Toxicity of Ag to aquatic plants drives Ag fate

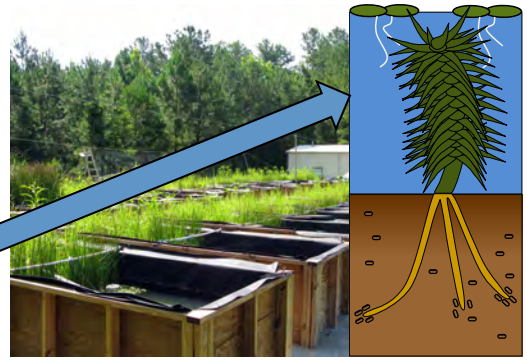
Benjamin P. Colman[1], Curtis J. Richardson[2], Emily S. Bernhardt[1]

Ag added to aquatic ecosystems

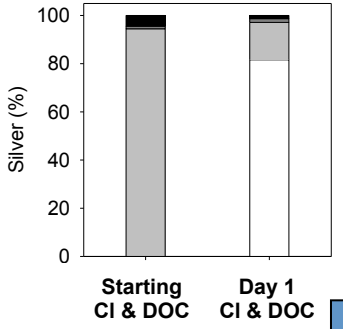
Prediction:
Stability
&
Toxicity

Ag^+ > ● > ○

$AgNO_3$ 12 nm 49 nm
AgNPs

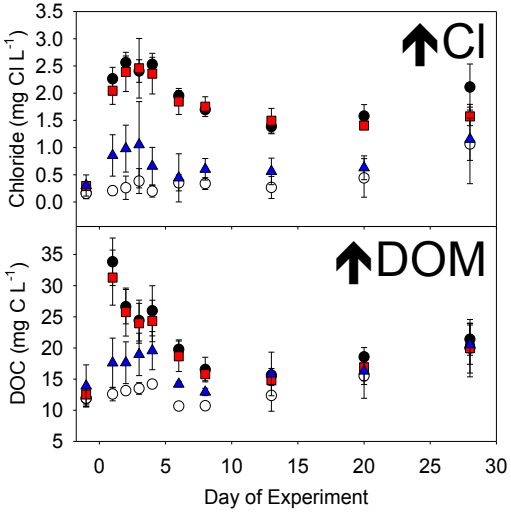


Changing water chemistry decreases Ag^+ solubility in $AgNO_3$ treatment



Speciation model consistent with large loss of Ag in $AgNO_3$ between days 0 and 1 (see below)

Toxicity to plants changes water chemistry



Increased DOC and Cl^- result from Ag toxicity to plants

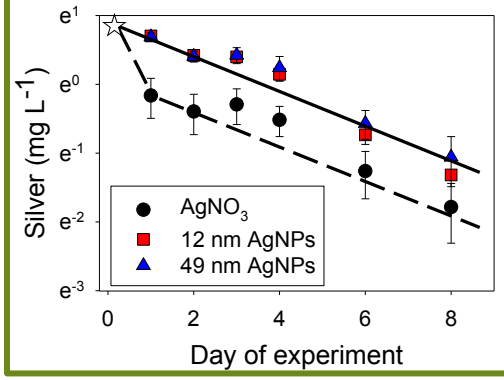
Observation:
Toxicity

Ag^+ = ● > ○

Kinetics equivalent after day 1

1st order rate law: $[Ag]_t = [Ag]_0 * e^{-kt}$

where: $[Ag]_t$ and $[Ag]_0$ – [Ag] at time t and initial
k – rate constant



Observation:
Stability
k (rate constant)

Ag^+ = ● = ○

$k = 0.21 \pm 0.066\ day^{-1}$
Suggests similar removal mechanism In all Ag treatments

Colman *et al.* 2014 *ES&T*

[1]Biology, Duke University, [2]Nicholas School, Duke University

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EF-0830093

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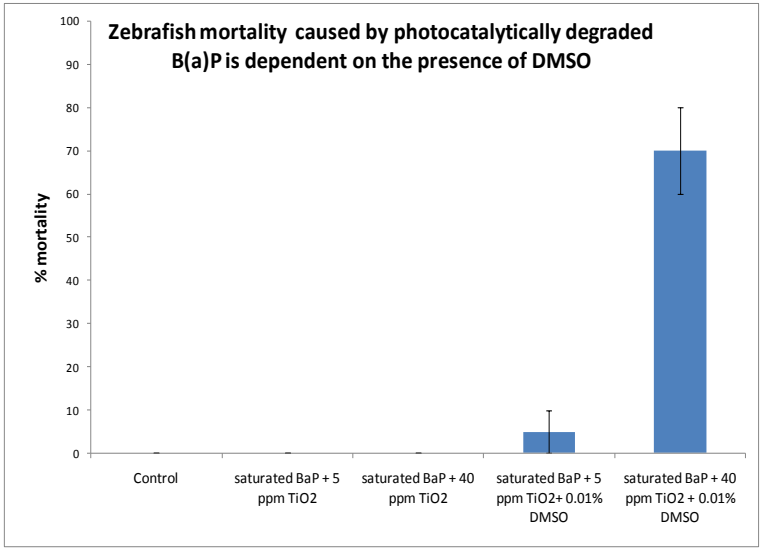
TiO_2 NP Photocatalyzed Degradation of Benzo(a)pyrene

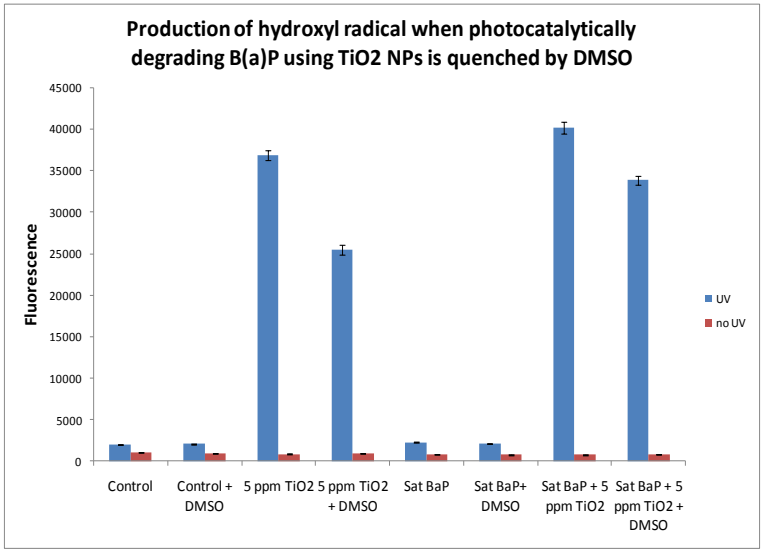
A. Bone[1], R. Di Giulio[1]

[1]*Nicholas School of the Environment, Duke University*

Objective: Determine the effects of photocatalytically degrading benzo(a)pyrene (BaP) using TiO_2 NP on toxicity of BaP to embryonic zebrafish.

- Solutions of BaP photocatalytically degraded with TiO_2 NPs are more toxic to embryonic zebrafish than unilluminated BaP. However, this toxicity is dependent on the presence of DMSO as a carrier solvent. (A)
- While the production of hydroxyl radical by illuminated TiO_2 NPs is assumed to be the driver of increased degradation and thus more toxic degradation products; in the presence of DMSO production of hydroxyl radical is in fact quenched and is thus the increased toxicity seen is not due to DMSO increasing hydroxyl radical production.





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EF-0830093

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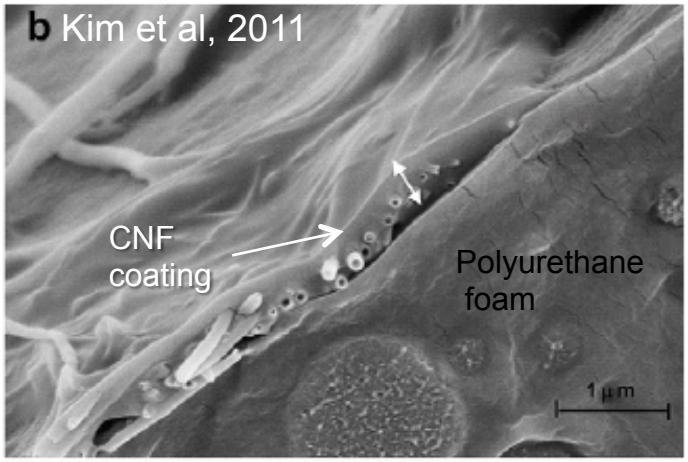
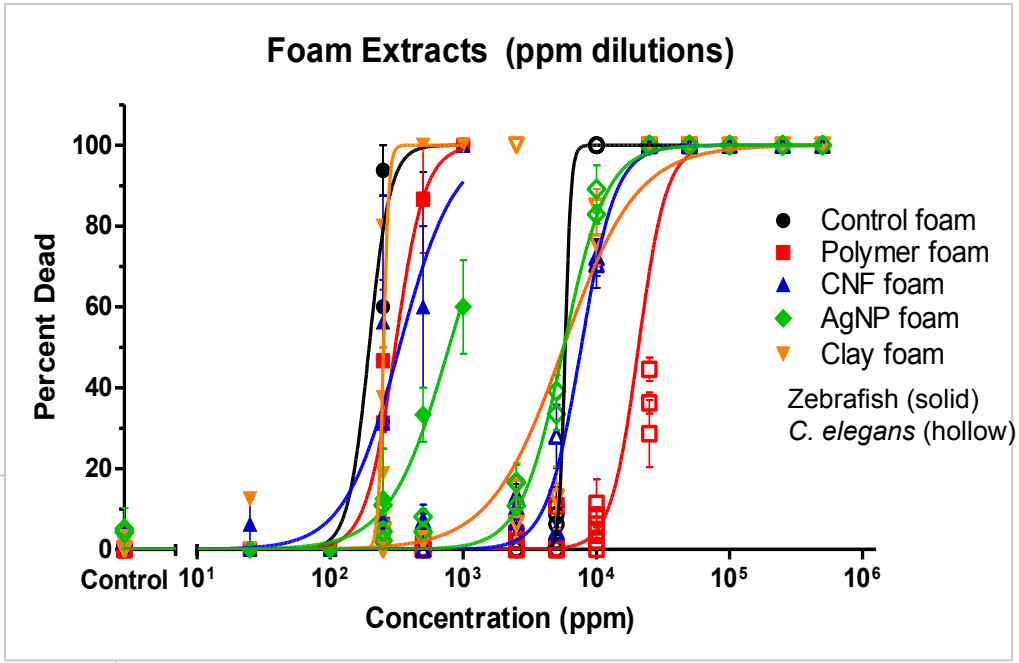
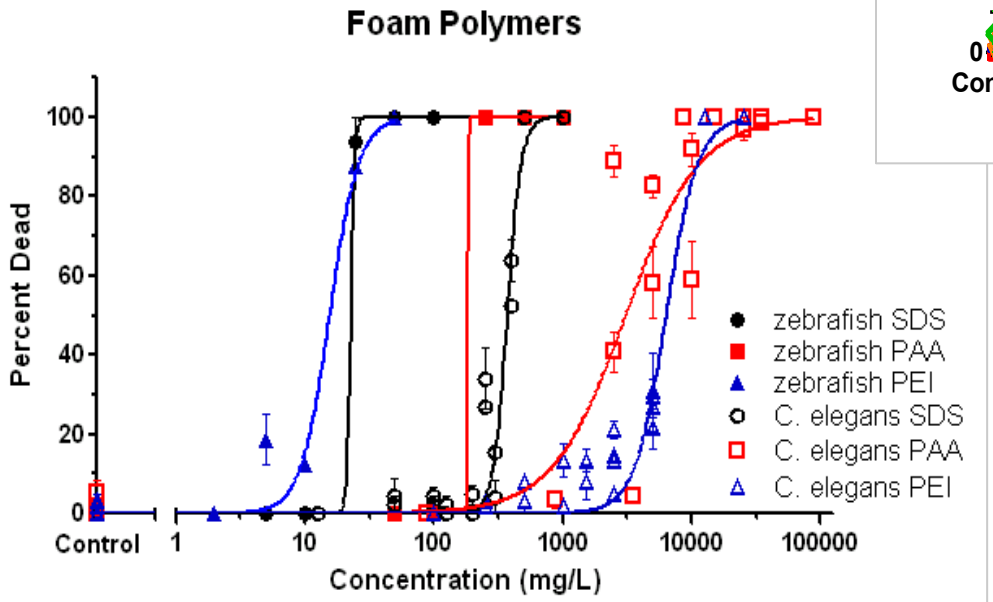
Nanocomposite Foams

