Nanomaterials and the Food Supply: Assessing the Balance Between Applications and Implications

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The Connecticut Agricultural Experiment Station, New Haven CT

Presented at the Environmental Sciences: Water, Gordon Research Conference
Holderness, NH June 29, 2016

What are Nanoparticles (NPs)?

- Nanoparticles (less than 100 nm) are generated *naturally* by erosion, fires, volcanoes, and marine wave action
- **A key point**- People have been exposed to nanoparticles for as long as there have been people; in other words, “nano” isn’t inherently bad
- Nanoparticles are also produced by human activities such as coal combustion, vehicle exhaust, and weathering rubber tires

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What are Engineered Nanomaterials?

- Our ability to construct and manipulate materials at the nano-scale has increased dramatically in the last decade
- Why does this matter? Materials at the nano-scale behave *differently* than the same material at the bulk or non-nano scale
- Have higher surface area to volume; can engineer for surface reactivity or other desired characteristics
- Frequently, this unique behavior can be both useful and profitable
- Nanotechnology was a $1 billion industry in 2005; will be a $3 trillion industry by 2020

Different size gold NPs reflect different wavelengths of light

Changes in properties		
	Bulk-scale	**Nano-scale**
Si	Insulator	Conductive
Cu	Malleable and ductile	Stiff
TiO_2	White color	Colorless
Au	Chemically inert	Chemically active

National Nanotechnology Initiative (NNI)(http://nano.gov/)

- Started in 2000; Clinton administration
- 2016/2017 Budget Request is $1.5 Billion across 20+ Federal agencies. Applications- 93%; Implications- 7%.
- "The NNI consists of the individual and cooperative nanotechnology-related activities of Federal agencies with a range of research and regulatory roles and responsibilities."

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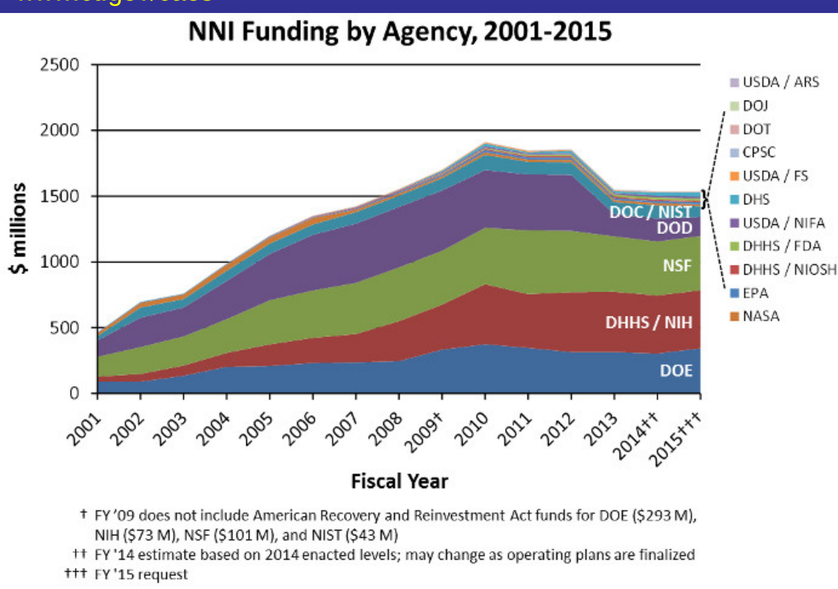
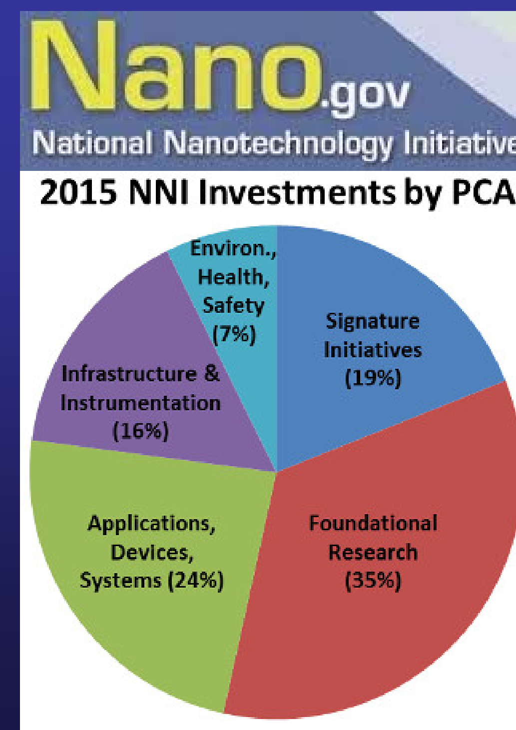
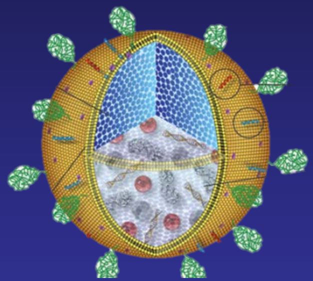
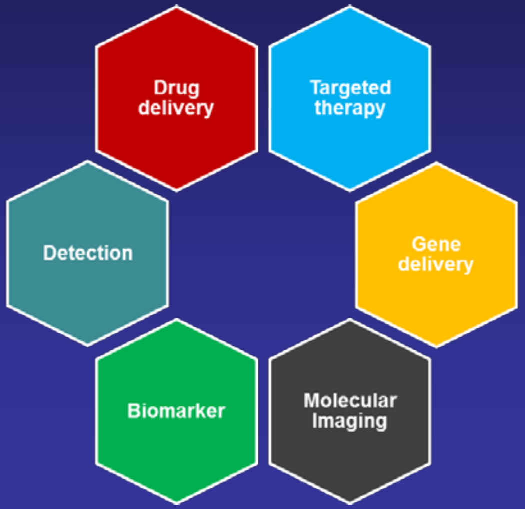




Nanotechnology- Applications

- Nanomedicine
- Water treatment
- Communication\electronics
- Energy
- **Agriculture\food**
- Textiles
- Cosmetics





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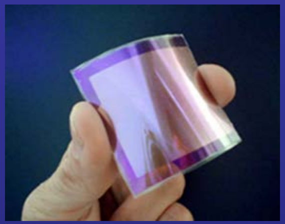
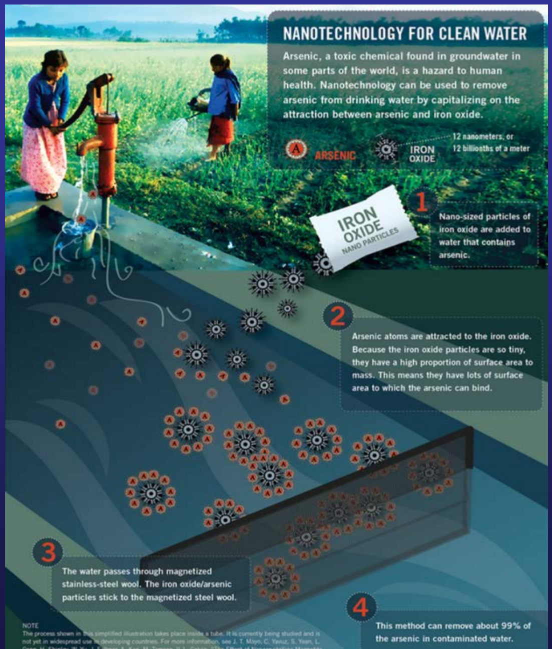
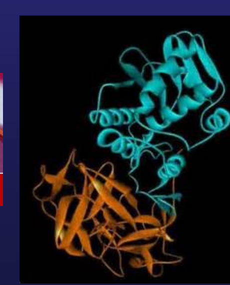


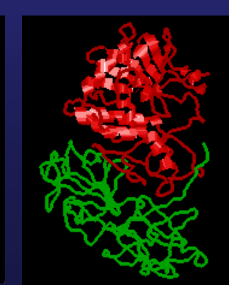


Nanomaterials and Food Protection

- Food Safety- microbes and chemicals/elements
  - Antimicrobials in food packaging
  - Nano-enabled coatings for food and equipment
  - Nanosensors for pathogen detection

- Food Defense- microbes and chemicals/elements
  - Nanosensors for specific agents of concern (biological weapons such as *B. anthracis,* Ebola [Harvard/MIT]) and others; plant proteins such as ricin and abrin.





Nanomaterials and Agriculture

- There has been significant interest and research in using nanotechnology in agriculture
- The goals fall into several categories
  - Increase production rates and yield
  - Increase efficiency of resource utilization
  - Minimize waste production
- Specific applications include:
  - Nano-fertilizers, Nano-pesticides
  - Nano-based treatment of agricultural waste
  - Nanosensors

2015

Biotechnology Advances 32 (2014) 1550–1561

Contents lists available at ScienceDirect

Biotechnology Advances

journal homepage: www.elsevier.com/locate/biotechadv

ELSEVIER

Research review paper

Application of nanotechnology for the encapsulation of botanical insecticides for sustainable agriculture: Prospects and promises

Jhones Luiz de Oliveira [a,1], Estefânia Vangelie Ramos Campos [a,b,1], Mansi Bakshi [c], P.C. Abhilash [c], Leonardo Fernandes Fraceto [a,b,*]

[a] Department of Biochemistry, State University of Campinas, Campinas, SP, Brazil
[b] Department of Environmental Engineering, São Paulo State University – UNESP, Sorocaba, SP, Brazil
[c] Institute of Environment & Sustainable Development, Banaras Hindu University, Varanasi 221005, India

IB IN DEPTH—Special Section on Nanobiotechnology, Part 1

2012

NORMAN SCOTT AND HONGDA CHEN, GUEST EDITORS

(Part 2 of the IB IN DEPTH—Special Section on Nanobiotechnology will appear in the February 2013 issue)

Overview

Nanoscale Science and Engineering for Agriculture and Food Systems

frontiers in Chemistry

PERSPECTIVE
published: 16 November 2015
doi: 10.3389/fchem.2015.00064

2015

Nanopesticides and Nanofertilizers: Emerging Contaminants or Opportunities for Risk Mitigation?

