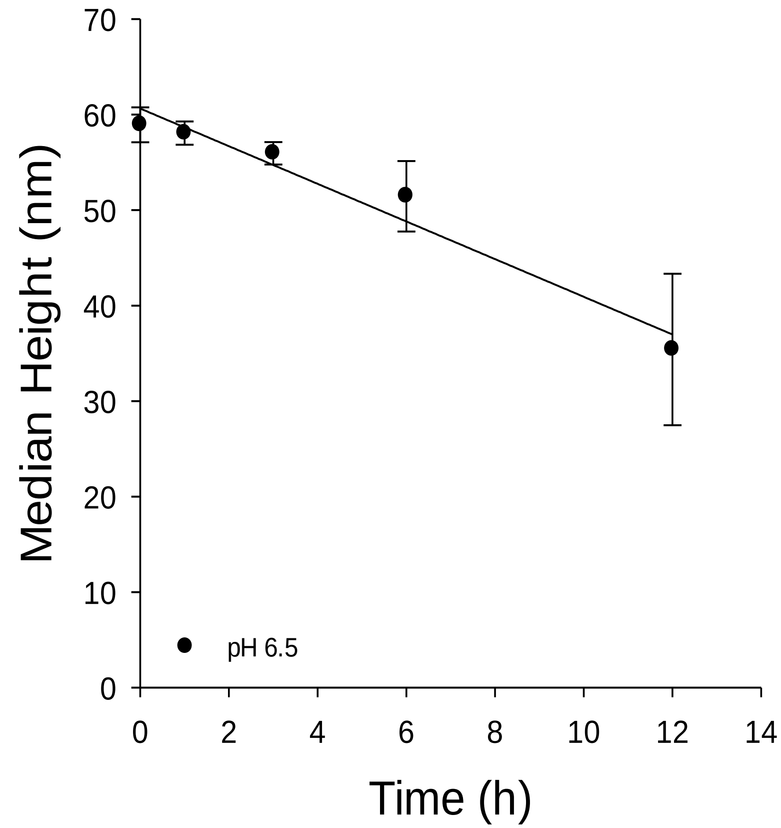
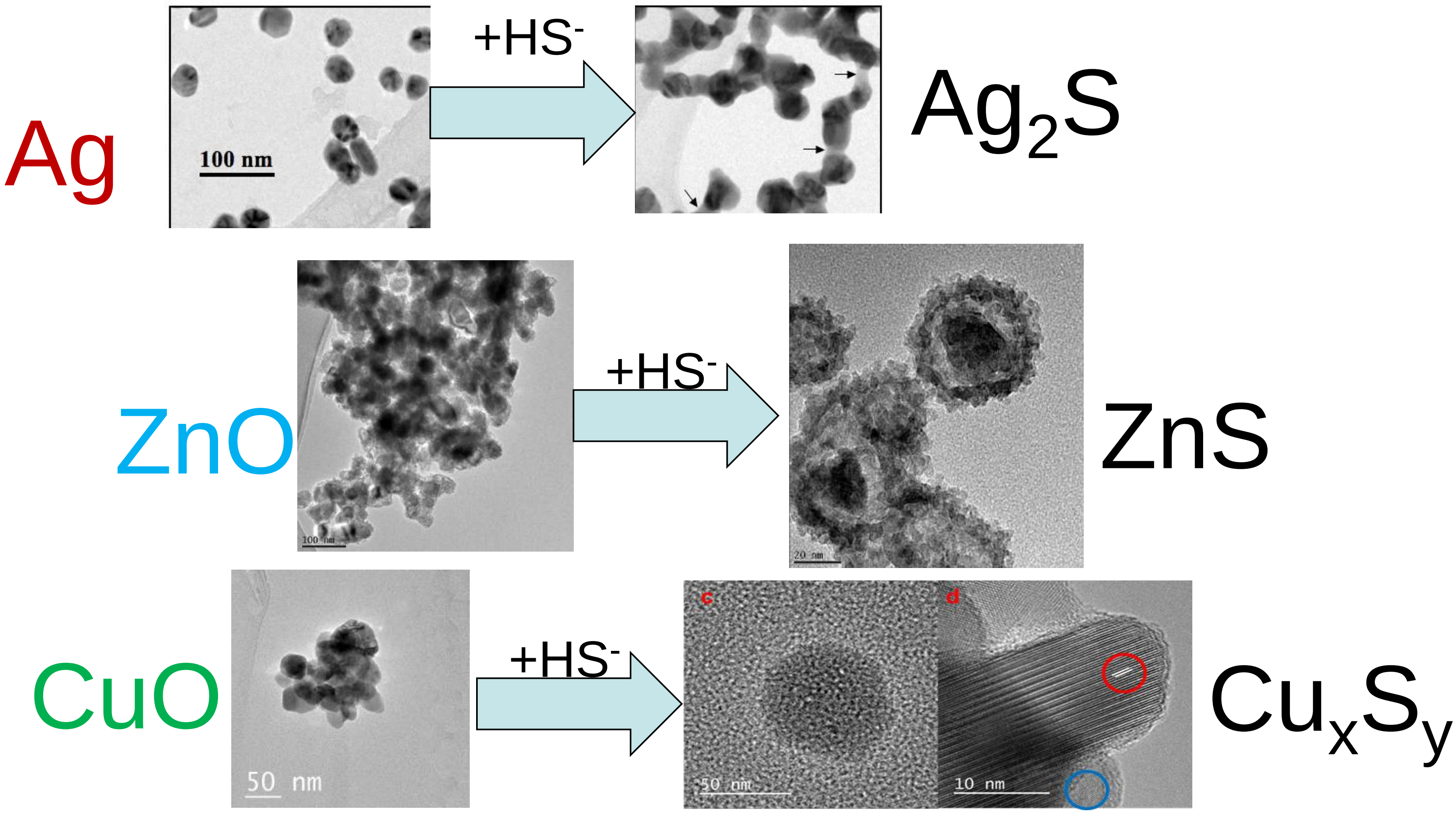


Figure 3. AgNP dissolution in 1 mg/L NaOCl at pH 6.5. Error bars are standard deviations of triplicate samples.

Sulfidation of Ag, ZnO, and CuO NPs



Ma et al., 2013 *ES&T* 47 (6), pp 2527–2534; Levard et al., *ES&T 2011 45 (12),* 5260.

Ma et al., 2014 *ES Nano*

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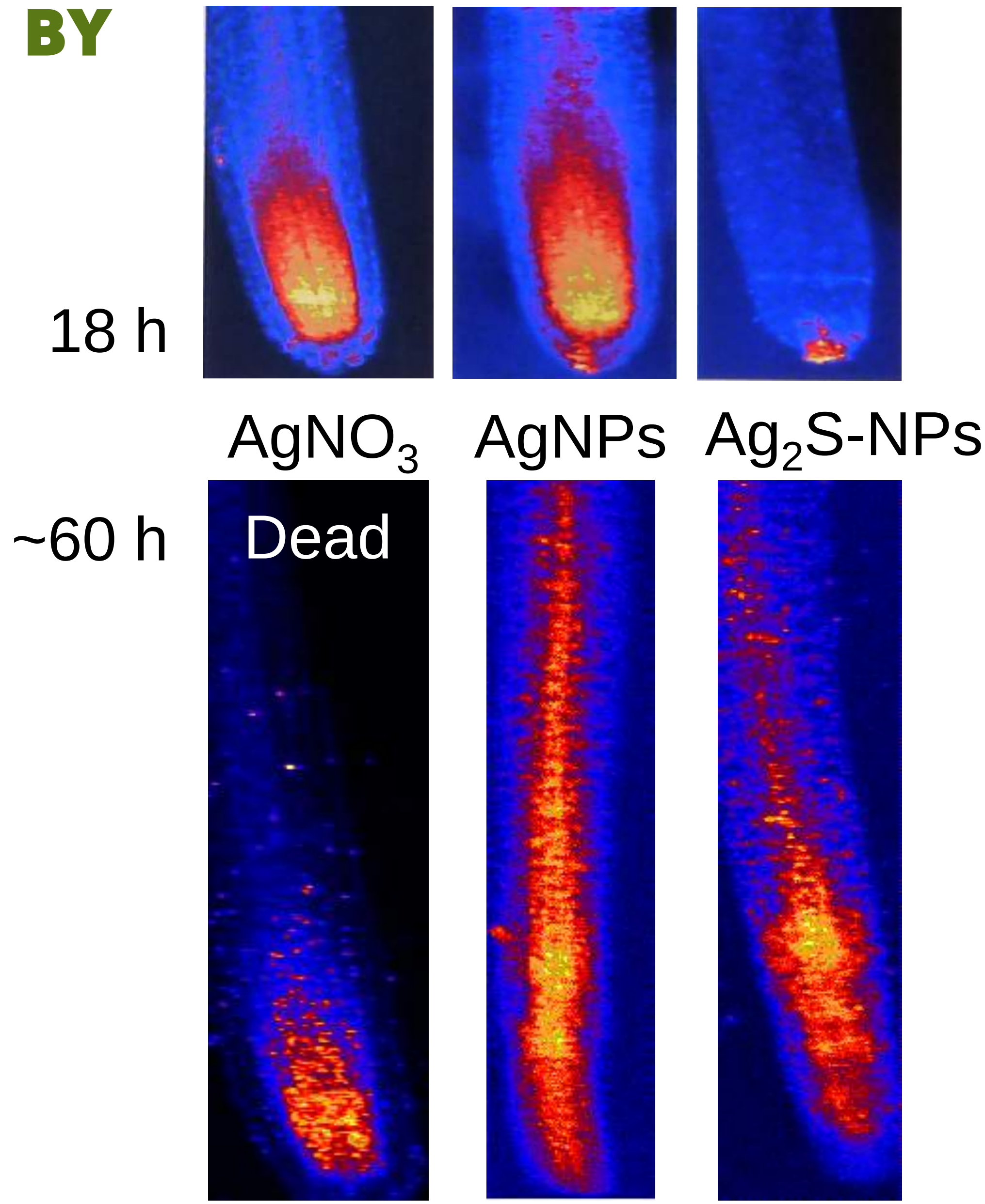
Mode of Uptake of Ag by Duckweed