J. Osterberg[1], M. Wiesner[2], R. Di Giulio[1]
[1]Nicholas School of the Environment, Duke University,
[2]Department of Civil and Environmental Engineering, Duke University,







- Nanocomposites are being investigated as flame retardants to replace persistent and endocrine-disrupting poly-halogenated compounds.
- 24 hr acute tox assays of zebrafish (*Danio rerio*) and the nematode *C. elegans* of extracts of polyurethane foam coated with Carbon nanofibers, nano clay or AgNP.
- Zebrafish more sensitive than *C. elegans*.
- Much of the toxicity seems to be linked to the polymers in the coating and the polyurethane foam itself rather than any nanoparticle component.

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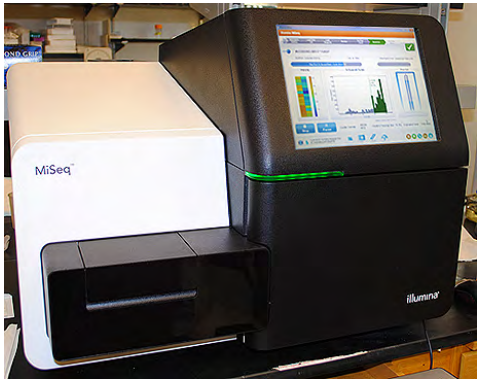
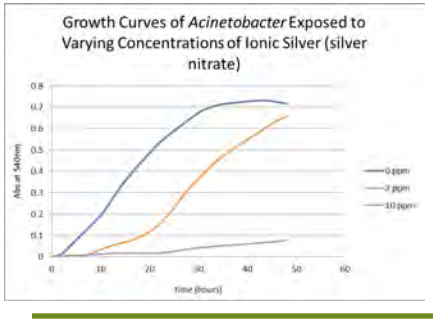
Nanoparticle Impacts on Wastewater Microbial Functions and Communities

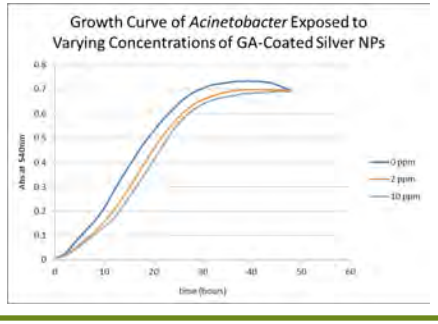
Carley Gwin[1], Claudia Gunsch[1]

[1]*Department of Civil and Environmental Engineering, Duke University*

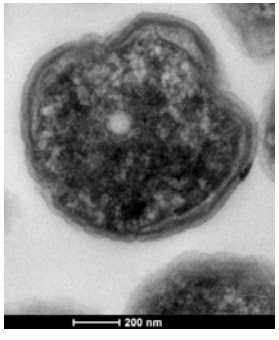
Metatranscriptomic Analysis of *Acinetobacter sp.* exposed to Ag+ and AgNPs

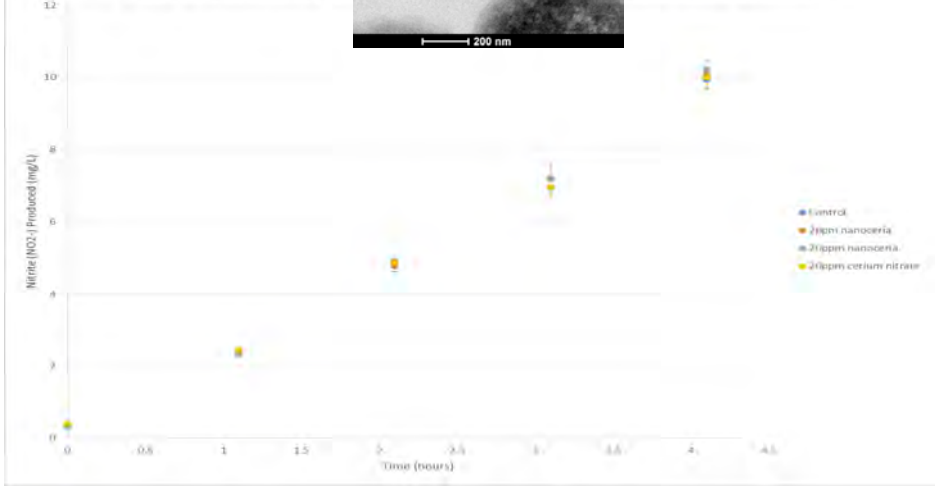






Impacts of nanoceria on *Nitrosomonas europaea*





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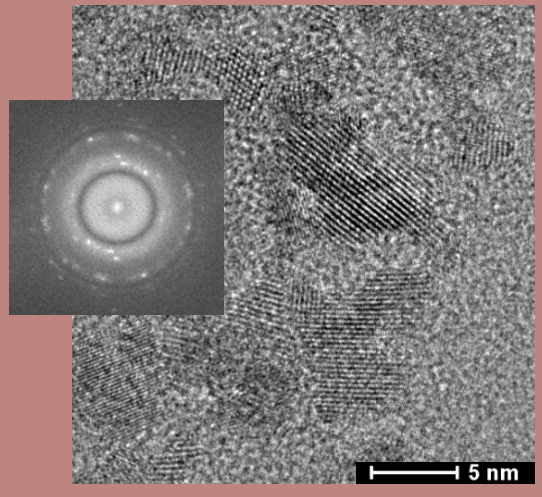
Tracking and characterizing cerium from a commercial diesel additive to exhaust to simulated environments

James Dale[1], Linsey Marr[2], Michael F. Hochella, Jr.[1]

Additive characterization



CeO_2		Additive	
Plane	d-spacing	d-spacing	δ
1 1 1	3.12	3.12	0%
0 0 2	2.71	2.75	1%
0 2 2	1.91	1.92	1%
1 1 3	1.63	1.64	1%
2 2 2	1.56	1.56	0%
0 0 4	1.35	1.37	1%

Pre-combustion particles are $Ce(IV)O_2$ nanoparticles between 5 and 9 nm

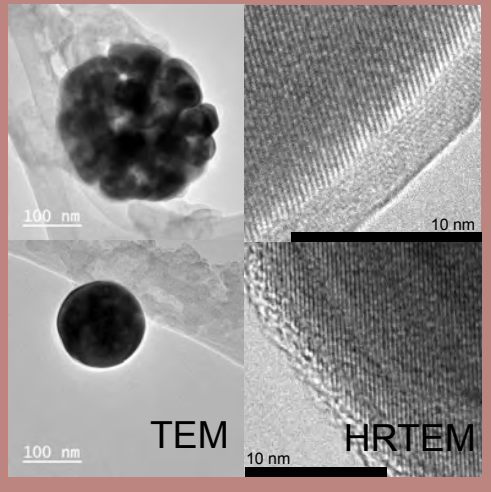
Combustion

35 kW Kubota diesel generator under load

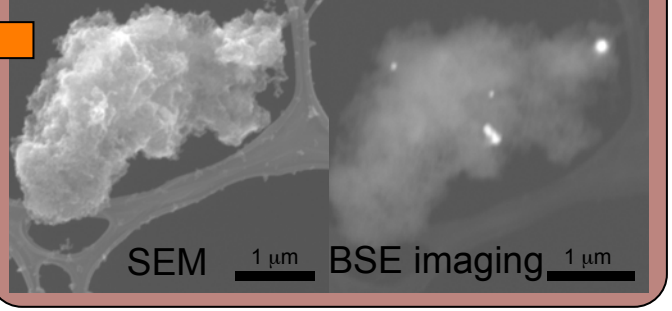
Mesocosms

Dosed by soil amendment with cerium doped exhaust (in process)

