Presidential Faculty/Student Collaboration and Publication Grant
Deadline Monday, February 20, 2017

Please use this checklist and budget. Include with your completed application. For more information about Presidential Faculty/Student Collaboration and Publication grants, please see https://gustavus.edu/kendallcenter/grant-opportunities/presidential-grant.php.

FACULTY INFORMATION

Name: Amanda M. Nienow Email: anienow@gustavus.edu

Department: ACS Chemistry Rank: Associate Professor

STUDENT INFORMATION

Name: Brittany Courteau Email: bcourtea@gustavus.edu

Major(s): Chemistry Graduation Year: 2018

CHECKLIST

Project Details

- ☒ Brief description of the proposed project including its collaborative nature
- ☒ Clear statement of anticipated outcomes
- ☒ Likely placement for publication or performances
- ☒ Anticipated research completion date

Participant Details

- ☒ Names and brief biographies of all participants
- ☒ Explanation of how this project fits into the career of the faculty member
  Note: Applications from faculty at all career stages are encouraged
- ☒ Explanation of how this project fits into the educational trajectory of the student
  Note: Statement should be written by the student; include year of graduation; student eligibility is limited to full-time returning students

- ☒ **Presidential Budget Proposal Form**

- ☒ If successful, my proposal can be used as an example to assist future applications. Check to give permission. This decision will not influence the application evaluation.

Submit electronically as a PDF to cblaukat@gustavus.edu at the John S. Kendall Center for Engaged Learning.

Presidential Faculty/Student Collaboration Grant

Budget Information

Faculty Stipend ($300 per week, up to $3,000 for a maximum of 10 weeks)
Student Summer Stipend ($400 per week, up to $4,000 for a maximum of 10 weeks)
Student Summer Campus Housing ($60 per week, for a maximum of 10 weeks)
Budget Maximum ($8,100 for all categories)

Item		**Amount**
Equipment (e.g., transcription machine, camera, cassette recorder – but not to include computer hardware)		**$**
1:	Cost:	
2:	Cost:	
3:	Cost:	
Materials (e.g., books, printing, software, lab supplies)		**$** 750
1: Lab Supplies	Cost: $250	$250
2: HPLC Column	Cost: $500	$500
3:	Cost:	
Travel Costs (cannot include conference travel, see http://gustavus.edu/finance/travel.php for allowable travel expenses)		**$**
Airfare:		
Mileage: Number of miles____ @ $0.53.5/mile		
Lodging:		
Meals:		
Stipends & Housing		**$** 7000
Faculty Stipend	$300 per week, up to $3,000 for a maximum of 10 weeks	$2400
Student Summer Stipend	$400 per week, up to $4,000 for a maximum of 10 weeks	$4000
Student Summer Campus Housing	$60 per week, up to 10 weeks	$600
Total Expenses		**$** 750
Amount Requested (Total Expenses + Requested Stipends + Housing)		**$** 7750

Have you applied for, or received funding from, another source to help support this project? (If no, skip a, b, and c below.)

☒ Yes ☐ No

a. Funding Source: National Science Foundation
b. Amount: $196639
c. Please explain how the Presidential grant will be used in addition to the other funding, and (if relevant), how the Presidential grant project would be impacted if external funding is not approved**.**

If this grant were to be funded in full prior to summer 2017 (although unlikely due to timing for NSF proposal reviews), some of the Presidental grant funds would be returned to the College. Specifically, the faculty stipend and lab costs would be returned, but I would likely keep the student portion of these funds. If external funding is not approved, the project is viable as presented here and the project will be even more crucial to the larger scope of Dr. Nienow's work as a way to obtain data ahead of a grant resbumission to the NSF.