Duckweed
Landoltia punctata

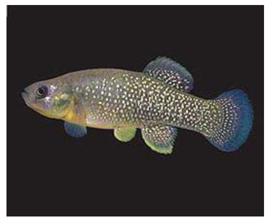


Stegemeier et al., *ES&T* (in preparation)

Sulfidation Decreases Toxicity

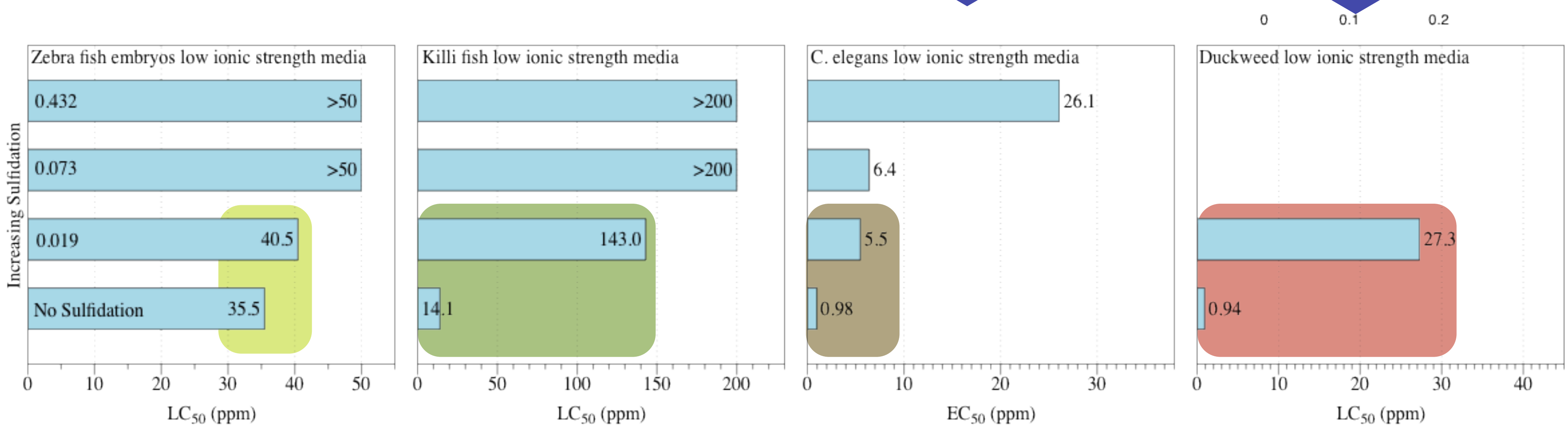
Zebrafish

Killifish



C. Elegans

Duckweed



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Levard, Hotze, et al., *ES&T 2013, 47, 13440−13448*

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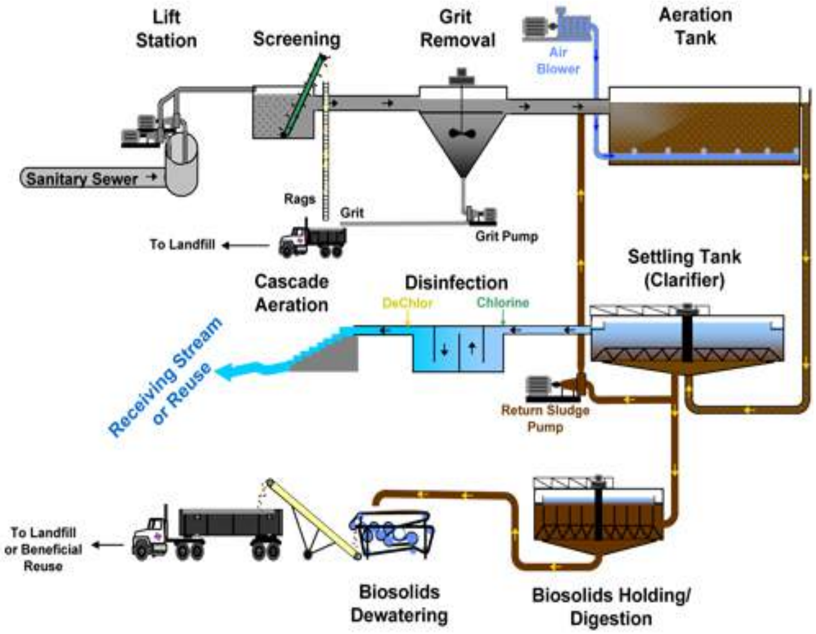
"Real World" Transformations

Wastewater Treatment Plant



Freshwater Wetland

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ZnO Fate in the Wastewater System?

Primary clarifier (180 L)

Anaerobic digester (150 L)

Secondary clarifier (150 L)

Zn^{2+}

Control

ZnO NP

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ROTHAMSTED RESEARCH

NATURAL ENVIRONMENT RESEARCH COUNCIL

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Mesocosms:
Controlled Release Field Sites

- 30 mesocosms
- year-long experiments
- pulse & chronic inputs
- Nano- Ag, CeO2, Cu, Au, TiO2, SWCNTs
- NPs+conventional contaminants
- Release form commercial productions

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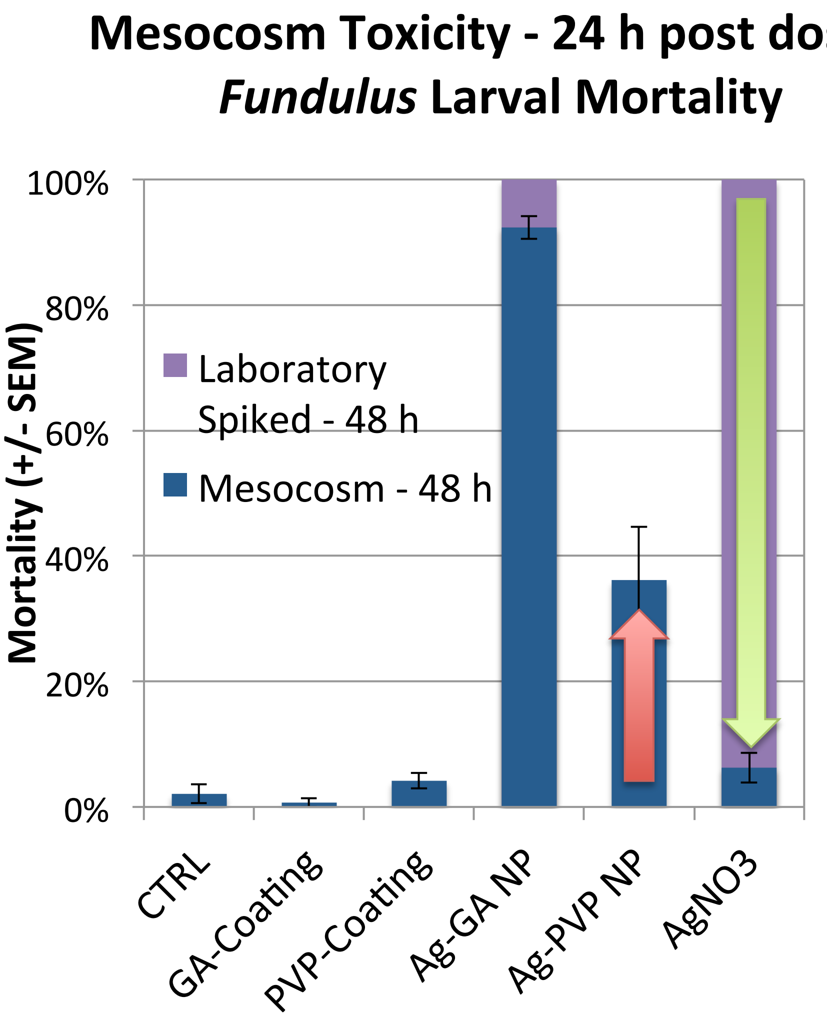
Mesocosm Results



