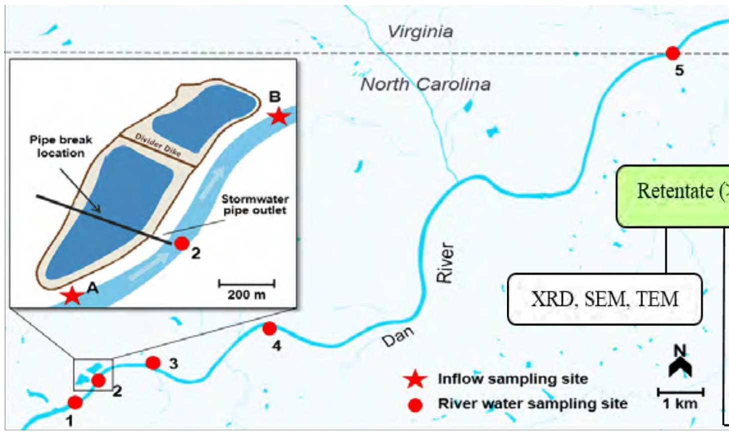
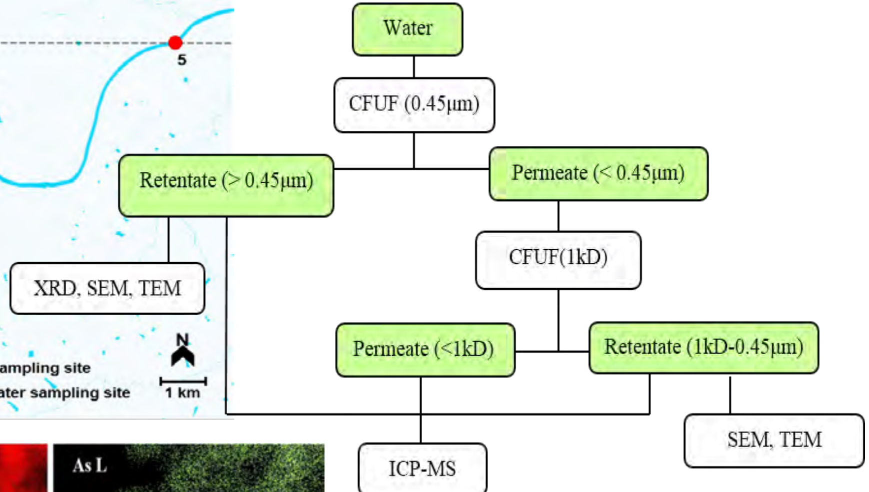
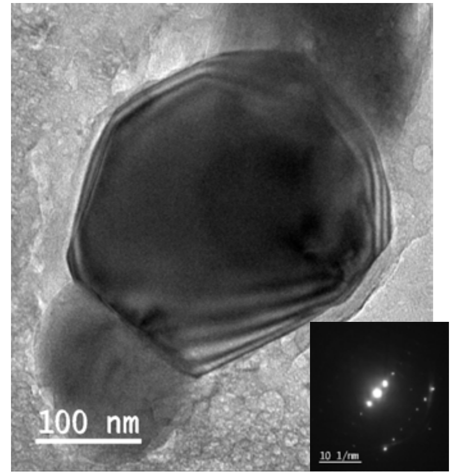
Importance of a Nanoscience Approach in the Understanding of Major Aqueous Contamination Scenarios: Case Study from a Recent Coal Ash Spill

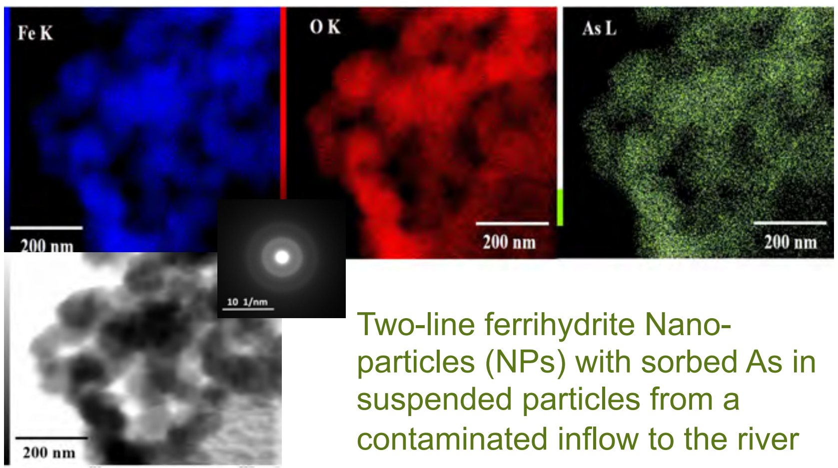
Yi Yang [a,c], Benjamin P. Colman [b], Emily S. Bernhardt [b], Michael F. Hochella, Jr.[a]







Anatase NPs in river water



Two-line ferrihydrite Nano-particles (NPs) with sorbed As in suspended particles from a contaminated inflow to the river

- Arsenic is the principal contaminant in this spill; the majority was found to be sorbed to aggregates dominated by incidental ferrihydrite NPs; the minority is a truly dissolved (molecular aqueous) component.
- A photocatalytic nano-TiO_2 phase (anatase) was identified in the coal ash impacted river water.

More info. refer to ES&T 2015 DOI: 10.1021/es505662q

[a] The Center for NanoBioEarth, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA
[b] Biology Department, Duke University, Durham, NC, 27708, USA
[c] Department of Geosciences, East China Normal University Shanghai, China

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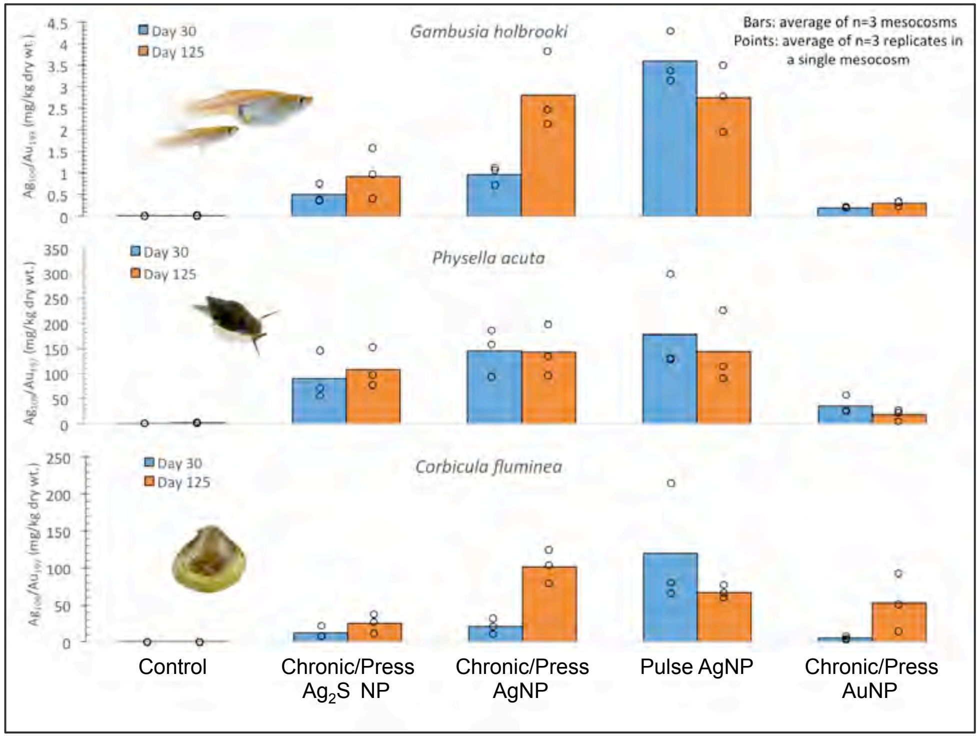
Bioavailability of Nanoparticles in Environmentally-Relevant Exposure Scenarios

Leanne Baker[1], Ryan King[1], Ben Colman[2], Emily Bernhardt[2], and Cole Matson[1]

Ag and Au NP uptake in Duke wetland mesocosms



- **Press versus Pulse Dosing:** Equal or higher concentrations of Ag in organisms from chronic AgNP treatments, compared to Pulse AgNP treatments, by day 125. Note that chronic treatment was only 34% of pulse treatment by day 125 (of 365).
- **Dissolution:** Ag from AgNPs is taken up with greater efficiency than AuNP, likely due to AgNP dissolution. Filter-feeding *Corbicula* are the only exception.