Exhaust Characterization



$Ce(IV)O_2$, 80 to 300 nm, single crystal and polycrystalline aggregates, found inside and outside of carbon aggregates



[1]Department of Geosciences, Virginia Tech
[2]Department of Civil and Environmental Engineering, Virginia Tech

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EF-0830093
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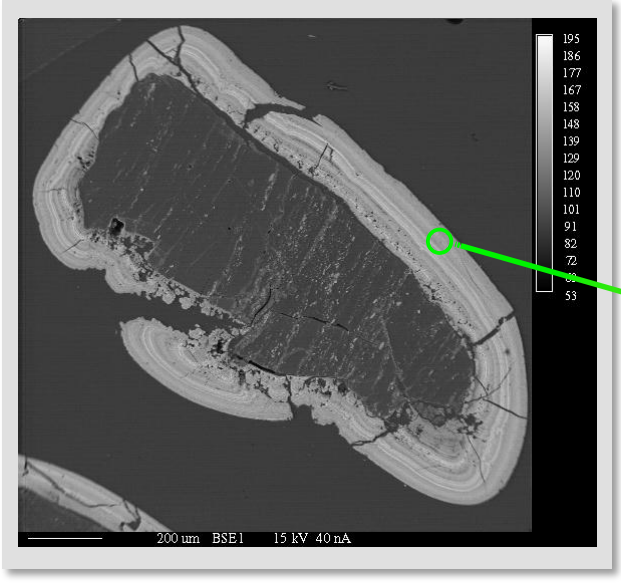
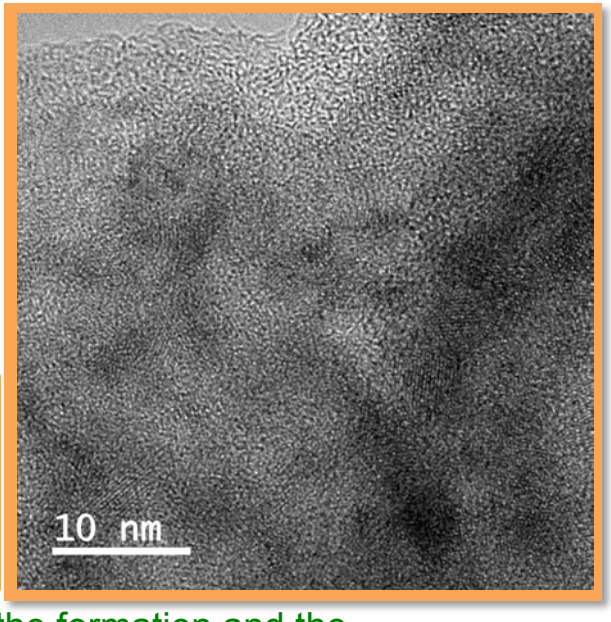
How fresh water facilities remove metals from drinking water: Seeking the mechanism at the nanoscale

Michel Vargas[1], Gary Hinds[2], William Knocke[2], Michael Hochella[3], Mitsu Murayama[1]
Department of [1]Materials Science and Engineering, [2]Civil and Environmental Engineering, [3]Geosciences, Virginia Tech



Classical Macro-scale based view: an anthracite coal filter media from a water treatment plant in Newport News, VA, showing growth ring-like surface layers after long-time exposure. The dark/bright layers are **believed to result from Mn/Al enrichment, respectively**.



What we found so far: Mn and Al interact strongly, forming multicomponent surface layers on filter media containing MnO_x nanoparticles and nanosized (Mn,Al)-O amorphous flakes.

- Nanoparticles and nano-scale interactions likely play the key role in the formation and the chemical behavior of transition metal oxide surface layers in water filtration systems.
- The media's properties seem to be a critical factor in the MnO_x(s) surface formation mechanism.
- This is contrary to the generally accepted "uniform film-like" surface layer description.

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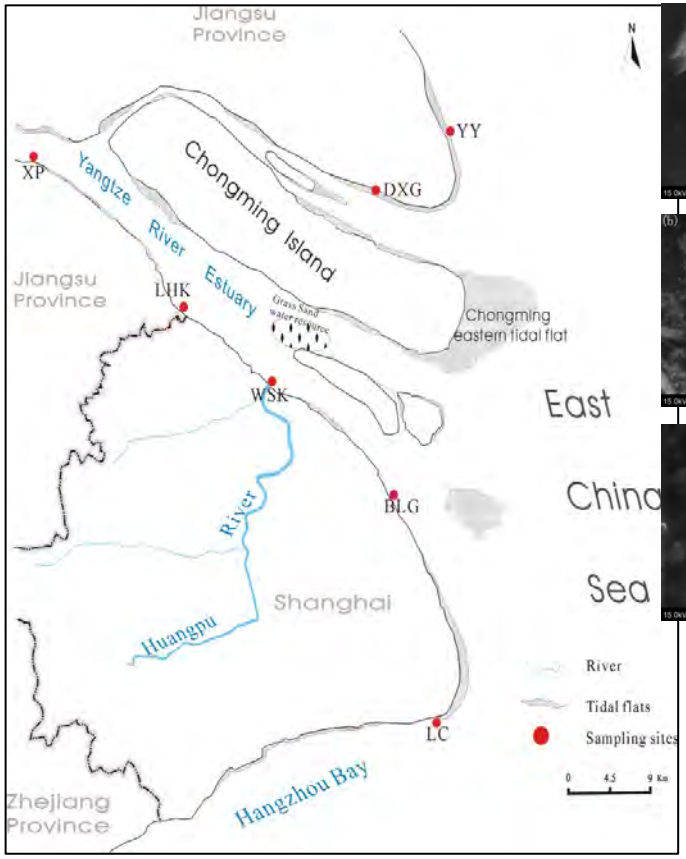
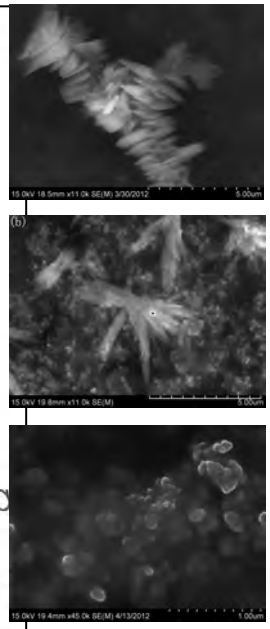
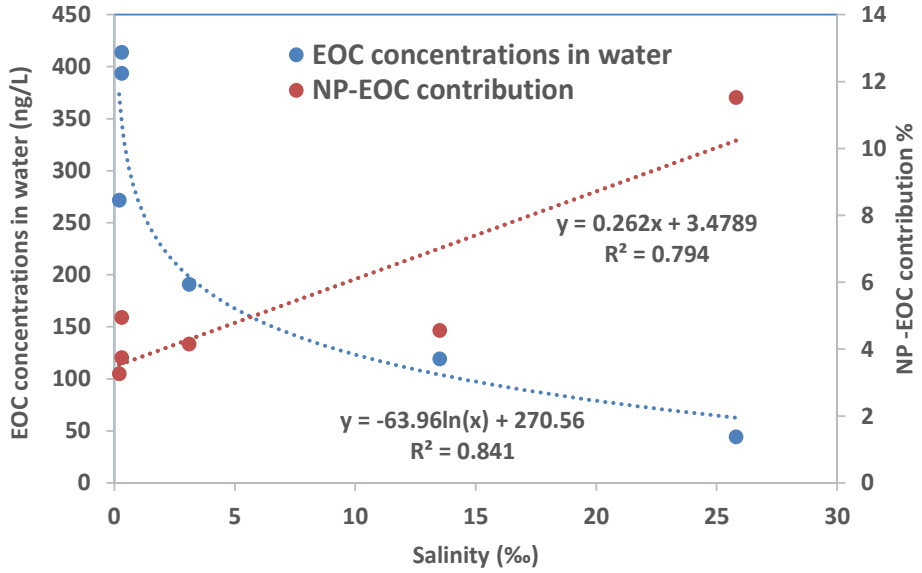
Nanoparticles as a sink for emerging organic contaminants (EOCs) in the Yangtze Estuary, China

Yi Yang [1,2], Caixia Yan [2], Michael F. Hochella Jr. [1]







Forty two emerging organic contaminants were analyzed using LC-MS-MS. Nanoparticles (NP) were isolated using CFUF.

- NP-EOCs contributes up to 60 % of the total EOC in water.
- NP properties control its association with EOCs.
- Salinity plays a critical role in EOCs-NP interaction in an estuarine system.

[1] The Center for NanoBioEarth, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA
[2] State Key Laboratory of Estuarine and Coastal Research, East China Normal University Shanhgai, China

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EF-0830093
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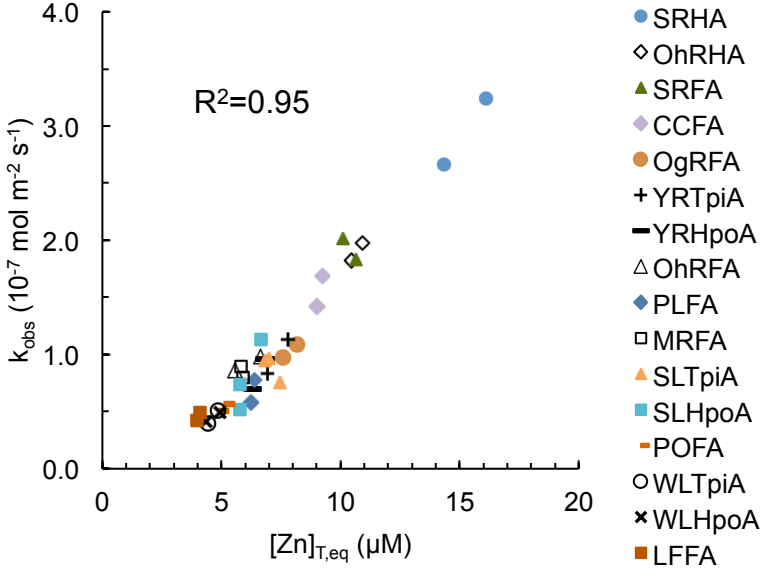
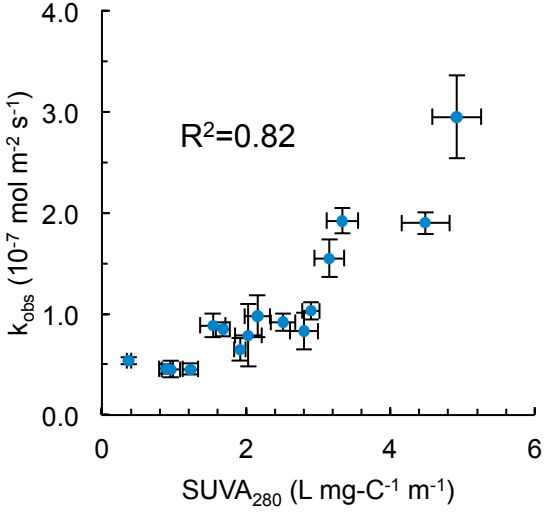
Effects of natural organic matter properties on the dissolution kinetics of ZnO NPs

Chuanjia Jiang[1], George R. Aiken[2], Heileen Hsu-Kim[1]

[1]Duke University, Department of Civil & Environmental Engineering. [2]US Geological Survey





- Dissolution kinetics of ZnO NPs monitored by anodic stripping voltammetry (ASV).
- Dissolution rate constant (k_{obs}) related to equilibrium dissolved zinc concentration ($[Zn]_{T,eq}$) in a linear fashion for the different NOM isolates.
- k_{obs} is positively correlated with Specific UV Absorbance (SUVA) of NOMs, an indicator of aromatic carbon content.

