AGRICULTURAL RESEARCH FOUNDATION
FINAL REPORT
FUNDING CYCLE 2014 – 2016

TITLE: Comparative analysis of the fate & transformation of nanotechnology-based pesticides & their conventional formulations

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SUMMARY: Dr. Hooven, Dr. Sagili and Dr. Harper were awarded a grant from USDA/NIFA for two years to work on the "Effects of Pesticide Nanotechnology on Vulnerable Organisms". We requested this ARF funding to extend on the work proposed in the NIFA grant. That is, the work is focused on the environmental fate and potential transformation of nanotechnology-based pesticides (NBPs) in the environment, in which NBPs will be compared to findings for conventional pesticide formulations. The ARF funding has thus far been used to cover reagents and chemicals necessary for the studies in addition to support for an undergraduate working on the project. The information gained complements the research conducted through the NIFA grant but does not overlap.

OBJECTIVES: The major objective of this project was to determine how nano-sized capsules differ from micron-sized capsules with regards to toxicity, stability and persistence. The project used embryonic zebrafish as a model organism to determine the impacts that nano-sized pesticide carriers exert on the environment compared to that of micron sized carriers. The results help us better understand the possible elevated risks associated with nano-sized carriers utilized for pesticide delivery and help inform pesticide development and pesticide risk assessment. This research provided some of the first data of its kind on the toxicity of nanotechnology-based pesticides to non-target organisms and their differential interactions with biota and the environment. Ultimately, this project provides knowledge necessary to promote innovative ways to maintain food security while minimizing negative effects to public health and the environment.

PROCEDURES: The research is being conducted across a range of non-selective systemic pesticides designed for use as herbicides (glyphosate based), insecticides (neonicotinoid based), and fungicides (propiconazole based). Considering the broad use of these pesticides, possible alterations may need to be considered in the future to combat resistance and enhance bioactivity in regards to target organisms. A commercial pyrethroid capsule suspension formulation was partitioned into two size fractions by centrifugation. Once the nano-sized and micron-sized capsules have been isolated and concentrated, size characterization and active ingredient quantification will be completed. Embryonic zebrafish were exposed to the two suspensions based on equivalent active ingredient concentrations. Embryonic tremoring, a pyrethroid specific response observed in the fish after exposure to the pesticide, was quantified and differences between the two exposures recorded. Mortality and sublethal endpoints were also compared.

The proximity of waterways in agricultural areas coupled with the frequent lack of robust riparian buffers to protect waterways from adjacent land uses makes rivers, lakes and streams particularly

vulnerable to agricultural runoff. Since agricultural soil characteristics are major factors in determining the amount and the state of pesticides entering waterways, soil impacts on NBPs will be assessed. The researcher are thoroughly characterizing the different versions of the pesticides including parameters such as size of the capsules, octanol/water partitioning, thermal and kinetic stability, photolysis, hydrophobicity, as well as bioaccumulation and bioconcentration potential.

Aquatic toxicity assays were used to characterize the uptake and impacts of nano-enabled pesticides relative to their traditional version following exposure of the pesticides to agricultural soils. A rapid, high throughput embryonic zebrafish assay was used to better understand the toxicity of both forms of the pesticide (Harper et al., 2008; Truong et al., 2011). Zebrafish body burden studies will be used to study how the chemical partitions in the embryo and the role of the chorionic membrane to protect from or enhance an exposure.

SIGNIFICANT ACCOMPLISHMENTS:

Peer-Reviewed Publications

Son, J., Hooven, L.A., Harper, B., and S.L. Harper, 2015. Effect of pH and ionic strength on the fate and toxicity of encapsulated lambda-cyhalothrin to *Daphnia magna*. Science of the Total Environment 538: 683-691.

Meredith, A., Harper, B. and S.L. Harper. 2016. The influence of size on the toxicity of an encapsulated pesticide: a comparison of micron- and nano-sized capsules. Environment International 86: 68-74.