Determination of the Kinetic Expression and Mechanism of the Photochemical Degradation of the Herbicide Dicamba in Aqueous Solution

Project Description

Background

Agrochemicals are widely used around the world. In 2007, the last year the U.S. EPA publicly provides usage amounts, 1,133 million pounds of pesticides were used in agriculture, 531 million pounds of that amount was herbicides dedicated to the eradication of weeds.[1] For over 50 years, dicamba, 3,6-Dichloro-2-methoxybenzoic acid, has been one of the agrochemicals used in the United States, historically mostly on corn or grain crops. Although use of dicamba decreased upon the rise of glyphosate (Round-Up) in the early 2000s, the recent development of glyphosate resistant weeds means dicamba use is increasing again. In 2016, Monsanto announced Roundup Ready 2 soybeans, genetically modified soybeans branded under the name Xtend, that can tolerate both dicamba and glyphosate.[2] In April 2016, the EPA proposed to allow the use of dicamba in sprays for these soybeans for five years; a decision on this proposal was expected in fall 2016 but is yet to be announced.[3] In July 2016, the Xtend soybeans gained EU import approval.[4] In the meantime, the USDA has declared Xtend soybeans unlikely to pose risks to other plants.[3] With the use of dicamba on soybeans, a crop it hasn't been applied to in the past, it is likely the usage of dicamba will increase dramatically in the next few years.

Dicmaba is a post-emergent herbicide, applied to crops in the early growth stages. Dicamba is moderately toxic to humans and can cause muscle cramps, nausea, vomiting, skin rashes, loss of voice, or swelling of cervical glands.[5] In addition, it can have adverse effects on non-target organisms in the environment. Biodegradation and photodegradation are the two main pathways for the elimination of pollutants from the environment. The biodegradation of dicamba has been examined in many publications,[6–9] but the photochemistry has not been examined in detail. This project will investigate the fundamental photochemical kinetics (i.e., how fast does it react) and mechanism (i.e,. how does it react) of dicamba photodegradation in aqueous solutions as a function of pH, natural organic matter (added to the solution to mimic river or lake water), and deoxygenated solutions. This is a first step in a larger project to examine the photochemistry on more relevant environmental surfaces such as corn and soybean leaves and to examine the photochemistry of dicamba when in commercial herbicide formulations.

Proposed Work

Under this Presidential Faculty-Student Collaboration grant, Dr. Nienow and Brittany Courteau will examine the photolysis reactions of dicamba in aqueous solutions of different water quality. This will involve changing the pH of the solution, varying the amount of dissolved solids, adding or removing oxygen from solution, examining the rates of reaction, and determining the products formed. Specifically this Presidential Faculty-Student Collaboration grant has four goals: to test the effects of pH, natural organic matter (NOM), and oxygen on the photochemical mechanism, and to determine the photoproducts of reaction.

1. **Effect of pH**

Since dicamba is a weak acid (see Figure 1),[10] the compound can exist in different forms depending on the pH, and therefore the pH of solution will impact the photochemistry.

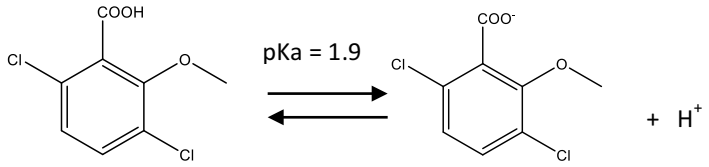

Figure 1: Dicamba speciation as a function of pH

The neutral form of dicamba (left side of Figure 1) will be present at pH values below 1.9 and is known to absorb light at wavelengths below 325 nm.[10] At environmentally relevant pH values (i.e., near neutral), the anionic form (right side of Figure 1) will be dominant. The absorption spectrum of the anionic species shows an increase in absorption relative to the neutral species.[10] To test the impact of pH on the kinetics of photodegradation of dicamba, phosophate buffers will be used to adjust pH to a unit above and a unit below the pKa (a pH range of about 1-4). UV-Vis absorption spectroscopy, a way to monitor how the molecule absorbs light, will be used to collect spectra for both the neutral and anionic dicamba species. The solutions will be irradiated in a Q-Sun solar simulator, purchased by Dr. Nienow in 2012 with NSF funds as a way to have a light source similar to the sun even in the winter or on a rainy day. Experiments in the Q-sun will allow measurement of how fast the reaction occurs as a function of wavelength and light intensity. Chromatography analysis will be used to determine the concentration of any remaining dicamba upon irradiation. These initial tests will show whether the species impacts the non-linear kinetics found in earlier experiments. The results will be used to develop a kinetic model.