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CEINT Creates New Middle School Student Engineers Network-Strengthening Opportunities in Research (SENSOR) Saturday Academy

What? Hands-on education/mentoring program to encourage careers in science and engineering by engaging underrepresented minority (URM) 8th grade students in water quality testing and sensor applications to CEINT mesocosm samples and CEINT curriculum: *Welcome to NanoScience: Interdisciplinary Environmental Explorations, Grades 9–12*

Goals? •Introduce students to careers in engineering and research
•Teach engineering design by sensor applications & math exercises
•Create network to support pursuit of degrees in science and engineering

Who? 8th grade URM students. Mentors include CEINT graduate and undergraduate students led by PI: Dr. Adrienne Stiff-Roberts and Co-PI: Dr. Glenda Kelly

When? 12 Saturday sessions (Sept.- May 2014-16)

Where? Duke University campus plus field trip to Duke Marine Laboratory

Duke UNIVERSITY
BURROUGHS WELLCOME FUND
NSF EF-0830093
CEINT

2008-14 CEINT Impacts Educational Infrastructure

- 20 new courses + 35 modified to infuse CEINT research across 6 universities
- 364 seminars and colloquia
- IGERT is creating core curriculum
  - "Educating at the Interface: Nanotechnology-Environmental Effects & Policy"
  - 2 new courses taught by distance learning across 3 universities
- Center-wide REU renewed 2014 creates international network for undergraduates
  - Duke, Virginia Tech, Carnegie Mellon and the CEREGE in France
  - 17 faculty mentors
  - >90% REU seniors accepted into 1st choice graduate programs science or engineering
  - Cross site integration- videoconferencing, student created websites & collaboratories
  - Virtual presentations link US students with international collaborators
- CEINT Scholars Steering Committee (CSSC) creates student/postdoc training network



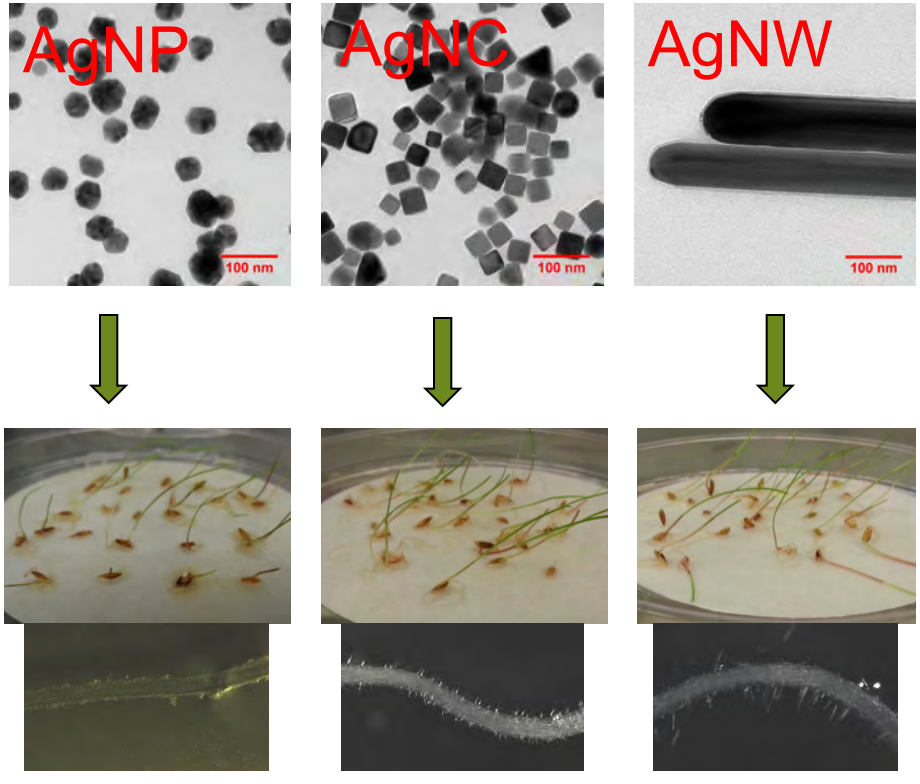

CEINT

Effect of Shape on Toxicity of AgNPs

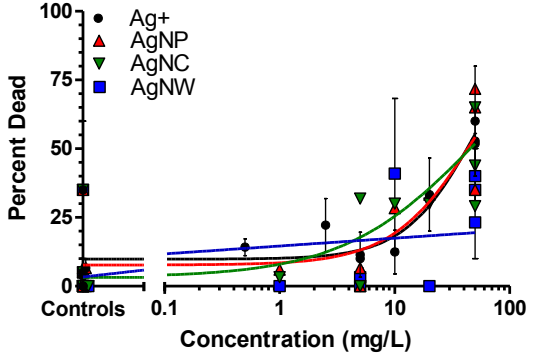
D. Gorka[1], J. Osterberg[3], B. Colman[2], J. Meyer[3], R. Di Giulio[3], E. Bernhardt[2], J. Liu[1]

[1]Department of Chemistry, Duke University, [2]Department of Biology, Duke University,

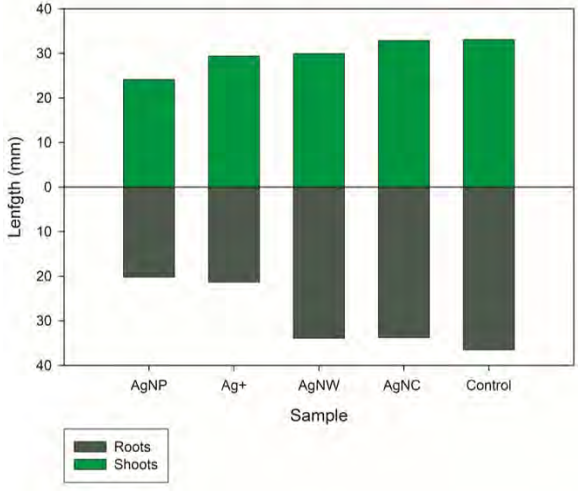
[3]Nicholas School of the Environment, Duke University



Danio rerio



Lolium multiflorum



Order of toxicity: AgNP > AgNC > AgNW > Control

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EF-0830093
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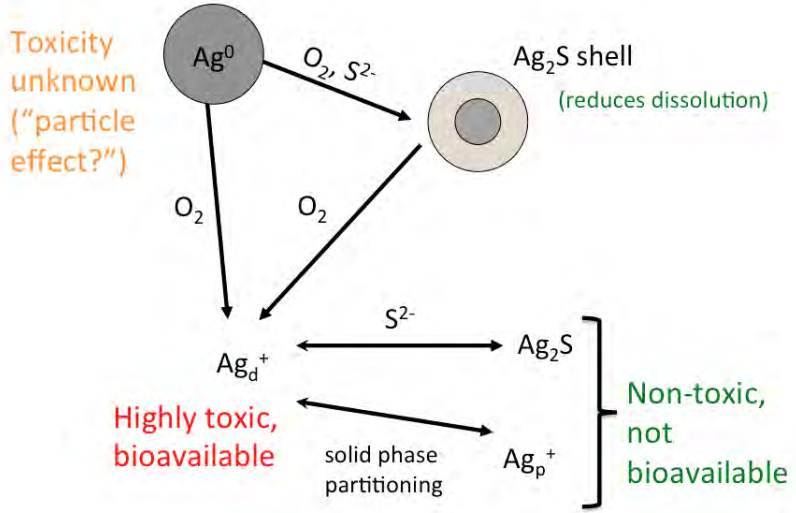
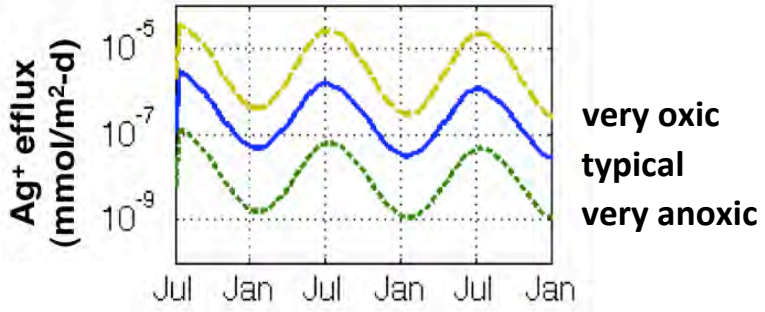
Modeling Nanosilver Transformations in Sediments

