Accumulation and Trophic Transfer of Engineered Nanomaterials by Plants

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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
  - Disease suppression

2014

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

ACS Select on Nanotechnology in Food and Agriculture: A Perspective on Implications and Applications

Powder that makes doughnuts white may have, until recently, been the most well-known food containing manufactured nanoscale particles. This may be rapidly changing. The growing ability to create and manipulate on the nanoscale indicates it is only a matter of time before more engineered nanomaterials (ENMs) are found on our farms, in our grocery stores, and on our plates. What we do not know yet is what forms these technologies will take. This causes simultaneous excitement for potentially better and healthier products and concern due to multifaceted new properties yet to be fully understood by the scientific community.

The budding nature of the field is reflected in this ACS Select on Nanotechnology in Food and Agriculture: Implications and Applications. As recently published papers from six ACS journals were being selected, it quickly became apparent that much work was being conducted on the implications of these ENMs. Papers focused on consequences of widespread use by examining effects on the environment, agriculture, and plants, and humans through direct consumption. However, work has also begun in the area of application of nanoscale science to food and agriculture. New nanosensors for improving food quality and safety and packaging techniques that will change the way food is stored and delivered have been the primary application foci among authors featured in this Select.

APPLICATIONS

Potential applications of nanoscale sciences to food and agriculture are limited only by the imagination. Papers in this ACS Select demonstrate that the majority of the work is being done on nanoscale biomaterials, packaging, and sensors to enhance the shelf life of foods and more carefully detect when undesirable compounds are present in food.

Encapsulation of active compounds in packaging in nanoscale electrospun fibers is an attractive option for enhancing the shelf life of packaged foods. Kayaci et al. describe their successful efforts to lend more stability to the eugenol molecule, a popular preservative choice in the food industry due to its natural origins and extraction from plants, as well as antibacterial, antifungal, and antioxidant activities.[1] Eugenol is quite susceptible to degradation by oxygen, light, and heat, but encapsulation in cyclodextrin inclusion complexes is shown to aid the thermal stability of the preservative. The controlled/slow release of active ingredients encapsulated is another advantage for many applications of delivery of valuable payloads. Nanocellulose is a biomaterial that is seeing growing use in food packaging and other applications. Although the end product is biodegradable and biocompatible, Li et al. perform a life cycle assessment examining the environmental impacts of fabricating this nanoscale form of cellulose.[2] The environmental footprint increases significantly when compared with a standard procedure for extraction of raw cellulose materials, but is much less than that of the production of carbon nanotubes.

Nanoscale sensors will be extremely important tools for food quality and safety in the near future. In a review of sensor science for food safety Farahi and coauthors concluded that nanotechnology is clearly a big part of the future in sensor science because of advantages such as "...greater effective functionalized sensing surface area in a compact form...high sensitivity due to their small size...unique optical and electrical properties...fast response due to high elastic (spring) constants; and...highly localized detection of entities of comparable size". These advantages go hand-in-hand with challenges; sensors have been laboratory-tested but few field tests, which would gauge progress toward overcoming these challenges, have been conducted.[3] Selectivity and sensitivity make them potentially transformative. In a nanoparticle-based immunoassay, where antibodies are immobilized on magnetic beads, Zhang et al. are able to monitor for marine toxins in seafood down to a concentration of picograms per milliliter.[4] Apak et al. provide a good example of selective nanoscale sensors by binding oxidant sensitive dyes to the surface of nanoscale TiO_2 and determining the catechin content of various types of tea (catechin molecules bestow teas with a majority of their beneficial health effects).[5] Zhang et al. have developed a time- and temperature-sensitive indicator for perishable products using gold and silver plasmonic nanocrystals that can be tuned to change color from red to green on the basis of the temperatures they are exposed to and the time since the food has been packaged.[6]

It is envisioned by scholars and stakeholders that the convergence between nanotechnology, biotechnology, and agricultural and environmental sciences will lead to revolutionary advances in the next 5−10 years. Some applications on the horizon may include, but are not limited to

- development of nanotechnology-based foods with lower calories and less fat, salt, and sugar while retaining flavor and texture;
- nanoscale vehicles for effective delivery of micronutrients and sensitive bioactives;
- re-engineering of crops, animals, and microbes at the genetic and cellular level;
- nanobiosensors for detection of pathogens, toxins, and bacteria in foods;
- identification systems for tracking animal and plant materials from origination to consumption;
- integrated systems for sensing, monitoring, and active response intervention for plant and animal production;
- smart field systems to detect, locate, report, and direct application of water;
- precision and controlled release of fertilizers and pesticides;
- development of plants that exhibit drought resistance and tolerance to salt and excess moisture; and
- nanoscale films for food packaging and contact materials that extend shelf life, retain quality, and reduce cooling requirements.

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DOI 10.1007/s11051-015-2907-7

2015

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

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

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

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Supporting Information

CAES Nanotoxicology Program

- Goal- To assess the effects of engineered nanomaterial exposure in agricultural systems. Exposure pathways include nano-enabled agrichemicals and biosolids. Focus is on plants but other species included.
- 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- Determine the impact of biochar on NM uptake and toxicity to crops and earthworm species.