2. Effect of Natural Organic Matter (NOM)

A series of experiments will be conducted with added NOM to model surface waters such as rivers and lakes. Suwanee River NOM will be added in amounts between 1-10 mg/L (typical NOM concentrations in the environment) into solutions of buffered dicamba. The differences in reaction rates will be used to determine if light screening (causing a slowing of the photochemical reaction), photosensitization (causing an increase of the photochemical reaction), or other mechanism will have an impact on dicamba photodegradation in the environment. The developed kinetic model will be edited to incorporate the role of NOM.

3. **Effect of Oxygen**

In all water samples, there is a small amount of dissolved oxygen so that all of the reactions discussed above (pH and NOM experiments) are done in the presence of oxygen. This oxygen can be removed by bubbling an inert gas (such as nitrogen) into the solutions prior to shining light on them. Understanding the role of oxygen will aid in the further development of the kinetic model, and will help in formulating an understanding of the fate of dicamba in the environment.

4. Development of Photoproducts

In addition to measuring the kinetic rate constants of the different reactions above, the photoproducts will be analyzed using both GC-MS and LC-MS. (GC-MS analysis will be completed at MSU-Mankato). A careful analysis of photoproduct formation and degradation as a function of irradiation time will be conducted to deduce the photochemical mechanism. The kinetic and mechanistic information gathered will be used to develop a kinetic model.

Brittany and Amanda will work closely together on all aspects of this project. Amanda will train Brittany to do the laboratory work, so that by the end of the summer she will be proficient in a suite of techniques. Amanda will do the experimental design for most of the plan described above while working with Brittany to put the designs into practice throughout the summer. They will work together to prepare presentations of the data and to edit a National Science Foundation grant resubmission, if warranted.

Anticipated Outcomes

Brittany will work full-time (10 weeks) during the summer of 2017, and will continue through the 2017-2018 academic year if possible. This Presidential grant will only fund the project during the summer, but there will likely be a few loose ends to complete during the school year, including the preparation of presentation and publication materials.

1. *Understanding of dicamba photochemistry in water:* The series of experiments described above will provide a fundamental understanding of the reactivity of dicamba in different model environments. Dr. Nienow and Brittany will obtain rate constants (a measure of how fast the reaction happens) and possible mechanisms (the pathways in which the molecule is changed during reaction) that can be used to develop a predictive model to understand the photoreactivity of the molecule in the environment. These experiments will also serve as a basis for future, more complex experiments involving dicamba. For example, commercial formulations of dicamba used in the field include other compounds (called adjuvants) that help the spray spread over the field and to remain stable. Once it is clear how the active ingredient (dicamba) reacts, the impact of the adjuvants can be investigated. The experiments described above will be complete by August, 2017 but will influence future work done by Dr. Nienow and research students in her lab.

2. *A competitive proposal for external funding:* Dr. Nienow submitted a National Science Foundation grant proposal related to this project in the fall of 2016. The major budget pieces of the NSF grant proposal were two summer student stipends per year, a faculty stipend each summer, lab supplies, and funds for new equipment (the latter in the range of $55,000). Given the NSF review timing process (sometimes nearly a year in length), the rate of grant success (about 15-20%), and the current governmental climate, Dr. Nienow sees two probable outcomes for the NSF proposal: a) the grant is funded but notification happens after summer 2017 (which is what happened with Dr. Nienow's previous NSF grant in 2012), b) the grant isn't funded. In the latter case, a resubmission of the grant will be completed in fall 2017. Under case (a), the Presidential Faculty-Student collaboration grant will allow Dr. Nienow to continue work in her lab, to start this project, and to better leverage the NSF funds. It is even more important to start this project in summer 2017 if the NSF grant isn't funded. This project will provide additional data, strengthening the NSF grant proposal upon resubmission. [Note: If the NSF grant were to be funded prior to summer 2017 (unlikely but best case scenario), Dr. Nienow would not use the faculty stipend or the lab supply funds from the Presidential Faculty-Student collaboration grant, but would maintain the student stipend. In this case, Brittany would serve as a mentor to other students who would be paid under the NSF grant.]

