Engineered Nanoparticles in Food: Implications for Food Safety and Consumer Health

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Presented at the International Association for Food Protection (IAFP) Annual Meeting
St. Louis, MO July 31-August 2, 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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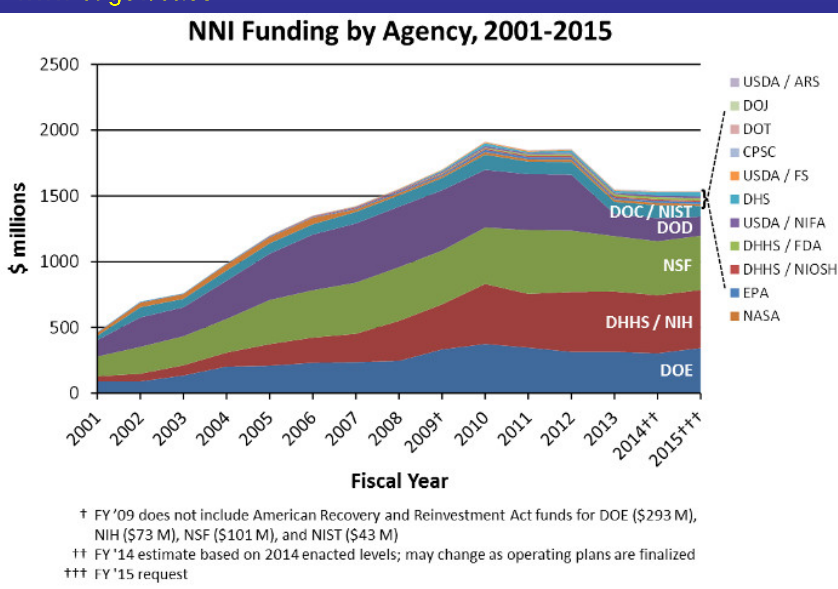
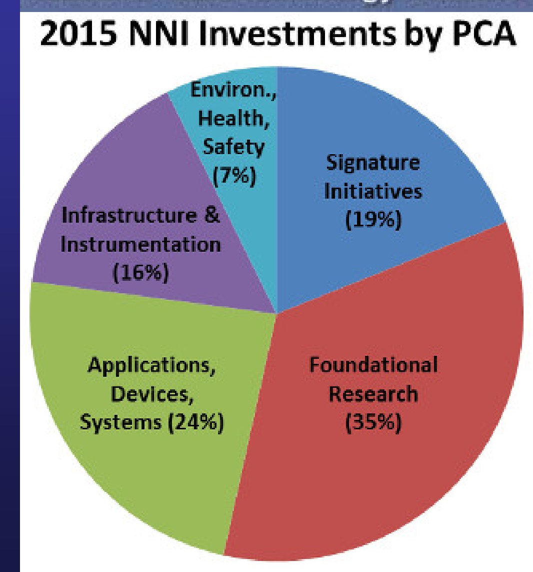


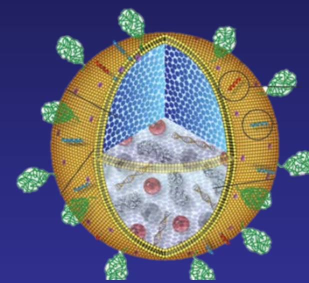
Finally, we can drink Coke with a straw.

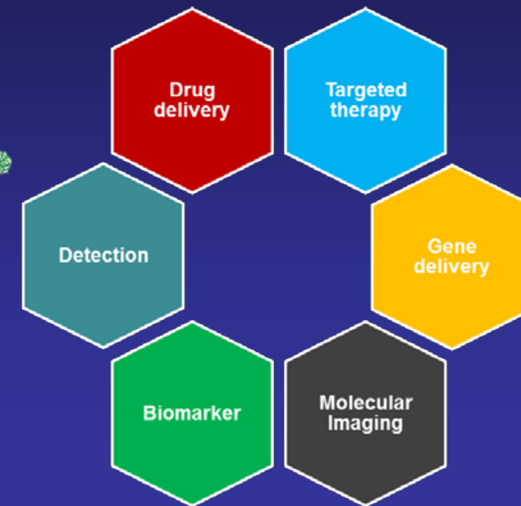
Nano.gov
National Nanotechnology Initiative



Nanotechnology- Applications

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





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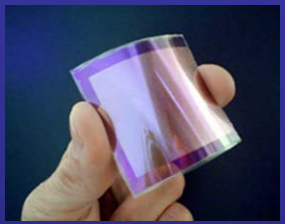

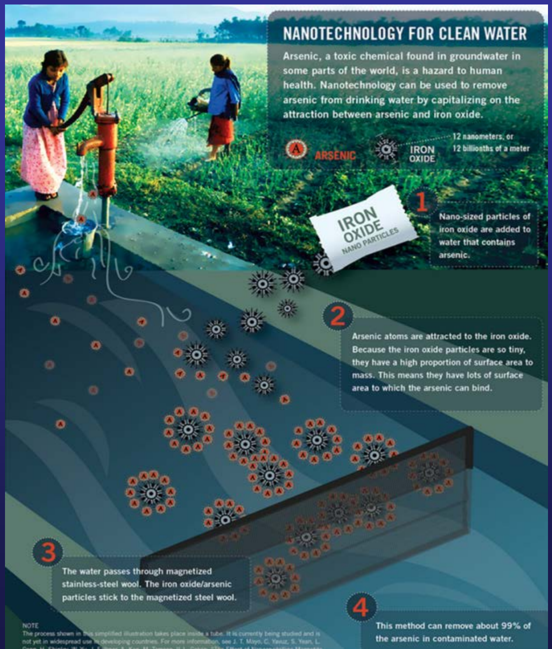

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Nanomaterials and Food Protection

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

- <u>Food Defense</u>- 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.

