

Nanoparticle Contamination of Agricultural Crop Species

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Project Objectives- Nanomaterials (NM), substances with dimensions less than 100 nm, possess unique properties as a function of small size. Over 1300 nanomaterial-containing products are now commercially available, including pesticide and fertilizer formulations. The current magnitude of exposure and the unique nature of engineered particulates warrant caution, especially given the regulatory framework that generally assumes that nanomaterials possess equivalent toxicity and risk to corresponding bulk materials. As a consequence of this assumption, until recently few data have been generated on nanomaterial impacts on agricultural plants and potential contaminant trophic transfer is largely unknown. This lack of understanding is disconcerting given that food crop contamination is a pathway of human exposure. This five year project will quantitatively characterize the impact of NM on common food crops, including a mechanistic assessment of toxicity, accumulation, and trophic transfer, as well as the potential effects on the fate of co-existing pesticides. The objectives of the project are as follows:

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

Approach and Progress- We are approximately half way through the project and have made significant progress on objectives one and four. Objective one is a high throughput screening study assessing the acute toxicity of 12 NM, as well as corresponding bulk and ion controls, to 12 crop species. Primary endpoints include biomass, transpiration, and element/particle content in root and shoot tissues as a function of exposure. The original goal of the screening study was to isolate the plant-NM systems of greatest concern so as to guide detailed mechanistic investigations. The screen is nearly half way complete, although it has already begun to serve its intended purpose of highlighting systems worthy of more intense investigation. To date, nanoparticle (NP) Ag, ZnO, CuO and CeO₂ have been studied with all 12 crops. From one to five plant species have been tested with Al₂O₃, fullerenes, SiO₂ or TiO₂. In all instances, toxicity (biomass, transpiration) data have been collected and analyzed. The elemental content analysis as determined by ICP-MS is proceeding; we have acquired data for about half of the shoots and roots of exposed plants. Current findings indicate species- and particle type-specific phytotoxicity, as well as concentration-dependent effects. Most importantly, particle-size specific toxicity has been observed repeatedly, with several types of nanoparticles being more toxic and accumulated to a greater extent than equivalent bulk or ion controls. A separate study was initiated to look specifically at CuO toxicity and uptake in corn. Similarly, NP CuO toxicity and translocation was found to be significantly greater than corresponding bulk and ion treatments [2]. Importantly, electron microscopy data confirmed xylem- and phloem-based nanoparticle transport and transformation. Last, a study was recently completed assessing the physiological and molecular response of a model plant (*Arabidopsis*) to NP CeO₂ and In₂O₃ exposure [3]. In this study, significantly greater gene regulation response upon In₂O₃-exposure was directly

related to significantly less observed phytotoxicity relative to CeO₂ treatment.

The third objective involves trophic transfer studies and experiments are currently underway assaying the toxicity and transfer of NP and bulk CeO₂ or La₂O₃ from soil to plants (zucchini, lettuce) to crickets to mantids. Some very preliminary data suggests greater transfer of NP CeO₂ from plants to crickets than bulk material but that a significant amount of the ingested ceria may be excreted in feces. Significant progress has been made on objective 4, which is quantifying the altered fate and effects of pesticides as a function of NM co-exposure. In two studies published in 2012 and 2013 [4,5], we noted that NP co-exposure (fullerenes, Ag) significantly altered the accumulation of pesticides (DDE) by several crops grown in vermiculite. However, a third study also published in 2013 was conducted in soil and showed far less impact of NP co-exposure on contaminant availability than observed in vermiculite [6]. A fourth study recently accepted for publication addresses the impact of multiwalled carbon nanotube (MWCNT) or fullerene co-exposure on the uptake of field weathered chlordane and DDx (DDT plus metabolites) by four plant species from soil [7]. Interestingly, MWCNT co-exposure consistently decreased pesticide phytoaccumulation in a concentration dependent fashion but fullerene effects were far more variable, ranging from decreased uptake to no measurable effect to actual increases in pesticide accumulation.

Collaborations- Several related collaborations have been initiated; in all cases, these collaborations involve separate lines of research that branch off from the work on our current proposal. Institutions with which we are actively collaborating with include Hampshire College, the University of Texas-El Paso, Muhlenberg College, the National Institute of Standards and Technology (NIST), the University of New Haven, the Ocean University of China, the University of Parma (Italy), and the Institute of Experimental Botany (Czech Republic).

Notable Discoveries- One discovery of significance has been the finding that engineered nanomaterials can significantly alter the accumulation of co-existing pesticides in food crops. This discovery may have significant implications for food safety, as well as for the movement of pesticides and other organic contaminants through various environmental compartments. A second discovery stems from our study on NP CuO toxicity and uptake by corn. Our findings show two new phenomena, both confirmed by transmission electron microscopy with energy dispersive X-ray spectroscopy (TEM-EDX). First, after significant root to shoot translocation, CuO NPs were reduced to CuO₂ or CuS. This is among the first reports to demonstrate NP biotransformation with plants. Second, the use of split root experiments enabled the discovery of shoot-to-root translocation of CuO NP in corn; this is the first demonstration of phloem-based NP transport in the literature.

References

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