



PROJECT TITLE: Quantifying Acrylamide Detoxification in Frac Sand Washwater

I. PROJECT STATEMENT

Frac sand processing facilities have the potential to release toxic organic chemicals into ground and surface waters. Virtually all facilities use polymeric organic chemicals called flocculants to improve the removal of fines (clays, silts, and undersized sands) from the sand washwater. Flocculants allow for the reuse of washwater and reduce the consumption of freshwater. The commercial formulations of the commonly used flocculants contain residual concentrations of the small monomeric subunits used to produce the polymers. The formulations for polyacrylamide contain trace concentrations of the acrylamide monomer. The acrylamide monomer is a recognized neurotoxin and the U.S. Environmental Protection Agency has established a *de facto* drinking water limit of 0.5 parts per billion (ppb).

Naturally-occurring microorganisms are capable of detoxifying acrylamide. Detoxification occurs when the acrylamide monomer is enzymatically hydrolyzed to yield acrylic acid (2-propenoic acid) and ammonia. The literature suggests that the rates of microbial detoxification for trace concentrations of acrylamide are site specific and will depend on the organic compound composition (concentrations and presence of certain types of organic compounds) created by adding water treatment chemicals to the source water. Laboratory testing of the washwater is required to determine the site-specific rates of detoxification and the risk to public health.

The project has two goals. The first is to establish the reproducibility of a laboratory testing protocol to quantify the ability of frac sand washwater to support the microbial detoxification of acrylamide. The second goal is to demonstrate a correlation between the rate information obtained from the laboratory testing protocol and the observed acrylamide removals in a water-unsaturated sand column (a conservative surrogate of an environmental soil column). Having the ability to quantify the site specific rates of acrylamide detoxification would allow the proposers of frac sand facilities, regulators, and the public to define environmental health risk and to assess the need for additional safeguards.

The laboratory work will evaluate the site-specific rates of acrylamide detoxification for three frac sand washwaters. The detoxification rates for each washwater will be determined in five attached-growth bioreactors operated in parallel. The five replicate bioreactors allow the statistical reproducibility of the laboratory protocol to be evaluated. Initial tests will be performed at room temperature with subsequent tests performed in a cold room. The verification tests will consist of one water-unsaturated sand column for each of the three frac sand washwaters. The sand column tests will be conducted both at room temperature and within a cold room.

II. DESCRIPTION OF PROJECT ACTIVITIES

Activity 1: *Construct and Test Laboratory Bioreactors*

Budget: \$ 55,240

This activity will focus on the construction and testing of the five attached-growth bioreactors. Testing will confirm that materials used in the construction of the bioreactors have no impact on water-phase acrylamide concentrations. In addition, the hydraulic properties of the sand column reactors will be characterized.

Outcome	Completion Date
1. Construction of Attached-Growth Bioreactors	SEP 2014
2. Confirmation of Acrylamide-Inert Bioreactor Construction	SEP 2014
3. Construction and Characterization of Sand Column Bioreactors	OCT 2014



Environment and Natural Resources Trust Fund (ENRTF)

2014 Main Proposal

Project Title: *Quantifying Acrylamide Detoxification in Frac Sand Washwater*

Activity 2: *Determine Acrylamide Detoxification Rates in Laboratory*

Budget: \$ 80,800

The ability of naturally-occurring microorganisms that are grown on the organic compounds found in frac sand washwater to detoxify acrylamide will be determined in laboratory completely-mixed attached-growth bioreactors. Five replicate bioreactors will be operated for each tested frac sand washwater. Assessing the reproducibility of acrylamide detoxification rates among the five bioreactors is a focus of this activity. Reproducibility would support the use of the laboratory protocol in environmental review and in permitting.

Outcome	Completion Date
1. Acrylamide Detoxification Rates for Three Frac Sand Washwaters	JUN 2015

Activity 3: *Verify Applicability of Results in Laboratory Sand Columns*

Budget: \$ 38,520

The ability of the rate information obtained from Activity 2 to characterize environmental rates of acrylamide detoxification will be assessed in laboratory sand columns. The water-unsaturated sand columns will be operated in a once-through mode.