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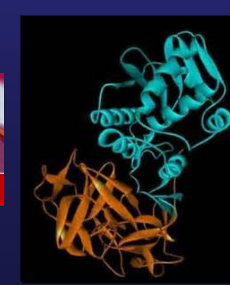
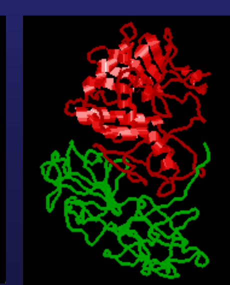




Nanomaterials and Agriculture

- There has been significant interest 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
ELSEVIER
Biotechnology Advances
journal homepage: www.elsevier.com/locate/biotechadv
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

www.ct.gov/caes

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

2007

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

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

2011

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

RESEARCH PAPER

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

Anindita Mondal · Ruma Basu · Sukhen Das · Papiya Nandy

2014

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

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

2012

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

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

www.ct.gov/caes

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[○,▲]

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

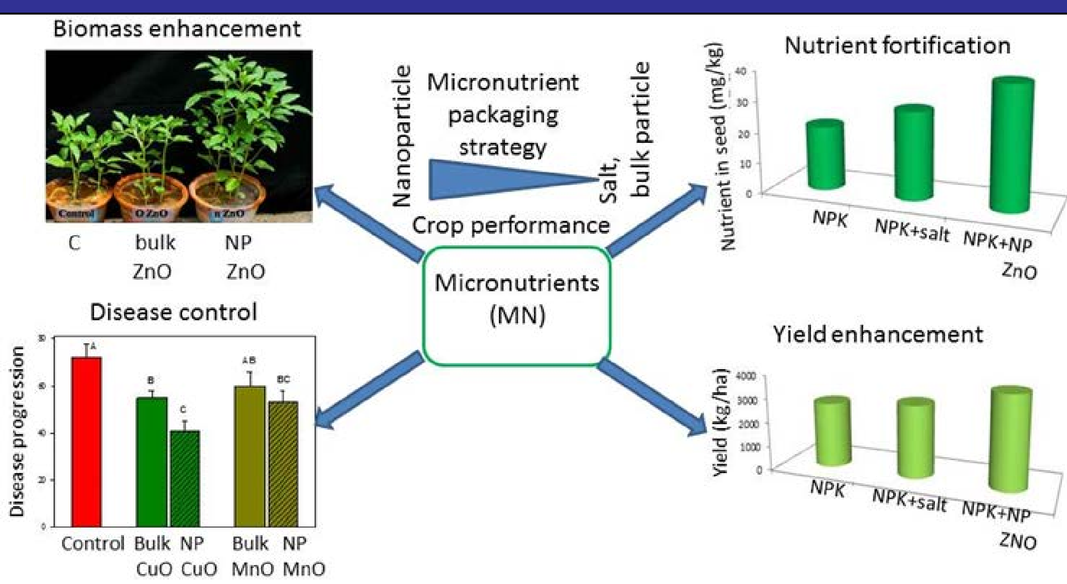
- Nanoscale based micronutrients for disease suppression (particularly root disease)
- A new research initiative at CAES
- Many micronutrients (Cu, Mn, Zn, Mg) stimulate or are part of plant defense systems.
- However, these nutrients have low availability in soil and are not readily transferred from shoot to root. What about nano versions of these nutrients?
- New USDA Grant- $480,000; 3/16-2/19.

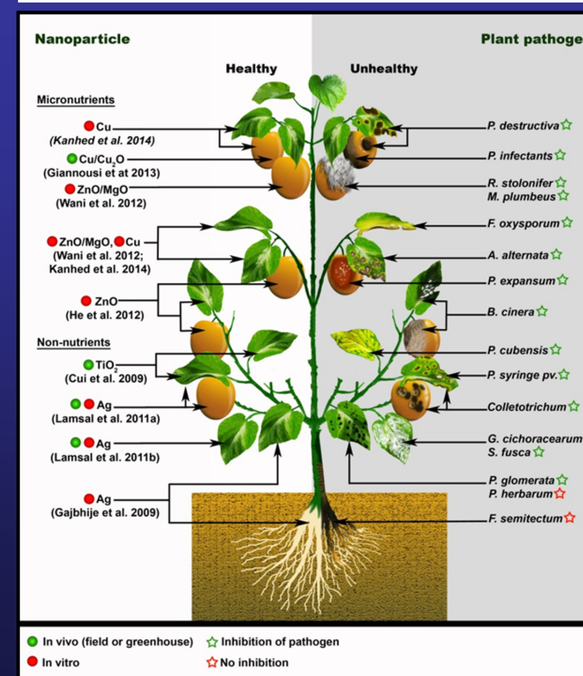
J Nanopart Res (2015) 17:92
DOI 10.1007/s11051-015-2907-7

REVIEW

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

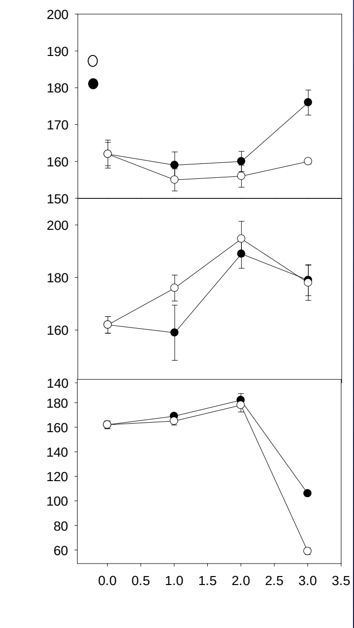
Alia Servin · Wade Elmer · Arnab Mukherjee · Roberto De la Torre-Roche · Helmi Hamdi · Jason C. White · Prem Bindraban · Christian Dimkpa