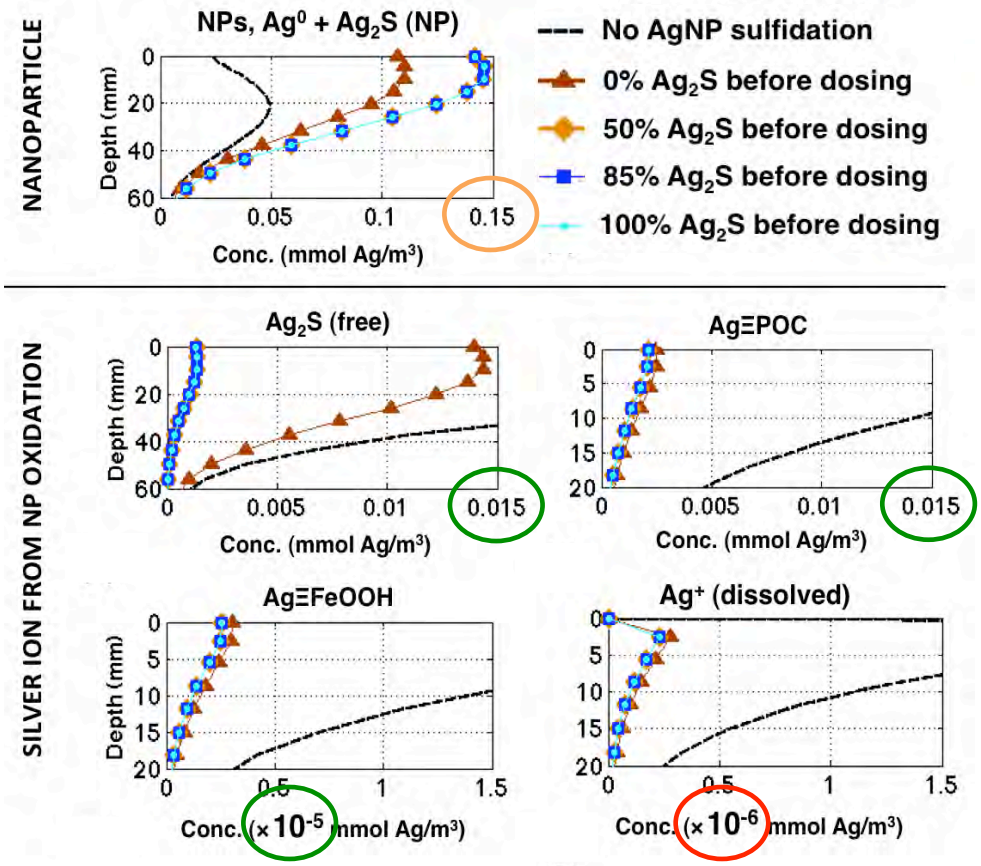
Amy Dale[1,2], Gregory Lowry[1], Elizabeth Casman[2]





Toxic Ag^+ formation and efflux from sediments increases in summer. Anoxic environments show less Ag^+ formation.

Speciation one year after dosing (July):



Nanosilver will persist as non-bioavailable species (Ag_2S and AgΞPOC) in sediments. Even pristine (0% Ag_2S) NPs sulfidize and behave as if fully sulfidized (100% Ag_2S) within a year of entering sediments.

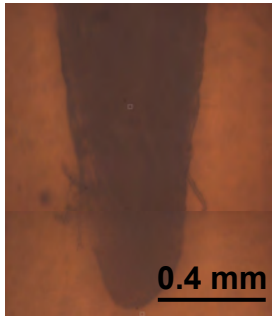
Dale, A. L.; Lowry, G. V.; Casman, E. A., Modeling Nanosilver Transformations in Freshwater Sediments. *Environ Sci Technol* **2013,** *47*, (22), 12920-12928.

[1]Department of Civil and Environmental Engineering, Carnegie Melon University;
[2]Department of Engineering and Public Policy, Carnegie Melon University

DBI-1266252 / EF-0830093

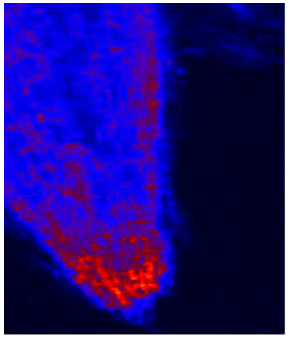
Measuring Bioavailability of Ag Nanoparticles in Plants with X-ray Absorption Spectroscopic (XAS) imaging

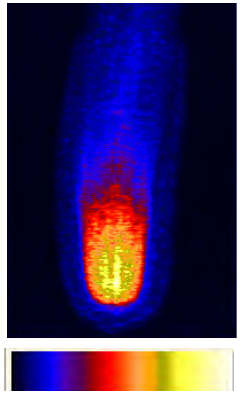
John Stegemeier[1], Ben Colman[2], Fabienne Schwab[2], Emily Bernhardt[2], Greg Lowry[1]
[1]Carnegie Mellon University, [2]Duke University

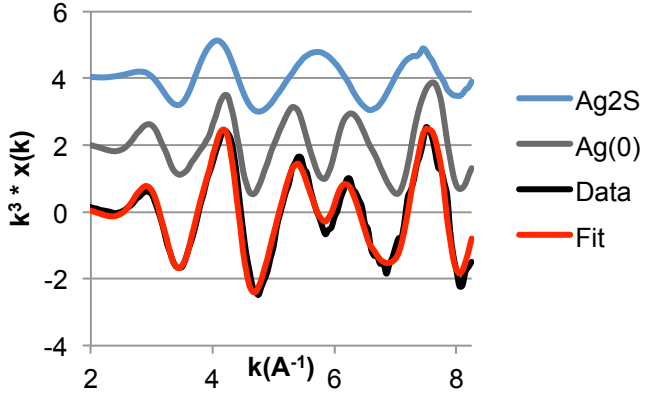


Alfalfa root

Duckweed root


Ag XAS map of roots exposed to Ag(0) NPs





X-ray based speciation shows transformation of metallic silver NPs into a silver sulfide species

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EF-0830093
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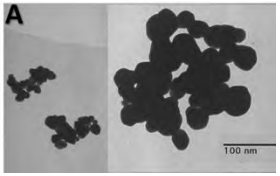
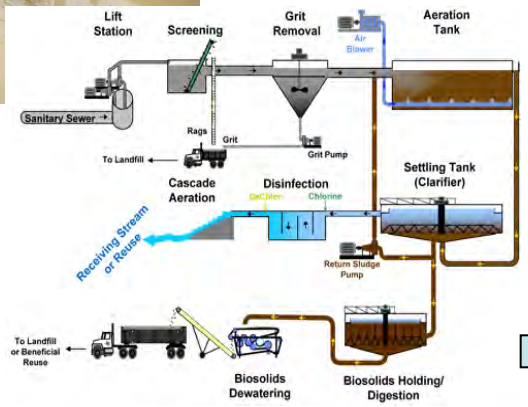
Sulfidation is a Key Environmental Fate Process for ZnO, CuO, and Ag Nanoparticles

Clement Levard (CEREGE), Gordon E. Brown, Jr. (Stanford), Jason Unrine (Kentucky), Gregory V. Lowry (CMU)

Ag Nanoparticles →

→ **Ag_2S Nanoparticles**





ZnO Nanoparticles →

→ **ZnS**
$Zn_3(PO_4)_2$
Zn-Ferrihydrite
(No ZnO!!)

CuO Nanoparticles → (S^{2-}) → **Cu_xS_y Nanoparticles**

Fate and toxicity will be that of the metal sulfide or metal phosphate products rather than the initial pristine nanomaterial.

DBI-1266252
EF-0830093

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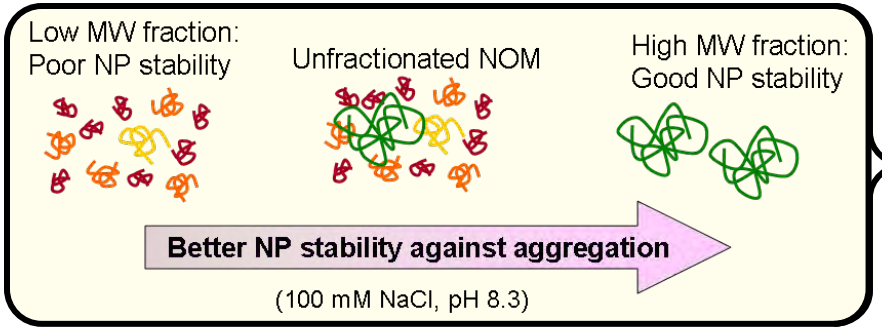
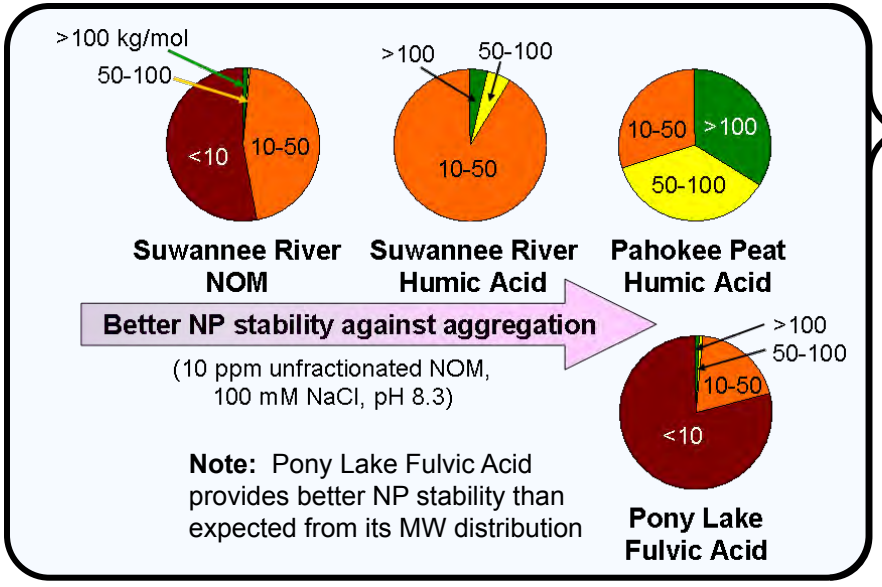
Properties of Natural Organic Matter that Govern Its Effects on Gold Nanoparticle Aggregation

Stacey M. Louie[1], Eleanor Spielman-Sun[2], Robert D. Tilton[1], Gregory V. Lowry[1]

[1]Carnegie Mellon University, Pittsburgh, PA 15213; [2]Oberlin College, Oberlin, OH 44074





Importance of the heterogeneity of each natural organic matter (NOM) sample

- Gold nanoparticle (NP) aggregation is sensitive to the presence of high molecular weight (MW) components, which stabilize the NPs against aggregation

Importance of variability among NOM sources

- MW distribution of the NOM explains NP aggregation behavior for some, but not all, of the NOM samples tested

Implications

- Quantitative prediction of NP fate and transport will require detailed knowledge of the physicochemical heterogeneity of the NOM in the environment of interest

Louie, S.M.; Tilton, R.D.; Lowry, G.V. Effects of molecular weight distribution and chemical properties of natural organic matter on gold nanoparticle aggregation. *Environmental Science and Technology* **2013**, *47*, 4245.