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Trophic Transfer Studies

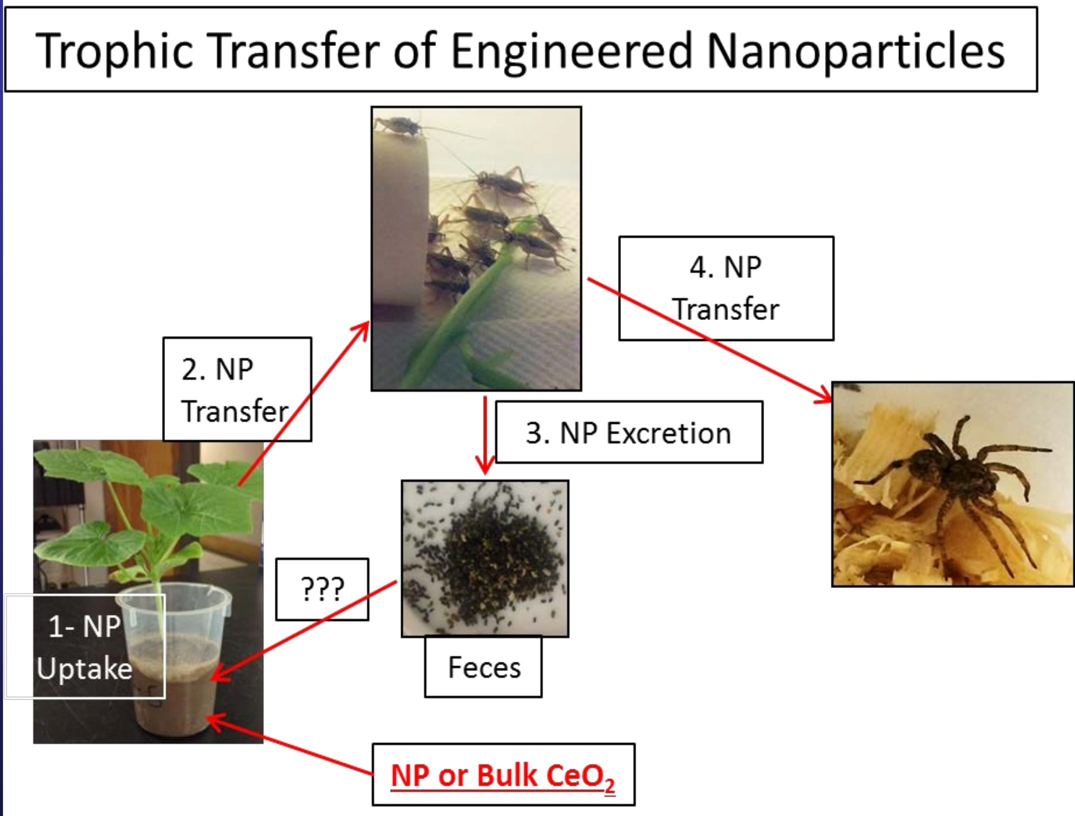
- A significant knowledge gap exists on the potential transfer of engineered nanomaterials from soil to crops and to the organisms (humans, non-humans) that consume those crops
- Some work in aquatic systems
- Only a few studies in soil with NP Au (Univ. of KY); transfer and biomagnification noted under some conditions
- Establishing differences between bulk and NP forms is key to understanding exposure

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

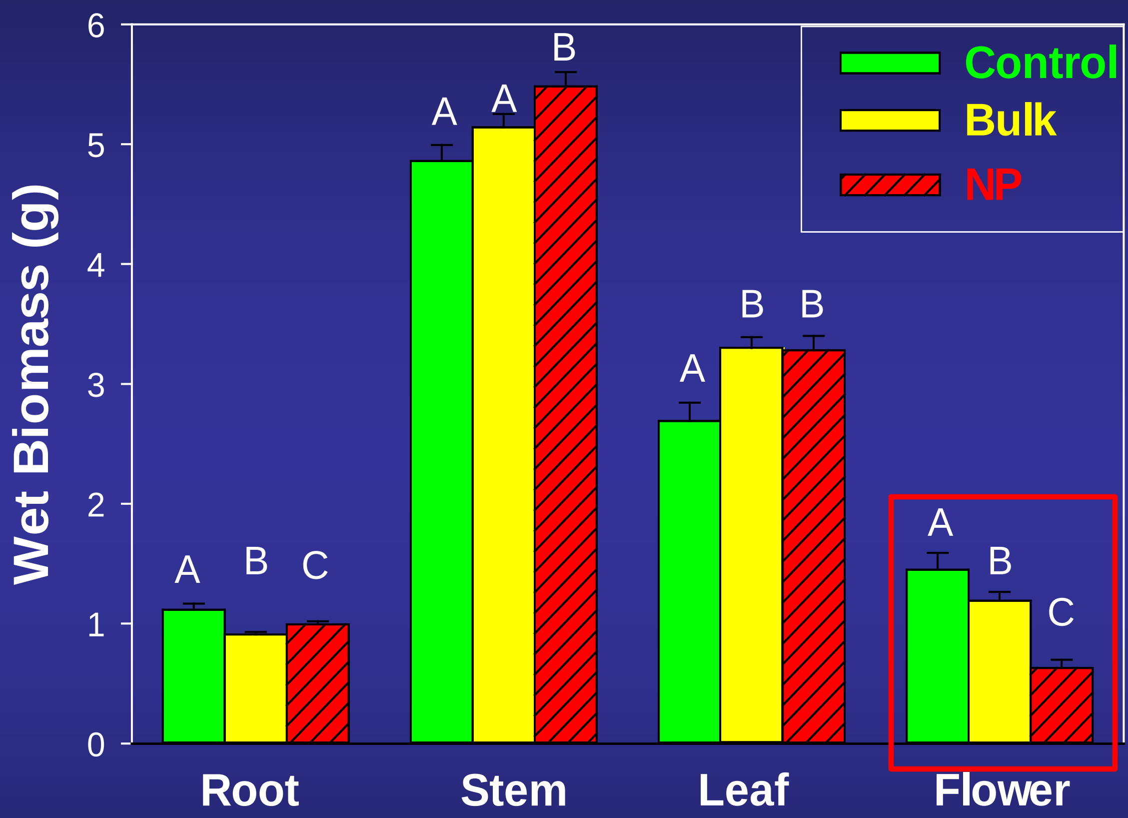
Objective 3- Determine the trophic transfer potential of NMs