[1]*Baylor University*, [2]*Duke University*

NSF EF-0830093
NSF DBI-1266252

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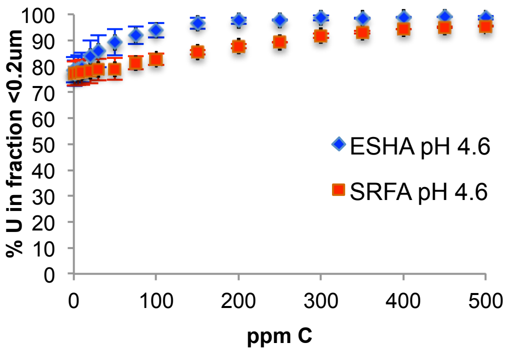
Partitioning of U(VI) between ferrihydrite and humic substances

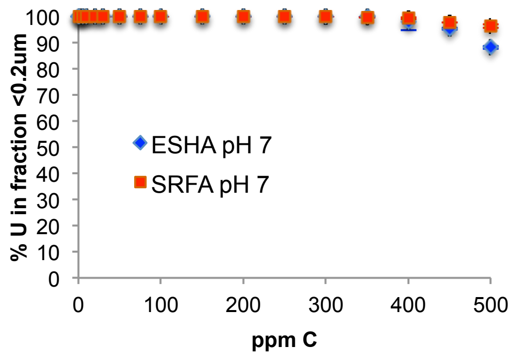
Gabrielle Dublet[1], Naresh Kumar[1], Juan Lezama Pacheco[2,3], John Bargar[3], Scott Fendorf[2] and Gordon Brown[1,3]

Question: What is the role of Natural Organic Matter (NOM) on U(VI) scavenging vs. dispersion in sediment?

U retained in the aggregate fraction <0.2μm

as a function of ESHA or SRFA concentration (expressed in ppm Carbon)





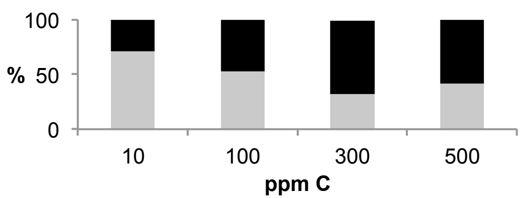
Proxy studied: batch reactions of 2g/L ferrihydrite (common nano Fe-hydroxides) with U(VI) 100 μM in presence of various concentrations of humic and fulvic acids (ESHA and SRFA)

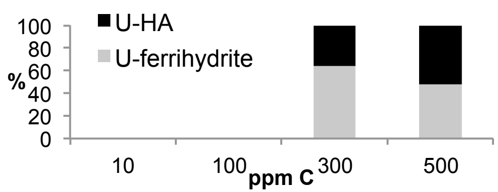
Effect of organic matter concentration:

- at acidic pH, U scavenging is enhanced
- At circumneutral pH, high NOM concentrations hinder U scavenging

What is the speciation of U in the organo-metallic aggregates?

%U bound to C vs. ferrihydrite in the aggregates





Approach: LCF fits of U LIII edge EXAFS spectroscopy as a function of ESHA or SRFA concentration (expressed in ppm Carbon)

Highlight result:
The proportion of U bound to C compounds is significant, and it increases with the concentration of NOM in the aggregates.

Other ongoing project in the group:

- the reactivity of iron hydroxides based on Fe and O isotope exchange
- sulfidation of Fe-oxides and oxyhydroxides

[1]Dept. of Geological Sciences, Stanford University, Stanford CA 94305-2115, USA
[2]Dept. of Earth System Science, Stanford University, Stanford CA 94305, USA
[3]Stanford Synchrotron Radiation Lightsource, 2575 Sand Hill Road, Menlo Park, CA, 94025, USA

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Hydrology and sediment transport dominate reactive metallic nanoparticle fate in rivers

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

Less than 6% NP-derived metal stays in a watershed!

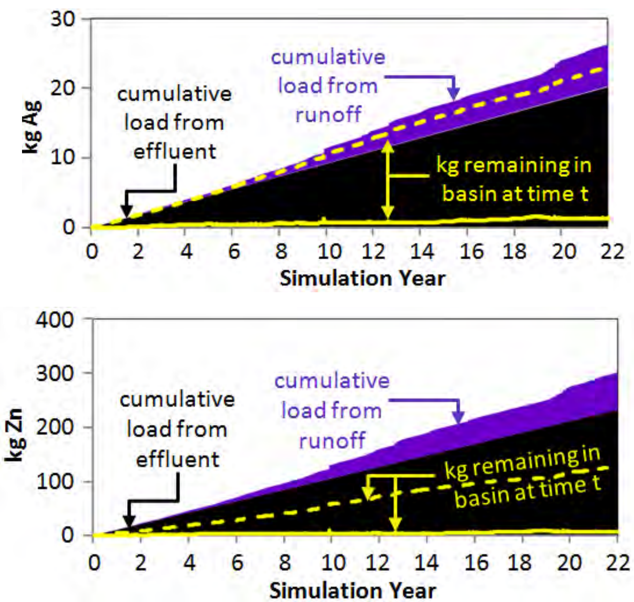

Figure 1. Comparison of the cumulative total NP derived metal load from effluent (black) and agricultural runoff (purple) to the total mass of NP metal in the simulation over time for Ag (top) and Zn (bottom). Solid yellow lines show metal mass remaining in the basin. Dashed yellow lines show metal remaining for a scenario where flow-dependence of sediment transport was disabled. [2]

Spatial variation of predicted NP-derived metal concentration within the basin varies by more than 5 orders of magnitude.

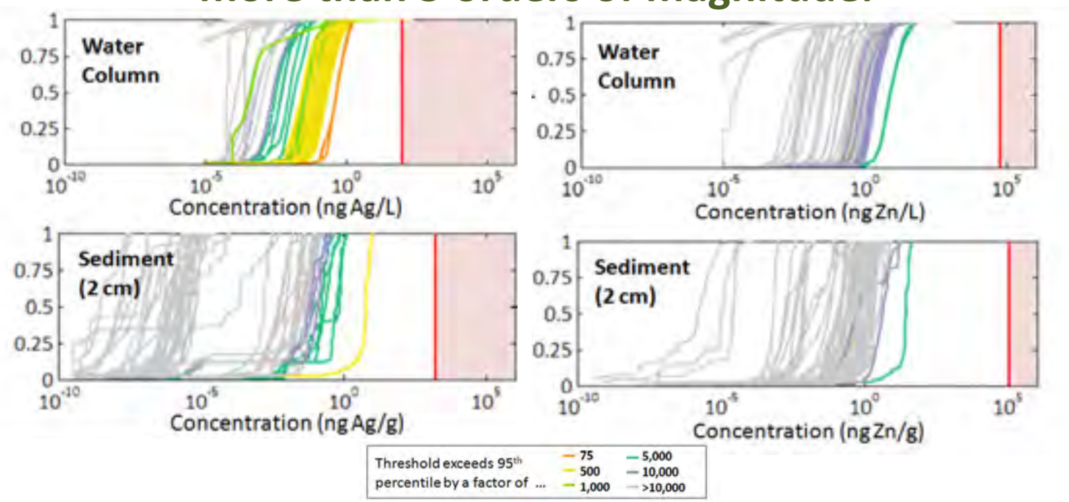

Figure 2. Cumulative distribution functions of predicted total metal concentrations over time in surface waters and sediments for each of the 68 river segments in the James River Basin for Ag (left) and Zn (right). Red vertical lines indicate EPA water and sediment quality thresholds for the metals. [a]

Overly-simplified hydrology in fate models will overestimate accumulation and underestimate variability in environmental concentrations of NP-derived metals.

[1] Engineering and Public Policy, Carnegie Mellon University
[2] Civil and Environmental Engineering, Carnegie Mellon University

a From Dale et al., "Watershed model prompts re-evaluation of prevailing approaches in fate modeling for engineered nanoparticles" (in review)

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Effect of UV on AgNP toxicity in zebrafish embryos

Audrey Bone[1], Richard Di Gulio[1]

Understanding the role of environmental factors such as UV in mediating behavior and toxicity of AgNPs to aquatic organisms is vital for risk assessment

PVP- and GA-AgNPs were irradiated using a solar simulator prior to dosing zebrafish embryos

UV-vis spectra of AgNPs exhibit changes in AgNP size and aggregation that could be responsible for the changes in toxicity. Dissolution studies are ongoing.