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NSF EF-0830093

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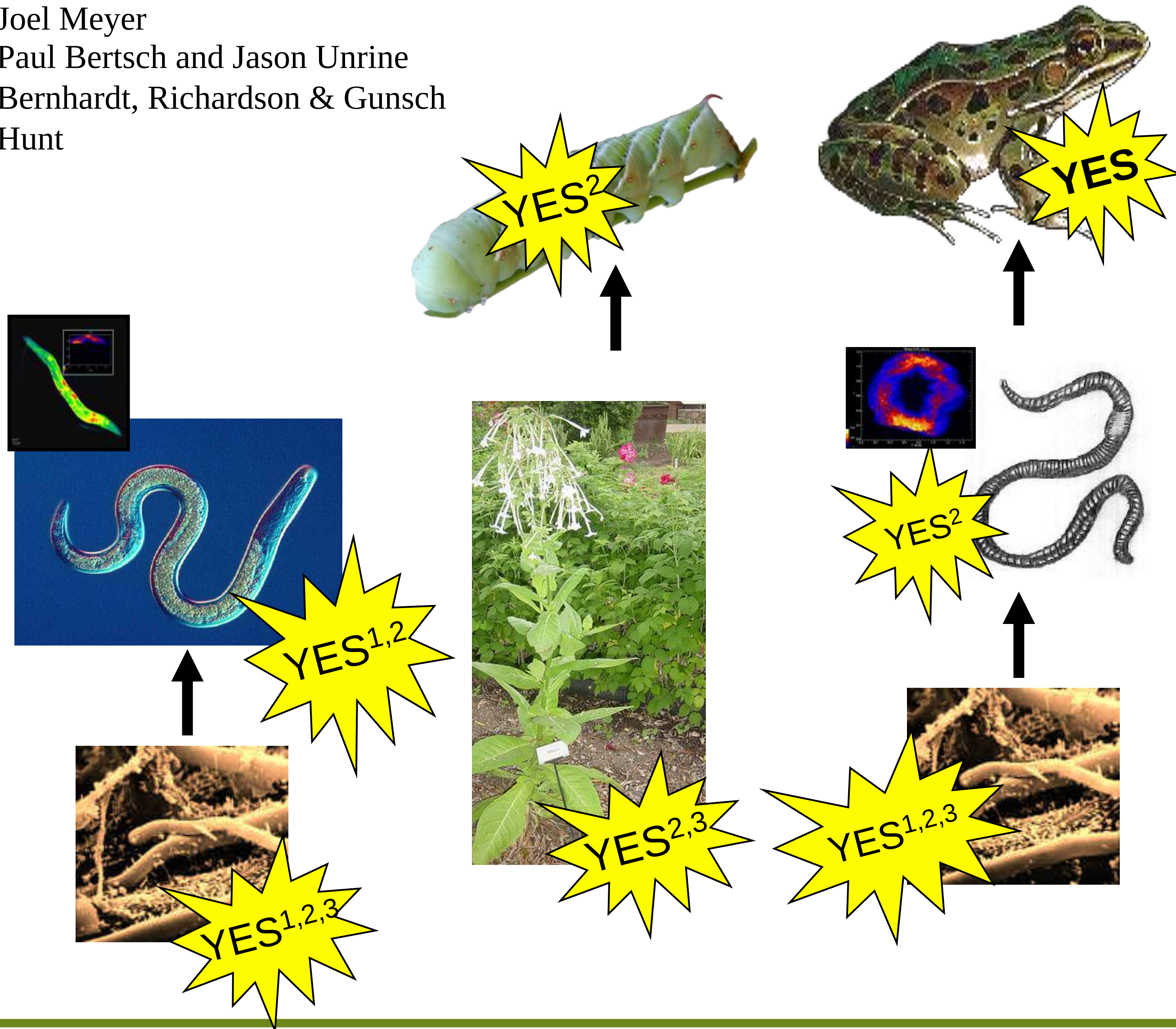
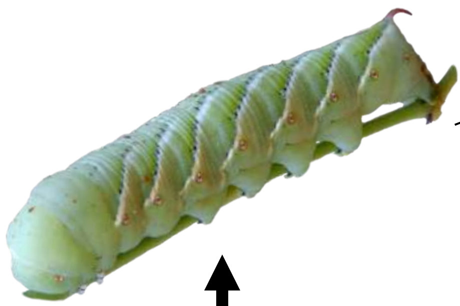
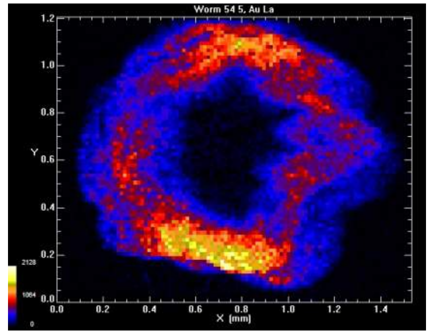
[1]Joel Meyer
[2]Paul Bertsch and Jason Unrine
[3]Bernhardt, Richardson & Gunsch
[4]Hunt

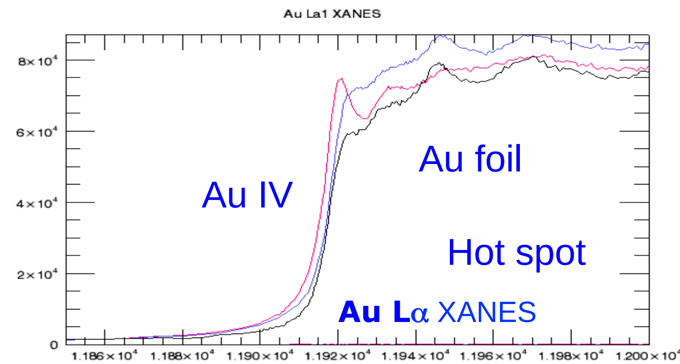


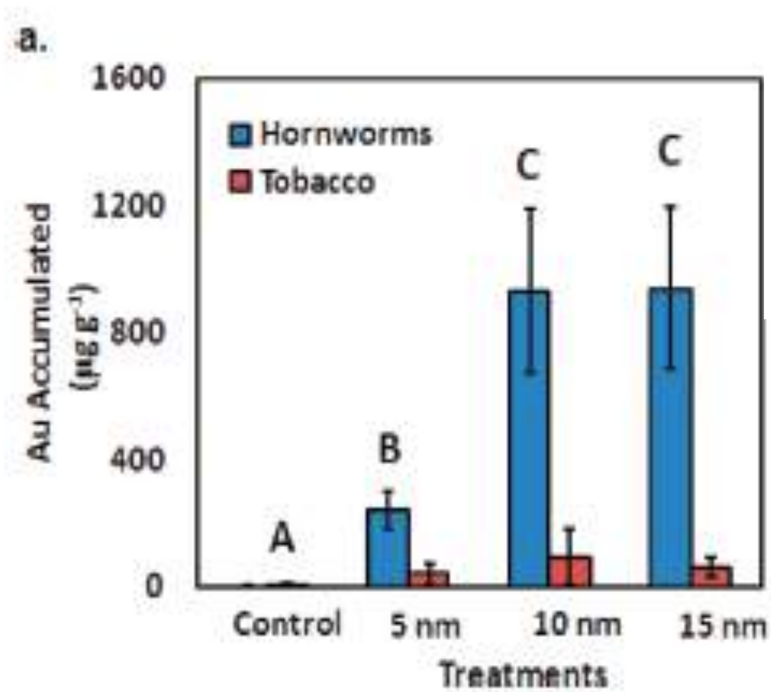
Evidence for Biomagnification of Gold Nanoparticles within a Terrestrial Food Chain

JONATHAN D. JUDY, JASON M. UNRINE, AND PAUL M. BERTSCH*










COVER STORY
CHEMICAL YEAR IN REVIEW
C&EN highlights the major research achievements of 2011 and revisits trends in research from a decade ago. PAGES 13, 17


NANOMATERIALS IN THE FOOD CHAIN

Nanoparticles show tremendous promise for drug delivery, and they are already being used as functional materials in consumer products such as paint and cosmetics. But scientists demonstrated this year that the tiny materials warrant additional scrutiny as they've begun to swirl down drains and otherwise end up in the environment. Studies showed that not only do some nanoparticles transfer from organism to organism in the food chain but that they also increase in concentration,

A hornworm caterpillar feeds on tobacco leaves containing gold nanoparticles; in the inset, a cross-sectional X-ray fluorescence map shows the nanoparticles (yellow and orange) collected around the caterpillar's gut.

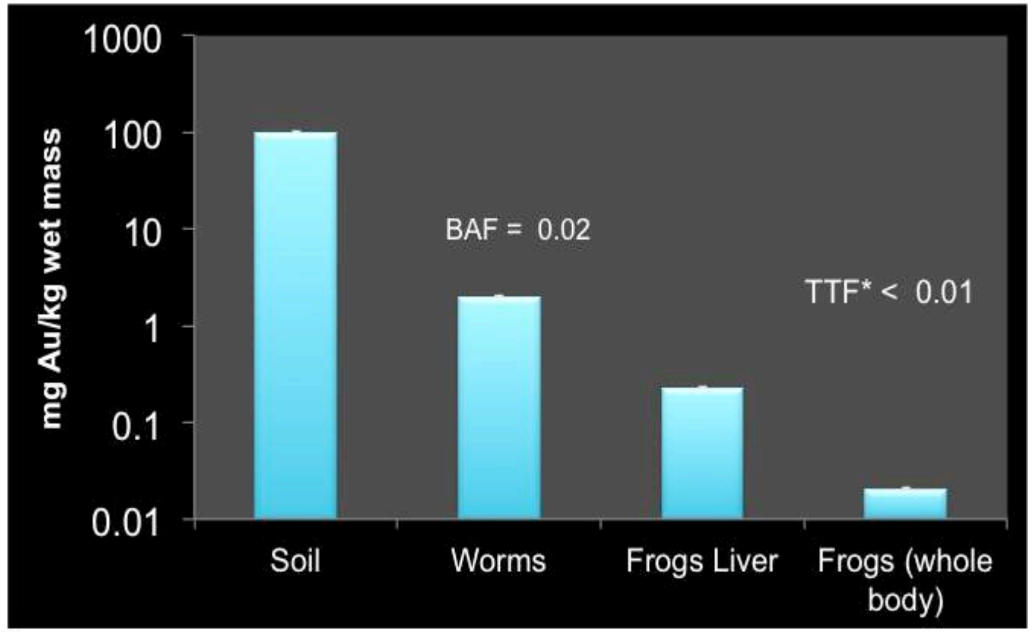
COURTESY OF PAUL BERTSCH & JONATHAN JUDY

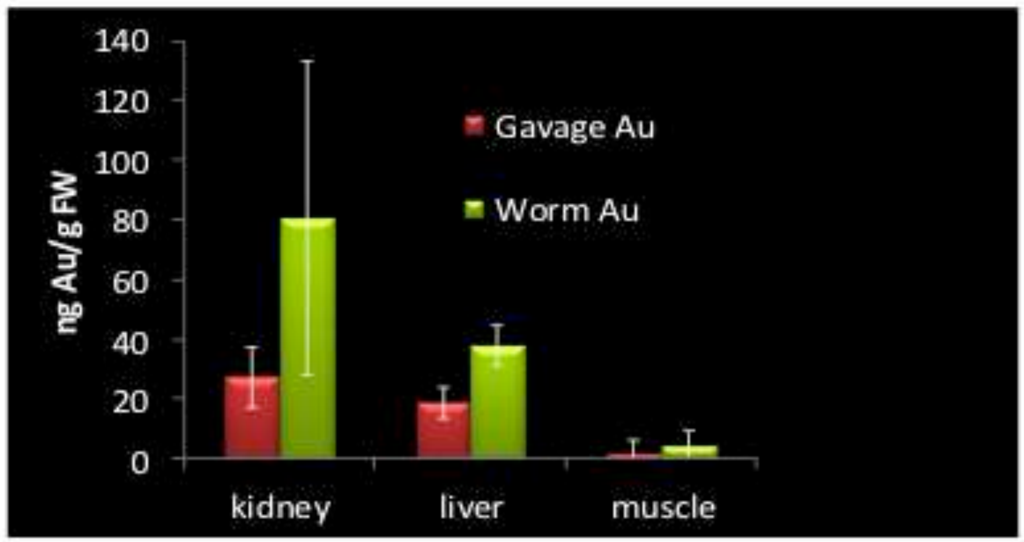
Judy et al., 2011 ES&T

Trophic transfer & dilution of Au NPs

Rana catesbeiana

Eisenia fetida





Unrine et al. *ES&T 2012*

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What parameters are needed to predict transport and fate of nanoparticles/