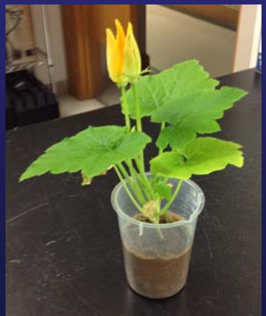
- Experiment 1- **NP/bulk** CeO_2 (0 or 1000 mg/kg) added to an agricultural loam.
- Zucchini grown for 28d from seedling.
- Roots, stems, leaves, and flowers analyzed by ICP-MS.
- Leaves used to feed crickets for 14d.
- Crickets used to feed wolf spiders for 7d.
- Insect tissues for ICP-MS; S/TEM-EDS.

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



NP/Bulk CeO_2: Biomass Effects

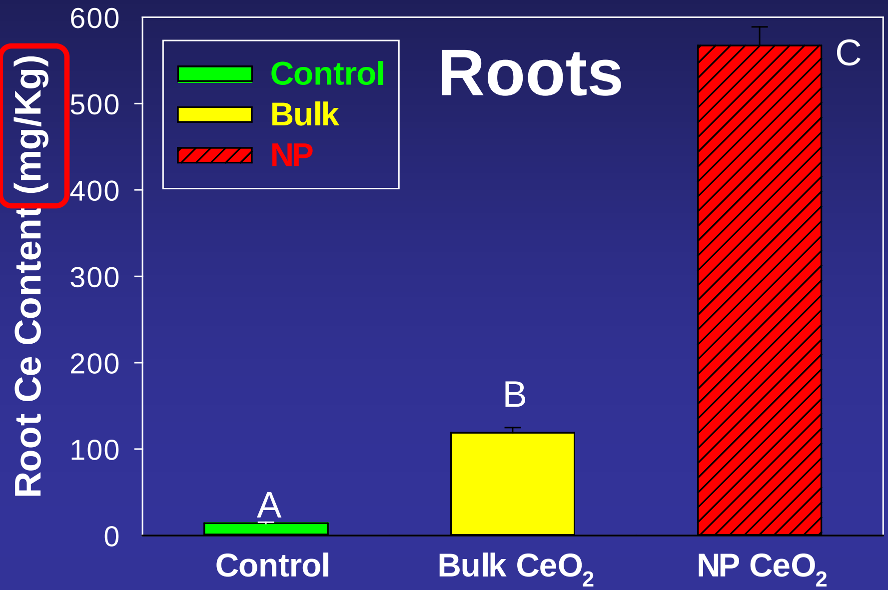


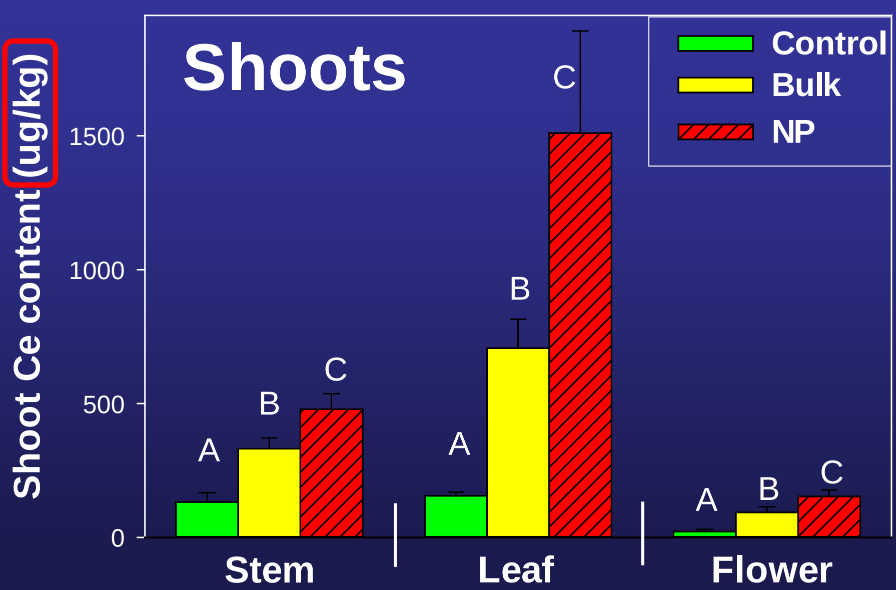


- No effect of Ce exposure on total wet or dry biomass
- Particle-size specific effects evident in root mass (decreases with exposure), stem mass (increase), and leaf mass (increase)
- NP CeO_2 reduced flower mass (reproductive tissues by more than 50%)

