

**Nebraska Water Center
Annual Technical Report
FY 2017**

Introduction

Dr. Chittaranjan Ray, Ph.D., P.E., professor in the University of Nebraska-Lincoln's Department of Civil Engineering, became director of the Nebraska Water Center on August 1, 2013. Steve Ress and Tricia Liedle respectively serve as communications coordinator and program specialist. Ben Beckman worked jointly for NWC, Daugherty Water for Food Global Institute and Nebraska Extension as a full-time outreach and education coordinator until his resignation in January 2018. Ben moved on to serve as a County Extension Educator in Hartington, NE. Serving part-time as NWC staff are Rachael Herpel, as legislative liaison and outreach coordinator; and Craig Eiting, as web developer and desktop publisher. Efforts are on the way to recruit a new research and extension communications specialist, and NWC became part of the Daugherty Global Institute in 2012, when its name was changed from the previous University of Nebraska-Lincoln (or UNL) Water Center.

The Nebraska Water Center is currently offices within the Daugherty Water for Food Global Institute at the new Nebraska Innovation Campus, at 2021 Transformation Dr., Ste. 3220, Lincoln, NE 68588-6204 U.S.A.

The Nebraska Water Center was the lead organizer for several events in 2017: (1) in April 2017, water researchers from around the world gathered in Bangalore, India from several universities in USA along with researchers in India where they “addressed the Nexus of Food, Energy, and Water in the Context of Societal Challenges.” The workshop jointly funded by the Indo-US Science & Technology forum and the National Science Foundation. A proposal to edit a book from the India workshop has been submitted to Springer Publishers; (2) the 46th annual water and natural resources tour visited the Central Platte River basin for three days in June; (3) Water Quality conference in October at Nebraska Innovation Campus. The event was partially sponsored by the USGS Nebraska Water Science Center with nearly 150 participating in the conference; and (4) a series of seven free, public lectures from January-April 2018 under the theme of “Advances in Irrigation Management” constituted the annual spring semester water seminar series, which the Nebraska Water Center co-hosts with the University of Nebraska-Lincoln's School of Natural Resources. More than a dozen undergraduate students enrolled in the seminar for 1-hour of course credit in addition to public attendance at the lectures.

Research Program Introduction

For the 2017 fiscal year, three research seed grants received funding through the USGS 104(b) program. These were: (1) Evaluation of Changing Irrigation Management on Ground Water Recharge and Quality; and (2) Water Usage in the Food Industry; and (3) Economic, Environmental, and Crop Performance Assessment Under Center Pivot, Subsurface Drip, and Furrow Irrigation Systems in a Changing Climate in West Central Nebraska.

Seed grants chosen for the upcoming year 2017 are: (1) Pesticide Exposure in Recreational Lakes; and (2) The Chemistry and Ecotoxicology of Microplastics - Water Quality Research Experience in Nebraska Waterways; and (3) Microalgae Treatment of Meat Processing Wastewater for Nutrient Removal and Water Reconditioning.

The Nebraska Water Sciences Laboratory (WSL) is a core research facility that is part of the Nebraska Water Center. Established in 1990, the WSL is a state-of-the-art research and teaching laboratory designed to provide technical services and expertise in analytical and isotopic methods. The facility provides specialized instrumentation and methods for organic, emerging contaminants, heavy metals, and for stable isotope mass spectrometry. It's mission extends to serve as a methodology development and teaching facility for both faculty and students. Faculty, staff, and students have analyzed thousands of samples at the facility.

Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater

Basic Information

Title:	Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater
Project Number:	2014NE265G
USGS Grant Number:	
Start Date:	9/1/2014
End Date:	8/31/2018
Funding Source:	104G
Congressional District:	
Research Category:	Water Quality
Focus Categories:	Hydrogeochemistry, Nitrate Contamination, Radioactive Substances
Descriptors:	None
Principal Investigators:	Karrie Anne Weber, Daniel Davidson Snow

Publications

1. Nolan, Jason; Karrie A. Weber, 2015. Natural Uranium Contamination in Major U.S. Aquifers Linked to Nitrate. *Environmental Science & Technology Letters*, 2 (8), 215-220.
2. Weber, Karrie A.; Olivia Healy; Jason Nolan; Don Pan; Kate Campbell; Abbey Heithoff; Trisha Spanbauer; Daniel Snow, Nitrate stimulated uranium mobilization in groundwater. in preparation.
3. Nolan, Jason P.; Sharon Bone; Kate Campbell; Don Pan; Olivia Healy; Chris Elofson; Robert M. Joeckel; Marty Stange; Todd Wilson; Paul Hanson, John Bargar; Daniel Snow; Karrie A. Weber, Naturally Occurring Uranium in an Oxidic Alluvial Aquifer. in preparation.
4. Nolan, Jason P., Don Pan, Olivia Healy, Marty Stange, Karrie A. Weber. Geogenic Aqueous Uranium in an Alluvial Aquifer. *Goldschmidt*. August 16-21, 2015. Prague, Czech Republic. (poster presentation)
5. Nolan, Jason; Karrie A. Weber, 2015. Natural Uranium Contamination in Major U.S. Aquifers Linked to Nitrate. *Environmental Science & Technology Letters*, 2 (8), 215-220.
6. Weber, Karrie A.; Olivia Healy; Jason Nolan; Don Pan; Kate Campbell; Abbey Heithoff; Trisha Spanbauer; Daniel Snow, Nitrate stimulated uranium mobilization in groundwater. in preparation.
7. Nolan, Jason P.; Sharon Bone; Kate Campbell; Don Pan; Olivia Healy; Chris Elofson; Robert M. Joeckel; Marty Stange; Todd Wilson; Paul Hanson, John Bargar; Daniel Snow; Karrie A. Weber, Naturally Occurring Uranium in an Oxidic Alluvial Aquifer. in preparation.
8. Nolan, Jason P., Don Pan, Olivia Healy, Marty Stange, Karrie A. Weber. Geogenic Aqueous Uranium in an Alluvial Aquifer. *Goldschmidt*. August 16-21, 2015. Prague, Czech Republic. (poster presentation)
9. Nolan, Jason P. Mobilization of Naturally Occurring Uranium in Sediment Into Groundwater (Dissertation). University of Nebraska, Lincoln.
10. Weber, K.A. Uranium and Nitrate in Groundwater. Nebraska Natural Resource District Conference, Kearney, NE, March 1, 2016.
11. Weber, K. A. Keynote. Life Beneath Our Feet: Influence on Water Quality. Iowa State University. Environmental Science Graduate Research Symposium. April 1, 2016.
12. Weber, K.A. Nitrate and Uranium in Groundwater, NRD Annual Conference, Kearney, NE, March 1, 2016.

Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater

13. Westrop, J., Nolan, J.P. , Pan, D. , Healy, O. , Bone, S., Campbell-Hay, K., Bargar, J., D. Snow, K.A. Weber. Nitrate-Stimulated uranium mobilization in groundwater. Nebraska Water Center Symposium. October 20, 2016. Lincoln, NE. (poster presentation)
14. Weber, K.A. Nolan, J.P. , Pan, D. , Healy, O. , Bone, S., Campbell-Hay, K., Bargar, J., and D. Snow. Nitrate-Stimulated Mobilization of Naturally Occurring Uranium in Groundwater. Geological Society of America Annual Meeting. September 25-28, 2016. Denver, CO. (poster presentation)
15. Nolan, J. P., C. Elofson, S. Bone, K. Campbell, D. Snow, J. Bargar, and K. A. Weber. Surface Complexation of Uranium(VI) in Suboxic Aquifers in the Presence of Uranium(IV) minerals. Geological Society of America Annual Meeting. September 25-28, 2016. Denver, CO.
16. Weber, K.A. Nolan, J.P. , Pan, D. , Healy, O. , Bone, S., Campbell-Hay, K., Bargar, J., and D. Snow. Nitrate-Stimulated Mobilization of Naturally Occurring Uranium in Groundwater. International Society for Microbial Ecology. August 21-26, 2016. Montreal, CA. (poster presentation)
17. Nolan, J.P., Pan, D., Healy, O., Bone, S., Campbell-Hay, K., Stange, M., Elofson, C., Wilson, T., Snow, D., Hanson, P., Joeckel, R.M., Bargar, J., and Weber, K.A. Sedimentary Natural Occurring Uranium in Alluvial Aquifers. 2016 Water for Food Global Conference, Lincoln, NE. April 2016. (poster presentation)
18. Pan, D., J. Nolan, K. H. Williams, M. J. Robbins, K. A. Weber. Abundance and Distribution of Microbial Cells and Viruses in an Alluvial Aquifer. (in review *Frontiers in Microbiology*)
19. Nolan, J. P. §; Bone, S.; Campbell, K.; Pan, D. ; Healy, O.; Elofson, C.; Joeckel, R. M.; Stange, M.; Wilson, T.; Hanson, P.; Bargar, J.; D., S.; Weber, K. A., Naturally Occurring Uranium in an Oxidic Alluvial Aquifer. (in preparation)
20. Nolan, J. P., R. Singh, C. Elofson, S. Bone, K. Campbell, D. Snow, J. Bargar, and K. A. Weber. Surface Complexation of Uranium(VI) in Suboxic Aquifers in the Presence of Uranium(IV)Minerals. (in preparation)
21. Nolan, Jason; Karrie A. Weber, 2015. Natural Uranium Contamination in Major U.S. Aquifers Linked to Nitrate. *Environmental Science & Technology Letters*, 2 (8), 215-220.
22. Weber, Karrie A.; Olivia Healy; Jason Nolan; Don Pan; Kate Campbell; Abbey Heithoff; Trisha Spanbauer; Daniel Snow, Nitrate stimulated uranium mobilization in groundwater. in preparation.
23. Nolan, Jason P.; Sharon Bone; Kate Campbell; Don Pan; Olivia Healy; Chris Elofson; Robert M. Joeckel; Marty Stange; Todd Wilson; Paul Hanson, John Bargar; Daniel Snow; Karrie A. Weber, Naturally Occurring Uranium in an Oxidic Alluvial Aquifer. in preparation.
24. Nolan, Jason P., Don Pan, Olivia Healy, Marty Stange, Karrie A. Weber. Geogenic Aqueous Uranium in an Alluvial Aquifer. *Goldschmidt*. August 16-21, 2015. Prague, Czech Republic. (poster presentation)
25. Nolan, Jason P. Mobilization of Naturally Occurring Uranium in Sediment Into Groundwater (Dissertation). University of Nebraska, Lincoln.
26. Weber, K.A. Uranium and Nitrate in Groundwater. Nebraska Natural Resource District Conference, Kearney, NE, March 1, 2016.
27. Weber, K. A. Keynote. Life Beneath Our Feet: Influence on Water Quality. Iowa State University. Environmental Science Graduate Research Symposium. April 1, 2016.
28. Weber, K.A. Nitrate and Uranium in Groundwater, NRD Annual Conference, Kearney, NE, March 1, 2016.
29. Westrop, J., Nolan, J.P. , Pan, D. , Healy, O. , Bone, S., Campbell-Hay, K., Bargar, J., D. Snow, K.A. Weber. Nitrate-Stimulated uranium mobilization in groundwater. Nebraska Water Center Symposium. October 20, 2016. Lincoln, NE. (poster presentation)
30. Weber, K.A. Nolan, J.P. , Pan, D. , Healy, O. , Bone, S., Campbell-Hay, K., Bargar, J., and D. Snow. Nitrate-Stimulated Mobilization of Naturally Occurring Uranium in Groundwater. Geological Society of America Annual Meeting. September 25-28, 2016. Denver, CO. (poster presentation)
31. Nolan, J. P., C. Elofson, S. Bone, K. Campbell, D. Snow, J. Bargar, and K. A. Weber. Surface Complexation of Uranium(VI) in Suboxic Aquifers in the Presence of Uranium(IV) minerals. Geological Society of America Annual Meeting. September 25-28, 2016. Denver, CO.

Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater

32. Weber, K.A. Nolan, J.P. , Pan, D. , Healy, O. , Bone, S., Campbell-Hay, K., Bargar, J., and D. Snow. Nitrate-Stimulated Mobilization of Naturally Occurring Uranium in Groundwater. International Society for Microbial Ecology. August 21-26, 2016. Montreal, CA. (poster presentation)
33. Nolan, J.P., Pan, D., Healy, O., Bone, S., Campbell-Hay, K., Stange, M., Elofson, C., Wilson, T., Snow, D., Hanson, P., Joeckel, R.M., Bargar, J., and Weber, K.A. Sedimentary Natural Occurring Uranium in Alluvial Aquifers. 2016 Water for Food Global Conference, Lincoln, NE. April 2016. (poster presentation)
34. Pan, D., J. Nolan, K. H. Williams, M. J. Robbins, K. A. Weber. Abundance and Distribution of Microbial Cells and Viruses in an Alluvial Aquifer. (in review *Frontiers in Microbiology*)
35. Nolan, J. P. §; Bone, S.; Campbell, K.; Pan, D. ; Healy, O.; Elofson, C.; Joeckel, R. M.; Stange, M.; Wilson, T.; Hanson, P.; Bargar, J.; D., S.; Weber, K. A., Naturally Occurring Uranium in an Oxidic Alluvial Aquifer. (in preparation)
36. Nolan, J. P., R. Singh, C. Elofson, S. Bone, K. Campbell, D. Snow, J. Bargar, and K. A. Weber. Surface Complexation of Uranium(VI) in Suboxic Aquifers in the Presence of Uranium(IV)Minerals. (in preparation)
37. Pan, D., J. Nolan, K. H. Williams, M. J. Robbins, K. A. Weber. 2017. Abundance and Distribution of Microbial Cells and Viruses in an Alluvial Aquifer. *Frontiers in Microbiology*. 8: 1199.
38. Weber, K. A., J Westrop, J. P. Nolan, S. Bone, J. Bargar, K. Campbell-Hay, and D. Snow. Microbially-mediated metal/radionuclide oxidation and mobility of naturally occurring uranium. International Society for Subsurface Microbiology Symposium. Rotorua, New Zealand. November 6-10, 2017.
39. Westrop, J., J. P. Nolan, S. Bone, J. Bargar, A. Kohtz, D. Snow, and K. A. Weber. Mobilization of naturally occurring uranium in response in response to nitrate inputs into subsurface sediments. Geological Society of America Annual Meeting. Seattle Washington, October 22-25.
40. Weber, K. A. Co-contaminants and Redox Chemistry: Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater. Water Quality Symposium, Water for Food Institute and Nebraska Water Center. October 26, 2017.
41. Weber, K.A. Nitrogen mediated metal redox cycling. American Chemical Society Spring Meeting, San Francisco, CA April 2-6, 2017.
42. Weber, K. A. Life beneath our Feet: Influence on Water Quality—Nitrate and Uranium. Indo-US Workshop Addressing the Nexus of Food, Energy and Water. Bangaluru, India. April 20, 2017

United States Geological Survey 104(g) Report (2017-2018)
Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater

Karrie A. Weber^{1,2} (PI), Daniel Snow³

¹School of Biological Sciences, University of Nebraska, Lincoln

²Department of Earth and Atmospheric Sciences, University of Nebraska, Lincoln

³Nebraska Water Center and School of Natural Resources, University of Nebraska, Lincoln

United States Geological Survey collaborator Kate Campbell

EXECUTIVE SUMMARY

This interdisciplinary project was conducted in collaboration between Drs. Karrie A. Weber and Daniel Snow, University of Nebraska-Lincoln (UNL) and Dr. Kate Campbell-Hay at the United States Geological Survey in Boulder, CO. Dr. Karrie A. Weber is an Associate Professor in the School of Biological Sciences (joint appointment in Department of Earth and Atmospheric Sciences) with expertise in microbial metabolisms mediating soil/sedimentary carbon, nitrogen, and metal/radionuclide biogeochemical cycling. She is responsible for project oversight, experimental design, sample collection, laboratory experiments, and geochemical analyses. Dr. Snow is an Associate Research Professor in the School of Natural Resources and Director of the Water Sciences Laboratory in the Daugherty Water for Food Institute. Dr. Snow is a geochemist overseeing development of new methods for stable isotope analyses. Dr. Campbell-Hay is a research chemist in the USGS NRP with an expertise in coupling UCODE to PHREEQC. She has conducted quantitative XRD analyses on oxic and anoxically preserved sediment samples as well as provided advice and support to students developing models based on data generated in the Weber laboratory. In an effort to identify the valence state of the uranium buried in subsurface sediments using X-Ray Adsorption Near Edge Spectroscopy (XANES) analysis we initiated a collaboration with Dr. John Bargar at Stanford Synchrotron Radiation Lightsource (SSRL) in 2015 which continues to date. Additional local collaborations have been initiated with city municipalities such as Hastings Utilities as well as Nebraska Natural Resource Districts to transfer to directly transfer knowledge gained from this research to regions experiencing nitrate and/or uranium water quality problems. In addition to the support of two female investigators, this project has supported the research of four graduate students at (2 Ph.D. students in the Department of Earth and Atmospheric Sciences (including one disabled veteran), 2 female Ph.D. student in the School of Biological Sciences) and four undergraduate students, including one female supported through the Undergraduate Creative Activity and Research Experience Program (UCARE) at UNL. Two postdoctoral scholars have participated in this project, one received direct support through the USGS funded project and another through the Water Advanced Research Innovation Fellowship program.

Experimental research results have been disseminated by the PI and two graduate students to date at national and international scientific conferences as well as locally in the state of the Nebraska to stakeholders and government agencies through workshops, meetings, and conferences (Department of Natural Resources, Natural Resource Districts local meeting).

BACKGROUND

Soluble uranium (U) is a regulated contaminant in public ground water supplies throughout the United States (Ayotte et al., 2011a), most notably in the High Plains and Central Valley Aquifers (Figure 1). Increasing occurrence of elevated U concentrations in drinking water in both urban and rural communities affects more than 6 million people increasing public supply treatment costs and human health concerns for private water supplies (Hakonson-Hayes et al., 2002). Health concerns and regulatory actions have prompted communities to seek alternative drinking water sources or seek expensive treatment options that can exceed millions of dollars and thus has significant economic impacts. Mechanisms driving U mobilization in these aquifers remains poorly understood. In order to develop management strategies and prevent further contamination of drinking water sources, it is necessary to gain a fundamental understanding of the mechanisms stimulating U mobilization and improve predictive models. Two fundamental mechanisms have been recognized to drive U mobilization: *i*) desorption of U as a result of increased alkalinity or ground water removal and *ii*) dissolution of reduced U minerals. Though increasing bicarbonate alkalinity plays a significant role in mobilization (Ayotte et al., 2011b; Jurgens et al., 2010), in areas where U sources are in the form of reduced minerals and solids, elevated U concentrations cannot be explained without some mechanism for oxidation.

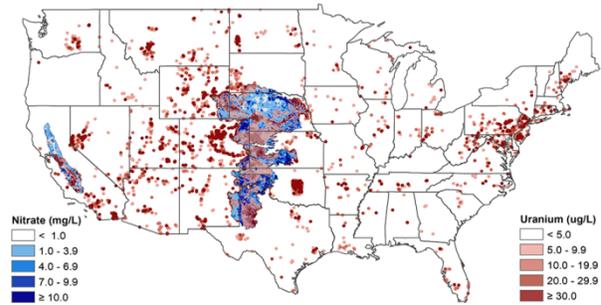


Fig. 1. Interpolated nitrate and U groundwater concentrations in the High Plains and Central Valley Aquifer from Nolan and Weber (2015).

PROJECT OBJECTIVE

The **objective** of this project is to determine the mechanisms governing the oxidative dissolution of U(IV) leading to U mobility and quantify the rate and extent of these reactions in order to develop a reactive transport model to predict U mobility in ground water.

SUMMARY OF HYPOTHESES AND APPROACH

1. *Microbial U reduction rates are slower than rates of oxidative dissolution of U (by O_2 , NO_3^- , and $Fe(III)$) thus resulting in U mobilization.*

Subsurface samples will be collected via GeoProbe[®] coring and geochemically characterized to identify zones of U(IV) bearing minerals as indicators of U reduction. Packed column experiments will be prepared from core sections containing U(IV) bearing minerals.

2. *Oxidation of U coupled to nitrate reduction can be traced using ^{18}O -labeled NO_3^- .*

Subsurface samples testing positive for microbial U(IV) oxidation coupled to nitrate reduction will be placed in column experiments and amended with ^{18}O labeled NO_3^- . ^{18}O in the U(VI) species will be quantified.

EXPERIMENTAL RESULTS

Uranium is a ubiquitous, naturally occurring radionuclide commonly deposited in organic carbon-rich regions subsequent to weathering of igneous rock. The majority of U exists in soils and sediments as insoluble reduced U(IV) minerals and is generally insoluble and thus immobile in suboxic groundwater. It has been recognized that exposing reduced U(IV) minerals to oxidizing groundwater leads to oxidative dissolution producing a dissolved U(VI) species which is mobile in groundwater. However, beyond sites directly contaminated with U from anthropogenic activity (mining, milling, nuclear testing, and disposal of spent nuclear fuel), U contamination has not been considered a risk. Yet, nitrate, a common groundwater contaminant, indirectly or directly solubilizes U(IV). Research resulting from this project was the first to demonstrate a link between groundwater nitrate and U concentrations in two major US aquifers, High Plains and Central Valley (Figure 1) (Nolan and Weber, 2015). Areas with U exceeding the MCL (30 μ g/L) have little to no direct anthropogenic U activity suggesting geogenic U contamination in these aquifers that may be driven by nitrate. These results were made publically available through *Environmental Science and Technology Letters* and can be located here <http://pubs.acs.org/doi/ipdf/10.1021/acs.estlett.5b00174>. This study also highlights that nitrate-mediated U mobilization is not restricted to isolated locations in Nebraska, but rather indicates that this may be a wide-spread issue.

Mobilization of Naturally Occurring U

Uranium in groundwater can originate from reduced U deposited in sediments. We have identified a shallow aquifer in Nebraska where the groundwater U concentration (302 μ g/L) exceeds the MCL by 10 times and nitrate concentration (30 mg/L) exceeds the MCL (10 mg/L) by three times. Both U and Fe in the sediment are in the reduced state and are associated with clays (Weber et al., *in prep*). Culture-based enumeration of nitrate-dependent U(IV) oxidizing microorganisms at this site (Weber et al., *in prep*) revealed an abundant community an order of magnitude higher than an aquifer contaminated with spent nuclear fuel (Weber et al., 2011). Culture-independent identification of the microbial community revealed *Pseudomonas* spp. and *Acidovorax* spp. as predominant community members (Weber et al., *in prep*). These are both species within genera Weber's prior research has previously described as capable of nitrate-dependent U(IV) oxidation (Byrne-Bailey et al., 2010; Weber et al., 2011), and could thus facilitate oxidative dissolution of U(IV). Microbial U biogeochemical cycling was experimentally verified through a series of MPN series.

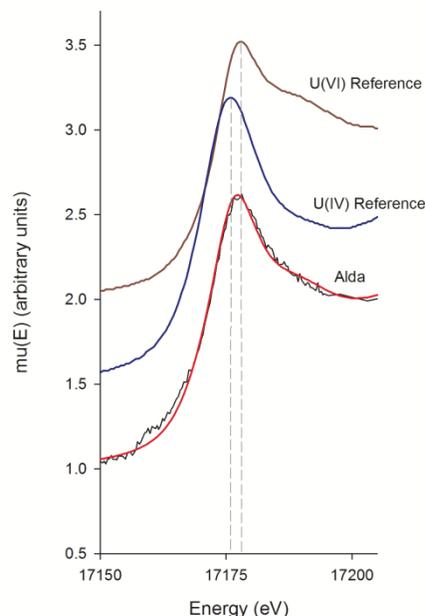


Figure 2. XANES data of natural sediments reveals U in both the reduced and oxidized state (50:50).

The potential of microbially-catalyzed uranium mobilization directly from uranium-rich subsurface sediments collected from an alluvial aquifer in the Platte River Floodplain (USA). Sediments and groundwater were collected from a region exhibiting fluctuating redox conditions. The reduction potential indicated a reduced environment and the presence of U(IV) (50% of total U) was confirmed by X-Ray Adsorption Near Edge Spectroscopy (XANES) (Figure 2). Upflow meso-scale column reactors were packed with sediment and sterile sand (50% mass/mass) with bicarbonate buffered (pH 7.1) artificial groundwater as the influent (Figure 3). Following pre-incubation the addition of nitrate with the influent stimulated the release of U(VI) into aqueous solution and did exceed the MCL relative to controls in which nitrate was omitted (Figure 4A). Nitrate was reduced to nitrite (Figure 4B) and is likely the result of the oxidation of natural organic carbon remaining in the sediments. Nitrite is recognized to rapidly oxidize U(IV) to U(VI). This result suggests that while nitrate-dependent U(IV) oxidizing microorganisms were identified in the sediment (3.0×10^6 cells g^{-1} sediment), nitrite production may be the



Figure 3. Upflow meso-scale column reactors inside an anaerobic glove bag.