Solutes	Nanomaterials
Distribution Coefficient	Distribution Coefficient
K_{ow}	Surface affinity
	Hydrophobicity, surface charge…
solubility	Dissolution rate
Henry's constant	N/A
Vapor pressure	??
Bioaccumulation factor	Bioaccumulation factor
Biodegradation rate	Bio-disassembly rate
Reaction rates	Transformation rates

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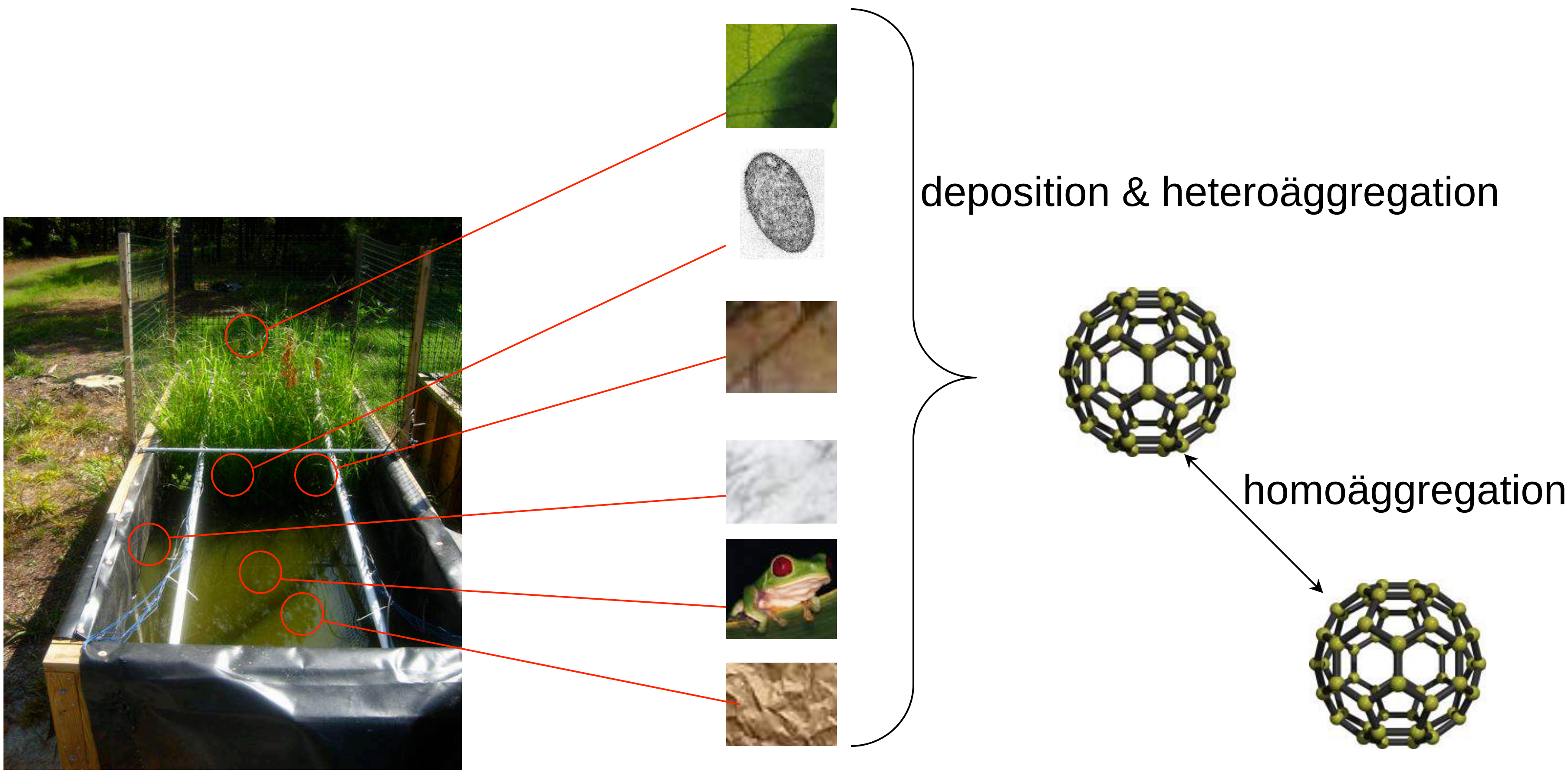
Affinity of nanoparticles for various surfaces



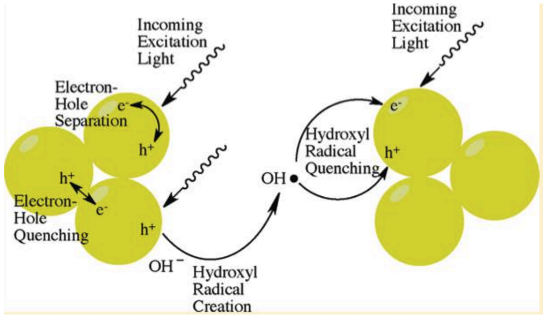
Aggregation, Transport and Surface affinity

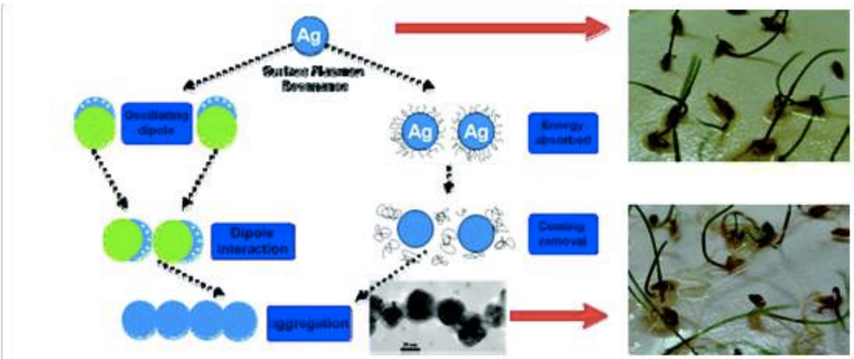
$$\frac{dn_k}{dt} = \frac{1}{2}\alpha \sum_{i+j \to k} \beta(i,j) n_i n_j - \alpha n_k \sum_i \beta(i,k) n_i$$

+/- breakup –settling – dissolution…

Aggregation:
- *Dissolution*
- *Reactivity*
  - *Photo-catalysis*
  - *Molecular Adsorption*
- *transport*

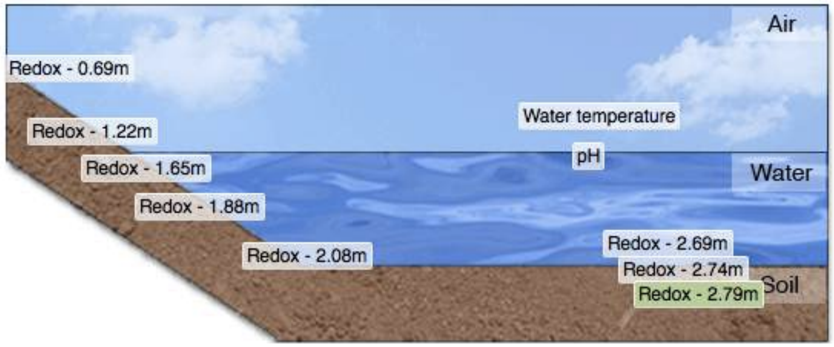
Deposition:
- *Environmental dispersal*
- *Biouptake*
- *Translocation in organisms*

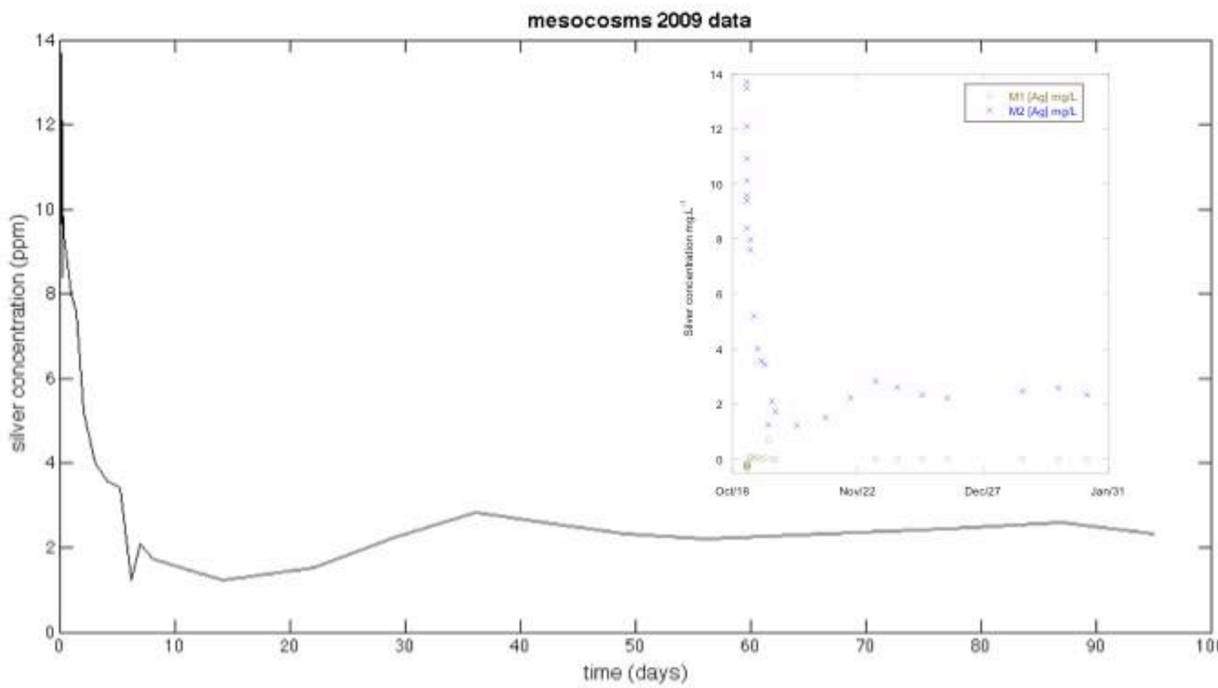




Hotze et al., *Langmuir* 2010, 26(13), 11170–11175
Jassby et al., *Environ. Sci. Technol*. 2012, 46, 6934−6941

