

Trophic Transfer Potential of Nanoparticles in Terrestrial Food Chains



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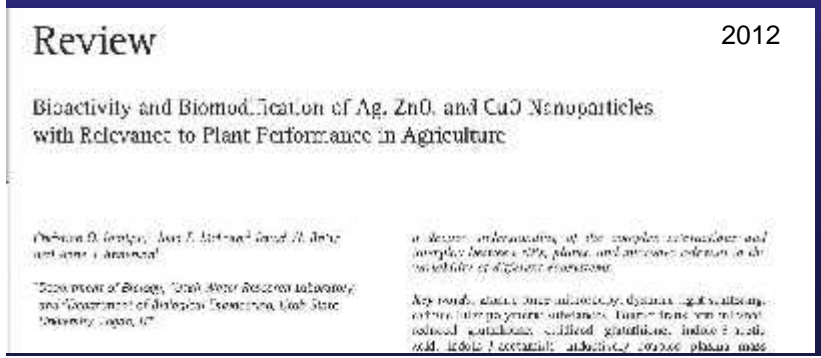
Presented at the SUN-SNO-GUIDENANO Sustainable Nanotechnology Conference 2015,
Venice Italy, March 9-11, 2015

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



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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...)



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Environ Monit Assess (2013) 179:1–15
DOI 10.1007/s12011-012-0615-5

The Improvement of Spinach Growth by Nano-anatase TiO₂ Treatment Is Related to Nitrogen Photoreduction

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

2012

JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Dissolution Kinetics of Macronutrient Fertilizers Coated with Manufactured Zinc Oxide Nanoparticles

Nargis Akbari,¹ Mike L. McLaughlin,^{1,2} Samuel P. Stang,³ Jason K. Kirby,⁴ Ganga M. Hettiarachchi,^{5,6} Douglas C. Haig,^{1,4} and Glenn Corcoran^{1,7}

J. Agric. Res. (2012) 15, 1519–1525
DOI 10.1007/s12011-012-0466-2

RESEARCH PAPER

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

Anamita Mondal · Runa Bhow · Sukleen Das · Pooja Nandy

Carbon Nanotubes Induce Growth Enhancement of Tobacco Cells 2012

Mariya V. Khodakovskaya,¹ Karisika de Silva,¹ Alexandru S. Biris,^{2,3} Erkelezi Dervishi,⁴ and Hector Villalobos¹

¹Department of Applied Sciences, The College of Southern Enterprise, University of Southern California, Los Angeles, CA 90089, United States

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

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Microbiology 2011, 1:26-32 (2011)
© The Korean Society of Mycology

DOI:10.1186/1229-8019-1-26

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

Kabir Lamsal, Sang-Woo Kim¹, Jin Hee Jung¹, Yui Seok Kim¹, Kyoung Su Kim¹ and Youn Su Lee^{2*}

Journal of Nanoparticles Technology: Nanoparticle Delivery (2011) 1:26-32
¹Department of Agricultural Biotechnology, Center for Tropical Genetic Resources and Center for Tropical Pathogenomics, Seoul National University, Seoul 151-747, Korea

(Received: October 21, 2010; Accepted: February 16, 2011)

2012

small

DNA Delivery

Parameters Affecting the Efficient Delivery of Mesoporous Silica Nanoparticle Materials and Gold Nanorods into Plant Tissues by the Biolistic Method

Susana Morthé-Ortizgosa, Justth S. Valenstein, Wef Sun, Lorena Moeller, Ning Fong, Brian G. Trewyn, Victor S.-Y. Lin, and Ken Weng*