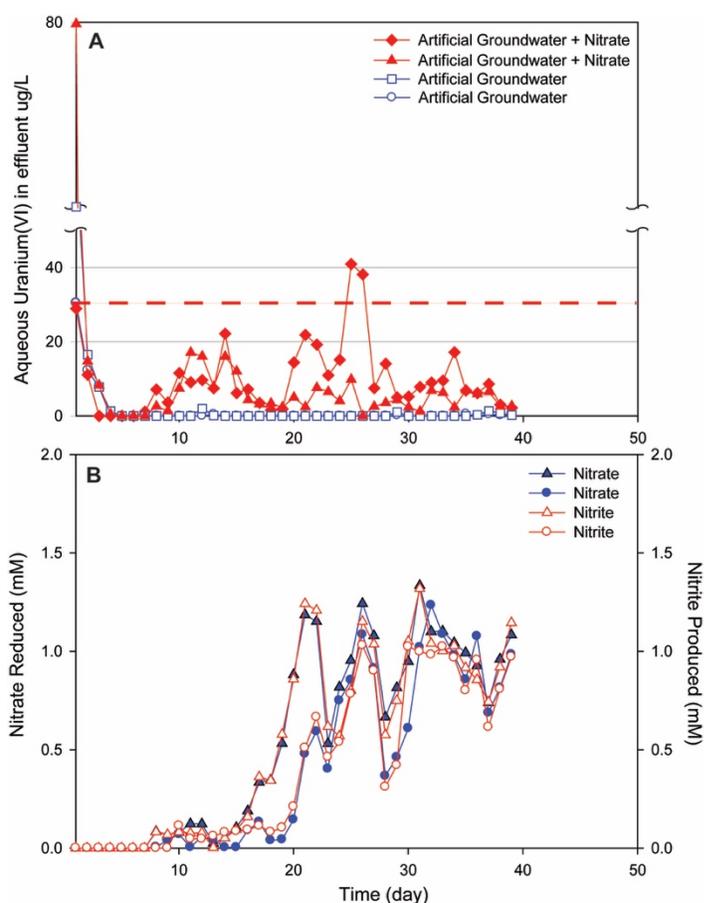


Figure 4. Upflow meso-scale column reactors packed with 50% sand and 50% sediment. Nitrate was amended into two column reactors and omitted from two reactors (A). Nitrate was reduced to nitrite in reactors receiving nitrate input (B).

mechanism driving the mobilization of U(VI) in these sediments.

Pseudomonas spp. capable of nitrate reduction to nitrite have been successfully stimulated in this aquifer and compose a majority of the microbial community (Pan et al., 2014). Thus, reactive intermediates of nitrate reduction could serve as the oxidant of naturally occurring solid-phase U(IV) present in the sediments contributing to increases in groundwater U concentrations above the MCL. A small amount of U(VI) was observed to release from sediments in which nitrate was omitted (Figure 4A). Thus indicating that release of U(VI) from the sediments may also occur via desorption processes.

Nitrate reduction was observed to closely follow the abundance of cells in the experiment. The mechanisms responsible for cell decreases is unknown. However in subsequent experiments we will continue to microbial activity and factors that may influence microbial activity.

In order to determine if microbial catalysis was responsible for nitrate-mediated U mobilization, an additional series of column studies was conducted. Columns were packed with reduced U(IV)-bearing sediments and acid-washed, combusted and autoclaved quartz sand (50% mass/mass). Influent was amended with a continuous flow of artificial groundwater (AGW; pH 7.2, 9mM bicarbonate) at a flow rate of 10 cm/day into columns receiving no nitrate amendment, a nitrate amendment, and/or a nitrate and azide amendment (inhibition of nitrate reduction). Sodium azide inhibit the transfer of electrons to the terminal reductase thus inhibiting nitrate reduction. Pre-equilibration with AGW (nitrate omitted) of all columns demonstrated desorption of surface associated U. Following desorption of U from sediments (effluent U concentrations <1 ppb), treatment columns were amended with nitrate or nitrate plus azide. No significant U elution was observed following pre-equilibration when microbial metabolism was inhibited (nitrate plus azide) or nitrate was omitted. Nitrate reduction was observed resulting transient production of nitrite in nitrate amended columns. A lag in U elution following nitrate reduction was observed, but U elution did begin from nitrate amended columns. The observed lag in U elution from the columns could be a result of U adsorbed to Fe(III) oxides precipitated via nitrate-dependent Fe(II) oxidation (see results described below). Thus these results demonstrate that microbially-catalyzed nitrate stimulated U mobilization.

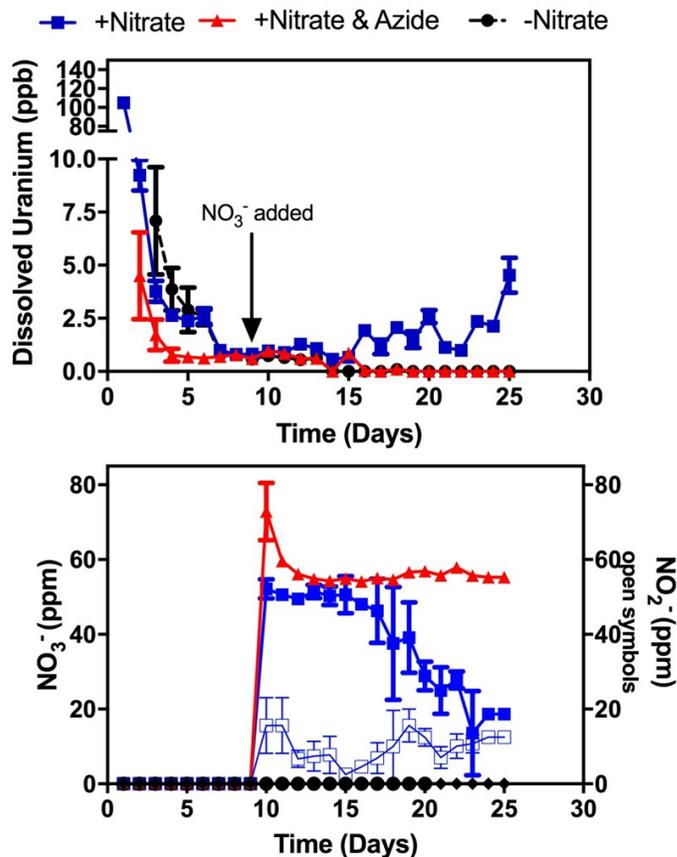


Figure 4. Effluent U concentrations from upflow meso-scale column reactors packed with 50% sand and 50% sediment receiving amendments of nitrate, nitrate and azide, and nitrate omitted (A). Nitrate was reduced in reactors receiving nitrate only input (B).

U adsorption

The mobility of naturally occurring U in aquifers is influenced by redox and as well as binding to the sediments via adsorption. As such adsorption reaction controlling mobility must be included in reactive transport models. Typically adsorption experiments are conducted after subsurface sediments have been exposed to oxidizing conditions. As such both Fe(II) and U(IV) can be oxidized as a result of O₂ exposure via biotic and abiotic mechanisms. A prior preliminary result in 2016-2017 revealed that oxidation could influence the outcome of adsorption experiments. These experiments were repeated to validate our prior results. In an effort to test the effect of oxidizing conditions on adsorption capacity of the subsurface sediments in which U(IV) was identified by XANES (Fig. 2). A series of equilibrium adsorption experiments was conducted to specifically determine whether or not with sediments exposed to O₂ and sediment that remained under anoxic conditions would differentially adsorb U. Treatments in which were exposed to O₂ resulted in the oxidation of 50% of the Fe(II) leading to Fe(III) oxide precipitation. Following pre-equilibration of sediments, U was added in varying

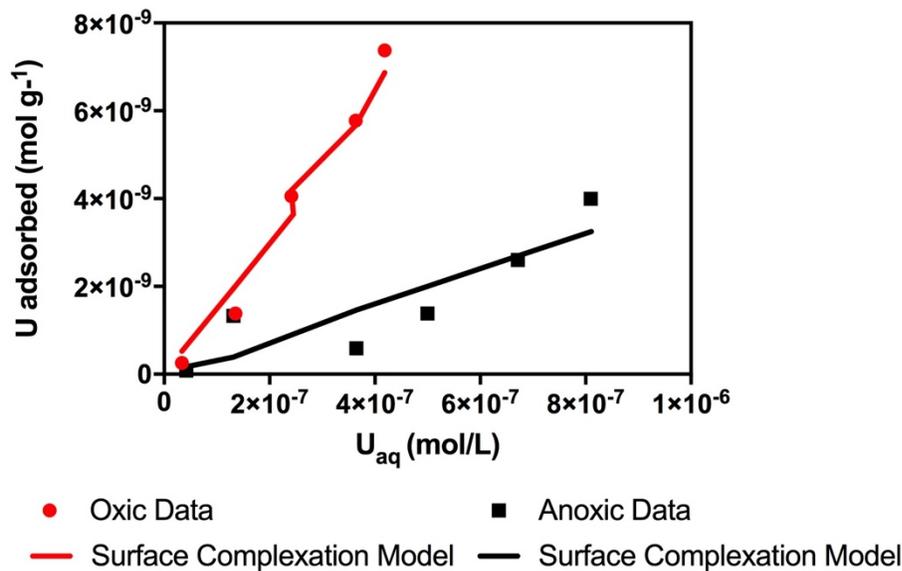


Figure 6. Equilibrium adsorption of U(VI) onto oxic and anoxic sediment.

concentrations to both oxidized and reduced sediments to concentrations which would be observed in the field. Oxidized sediments did adsorb more U than the reduced sediments (Fig. 6). A general composite surface complexation model developed from a series of adsorption experiments conducted under oxic versus anoxic conditions revealed precipitation of ferrihydrite increased adsorption sites under oxidizing conditions. These results indicate that reduced sediments will not adsorb as much U as oxidized sediments. Thus in order to accurately assess the adsorption of U in our column experiments we will need to quantify iron oxide precipitation under oxidizing conditions (with nitrate of O₂). Over the next few months additional experiments will be conducted to vary carbonate concentration for further development of the surface complexation models are currently in collaboration with Dr. Kate Campbell.

Summary

Together these data have demonstrated the widespread correlation between nitrate and uranium, that nitrate will stimulate the oxidation of naturally occurring U(IV) in sediments, and an additional mechanism where solid-phase U(VI) is released from sediments. Over the remainder of the grant we will continue to focus on the development of a novel model to predict

rate of U mobilization. The surface complexation model has been developed. Additional parameters will be tested to calibrate the model over a range of conditions. Dr. Weber will continue to work closely with Dr. Campbell to complete model development. Kinetic data will be obtained from a series of upflow meso-scale column reactors (Figure 5) as outlined below. In addition to the proposal submitted in 2017 to the Department of Energy, Subsurface Biogeochemistry Research program in collaboration with John Bargar we will also prepare a submission to the National Science Foundation to further explore this hypothesis and investigate the link between carbon, nitrate, and uranium in natural and contaminated environments expanding our research to Riverton, WY.

FUTURE PLANS:

Hypothesis 1: *Microbial U reduction rates are slower than rates of oxidative dissolution of U (by O₂, NO₃⁻, and Fe(III)) thus resulting in U mobilization.*

We have completed site and sediment characterization, adsorption experiments and development of surface complexation models are near completion, and we have completed a series of column studies demonstrating the mobilization of U(VI) in the presence of nitrate. We will continue to develop a surface complexation model and will determine the rates of U(VI) and Fe(III) reduction, U(IV) oxidation and U(VI) mobilization by O₂ and Fe(III) oxides to provide to Dr. Campbell for continued model development.