Press Coverage

OSU press release: "OSU study: Packaging insecticides in tiny capsules may make them more toxic". http://oregonstate.edu/ua/ncs/archives/2015/nov/osu-study-packaging-insecticides-tiny-capsules-may-make-them-more-toxic

Corvallis Advocate: Insecticides Toxic: Wait, What? How is that News? (12/2)
http://www.corvallisadvocate.com/2015/insecticides-toxic-wait-what-how-is-that-news/

Article in Modern Farmer on the project was picked up and republished by The Fern:
http://modernfarmer.com/2015/01/everything-need-know-nanopesticides/

http://thefern.org/2015/01/everything-need-know-nanopesticides/

Article highlighted in Nanowerk Nanotechnology Spotlight: Friedman, A, B.L. Adler, V. Cabral, M. Navati, J. Doerner, R. Charafeddine, D. Chandra, H. Liang, L. Gunther, A. Clendaniel, S.L. Harper, J.M. Friedman, and J.D. Nosanchuk. Curcumin-encapsulated nanoparticles as innovative antimicrobial and wound healing agent. Nanomedicine: Nanotechnology, Biology and Medicine, 11: 195-206.
http://www.nanowerk.com/spotlight/spotid=37448.php

Published Abstracts

Meredith, A., Harper, B., Harper, SL. 2015. The influence of size on the toxicity of encapsulated pesticides: a comparison between nano- and micro-capsules. Society of Environmental Toxicology and Chemistry North America annual meeting.

Oral Presentations

Son, J., L. A. Hooven, B. Harper and S. L Harper. Effect of pH and ionic strength on the fate and toxicity of encapsulated lambda-cyhalothrin to *Daphnia magna.* NANO KOREA 2015 Symposium, Seoul, Korea (July 1-3, 2015).

Hooven, L. and S.L. Harper. Do nanotechnology-based pesticide products increase risk to honey bees compared to cognate active ingredients? Society of Environmental Toxicology and Chemistry 35th Annual Conference, Vancouver, BC (November 12, 2014).

Clendaniel, A., Harper, B., Son, J., Hooven, L. and S.L. Harper. The influence of size on the toxicity of encapsulated pesticides: comparing micron and nano-sized capsules. Pacific Northwest - Society of Environmental Toxicology and Chemistry 35th Annual Conference, Vancouver, BC (May 1, 2015).

Bulovsky, H., Wahl, Z., Clendaniel, A. and S.L. Harper. The environmental fate of nano-pesticides and their subsequent toxicity in aquatic environments. College of Engineering Expo, Corvallis, OR (April 27, 2015).

Meredith, A., Harper, B., Harper, SL. The influence of size on the toxicity of encapsulated pesticides: a comparison between nano and micro capsules. Presented at SETAC North America. Salt Lake City, Utah. November 1-5, 2015).

Poster Presentations

Clendaniel, A., Harper, B., Son, J., L., Harper, SL. The influence of size on the toxicity of encapsulated pesticides: a comparison between nano and micro capsules. Presented at Gordon Research Conference on Nanoscale Science & Engineering for Agriculture and Food Systems. Waltham, MA. June 2015.

BENEFITS & IMPACT: The public health and environmental hazards from the usage of pesticides is commonly greater than estimated risks when uncertainty exists in the fate and transport of pesticides. The goal of this proposal is to reduce the uncertainty associated with nanotechnology-based pesticides that incorporate nano-emulsions. When changing the delivery method for chemicals, it is necessary to fully understand how the application technique affects fate and transport, and therefore potential for exposure and adverse impacts. The researcher's long-term goal is to better understand nanotechnology's involvement in agriculture. Since nano-emulsions are also used in a wide variety of foods, cosmetics and pharmaceuticals, findings from this research will be generally applicable to many other disciplines.

Upon completion of the proposed studies, the researcher will have developed relevant and efficient testing strategies to compare risks from NBPs to the conventional formulations. Nano-emulsified pesticides are not well characterized chemically, physically or biologically. Understanding the fate and transport associated with presenting chemicals to the environment as nano-emulsions will promote the development of the most environmentally benign yet effective pesticidal products. Testing the active ingredients, as well as the other ingredients, in a pesticide will help determine if the current policy on formulated pesticides is stringent enough to assess real life risks from their application.

ADDITIONAL FUNDING RECEIVED: None thus far.

FUTURE FUNDING: Two National Science Foundation Graduate Research Fellowship applications were submitted by graduate students in the Harper laboratory to extend on this work. A USDA NIFA proposal will be submitted in April, 2016 and an NSF proposal will be submitted in October, 2016 to advance the NIFA grant.