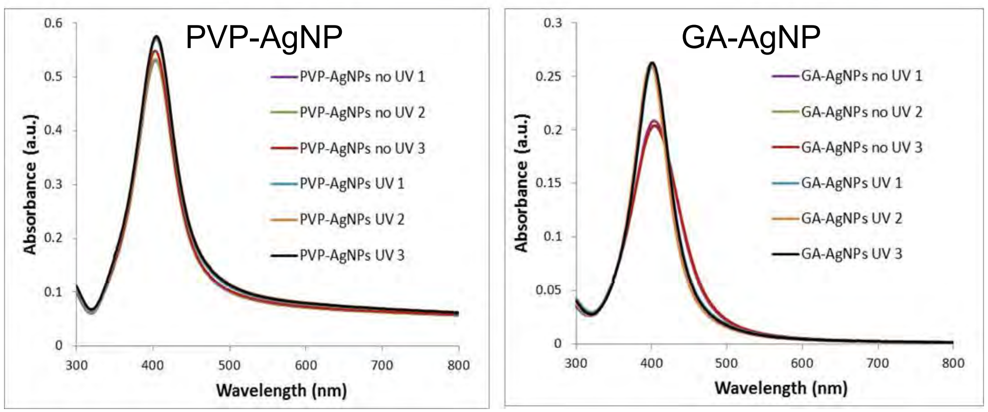
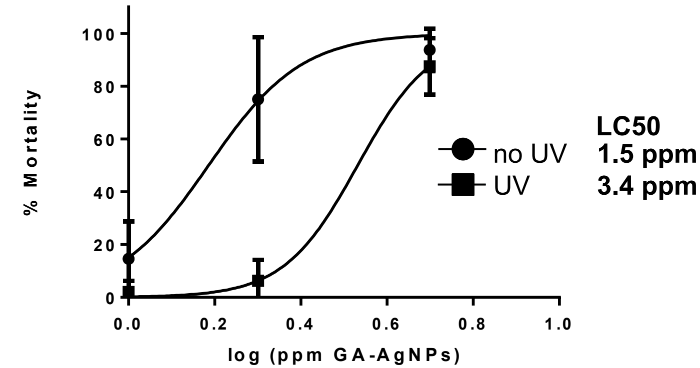


Figure 1. UV-vis spectra of PVP-AgNPs and GA AgNPs with and without exposure to UV light.

A. GA-AgNP toxicity **Reduced** after irradiation



B. PVP-AgNP toxicity **Increased** after irradiation

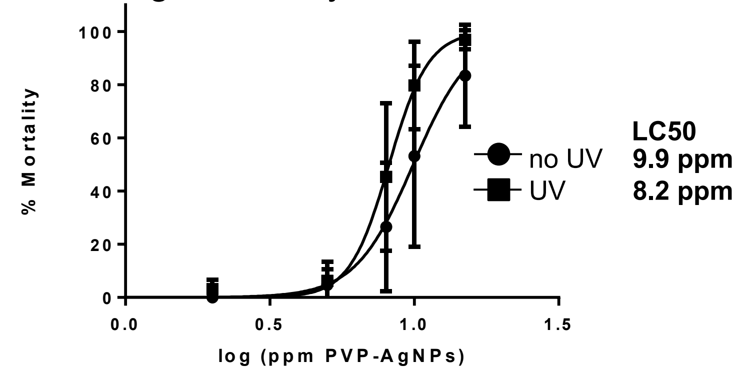


Figure 2. 48 hpd % mortality of 6 hpf zebrafish embryos exposed to (A) GA-AgNPs and (B) PVP-AgNPs previously illuminated with UV and without. Data presented as average ± SEM.

[1]Nicholas School of the Environment, Duke University

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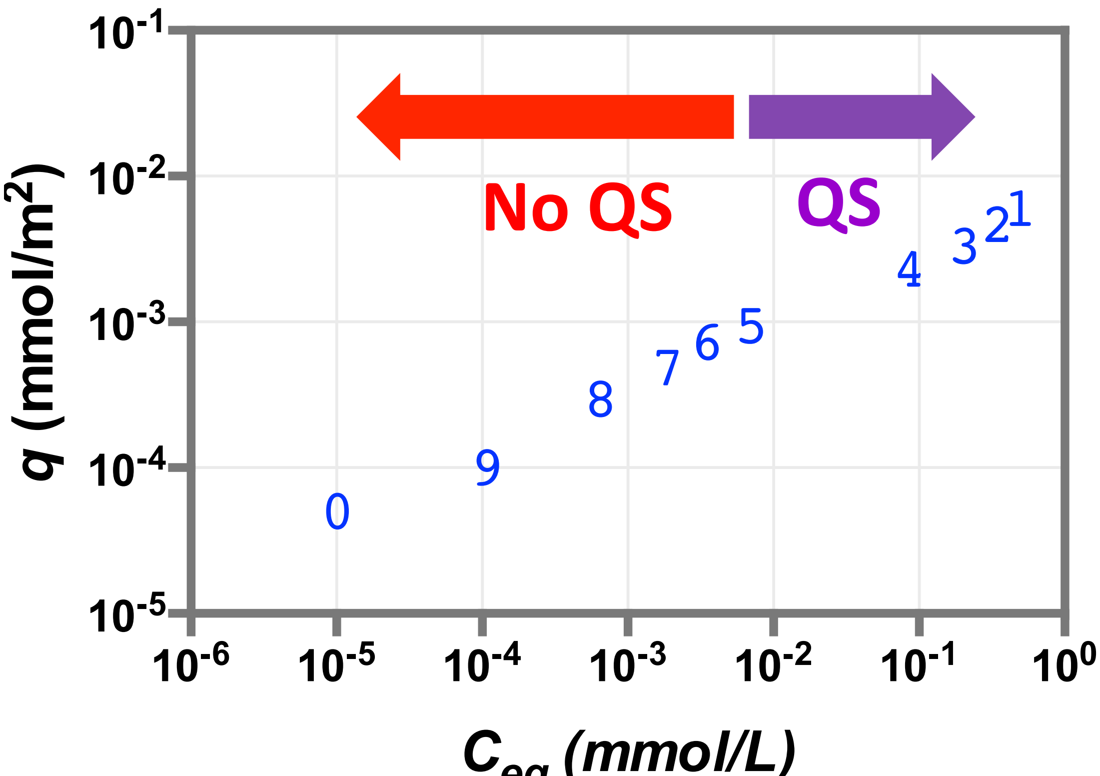
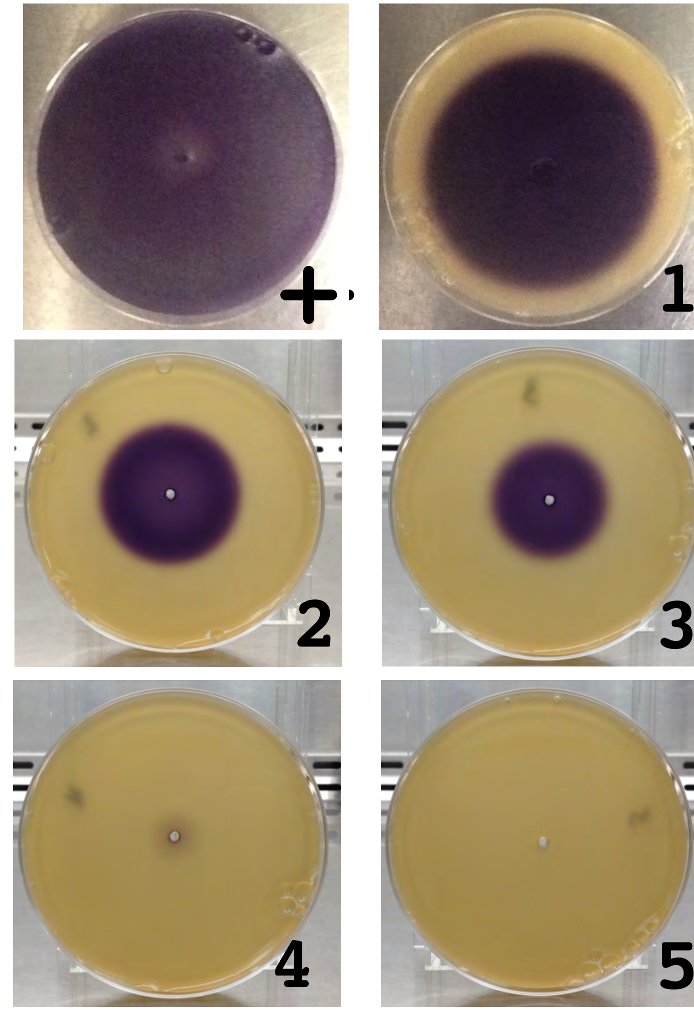
Disruption of Cell-to-Cell Signaling in Bacteria