Hypothesis 2: *Oxidation of U coupled to nitrate reduction can be traced using ¹⁸O-labeled NO₃⁻.*

Development of method to trace oxidized U(VI) species using ¹⁸O-labeled NO₃⁻ is currently underway. Experiments involving the use of ¹⁸O-labeled nitrate will be carried out after successful synthesis and analysis of uranium oxide (UO₂) of known oxygen isotope composition. One approach previously employed for uraninite synthesis uses a reduction of commercial uranyl chloride with hydrogen and could be adapted for this purpose using water with a known isotope composition (Weber et al., 2011). Because uranyl chloride already possess oxygen, and alternative approach to be investigated with involve reaction of depleted uranium metal with water (USDoE 2008). Moreover, we will try to take the ultraclave approach (Wang et al. 2008), where we plan to start with uranium tetrachloride as the starting material in ¹⁸O-labelled water as solvent. Reaction products for each reaction will be analyzed using high temperature pyrolysis and conversion to carbon monoxide (Yin and Chen, 2014). Because EA-IRMS has not been employed for oxygen isotope analysis of uranium minerals, oxygen yield will be quantified and precision of the measurements evaluated through standard procedures. Traditionally, uraninite reduction by fluorination and conversion to carbon dioxide for isotope ratio mass spectrometry has been used (Fayek et al., 2011), though many of these off-line conversions have become unnecessary with the advent of high temperature on-line conversion chemistry. UO₂ with varying isotopic composition will be prepared and used as standards for analysis of uranium minerals generated during reduction of ¹⁸O-labelled NO₃ in column studies and possibly in batch experiments and even in natural samples. Methods for oxygen isotope analysis of nitrate (Silva et al., 2000) and phosphate (McLaughlin et al., 2006) have already been developed and are regularly used at the Water Sciences Laboratory. A final goal of the project is to develop a method for measuring the δ¹⁸O of aqueous uranyl species which may be separated and concentrated using ion exchange and/or polymeric purification methods (Aly and Hamza, 2013).

Finally, development of a method for speciation of dissolved forms of reduced U(IV) and oxidized U(VI) uranium for the project will be facilitated by recent acquisition of a new Thermo ICAP RQ inductively coupled plasma mass spectrometer (ICP-MS) coupled to a ICS5+ gradient ion chromatography system. The ICAP RQ is replacing an obsolete, and nearly inoperative, ICP-MS at the Water Sciences Laboratory that has also slowed progress on this project.

PUBLICATIONS

‡Undergraduate/Post-baccalaureate Student Contributing Author

§Graduate Student Contributing Author

Published

Pan, D., J. Nolan, K. H. Williams, M. J. Robbins, K. A. Weber. 2017. Abundance and Distribution of Microbial Cells and Viruses in an Alluvial Aquifer. *Frontiers in Microbiology*. 8: 1199.

In preparation

Weber, K. A.; Healy, O. §; Nolan, J. §; Pan, D.; Campbell, K.; Heithoff, A.; Spanbauer, T. ‡; Snow, D., Nitrate stimulated uranium mobilization in groundwater. *in prep.*

Nolan, J. P. §; Bone, S.; Campbell, K.; Pan, D. §; Healy, O. §; Elofson, C. ‡; Joeckel, R. M.; Stange, M.; Wilson, T.; Hanson, P.; Bargar, J.; D., S.; Weber, K. A., Naturally Occurring Uranium in an Oxic Alluvial Aquifer. *in prep.*

WORKSHOP, SEMINAR AND CONFERENCE PROCEEDINGS

*Presenting Author

‡Undergraduate/Post-baccalaureate Student Contributing Author

§Graduate Student Contributing Author

Weber, K. A.*; J Westrop§, J. P. Nolan§, S. Bone, J. Bargar, K. Campbell-Hay, and D. Snow. Microbially-mediated metal/radionuclide oxidation and mobility of naturally occurring uranium. International Society for Subsurface Microbiology Symposium. Rotorua, New Zealand. November 6-10, 2017.

Westrop, J.§*, J. P. Nolan§, S. Bone, J. Bargar, A. Kohtz, D. Snow, and K. A. Weber. Mobilization of naturally occurring uranium in response in response to nitrate inputs into subsurface sediments. Geological Society of America Annual Meeting. Seattle Washington, October 22-25.

Weber, K. A. Co-contaminants and Redox Chemistry: Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater. Water Quality Symposium, Water for Food Institute and Nebraska Water Center. October 26, 2017.

Weber, K.A. Nitrogen mediated metal redox cycling. American Chemical Society Spring Meeting, San Francisco, CA April 2-6, 2017.

Weber, K. A. Life beneath our Feet: Influence on Water Quality—Nitrate and Uranium. Indo-US Workshop Addressing the Nexus of Food, Energy and Water. Bangaluru, India. April 20, 2017

REFERENCES CITED

- Aly, M. M., and Hamza, M. F., 2013, A Review: Studies on Uranium Removal Using Different Techniques. Overview: *Journal of Dispersion Science and Technology*, v. 34, no. 2, p. 182-213.
- Ayotte, J. D., Gronberg, J. M., and Apodaca, L. E., 2011a, Trace Elements and Radon in Groundwater Across the United States: U.S. Geological Survey Scientific Investigations Report
- Ayotte, J. D., Szabo, Z., Focazio, M. J., and Eberts, S. M., 2011b, Effects of human-induced alteration of groundwater flow on concentrations of naturally-occurring trace elements at water-supply wells: *Applied Geochemistry*, v. 26, no. 5, p. 747-762.
- Byrne-Bailey, K. G., Weber, K. A., Chair, A. H., Bose, S., Knox, T., Spanbauer, T. L., Chertkov, O., and Coates, J. D., 2010, Completed Genome Sequence of the Anaerobic Iron-Oxidizing Bacterium *Acidovorax ebreus* Strain TPSY: *J. Bacteriol.*, v. 192, no. 5, p. 1475-1476.
- Fayek, M., Horita, J., and Ripley, E. M., 2011, The oxygen isotopic composition of uranium minerals: A review: *Ore Geology Reviews*, v. 41, no. 1, p. 1-21.
- Hakonson-Hayes, A. C., Fresquez, P. R., and Whicker, F. W., 2002, Assessing potential risks from exposure to natural uranium in well water: *J Environ Radio* v. 59, no. 1, p. 29-40.
- Jurgens, B. C., Fram, M. S., Belitz, K., Burow, K. R., and Landon, M. K., 2010, Effects of Groundwater Development on Uranium: Central Valley, California, USA: *Ground Water*, v. 48, no. 6, p. 913-928.
- Kinniburgh, D., and Cooper, D., 2011, PhreePlot: Creating graphical output with PHREEQC.
- McLaughlin, K., Paytan, A., Kendall, C., and Silva, S., 2006, Oxygen isotopes of phosphatic compounds--Application for marine particulate matter, sediments and soils: *Marine Chemistry*, v. 98, no. 2-4, p. 148-155.
- Nolan, J., and Weber, K. A., 2015, Natural Uranium Contamination in Major U.S. Aquifers Linked to Nitrate: *Environmental Science & Technology Letters*, v. 2, no. 8, p. 215-220.
- Pan, D., Watson, R., Wang, D., Tan, Z. H., Snow, D. D., and Weber, K. A., 2014, Correlation between viral production and carbon mineralization under nitrate-reducing conditions in aquifer sediment: *ISME J*, v. 8, no. 8, p. 1691-1703.
- Parkhurst, D. L., and Appelo, C. A. J., 2013, Description of input and examples for PHREEQC version 3: a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: US Geological Survey, 2328-7055.
- Silva, S. R., Kendall, C., Wilkison, D. H., Ziegler, A. C., Chang, C. C. Y., and Avanzino, R. J., 2000, A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios: *Journal of Hydrology*, v. 228, no. 1-2, p. 22-36.

- Weber, K. A., Healy, O., Nolan, J., Pan, D., Campbell, K., Heithoff, A., Spanbauer, T., and Snow, D., *in prep*, Nitrate stimulated uranium mobilization in groundwater.
- Weber, K. A., Thrash, J. C., Van Trump, J. I., Achenbach, L. A., and Coates, J. D., 2011, Environmental and Taxonomic Bacterial Diversity of Anaerobic Uranium(IV) Bio-Oxidation *Appl Envir Microbiol*, v. 77, p. 4693 - 4696.
- Yin, X., and Chen, Z., 2014, Measuring oxygen yields of a thermal conversion/elemental analyzer-isotope ratio mass spectrometer for organic and inorganic materials through injection of CO: *J Mass Spectrom*, v. 49, no. 12, p. 1298-1305.

Impact of Variable Rate Irrigation on Consumptive Use of Water Resources

Basic Information

Title:	Impact of Variable Rate Irrigation on Consumptive Use of Water Resources
Project Number:	2017NE291B
Start Date:	3/1/2017
End Date:	2/28/2018
Funding Source:	104B
Congressional District:	NE-001
Research Category:	Engineering
Focus Categories:	Irrigation, Water Quantity, None
Descriptors:	None
Principal Investigators:	Derek Michael Heeren, Daran Ray Rudnick, Francisco MunozArriola

Publications

1. Barker, J. B., D. M. Heeren, C. M. U. Neale, and D. R. Rudnick. 2018. Evaluation of variable rate irrigation using a remote-sensing-based model. *Agricultural Water Management* 203: 63-74, doi: 10.1016/j.agwat.2018.02.022.
2. Heeren, D. M., J. B. Barker, T. H. Lo, S. R. Melvin, D. L. Martin, and J. D. Luck. 2017. Considerations in adopting variable rate irrigation. Online extension article, UNL Water. Available at: <https://water.unl.edu/article/agricultural-irrigation/considerations-adopting-variable-rate-irrigation>.

Annual Technical Report

Water Resources Institute Program

May 28, 2018

Project #: 2017NE291B

Funding Period: March 1, 2017 through February 28, 2019 (was extended)

Title: Impact of Variable Rate Irrigation on Consumptive Use of Water Resources

PI(s): Derek Heeren, Daran Rudnick, and Francisco Munoz-Arriola

RESEARCH: See the “synopsis” below.

PUBLICATIONS: One journal manuscript and one extension publication are under development. Part of the matching funds (Heeren faculty time) were used for the following publications:

Barker, J. B., D. M. Heeren, C. M. U. Neale, and D. R. Rudnick. 2018. Evaluation of variable rate irrigation using a remote-sensing-based model. *Agricultural Water Management* 203: 63-74, doi: 10.1016/j.agwat.2018.02.022.

Heeren, D. M., J. B. Barker, T. H. Lo, S. R. Melvin, D. L. Martin, and J. D. Luck. 2017. Considerations in adopting variable rate irrigation. Online extension article, UNL Water. Available at: <https://water.unl.edu/article/agricultural-irrigation/considerations-adopting-variable-rate-irrigation>.

INFORMATION TRANSFER PROGRAM: Information transfer activities included several presentations:

Bhatti, S., J. B. Barker, D. M. Heeren, C. M. U. Neale, D. R. Rudnick, W. E. Woldt, J. D. Luck, Y. Ge, G. E. Meyer, A. L. Boldt, and M. Maguire. October 26-27, 2017. Water and crop response to variable rate irrigation using remote sensing model and soil moisture content monitoring. Nebraska Water Center (NWC) Nebraska Water Symposium, Lincoln, Nebr. Poster presentation.

Bhatti, S., J. B. Barker, D. M. Heeren, C. M. U. Neale, M. Maguire, W. E. Woldt, and D. R. Rudnick. April 10-12, 2017. Water and crop response to variable rate irrigation. Water for Food Global Institute (WFI) Water for Food Global Conference, Lincoln, Nebr. Poster presentation.

Heeren, D. M., J. B. Barker, M. Maguire, W. E. Woldt, and C. M. U. Neale. January 15, 2018. Drones are buzzing toward increased crop production. IHE Delft Lunch Seminar, Delft, Netherlands.

Heeren, D. M. October 4, 2017. Variable rate irrigation (VRI): Potential benefits and management practices. Department Colloquium, Biological Systems Engineering Department, Lincoln, Nebr.

Heeren, D. M., and J. B. Barker. June 8, 2017. Variable rate irrigation (VRI): Principles, example problems, and current research. Irrigation Association (IA) Irrigation Faculty Academy, Grand Island, Nebr.

STUDENT SUPPORT: This grant supported one MS student, Sandeep Bhatti, who is planning to graduate in December 2018 and is looking for opportunities to pursue a PhD in irrigation or a related field. This grant also supported one undergraduate research assistant in summer 2017, Isabella Possignolo, who went on to pursue an MS degree in irrigation at UNL.

	Section 104 Awards		NIWR-USGS Internship	Supplemental Awards	Total
	Base Grants	Competitive Awards			
Undergrad.	1				
Masters	1				
PhD.					
Post-Doc.					
Total	2				

NOTABLE ACHIEVEMENTS AND AWARDS: Sandeep Bhatti, MS student supported by this grant, placed 2nd in the graduate student poster contest at the Nebraska Water Symposium for the following poster:

Bhatti, S., J. B. Barker, D. M. Heeren, C. M. U. Neale, D. R. Rudnick, W. E. Woldt, J. D. Luck, Y. Ge, G. E. Meyer, A. L. Boldt, and M. Maguire. October 26-27, 2017. Water and crop response to variable rate irrigation using remote sensing model and soil moisture content monitoring. NWC Nebraska Water Symposium, Lincoln, Nebr.

