



Environment and Natural Resources Trust Fund

M.L. 2023 Approved Work Plan

General Information

ID Number: 2023-107

Staff Lead: Mike Campana

Date this document submitted to LCCMR: May 24, 2023

Project Title: Ecotoxicological Impacts of Quinone Outside Inhibitor (QoI) Fungicides

Project Budget: \$279,000

Project Manager Information

Name: Kristine Wammer

Organization: University of St. Thomas

Office Telephone: (651) 962-6012

Email: khwammer@stthomas.edu

Web Address: <https://www.stthomas.edu/>

Project Reporting

Date Work Plan Approved by LCCMR: June 22, 2023

Reporting Schedule: April 1 / October 1 of each year.

Project Completion: June 30, 2025

Final Report Due Date: August 14, 2025

Legal Information

Legal Citation: M.L. 2023, Chp. 60, Art. 2, Sec. 2, Subd. 04f

Appropriation Language: \$279,000 the first year is from the trust fund to the commissioner of natural resources for an agreement with the University of St. Thomas to assess the ecological hazards associated with QoI fungicides and their major environmental transformation products.

Appropriation End Date: June 30, 2026

Narrative

Project Summary: This work will provide a more comprehensive assessment of the ecological hazards associated with quinone outside inhibitor (QoI) fungicides and their major environmental transformation products

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

Quinone outside inhibitors (QoIs) are widely used fungicides representing 15% of the fungicide market share. Due to their efficacy, QoIs are used extensively throughout the USA, particularly in the agricultural Midwest. With increasing concerns over antifungal resistance, fungicide use has rapidly increased in recent years; worldwide, QoI sales increased from \$620 million (1999) to \$1.636 billion (2007). In 2017, the most widely used fungicide in the world, azoxystrobin, was applied up to 16,000 kilograms per county in the USA.

Because QoIs are applied as seed treatments and/or aerially to crops as many as 10 times throughout the growing season, QoI-containing runoff and contamination of water resources is almost certain. Azoxystrobin was detected in 45 out of 103 water samples taken from 29 streams draining agriculture areas in the USA. QoI occurrence in water combined with the findings that azoxystrobin causes mortality and developmental malformations in fish has heightened concerns over ecological impacts. Recent reports indicating QoI exposure in pollinators and humans (70% of the children, 100% of the pregnant women studied) combined with findings that QoIs affect pollinator survival and increase markers associated with neurodegenerative diseases (i.e., Alzheimer's disease) bring further urgency to this issue.

What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.

Because of their widespread occurrence and growing awareness of previously overlooked potential health impacts, additional investigation of QoIs is necessary. Moreover, recent research by our team has found that many QoIs degrade readily in the environment through reactions common in natural (e.g., surface water) and engineered (e.g., water and wastewater treatment) aquatic systems. These reactions with sunlight (i.e., photochemical processes) and chemicals used in water and wastewater treatment (i.e., disinfection with free chlorine) often produce new chemical species, or QoI transformation products. Because these transformation products retain structural similarity to their parent QoI compounds, we hypothesize that these QoI transformation products retain biological activity that pose new risks to ecosystem and human health and must also be investigated.

To address existing knowledge gaps over the safety of their widespread use, we propose to investigate adverse effects associated with common QoI fungicides and their major environmental transformation products. This work capitalizes on the unique capabilities of the research team, who collectively have previously identified common transformation products of QoI photochemical and chlorination reactions and have extensive expertise in the use of bioassays, for a variety of species and toxicological endpoints, to assess hazards of emerging pollutant classes.

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

This work will provide a more comprehensive assessment of the ecological hazards associated with QoI fungicides and their major environmental transformation products. We will produce new knowledge of the adverse effects of this fungicide class used widely across Minnesota, including the first hazard assessment of their major transformation products. This should enable improved regulatory oversight of QoI use, as well as the disposal of fungicide-treated seeds, to better protect and enhance Minnesota's natural resources and by extension human health.

Project Location

What is the best scale for describing where your work will take place?

Statewide

What is the best scale to describe the area impacted by your work?

Statewide

When will the work impact occur?

During the Project and In the Future

Activities and Milestones

Activity 1: Evaluation of Qol environmental fate with identification of major transformation products

Activity Budget: \$183,000

Activity Description:

Working with the Qols most predominantly used in Minnesota (e.g., fenamidone, azoxystrobin and pyraclostrobin, among others), we will evaluate two processes we have identified as critical determinants to their persistence and fate in aquatic environments. We have found that Qols degrade in sunlight, both by direct and indirect reaction pathways, yielding as yet unidentified transformation products. This process occurs readily enough it should be anticipated in sunlit Minnesota surface waters and on surfaces including soils and seeds treated with Qols. Moreover, we know Qols are reactive toward chemical disinfectants like free chlorine, yielding products that are structurally similar to parent Qol species. These may be present in wastewater effluents discharged into Minnesota surface waters. Here, we will conduct experiments that will allow us to quantify the timescales over which these processes occur and develop process descriptors (like rate constants) that can be used to better model and predict Qol behavior. We will also use advanced chemical identification methods to structurally identify the remaining transformation products not yet identified through our preliminary work. We will then conduct experiments at sufficient scale such that we can isolate these products, thereby allowing us to test their ecotoxicological impacts in Activity 2.