Nanosilver concentration in water column of mesocosm following pulse input





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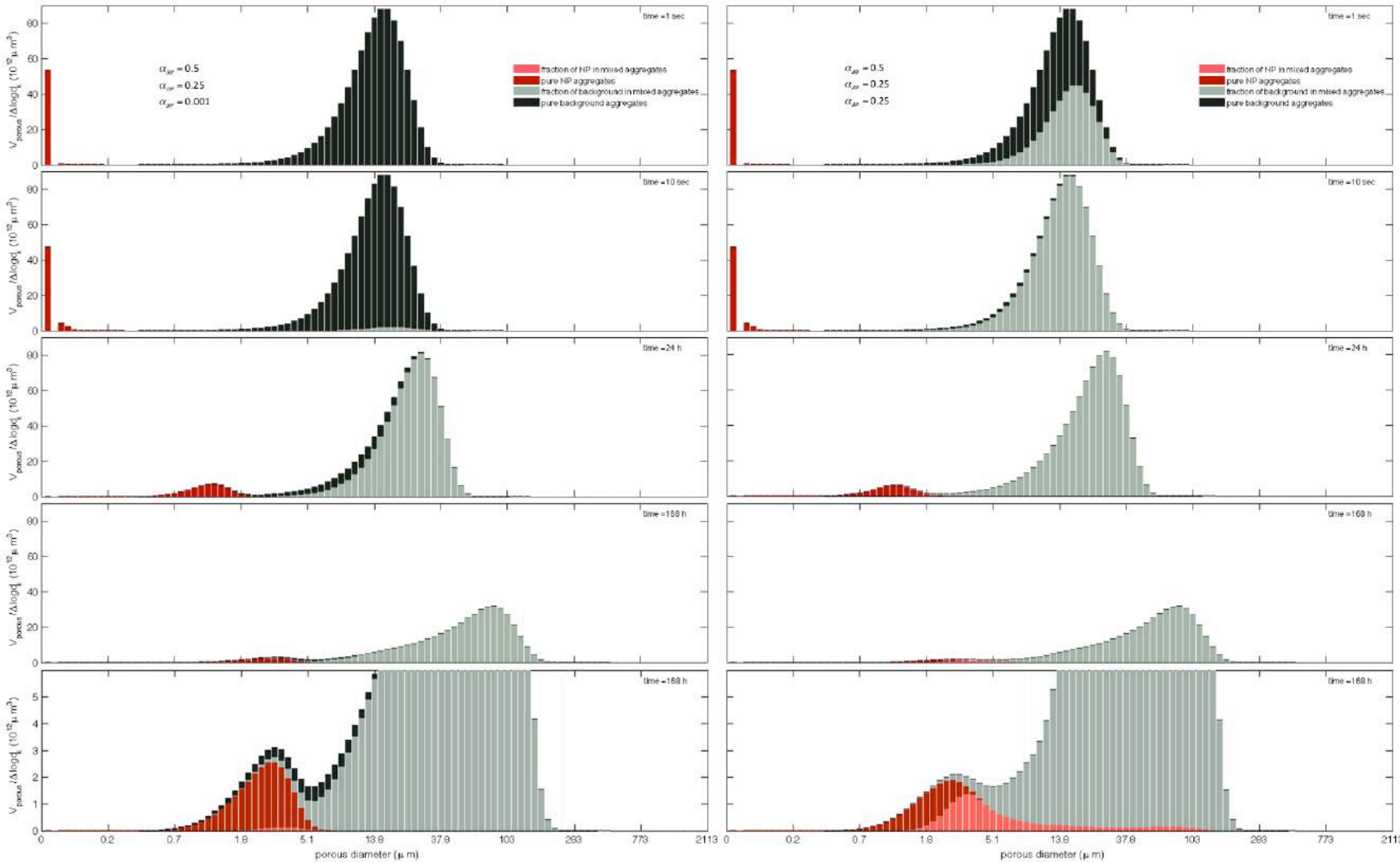
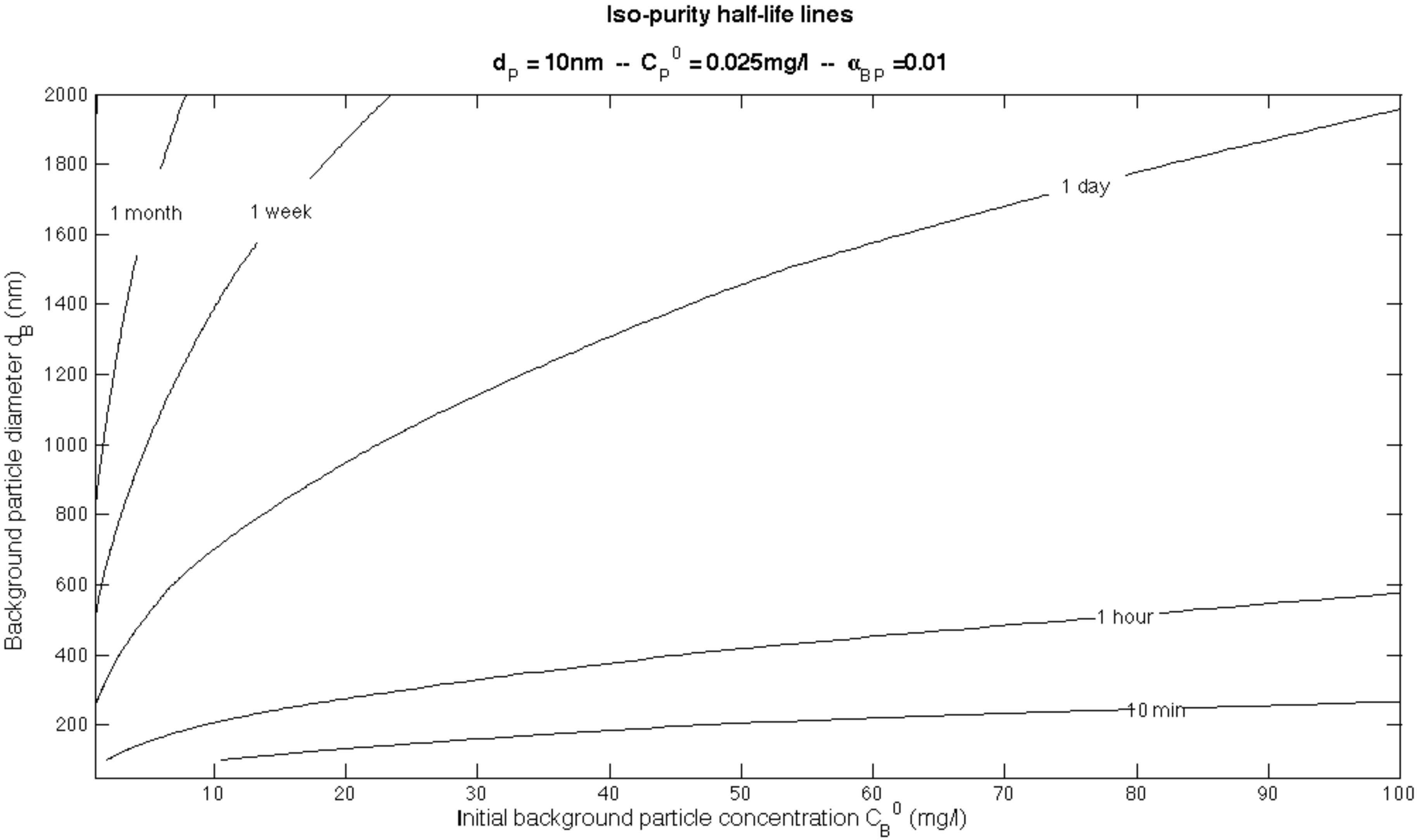
Simulations of heteroaggregation