Outcome	Completion Date
1. Verification Sand Column Tests for Three Frac Sand Washwaters	AUG 2015

III. PROJECT STRATEGY

A. Project Team/Partners

Barr Engineering Company, located in Minneapolis, Minnesota, will construct and operate the laboratory bioreactors, interpret the results, and prepare the reports. Barr will subcontract with an outside laboratory to measure the trace concentrations of acrylamide found within the laboratory bioreactors and in the feed solutions. Barr will manage all Environment and Natural Resources Trust Fund monies awarded to the project. The total request is \$174,560.

Charles Gantzer (Ph.D., University of Illinois, 1986) of Barr Engineering will modify the experimental protocols used in characterizing the biodegradation of trace concentrations of taste and odor compounds to the biological detoxification of acrylamide. He will lead data interpretation and report preparation. Don Richard PE (Ph.D., University of Minnesota, 2004) of Barr Engineering will be responsible for overall project management.

B. Timeline Requirements

The estimated project duration is 15 months. A final report will be delivered by October 1, 2015. The primary driver is the time requirements for the growth and accumulation of microbial biomass under the anticipated low concentrations of biodegradable organic compounds found in frac sand washwater. Each set of bioreactor tests is anticipated to require 3 months. If only 2 months per bioreactor are required, then project duration would be shortened accordingly. No subsequent project phases are anticipated: this is a stand-alone project.

C. Long-Term Strategy and Future Funding Needs

Protection of Minnesota’s ground and surface waters requires knowing the site-specific rates at which naturally-occurring microorganisms can detoxify acrylamide. With the proposed demonstration of reproducibility and verification of suitability, the evaluated laboratory testing protocol will be recognized as an acceptable approach for obtaining the site-specific detoxification rates by the frac sand industry, the State’s regulatory agencies, and other interested parties. With an accepted laboratory protocol, proposers of frac sand facilities would determine the site-specific detoxification rates during the environmental review and permitting process.

2014 Detailed Project Budget

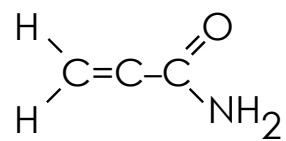
Project Title: *Quantifying Acrylamide Detoxification in Frac Sand Washwater*

IV. TOTAL ENRTF REQUEST BUDGET 1.25 years

<u>BUDGET ITEM</u>	<u>AMOUNT</u>
Personnel: Project Principal, Dr. Don Richard, 2.5% time to project, \$12,210 Project Manager, Dr. Charles Gantzer, 10.2% time to project, \$34,000 Laboratory, 3 engineers and scientists, total of 20.6% time to project, \$53,600 Administration, 1.9% time to project, \$3,750 Distribution of State Funds: 38.5% to salary, and 61.5% to benefits and other non-salary	\$ 103,560
Contracts:	\$ -
Equipment/Tools/Supplies: Bioreactors and sand columns, \$20,000 Laboratory supplies, \$5,500 Laboratory expendables and space rental, \$5,600	\$ 31,100
Acquisition (Fee Title or Permanent Easements):	\$ -
Travel:	\$ -
Additional Budget Items: Acrylamide analysis (trace concentrations) at outside laboratory, 114 samples at \$350/sample, \$39,900	\$ 39,900
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND \$ REQUEST =	\$ 174,560

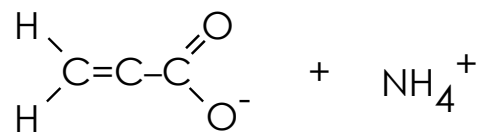
V. OTHER FUNDS

<u>SOURCE OF FUNDS</u>	<u>AMOUNT</u>	<u>Status</u>
Other Non-State \$ Being Applied to Project During Project Period: <i>Indicate any additional non-state cash dollars to be spent on the project during the funding period. For each individual sum, list out the source of the funds, the amount, and indicate whether the funds are secured or pending approval.</i>	\$ -	<i>Indicate: Secured or Pending</i>
Other State \$ Being Applied to Project During Project Period: <i>Indicate any additional state cash dollars (e.g. bonding, other grants) to be spent on the project during the funding period. For each individual sum, list out the source of the funds, the amount, and indicate whether the funds are secured or pending approval.</i>	\$ -	<i>Indicate: Secured or Pending</i>
In-kind Services During Project Period: <i>Indicate any in-kind services to be provided during the funding period. For each type of service, list type of service(s), estimated value, and indicate whether it is secured or pending. In-kind services listed must be specific to the project.</i>	\$ -	<i>Indicate: Secured or Pending</i>
Remaining \$ from Current ENRTF Appropriation (if applicable): <i>Specify dollar amount and year of appropriation from any current ENRTF appropriation for any directly related project of the project manager or organization that remains unspent or not yet legally obligated at the time of proposal submission. Be as specific as possible. Describe the status of funds in the right-most column.</i>	\$ -	<i>Indicate: Unspent? Not Legally Obligated? Other?</i>
Funding History: <i>Indicate funding secured prior to July 1, 2014, for activities directly relevant to this specific funding request, including past ENRTF funds. State specific source(s) of funds.</i>	\$ -	