Activity Milestones:

Description	Approximate Completion Date
Measure rates of Qol chlorination during simulated water and wastewater treatment	July 31, 2024
Measure photodegradation rates of Qols in water, bound to soils, and coated on seeds	December 31, 2024
Identify, scale up, and isolate photodegradation and chlorination transformation products for testing in Activity 2	March 31, 2025
Submit publication for peer review	June 30, 2025

Activity 2: Evaluation of toxicity of Qols and their major transformation products

Activity Budget: \$96,000

Activity Description:

First, the effects of Qols and their major transformation products on 70 molecular targets indicative of different toxicity types (including carcinogenesis, DNA damage, endocrine disruption, neurotoxicity) will be evaluated using cutting-edge, rapid, and cost-effective techniques where living cells are exposed to chemicals of interest and screened for changes in biological activity. Second, the effects on mitochondria (cell “power plants” that generate energy essential for survival) will be measured because chemical properties of Qols make them very likely to exert toxicity by affecting mitochondrial energy generation processes. Third, Qols and their major transformation products that initiate molecular responses and/or mitochondrial effects will be also evaluated for the effects on physiological and behavioral responses that are important for growth and survival of fish.

Activity Milestones:

Description	Approximate Completion Date
Evaluate effects of Qols and their transformation products on 70 molecular targets indicative of toxicity	March 31, 2025
Evaluate effects of Qols and their transformation products on the fish mitochondrial function	March 31, 2025
Evaluate effects of Qols and their transformation products on the physiology and behavior of fish	June 30, 2025
Submit publication for peer review	June 30, 2025
Production of fact sheet(s) through Center for Health Effects of Environmental Contamination (CHEEC)	June 30, 2025

Project Partners and Collaborators

Name	Organization	Role	Receiving Funds
Dalma Martinovic-Weigelt	University of St. Thomas	Co-Project Manager	Yes
David Cwiertny	University of Iowa	Co-Project Manager	Yes

Dissemination

Describe your plans for dissemination, presentation, documentation, or sharing of data, results, samples, physical collections, and other products and how they will follow ENRTF Acknowledgement Requirements and Guidelines.

Findings will be disseminated and archived via reports to LCCMR, peer-reviewed publications, and presentations at conferences, including by undergraduate and graduate student contributors to the project. Acknowledgment of funding from the Environment and Natural Resources Trust Fund will be included on all presentations and all published manuscripts.

Dissemination efforts will also be led by the Center for Health Effects of Environmental Contamination (CHEEC), directed by Prof. Cwiertny at the University of Iowa. While funded by the state of Iowa, CHEEC is well known across the Midwest region for its work related to the links between environmental pollutants and public health effects. CHEEC frequently produces fact sheets and infographics for their research, and such documents will be developed and posted on the CHEEC website based upon findings from the proposed work. Project outcomes will also be shared via the CHEEC social media accounts, and through presentations given across Iowa and in neighboring states by CHEEC personnel. CHEEC will also be made aware of the responsibility to follow ENRTF Acknowledgement Guidelines.

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?

We anticipate significant interest of the public and managers in this work. Baseline data regarding occurrence/ hazards will aid with determining whether and which QoIs and transformation products need to be added to the monitoring list of Minnesota Pollution Control Agency and/or become a candidate for Minnesota Department of Health screenings of toxicity and exposure potential as a part of the Protecting Minnesota's Water Resources Initiative. Such review may result in the development of Health Based Values and aquatic life screening values that are important for human and ecosystem health. Raised awareness of the hazards should reduce non-essential uses.

Other ENRTF Appropriations Awarded in the Last Six Years

Name	Appropriation	Amount Awarded
Assessing Techniques for Eliminating Contaminants to Protect Native Fish and Mussels	M.L. 2016, Chp. 186, Sec. 2, Subd. 04d	\$287,000
Reassessing Toxicity of Petroleum Spills on Groundwater and Surface Water	M.L. 2017, Chp. 96, Sec. 2, Subd. 04e	\$300,000
Mapping Antibiotic Resistance in Minnesota to Help Protect Environmental, Animal, and Human Health	M.L. 2018, Chp. 214, Art. 4, Sec. 2, Subd. 04h	\$750,000
Microgeographic Impact of Antibiotics Released from Identified Hotspots	M.L. 2021, First Special Session, Chp. 6, Art. 6, Sec. 2, Subd. 04d	\$508,000