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

NP/Bulk CeO_2: Plant Ce content

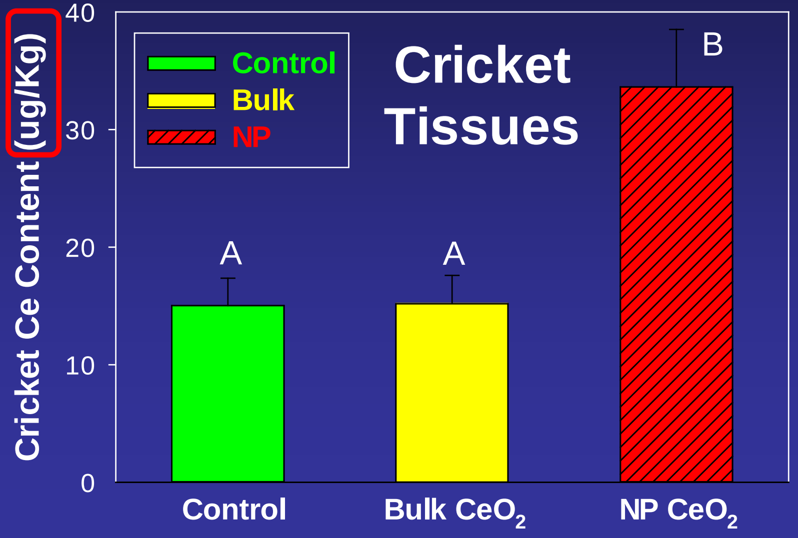


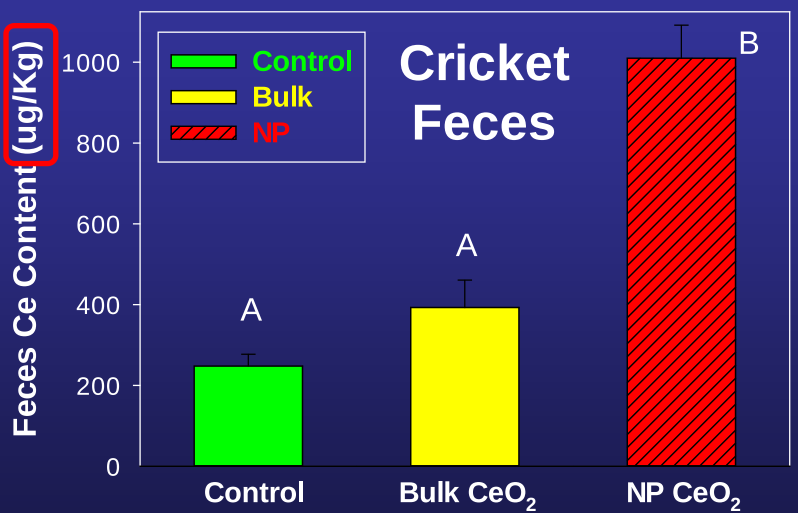


- Soil had background Ce at 21 mg/kg so Ce present in controls
- NP-exposed tissues contained significantly more Ce than did bulk treatments
- Bulk and NP-exposed roots contained Ce at 119 and 576 mg/kg (dilute acid-rinsed)
- NP-exposed shoot tissues contained 30-53% more Ce than bulk plants

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

NP/Bulk CeO_2: Cricket Ce Content





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

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

NP/Bulk CeO_2: Spider Ce Content

- All replicates (3 each) of control and bulk CeO_2-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 µg/kg; the third replicate was below the LOQ

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

<u>Trophic Transfer I:</u> Summary and Unanswered Questions

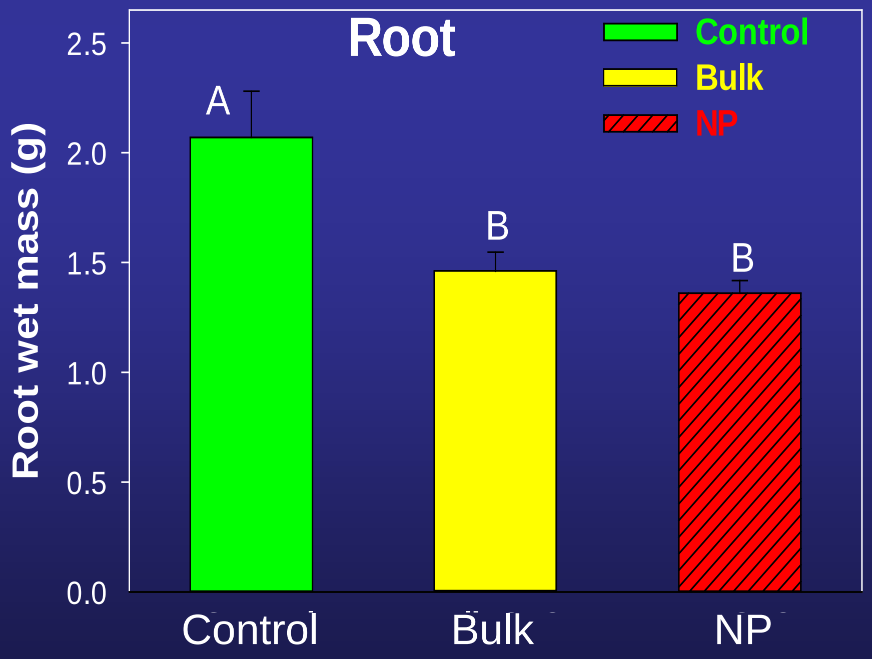
- Ce transfer from soil to plant does differ with particle size
- This greater NP exposure to the plant carries through herbivore and carnivore trophic levels
- Although trophic transfer occurs, biomagnification does not (order of magnitude or more decreases at each level)
- Significant release in feces (10 times more than tissues)
- <u>Questions</u>- Why does particle size matter? What form is accumulated and transferred? What form is excreted? Exposure issues with fecal Ce?