In memory of Professor Victor S.-Y. Lin, deceased May 4, 2010

Appl. Microbiol. Biotechnol. (2011) 91:1191–1201
DOI 10.1007/s00253-011-1201-4

MINI-REVIEW

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

Mahendra Rai¹ Animesh Ingle²

Microbiological Research 166 (2011) 400–410



Available online at www.sciencedirect.com

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Research

www.elsevier.de/micro

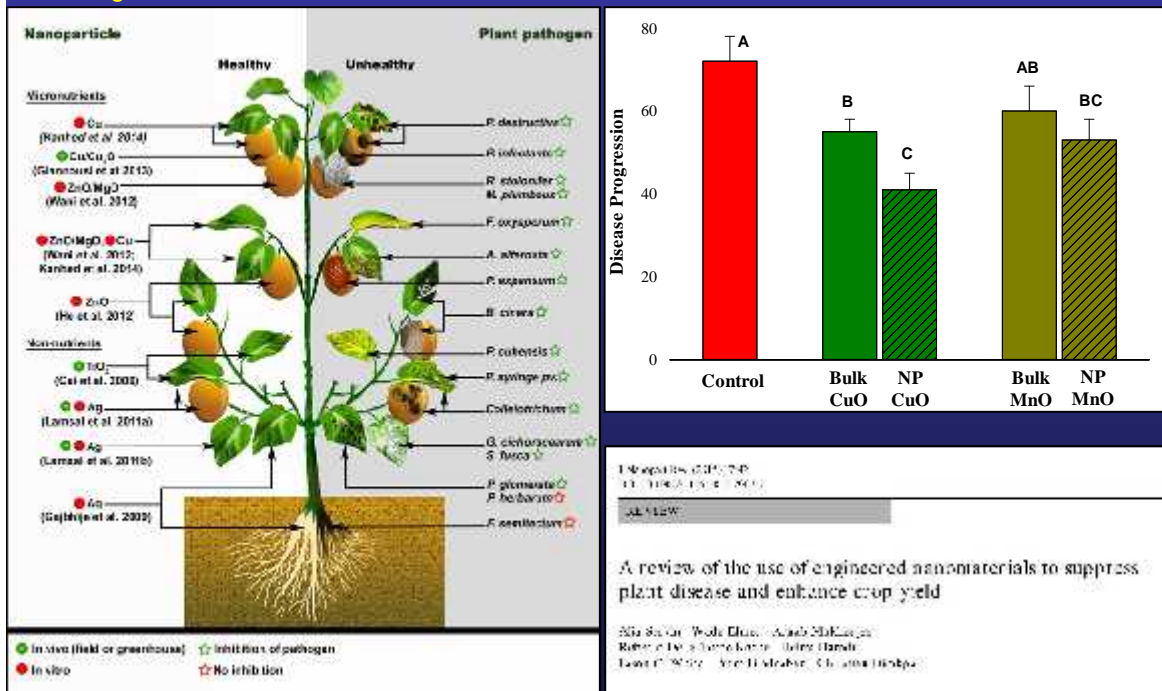
Antifungal activity of zinc oxide nanoparticles against *Botrytis cinerea* and *Penicillium expansum*

Lili He¹, Yang Liu¹, Azlin Mustapha, Mengshi Lin*

Nanomaterials and Agriculture

- Nanoscale based micronutrients or other elements for disease suppression
- A new research initiative at CAES
- Many micronutrients (Cu, Mn, Zn, Mg) stimulate plant defense systems

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Nanoscale Micronutrients Suppress Disease

VFRC Report 2014/x

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

VFRC CAES



Nanomaterials and Agriculture



- Prior to 2010, data on NM interactions with plants was limited. Many early studies looked only at NPs with no bulk material/ion comparison.
 - This is a key point. It is irrelevant whether a NP/NM is toxic. The key questions are is that NM/NP more toxic than the bulk/ion and if so, is it by a different mechanism?
- Are NM an emerging class of contaminants?
- There have been a number of recent studies assessing the effects of specific NPs on germination, root elongation, and other physiological/"omic" parameters
- These studies have tended to focus on acute toxicity; relatively short exposure to high concentrations. This is where we start in toxicology but as is frequently the case, chronic low dose exposure may be more important.
- Larger issue may be food chain contamination and an uncharacterized pathway of human exposure.



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CAES Nanotoxicology Program



- The entire program is based on a simple question- From a regulatory standpoint, bulk/ion and NMs are considered equal. Is that true? Or are there important instances where NM “behave” differently? The follow up question; does it matter (hazard and risk assessment)?



- USDA NIFA Grant 1- “Addressing Critical and Emerging Food Safety Issues.” A 5-year \$1.5 million grant “Nanomaterial contamination of agricultural crops.”

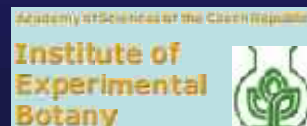
- Obj. 1: Determine the uptake, translocation, and toxicity of NM to crops.
- Obj. 2: Determine the impact of environmental conditions on NM uptake, translocation, and toxicity to crops.
- Obj. 3: Determine the potential trophic transfer of NMs.
- Obj. 4: Quantify the facilitated uptake of pesticides through NM-chemical interactions.



- USDA NIFA Grant 2- Determine the impact of biochar on NM uptake and toxicity to crops and earthworm species.



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Objective 3- Determine the trophic transfer potential of NMs

- Trophic transfer potential of engineered nanoparticles remains largely unknown
- There have been a few nice studies in aquatic systems
- For terrestrial systems, the published work is limited to group of 3 papers on Au NPs from the University of Kentucky
- For us, it is a three part question-
 - Does trophic transfer occur?
 - Is the rate and extent different for nanoparticles?
 - What is transferred? Ions or NPs or Both?