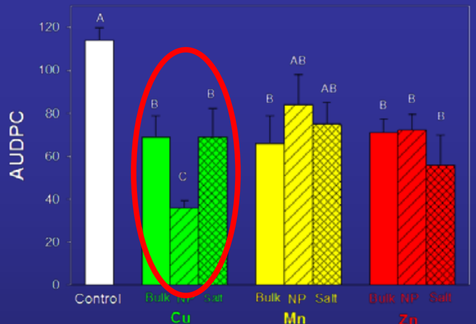


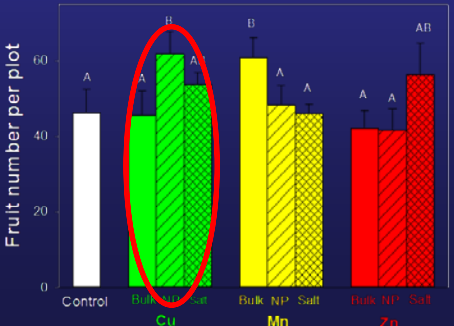


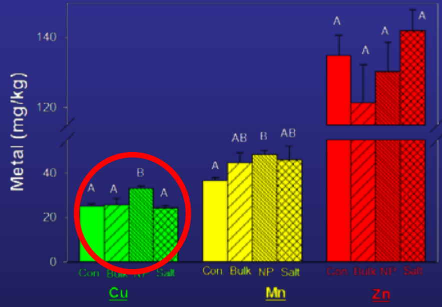
Nanoscale micronutrients for disease suppression

- 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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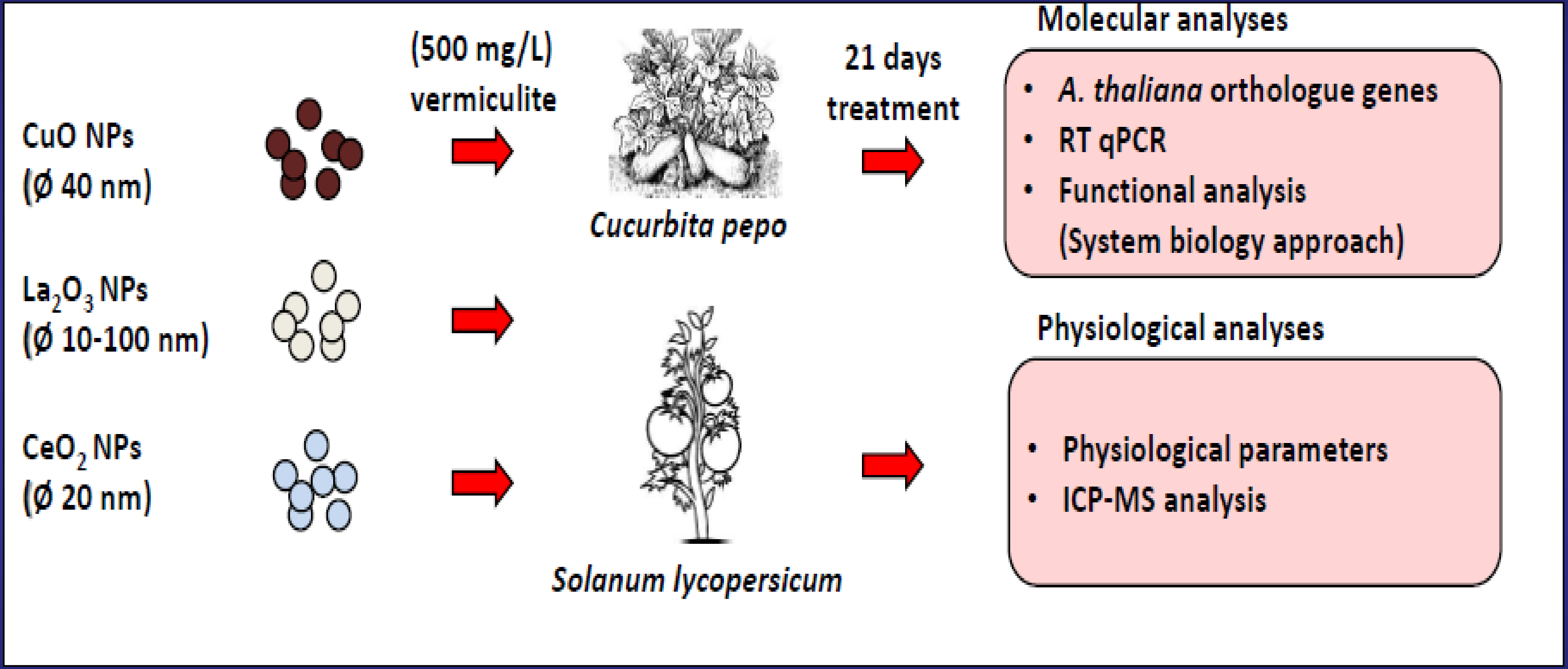
Implications: Nanotoxicology at CAES

- Two "simple" questions- Do NM behave differently? Does it matter (Is that difference of concern with regard to exposure and risk)?
- USDA NIFA -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: Impact of environmental conditions on NM fate.
  - Obj. 3: Determine the potential trophic transfer of NMs.
  - Obj. 4: Quantify co-contaminant interactions.
- USDA NIFA- Nanotechnology for Ag. and Food Systems- "Nanoscale interactions between engineered nanomaterials and biochar"
- USDA Hatch- "Impact of particle coating and weathering on nanomaterial fate and effects on crops"