Melanie Kah *

Department of Environmental Geosciences, University of Vienna, Vienna, Austria

2012

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Review

pubs.acs.org/JAFC

Nanomaterials in Plant Protection and Fertilization: Current State, Foreseen Applications, and Research Priorities

Alexander Gogos,[†] Katja Knauer,[‡] and Thomas D. Bucheli[*,†]

[†] Agroscope Reckenholz-Tänikon Research Station ART, 8046 Zurich, Switzerland
[‡] Federal Office for Agriculture, 3003 Berne, Switzerland

Supporting Information

Nanomaterials and Agriculture

- Nano-fertilizers often contain nutrients/growth promoters encapsulated in nanoscale polymers, chelates, or emulsions
  - Slow, targeted, efficient release becomes possible.
  - In some cases, the nanoparticle itself can stimulate growth
- Nanosensors can be used to detect pathogens, as well as monitor local, micro, and nano-conditions in the field (temperature, water availability, humidity, nutrient status, pesticide levels…)

www.ct.gov/caes

Biol Trace Elem Res (2007) 119:77–88
DOI 10.1007/s12011-007-0046-4

2007

The Improvement of Spinach Growth by Nano-anatase TiO_2 Treatment Is Related to Nitrogen Photoreduction

Fan Yang · Chao Liu · Fengqing Gao · Mingyu Su · Xiao Wu · Lei Zheng · Fashui Hong · Ping Yang

J Nanopart Res (2011) 13:4519–4528
DOI 10.1007/s11051-011-0406-z

2011

RESEARCH PAPER

Beneficial role of carbon nanotubes on mustard plant growth: an agricultural prospect

Anindita Mondal · Ruma Basu · Sukhen Das · Papiya Nandy

Agric Res
DOI 10.1007/s40003-014-0113-y

2014

FULL-LENGTH RESEARCH ARTICLE

Development of Zinc Nanofertilizer to Enhance Crop Production in Pearl Millet (*Pennisetum americanum*)

J. C. Tarafdar · Ramesh Raliya · Himanshu Mahawar · Indira Rathore

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
Article
pubs.acs.org/JAFC

2012

Dissolution Kinetics of Macronutrient Fertilizers Coated with Manufactured Zinc Oxide Nanoparticles

Narges Milani,[*,†] Mike J. McLaughlin,[†,‡] Samuel P. Stacey,[†] Jason K. Kirby,[‡] Ganga M. Hettiarachchi,[‡,§] Douglas G. Beak,[‡,∥] and Geert Cornelis[†,⊥]

Nanomaterials and Agriculture

- Nano-pesticides often follow a similar model to nano-fertilizers; active pesticidal (insecticide, fungicide,…) ingredient associated with or within a nanoscale product or carrier
  - Increased stability/solubility, slow release, increased uptake/translocation, and in some cases, targeted delivery (analogous to nano-based delivery in human disease research)
  - Can result in lower required amounts of active ingredients

2015

Journal of Agricultural and Food Chemistry
Perspective
pubs.acs.org/JAFC
Terms of Use

Nanopesticides: Guiding Principles for Regulatory Evaluation of Environmental Risks

Rai S. Kookana,*,†,‡ Alistair B. A. Boxall,§ Philip T. Reeves,∥ Roman Ashauer,§ Sabine Beulke,⊥ Qasim Chaudhry,⊥ Geert Cornelis,# Teresa F. Fernandes,□ Jay Gan,● Melanie Kah,△ Iseult Lynch,▼ James Ranville,○ Chris Sinclair,⊥ David Spurgeon,■ Karen Tiede,⊥ and Paul J. Van den Brink○,▲

www.ct.gov/caes

Mycobiology 39(1) : 26-32 (2011)
© The Korean Society of Mycology
DOI:10.4489/MYCO.2011.39.1.026

2011

Inhibition Effects of Silver Nanoparticles against Powdery Mildews on Cucumber and Pumpkin

Kabir Lamsal[1], Sang-Woo Kim[1], Jin Hee Jung[1], Yun Seok Kim[1], Kyoung Su Kim[2] and Youn Su Lee[1]*
[1]*Division of Bio-Resources Technology, Kangwon National University, Chuncheon 200-701, Korea*
[2]*Department of Agricultural Biotechnology, Center for Fungal Genetic Resources and Center for Fungal Pathogenesis, Seoul National University, Seoul 151-724, Korea*

Appl Microbiol Biotechnol (2012) 94:287–293
DOI 10.1007/s00253-012-3969-4

2012

MINI-REVIEW

Role of nanotechnology in agriculture with special reference to management of insect pests

Mahendra Rai · Avinash Ingle

2014

Environment International 63 (2014) 224–235
Contents lists available at ScienceDirect
Environment International
journal homepage: www.elsevier.com/locate/envint
ELSEVIER

Review

Nanopesticide research: Current trends and future priorities

Melanie Kah *, Thilo Hofmann *
Department of Environmental Geosciences, University of Vienna, Althanstrasse 14, 1090 Vienna, Austria

2011

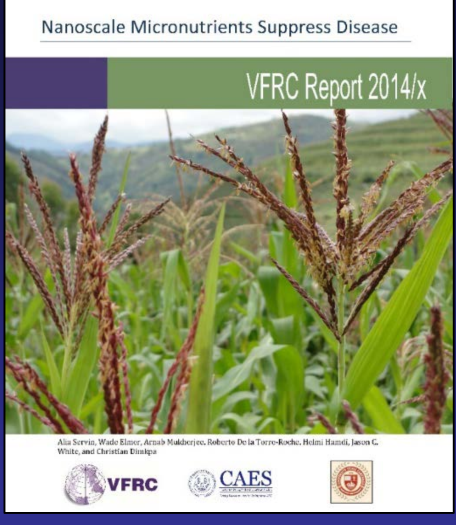
ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Microbiological Research
www.elsevier.de/micres

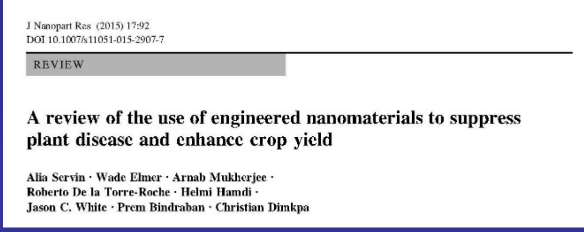
Antifungal activity of zinc oxide nanoparticles against *Botrytis cinerea* and *Penicillium expansum*

Lili He[1], Yang Liu[1], Azlin Mustapha, Mengshi Lin*

Nanomaterials and Agriculture

- Nanoscale based micronutrients for disease suppression (particularly root disease)
- A new research initiative at CAES
- Many micronutrients (Cu, Mn, Zn, Mg) stimulate or are part of plant defense systems.
- However, these nutrients have low availability in soil and are not readily transferred from shoot to root. What about nano versions of these nutrients?
- New USDA Grant- $480,000; March 2016-Feb. 2019

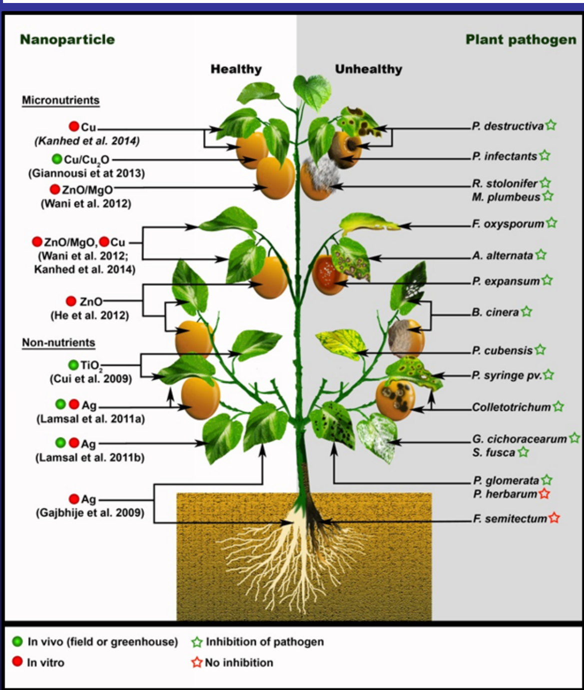


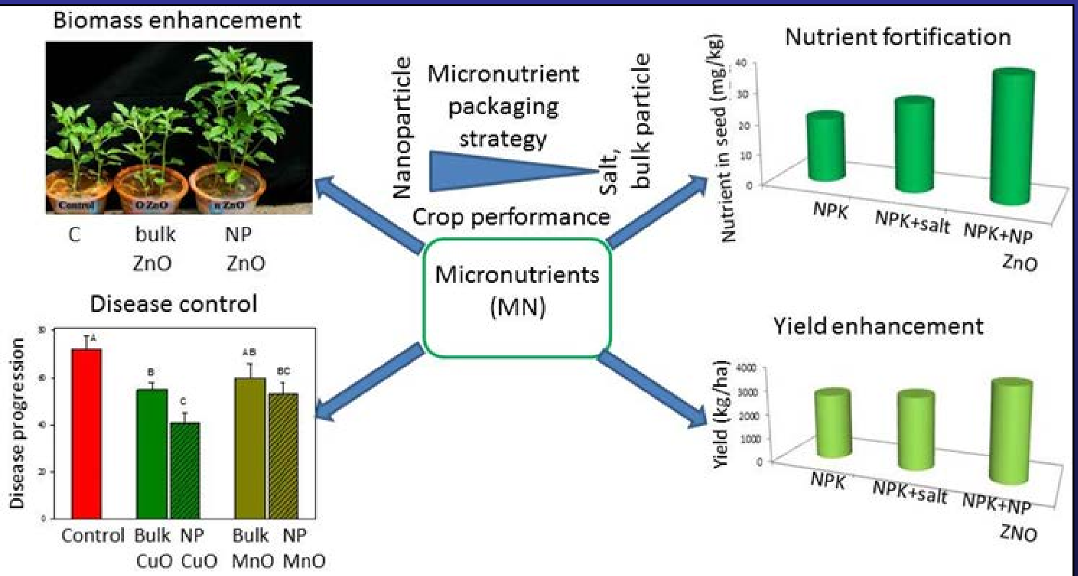

J Nanopart Res (2015) 17:92
DOI 10.1007/s11051-015-2907-7

REVIEW

A review of the use of engineered nanomaterials to suppress plant disease and enhance crop yield

Alia Servin · Wade Elmer · Arnab Mukherjee · Roberto De la Torre-Roche · Helmi Hamdi · Jason C. White · Prem Bindraban · Christian Dimkpa

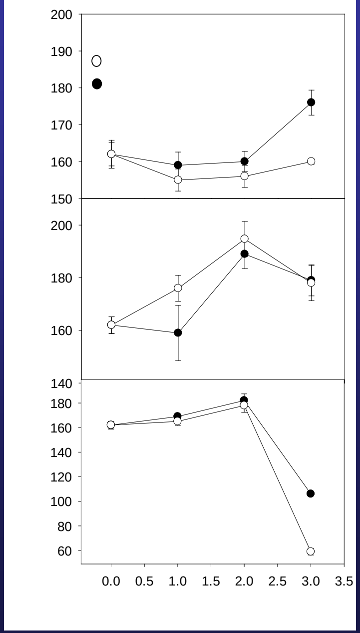


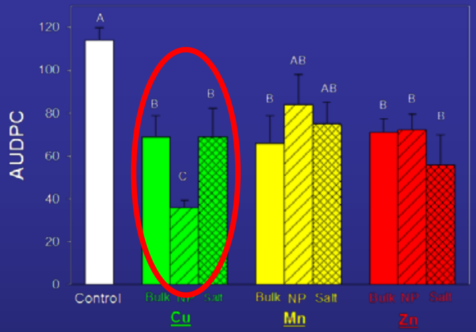


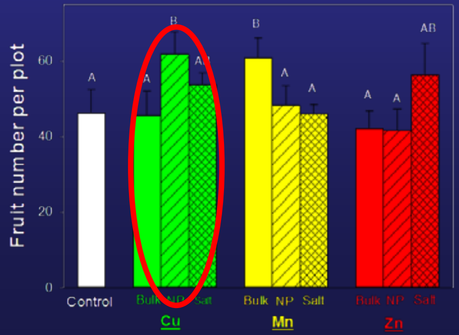
Nanoscale micronutrients for disease suppression