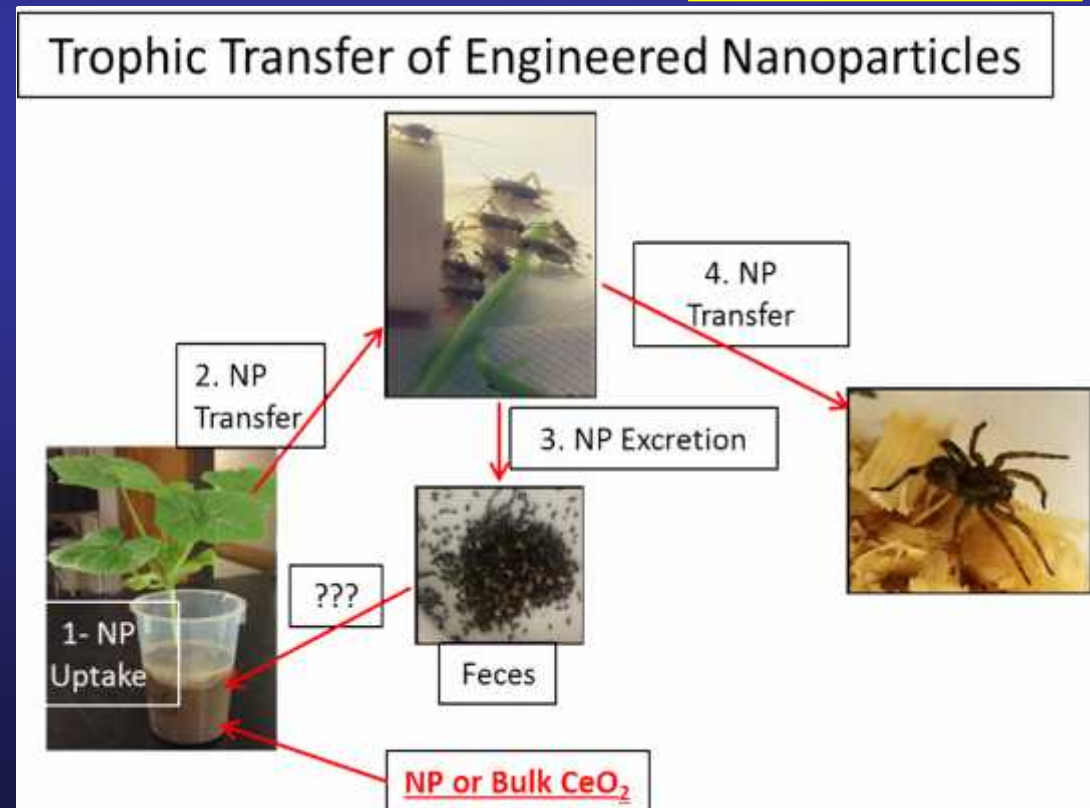




Objective 3- Determine the trophic transfer potential of NMs

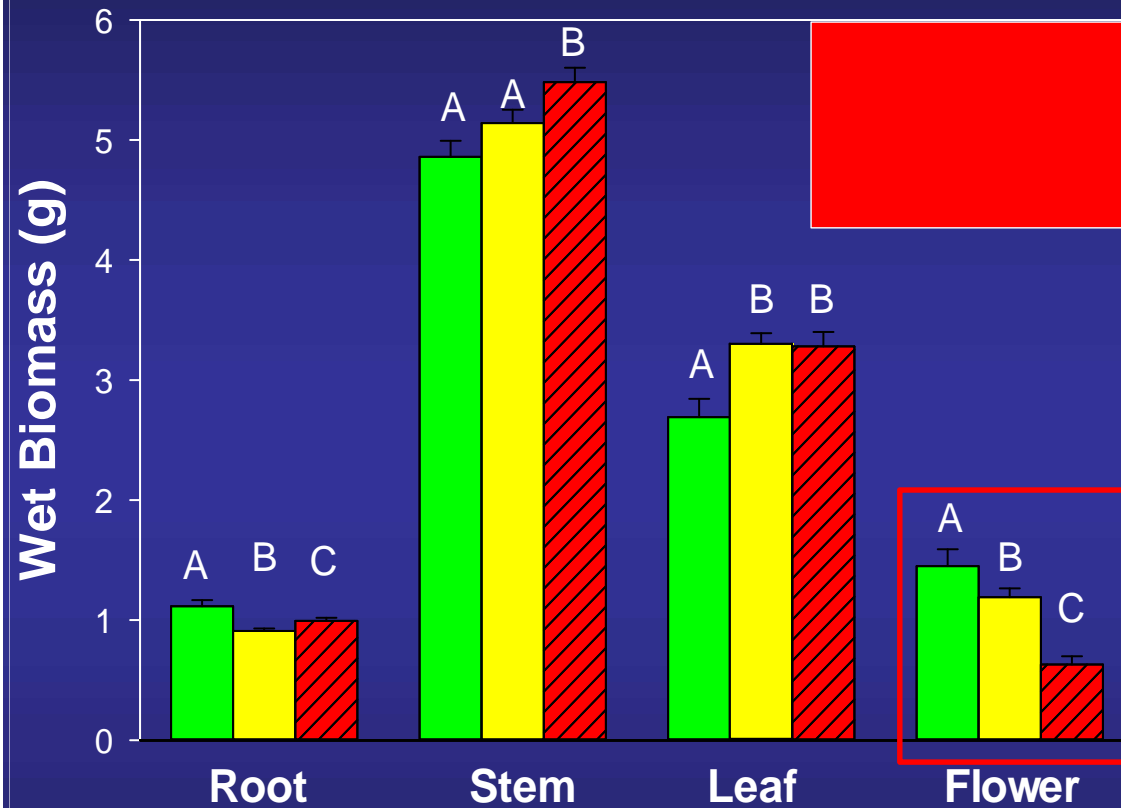
- Experiment 1- **NP or bulk** CeO₂ (0 or 1000 mg/Kg) added to an agricultural loam.
- Zucchini grown for 28d from seedling.
- Roots, stems, leaves, and flowers analyzed by ICP-MS.
- Leaves used to feed crickets for 14d.
- Crickets used to feed wolf spiders for 7d.
- Insect tissues for ICP-MS