DBI-1266252
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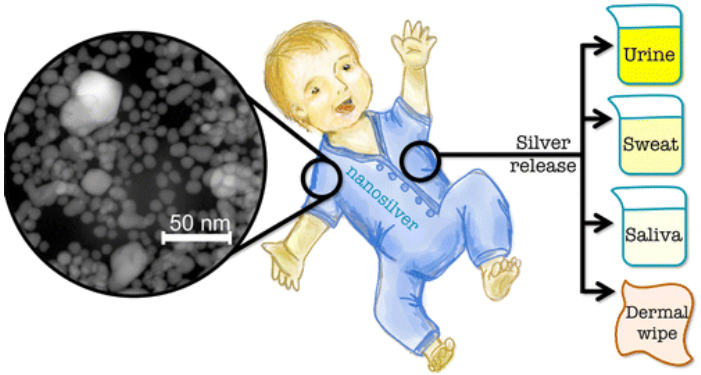
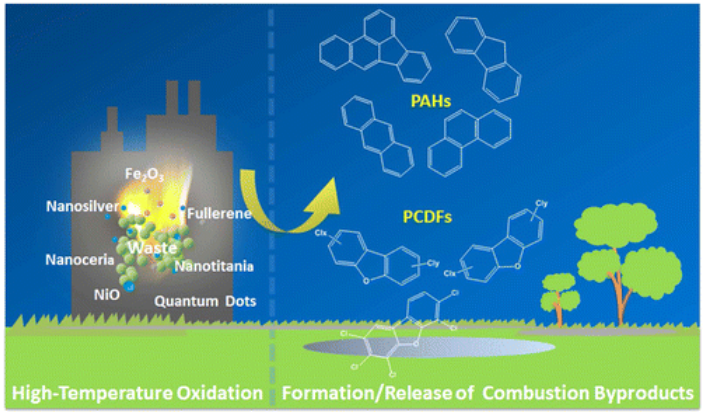
Exposure to and Transformations of Nanomaterials in Air

Marina Quadros, Andrea Tiwari, Eric Vejerano, Linsey C. Marr

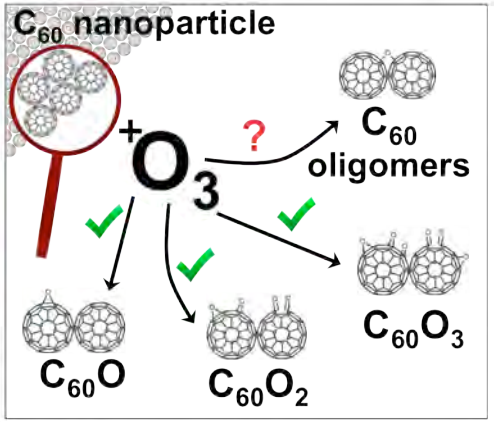
Department of Civil and Environmental Engineering, Virginia Tech



Levels of silver to which children may potentially be exposed during use of selected consumer products is predicted to be low, and bioavailable silver is expected to be in ionic rather than particulate form.



Incineration of waste containing nanomaterials v. their bulk counterparts produces ~6 times more PAHs. Chlorinated furans are formed at elevated concentrations with waste containing nanosilver and TiO_2.



Aerosolized C_{60} exposed to environmentally relevant concentrations of O_3 produces $C_{60}O$, $C_{60}O_2$, $C_{60}O_3$ and other O-containing species on the aerosol surface. Oxidative stress as measured by the DCF assay is higher.

Quadros et al. (2013). Release of silver from nanotechnology-based consumer products for children, ES&T, 47(15), 8894-8901. Vejerano et al. (2013). Emissions of polycyclic aromatic hydrocarbons, polychlorinated dibenzo-p-dioxins, and dibenzofurans from incineration of nanomaterials, ES&T, 47(9), 4866-4874. Tiwari et al. (2014). Oxidation of C_{60} aerosols by atmospherically relevant levels of O_3, ES&T, in press, doi:10.1021/es4045693.

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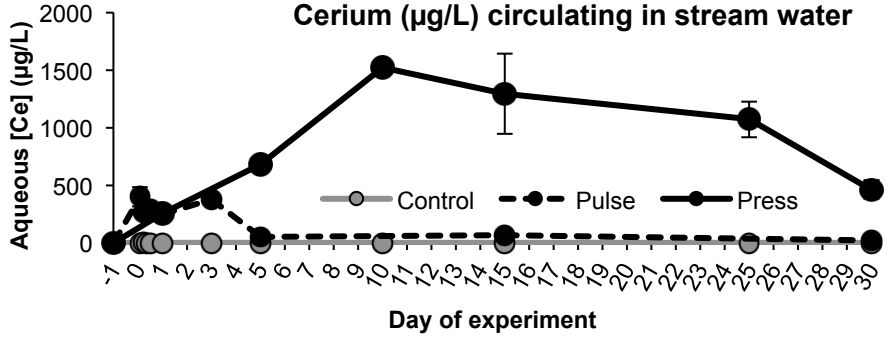
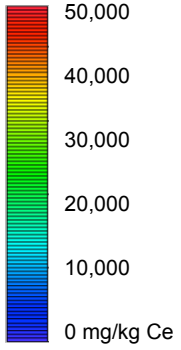
Environmental fate and transport of CeO_2 nanoparticles in stream mesocosms

Leanne Baker[1], Ryan S. King[1], Greg Lowry[2], Jason Unrine[3], and Cole W. Matson[1]

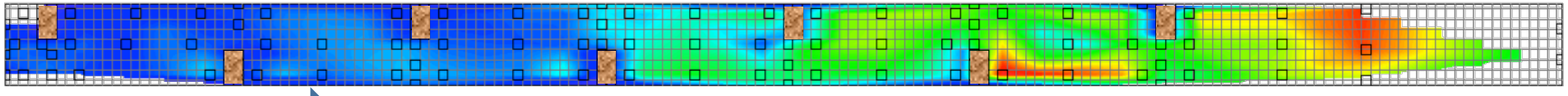
[1]Baylor University, [2]Carnegie Mellon, [3]University of Kentucky





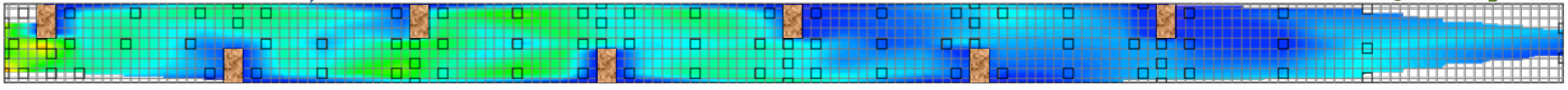
Cerium deposition in periphyton along stream riffle section

Pulse Addition 10 mg/L CeO_2 NP



Water flow

Press Addition 10 mg/L CeO_2 NP



- CeO_2 NPs added via press addition are more stable in the water column, resulting in substantially higher water concentrations
- Pulse and press additions result in significantly different patterns of NP deposition

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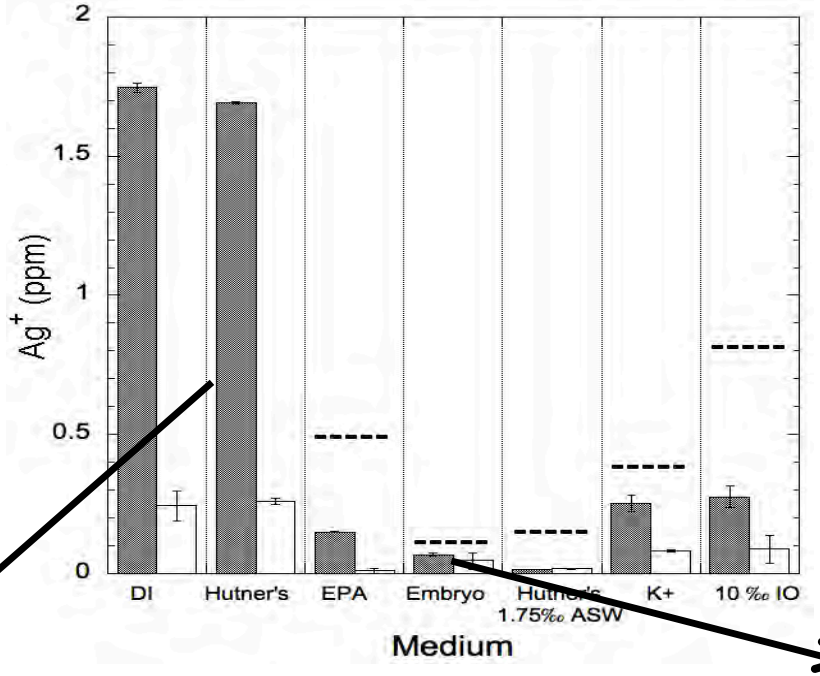
Toxicity of Ag Nanoparticles is from Dissolved Ag Species for four Test Organsims

Clement Levard (CEREGE), Joel Meyer (Duke), Ben Colman (Duke), Emily Bernhardt (Duke), Mark Wiesner (Duke), Rich DiGuilio (Duke), Gordon E. Brown, Jr. (Stanford), Gregory V. Lowry (Carnegie Mellon)