Eric McGivney, Kelvin B. Gregory
Civil and Environmental Engineering, Carnegie Mellon University

Acyl-homoserine lactones, chemical signals secreted and sensed by bacteria are intercepted by adsorption on ENP, stopping important cell-to-cell communications; Coatings may be used to fine-tune





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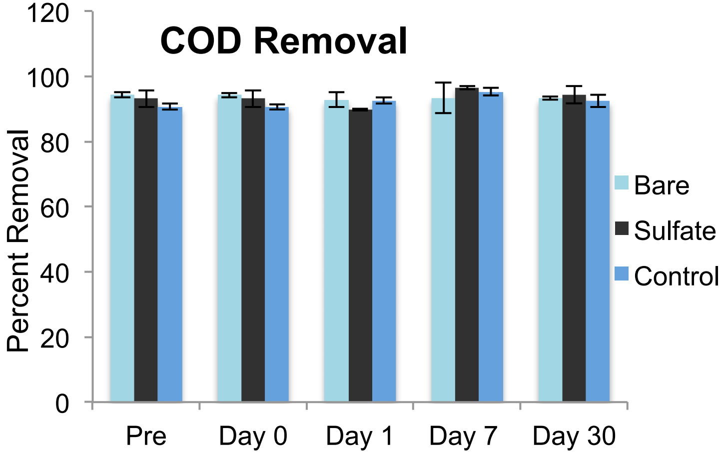
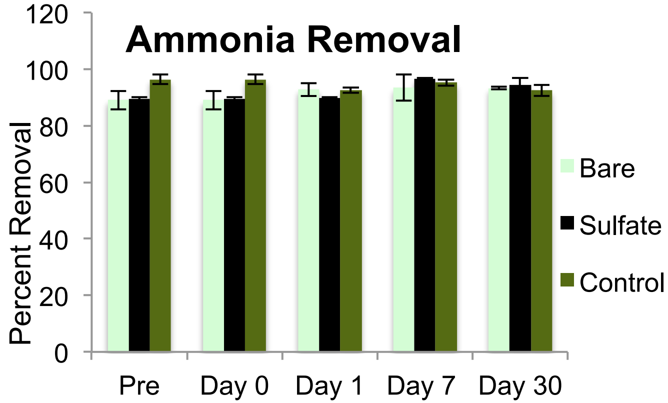
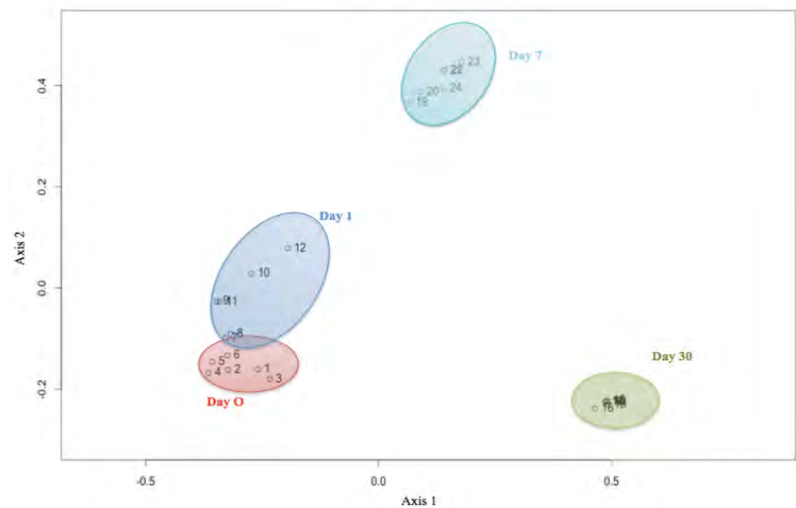
CeO_2 Nanoparticle Impacts on Wastewater Microbial Communities

Carley A. Gwin and Claudia K. Gunsch
Department of Civil and Environmental Engineering, Duke University





Microbial Community Analysis



CeO_2 Nanoparticles did not significantly affect wastewater treatment performance (in terms of COD and Nitrogen Removal) as well as microbial community structure

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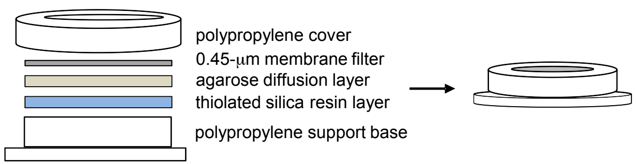
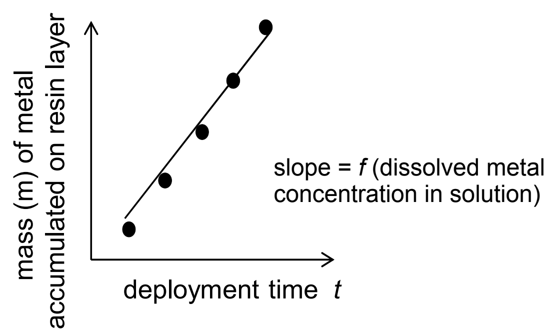
Passive Samplers for Dissolved Metal Analysis: What is the Influence of Nanoparticles?

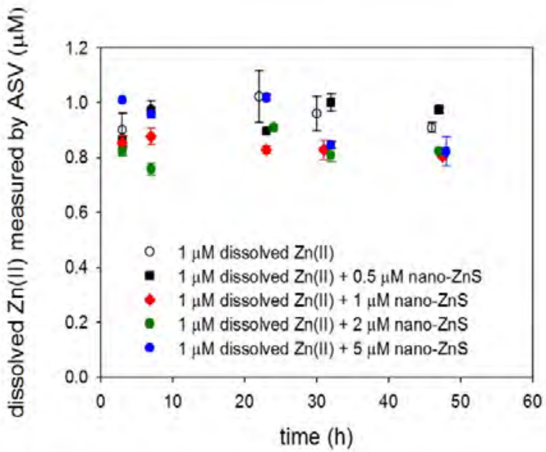
Anh Pham, Carol Johnson, Devon Manley, Heileen Hsu-Kim
Duke University, Department of Civil & Environmental Engineering

Diffusive Gradient in Thin-Film (DGT) passive samplers are used to quantify dissolved metals concentrations in water and sediment.

What are the effects of nanoparticles for measurements by DGTs?

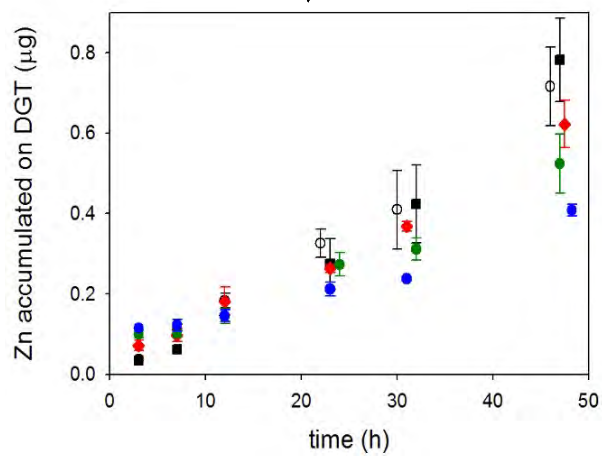






In mixtures with approximately the same dissolved [Zn],

the addition of ZnS nanoparticles yielded slower uptake of Zn on the sampler.



Implications: The presence of nanoparticles results in underestimates of dissolved metal concentration by the DGT sampler.

Future work: What is the relevance of DGT data for metal bioavailability?