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





NP/Bulk CeO₂: Biomass Effects

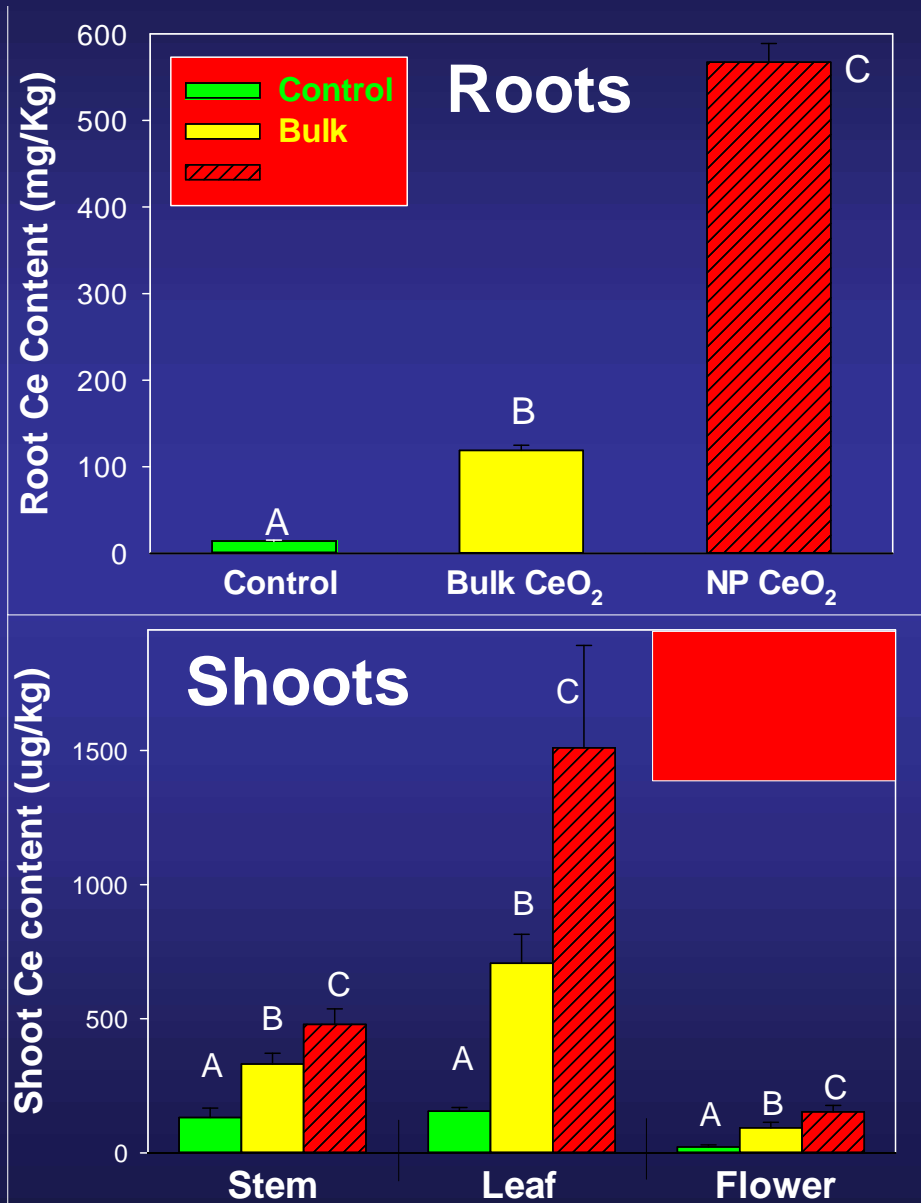


- No effect of Ce exposure on total wet or dry biomass
- Particle-size specific effects evident in root mass (decreases with exposure), stem mass (increase), and leaf mass (increase)
- NP CeO₂ reduced flower mass (reproductive tissues by more than 50%)