Killifish

Most Toxic, greatest dissolved Ag

Duckweed



Nematode

Least Toxic lowest dissolved Ag

Zebrafish

Levard et al., 2013 *Environ. Sci. Technol.* 2013, 47, 13440−13448

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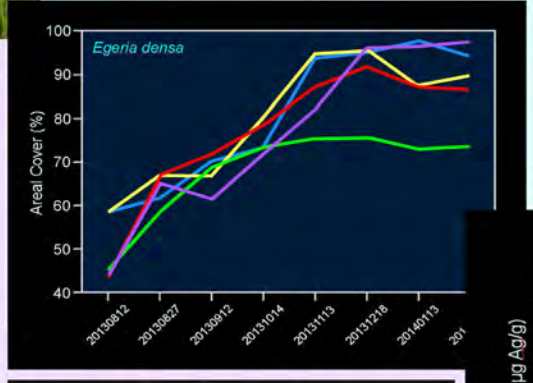
Biological and Chemical Responses of *Egeria densa* to Acute and Chronic Doses of Nanosilver

Curtis J. Richardson[1], Lin Yuan[2], and Mengchi Ho[1]

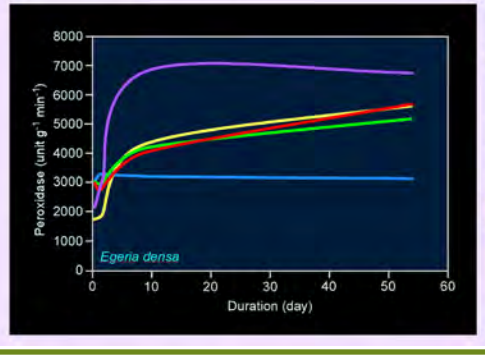
Four treatments, in addition to controls, with 3 replicates each of pulse Ag^0–GA (6 nm), chronic Ag^0–GA (6 nm), Ag_2S–GA (26 nm), and Au^0–GA (36 nm) were established to test the biological and chemical responses of *Egeria densa*.

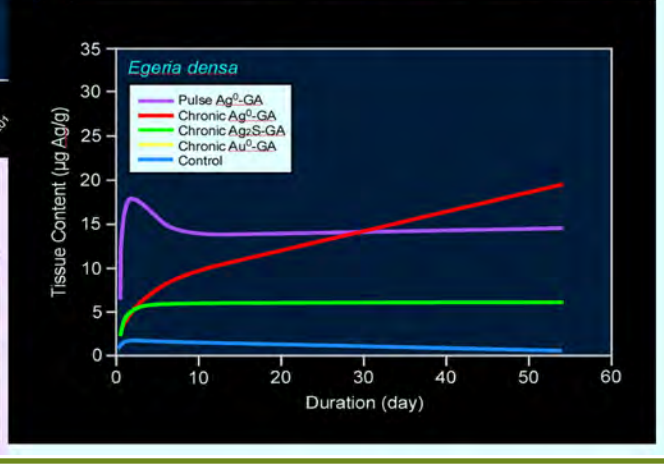
- Ag_2S–GA resulted in the smallest areal cover of *Egeria* (an analog to biomass) in the mesocosm, whereas all other treatments are not discernible from the control.
- *Egeria* tissue Ag content for the pulse addition peaked over other treatments in the first few days as expected. Ag contents under chronic addition of Ag^0–GA surpasses that under pulse treatment of Ag^0–GA after 30 days of exposure. The larger particle Ag_2S–GA treatment appeared to reach saturation in <5 days.



We carried out bioassays to determine to what degree the plant tissues are damaged and its defense systems are being activated.

- peroxidase (POD)
- superoxide dismutase (SOD)
- malondialdehyde (MDA)
- chlorophyll *a* and *b*





[1] Duke University Wetland Center, Nicholas School of the Environment, Durham, NC. USA
[2] Visiting from State Key Laboratory of Estuarine and Coastal Research, ECNU, Shanghai, China

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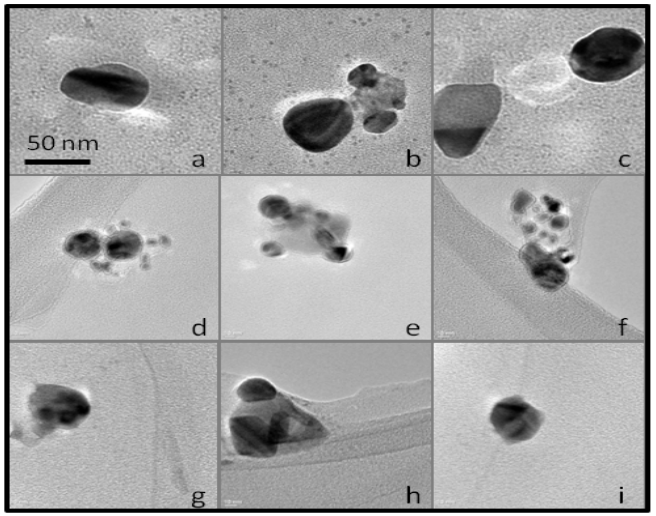
Influence of coating, sewage sludge amendment and aging on fate of Ag NPs in soil

Whitley, AR[1]; Levard, C[2]; Oostveen, E; Bertsch, PM[1]; Matocha, CJ[1]; vd Kammer, F[1]; Unrine, JM[1]

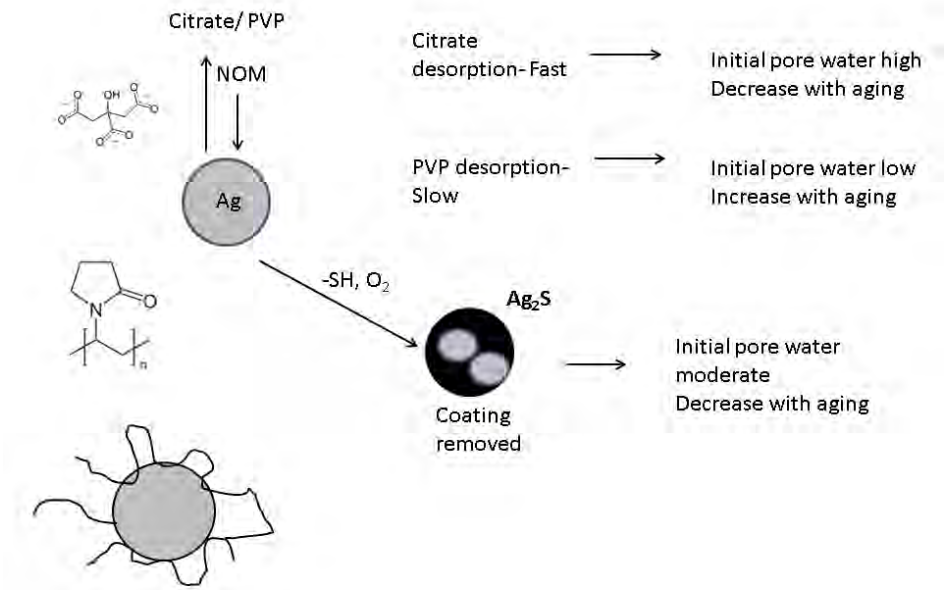
[1]Plant and Soil Sciences, University of Kentucky, [2]CEREGE, France



Citrate – No Sludge

PVP – 3% Sludge

Citrate – 3% Sludge



- Without sludge amendment, coating has profound impact on partitioning of Ag nanoparticles (NPs) to pore water, but when introduced through sewage sludge there is little effect of coating.
- Far more colloidal Ag when sludge spiked with Ag NP than with $AgNO_3$.

Whitley, AR; Levard, C; Oostveen, E; Bertsch, PM; Matocha, CJ; vd Kammer, F; Unrine, JM*. 2013. Behavior of Ag nanoparticles in soil: Effects of particle surface coating, aging and sewage sludge amendment. Environmental Pollution. 182: 141-149.

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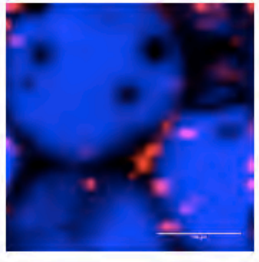
Raman Based Tracking of Gold Nanoparticle Aggregation and Transport

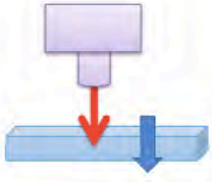
Matthew Chan and Dr. Peter Vikesland

Department of Civil and Environmental Engineering, Virginia Tech

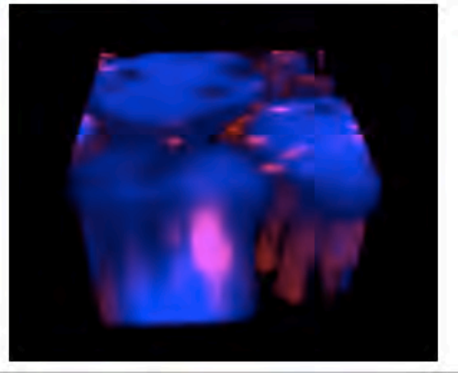
Research objectives:

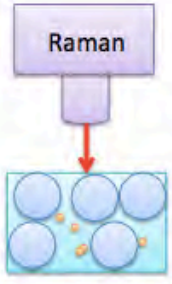
1. **Develop a novel, Raman based protocol to track the aggregation and transport of gold nanoparticles in porous media.**
2. **Once fully developed this protocol will be used to examine how changes in salt identity, nanoparticle size, and porous media structure and composition alter transport.**





- By stacking all the images, we can interpolate a 3D projection of the packed-bed interior



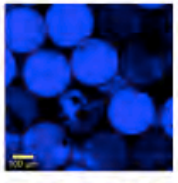


Quartz packed-bed filled with glass beads, AuNP aggregates, and NaCl

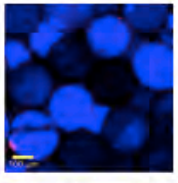
Silica

AuNP-Cl

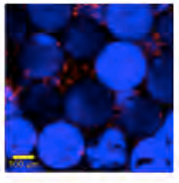
Increase [NaCl]; Increase AuNPs Aggregation