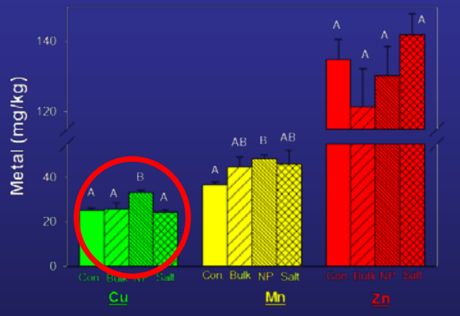
- Greenhouse and field trials with eggplant and tomato
- Single foliar application of NP (bulk, salt) CuO, MnO, or ZnO (100 mg/L) during seedling stage. Transplant to infested soil.
- NP CuO had greater disease suppression, higher Cu root content, and increased yield. NP CuO had no direct affect on the pathogen.
- $44 per acre for NP CuO suppressed a root pathogen of eggplant, increasing yield from $17,500/acre to $27,650 acre.

Elmer and White. *Environ. Sci.: Nano;* submitted









Nanoscale based micronutrients for disease suppression

- Current field trials in CT involve eggplant, watermelon and asparagus
- Single foliar applications of NP CuO, ZnO, MnO alone or in combination.
- Two separate experimental farms (soil types) being used. A range of concentrations used; salt only controls.
- Also, collaborative work in FL where field trials involve tomato growth with multiple applications during the growing season (Kocide, CuO and MgO NPs)

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Implications: Nanotoxicology at CAES

- Two "simple" questions- Do NM behave differently and if so, is that difference of concern with regard to exposure and risk?
- USDA NIFA Grant 1- Addressing Critical and Emerging Food Safety Issues- "Nanomaterial contamination of agricultural crops."
  - Obj. 1: Determine the uptake, translocation, and toxicity of NM to crops.
  - Obj. 2: Determine the impact of environmental conditions on NM uptake, translocation, and toxicity to crops.
  - Obj. 3: Determine the potential trophic transfer of NMs.
  - Obj. 4: Quantify the facilitated uptake of pesticides through NM-chemical interactions.
- USDA NIFA Grant 2- Nanotechnology for Ag. and Food Systems- "Nanoscale interactions between engineered nanomaterials and biochar"

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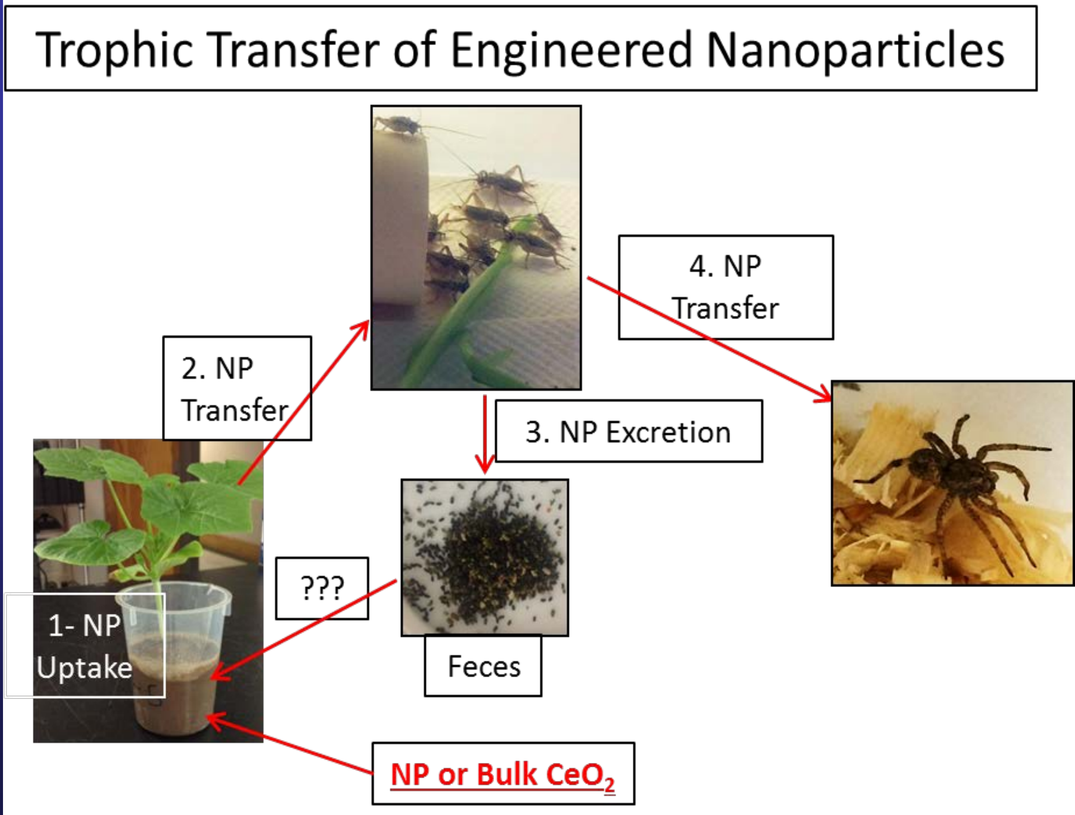
Determine the trophic transfer potential of NMs

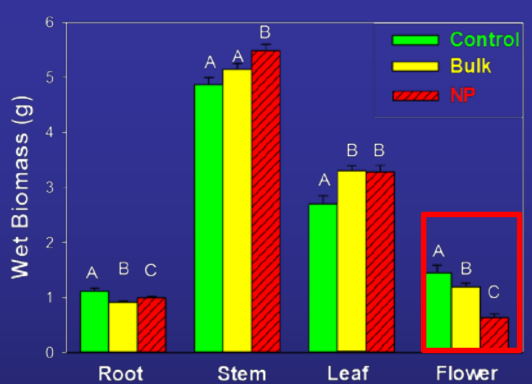
- Experiment 1- NP/bulk CeO_2 (0 or 1000 mg/Kg) added to an agricultural loam.
- Zucchini grown for 28d from seedling.
- Roots, stems, leaves, and flowers analyzed by ICP-MS.
- Leaves used to feed crickets for 14d.
- Crickets used to feed wolf spiders for 7d.
- Insect tissues/feces by ICP-MS.

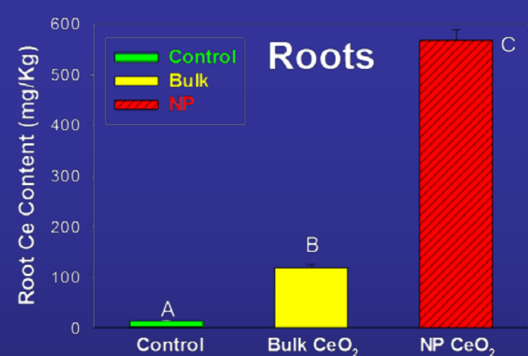
Hawthorne et al. 2014. *Environ. Sci. Technol.* 48:13102-13109

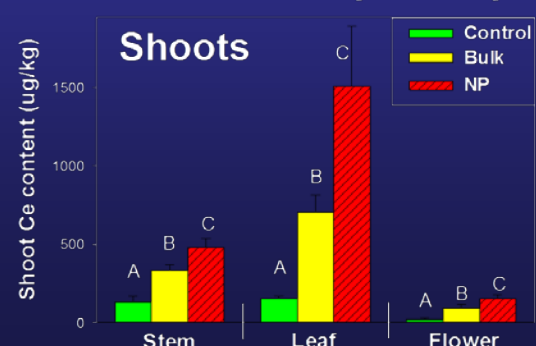


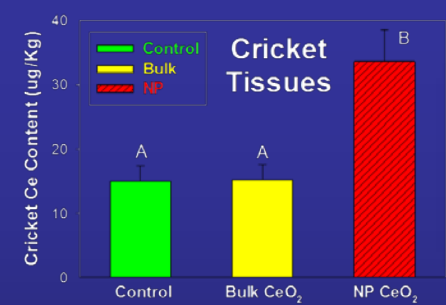
Determine the trophic transfer potential of NMs: Exp. 1

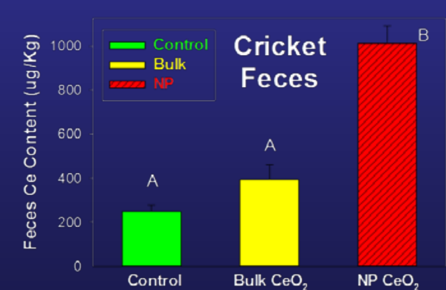
- Particle size-dependent transfer from soil → plant → herbivore → carnivore observed
- NP CeO_2 reduced biomass of reproductive tissues by 50%
- No biomagnification; 10-100 fold decreases at each level
- Insect feces contained 10x more Ce than insect tissues











Hawthorne et al. 2014. *Environ. Sci. Technol.* 48:13102-13109

Determine the trophic transfer potential of NMs: Exp. 2

- NP/bulk La_2O_3 (0 or 500 mg/Kg) in soil; lettuce grown for 50d from seedling.
- Leaves used to feed crickets and darkling beetles for 15 d.
- Crickets used to feed mantids for 7 days

De La Torre-Roche et al. 2015. *Environ. Sci. Technol.* 49:11866–11874.