PI Heeren received the following awards:

Honoree, recognized for performing highly impactful research, UNL College of Engineering. November 9, 2017. Research Recognition Reception, Lincoln, Nebr.

Distinguished Alumnus Award. October 26, 2017. Department of Agricultural and Biosystems Engineering, South Dakota State University. In recognition of significant contributions to society and accomplishments which have brought credit to the Department of Agricultural and Biosystems Engineering. Banquet of Excellence, Brookings, S.D.

SYNOPSIS

Title: Impact of Variable Rate Irrigation on Consumptive Use of Water Resources

Project Number: 2017NE291B

Start Date: 3/1/2017

End Date: 2/28/2018

Funding Source: 104B

Research Category

Focus Categories

Descriptors

Primary PI: Derek Heeren

Other PIs: Daran Rudnick and Francisco Munoz-Arriola

Project Class

Utilizing biotrickling filters to reduce water consumption at fermentation and dryer stacks in ethanol plants

Basic Information

Title:	Utilizing biotrickling filters to reduce water consumption at fermentation and dryer stacks in ethanol plants
Project Number:	2017NE292B
Start Date:	3/1/2017
End Date:	2/28/2018
Funding Source:	104B
Congressional District:	NE-001
Research Category:	Engineering
Focus Categories:	Water Quantity, Water Quality, Water Use
Descriptors:	None
Principal Investigators:	Ashraf AlyHassan

Publications

1. Duerschner, C. and Aly Hassan, A., (2018) Biofiltration of acetaldehyde emission resulting from drying operations at ethanol plants , 111th A&WMA annual conference, June 25-28, 2018, Hartford, CT
2. Aly Hassan, Ashraf (2017) "Towards more greener ethanol industry: Replacing scrubbers with biotrickling filters" Poster presented at the 2017 AEESP Research and Education Conference, held in Ann Arbor, MI, June 20-22, 2017.
3. Duerschner, Christopher (2018) "Utilizing Biotrickling filters for the treatment of recalcitrant industrial off-gases" Poster presented at the annual University of Nebraska graduate poster forum.
4. Duerschner, Christopher and Aly Hassan, Ashraf (Under Preperation) Biofiltration of acetaldehyde emissions using thermophilic and mesophilic bacteria Journal of Hazardous Material

FY 2017 ANNUAL TECHNICAL REPORT

Utilizing biotrickling filters to reduce water consumption at fermentation and dryer stacks in ethanol plants

NIWR Project Code: 2017NE292B

Project Type: Research

Start Date: 3/1/2017

End Date: 2/28/2018

Primary PI: Ashraf Aly Hassan, PhD, PE

Abstract

Biotrickling Filters (BTFs) are a desirable option for the treatment of dilute volatile organic compounds (VOCs). Replacing traditional air emission controls (air scrubbers and regenerative thermal oxidizers) at ethanol manufacturing plants result in economic and environmental benefits. Using BTFs to treat emissions from fermentation tanks and from distillers dried grains with solubles (DDGS) driers has not been studied. Two BTFs were operated in parallel under acetaldehyde loadings ranging from 1 to 34 g m⁻³ hr⁻¹. To examine the effect of temperature on the effectiveness of treatment, one of the BTFs was operated at room temperature while the other was heated to 60°C – the expected temperature of DDGS drier emissions. The unheated BTF reached an elimination capacity of 28 g m⁻³ hr⁻¹ at a removal efficiency of 83.2% and 31 seconds empty bed residence time. A removal efficiency of 100% was maintained up to a loading rate of 11.32 g m⁻³ hr⁻¹. The heated BTF reached an elimination capacity of 6.9 g m⁻³ hr⁻¹ at a loading rate of 9.6 g m⁻³ hr⁻¹. While high removal was achieved at low loading rates, removal suffered significantly at higher influent concentrations. Performance of the heated BTF was improved by reseeded with cooking compost resulting in increased thermophilic bacterial population. In the course of acetaldehyde degradation, the main byproduct formed was acetic acid with traces of formic acid. A mathematical model was used to successfully describe acetaldehyde concentration profiles.

Contents

Abstract	1
Contents	2
1. Background	3
2. Problem Statement	3
3. Overall Goal and Specific Objectives	4
4. Methodology	5
4.1. Experimental Apparatus.....	5
4.2. Analytical Methods.....	6
5. Principal Findings	6
5.1. Performance of the BTF A	8
5.2. Performance of BTF B.....	9
5.3. Improving the performance of BTF B	10
5.4. Identification of byproducts	10
5.5. Carbon mass balance.....	10
5.6. Modelling	11
6. Significance.....	15
7. References.....	15

1. Background

Development of alternative renewable energy sources has accelerated rapidly over the past few years as we seek to ease our dependence on expensive fossil fuels and to meet our growing energy demands. In the United States, the Energy Independence and Security Act of 2007 requires that U.S. energy providers produce at least 36 billion gallons of biofuel by 2022 [1]. Ethanol is widely viewed as an environmentally friendly alternative to fossil fuels as well as a replacement for methyl tertiary butyl ether, a gasoline oxygenate that has leaked from underground fuel storage tanks and contaminated groundwater aquifers across the United States [2]. The domestic production of ethanol from corn stocks is increasing steadily from recent 2 billion gallons in 2002 to 9 billion gallon in 2008 and finally a record 14.7 billion gallon in 2015. In fact, in 2015 the ethanol industry hit a production milestone of 1 million barrel per day [3]. Ethanol is the major type of biofuel produced in the United States and its production is expected to continue to increase.

The dry mill process of producing ethanol from corn dominates the ethanol production industry. In addition to producing ethanol, DDGS is sold as a high-protein animal feed and this product is important to the economic viability of these plants [4]. The US Environmental Protection Agency (USEPA) has investigated the emissions of air pollutants from ethanol production facilities and discovered that some of these facilities are a source of particulate matter (PM), volatile organic compounds (VOCs), and odors [5]. Air pollutants such as acetic acid, acetaldehyde, formaldehyde, and ethanol are emitted from DDGS dryers as well as from fermentation and distillation tanks [5]. Several of these compounds are classified as hazardous air pollutants (HAPs) by the USEPA.

2. Problem Statement

State environmental agencies limit the emission of the entire ethanol plant to 10 tons per year for each individual HAP and 25 tons per year for total HAPs in order to remain an area source and avoid class I threshold under Title V program. Control equipment on fermentation tanks and dryers are mandatory to control PM and VOCs under the Prevention of Significant Deterioration Program (PSD). The Best Available Control Technology (BACT) identified under the RACT/BACT/LAER Clearinghouse database maintained by the US EPA is CO₂ scrubber, distillation scrubber, and regenerative thermal oxidizer (RBLC ID: IA-0095) [6]. The operation scrubber requires vast amount of water and energy. A practical estimation of the amount of the water blowdown at an average scrubber is estimated at 29,000 gallons per day. In addition, elevated energy is required to operate the scrubber to account for high rate of water recirculation. The smallest ethanol plant will include at least one scrubber controlling the fermentation tank, however, more than one scrubber is expected to be onsite amounting for large water consumption.

A 2014 performance test on a fluid bed germ dryer in Columbus, Nebraska showed the concentrations given in Table 1. The dryer has a rated capacity of 36.4 MMBtu/hr. Emissions from the dryer are controlled by a scrubber. The scrubber liquid flow rate was 20.02 GPM (450 GPM recirculation), the scrubber pH 7.5, and differential pressure 8.6 inches of H₂O. The production rate was rated at 239,018 bushels. The stack temperature was 155 F, moisture content 30 (%v/v), actual cubic foot per minute 33,200, and total VOC 6.47 lb/hr on average. These are typical amount and composition expected from controlled dryers in the ethanol industry. Assuming that the scrubber operated at 90% removal efficiency, the main HAP constituents of the dryer are ethanol at 243 ppm_v, acetaldehyde at 28 ppm_v, acrolein 22 ppm_v, and formaldehyde at 17 ppm_v. Another study has reported the effluent concentrations of acetaldehyde and formaldehyde from a DDGS dryer to be 20.7 and 16.4 ppm_v with HLC ($L_{\text{liquid}}/L_{\text{gas}}$) equals to 4×10^{-3} and 6.8×10^{-6} , respectively [7]. Therefore, both compounds are selected for the study, because they compose a significant fraction of DDGS dryer exhaust gases.

Table 1: Actual HAPs concentration out of an ethanol plant in Columbus, NE

Constituent	Concentration, ppm _v			
	Test 1	Test 2	Test 3	Average
Acetaldehyde	2.75	2.49	3.14	2.79
Acetic Acid	0.85	0.53	0.53	0.64
Acrolein	2.43	2.36	1.75	2.18
Ethanol	27.7	24.0	21.1	24.3
Ethyl Acetate	< 0.41	< 0.41	< 0.41	< 0.41
Formaldehyde	< 1.72	< 1.72	< 1.72	< 1.72
Formic Acid	< 0.32	< 0.32	< 0.32	< 0.32
Methanol	< 0.52	< 0.48	1.26	< 0.75

The best available technology for the treatment of dilute HAPs is biological systems, specifically biofiltration [8]. Biological systems provide an environmentally-friendly and low-cost alternative as compared to other methods such as incineration, catalytic oxidation, and adsorption. They work best for the treatment of large volumes of off-gases, which contain low concentrations of biodegradable contaminants [8-10]. One of the main advantages of biological treatment is that it does not produce secondary effluent. Another advantage is low demand for supplementary material addition while in operation. Two types of biological treatment could be employed; biotrickling filter (BTF) and bioscrubber. The bioscrubber is very similar to the currently used scrubbers but it includes bed media for microorganisms' growths. On the other hand, BTFs are essentially a bioscrubber without liquid recirculation. BTF technology is superior to scrubbing because of several reasons; 1) water consumption is cut to an average of 1/20, 2) energy utilization is minimal because there is no recirculation, and 3) chemical addition is reduced significantly to green nutrients used by the organisms.

BTFs are packed columns with biologically active materials such as immobilized cells and compost or inorganic or polymeric media on which immobilized microbial mass is attached [9]. A schematic of one of the two BTFs proposed in the study is presented in Figure 1. The BTF bed media will be seeded with activated sludge obtained from the local wastewater treatment plant. The BTF will be constructed of seven cylindrical glass sections with an internal diameter of 7.6 cm and a total length of 130 cm. It will be packed with pelletized diatomaceous earth biological support media to a depth of about 60 cm (Celite 6 mm R-635 Bio-Catalyst Carrier; Celite Corp., Lompoc, CA). Both BTFs will run at two sets of constant operating temperature of 20 °C and 50 °C and operated in a co-current gas and liquid downward flow mode. The air flowrate will be set up to correspond to a reasonable empty bed resident time (EBRT) similar to the one currently practiced in scrubbers. EBRT is the determinant factor in sizing the BTF and associated manufacturing costs. HAPs will be injected via a syringe pump and vaporized into the air stream. Buffered nutrient solution will be supplied at a rate of 2 L d⁻¹, the composition of the nutrient solution is similar to that reported by others [11].

3. Overall Goal and Specific Objectives

The overall goal of this study is to minimize water and energy utilization as part of emissions control at ethanol plant by studying the feasibility of biotrickling filters (BTF) as a green biological alternative. BTF utilization has the potential of water quantity reduction to 1/20 of that of the scrubber. The overall goal addresses at least two of the top 10 water challenges in Nebraska as cited by the Nebraska Water Center.

On one hand the project addresses a water quantity challenge represented in the effect of water consumption and conservation (including ethanol production) and water institutions challenge, where real-time water monitoring is a goal.

The overall goal of the study was achieved by fulfilling the following objectives:

- Examine the potential biodegradation of acetaldehyde as the major HAP constituent in a BTF
- Compare the impact of elevated temperature and room temperature on the removal of acetaldehyde
- Demonstrate BTF as a viable alternative to water scrubbers

4. Methodology

The experimental plan was designed to evaluate the long-term performance of two independent BTFs removing acetaldehyde fumes. ‘BTF A’ is operated at room temperature and ‘BTF B’ is operated at 50 °C. Apart from temperature, the conditions of each BTF are identical. Several strategies were investigated to improve the performance of the BTF B including increase the liquid flowrate and utilizing different thermophilic bacterial seeds. The study designed is to examine removal efficiency under increasing loading rates with an emphasis on carbon balance closure and formation of byproducts.