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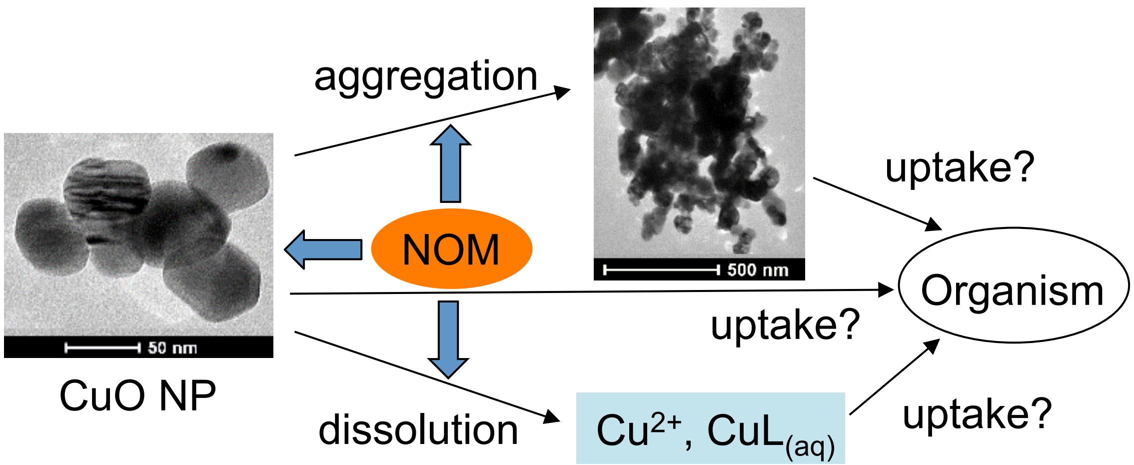
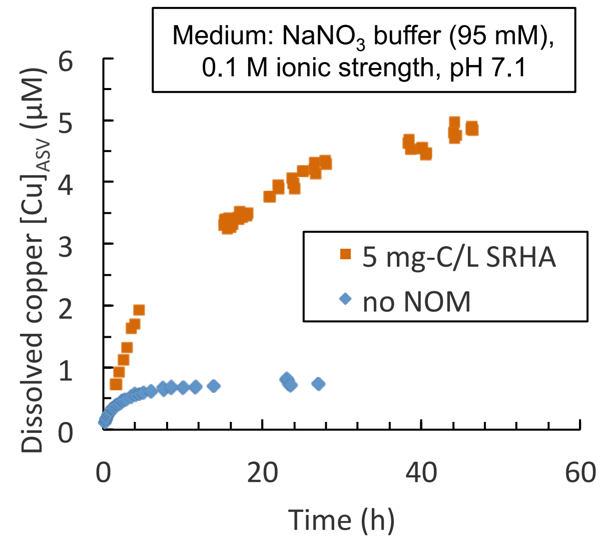
Effects of natural organic matter on the dissolution, aggregation and uptake kinetics of CuO NPs

Chuanjia Jiang[1,§], Benjamin T. Castellon[2,§], Cole W. Matson[2], George R. Aiken[3], Heileen Hsu-Kim[1]





- The uptake of copper by organisms exposed to CuO NPs can occur through release of soluble Cu from the NP or direct uptake of the NP.
- NOM affects the aggregation and dissolution kinetics of the NP, modifies particle surface, and thus may affect rate of copper uptake.
- The research will explore how different types of NOM isolates will affect these processes.

[1] Duke University [2] Baylor University [3] US Geological Survey
[§]These authors contributed equally to this work.

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Impacts on Educational Infrastructure 2008-15

22 new courses + 46 modified- infuses research into curriculum for 6 universities

445 seminars and colloquia across core university partners

IGERT creates core graduate level nano-science courses

REU is creating international training network & pipeline for graduate school

- ❑ Duke, VT, CMU & CEREGE   17 FACULTY mentors
- ❑ >90% REU seniors accepted into 1st choice graduate school science/engineering
- ❑ Applications increased over 5-fold-   increased retention for graduate school

➢CEINT Scholars Steering Committee (CSSC) major input into training

- ❑ Student/postdocs input annual meeting, posting instrumentation list, highlights and publication updates on website, new FACEBOOK page




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CEINT: Value Added Center Impacts

ALL Participants **Address bigger picture research questions**

Student/Post-docs

- ↑ access to faculty/students beyond home base
  learn cross discipline experimental design, toxicity endpoints
- rich interdisciplinary, cross-site & international collaborations
- ↑ nano-science content knowledge & research skills

Faculty Impacts

- ↑ **collaborations across discipline/for grants & research publications**
- ↑ cross-discipline presentations **> 1025 major presentations 14+ disciplines**
- allows going further in data interpretation- including follow-up design
- **address research areas not possible with simple sharing of resources**

Expanded national/international nano-research and publication networks

- **33 proposals funded** last 7 years- majority collaborative
  US-UK *Transatlantic Initiative for Nanotechnology and the Environment*
  Renewal Duke Superfund Research Center (*Developmental Toxicants)*
  Safe Ecodesign & Sustainable Research & Education Applied to Nanomaterial Development, 11 million euros
- **369** publications-majority collaborative; **14** online protocols
- leader in nano-informatics- shaping major initiatives

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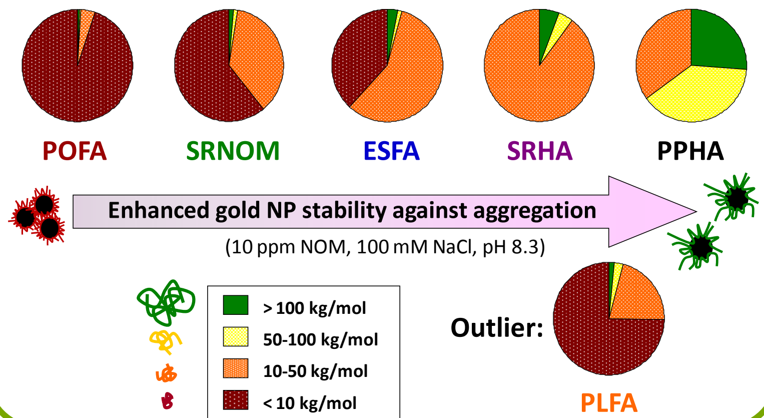
Correlation of the Properties of Fractionated Natural Organic Matter to Stabilization of Gold Nanoparticles Against Homoaggregation

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

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

NOM molecular weight distribution



Qualitative trends

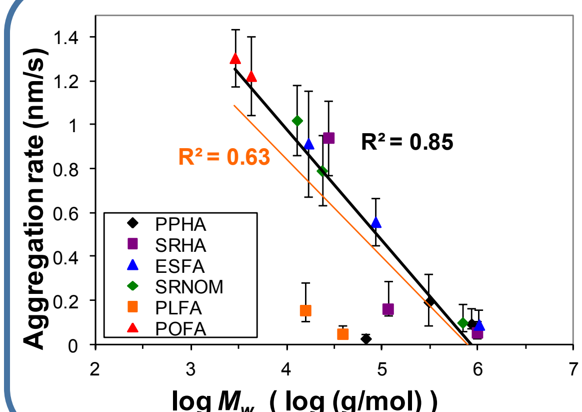
- Highest molecular weight (MW) NOM isolates produced the strongest gold NP stability, except for Pony Lake fulvic acid (PLFA)
- Highest MW components enhanced NP stability, even at low fractions of the NOM mixture

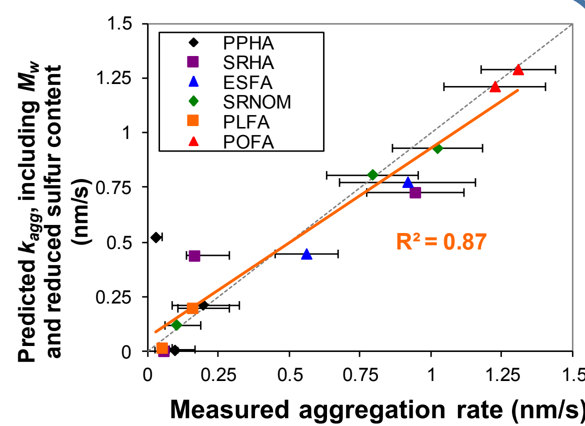
Implications:

- High MW NOM components have strong affinity to adsorb
- Steric stabilization mechanisms dominate (at high ionic strength)
- Polydispersity of NOM is important for predicting NP stability

Empirical correlations

- Weight-averaged MW of the NOM (*left*) was the best single predictor of gold NP aggregation rates
- Inclusion of reduced sulfur (*right*) or nitrogen content as additional parameters with MW improved the correlation for the chemically distinct PLFA isolate
- Assessment of NOM isolates with broader range of chemistries is needed to confirm the importance of functional group content





Louie, S.M.; Spielman-Sun, E.R.; Small, M.J.; Tilton, R.D.; Lowry, G.V. Correlation of the Physicochemical Properties of Natural Organic Matter Samples from Different Sources to Their Effects on Gold Nanoparticle Aggregation in Monovalent Electrolyte. *Environmental Science and Technology* **2015**, *49*, 2188.