Determine the trophic transfer potential of NMs: Exp. 2

- NP/bulk La were phytotoxic (25-30% biomass reduction)
- La accumulation and transfer were unaffected by particle size
- No biomagnification; 10-100 fold decreases at each level
- Insect feces contained 10x more La than insect tissues

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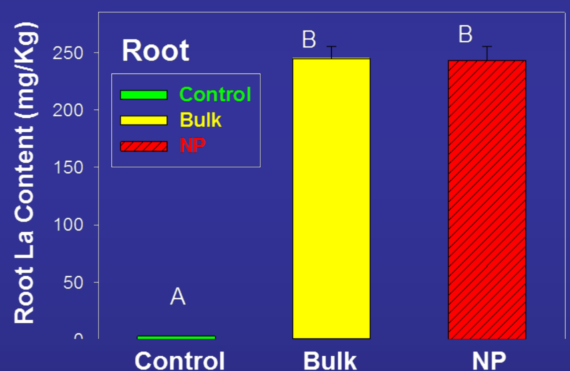
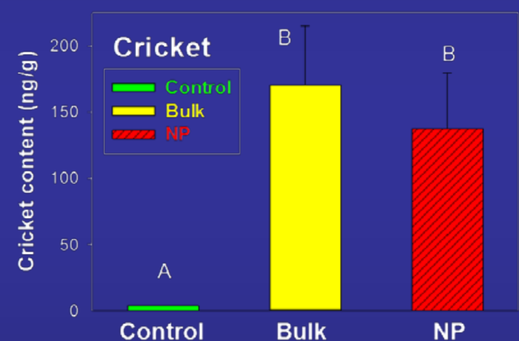
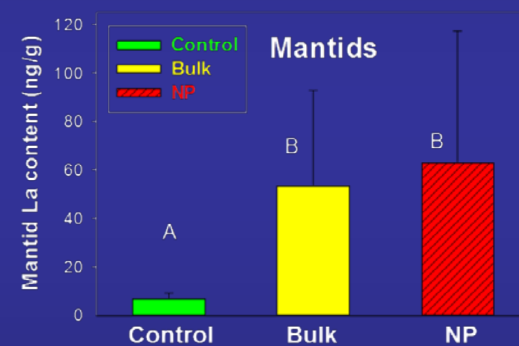
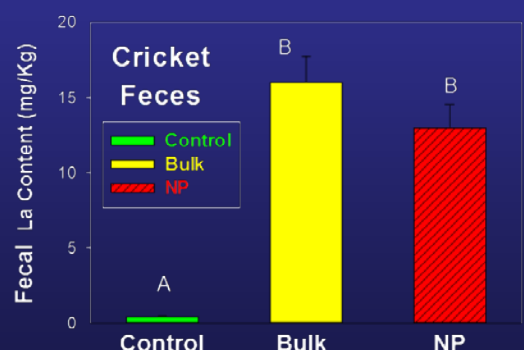
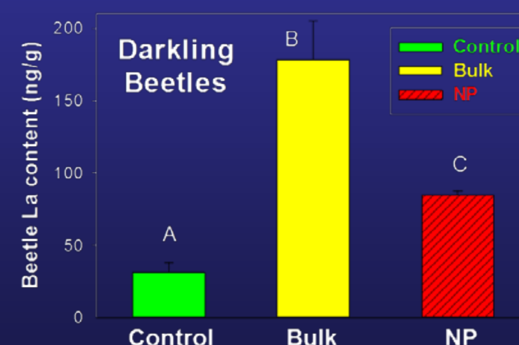






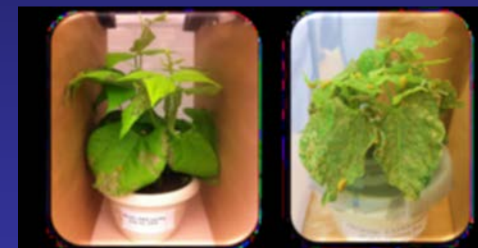


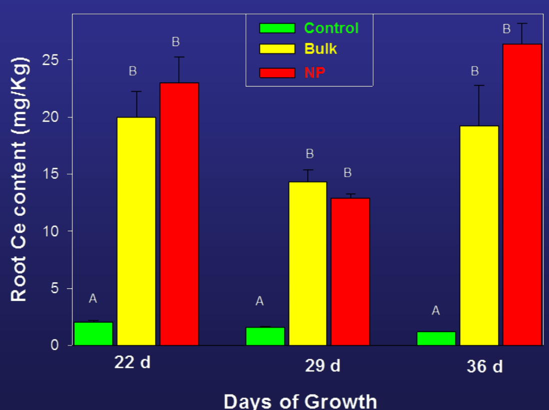


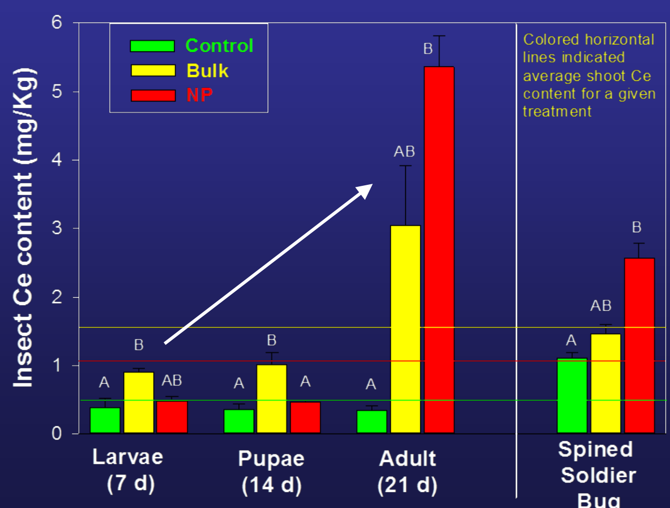
De La Torre-Roche et al. 2015. *Environ. Sci. Technol.* 49:11866–11874.

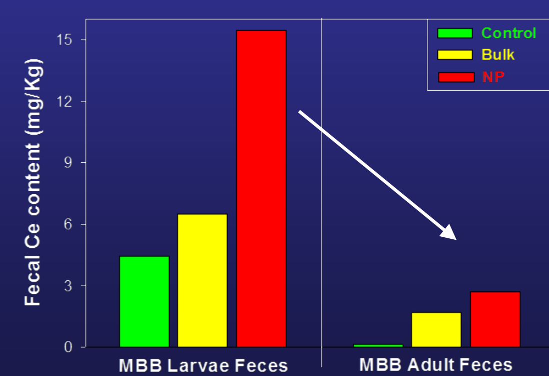
Determine the trophic transfer potential of NMs: Exp. 3

- NP/bulk CeO_2 (1000 mg/kg) added to a TX soil; kidney bean grown for 35 d
- Leaves fed to bean beetle (larvae, pupae, adult);
- Beetles fed to spined soldier bugs
- Ce root\shoot content was unaffected by particle size
- Time-dependent Ce *increase* in the beetle; biomagnification in the adult.
- Time dependent *decrease* in fecal Ce content.









Determine the trophic transfer potential of NMs: Exp. 4

- Trophic transfer of NP and bulk CuO
  - 500 mg/kg in soil for 0 or 60 days, lettuce, cricket, Anolis lizards.
  - Soil was contaminated with weathered chlordane (3 mg/kg) and DDX (0.2 mg/kg)
  - Tracked Cu, chlordane and DDX content and form (ICP-MS, µXRF, XANES, biomass, and gene expression in the plant (transcriptomics)

Servin et al. In preparation

Determine the trophic transfer potential of NMs: Exp. 4

- Leaf Cu content unaffected by particle type or weathering
- Root Cu content affected by particle size and weathering
- Cricket and fecal Cu content largely unaffected by particle type, weathering or even Cu amendment
- Lizard Cu content (head, intestine, body, feces) unaffected by Cu amendment, type or weathering

☹

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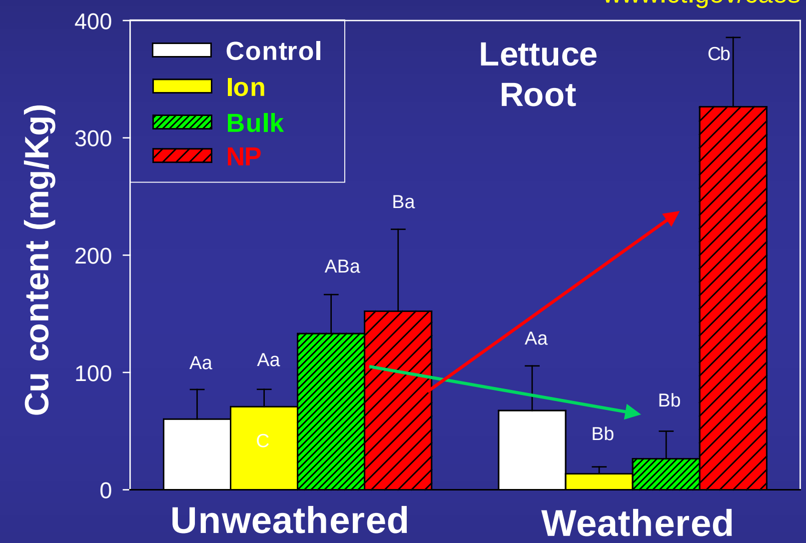
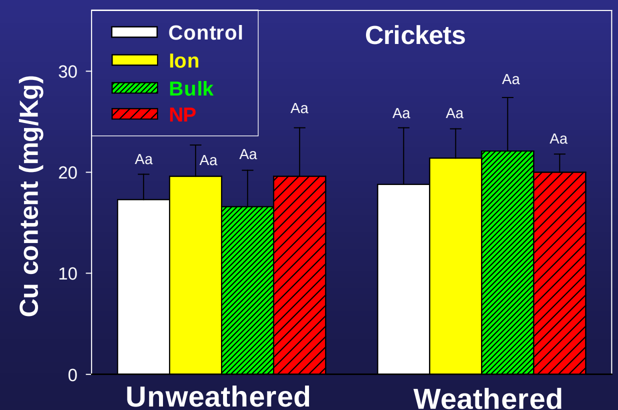
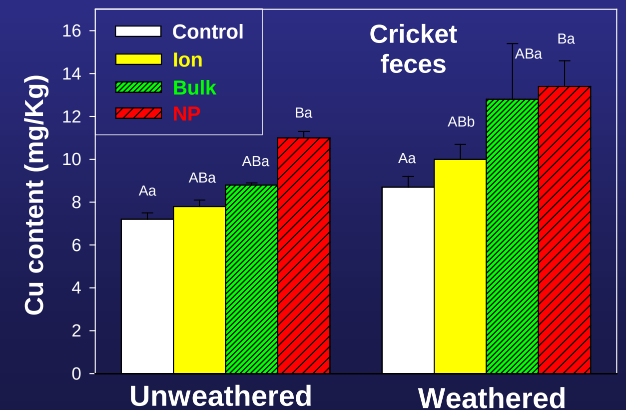






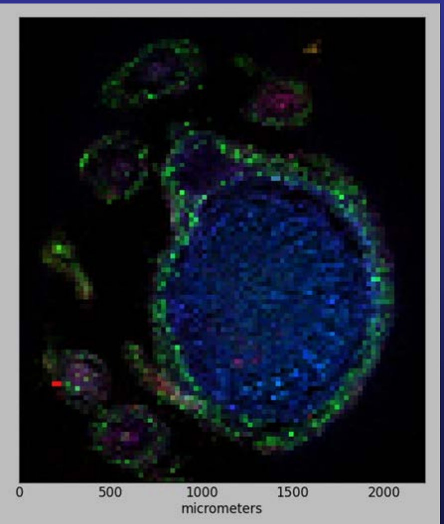
Servin et al. In preparation

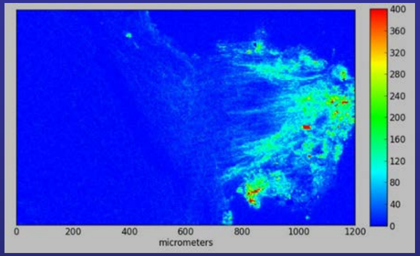
Determine the trophic transfer potential of NMs: Exp. 4