Acrylamide

Enzymatic
Hydrolysis



Acrylate

Ammonium

Chemical Pathway for the Detoxification of Acrylamide



Environment and Natural Resources Trust Fund (ENRTF)
Proposing Organization and Project Manager Qualifications
Project Title: *Quantifying Acrylamide Detoxification in Frac Sand Washwater*

Proposing Organization: Barr Engineering Company

Barr Engineering provides engineering and environmental consulting services to clients across the Midwest, throughout the Americas, and around the world. We have been employee owned since 1966 and trace our origins to the early 1900s. Working together, our engineers, scientists, and technical specialists help clients develop, manage, and restore natural resources. Our corporate headquarters is located in Minneapolis, Minnesota.

Project Manager: Charles J. Gantzer, Ph.D.

Dr. Gantzer's work involves evaluating the technical feasibility of chemical and microbial processes in engineered and natural environments. His research interests include the determining the ability of microorganisms found in sediments and found in attached films (biofilms) to biodegrade trace concentrations of organic compounds. Dr. Gantzer has been involved with the commercialization of environmental technologies developed at the University of Minnesota and he has taught courses in environmental engineering and environmental microbiology in the Department of Civil Engineering.

Education: Ph.D., Environmental Science in Civil Engineering, University of Illinois, 1986.
M.S., Environmental Science in Civil Engineering, University of, 1981.
B.S., Ecology, Ethology, and Evolution, University of Illinois, 1978.

Selected Articles: Manous, J. D., Gantzer, C. J., and Stefan, H. G. 2007. Spatial variation of sediment sulfate reduction rates in a saline lake. *Journal of Environmental Engineering, ASCE* 113(12): 1106-1116.
Higashino, M., Gantzer, C. J., and Stefan, H. G. 2004. Unsteady diffusional mass transfer at the sediment/water interface: theory and significance for SOD measurement. *Water Research* 38(1): 1-12.
Gantzer, C. J. and H. G. Stefan. 2003. A model of microbial activity in lake sediments in response to periodic water-column mixing. *Water Research* 137(12): 2833-2846.
Higashino, M., Stefan, H. G., and Gantzer, C. J. 2003. Periodic diffusional mass transfer near sediment/water interface: theory. *Journal of Environmental Engineering, ASCE* 129(5): 447-455.
Gantzer, C. J. and Wackett, L. P. 1991. Reductive dechlorination catalyzed by bacterial transition-metal coenzymes. *Environmental Science and Technology* 25(4): 715-722.
Gantzer, C. J. 1989. Inhibitory substrate utilization by steady-state biofilms. *Journal of Environmental Engineering, ASCE* 115(2): 302-319.
Gantzer, C. J., Rittmann, B. E., and Herricks, E. E. 1988. Mass transport to streambed biofilms. *Water Research* 22(6): 709-722.
Gantzer, C. J., Kollig, H. P., Rittmann, B. E., and Lewis, D. L. 1988. Predicting the rate of trace-organic compound removal by natural biofilms. *Water Research* 22(2): 191-200.

Book Chapters: Rittmann, B. E., Gantzer, C. J., and Montiel, A. 1995. Biological treatment to control taste-and-odor compounds in drinking-water treatment. In: I. H. Suffet, J. Mallevalle, and E. Kawczynski (eds.), *Advances in Taste-and-Odor Treatment and Control*, American Water Works Association Research Foundation, Denver, CO, pp. 209-246.
Gantzer, C. J., *et al.* 1989. Exchange processes at the fluid-biofilm interface. In: W. Characklis and P. Wilderer (eds.), *Dahlem Workshop on the Structure and Function of Biofilms*, John Wiley & Sons, Chichester, pp. 73-89.