TiO₂ NP Photocatalyzed Degradation of Benzo(a)pyrene Increases Toxicity to Zebrafish

A. Bone¹ and R.T. Di Giulio¹

Objective: Determine effect of photocatalytically degrading benzo(a)pyrene using TiO₂ NP on larval zebrafish.

A. Solutions of BaP photocatalytically degraded with TiO₂ NP (1ppm) induced more PAH-related toxicity and exposure than solutions of BaP exposed to UV alone, or unilluminated BaP.

B. At higher levels of TiO₂ NP (>2 ppm), mortality is seen only in these solutions. No mortality occurs in any other treatments (B). Mortality is dose-responsive to both BaP and TiO₂ NP concentrations.

C. Increased toxicity is likely due to production of a more toxic BaP daughter product. Chemical analysis of degradation products is underway.

¹ Nicholas School of the Environment, Duke University
Environmental Transport & Transformations: Nano Examples from Natural and Engineered Highly Complex (Real) Environments

Carol Johnson¹, Bojeong Kim¹, and Michael F. Hochella, Jr.¹

Nano Iron Oxide Redox Transformations in Minewater Outflow

Observations

U mine groundwater outflow (anoxic)

- Redox boundary

Green Rust nano-platelets

Fe²⁺Fe³⁺(OH)₁₀•4(H₂O)

Outflow stream water (oxic)

- Fe²⁺(aq)
- Fe³⁺(aq)
- Dissolution, precipitation

- Sedimentation, aging

Underlying sediment (oxic)

- Amorphous iron (oxyhydr)oxides coated with amorphous silica
- Particles grow, goethite nanoneedles form from surface

Proposed Mechanism

Nano Titanium Dioxide (TiO₂) in Sewage Sludge and Sewage-Amended Soils

TiO₂ Nanoparticles (NPs) Production & Use

Sewage Treatment Plant Sewage Sludge Products

- TiO₂ NPs were repeatedly identified across the sewage sludge types tested.
- They have faceted shapes with the rutile crystal structure, and typically form small, loosely packed aggregates.

Terrestrial Environment Agricultural Soils

- 8 weeks incubation in the field after soils amended with Ag NPs-spiked sewage sludge materials.
- TiO₂ NPs from sewage sludge products interact with Ag and then enter the environment as a soil amendment.

¹Department of Geosciences, Virginia Tech University

NSF EF-0830093
Silver Nanoparticles affect *Drosophila*

Najealicka Armstrong, Malai Ramamoorthy, Delina Lyon, Kimberly Jones, Atanu Duttaroy
Department of Civil and Environmental Engineering, Howard University

AgNPs interfere with Cu-dependent enzymes, affecting biological processes in the fruit flies.


NSF EF-0830093
Attachment Efficiency: 
Predicting ENM transport and attachment

Delina Lyon¹, Shihong Lin², Stacey Louie³, Ricardo Charles¹, Greg Lowry³, Mark Wiesner², Kimberly Jones¹

- Attachment efficiency, $\alpha$, can be used to predict NP transport in the environment by using compositional weighted averaged $\alpha$ values.
- Models/theories can be developed to predict $\alpha$ for ENMs and coated ENMs.

¹ Department of Civil and Environmental Engineering, Howard University
² Department of Civil and Environmental Engineering, Duke University
³ Department of Civil and Environmental Engineering, Carnegie Mellon University
Modeling Nanosilver Transformations in Freshwater Sediments

Amy Dale¹, Greg Lowry², and Elizabeth Casman¹

¹ Department of Engineering and Public Policy, Carnegie Mellon University
² Department of Civil and Environmental Engineering, Carnegie Mellon University

- Due to their tendency to aggregate, nanomaterials are expected to accumulate in the sediments of aquatic systems, where they will undergo chemical transformations that will affect their toxicity as well as their mobility.

- We have developed a 1-dimensional diagenetic model for nano-silver speciation and distribution in freshwater sediments and calibrated it to CEINT mesocosm data.

- This model will be part of an integrated fate and transport model for nanomaterials to be used in environmental risk assessment and will enable the formulation of science-based policy for the regulation of nanomaterials.
Meta-Analysis of *in vivo* pulmonary toxicity studies
Jeremy Gernand and Elizabeth Casman
Department of Engineering and Public Policy, Carnegie Mellon University

Machine learning techniques produce models relating nanoparticle properties and experimental conditions to indicators of pulmonary toxicity.

Results facilitate the quantitative comparison of factors contributing to toxicity across studies and elucidate the interactions between such factors.

Insights gained from these models test hypotheses relating to nano-particle-specific causes of pulmonary toxicity.