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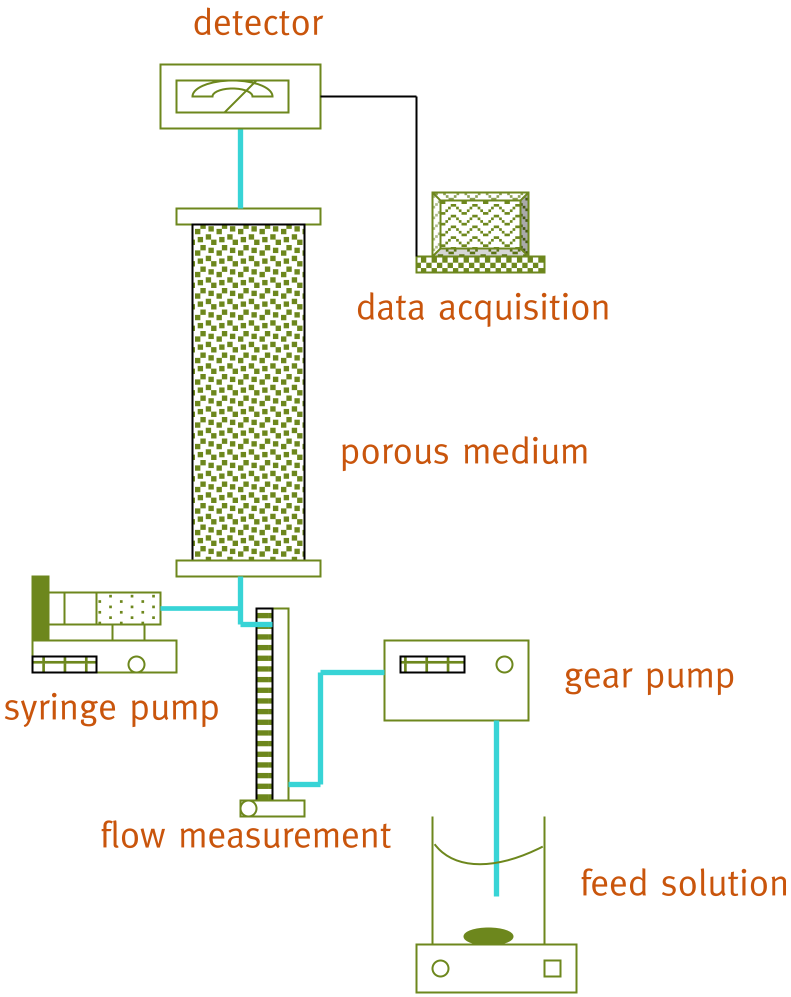
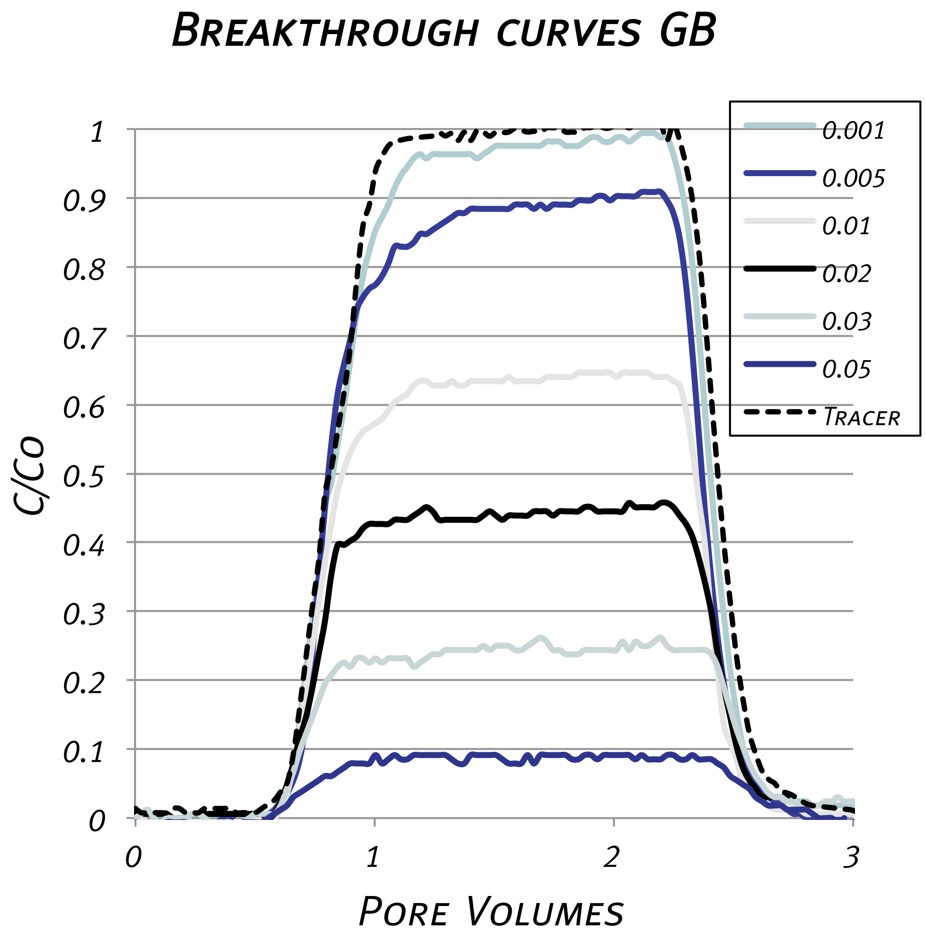
Measuring surface affinity (alpha) in model systems





Measuring surface affinity in complex systems

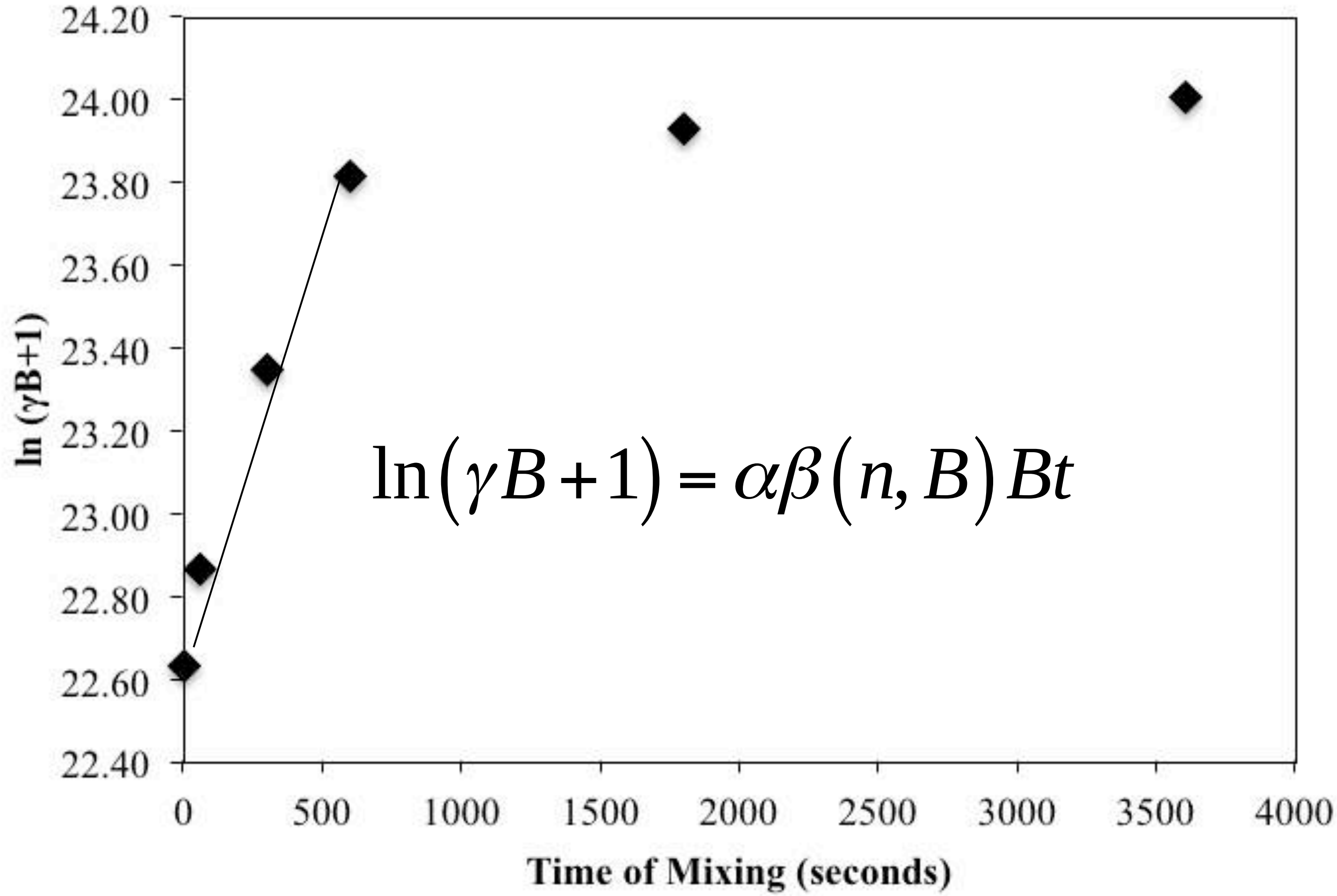
$$\frac{dn_k}{dt} = \frac{1}{2}\alpha \sum_{i+j \to k} \beta(i, j) n_i n_j - \alpha n_k \sum_i \beta(i, k) n_i - breakup$$

$$\frac{dn}{dt} = -\alpha\beta(n, B)nB + k_B(n_0 - n)$$

$$\ln(\gamma B + 1) = \alpha\beta(n, B)Bt$$

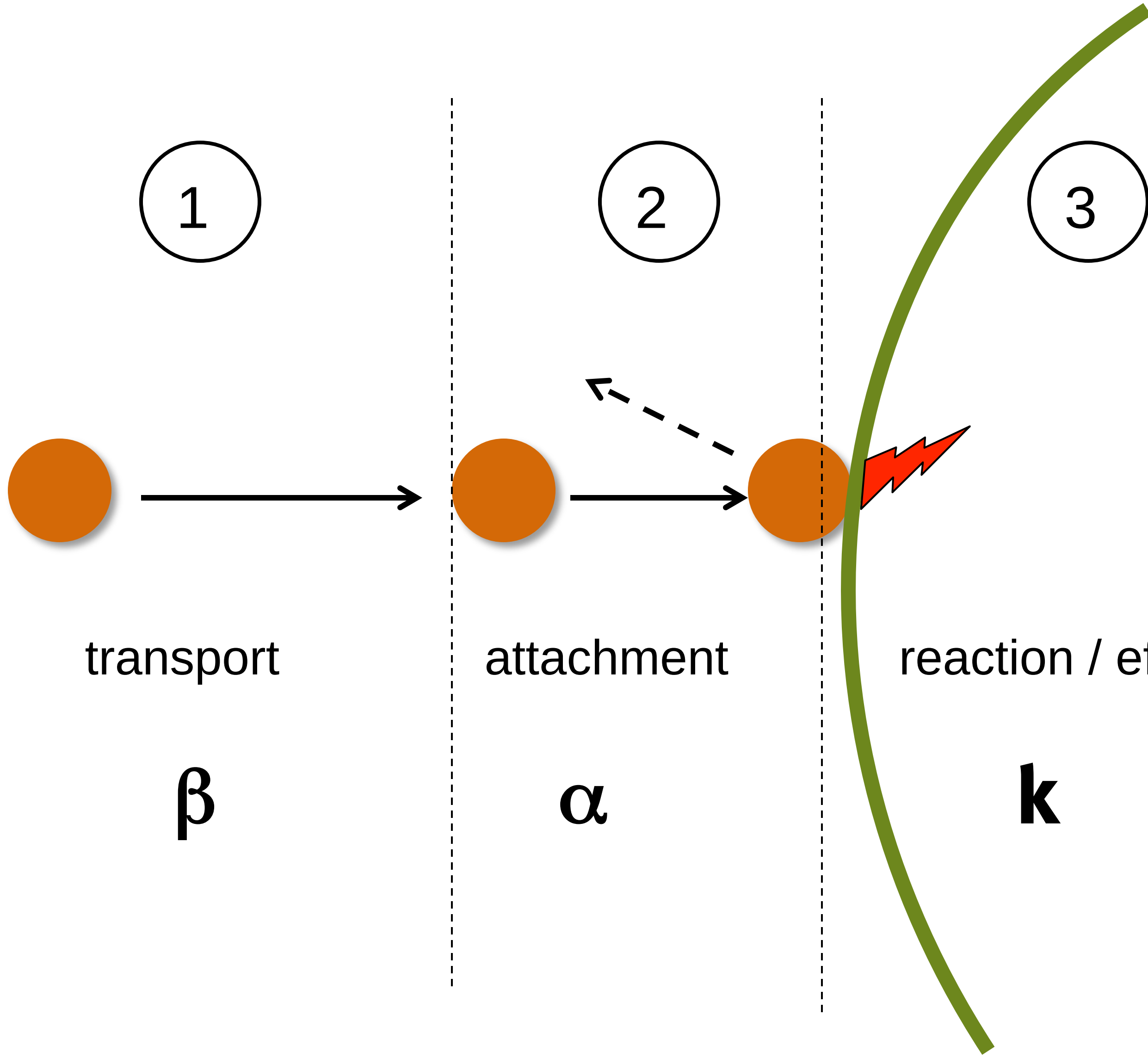
Barton et al., ENVIRONMENTAL ENGINEERING SCIENCE
Volume 31, Number 7, 2014