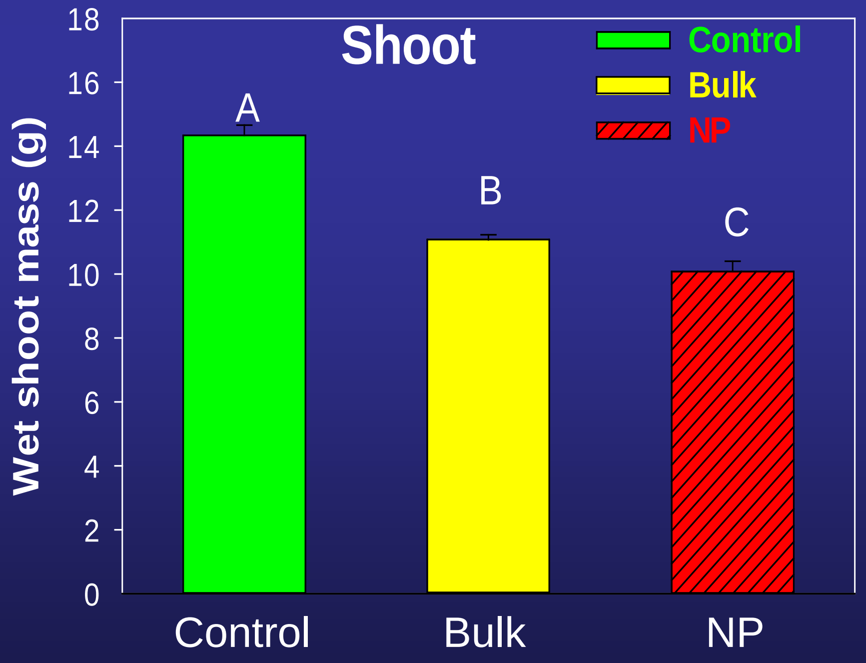
Trophic Transfer II: Lanthanum Oxide

- Experiment 2- **NP/bulk** La_2O_3 (0 or 500 mg/kg) added to an agricultural loam
- Lettuce grown for 50d from seedling.
- Roots and shoots analyzed by ICP-MS.
- Leaves used to feed crickets and darkling beetles for 15 days.
- Crickets used to feed mantids for 7-10 days.
- Arthropod tissues for ICP-MS; S/TEM-EDS for tissues.

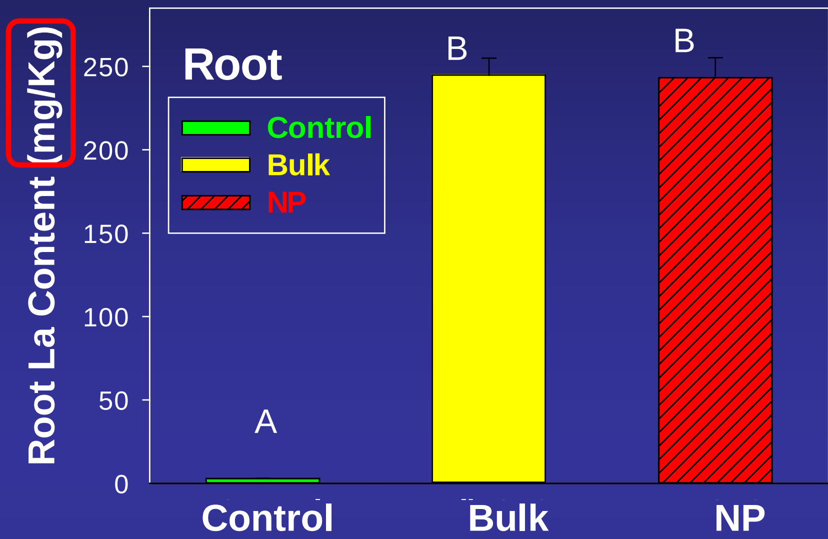
NP/Bulk La_2O_3: Biomass Effects

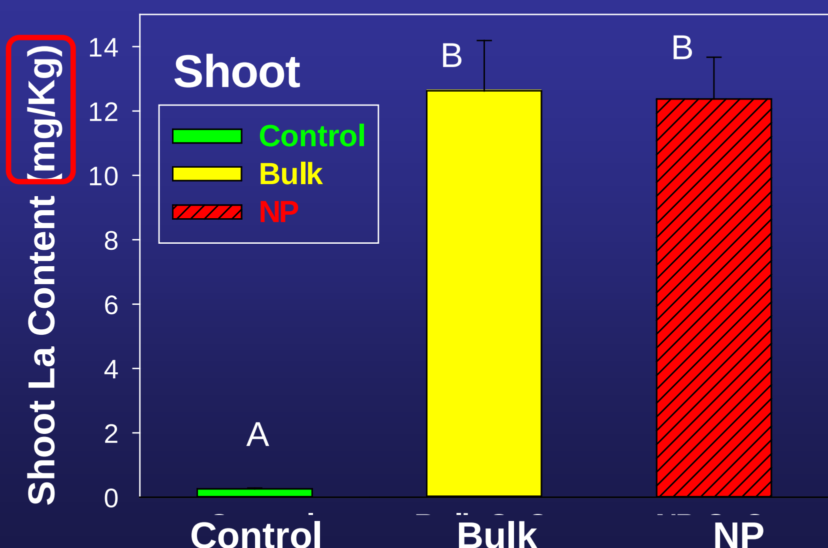
- La_2O_3 reduced root mass regardless of particle size
- La_2O_3 NPs reduced shoot biomass significantly more than did the bulk metal oxide