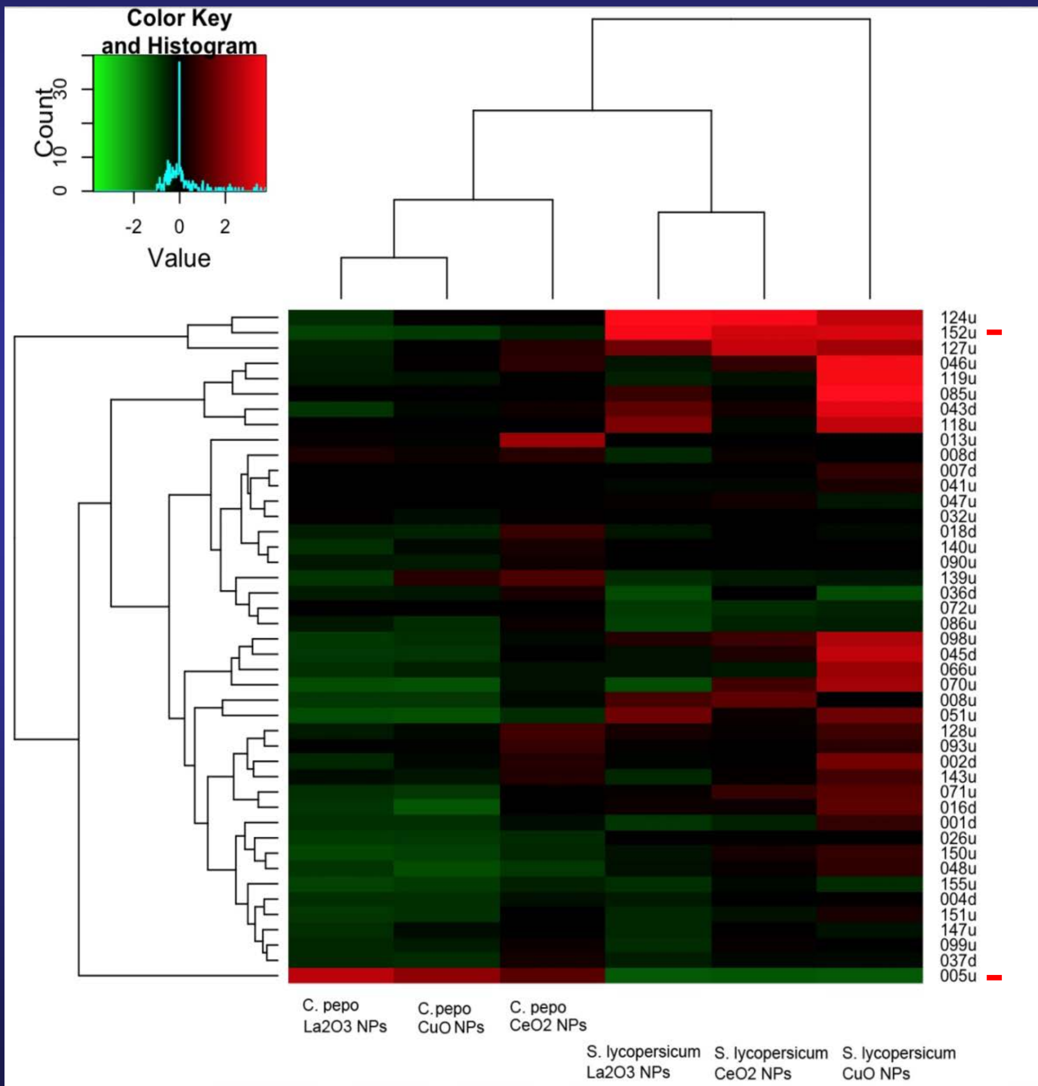
Obj. 1: Toxicity, Mechanisms, and Biomarkers



About 70 candidate/target genes identified in *A. thaliana* were located and validated through transcriptomic analyses in zucchini (*C. pepo*) and tomato (*S. lycopersicum*).

Pagano *et al.* 2016 *Environ. Sci. Technol.* 50:7198–7207

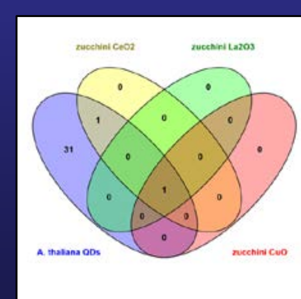
Response: Zucchini vs Tomato

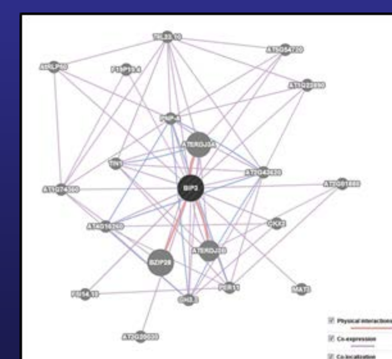


Comparison between the tomato and zucchini:

- **005u** (heat shock protein) up regulated in all the treatments of zucchini, down regulated in all the treatments of tomato

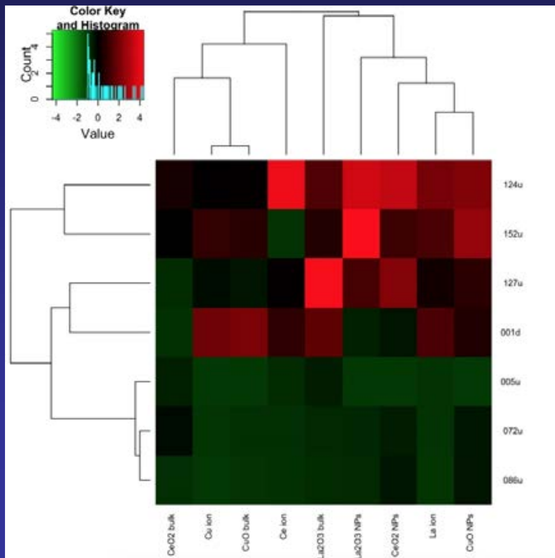
- **152u** (chloroplast electron carrier) up regulated in all the treatments of tomato, down regulated in all the treatments of zucchini



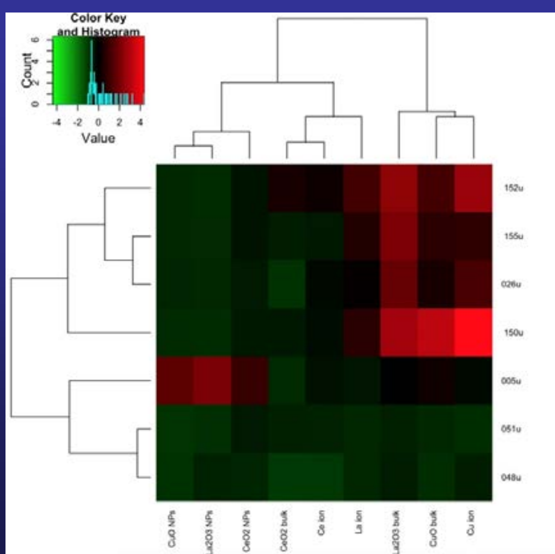


Pagano *et al.* 2016 *Environ. Sci. Technol.* 50:7198–7207

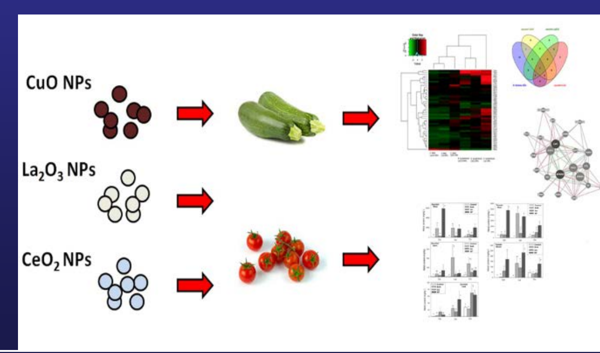
Bulk & Ion Exposure?