Transformed distribution coefficient aggregation time

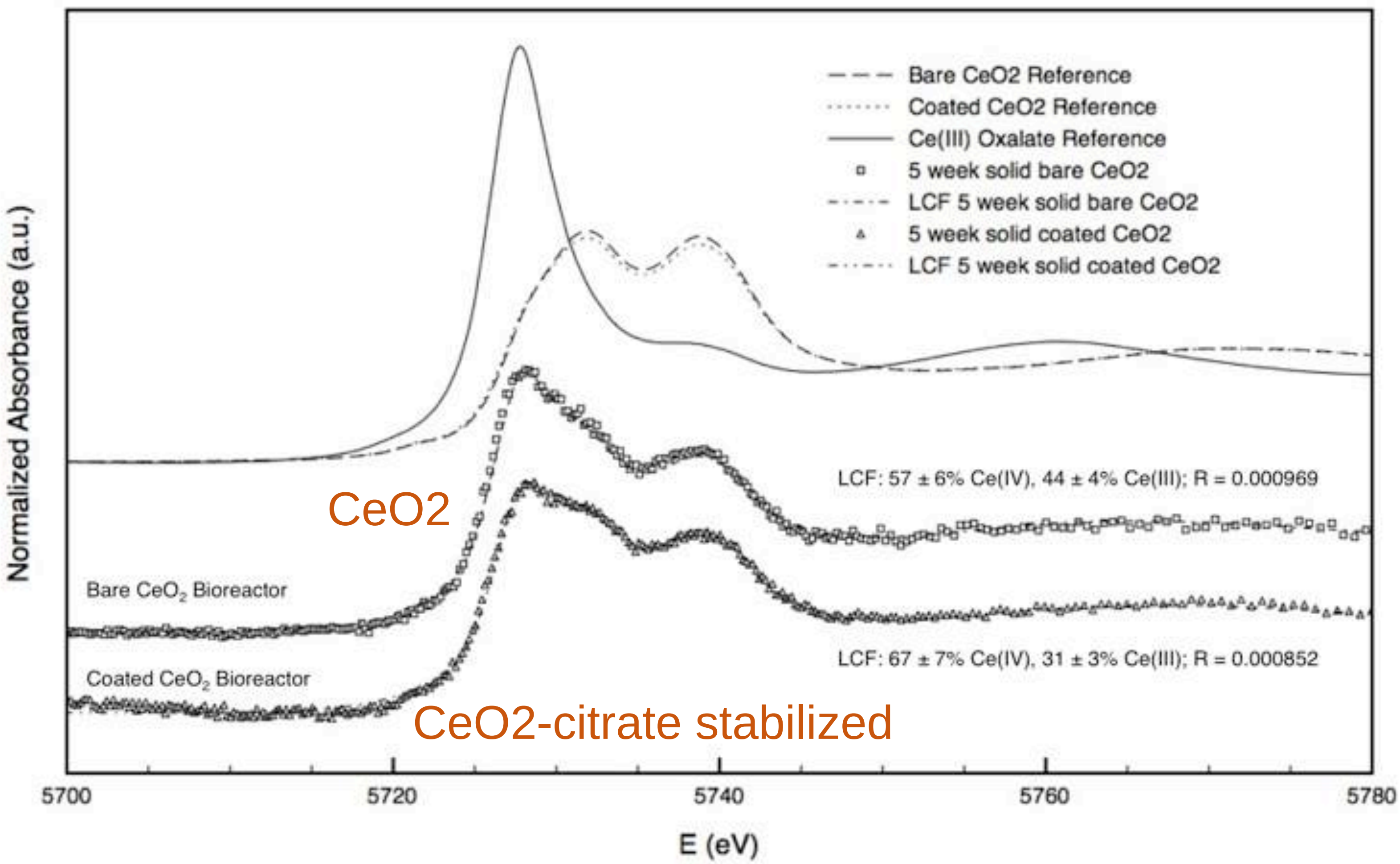


$$\ln\left(\gamma B+1\right)=\alpha\beta\left(n,B\right)Bt$$

Conceptual model for nanoparticle reactivity



Importance of surface affinity for transformtion: CeO2



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Barton et al. 2014 (in review)

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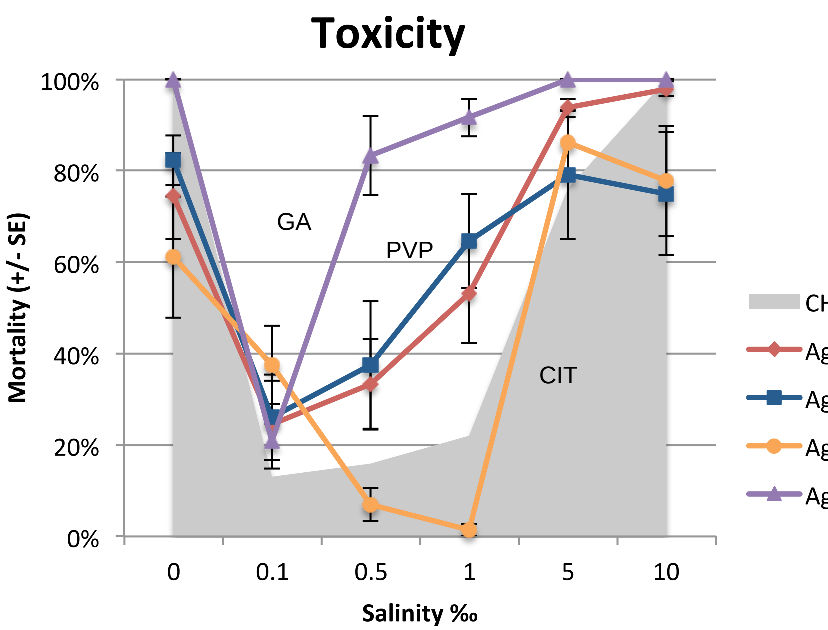
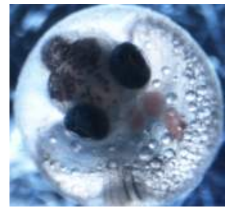
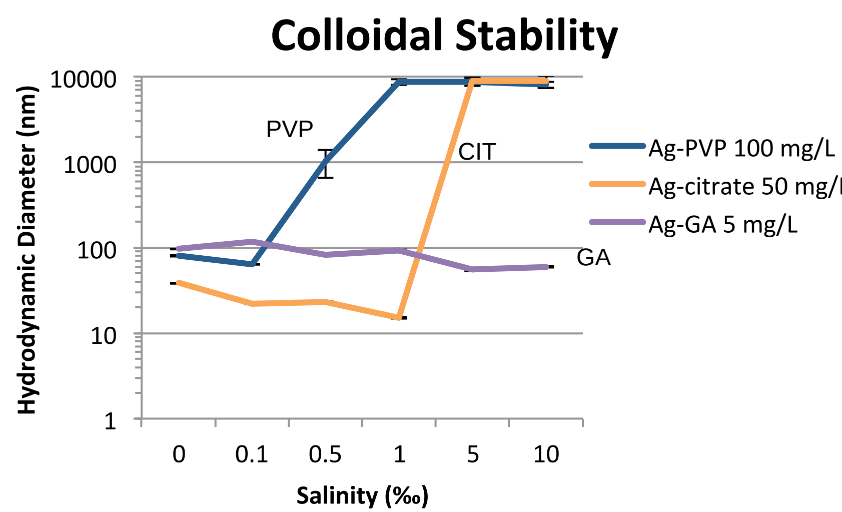
Ag NP Embryotoxicity across a Salinity Gradient – The Role of Coatings and Dissolved Silver





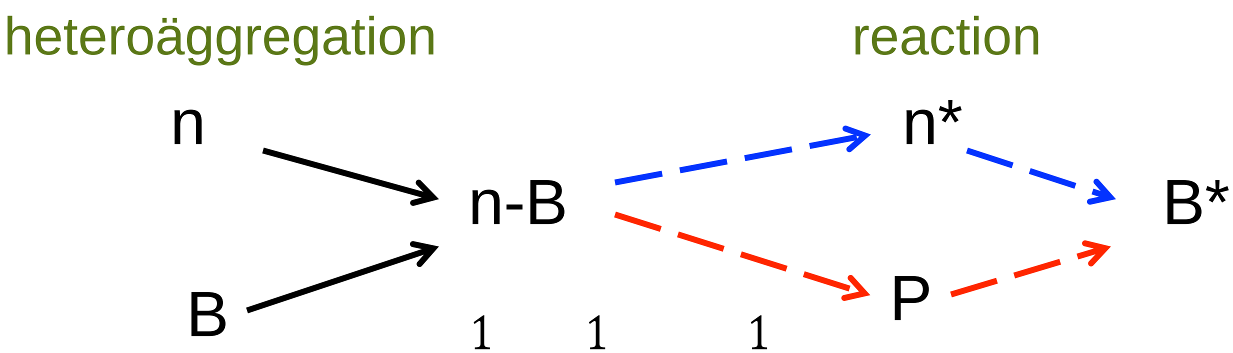
Atlantic killifish
Fundulus heteroclitus