NP/Bulk CeO₂: Plant Ce content



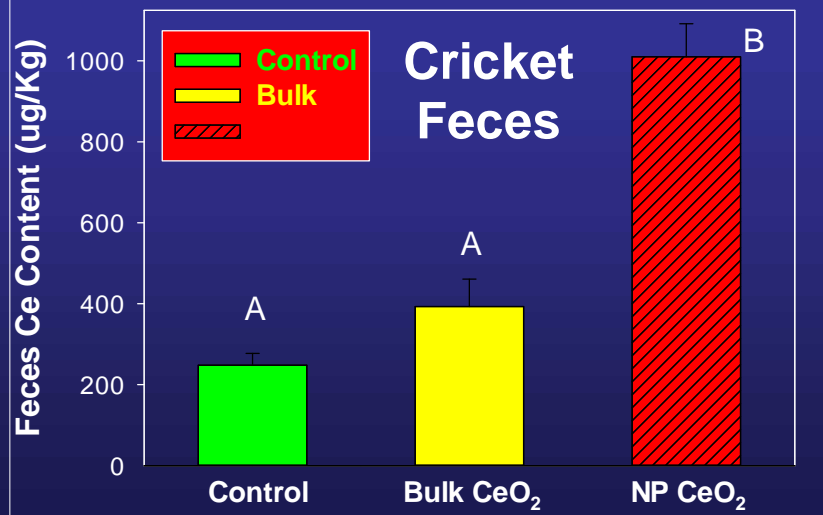
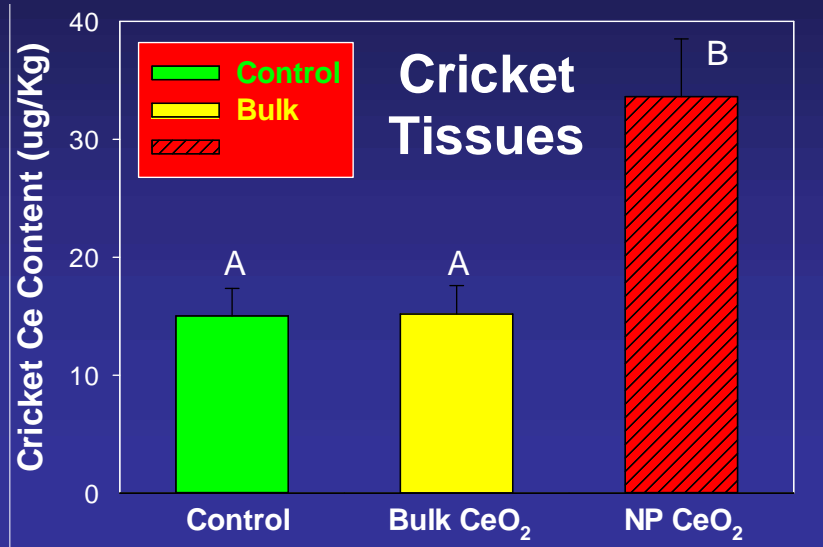
- Soil had background Ce at 21 mg/Kg so Ce present in controls
- NP-exposed tissues contained significantly more Ce than did bulk treatments!!
- Bulk and NP-exposed roots contained Ce at 119 and 576 mg/Kg (dilute acid-rinsed)
- NP-exposed shoot tissues contained 30-53% more Ce than bulk plants

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





NP/Bulk CeO₂: Cricket Ce Content



- Crickets fed bulk Ce contaminated leaves contained Ce at 15 ng/g
- NP exposed crickets had Ce at 33 ng/g
- Cricket feces for control and bulk-exposed insects were 250-380 ng/g
- Feces from NP-exposed crickets contained nearly 1000 ng/g





NP/Bulk CeO₂: Spider Ce Content

- All replicates (3 each) of control and bulk CeO₂-exposed spiders contained Ce at levels below the LOQ (4.6 μg/Kg)
- Two of the three NP-exposed spiders contained Ce at 8.8 and 5.9 ng/g; the third replicate was below the LOQ

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Objective 3- Determine the trophic transfer potential of NMs