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Jeremy Gernand and Elizabeth Casman (in review) *A meta-analysis of carbon nanotube pulmonary toxicity studies – how physical dimensions and impurities affect the toxicity of carbon nanotubes. Risk Analysis*

NSF EF-0830093
Toxicogenomic Effects of Au-NPs on *C. elegans*


Department of Plant and Soil Sciences, University of Kentucky

- Demonstrated that *rme-2* from the endocytosis pathway is involved in Au-NP uptake
- Genes from a *C. elegans*-specific UPR pathway, such as *pqn-5*, plays a role in detoxification of Au-NPs

Tsyusko et al. *ES&T* 2012 46: 4115
Trophic Transfer Enhances Bioavailability of Au Nanoparticles

J. Unrine, O. Zhurbich, A. Shoults-Wilson, O. Tsyusko and P. Bertsch

Department of Plant and Soil Sciences, University of Kentucky

- Demonstrated trophic transfer of Au nanoparticles.
- Showed that trophic transfer enhances bioavailability of nanoparticles.
- Modeled concentrations over lifespan of predator using a biodynamic model.

Unrine et al. ES&T 2012 46: 9753

NSF EF-0830093
Batch and column studies allow investigation of TiO$_2$ attachment at low concentrations (~100 ppb).
CEINT-NISE Net Partnership- Highlighted as Model

NISE Net invites CEINT Associate Director to highlight museum-university partnerships

CEINT Partnered with NISE Net since 2009- 3 national museum partners

Over 17,000 visitors to CEINT partner museums: NanoDays 2009-13

NanoDays ➔ NanoNights ➔ Nano Camps ➔ Science Cafes ➔ Educational Video

Field trips for museum educators to CEINT ➔ Partner on new Museum grants

Benefits of Museum Partnerships to University Research Center

Interested audiences - broad engagement - network facilitates national expansion

NISE Net templates help students pitch level for science translation

CEINT students value learning science translation

Activities demo CEINT research for broad, continuing use

Allows more depth face-to-face public engagement:

What roles do microbes play in the environment?

How could nanoparticles influence those roles?

Do coatings change where nanoparticles go?

Why are medaka used in CEINT research?

CEINT Video on NISE Net Website

Does Every Silver Lining Have a Cloud?

NSF EF-0830093
Gold NPs with Positive or Negative Charge
Synthesized to explore the effect of surface charges on transport, transformations, biouptake and toxicity

Stella Marinakos and Jie Liu
Department of Chemistry, Duke University

zeta potential: -42 mV

zeta potential: +43 mV

Au-S

\[ \text{Au-S} \]

\[ \text{NH}_3^+ \]

\[ \text{Au-S} \]

FT-IR

\[ \text{Au@NH}_3^+ \]

\[ \text{Au@COO}^- \]

\[ \text{NH bend} \]

\[ \text{COO}^- \text{ stretches} \]

Wavenumber (cm\(^{-1}\))

% Transmission

Wavenumber (cm\(^{-1}\))

Au-S

\[ \text{NH}_3^+ \]
Environmental properties are at least as important as nanomaterial properties in assessing behavior and effects

Ben P. Colman¹, Emily Bernhardt¹, Jason M. Unrine², Audrey J. Bone¹, Rich Di Giulio¹, Paul Bertsch², Cole W. Matson³, Mark R. Wiesner¹, and Gregory V. Lowry⁴

¹Duke University, ²University of Kentucky, ³Baylor University, ⁴Carnegie Mellon University

Research must identify macroscopic behavior of nanomaterials in representative environments (e.g. transformations), and the impacts of those behaviors on observed effects.

Organic carbon level in sediment controls Ag NP sulfidation and Ag⁺ efflux

Resulting sulfidation of AgNPs dramatically decreases toxicity

More Sulfdizened
Darkfield Hyperspectral Imaging Microscopy: Nanoparticle Characterization and Analysis in Complex (Real) Environments

Appala Raju Badireddy¹, Jie Liu² and Mark R. Wiesner¹

Type of coating affects the hydrodynamic size of AgNPs

Bundled carboxylated carbon nanotubes in synthetic water

AgNPs in the gut of C. elegans

¹ Department of Civil and Environmental Engineering, Duke University
² Department of Chemistry, Duke University

NSF EF-0830093
Modeling the Environmental Release, Transport, Transformation and Biouptake of Nanomaterials: An Integrated Center-wide Initiative

Christine O. Hendren¹, Lauren E. Barton¹, Paul M. Bertsch², Elizabeth Casman³, Amy L. Dale³, Gregory V. Lowry³, Mathieu Thérezien¹, Jason M. Urine², and Mark R. Wiesner¹

¹Duke University, ²University of Kentucky, ³Carnegie Mellon University

NSF EF-0830093