- For tomato, *CuO NPs response was unique* (as compared to bulk and ion)
- Lanthanides behave differently, with bulk and NP La_2O_3 grouping closely together but CeO_2 has a significant “nano” effect on transcription.



- For zucchini, of the 7 commonly expressed genes, *all 3 NP treatments group separately* from the correspond-ing bulk and ionic exposures.

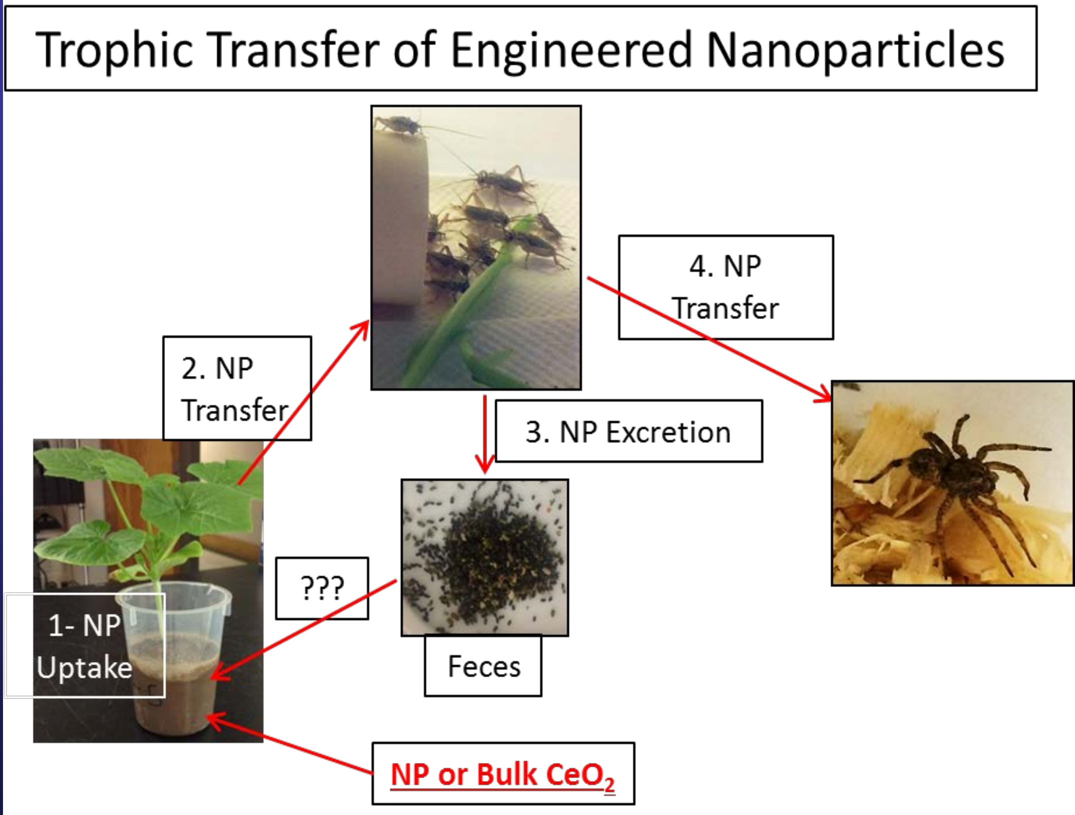


Pagano *et al.* 2016 *Environ. Sci. Technol.* 50:7198–7207

Determine the trophic transfer potential of NMs

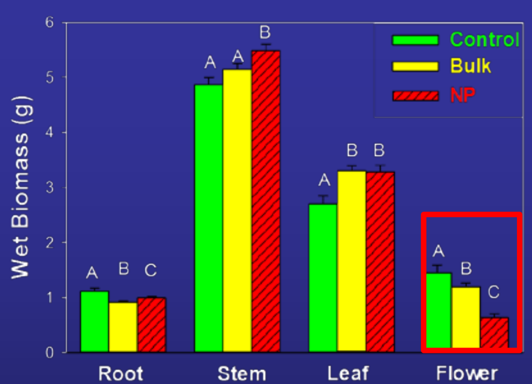
- Experiment 1- NP/bulk CeO_2 (0 or 1000 mg/Kg) added to an agricultural loam.
- Zucchini grown for 28d from seedling.
- Roots, stems, leaves, and flowers analyzed by ICP-MS.
- Leaves used to feed crickets for 14d.
- Crickets used to feed wolf spiders for 7d.
- Insect tissues/feces by ICP-MS.

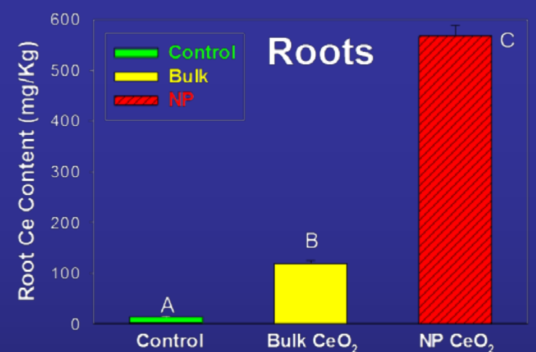
Hawthorne et al. 2014. *Environ. Sci. Technol.* 48:13102-13109