3. *Scholarly presentations:* The results of the experiments described above will be presented in several venues. Brittany will present the project at the Gustavus summer research student weekly symposia, at the Midstates Consortium for Math and Sciences Undergraduate Research Symposia in fall of 2017, and at the Celebration of Creative Inquiry. Dr. Nienow will try to get on the schedule for Teacher's Talking in 2017-2018 (or later if necessary) to present the work to the faculty. In addition, if there is a complete narrative of the photochemistry of dicamba in the summer of 2017 (or maybe J-term 2018), the work would be written up in a collaborative writing process between

Brittany and Dr. Nienow, resulting in a manuscript to be sent through peer-review. A manuscript would most likely be submitted to the *Journal of Agricultural and Food Chemistry* or *Environmental Science: Processes and Impacts*.

4. *Applied research experience for Brittany Courteau:* Brittany is thrilled about the possibility of collaborating with Dr. Nienow for summer research. She will broaden her knowledge of instrumental and chemistry techniques, improve her ability to plan, analyze, synthesize, and communicate scientific results to the PI, to other Gustavus students, and to the larger scientific community. This kind of exposure to research experience is essential for admittance into graduate school programs and a career in the field of chemistry.

Participant Information

Amanda Nienow is an associate professor of Chemistry and has been teaching and conducting research at Gustavus since 2007. For the past four years, Amanda has been working with Gustavus students examining the photochemistry of imidazolinone herbicides in water and on plants. She earned her Ph.D. at the University of Minnesota in physical chemistry, working on a project related to the oxidation of soot nanoparticles and completed a postdoctoral fellowship at Purdue University examining the photochemistry of pesticides using advanced oxidation processes.

Brittany Courteau (2018) is currently a junior studying chemistry and statistics at Gustavus Adolphus College. She plans to graduate with a degree in ACS Chemistry and a minor in Statistics. Brittany plans to continue her education by going to graduate school. She is interested in physical chemistry, and the impact it has on the world. While at Gustavus, Brittany has been enthusiastic about chemistry and pursued it through her work in the Chemistry Department and Chemistry Club. She was a part of the outreach program, Science on Saturdays' for children. Through these experiences she strengthened her skills in organization, attention to detail and problem solving. Brittany also showed her ability to communicate with others. She is comfortable being part of a team or working independently, and is excited to do research.

Career and Education Trajectories

Amanda Nienow

The examination of the photochemistry of dicamba is a new direction in the Nienow research group, but builds off of previous work looking at the photochemistry of imidazolinone herbicides. The imidazolinone project began with a Presidential Faculty-Student Collaboration grant (2012) which provided sufficient preliminary data used to prepare a successful National Science Foundation grant. During the duration of the NSF grant, Amanda trained five full-time summer research students and seven part-time students during the school year (a total of 12 students). The previous NSF supported work was done mostly at Gustavus but a portion was done with a collaborator at the University of Blaise Pascal in Clermont-Ferrand, France (two Gustavus students worked with Dr. Nienow at the UBP labs for a week) and with collaborators at the University of Minnesota and MSU – Mankato. The work has led to two peer-reviewed journal articles with another partially completed (planned submission May 2017). Amanda is at a

critical junction in her research projects and the current Presidential Faculty-Student Collaboration proposal will provide her data for use in future external grant proposals.

The dicamba project described in this proposal began as a student driven project in Dr. Nienow's lab. After visiting a family farm, the student returned with a jar of commercially formulated dicamba, eager to subject the solution to the tests being developed for the imidazolinone herbicides. It was quickly determined that dicamba, as a molecule containing chlorine, was reacting with more complex mechanisms than the previous work. Although a lot of Dr. Nienow's research has applicability to environmental and herbicide chemistry, she remains interested in fundamentally understanding the photochemical reactions. Dicamba presents a unique challenge in this regard. In addition, with the commercial formulation in hand, the research can be expanded to examine the roles of adjuvants (the additional compounds in the commercial formulations). This is an exciting addition to the repertoire of work completed to date. Dr. Nienow's long-term goals for her research project is to examine the chemistry of pesticides in the most environmentally relevant systems. Since the environment is complex, it is important to build projects from fundamental understanding through the more complex systems. This Presidential Faculty-Student Collaboration grant will allow the group to keep building toward the complex systems.