4.1. Experimental Apparatus

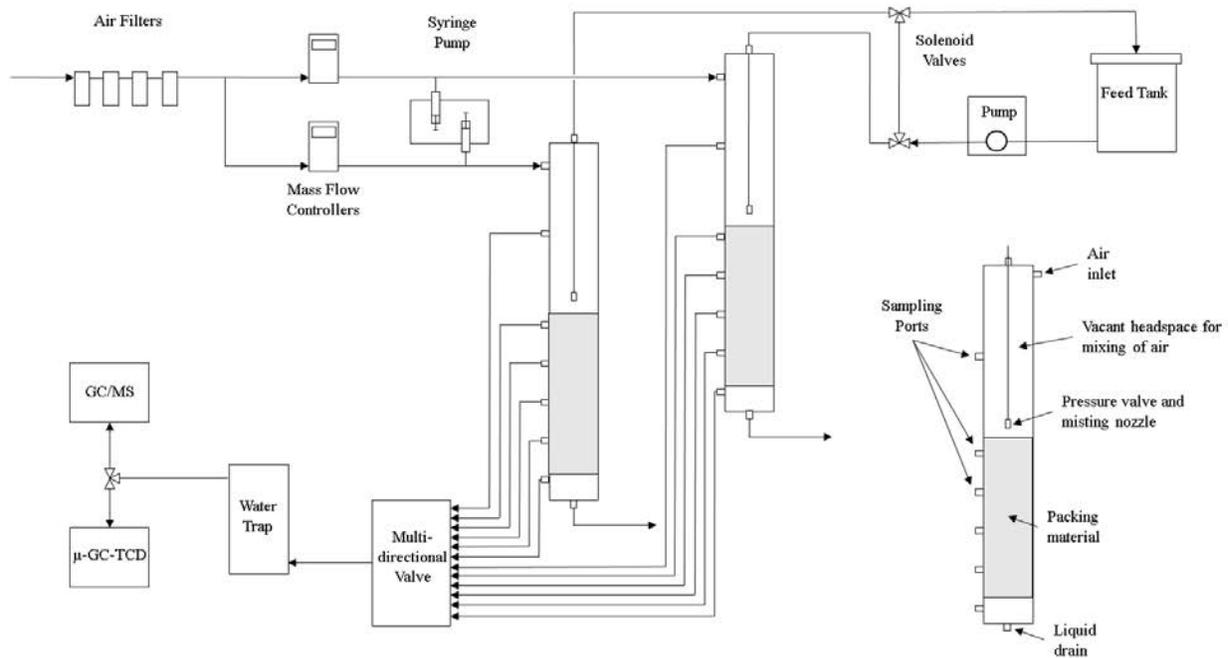


Fig 1: Schematic of the BTF experimental apparatus

Error! Reference source not found. shows a full schematic of the experimental apparatus. The BTF media consisting of 3’ pellets of diatomaceous earth, was housed in a three-inch internal diameter glass column. The bed was seeded with initially by microorganisms. Each column was filled with activated sludge and glucose solution and left overnight. The columns extend for 3’ above the top of the packing material, where the acetaldehyde laden air was introduced at the top to allow uniform mixing. The BTF is equipped with sampling ports located at packed depths of 3, 13, 23, 33, and 36 inches. All connections are

airtight. Heating of BTF B is managed by a heat tape wrapped around the packed length of the column. Approximately half of the surface area of the column is covered by the heat tape. A thermocouple placed through the fifth sampling port allows for feedback control.

House air is filtered through a Parker Filtration 2000 series compressed air and Balston sterile air filter followed by a Parker compressed air gas water separator. Following filtration, the air stream is split and flowrate is regulated by two Aalborg mass flow controllers. Acetaldehyde is infused into the air stream through a septum housed in a stainless-steel tee union. A Harvard Apparatus Pump 11 Elite syringe pump and Hamilton Gastight syringes were used to regulate the infusion.

Nutrient/Buffer solution is pumped via a Cole Parmer cavity style pump head equipped with a variable speed pump and controlled by a timer. The pipe delivering solution to each BTF is terminated by a pressure valve and a misting nozzle. The composition of the nutrient/buffer solution is provided in the supplemental material. The outlet to this column leads to a manual three-way valve, which can be manipulated to deliver air to either an Agilent Technologies 490 Micro GC with a TCD or an Agilent GC/MS instrument.

4.2. Analytical Methods

Acetaldehyde was measured using an Agilent 7820A GC system with an MS detector and 30 m, 0.25 mm I.D. HP-5MS column. The GC was operated in 'Splitless mode' with an inlet temperature of 250°C and an isothermal oven temperature of 30°C. The carrier gas was helium at a flow rate of 1 mL/min. The injection valve was maintained at 80°C and contained a 0.25 mL loop. A retention time of 1.46 min. for acetaldehyde was obtained under the conditions used. The detection limit was 0.5 ppmv.

Additional gas species, including CO₂, O₂, and N₂ were measured using a 490 µ-GC equipped with a thermal conductivity detector and a two-channel module. One channel used to measure O₂ and N₂ contained a 10 m MS5A heated injector maintained at 60°C with a channel temperature of 75°C. The other channel used to measure CO₂ contained a 4m PPQ module with an injector temperature of 50°C and a column temperature of 55°C. For both channels, the sample inline temperature was 35°C and the injection pump run time was 5 sec.

Analysis of the liquid effluent included volatile suspended solids (VSS), chemical oxygen demand (COD), nitrate, and pH. VSS was determined using Methods 2540 D and 2540 E in Standard Methods, COD was determined using Hach 820 vials. Nitrate concentration was determined using a Dionex IonPa™ AS22 ion chromatography instrument equipped with an analytical 4 x 250 mm column and a suppressed conductivity detector. The eluent used was 4.5 mM Na₂CO₃ and 1.4 mM NaHCO₃ with a flow rate of 1.2 mL/min. Temperature was 30°C, applied current was 31 mA, injector volume was 10µL and the storage solution was 100 mM NaHCO₃. Nitrate retention time was 6.93 min. at these conditions.

5. Principal Findings

Each BTF was operated at constant inlet concentration, which was increased in a step-wise manner to form a total of six phases. The inlet concentration, loading rate and corresponding average elimination capacity are shown in Table 2 for each BTF. Table 3 shows the removal efficiency at different EBRTs. The duration mentioned in Table 2 represents stable operation after a brief acclimation period. Acclimation periods were observed only during Phases I and II and were 5 and 3 days, respectively.

Table 2: Different phase of operation including duration, inlet concentration, loading rate, elimination capacity, and removal efficiency for both BTFs

Phase	Duration (days)	Inlet Concentration (ppmv)	Loading Rate ($\text{g m}^{-3} \text{hr}^{-1}$)	Average Elimination Capacity ($\text{g m}^{-3} \text{hr}^{-1}$)		Average Removal Efficiency (%)	
				BTF A	BTF B	BTF A	BTF B
				I	18	20	1.05
II	21	40	2.10	2.1±0.71	2.1±0.75	100±0.0	84.9±17.8
III	18	100	5.66	5.0±1.3	4.2±1.3	100±0.0	58.4±16.8
IV	28	200	11.32	9.6±2.8	6.9±4.4	99.8±0.3	60.8±29.5
V	42	400	22.64	18.6±6.5	6.4±6.2	90.8±13.8	19.4±23.2
VI	23	600	34.01	28.2±3.8	0.67±4.1	83.2±12.5	9.3±15.2

Table 3: Removal efficiency for both BTFs at different phases of operation and varying EBRTs

Phase	BTF A					BTF B				
	EBRT (s)									
	3	13	23	33	36	3	13	23	33	36
I	96.2±4.2	100±0.0	100±0.0	100±0.0	100±0.0	79.9±27.9	98.8±3.0	98.0±8.0	94.5±11.8	96.2±10.4
II	35.2±7.9	96.8±4.6	100±0.0	100±0.0	100±0.0	50.4±20.4	90.5±10.9	NA*	89.1±12.0	84.9±17.8
III	14.6±11.5	82.4±7.4	99.6±0.9	100±0.0	100±0.0	42.2±22.4	66.9±13.8	63.5±16.8	NA	58.4±16.8
IV	17.7±12.3	94.2±6.6	96.7±2.8	99.7±0.4	99.8±0.3	54.3±29.2	47.0±19.5	57.6±29.2	NA	60.8±29.5
V	10.1±7.8	50.1±26.6	79.2±15.6	89.7±15.8	90.8±13.8	18.6±22.4	18.9±16.0	23.0±25.6	NA	19.4±23.2
VI	37.4±10.3	59.5±14.3	77.6±14.7	81.2±13.9	83.2±12.5	7.3±8.7	4.1±7.0	4.3±5.4	NA	9.3±15.2

* Data not available - sampling port used to house thermocouple.

Starting from Phase III stagnation, a biomass control technique, was applied. During stagnation, liquid and water inputs to the BTFs were halted. Variability in the measured inlet concentration was observed in each BTF, starting at Phase IV. This could be explained by the high vapor pressure of acetaldehyde which results in rapid volatilization affecting high syringe pump flow rates. While target influent concentrations are presented in Table 2, actual measured concentrations in ppmv at phases IV, V, and VI, were 170±49.3, 361±117, and 417±77 for BTF A and 168±66.2, 330±128, and 352±112 for BTF B, respectively. During Phase IV, plastic syringes were initially used to inject acetaldehyde. After coloration of the syringes was noted, it was suspected that a reaction between acetaldehyde and the syringe material causes this variation in the influent concentration. Hamilton glass syringes were used to inject acetaldehyde for an additional week. No differences were observed in the influent concentration. The standard deviation amplified as the concentration increased. There was no significant difference between A and B although they are independently fed. It should be noted that the daily reported concentration is the average of 5 consecutive injections. The observed differences among these injections

were significantly less than that observed day to day. Complete uptake of nitrates in BTF A prompted an extension to Phase V. The nitrate concentration of the influent solution was increased from 495 to 741 for an additional two weeks. This is conducted to ensure that the removal of acetaldehyde would not be limited by nitrate availability. This same amount of additional nitrate was supplied through phase VI.

Figure 1 shows the loading rate versus the elimination capacity for both BTFs. For BTF A, the elimination capacity increased proportionally to the loading rate up to 9 g/m³/hr. High elimination capacity was still observed at higher loading rates. A maximum elimination capacity could not be established. BTF B performed more poorly than BTF A at higher concentrations. The maximum elimination capacity was obtained at a loading rate of 9 g/m³/hr. at a value of 6.9 g/m³/hr. Additionally, the elimination capacity for BTF B is seen to decline suggesting biomass loss.

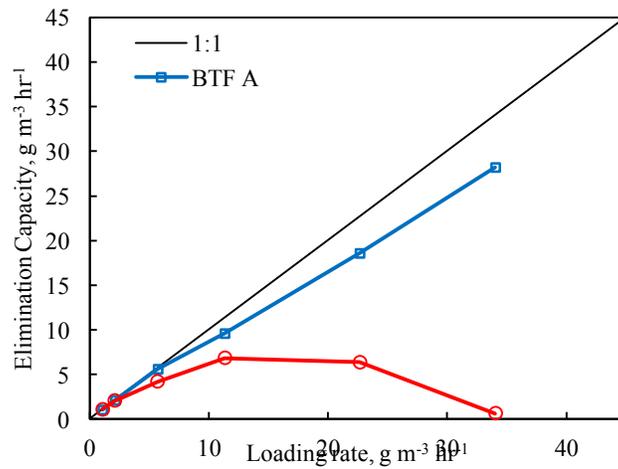


Figure 1: Elimination capacity versus loading rate for each BTF.