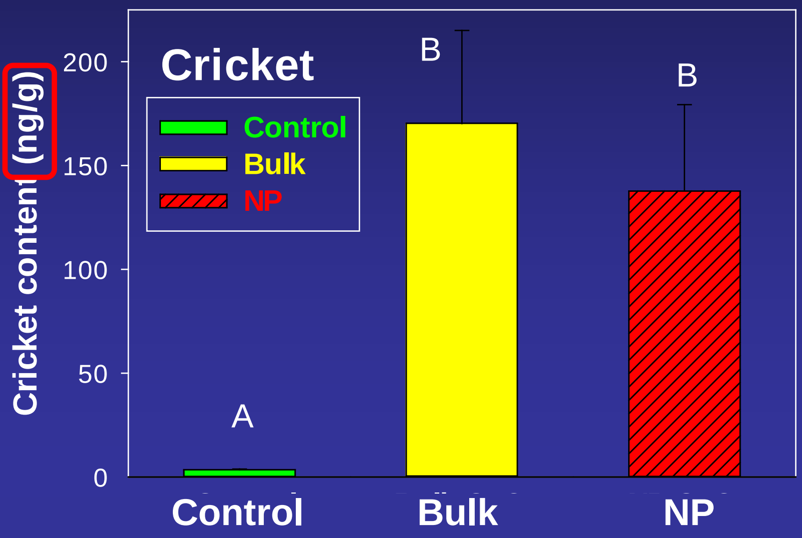
NP/Bulk La_2O_3: Plant La Content



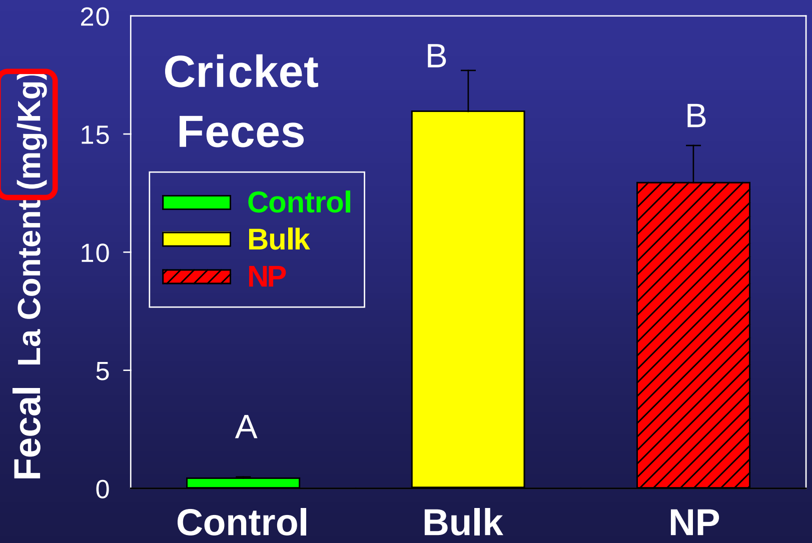


- La root and shoot content was unaffected by particle size

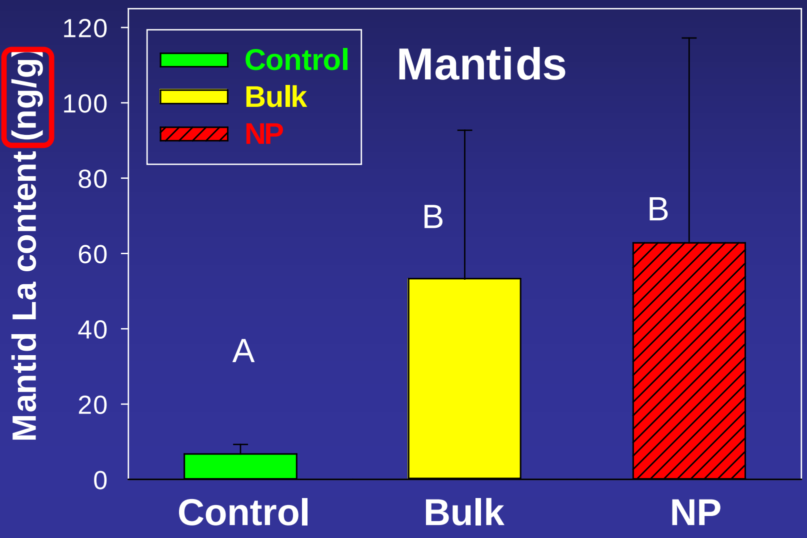
NP/Bulk La_2O_3: Insect La Content

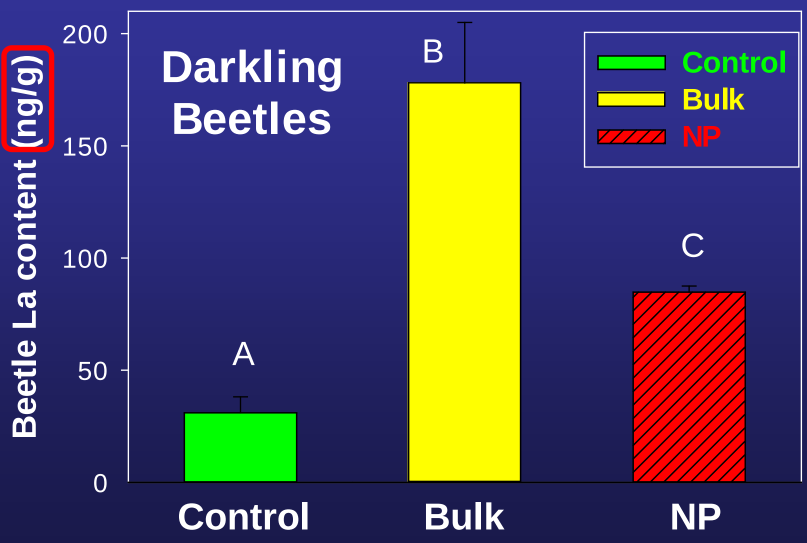


- La content in crickets and cricket feces was unaffected by particle size



NP/Bulk La_2O_3: Insect La Content





- La content in mantids and beetles was unaffected by particle size

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.