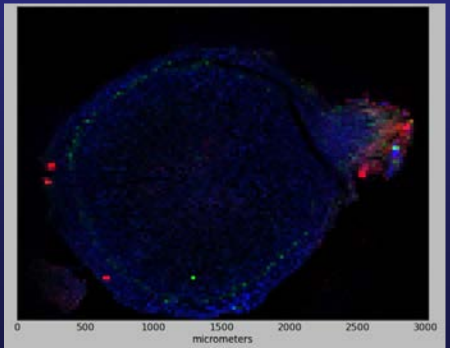
- In NP exposed roots, Cu distribution and speciation varied with weathering status (ESRF, Grenoble France)
- Unweathered treatment had Cu hot spots in the roots; the weathered treatment had homogeneous Cu
- Cu in the weathered roots was more reduced/transformed to Cu_2O and Cu_2S forms

www.ct.gov/caes

Servin et al. In preparation







Unweathered

Spot	Components: CuO	Cu2O	Cu2S	R-factor
SR(175)	0.6580	0.342	0.0000	0.004
SR(178-)	0.0000	0.554	0.446	0.002
SR(192-)	0.458	0.355	0.187	0.001
ASR (208)	1	0.0000	0.0000	0.000
SR(231-)	0.635	0.430	0.0000	0.006
SR(242-)	0.229	0.353	0.417	0.004
AMR(263)	1	0.0000	0.0000	0.000
EMR(250-)	0.314	0.238	0.447	0.009

Weathered

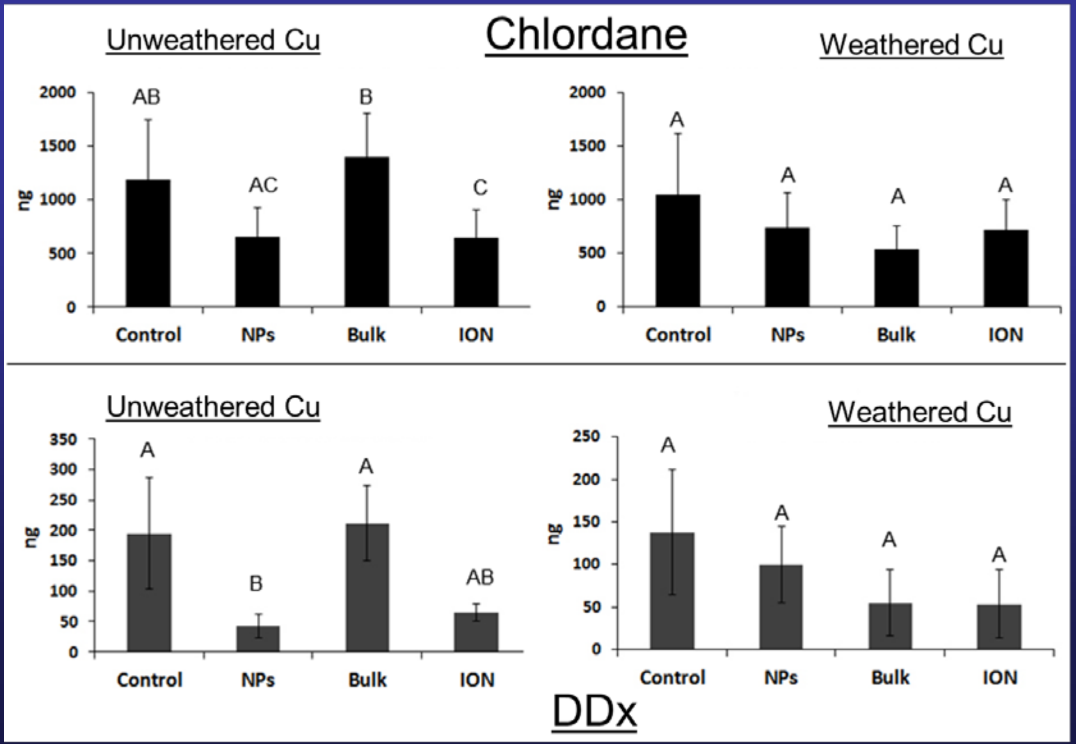
Spot	Components: CuO	Cu2O	Cu2S	R-factor
A	0.0000	0.9425	0.0575	0.0009
E	0.0000	0.4599	0.4354	0.0009
SR	0.0000	0.3402	0.6239	0.0029
MR	0.0000	0.0877	0.8511	0.0019
C	0.0000	0.4647	0.4835	0.0029

A; aggregate sec root, E; Epidermis, SR; secondary root, MR; Main root, C; Cortex

Determine the trophic transfer potential of NMs: Exp. 4

- Soil contained weathered chlordane (3 mg/kg) and DDx (0.2 mg/kg).
- Pesticide content in roots and shoots determined by GC-MS; below is whole plant content (ng)
- Unweathered Cu type/size seems to differentially impact pesticide uptake
- Upon weathering, these differences based on type disappear
- Interesting changes between unweathered and weathered pesticide for bulk and NP Cu

Servin et al. In preparation



NM Trophic Transfer?

- Element transfer from metal oxides in soil to biota does occur and it can be particle-size dependent
- Nanoparticles can be found in biota
- Biomagnification appears possible but perhaps atypical
- Insects often (but not always) excrete much of what they ingest
- Species and soil type seem to have significant impacts
- NP transformation processes in the soil and biota are important to fate (and effects?)
- Overall risk? Seems low?

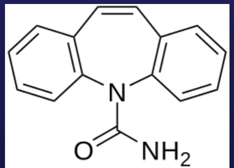
Nanomaterial interactions with co-existing contaminants

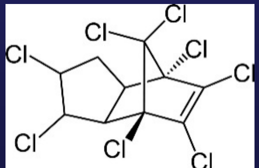
- NMs are entering agricultural systems directly (pesticide/ fertilizers) or indirectly (biosolids)
- Agricultural soils contain a number of other organic chemicals
- Interactions between NM and these co-existing contaminants may be important
  - Could bioavailability of legacy pesticides be affected? A food safety issue?
  - Could efficacy of intentional agrichemicals be affected? An economic issue?
- Multiple publications since 2012; three more underway

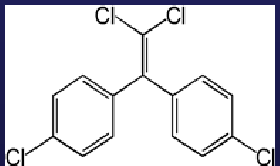
Nanomaterial interactions with co-existing contaminants

- Impact of C_{60} or Ag on DDE accumulation by crops in vermiculite (De La Torre Roche et al. 2012. *Environ. Sci. Technol.*; De La Torre Roche et al. 2013a. *Environ. Sci. Technol.*).
- Impact of C_{60} on weathered DDE accumulation from soil by crop and worm species (Kelsey and White, 2013. *Environ. Toxicol. Chem.*).
- Impact of C_{60} on weathered chlordane and DDE accumulation by 4 crops in soil (De La Torre Roche et al. 2013b. *Environ. Sci. Technol.*).
- Impact of functionalized/non-functionalized MWCNT on chlordane and DDE uptake by lettuce in vermiculite (Hamdi et al. 2015 *Nanotox*.)
- Impact of NP TiO_2 on Pb accumulation by hydroponic rice (Cai et al., in review)
- Impact of functionalized/non-functionalized MWCNT on carbamazepine accumulation by collard greens (Deng et al. in prep.)
- Impact of coated and uncoated NP Ag on chlordane and DDx accumulation by earthworms in soil (Mukherjee et al. in prep.)



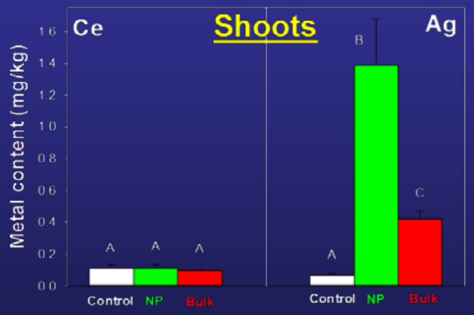



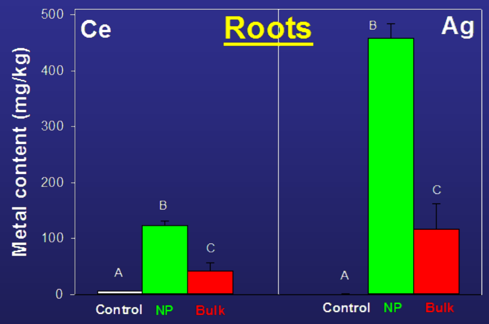


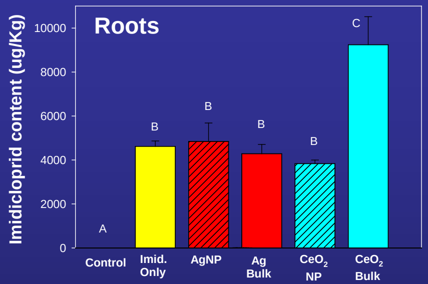


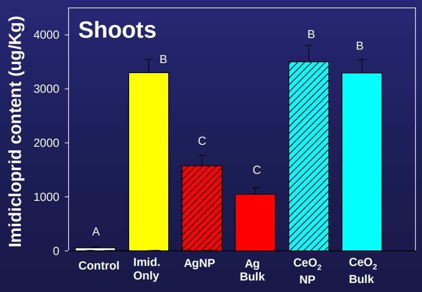

Nanomaterial interactions with co-existing contaminants

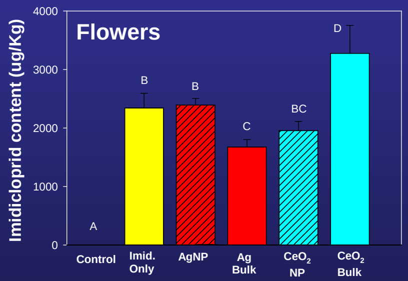
- Completing an experiment where zucchini was grown for 28-d in soil that contained Ag or CeO_2 NPs (or bulk) and imidicloprid
- Roots, shoots, flowers and pollen were analyzed for metals by ICP-MS and imidicloprid + metabolites by LC-MS/MS
- NP were accumulated at greater levels than bulk forms
- NP Ag increased pollen imidicloprid content; bulk Ce increased root and flower imidicloprid content;