5.1. Performance of the BTF A

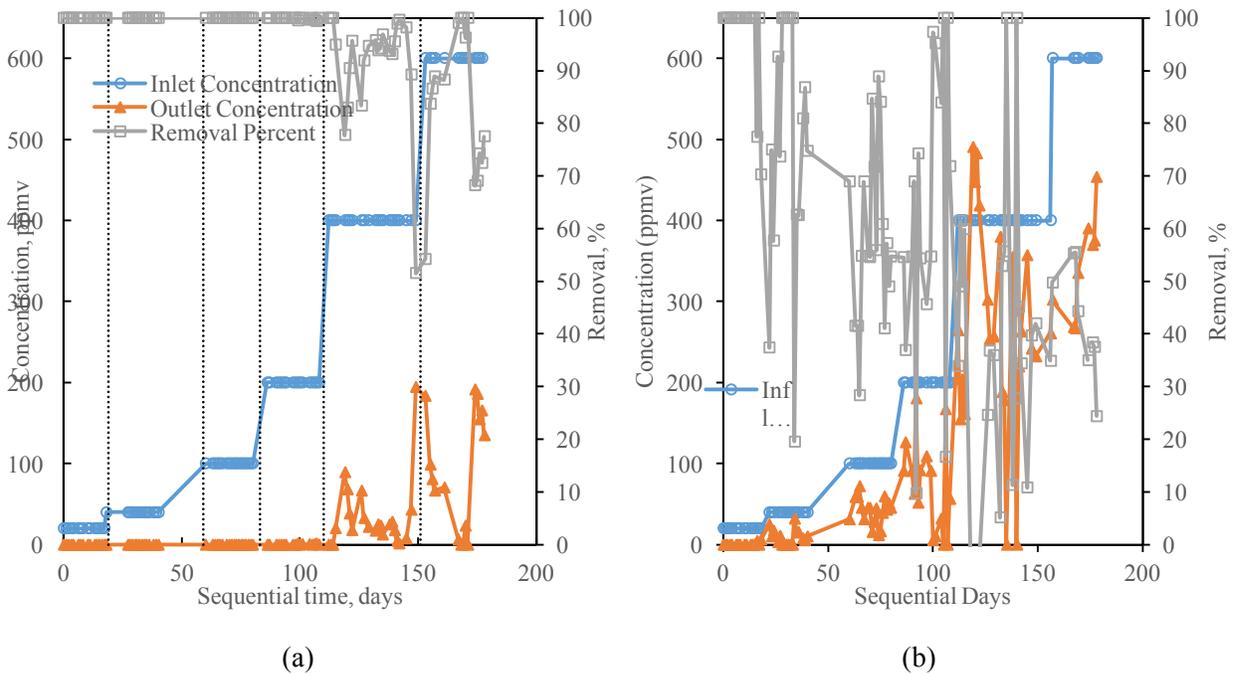


Figure 2: Inlet concentration, outlet concentration and percent removal for (a) BTF A and for (b) BTF B. Dotted lines separate the different operating phases.

As seen in Figure 2a, complete removal of acetaldehyde was achieved through phase IV. In phase V, approximately 90% removal was achieved. The removal efficiency was changing erratically in phase VI due to variability in the loading conditions however the removal dropped below 50% only once and below 60% on only three days.

Detailed VSS, pH and COD measurements are presented in supplemental Table S2. The measured pH of the nutrient solution in the holding tank was on average 8.53 ± 0.44 . The average change in pH between the influent and effluent was 0.83 ± 0.27 , 0.36 ± 0.31 and 0.26 ± 0.37 for Phases IV, V, and VI, respectively. It is expected that the pH will increase due to aerobic degradation of acetaldehyde. At higher concentration other acidic byproducts were formed. Their concentration was increased with elevated influent acetaldehyde concentration decreasing the pH of the effluent liquid.

VSS of the liquid effluent increased with increasing loading rates, however VSS spiked considerably in phase VI. The maximum VSS measured in Phases III, IV, and V were 21.0, 24.7, and 27.3 mg/L respectively while in Phase VI the maximum VSS was 86.4 mg/L. The increase in VSS during phase VI suggests biomass growth greater than the media holding capacity. Effluent COD in mg/L averaged 77.9 ± 33.2 , 915.8 ± 87.0 and 1960 ± 1387 during Phases IV, V, and VI, respectively. This is again attributable to loss of biomass but also to increased byproduct concentrations. The composition of the effluent COD will be discussed in detail in section Carbon mass balance.

5.2. Performance of BTF B

The heated BTF achieved 96% removal in Phase I, however through the later phases, removal steadily declined reaching 85%, 58%, 61% in phases II, III, and IV, respectively. In phases V and VI, the removal decreased significantly reaching only 19% and 9.3%, respectively. The most probable explanation for this poor performance is the lack of nutrient liquid and sufficient thermophilic organisms in BTF B, as discussed in Section 3.3. Exposure to these conditions over time led to biofilm deterioration. Visual inspection strongly indicated that BTF B contained significantly less biomass than BTF A. Furthermore, while the biomass in BTF A was observed to both grow thicker and to move downward through the media as the concentration of acetaldehyde was increased, no such changes were noticeable in BTF B.

The poor performance is attributed to other factors as well. First, the solubility of acetaldehyde decreases by approximately a factor of ten as temperature increases from 20°C to 60°C resulting in low availability of acetaldehyde for biodegradation in the liquid phase. At an air flowrate of 8 L/min and a saturated water vapor pressure of 19.92 kPa at 60°C, the amount of vaporized water is equal to 1.5 L/day of liquid equivalent. This is a comparable amount to the volume of water fed and suggests that BTF B may have had little liquid water available. It is also possible that the temperature in the interior of BTF B may have been greater than that measured on its outer wall. Temperature control was performed using a thermocouple placed in the fifth sampling port. This thermocouple measured the temperature just at the edge and did not extend into the interior of the media. The temperature of the column was measured manually using an infrared thermometer gun and the temperature set point was adjusted until the apparent temperature reading was 60°C. Furthermore, the thermostat exhibited significant lag time and occasional overshoot. During overshoot, the infrared thermometer would read temperatures up to 100°C. These periods of extreme temperature prevented biofilm from forming.

Other phenomena were also observed as a result of the heating of BTF B. Due to the vaporization of the nutrient solution supplied to BTF B, accumulation of salts was observed. This accumulation resulted in

periodic ‘flushing events’ whereby during a dip in temperature, deposited salts would be flushed in the effluent liquid by a sudden increase in flow rate. The effluent during these events appeared dark in color due to concentrated ferric ion. The effluent from one of these events registered a total fixed solids concentration of 6,200 mg/L. The pH of the effluent during one of these events was 10.2, an increase of 2.6 log units from the influent solution on that day.

The average change in pH between the effluent and the influent solution was 0.11 ± 0.77 , -0.64 ± 1.23 , and 0.66 ± 1.69 during Phases IV, V, and VI, respectively. These results show that within the same phase, pH changed erratically. This behavior could be explained by the frequent observed flushes. VSS for BTF B increased on average from 34.1 mg/L in Phase III to 39.5 mg/L in Phase IV. In Phases V and VI, the VSS decreased to 21.3 and 12.8 mg/L respectively. Although VSS decreased as loading rate increased, COD exhibited the opposite trend. Average COD for Phases III through VI were 171, 144, 242, and 375 mg/L respectively. As with BTF A, this trend suggests an increase in soluble byproducts. At lower concentrations, BTF B generated larger concentrations of COD than BTF A suggesting that increased temperature results in incomplete degradation of acetaldehyde. In Phases V and VI, there was not enough biomass to support the biodegradation in BTF B resulting in lower COD concentrations than in BTF A.

5.3. Improving the performance of BTF B

Several attempts were made to remedy the deficiency in removal of BTF B at 600 ppmv influent. Since the BTF was losing influent nutrient liquid in the form of vapor, the liquid flowrate was increased from 1.2 to 2.7 L/day. After deducting 1.5 L/day for evaporation, the remaining 1.2 L/day is comparable to BTF A. Collected effluent volume increased from 0.87 ± 0.34 to 2.7 ± 0.22 L/day. The increase in water volume did not result in the expected increase in removal efficiency.

Since BTF B had lost most of its biomass, a new inoculant was needed. Initially, the column was seeded with anaerobic sludge kept at 35°C. The availability of additional thermophilic bacteria consortium could enhance the performance. Therefore, compost from a cooking pile at 120°F was used to reseed the column. The compost was suspended in water and acetaldehyde fumes were bubbled through the slurry for one week while heated to a temperature of 40°C. Finally, the slurry was strained and used to submerge the media for six hours. The results from this change are not yet available.

5.4. Identification of byproducts

COD causing compounds are formed within the BTF bed. They consist of soluble byproducts, undegraded acetaldehyde, and some microorganisms. Expected degradation byproducts are acetate, formate, ethanol, methanol and formaldehyde. To identify byproducts, IC samples were introduced in phase V. Acetate was identified as a major byproduct; however, it was still a fraction of the total COD. Formate was also identified, however no formate was detected in BTF A and only trace amounts were detected in BTF B. For BTF A, 140 mg/L of acetate was detected during phase V and up to 625 mg/L was detected during phase VI. For BTF B, up to 227 mg/L of acetate were detected during phase V and up to 401 mg/L were detected during phase VI. A maximum of 0.8 mg/L of formate was detected throughout all phases.

Liquid samples were also collected from each sampling port of BTF A during phase VI to identify depth-wise trends in byproduct formation, however neither acetate nor formate were detected in these samples. Liquid samples were not able to be collected from BTF B, even the period of increased water supply. The creation of ethanol, methanol, and formaldehyde as volatile byproducts was investigated using a DB wax column in the GC/MS, nevertheless, none were detected.

5.5. Carbon mass balance

Figure 3 shows the carbon mass balance for each BTF. The only source of input carbon considered in this figure is the feed of acetaldehyde in the gaseous phase. Inorganic carbon, such as the carbonate found in the nutrient solution is not considered. Background CO₂ found in the house air is considered, but is subtracted from effluent CO₂ and so is not depicted in the figure. Sources of effluent carbon in the gas phase include undegraded acetaldehyde and CO₂ produced by degradation processes. COD is the only source of effluent carbon in the liquid phase. COD composition includes microorganisms, soluble byproducts, and dissolved acetaldehyde. The major byproduct identified was acetate, and the COD contributed by acetate is of great relevance. For BTF A, acetate composed 20% of effluent COD for phase V and 42% for phase VI. The COD contribution from dissolved acetaldehyde is not expected to be significant because the liquid collection containers are open to the atmosphere. The remaining COD contribution is expected to result from microorganisms. Effluent water in the unheated BTF was visibly cloudy throughout the highest two concentration phases, suggesting that some loss of biomass was indeed occurring. The relative amounts of influent carbon transferred to CO₂ and to biomass are also of interest. For BTF A, between 48% and 59% of influent carbon was transferred to CO₂ except for Phase III, during which 89% of carbon was transferred. For BTF B, acetate accounted for almost all the effluent COD in both phases V and VI. The mass balance shows that undegraded acetaldehyde accounted for the majority of effluent carbon and that CO₂ production and COD generation did not increase with loading rate. The consistent CO₂ and COD values over the operating period suggest that a maximum elimination capacity was reached and that increased loading rate does not result in increased biodegradation.

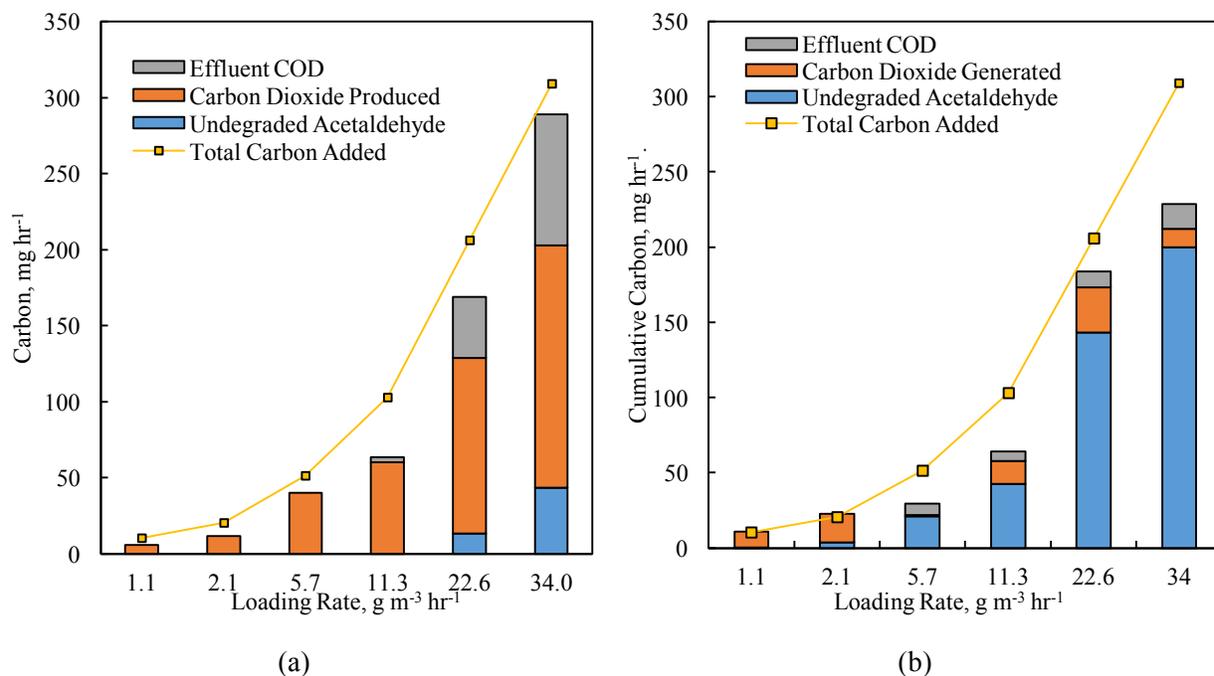


Figure 3: Carbon mass balance for (a) BTF A and (b) BTF B

5.6. Modelling

Two mathematical models were developed to describe the variations in acetaldehyde concentration throughout the bed depth. Model 1 operates on the principle that acetaldehyde is transferred to the liquid phase. As acetaldehyde is degraded in the liquid, it is instantaneously repartitioned to achieve vapor liquid equilibrium (VLE). While all parameters could be physically determined, the only unknown

parameter is the degradation rate constant. The value of this parameter can then be obtained for each influent concentration individually. A full list of assumptions follows.