Trophic Transfer Studies- Key Exposure and Effects Questions

- Why does CeO_2 bioaccumulate in a particle-size specific fashion and La_2O_3 does not?
- Ion release from metal oxides in soil?
- Impact of root exudation on metal oxide dissolution?
- Use sensitive “omics” endpoints
- What is the nature of the accumulated Ce and La?
  - S/TEM-EDX
  - Synchrotron (µXRF, XANES)

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

Obj. 4: Nanomaterial interactions with co-existing organic chemicals

- Nanomaterials may represent a novel class of contaminants entering agricultural systems directly (agrichemicals) or indirectly (biosolids)
- Agricultural systems contain a number of other organic chemicals and metals
- Interactions between nanomaterials and these co-existing contaminants/chemicals are unknown
    - Could bioavailability of legacy pesticides be affected? A food safety issue?
    - Could efficacy of intentional pesticides be affected? An economic issue?
- Five publications since 2012; a sixth in preparation





Effect of MWCNT or C_{60} on weathered chlordane/DDE accumulation from soil

- Soil with 2,150 µg/kg weathered chlordane; 120 µg/kg DDE
- Chlordane residues summed as 3 components; cis-chlordane (CC), trans-chlordane (TC), trans-nonachlor (TN)
- Plants- zucchini, tomato, soybean, corn
- Carbon nanomaterials- C_{60} fullerenes or MWCNTs at 0, 500, 1000, or 5000 mg/kg
  - Tissue biomass
  - GC-MS analysis for TC, CC, TN, and DDE content in roots, stems, leaves



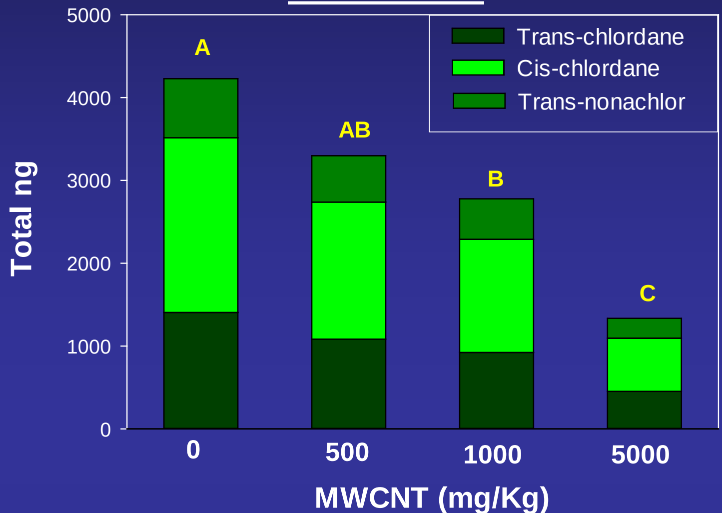
De La Torre Roche et al. 2013. *Environ. Sci. Technol.* 47:12539-12547

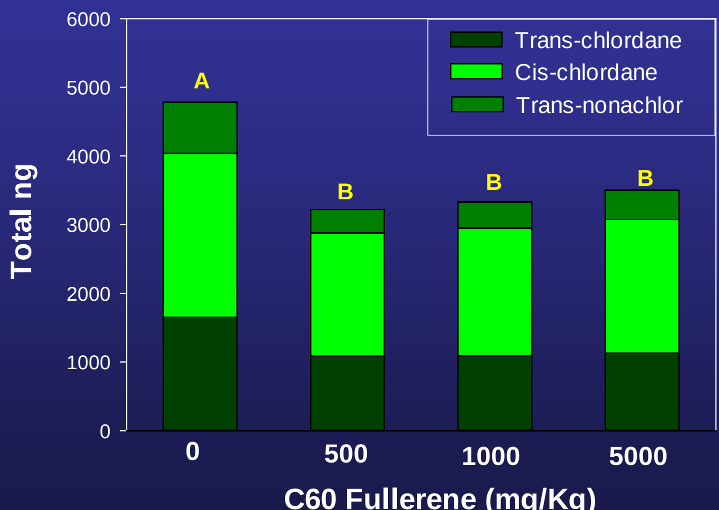
State University of New York
College of Environmental Science and Forestry

Southern Illinois University Carbondale

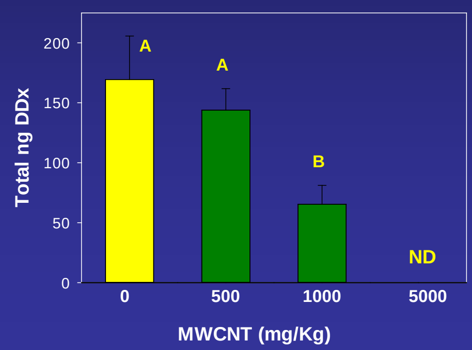
MWCNTs or C_{60} differentially impact pesticide accumulation by zucchini

