Western Washington University
Western CEDAR

WWU Honors Program Senior Projects | WWU Graduate and Undergraduate Scholarship

Summer 2020

# Evaluating Impacts of Nanopesticides and Microplastics in an Agricultural Rhizosphere

Emma Nordlund
*Western Washington University*

Manuel Montaño
*Western Washington University*

Follow this and additional works at: https://cedar.wwu.edu/wwu_honors

 Part of the Environmental Sciences Commons

## Recommended Citation

Nordlund, Emma and Montaño, Manuel, "Evaluating Impacts of Nanopesticides and Microplastics in an Agricultural Rhizosphere" (2020). *WWU Honors Program Senior Projects*. 419.
https://cedar.wwu.edu/wwu_honors/419

This Project is brought to you for free and open access by the WWU Graduate and Undergraduate Scholarship at Western CEDAR. It has been accepted for inclusion in WWU Honors Program Senior Projects by an authorized administrator of Western CEDAR. For more information, please contact westerncedar@wwu.edu.

Emma Nordlund

Advisor: Dr. Manuel Montaño

August 2020

# Evaluating Impacts of Nanopesticides and Microplastics in Agricultural Rhizospheres

## Introduction

The prevalence of microplastics in biosolids has led to the contamination of agricultural fields. With over 380 million metric tons of plastic produced globally each year, it is critical to understand how microplastic pollution will interact with both abiotic and biotic components of the environment (Ritchie and Roser 2018). Additionally, recent advances in the agrochemical industry have led to the production and sale of nanopesticides, which are characterized by their size (1 – 100 nm in at least one dimension) and unique size-based properties (Auffan et al. 2009). Their high surface area to volume ratio affects their fate and transport, particularly regarding dissolution, degradation, and sorption behavior, in turn altering their bioavailability and toxicity (Chen 2018; Kah et al. 2018). The purpose of this study was to develop a methodology for assessing the fate, transport, and impacts of emerging contaminants in an agricultural setting. Two contaminants of concern were investigated: Kocide-3000-O (a copper-based nanofungicide) and polyester microplastics.

## Materials and Methods

Greenhouse experiments were conducted to assess its impacts to corn (*Zea mays*), a common agricultural crop. The two treatment groups were dosed twice with approximately 6.68 mg of $Cu(OH)_2$ through a foliar application of Kocide-3000-O, and one treatment group contained 500 mg of polyester microfibers in the soil to represent a microplastic-contaminated environment. Plant tissue and root exudates were collected for analysis after 36 days of growth. Root exudate was collected by removing soil from the plant body, then placing the plant in 450 mL of water for 24 hours.

Total copper content in root/shoot tissue was determined via a nitric acid digestion. Briefly, 1-2 g of tissue (dw) was cut into 1 cm pieces, ashed at 550°C, then heated with 6 mL water and 3

mL 50% $HNO_3$ until liquid evaporated. The samples were ashed again at 550°C, then dissolved in 5 mL 18.5% HCl. This solution was diluted to 25 mL with water and analyzed via FAAS.

The remaining plant tissues were flash-frozen in liquid nitrogen, then stored in a freezer at -80°C until MALDI-TOF-MS analysis. Root exudates was analyzed on a Horiba Aqualog to characterize the dissolved organic matter. Excitation-Emission Matrices (EEMs) were created using a scanning wavelength of 240 – 450 nm with a 0.1 second integration time. Origin software was used to construct plots and determine peak intensities. To identify and quantify the low-molecular-weight compounds present in root exudate, UPLC-QTOF-MS will be used. Root exudate is being stored in the fridge until analysis.

For benchtop laboratory experiments, a synthetic root exudate was prepared using a modified formula from Huang et al. (2017). A 44:43:13 ratio of sugars, organic acids, and amino acids, was used to mimic a C4 plant's root exudate composition (Vranova et al. 2013).

The polyester microfibers used in this study were prepared by blending 100% polyester yarn with water, followed by 20 hours of drying at 85°C. To evaluate the effects of root exudate on microplastic composition, microfibers were placed in glass test tubes containing 0, 0.1, 1.0, or 9.0 g/L carbon in the form of synthetic root exudate. After 31 days, fibers were analyzed on FTIR. A similar process was conducted using pre-made low-density polyethylene beads with a 24-day interval.

The morphology and bioavailability of Kocide-3000-O was characterized using scanning electron microscopy (SEM) and batch sorption experiments with flame atomic absorption spectroscopy (FAAS). In the sorption experiments, a range of Kocide was added to 50 mL centrifuge tubes containing 2.0 g (dw) soil and one of three treatments: 1 mg polyester microfibers, 1 g/L synthetic root exudate, and both microfibers and synthetic root exudate. After a 14-day equilibration period, samples were centrifuged and filtered to remove all particles greater than 0.2 microns in diameter, acidified with one drop of concentrated $HNO_3$, and analyzed via FAAS.

**Results and Discussion**

In water, Kocide-3000-O dissolves readily into sheet-like fragments of copper-based nanorods (Figures 1). Furthermore, the batch sorption experiments showed that copper solubility and bioavailability increase in the presence of root exudate (Figure 2).