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Getting from Data to Knowledge in the CEINT NanoInformatics Knowledge Commons (NIKC)

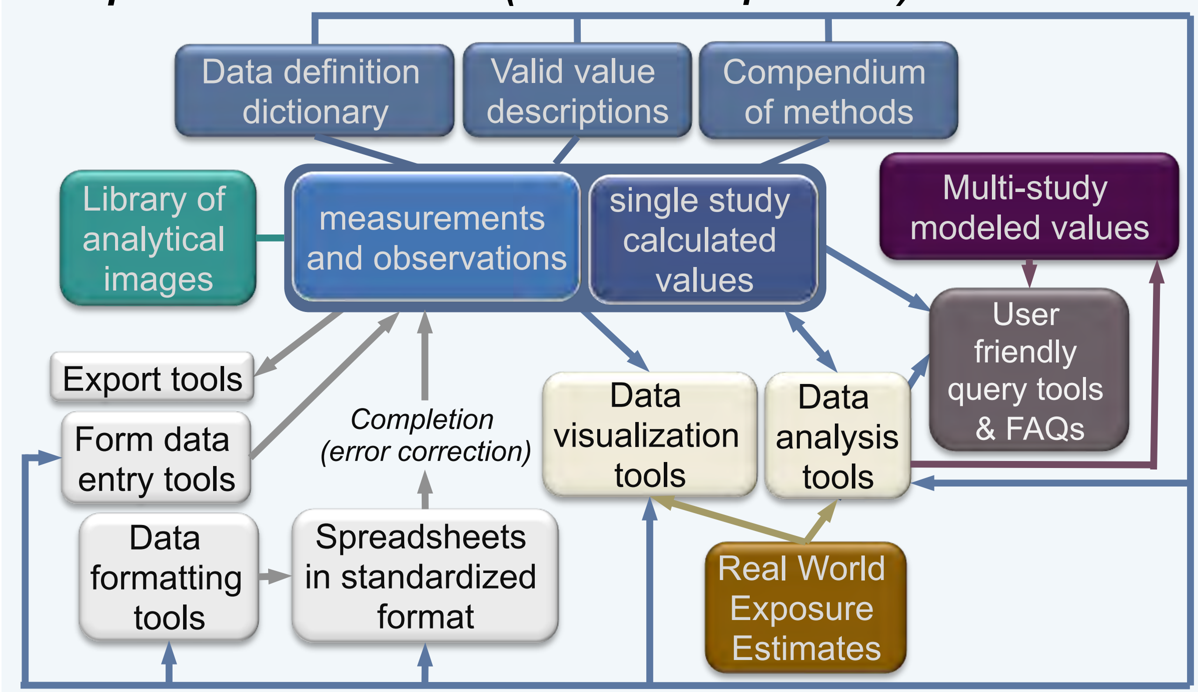
Sandra C. Karcher[1], Christine Ogilvie Hendren[2], Yuan Tian[3], Jeanne M. VanBriesen[1], Gregory V. Lowry[1], Mark R. Wiesner[2,3]

Targeted For Inclusion in CEINT NIKC:

- Nanomaterial characterization and associated metadata
- System characterization and associated metadata
- Nanomaterial dosing information
- Experimental methods and results
- Single study calculated values

Photo: May 2014 brainstorming session. The CEINT Data Integration Team (DIT) met with experimental researchers to develop database use case scenarios.

Components of the NIKC (realized and potential)



Status of CEINT NIKC:

- Components of the NIKC identified and prioritized
- Structure to hold the measurements and observations and single study calculated values has been designed and documented
- Targeted data being added to the data structure; accessible via query
- Pathways are being developed to get from data to knowledge in a way that is consistent with researcher identified use case scenarios

1 Carnegie Mellon University, Department of Civil and Environmental Engineering
2 Center for the Environmental Implications of NanoTechnology, Duke University
3 Duke University, Department of Civil and Environmental Engineering

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Bioavailability of Silver and Silver Sulfide Nanoparticles to Alfalfa (*Medicago* sativa)

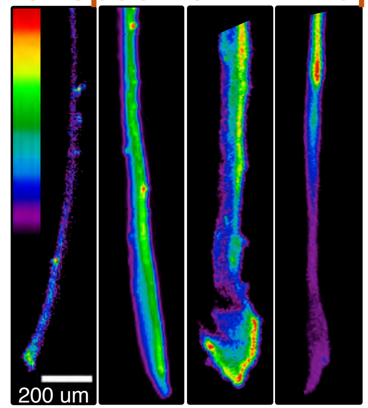
John Stegemeier[1], Fabienne Schwab[2], Ben Colman[2], Gregory V. Lowry[1]

[1]Carnegie Mellon University, Pittsburgh, PA [2]Duke University, Durham, NC

Experimental Setup

- Alfalfa sprouts were exposed hydroponically to three Ag treatments: suspensions of Ag^0 and Ag_2S nanoparticles and the control, $AgNO_3$
- Root tips were examined using Synchrotron-based X-ray Fluorescence (XRF) and Transmission Electron Microscopy (TEM)
- Silver specific XRF maps were generated to visualize the distribution of Ag in the plant tissue while TEM was used to identify dense particles in the cell walls.

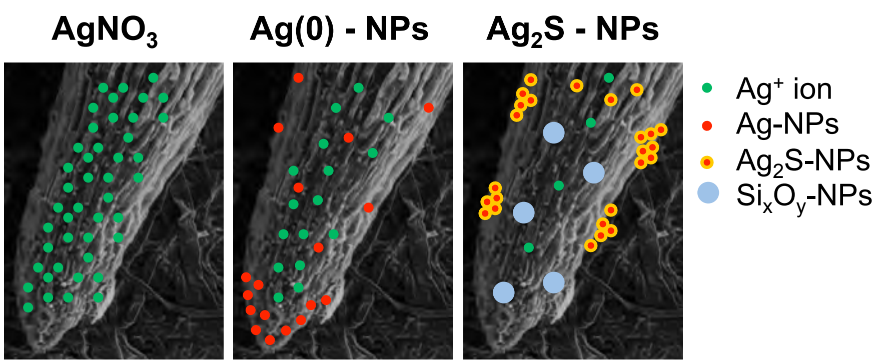
Silver specific XRF maps



Alfalfa root tips

- An unexposed alfalfa root is shown (1st)
- Ag is pervasive in the $AgNO_3$ exposure (2nd)
- Ag is more discrete in Ag^0 and Ag_2S NP treatments (3rd and 4th column, respectively)

Silver exposed alfalfa root tips



Major Results

- Silver accumulated similarly in/on the roots of alfalfa plants for Ag^+ and Ag^0 & Ag_2S nanoparticles.
- Distribution and speciation of Ag in the roots was different of Ag NPs compared to Ag ions.

Implications:

- The low solubility of the Ag_2S NP does not prevent the uptake and translocation throughout plant tissue.
- This suggests Ag solubility, although directly related to toxicity, may not predict the fate of these NPs exposed to plants.

Stegemeier, J.P.; Schwab F.; Colman, B.P.; Webb, S.; Newville, M.; Lanzirotti, A.; Winkler, C.; Wiesner, M.; Lowry, G.V. Speciation Matters: Bioavailability of Silver and Silver Sulfide Nanoparticles to Alfalfa (*Medicago* sativa). Environmental Science and Technology Submitted - 2015,