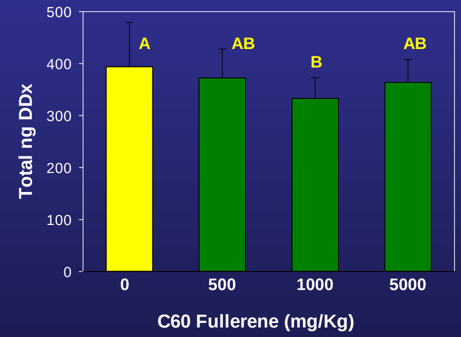
Chlordane





DDx



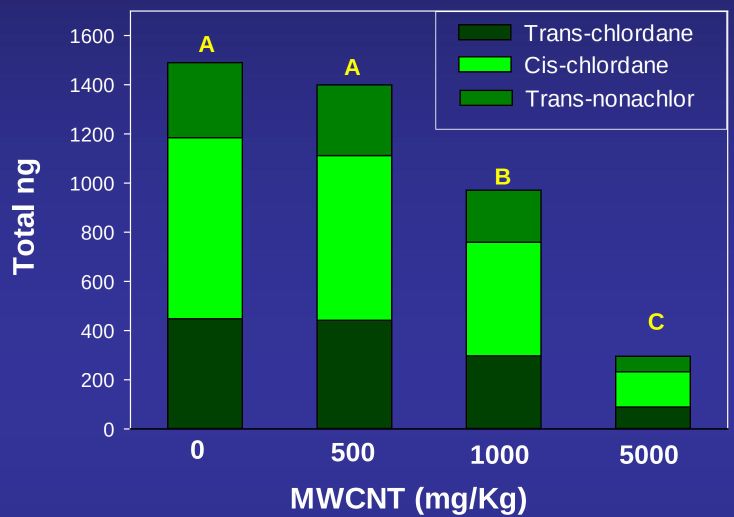


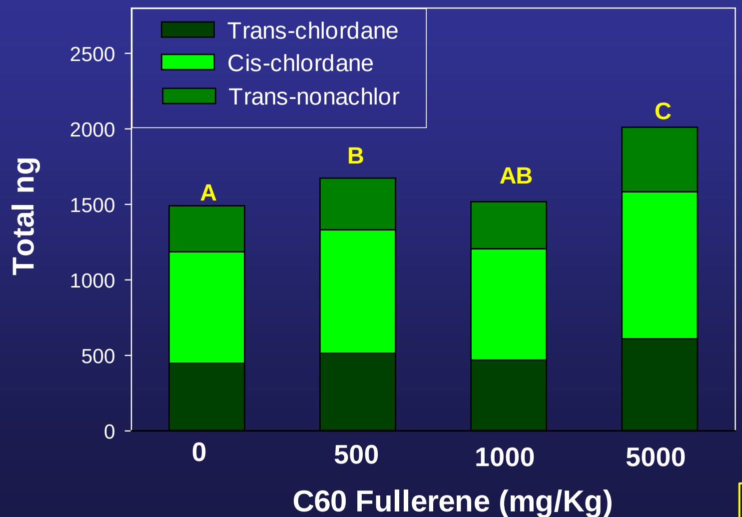
- MWCNTs decrease the accumulation of weathered residues in a dose-dependent fashion
- C_{60} fullerenes have much more modest effects on residue accumulation

De La Torre Roche et al. 2013. *Environ. Sci. Technol.* 47:12539-12547

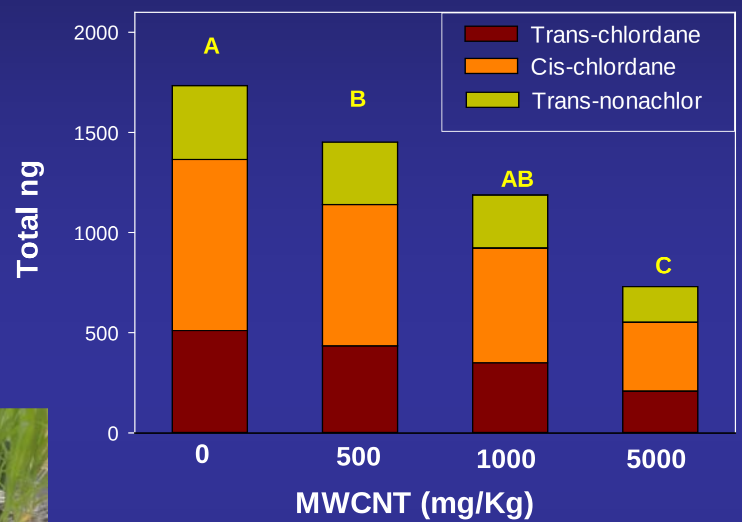
MWCNTs or C_{60} differentially impact pesticide accumulation by tomato and corn

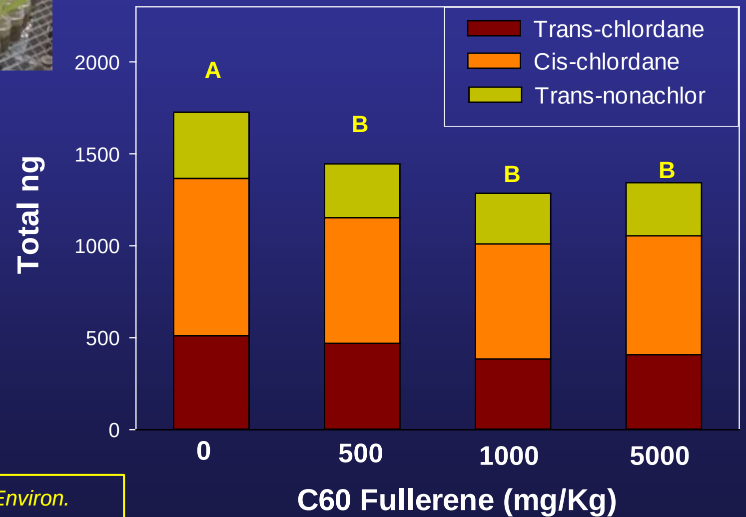
Tomato





Corn





De La Torre Roche et al. 2013. *Environ. Sci. Technol.* 47:12539-12547

Conclusions

- Are engineered nanomaterials an emerging class of contaminants in agricultural systems?
- Exposure may occur directly through NM-containing pesticide/ fertilizer formulations, as well as spills, or indirectly through the application of NM-containing biosolids
- Trophic transfer studies shows that particle size specific uptake and transfer can occur; biomagnification not evident
- NM have been shown to significantly impact the fate and effects of co-existing contaminants under model and soil-based conditions
- <u>Exposure</u>: Long term, low dose studies under realistic conditions are needed

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- **Wang et al**- Ocean University of China
- **Marmiroli et al.**- Univ. of Parma, Italy

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- 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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