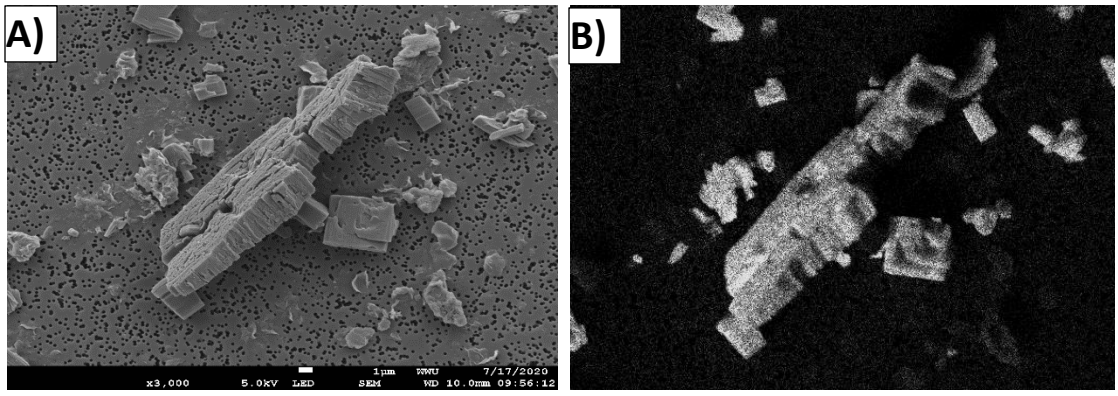


Figure 1. A) Field emission SEM image of Kocide-3000-O after aging 48 hours in water. B) EDX mapping of copper content of image.

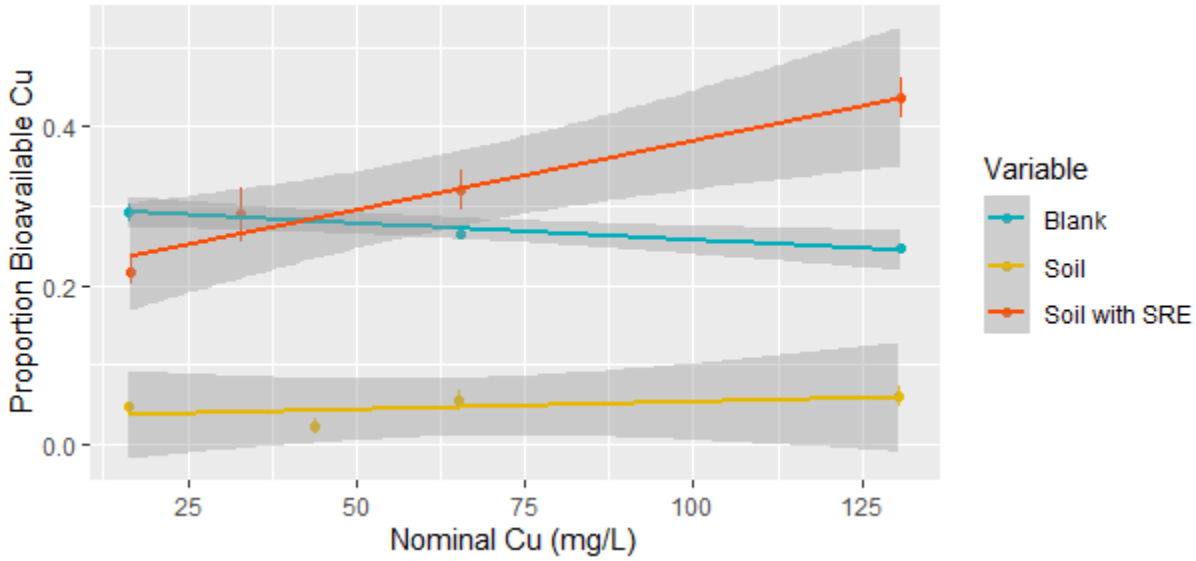


Figure 2. Proportion of bioavailable copper vs nominal copper concentration added. Shaded areas represent 95% confidence intervals for the linear models.

There were no significant differences in copper concentration of plant tissue, or in shoot height, shoot dry weight, and root dry weight. Spectral analysis of the root exudate confirmed the presence of protein-like dissolved organic carbon in all samples with no significant difference in signal intensity. Further work will involve the use of metabolomics analysis using UPLC-QTOF-MS and MALDI-TOF-MS on the root exudate and preserved plant tissues to provide information

regarding the plants' biochemical responses to these stressors. Our work to-date shows that under realistic dosing conditions, minimal differences between plant health are identified; however, the metabolomic effects have yet to be determined.

**Works Referenced**


Auffan, M., Rose, J., Bottero, J. Y., Lowry, G. V., Jolivet, J. P., & Wiesner, M. R. (2009). Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nature nanotechnology*, 4(10), 634-641.

Chen, H. (2018). Metal based nanoparticles in agricultural system: behavior, transport, and interaction with plants. *Chemical Speciation & Bioavailability*, *30*(1), 123-134.

Huang, Y., Zhao, L., & Keller, A. A. (2017). Interactions, transformations, and bioavailability of nano-copper exposed to root exudates. *Environmental science & technology*, 51(17), 9774-9783.

Kah, M., Kookana, R. S., Gogos, A., & Bucheli, T. D. (2018). A critical evaluation of nanopesticides and nanofertilizers against their conventional analogues. Nature nanotechnology, 13(8), 677-684.

Ritchie, H., & Roser, M. (2018). Plastic pollution. *Our World in Data*.

Vranova, V., Rejsek, K., Skene, K. R., Janous, D., & Formanek, P. (2013). Methods of collection of plant root exudates in relation to plant metabolism and purpose: a review. *Journal of Plant Nutrition and Soil Science*, 176(2), 175-199.