DGE-0966227
EF-0830093

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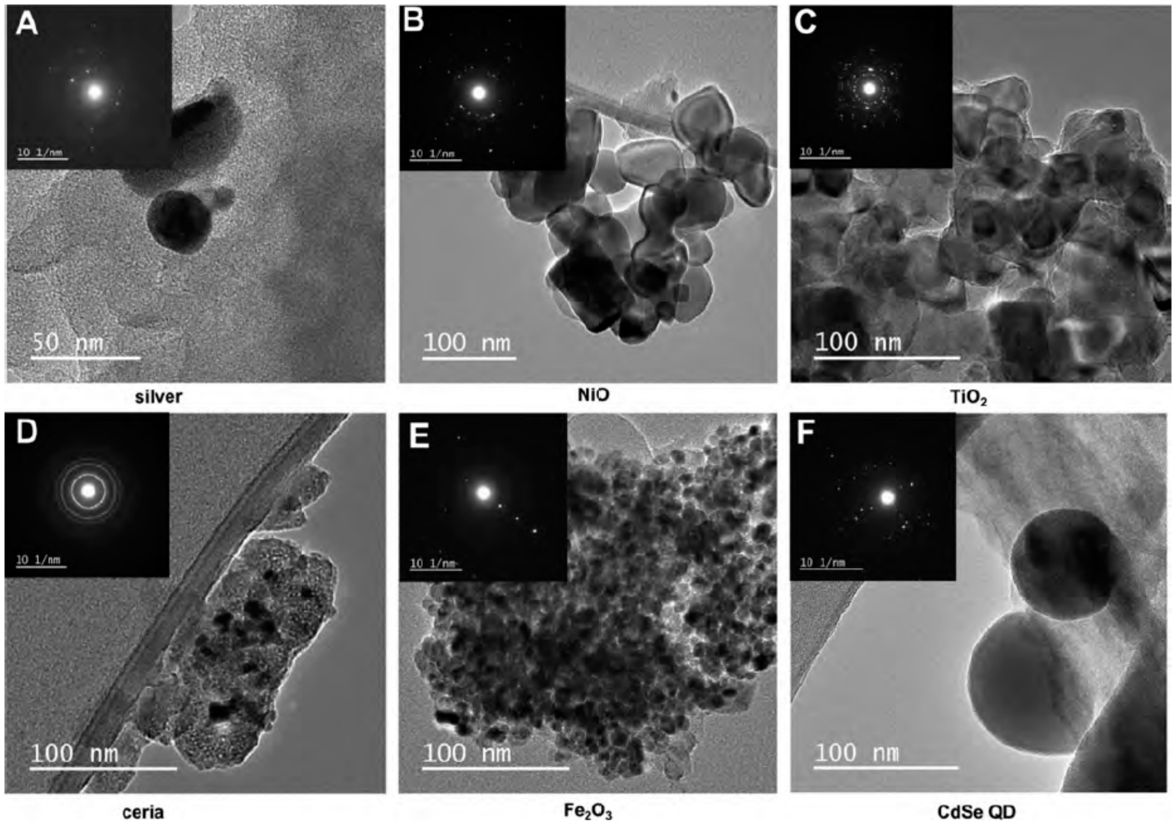
Exposure to and Transformations of Nanomaterials in Air

Eric Vejerano, Linsey C. Marr

Civil and Environmental Engineering, Virginia Tech



Following incineration, some nanomaterials are unchanged while others undergo transformations, as shown in this TEM image of six types of nanoparticles. Silver nanoparticles are unchanged, NiO nanoparticles grow and remain separate, TiO_2 nanoparticles retain their size but aggregate and become encapsulated, ceria and Fe_2O_3 nanoparticles form aggregates, and CdSe QD nanoparticles grow and form spheres. The insets show diffraction patterns of the particles.

Vejerano et al. (2014). Characterization of particle emissions and fate of nanomaterials during incineration, Environmental Science: Nano, 1, 133-143.

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Chronic AgNP additions lead to higher long-term exposure

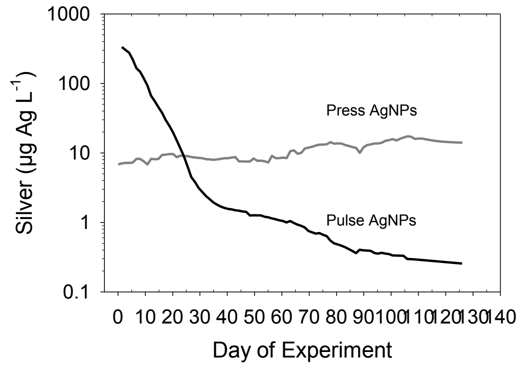
Benjamin P. Colman[1], Leanne Baker[2], Cole Matson[2], Ryan King[2], Emily S. Bernhardt[1]

Pulse exposure vs. more realistic Press

Pulse AgNPs:
450mg Ag`
Single addition on Day 0

Press AgNPs:
450mg Ag
52 weekly additions

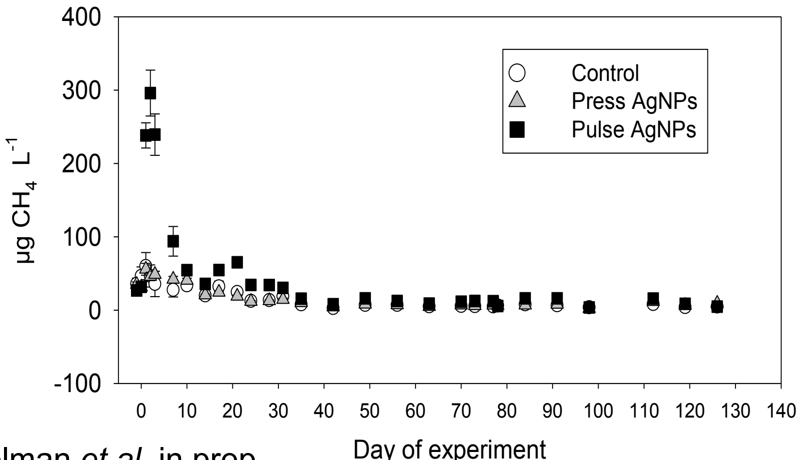
Higher long-term exposure in Press AgNPs



Smoothed data show Press AgNPs have higher average water column concentration by Day 28 (only 8% silver added)

Pulse AgNPs →Acute toxicity to plants

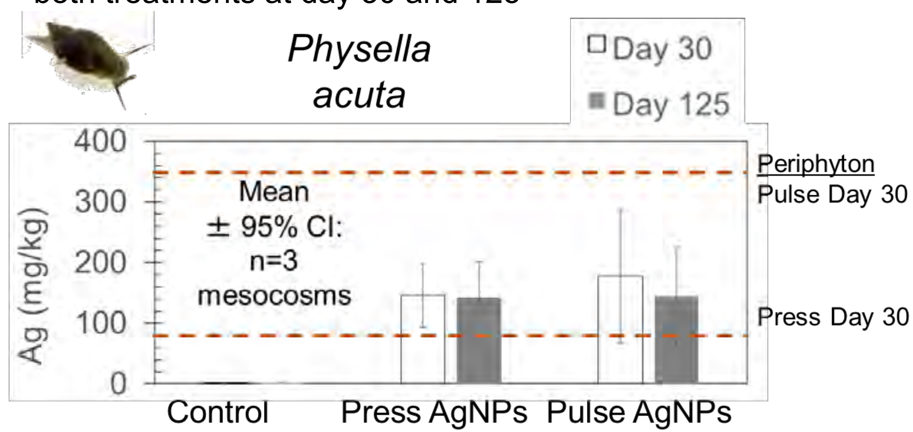
Ag toxicity to plants caused short termrelease of organic matter, and organic matter stimulated methane production



Colman *et al.* in prep

Uptake similar Pulse vs. Press by day 125

Periphyton (microbe/algal biofilms) show elevated Ag in Pulse AgNPs at day 30, but snails showed similar uptake in both treatments at day 30 and 125



[1]Duke University; [2]Baylor University

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Impact of sulfidation on the bioavailability and toxicity of silver nanoparticles to *Caenorhabditis elegans*

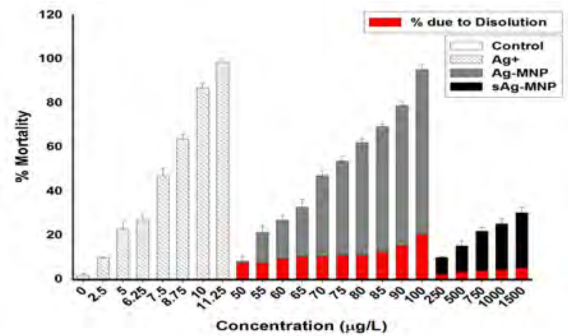
Daniel L. Starnes, Jason M. Unrine, Catherine P. Starnes, Blanche E. Collin, Emily K. Oostveen, Rui Ma, Gregory V. Lowry, Paul M. Bertsch, and Olga V. Tsyusko

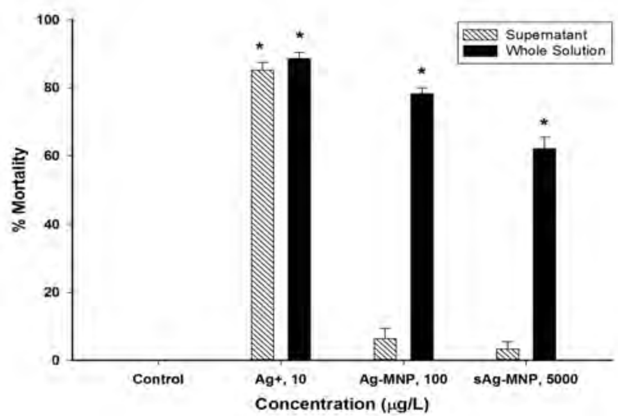
Department of Plant and Soil Sciences, University of Kentucky, 1100 South Limestone Street, Lexington, Kentucky 40546, United States

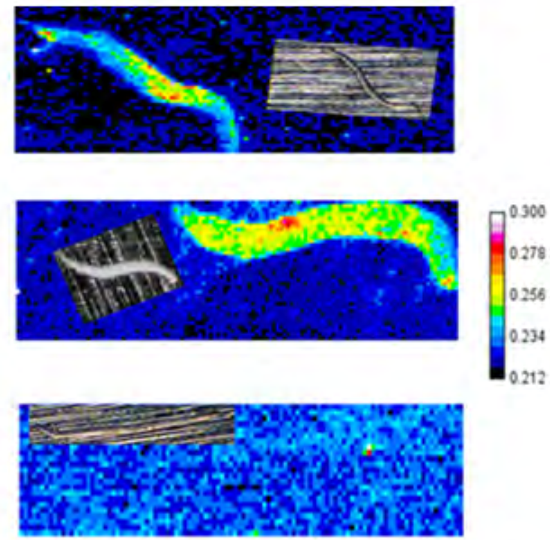
Department of Civil & Environmental Engineering, Carnegie Mellon University, Pittsburgh, Pennsvlvania 15213. United States

- Toxicity of both pristine (Ag-MNP) and sulfidized manufactured Ag nanoparticles (sAg-MNP) due to release of ions in exposure media decreases with increasing exposure concentration (two figures on left).