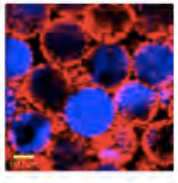
0 mM NaCl



3 mM NaCl



10 mM NaCl



100 mM NaCl

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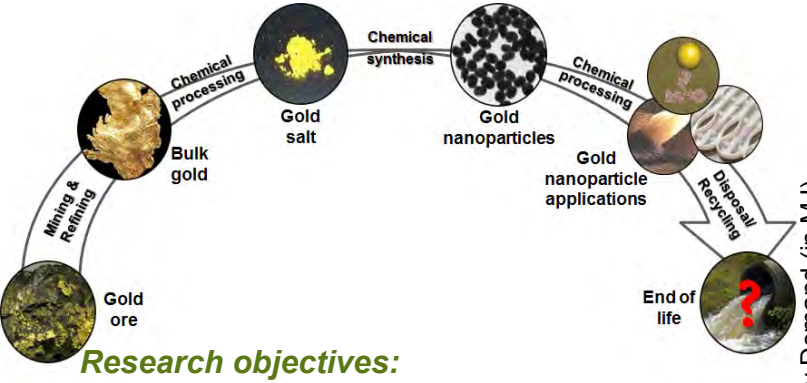
“Green” Synthesis of Gold Nanoparticles: Mechanistic Studies and Life Cycle Assessment

Paramjeet Pati[1], Dr. Peter Vikesland[1], Dr. Sean McGinnis[2]

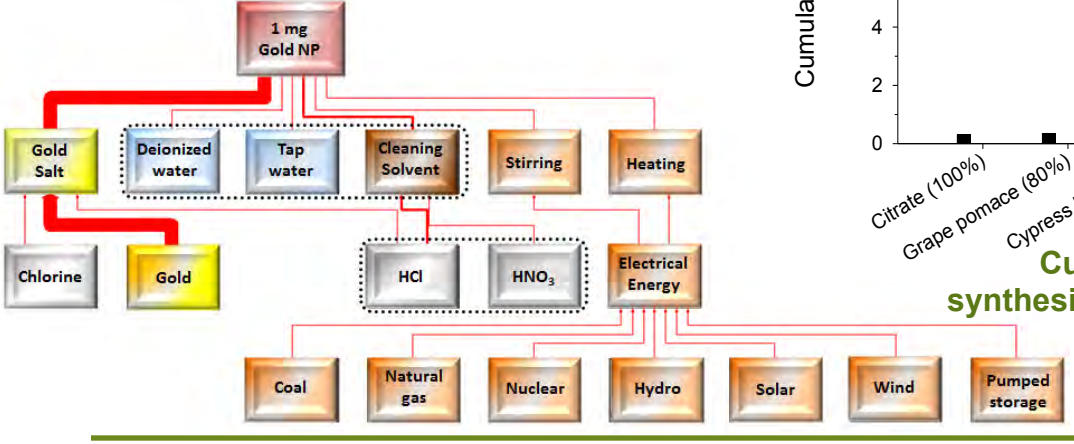
[1]Department of Civil and Environmental Engineering, [2]Department of Materials Science and Engineering, Virginia Tech



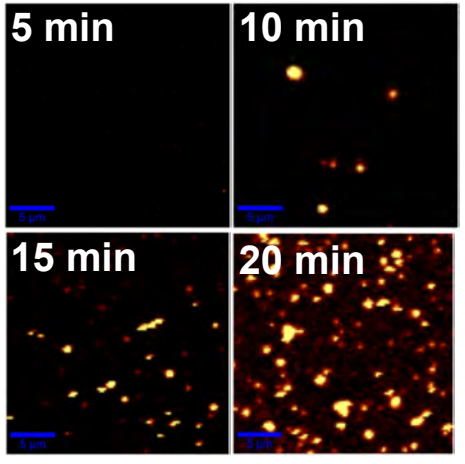
Research objectives:

1. Estimate the life cycle impacts of AuNPS

2. Improve mechanistic understanding of green synthesis processes to develop design rules



Formation of carbohydrate-reduced gold nanoparticles over time.



Cumulative Energy Demand of 1 mg of AuNPs synthesized using “green” reducing and stabilizing agents

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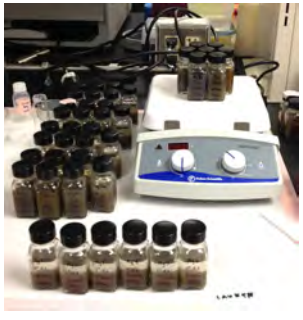
Heterogeneous Attachment Efficiency:
Batch measurements in environmental matrices

Lauren Barton[1], Mathieu Therezien[1], Mark Wiesner[1]

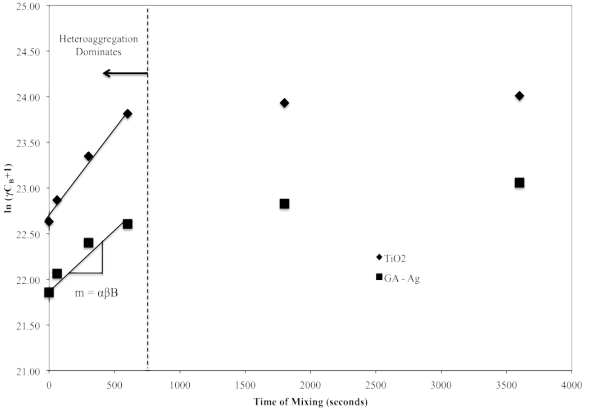
WWTP



batch experiments

$$\gamma(t) = \frac{M_S / M_B}{C_L}$$

distribution of NPs between the solid and liquid phases



$$Ln\left(\gamma(t)\cdot C_B + 1\right) = \alpha\cdot\beta(n,B)\cdot B\cdot t$$

- Distribution coefficient $\gamma(t)$ measured from batch experiments.
- Attachment efficiency α_{hetero} calculated from slope at the early aggregation stages.

[1] Department of Civil and Environmental Engineering, Duke University

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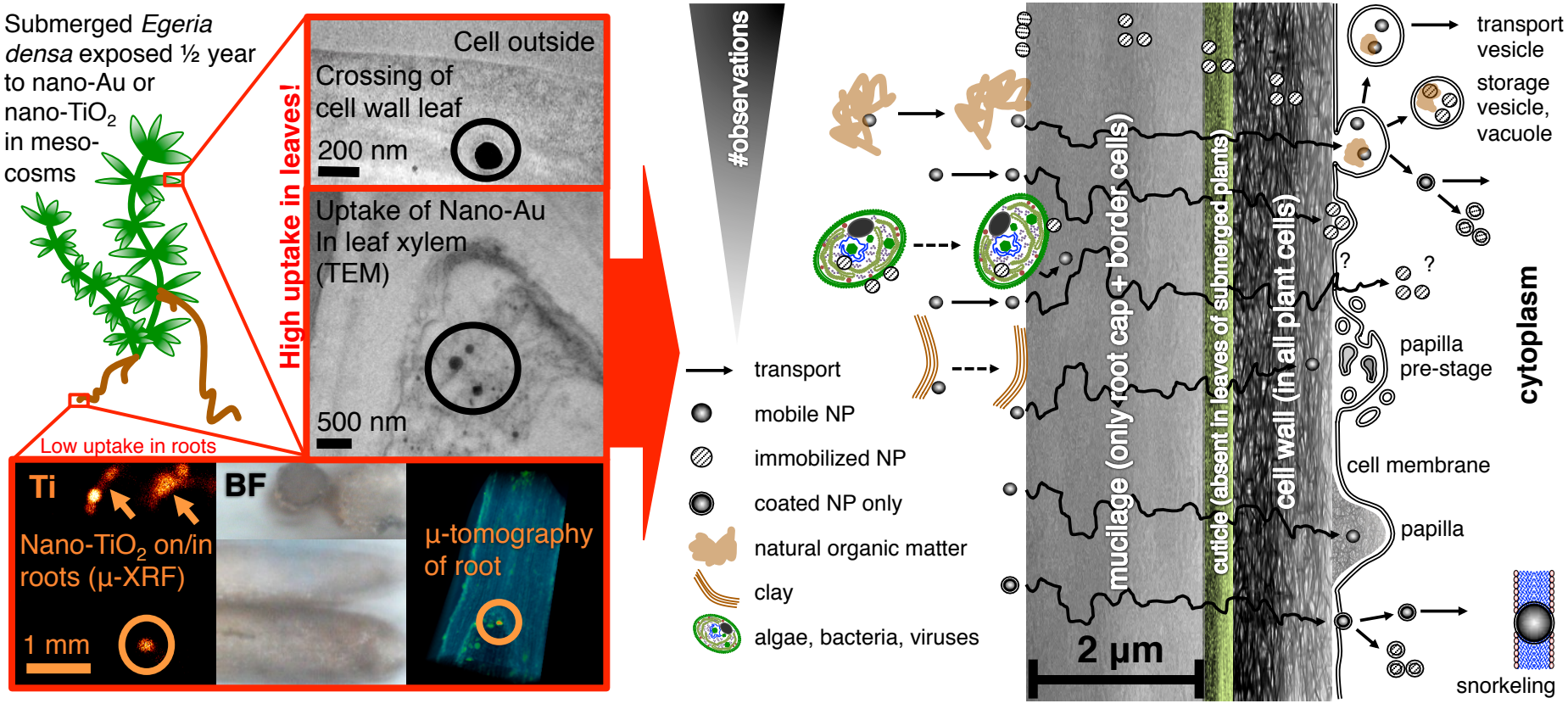
Nanoparticle Uptake Pathway Identification and Characterization in Plant Cells

Using Transmission Electron Microscopy (TEM), μ-X-Ray Analysis, Hyperspectral Imaging

F. Schwab[1], S. Marinakos[1], W. Liu[2], M. Auffan[1,2], C. Levard[2], B. P. Colman[1], E. S. Bernhardt[1], J.-Y. Bottero, M. Wiesner[1]

[1] Duke University, Civil & Environmental Engineering Department / Biology Department, USA

[2] Centre de Recherche et d'Enseignement de Géosciences de l'Environnement (CEREGE), France



Schwab et al., manuscripts in prep.

FNSNF Fonds National Suisse Schweizerischer Nationalfonds Fondo Nazionale Svizzero Swiss National Science Foundation

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