- Ag NP coatings significantly affect particle behavior
  - Stability/Aggregation (Ag-gum arabic most stable)
  - Toxicity (Ag-gum arabic most toxic)
- Dissolved silver and silver speciation play a significant role in toxicity
  - Toxicity curve shape related to silver speciation (total dissolved Ag, not Ag^{+})

Examples of nanoparticle reactivity

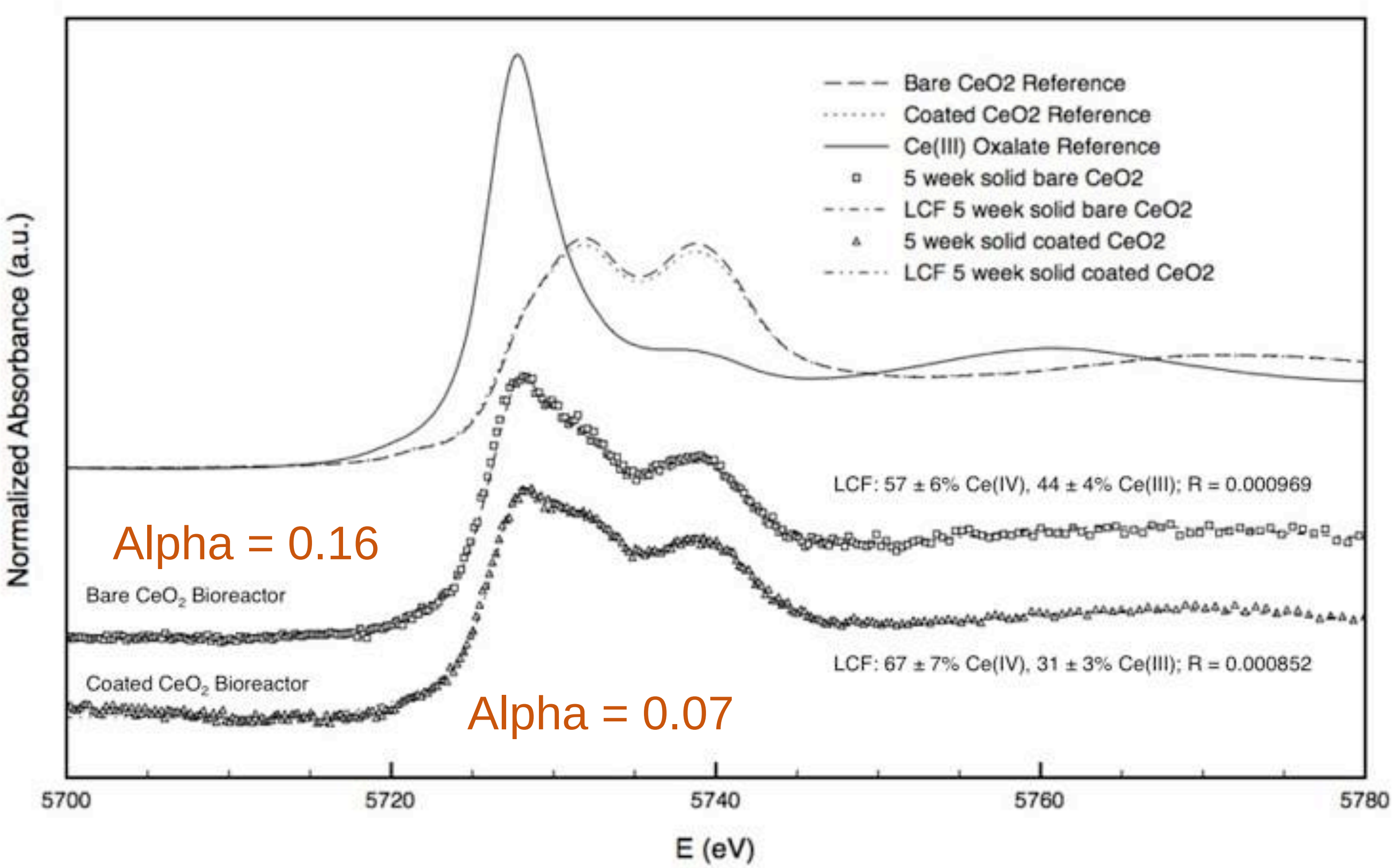
Effect	Underlying reaction
Toxicity to plants and fish by nano Ag	Nano silver dissolution
Viral inactivation by fullerol	Singlet oxygen generation
Bacterial inactivation by CeO2	Ce reduction



$$\frac{1}{k_T} = \frac{1}{k_{red}} + \frac{1}{\alpha_{NB}\beta nB}$$

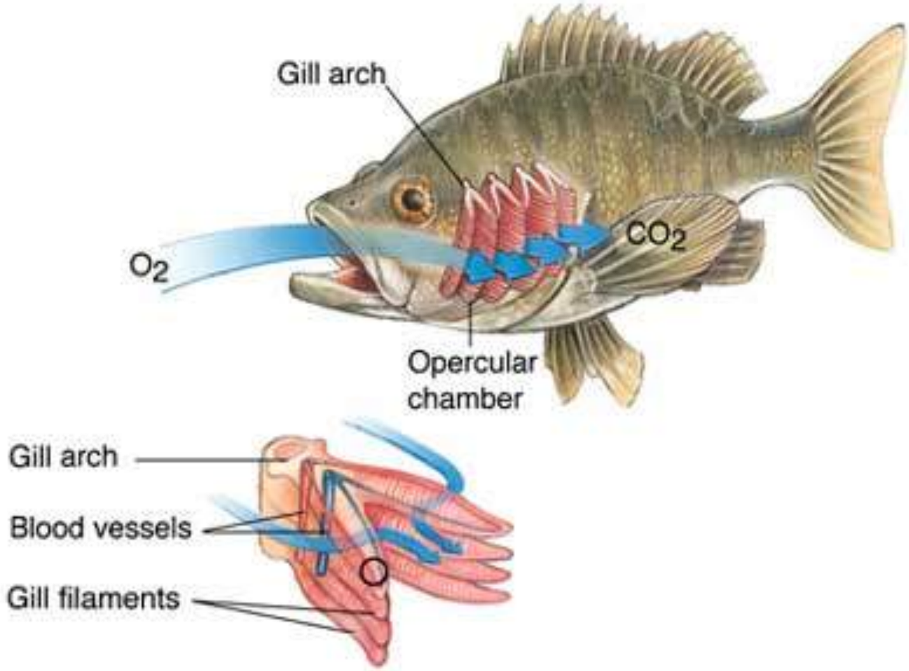
$$k_T = \frac{k_{red}\,\alpha_{NB}\,\beta nB}{k_{red} + \alpha_{NB}\,\beta nB}$$

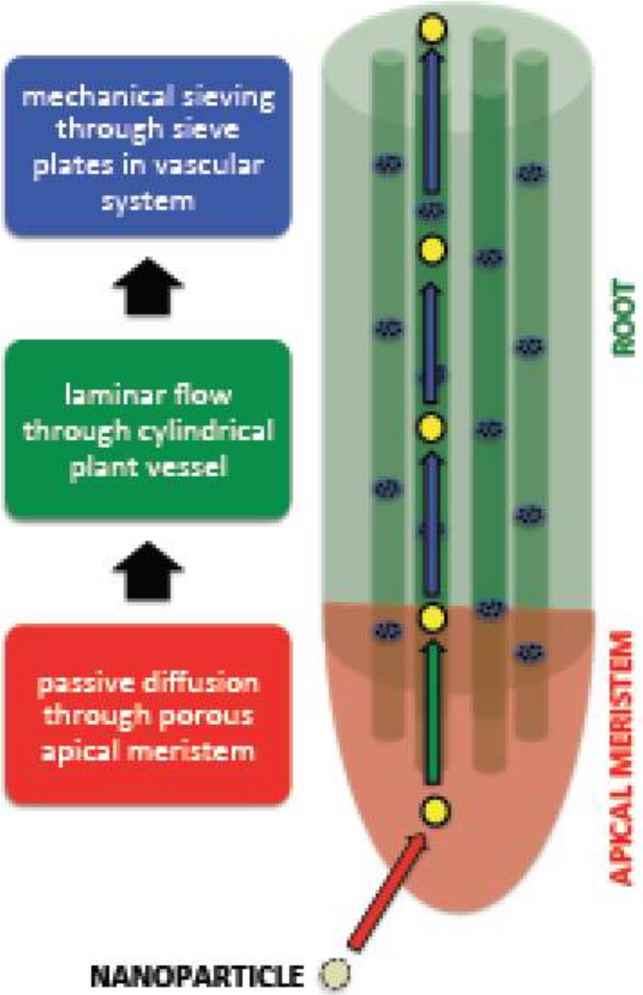
Importance of surface affinity for transformtion: CeO2



Barton et al. 2014 (in review)

Particle deposition and translocation in organisms





Summary

1. Need for functional assays (like surface affinity) for key processes (Transport, transformation, bioüptake…)

2. Many interactions between nano-scale materials, organisms and ecosystems- RICH SCIENTIFIC TERRAIN

Some take home points:

(WPB addition, based on summary comments from MRW)

- Nanoparticles (whether engineered [“ENPs”] or natural):
  can be taken up by plants and animals;
- NPs are subject to trophic transfer- in some cases with biomagnification, in some with dilution;
- Attachment efficiencies appear to be a promising way of predicting NP behavior.
- The toxicity issue is secondary.
  Most important -- growing awareness of:
  - Complexity of nanometric phases in their interactions with living systems; and
  - Potentially important roles of NPs in uptake of chemicals, nutrient cycling, transport of other species, etc.

Thank You

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