- Sulfidized AgNPs elicit toxicity without measurable (by XRF) uptake of Ag. Toxicity may be related to cuticle damage (figure on right).







Ag K_{α} fluorescence of *Caenorhabditis elegans* specimens (stage L4) that were exposed to the LC_{30} concentration(at 4 hr) for $AgNO_3$ (Top), pristine silver manufactured nanoparticles (Middle), and artificially sulfidized manufactured silver nanoparticles (Lower) in moderately hard reconstituted water in the absence of bacterial food, as determined using a synchrotron-based X-ray fluorescence microprobe. Color bar indicates normalized Ag K_{α} fluorescence intensity. The data are normalized to the incident beam ion chamber reading, so they are normalized with respect to each other.

Starnes, D. L.; Unrine, J. M.; Starnes, C. P.; Collin, B. E.; Oostveen, E. K.; Ma, R.; Lowry, G. V.; Bertsch, P. M.; Tsyusko, O. V., Impact of sulfidation on the bioavailability and toxicity of silver nanoparticles to Caenorhabditis elegans. *Environmental Pollution* ***2015, 196, 239-246.***

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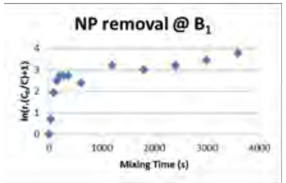
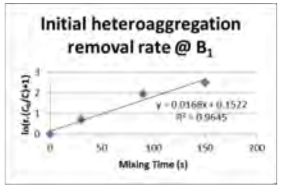
A Method for Heterogeneous NP Attachment in Mixed Systems

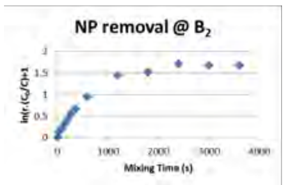
Niall O'Brien[1,2], Mark Wiesner[1]

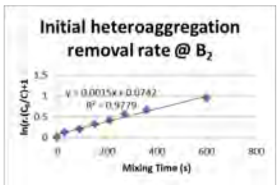
1. Experimentally determine collision frequency, β, for defined mixed system.





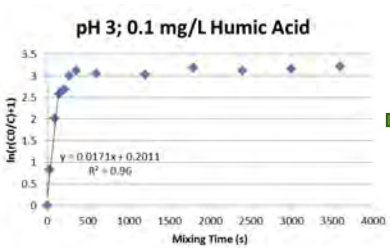
αβB = 0.0168

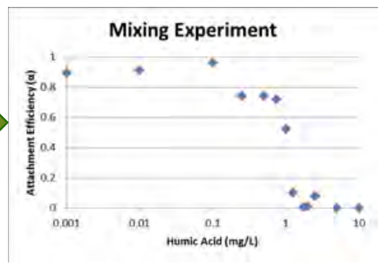




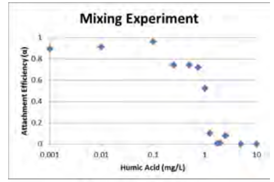
αβB = 0.0015

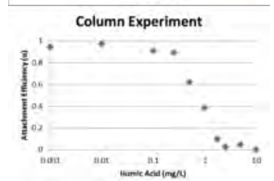
2. Alter material/environmental conditions to observe change in attachment, α, determined from initial rate of heteroäggregation, αβB.

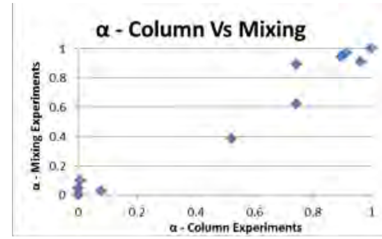




3. Validate method with porous media attachment.







Method yields a NP-appropriate fate descriptor for nanomaterial distribution as determined by their affinity for the surface they encounter and their relative abundance.

α βB

(Attachment)*(Defined_System)*(Time) → Distribution

Describes dynamic nature of NP attachment and heteroäggregation.

Surface affinities determined by mixing experiment compare well to those obtained in column studies.

Column vs mixing $R^2>0.9$

Provides NP homoäggregation control; equivalent unavailable for porous media method.

[1] Department of Civil and Environmental Engineering, Duke University
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NP Release from Commercial Wood Products:

Impact of form on environmental fate

Niall O'Brien[1,2], Gretchen Gherke[1], Mélanie Auffan[3], Jean-Yves Bottero[3], Mark Wiesner[1]

Citrate-coated CeO_2 NP wood stain additive (NanoBYK)

Scenario 1: Dried stain (Form: surface bound / solid suspension)

Scenario 2: Liquid stain spill (Form: liquid suspension)

Micronized copper azole (MCA) pressure treated lumber

Scenario 1: Freshly cut lumber (Form: solid suspension)

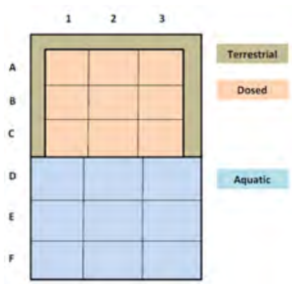
Scenario 2: Soil applied fungicide (Kocide) (Form: liquid suspension)

Soil release

Ce: Dried stain (Surface bound/solid suspension) → Weathering

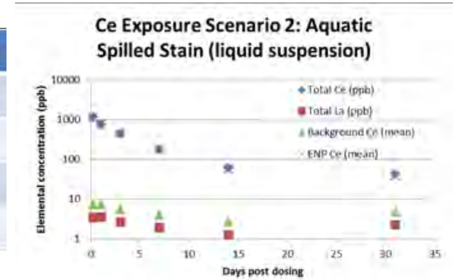
Ce: Liquid stain (Liquid suspension) / Cu: Liquid fungicide (Liquid suspension) → Direct release

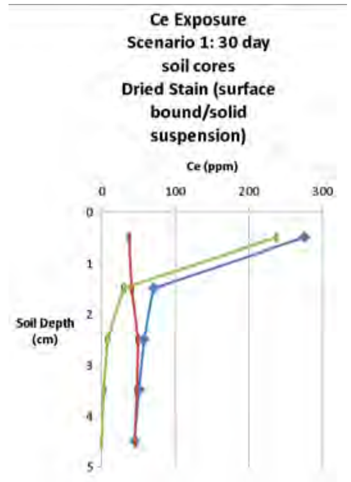
Cu: Pressure treated lumber (Solid suspension) → Leaching

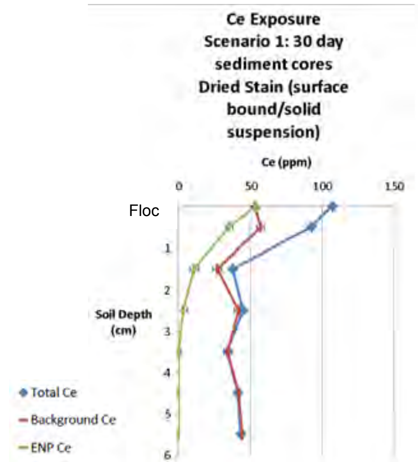


Detection above variable and relatively high background levels of Ce (40-80 ppm) and Cu (5-15 ppm) achieved through analysis of elemental ratios.

Elements	Ce/La	Ce/Nd
Ratio	2.14	1.83
Std Dev	0.09	0.10
5th percentile	2.00	1.69
95th percentile	2.27	1.97







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