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified Staff?	\$ Amount
Personnel								
Dalma Martinovic-Weigelt		Co-Project Manager			7%	0.16		\$23,970
Undergraduate research assistants (academic year)		Conduct lab experiments, analyze data			0%	1		\$34,680
Undergraduate research assistants (summer)		Conduct lab and field experiments, analyze data			7%	1.4		\$52,877
							Sub Total	\$111,527
Contracts and Services								
University of Iowa	Sub award	Personnel (\$81,324, salary + fringe. 0.11 month effort for year for Dr. Cwiertny, 12 mo effort per year for PhD student.) Materials/supplies (\$5,000). Tuition/Fees for Ph.D. student (\$18,325) Perform reactions with free chlorine, identify and scale up transformation products.		X		2.02		\$104,649
							Sub Total	\$104,649
Equipment, Tools, and Supplies								
	Tools and Supplies	High throughput assay supplies. Attagene assay runs and assay setup. \$3.64 per sample per endpoint.	To conduct comprehensive molecular toxicity evaluation					\$27,540
	Tools and Supplies	Miscellaneous disposable biological analyses lab supplies – cells, cell media and FBS, larvae, reagents, filters, buffers, sample processing supplies, animal microcosm setups, and molecular biology supplies.	Used to set up transformation experiments, to conduct extractions and fractionations and to conduct traditional toxicity analyses					\$15,304

	Tools and Supplies	Miscellaneous disposable chemical analyses lab supplies - reagents, filters, buffers, sample processing supplies (disposable sampling containers, pipette tips, chemicals, extraction columns) and instrument time	Used to conduct photolysis experiments and generation of transformation products in Activity 1					\$19,980
							Sub Total	\$62,824
Capital Expenditures								
							Sub Total	-
Acquisitions and Stewardship								
							Sub Total	-
Travel In Minnesota								
							Sub Total	-
Travel Outside Minnesota								
							Sub Total	-
Printing and Publication								
							Sub Total	-
Other Expenses								
							Sub Total	-
							Grand Total	\$279,000

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
Contracts and Services - University of Iowa	Sub award	Personnel (\$81,324, salary + fringe. 0.11 month effort for year for Dr. Cwiertny, 12 mo effort per year for PhD student.) Materials/supplies (\$5,000). Tuition/Fees for Ph.D. student (\$18,325) Perform reactions with free chlorine, identify and scale up transformation products.	<p>At the University of Iowa, Cwiertny and his research group have already conducted preliminary work to identify and isolate the transformation products generated from the reaction of quinone outside inhibitor (Qoi) fungicides with free chlorine during simulated water/wastewater treatment. To the best of our knowledge, they are the only group to date to have developed methods to isolate sufficient quantities of these transformation products for use in ecotoxicity testing that we have proposed. Partnering with this group and leveraging their already established methodologies enables the research team to achieve all of the stated research goals within the 2-year project period and at the funding level requested. Developing these capabilities without the participation of the University of Iowa collaborators would add more time and require more financial support to complete the work as proposed.</p> <p>The work conducted at the University of Iowa will still directly benefit the state of Minnesota, as chemicals generated and isolated in the Cwiertny laboratory will be used in ecotoxicity testing at the University of St. Thomas. Moreover, data derived from these studies will be valuable to environmental fate and risk assessment associated with the use of Qoi fungicides in Minnesota, where these chemicals are widely used and have been detected in Minnesota water resources.</p>

Non ENRTF Funds

Category	Specific Source	Use	Status	\$ Amount
State				
			State Sub Total	-
Non-State				
			Non State Sub Total	-
			Funds Total	-

Attachments

Required Attachments

Visual Component

File: [bf9a4d95-9d4.pdf](#)

Alternate Text for Visual Component

The figure depicts estimated use of a commonly applied QoI fungicide, a picture of seeds treated with QoIs, and a schematic overview of the proposed chemistry and toxicology experimental approaches....

Financial Capacity

File: [b3193e12-e72.pdf](#)

Optional Attachments

Support Letter, Photos, Media, Other

Title	File
Background check certification form	a7618245-d6d.pdf
Wammer 2023-107 research addendum	ca533211-7d3.pdf

Difference between Proposal and Work Plan

Describe changes from Proposal to Work Plan Stage

No significant changes; small budget changes were made to meet new budget target (\$3,000 reduction)

Additional Acknowledgements and Conditions:

The following are acknowledgements and conditions beyond those already included in the above workplan:

Do you understand and acknowledge the ENRTF repayment requirements if the use of capital equipment changes?

N/A

Do you agree travel expenses must follow the "Commissioner's Plan" promulgated by the Commissioner of Management of Budget or, for University of Minnesota projects, the University of Minnesota plan?

N/A

Does your project have potential for royalties, copyrights, patents, or sale of products and assets?

No

Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10?

N/A

Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF?

N/A

Does your project include original, hypothesis-driven research?

Yes

Does the organization have a fiscal agent for this project?

No