This is Dr. Nienow's tenth year at Gustavus, and every summer (including a summer in which she was on maternity leave), she has supervised student researchers. She has built a research program that is accessible to Gustavus students, and given St. Peter's location in agricultural Minnesota, of immediate interest to students. The research provides students the opportunity to learn wet chemistry techniques, oral and written communication skills, and understand a bit of the environment around them. During her time at Gustavus, Dr. Nienow has supervised 14 full-time summer research students; three of these students worked in her lab for multiple summers. Five of these students were funded from external grants and three of the students were funded by the Howard Hughes Medical Institute Grant obtained by a team at Gustavus in 2008. The remainder of the students were supported by internal funds: one student was funded by the First Year Research Experience (FYRE) program; one was funded by a Presidential Faculty-Student Collaboration grant (2011); and four were funded by Chemistry Department funds, all in the first four years of her time at Gustavus. Dr. Nienow has mentored an additional 14 students during the academic year (for credit or as volunteers in the lab), many who have gone on to graduate school, medical school, and dental school. Dr. Nienow has a good track record of obtaining external funds, and believes that if she was awarded a Presidential grant it will help her obtain additional external funding for upcoming years, as well as helping to train new scientists.

Brittany Courteau (2018)
I am excited about collaborating with Dr. Nienow on this project. I look forward to learning from her and acquiring new skills while working on the project. This research experience would not only be a great way to learn from Dr. Nienow, but is also important for my future in chemistry. I am an aspiring chemist and I plan on attending graduate school. This opportunity would be a great start for graduate school and my career as a researcher. If selected, I would use this project to gain new skills from Dr. Nienow and strengthen skills I have learned in the classroom, the laboratory and the Chemistry Department in a practical way. I would be grateful for this opportunity to work on the project with Dr. Nienow.

(1) Grube, Arthur; Donaldson, David; Kiely, Timothy; Wu, La. *Pesticides Industry Sales and Usage: 2006 and 2007 Market Estimates*; U.S. Environmental Protection Agency, 2011.
(2) *Roundup Ready 2 Xtend Soybeans: Currently in Phase IV of Monsanto's R&D Pipeline*; Monsanto.
(3) Erickson, Britt E. Illegal dicamba use damaging soybeans in U.S. *Chemical and Engineering News*. August 8, 2016, p 15.
(4) *Roundup Ready 2 Xtend Soybeans Gain EU Import Approval*; Monsanto: St. Louis, MO, 2016.
(5) Rahman, M. A.; Muneer, M. Heterogeneous Photocatalytic Degradation of Picloram, Dicamba, and Floumeturon in Aqueous Suspensions of Titanium Dioxide. *J. Environ. Sci. Health Part B* **2005**, *40* (2), 247–267.
(6) Fogarty, A. M.; Tuovinen, O. H. Microbiological degradation of the herbicide dicamba. *J. Ind. Microbiol.* **1995**, *14* (5), 365–370.
(7) Krueger, J. P.; Butz, R. G.; Cork, D. J. Aerobic and anaerobic soil metabolism of dicamba. *J. Agric. Food Chem.* **1991**, *39* (5), 995–999.
(8) Pavel, E. W.; Lopez, A. R.; Berry, D. F.; Smith, E. P.; Reneau, R. B.; Mostaghimi, S. Anaerobic degradation of dicamba and metribuzin in riparian wetland soils. *Water Res.* **1999**, *33* (1), 87–94.
(9) Milligan, P. W.; Häggblom, M. M. Biodegradation and Biotransformation of Dicamba under Different Reducing Conditions. *Environ. Sci. Technol.* **1999**, *33* (8), 1224–1229.
(10) Aguer, J.-P.; Blachère, F.; Boule, P.; Garaudee, S.; Guillard, C. Photolysis of dicamba (3,6-dichloro-2-methoxybenzoic acid) in aqueous solution and dispersed on solid supports. *Int. J. Photoenergy* **2000**, *2* (2), 81–86.