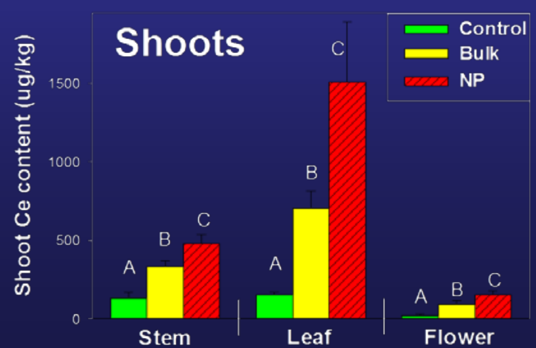


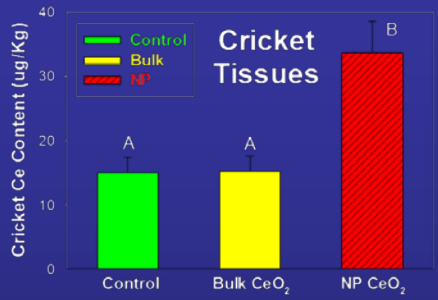
Determine the trophic transfer potential of NMs: Exp. 1

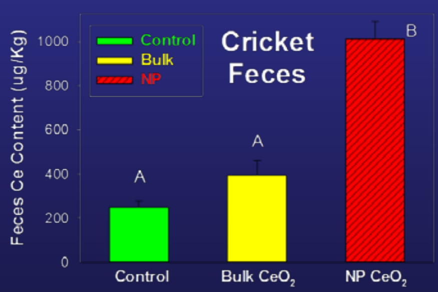
- Particle size-dependent transfer from soil → plant → herbivore → carnivore observed
- NP CeO_2 reduced biomass of reproductive tissues by 50%
- No biomagnification; 10-100 fold decreases at each level
- Insect feces contained 10x more Ce than insect tissues







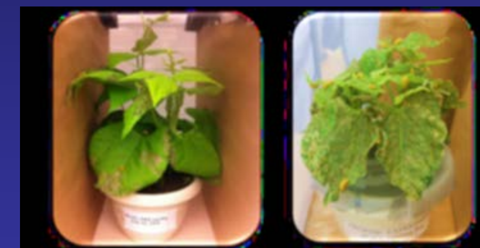




Hawthorne et al. 2014. *Environ. Sci. Technol.* 48:13102-13109

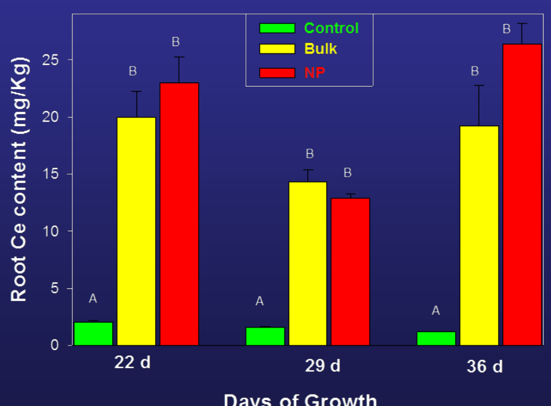
Determine the trophic transfer potential of NMs: Exp. 2

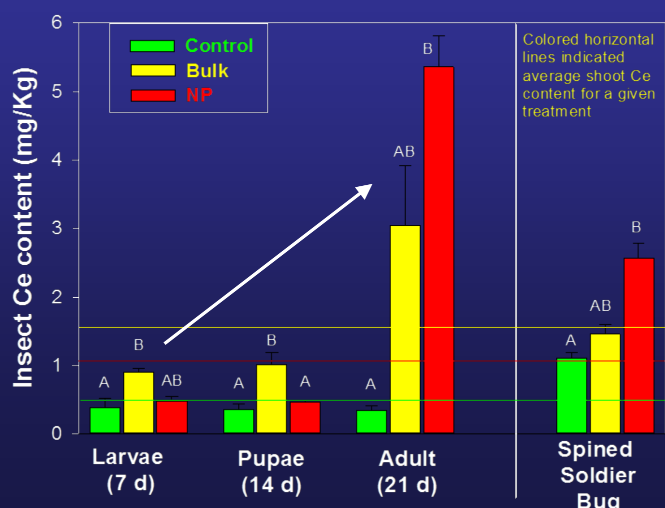
- NP/bulk CeO_2 (1000 mg/kg) added to a TX soil; kidney bean grown for 35 d

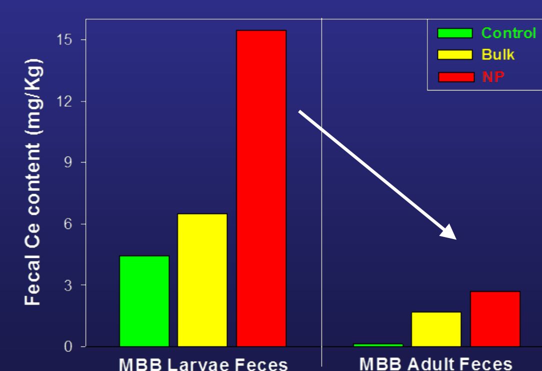


- Leaves fed to bean beetle (larvae, pupae, adult);
- Beetles fed to spined soldier bugs
- Ce root\shoot content was unaffected by particle size
- Time-dependent Ce *increase* in the beetle; biomagnification in the adult.

- Time dependent *decrease* in fecal Ce content.