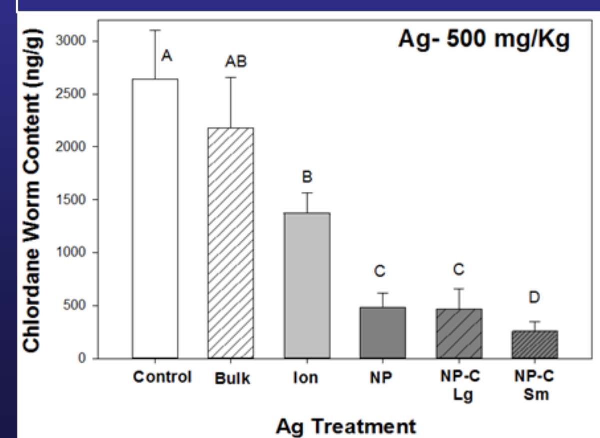




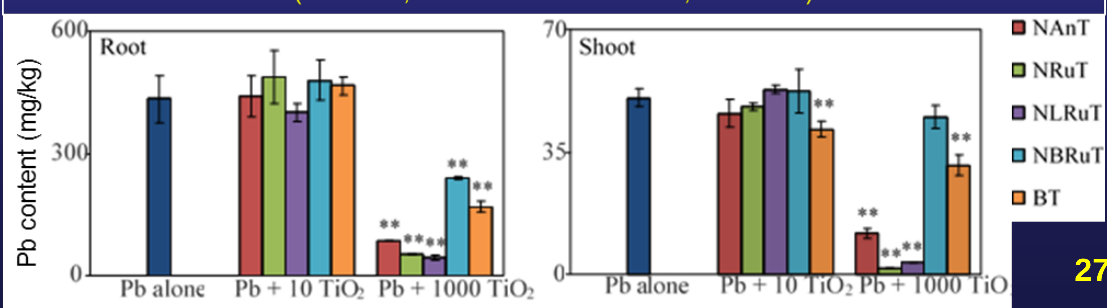
Nanomaterial interactions with co-existing contaminants?

- In both model media and soil, exposure to NM/NP can influence the bioavailability of co-existing organic contaminants
- Evident in abiotic and biotic (plants, worms) exposure assays
- Whether availability is increased or decreased depends on NP/NM type, morphology (tubes vs fullerenes), and concentration; as well as species.
- Decreased co-contaminant availability upon NP exposure seems more common

Impact of Ag types on chlordane accumulation by earthworms
(Mukherjee et al.; in prep)



Impact of different TiO2-types on Pb accumulation by rice
(Cai et al; *Environ. Sci. Technol.*, in review)



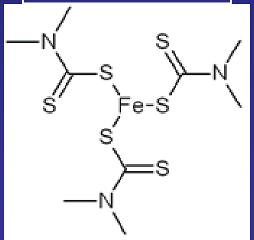
NP/NM Detection in Complex Matrices

- Current NP detection techniques (ICP-MS, sp-ICP-MS, FFF-ICP-MS, S/TEM-EDS, µXRF/XANES) all have significant shortcomings
- Concerns over human exposure to and risk from NPs have increased interest in novel detection strategies.
- A group at UMass Amherst is investigating the feasibility of Surface-enhanced Raman Spectroscopy (SERS) as a method for NPs detection and quantification in complex matrices.
- An initial study published last year used ferbam (a fungicide) as an indicator molecule that binds strongly onto AgNPs.
- Detection and quantitation based on the signature SERS response of AgNPs-ferbam complex.
- A novel approach: NPs have been used to detect pesticides; we are using a pesticide to detect NPs.

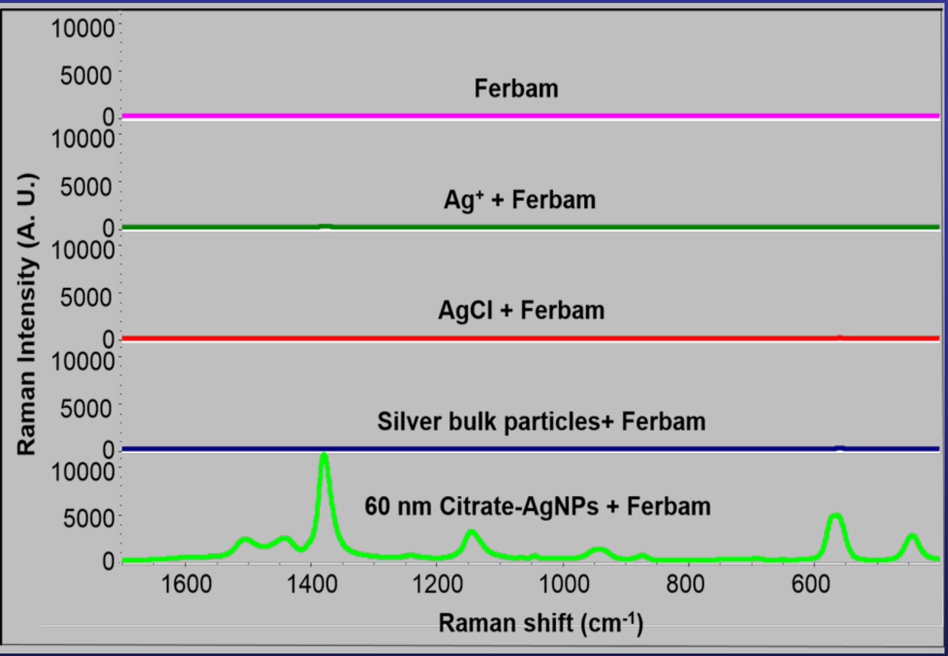
Guo et al. 2015. *Environ. Sci. Technol.* 49:4317-4324.

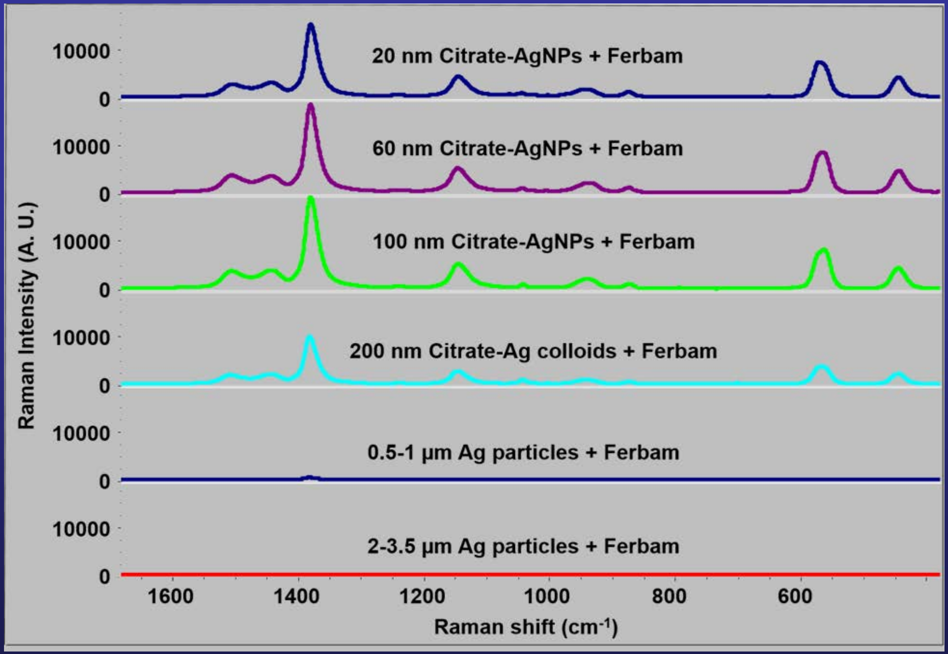
SERS and NP Ag detection

Ferbam



- SERS is able to specifically detect and discriminate NP with ferbam (10 mg/L) as an indicator.
- The largest peak was located at 1379 cm-1, which can be attributed to deformation of ferbam upon Ag binding

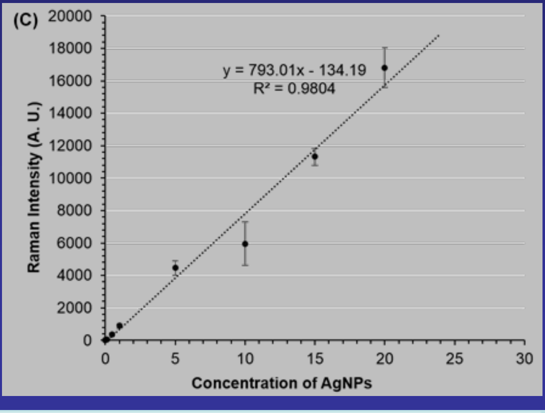


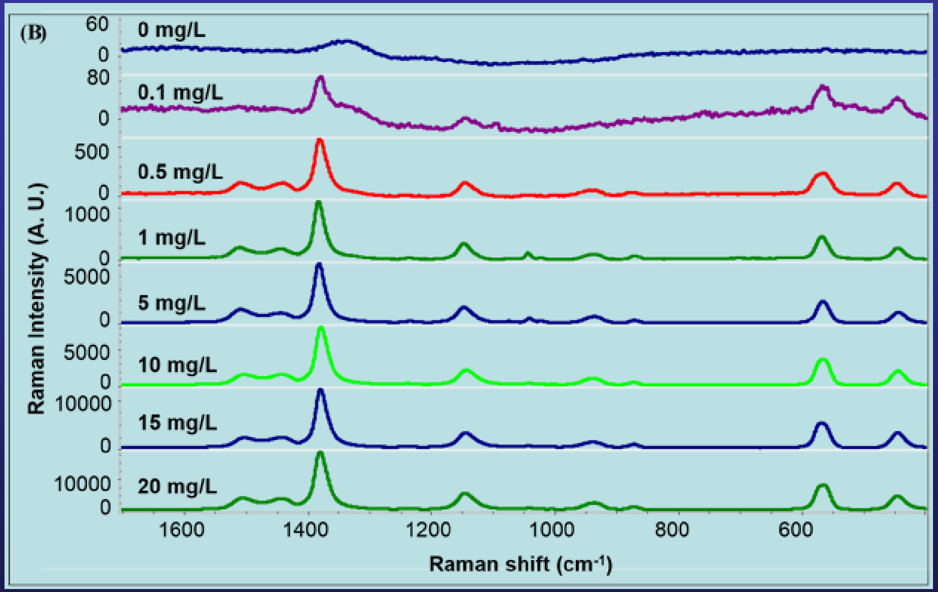


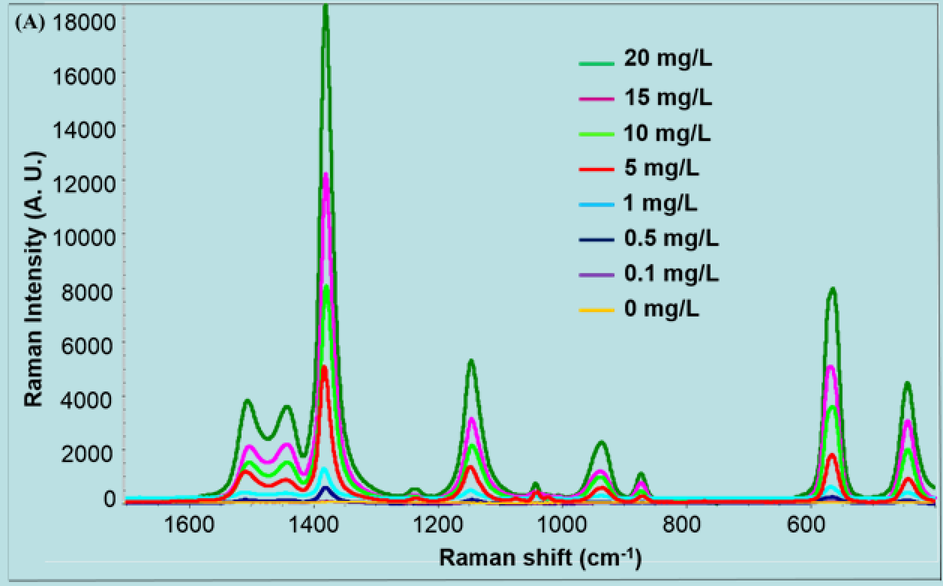
Guo et al. 2015. *Environ. Sci. Technol.* 49:4317-4324.