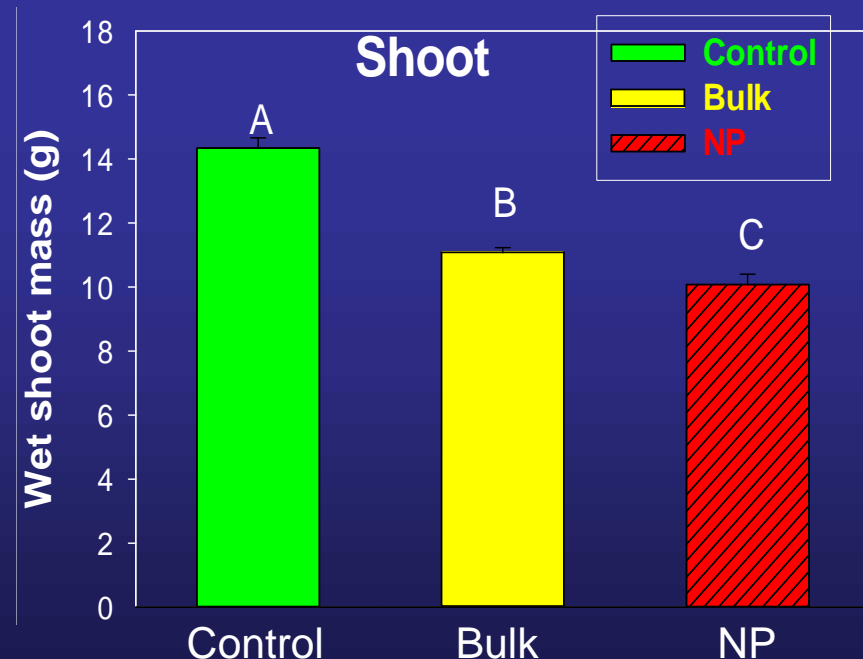
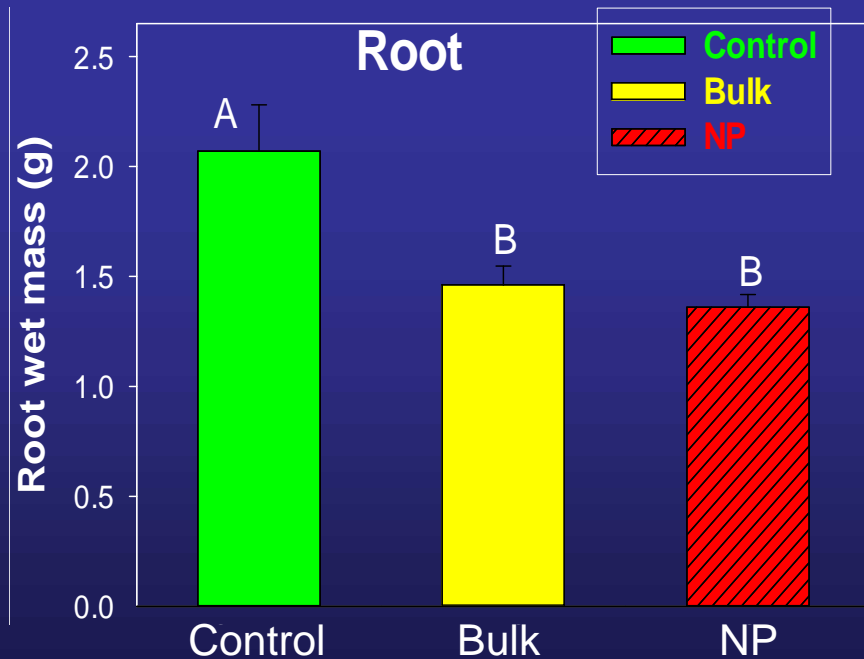
- Experiment 2- **NP or bulk** La_2O_3 (0 or 500 mg/Kg) added to an agricultural loam (a January soil-run in CT by post-docs from Texas...)
- Lettuce grown for 50d from seedling.
- Roots and shoots analyzed by ICP-MS.
- Leaves used to feed crickets and darkling beetles for 15d.
- Crickets used to feed mantids for 10d.
- Arthropod tissues for ICP-MS; S/TEM-EDS.





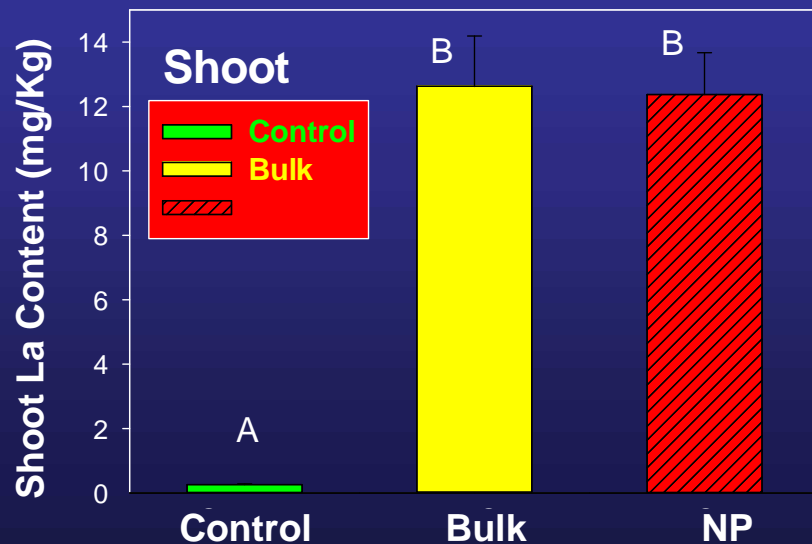
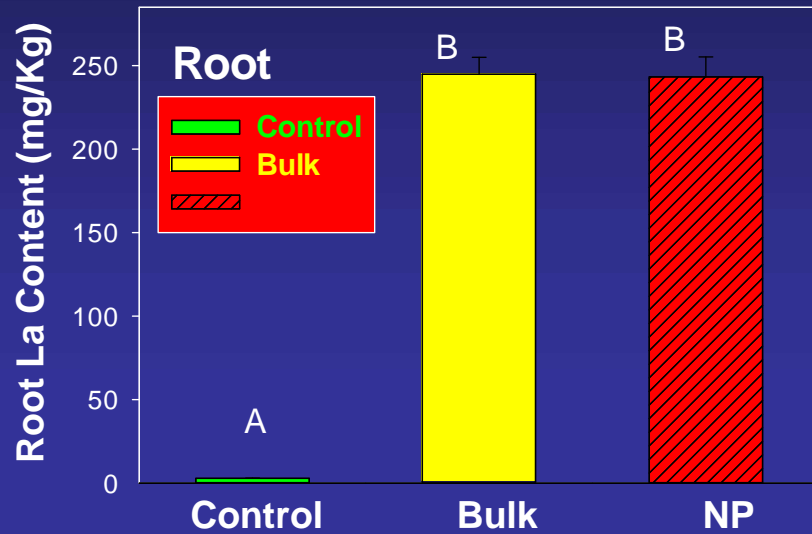
NP/Bulk La_2O_3 : Biomass Effects