Determine the trophic transfer potential of NMs: Exp. 3

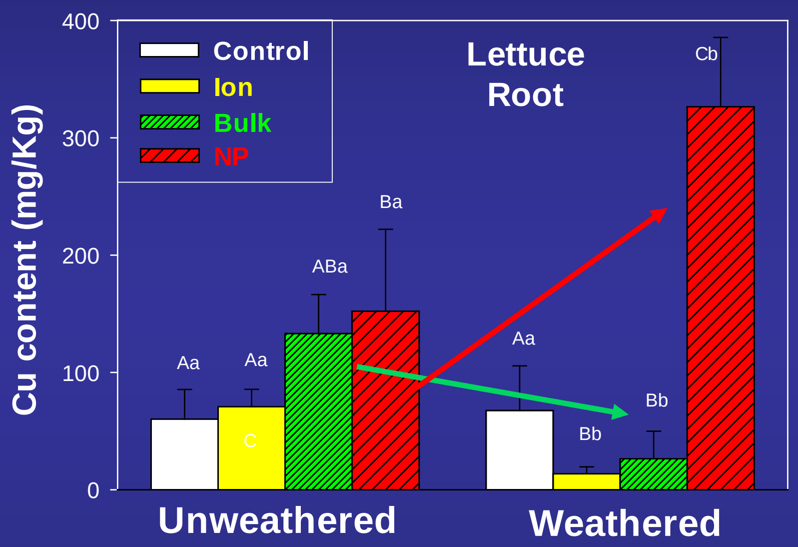
- Trophic transfer of NP and bulk CuO
  - 500 mg/kg in soil for 0 or 60 days, lettuce, cricket, Anolis lizards.
  - Soil was contaminated with weathered chlordane (3 mg/kg) and DDX (0.2 mg/kg)
  - Tracked Cu, chlordane and DDX content and form (ICP-MS, µXRF, XANES, biomass, and gene expression in the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

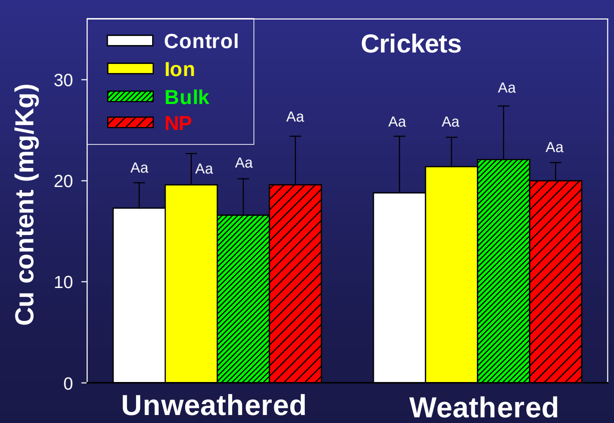
Servin et al. In preparation

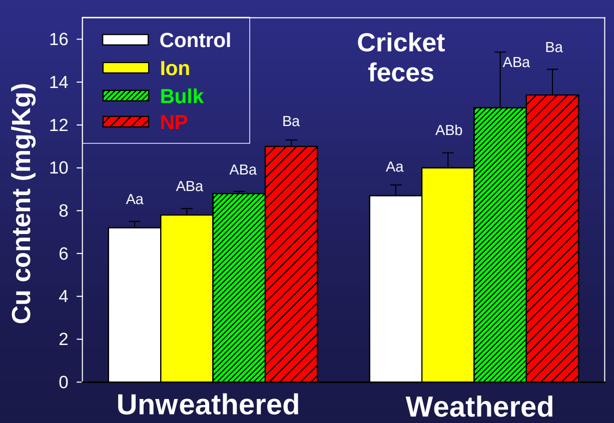
Determine the trophic transfer potential of NMs: Exp. 4

- Leaf Cu content unaffected by particle type or weathering
- Root Cu content affected by particle size upon 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

☹







Servin et al. In preparation

Determine the trophic transfer potential of NMs: Exp. 3

- 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

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

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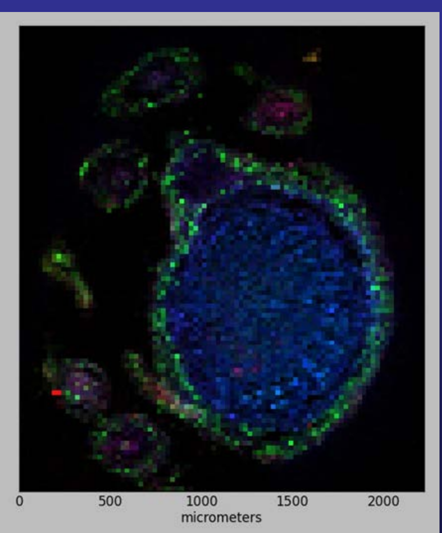
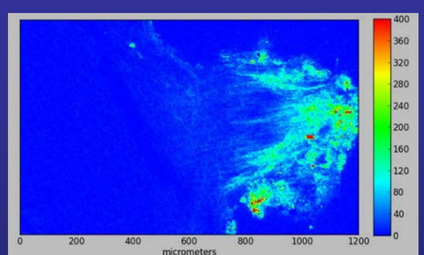
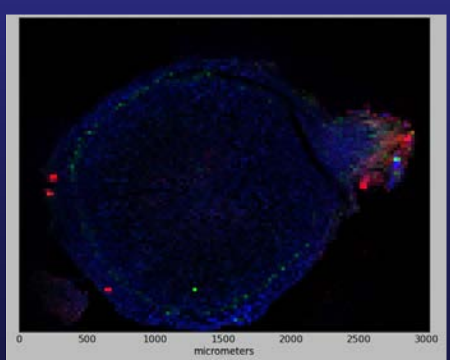






Nanomaterial interactions with co-existing contaminants

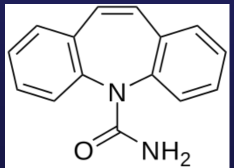
- NMs are entering agricultural systems directly (pesticide/ fertilizers) or indirectly (biosolids)
- Agricultural soils contain a number of other organic chemicals
- Interactions between NM and these co-existing contaminants may be important
  - Could bioavailability of legacy pesticides be affected?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

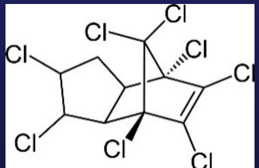


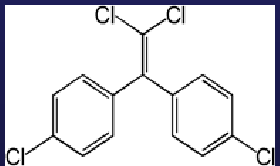


Nanomaterial interactions with co-existing contaminants

- 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.)