SERS and NP Ag quantitation

- The concentration-dependent SERS spectra of AgNPs (citrate, 60 nm) with ferbam as an indicator.
- The linear relationship between Raman intensity and AgNPs concentration.



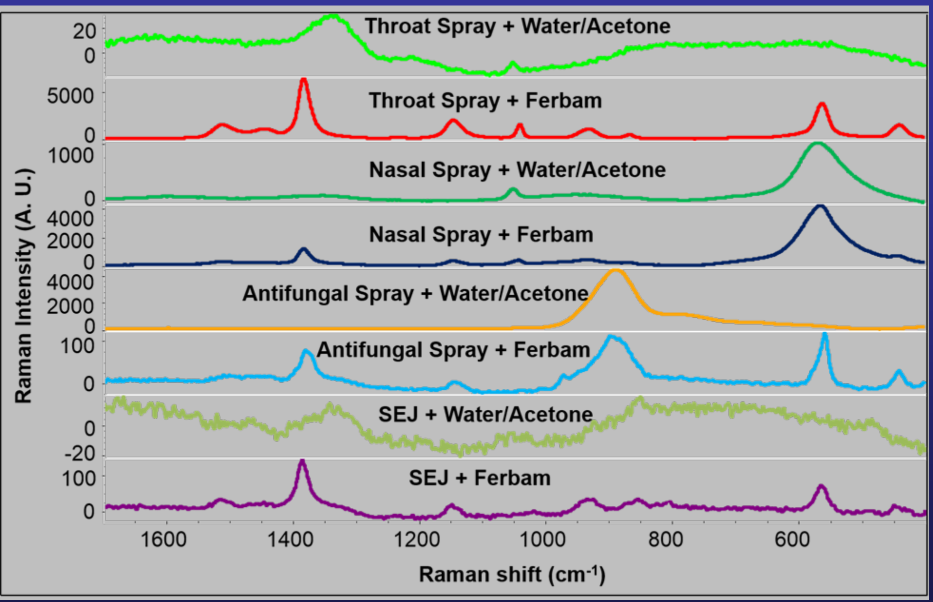




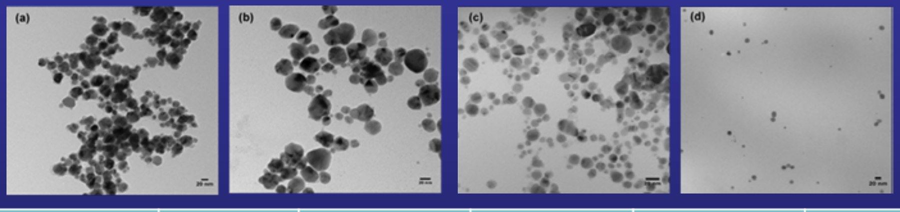
Guo et al. 2015. *Environ. Sci. Technol.* 49:4317-4324.

SERS for Ag NP quantitation in commercial products

- SERS spectra for 4 Ag NPs-containing antimicrobial products confirm the effectiveness of ferbam for Ag NP binding and NP detection.



- TEM images of the four commercial products confirmed the presence of significant quantities of Ag NPs
- Ag concentration as determined by SERS and by ICP-MS were similar for 3 of the 4 products



Product	Average Size (nm, TEM)	Advertised concentration of AgNPs (mg/L)	Total silver concentration (mg/L)[a]	Concentration of Ag by ICP-MS (mg/L)	SERS intensity
Throat spray	28.9 ± 0.8	30	29.9 ± 0.2	21.5 ± 0.6	6335
Nasal spray	33.2 ± 1.0	10	10.2 ± 0.1	6.5 ± 0.1	1253
Antifungal spray	15.4 ± 0.5	30	30.2 ± 0.2	10.0 ± 1.2	78
SEJ	14.0 ± 0.4	-[b]	340.7 ± 3.1[c]	75.3 ± 2.1[c]	141

Guo et al. 2015. *Environ. Sci. Technol.* 49:4317-4324.

Optimizing SERS

- The ferbam-based approach was a first step but sensitivity (>0.1 mg/L) is insufficient for many matrices.
- Surface modification and microextraction approach used to separate AgNPs in the matrix
  - Use a surfactant ligand to bind to the AgNPs
  - Modify the surface hydrophobicity so that the bound AgNPs can be extracted by an organic solvent
  - Produce a strong and distinct SERS signal for detection and quantification of the extracted/concentrated AgNPs

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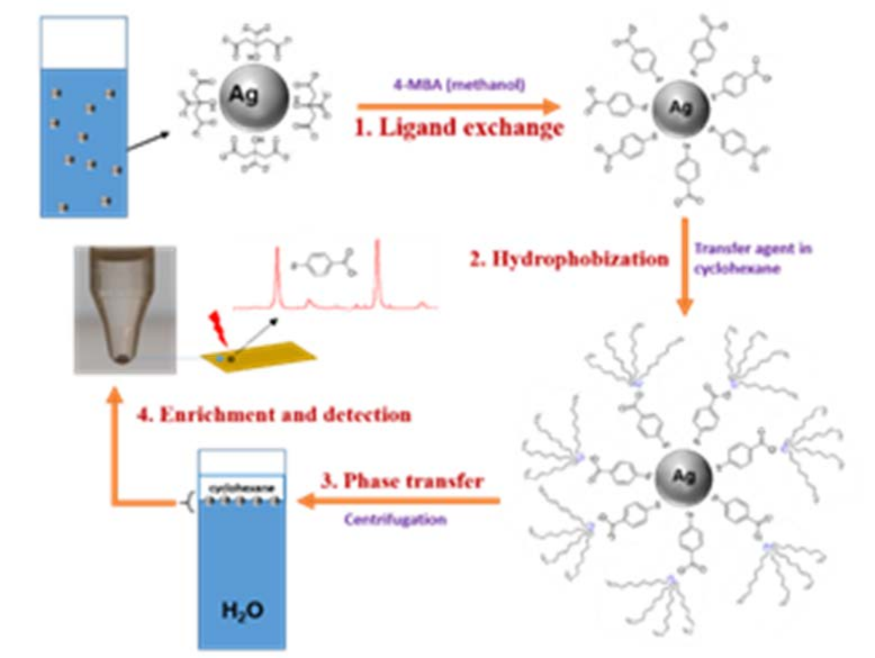

Fig. 1 Schematic diagram illustrating the determination of AgNPs by SERS after hydrophobization-mediated extraction.

Guo et al. 2016. *Chem. Comm.* Submitted for publication.

Optimizing SERS

- 4-mercaptobenzoic acid (4-MBA) modifies the surface of the coated AgNPs by displacing citrate with a thiol group.
- The 4-MBA forms acid-base pairs with tetraoctyl-ammoniumbromide (TOAB), which significantly increases AgNPs hydrophobicity.
- 4-MBA has distinct SERS peaks at 1080 and 1590 cm−1, effectively serving as an AgNP probe
- The data to the right shows that nearly all of the AgNPs are extracted from the water

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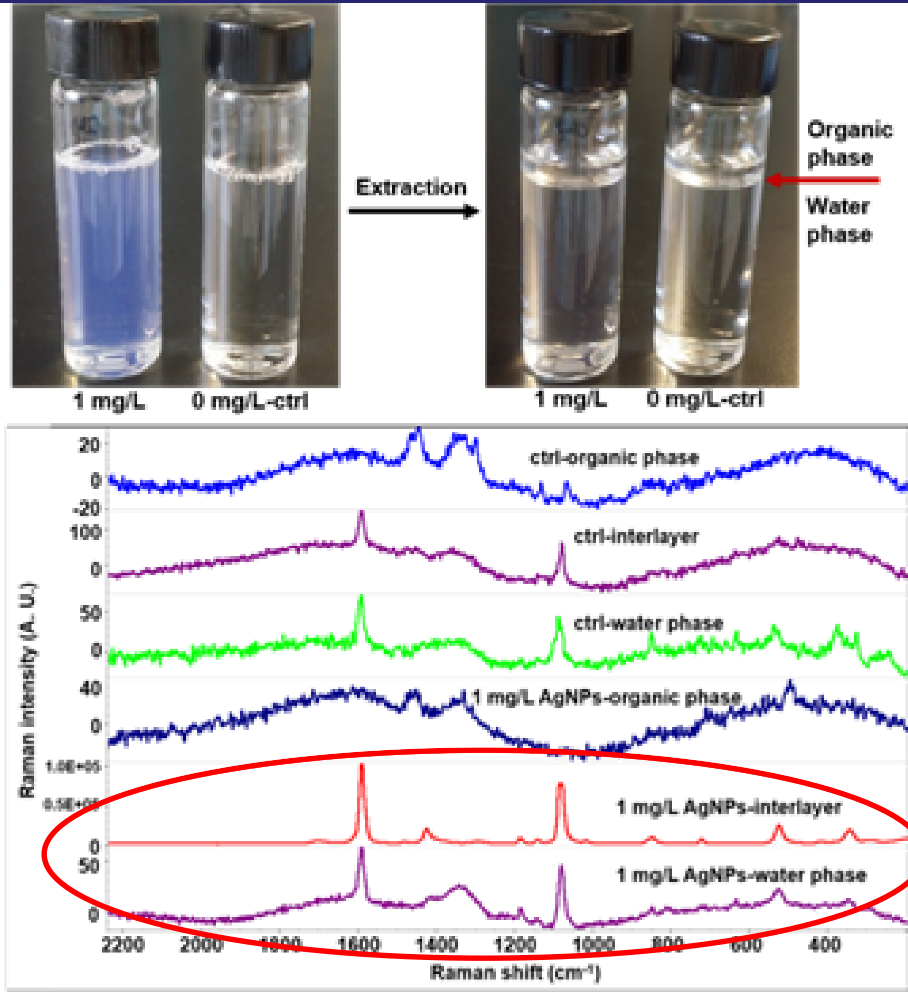


Fig. 2 Phase separation and comparison of the SERS intensities of organic phase, interlayer and water phase after extraction.