- La_2O_3 reduced root mass regardless of particle size
- La_2O_3 NPs reduced shoot biomass significantly more than did the bulk metal oxide





NP/Bulk La_2O_3 : Plant La Content

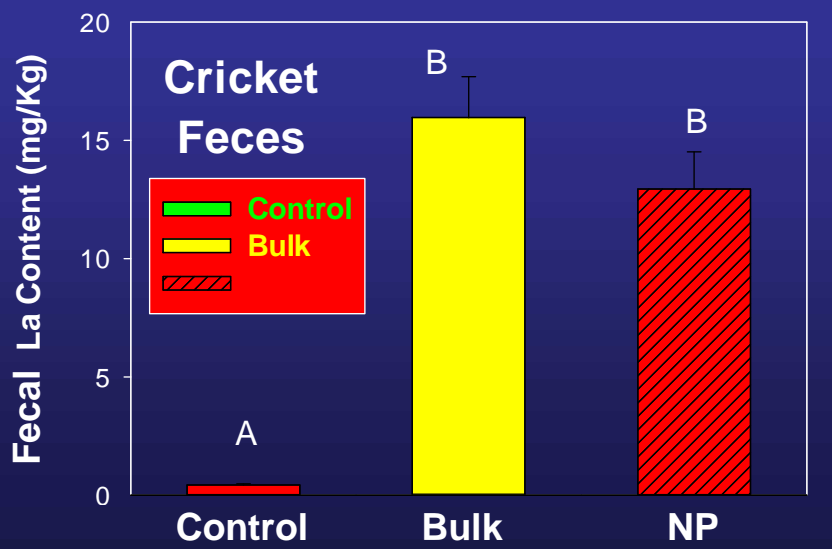
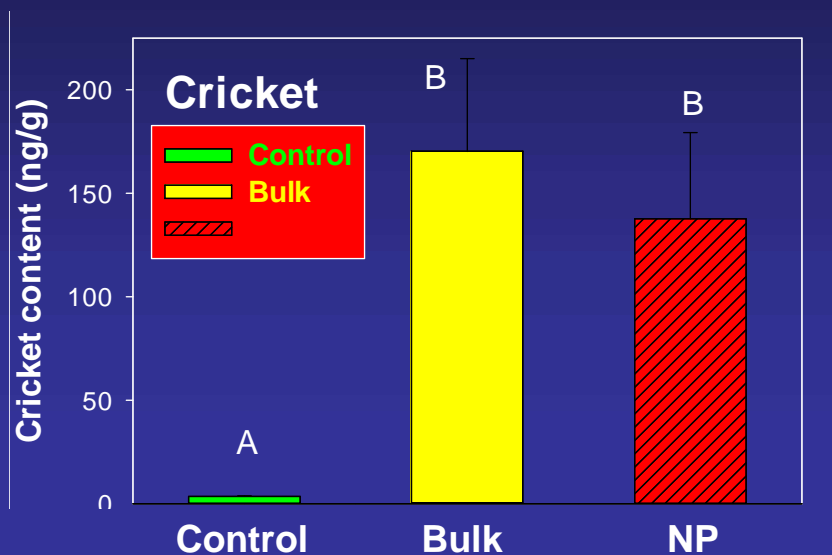


- La root and shoot content was unaffected by particle size
- La translocation much greater than Ce in zucchini