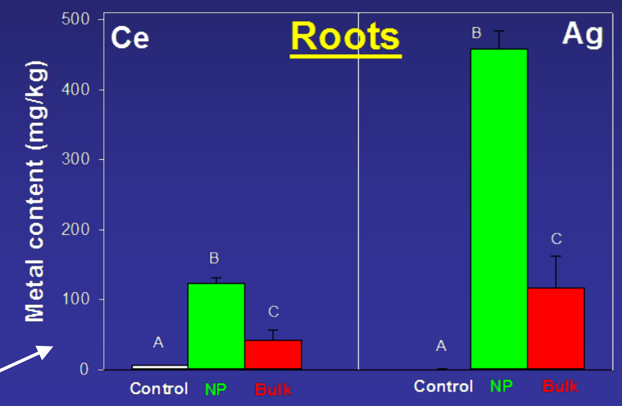


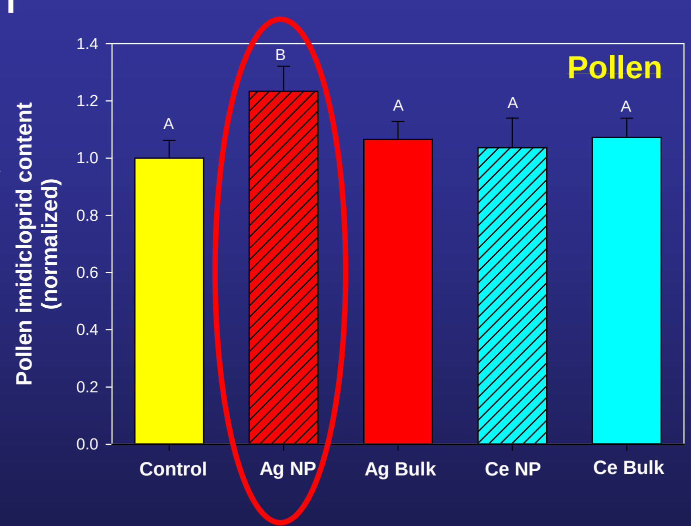


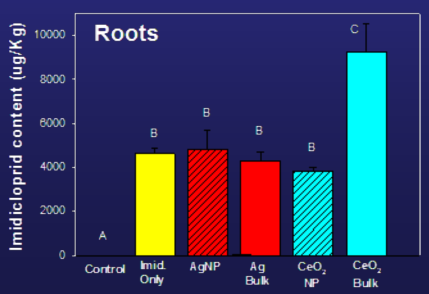


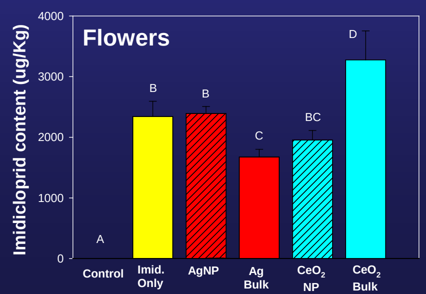
Quantify the facilitated uptake of pesticides through NM-chemical interactions

- Zucchini was grown for 28-d in soil that contained NP Ag or CeO_2 (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;









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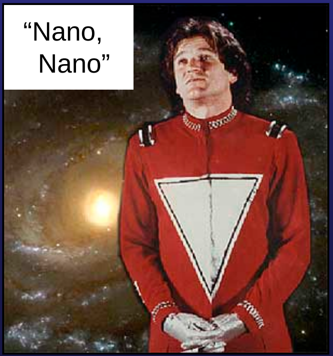
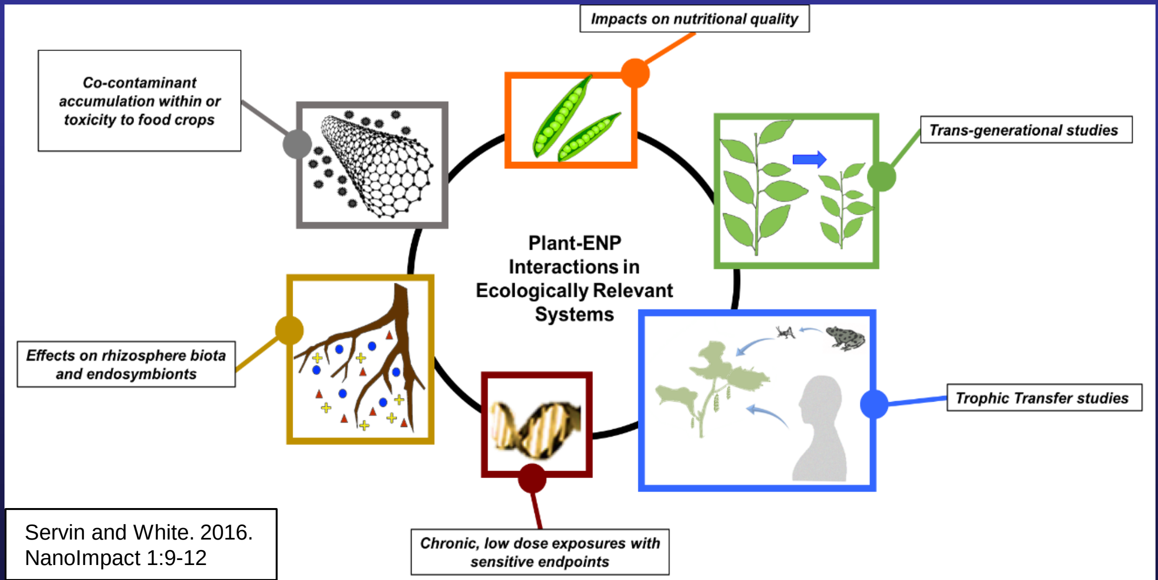
Conclusions

- Are NM significant emerging class of contaminants in agriculture?
- Exposure through NM-containing pesticide/fertilizers, biosolids, food packaging/processing, and as flavor/quality amendments.
- Trophic transfer, biomagnification, food chain contamination can occur. Species-, soil-, and particle type-variability seems high.
- NMs can significantly alter the of co-contaminants. Species-, soil-, and particle type-variability seems high.
- Detailed mechanistic studies are needed; robust detection platforms are needed
- The benefits of nanotech-nology to food are great but there are some EHS issues





Servin and White. 2016. NanoImpact 1:9-12

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- **Wang et al**- Ocean Univ. of China
- **Marmiroli et al.**- Univ. of Parma, Italy
- **T. Vanek**- Czech Republic
- **J. Vangronsveld et al.**- Hasselt Univ., Belgium
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