Guo et al. 2016. *Chem. Comm.* Submitted for publication.

Optimizing SERS

- Detection down to 100 ng/L is possible (below, left).
- The response is linear with AgNPs concentration (below, center).
- The technique was used to detect 20 and 2 µg/g AgNPs in wheat leaves (below, right).
- Current work looking at method efficacy with different size Ag NPs and with different coatings.

Guo et al. 2016. *Chem. Comm.* Submitted for publication.

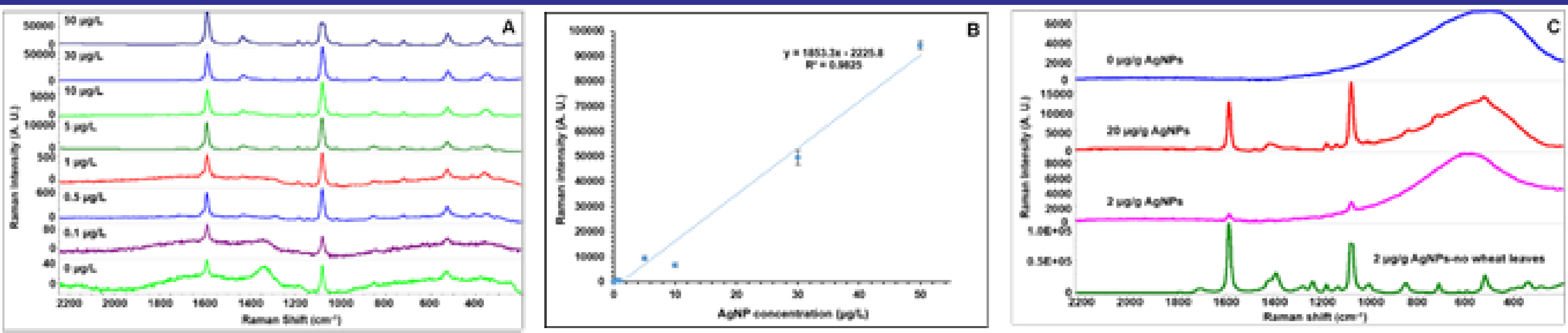


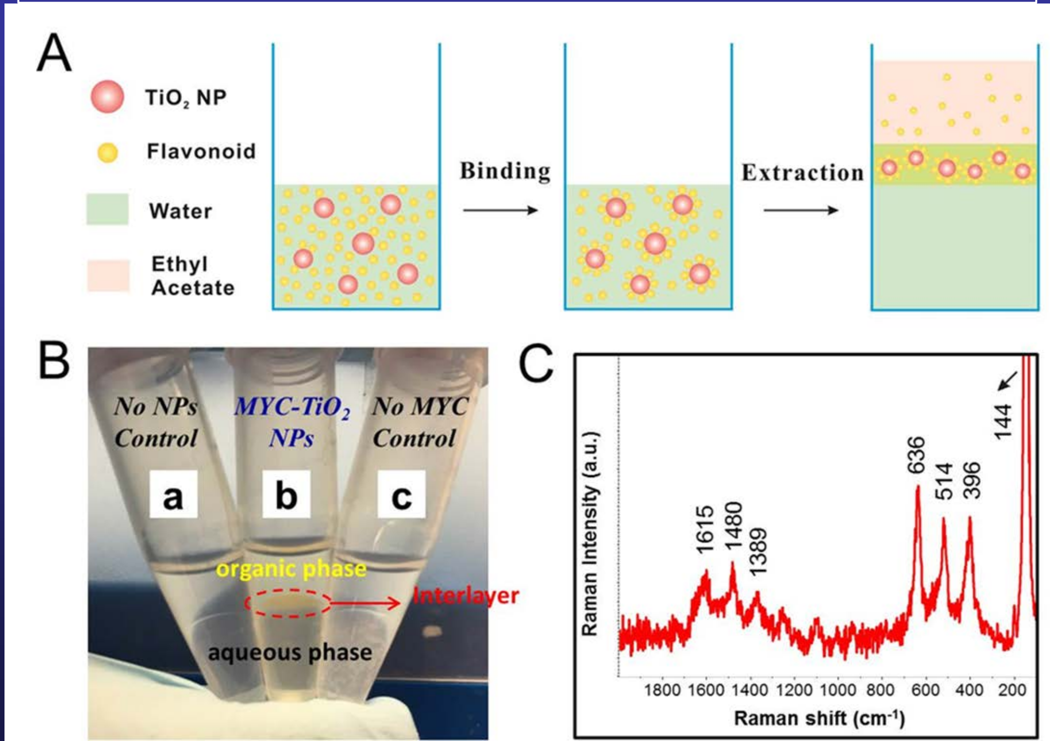
Fig. 3 Concentration-dependent SERS response to AgNPs via hydrophobization-mediated extraction assisted SERS (A). A linear relationship (B) was constructed between Raman intensity and AgNP concentration. The error bars represent the standard errors of ten parallel SERS measurements. The developed method was applied to detect AgNPs in wheat leaves (C).

Optimizing SERS

- SERS approach for Titanium dioxide (TiO_2) detection
- Developing a method using flavonoid-assisted microextraction and SERS for TiO_2 NPs (anatase, 21 nm) detection in complex liquid matrices.
- Flavonoids bind TiO_2 NPs, enabling the extraction of the particles by ethyl acetate and sodium chloride.
- Using the flavonoid, myricetin (MYC), we were able to achieve detection at 0.2 mg/L TiO_2 NPs in water.

Zhao et al. 2016. *Anal. Chem.* Submitted for publication

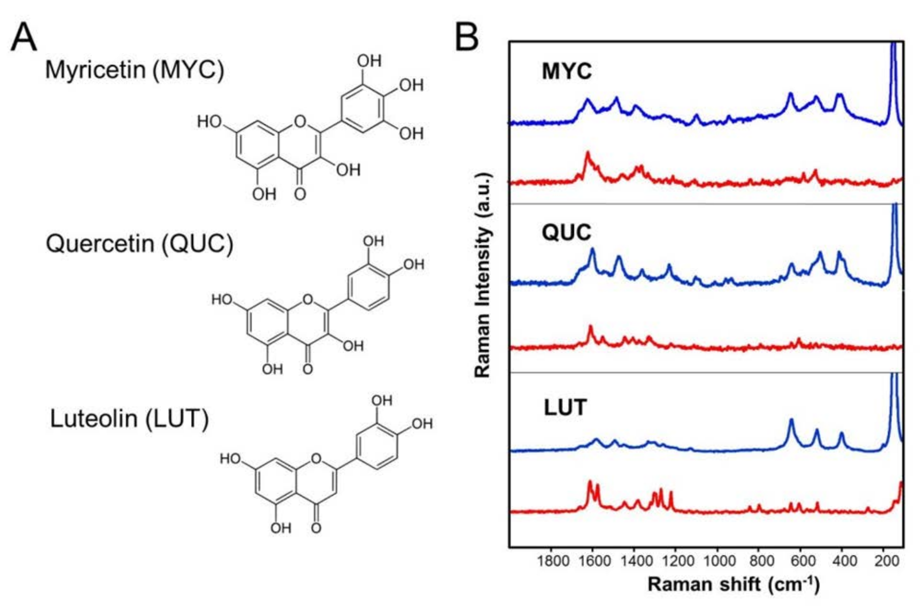
(A) Schematic illustration of flavonoid-assisted extraction method for TiO_2 NPs from water. (B) Photographs of flavonoid-based phase separation. (C) SERS spectra of MYC-adsorbed TiO_2 NPs from the interlayer.

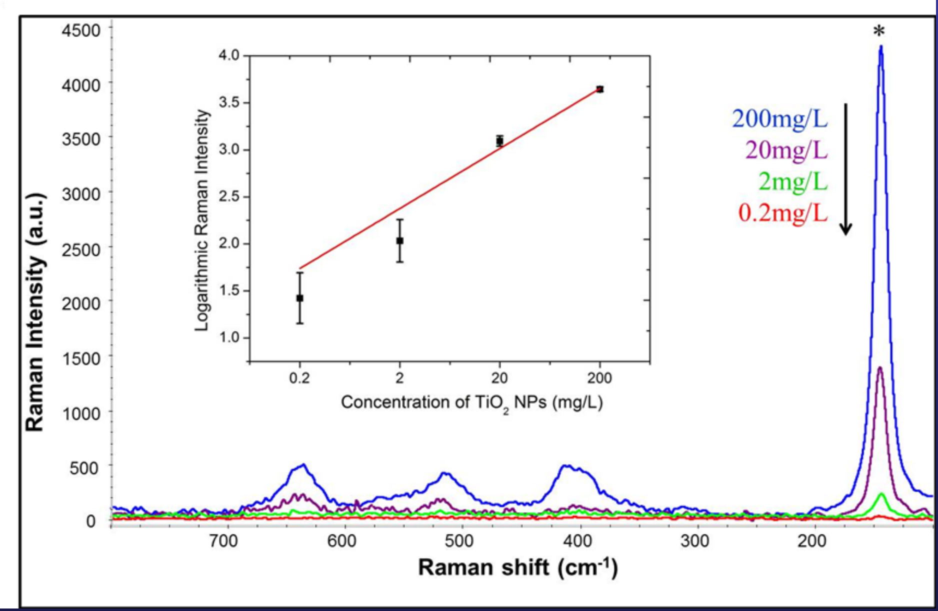


Optimizing SERS

- Three flavonoids: Myricetin (MYC), Quercetin (QUC) and Luteolin (LUT).
- Raman spectra (red) of three flavonoids, and SERS spectra (blue) of flavonoid adsorbed TiO_2 NPs. The Raman signature of sorbed TiO_2 NPs at 144 cm^{-1} could be clearly observed with flavonoid-binding.

- Raman characteristic peaks of TiO_2 NPs in the range from 100 cm^{-1} -800 cm^{-1}. Inset: Linear fitting curve for quantification of TiO_2 NPs based on 144 cm^{-1} Raman peak.





Zhao et al. 2016. *Anal. Chem*. Submitted for publication

Conclusions

- Are NM significant emerging class of contaminants in agricultural/food systems? This is the key Pro vs Con question.
- Exposure may occur through NM-containing pesticide/fertilizers, biosolids, food packaging/processing, and as flavor/quality amendments.
- Trophic transfer/food chain contamination can occur but biomagnification seems uncommon and species-, soil-, and particle-variability seems high
- Some NMs may significantly alter the fate and effect of co-contaminants by some biota in soil and non-soil systems
- Again, these interactions seem to differ with species, particle size/charac--teristics (coating, functionalization) and exposure conditions
- Robust and accurate NPs detection platforms are needed
- Although the benefits of nanotechnology to food production are huge, there are some EHS warning signs

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