NP/Bulk La_2O_3 : Insect La Content



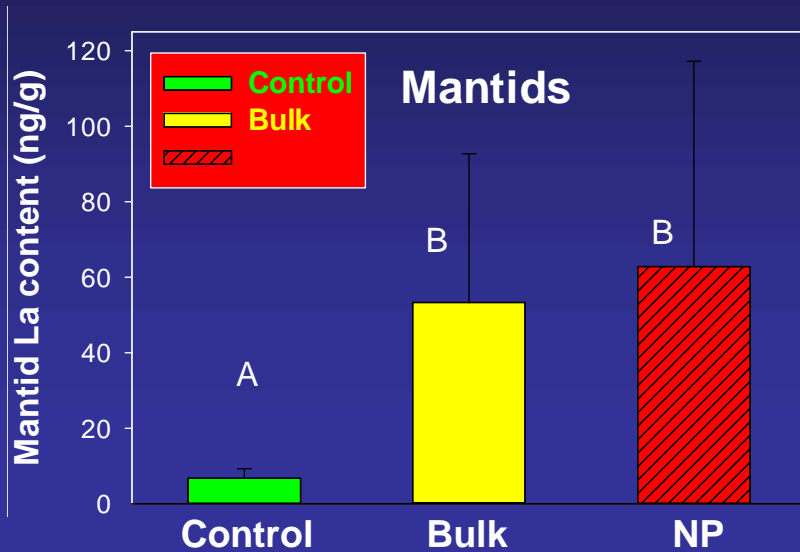
- La content in crickets and cricket feces was unaffected by particle size
- Similar to Ce, fecal content was **much** higher than tissue content



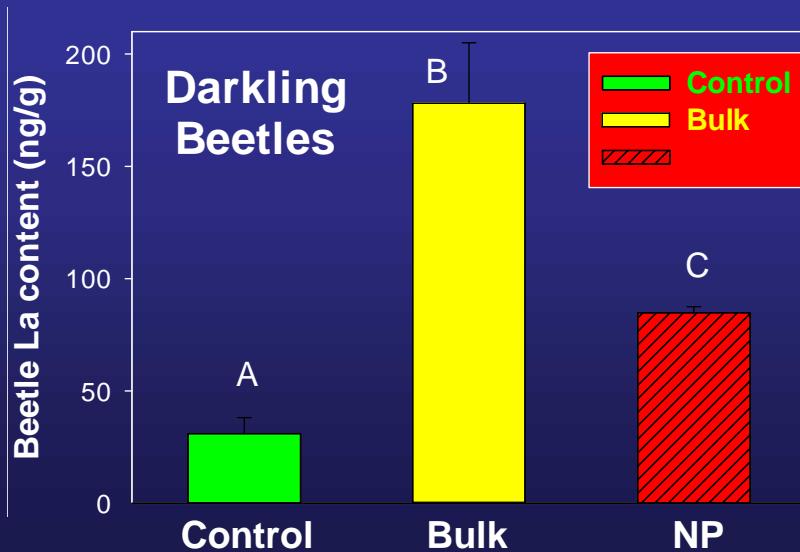
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NP/Bulk La_2O_3 : Insect La Content



- La content in mantids was unaffected by particle size
- La content in beetles was actually decreased for the NP





Trophic Transfer Studies- Ongoing Work

- NP and bulk cerium trophic transfer part II- conducted at UTEP with TX soil (1000-2000 mg/kg CeO_2), kidney bean, Mexican bean beetle Majumdar et al; in preparation.
- Trophic transfer of NP and bulk CuO- 500 mg/kg in soil for 0 or 60 days, lettuce, cricket, anolis lizards.



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Gardea-Torresdey et al. *Environ. Sci. Technol.*, 2014, 48 (5), pp 2526–2540



Trophic Transfer Studies- Future Work

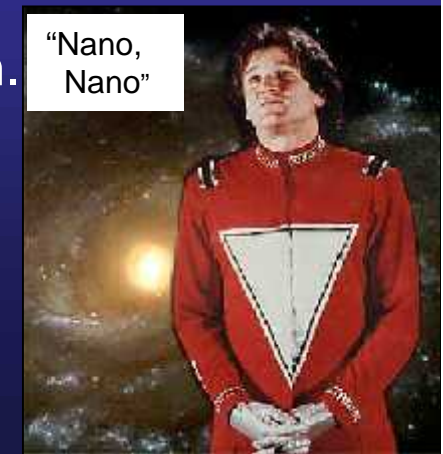
- Determine why CeO_2 bioaccumulates in a particle-size specific fashion and La_2O_3 does not
- Measure ion release from metal oxides in soil
- Determine impact of root exudation on metal oxide dissolution
- “omics” endpoints
- Determine the nature of the accumulated Ce and La
 - S/TEM-EDX
 - Synchrotron (μXRF , XANES)





Conclusions

- Are engineered nanomaterials an emerging class of contaminants in agricultural systems? Do they behave different from their non-nano counterparts in a toxicologically significant fashion?
- In agriculture, exposure routes are numerous and can occur directly through NM-containing pesticide/ fertilizer formulations, as well as spills, or indirectly through the application of NM-containing biosolids
- Trophic transfer studies just completed or underway
 - NP CeO_2 seems to be accumulated from soil and trophically transferred in particle size specific fashion.
 - NP La_2O_3 presents a different scenario, albeit with a different plant
- Clearly, much more work is needed





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- 2011-2016: USDA AFRI -Addressing Critical and Emerging Food Safety Issues-
“Nanomaterial contamination agricultural crops”
- 2012-2015: USDA AFRI –Nanotechnology for Agricultural and Food Systems-
“Nanoscale interactions between engineered nanomaterials and black carbon (biochar) in soil”

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