1. The system attains instantaneous VLE
2. No radial variation in parameters is expected
3. Flow of water through the bed is continuous and uniform
4. Degradation reactions occur by a first order rate law
5. The ideal gas law applies to all gaseous species
6. Variation in biofilm density does not affect the void ratio or rate constant

Definitions for all terms in subsequent equations are available in Table 5. VLE for a highly volatile species is described by Henry's law, where C is the liquid phase concentration, H is the Henry's law constant, and y is the gas phase mole fraction.

$$C = Hy \quad (1)$$

The total moles of a volatile species at an arbitrary location in the BTF is the sum of the moles in the liquid and gaseous phases. Substitution of Henry's law into this mole balance yields an expression relating the gas phase mole fraction of acetaldehyde to the total moles of acetaldehyde in both phases.

$$y = \frac{n}{\frac{Q_G}{\bar{V}_{ig}} + Q_L H} \quad (2)$$

Here, n is the total moles of acetaldehyde, Q_G is the volumetric gas flow rate, Q_L is the volumetric liquid flow rate and \bar{V}_{ig} is the specific volume of an ideal gas. A mole balance over a differential volume of BTF in the liquid phase shows that the total moles of acetaldehyde varies according to

$$dn = -Q_L k H y \frac{dz}{v_L} \quad (3)$$

Combining Eq. 2 with Eq. 3 and integrating results in

$$n = n_0 e^{-\alpha z} \quad (4)$$

where

$$\alpha = \frac{Q_L k H \bar{V}_{ig}}{v_L (Q_G + Q_L H \bar{V}_{ig})} \quad (5)$$

One additional substitution of Eq. 2 provides an expression for the variation of gas phase mole fraction with depth.

$$y = y_0 e^{-\alpha z} \quad (6)$$

Concentration profiles of acetaldehyde were collected at all phases. An example of one of these profiles for phase VI is shown in **Error! Reference source not found.** The profiles were used to generate apparent exponential decay in accordance with Eq. 6 fitting for 'k' using least square methods. The values obtained for each phase are shown in Table 4.

Table 4: Best fit rate constants and overall mass transfer coefficients for BTF A

Phase	k (s ⁻¹)	$K_L * 10^6$ (m/s)	$K_G * 10^8$ (s ² m ⁻⁴)
I	0.01058	2.169	10.36
II	0.00152	1.483	2.00
III	0.00101	1.518	2.00
IV	0.00124	1.500	2.00
V	0.00055	1.544	2.01
VI	0.00040	1.544	2.01

Model 2 does not assume instantaneous equilibrium and instead considers the rate of mass transfer between gas and liquid phases. The assumptions of this model are identical to those of the VLE model, except assumption 1. It is also assumed that mass transfer of acetaldehyde between phases is represented by a two-resistance film approach. The equations that result from this model are

$$\frac{dC}{dz} = \left(\frac{K_L a_i A H}{Q_L} \right) y - \frac{A}{Q_L} (K_L a_i + k) C \quad (7)$$

$$\frac{dy}{dz} = - \left(\frac{K_G a_i A P}{Q_G} \right) y + \left(\frac{K_G a_i A P}{Q_G H} \right) C \quad (8)$$

with initial conditions given by:

$$C(0) = 0$$

$$y(0) = y_0$$

The analytical solution to these equations is:

$$y(z) = \frac{y_0}{2C_2} \left((C_2 + C_4 + a_i C_5 - a_i C_6) e^{\frac{A(C_2 - C_1)z}{C_3}} + (C_2 - C_4 - a_i C_5 + a_i C_6) e^{-\frac{A(C_1 + C_2)z}{C_3}} \right) \quad (9)$$

$$C(z) = \frac{y_0 a_i H C_5}{C_2} \left(e^{\frac{A(C_2 - C_1)z}{C_3}} - e^{-\frac{A(C_1 + C_2)z}{C_3}} \right) \quad (10)$$

where constants C_1 through C_6 are defined as

$$C_1 = HkQ_G + a_i H K_L Q_G + a_i H K_G P Q_L$$

$$C_3 = 2H Q_G Q_L$$

$$C_5 = H K_L Q_G$$

$$C_2 = \sqrt{C_1^2 - 4a_i H^2 k K_G P Q_G Q_L}$$

$$C_4 = HkQ_G$$

$$C_6 = H K_G P Q_L$$

The values of the mass transfer coefficients K_L and K_G were obtained using a two-dimensional least squares regression using the values for 'k' obtained previously. Except for Phase I, the results were identical to those obtained model 1. This supports the assumption in model 1 that VLE is quickly established.

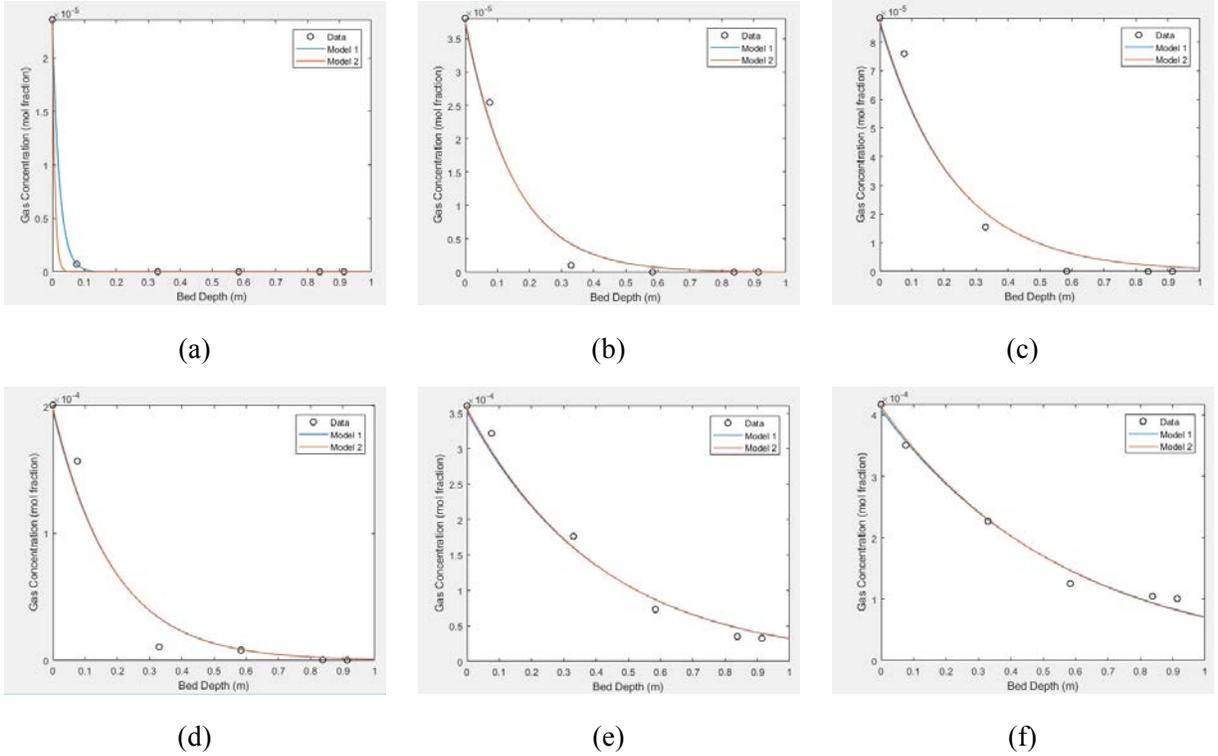


Figure 4: Plots comparing the best fit curves of models 1 and 2 to measured gas phase acetaldehyde concentration profiles. Panels (a) through (f) correspond to Phases I through VI, respectively.

Table 5: Definition of terms in model equations

Symbol	Definition
A	cross sectional area of BTF
a_i	specific phase interfacial area
C	mole concentration of contaminant in liquid phase
H	Henry's Law Constant
ΔH_{sol}	enthalpy of solution
ΔH_{rxn}	enthalpy of reaction
k	first order rate constant
K_G	combined gas mass transfer coefficient
K_L	combined liquid mass transfer coefficient
n	total molar flow rate
P	pressure

ϕ	void ratio
R	ideal gas law constant
t	time
Q_G	volumetric flow rate of gas
Q_L	volumetric flow rate of liquid
V_{ig}	specific volume of an ideal gas
v_L	downward velocity component of liquid in the BTF
y	mole fraction of contaminant in gas phase
z	bed depth coordinate

6. Significance

Utilization of BTF as the main air emission control device in place of scrubbers and RTOs is feasible. Large cost and energy savings will result from this switch. The capital cost required to transform an existing scrubber to a BTF is minimal. A mathematical model developed may be used to design BTFs successfully based on air flow rate and generated concentrations.

This study examined the effect of air stream temperature on the biodegradation ability of BTFs to successfully destroy acetaldehyde. Results from the 60°C column suggest that treatment of air at elevated temperature is not as effective as at room temperature however it could still be used at ethanol production plants for dryer's emissions. At room temperature, a removal efficiency of 100% was achieved in target operating conditions of ethanol plants compared to 85% at 60°C. At elevated temperatures, seeding with cultivated thermophilic bacteria will be necessary and care must be taken to ensure adequate water supply. Microbial cultures extracted from cooking compost piles have proven superior performance and resilience against harsh operating conditions. In order to remedy the deficiency in performance at elevated temperature, air streams from fermenters and DDGS driers may be mixed together. This will decrease the resulting temperature and will supply the required oxygen for the fermenter stream.

7. References

1. United States Congress, *Energy Independence and Security Act of 2007*, in H.R. 6, s.s. 110th Congress, Editor. 2007, Government Printing Office: Washington, DC.
2. Bradley, P.M., J.E. Landmeyer, and F.H. Chapelle, *Widespread potential for microbial MTBE degradation in surface-water sediments*. Environmental science & technology, 2001. **35**(4): p. 658-662.
3. Renewable Fuels Association, *Fueling a high octane future*, in *2016 Ethanol Industry Outlook*. 2016.
4. McAloon, A., et al., *Determining the Cost of Producing Ethanol from Corn Starch and Lignocellulosic Feedstocks*, N.R.E. Laboratory, Editor. 2000, A Joint Study Sponsored by: U.S. Department of Agriculture and U.S. Department of Energy.
5. Brady, D. and G.C. Pratt, *Volatile Organic Compound Emissions from Dry Mill Fuel Ethanol Production*. Journal of the Air & Waste Management Association, 2007. **57**(9): p. 1091-1102.

6. US Environmental Protection Agency, *RACT/BACT/LAER Clearinghouse*. 2016, Technology Transfer Network, Clean Air Technology Center.
7. Chen, L.-J., et al., *Biofiltration of simulated air pollutants from distillers dried grains with solubles (DDGS) dryer vents at corn-derived ethanol production facilities*. *Environmental Progress & Sustainable Energy*, 2010. **29**(1): p. 116-126.
8. Delhoméie, M. and M. Heitz, *Biofiltration of air: A review*. *Critical Reviews In Biotechnology*, 2005. **25**(1-2): p. 53-72.
9. Crocker, B. and K. Schnelle, *Air pollution control for stationary sources*, in *Encyclopedia of Environmental Analysis and Remediation*, R.A. Meyers, Editor. 1998, John Wiley and Sons, Inc.: New York. p. 151-213.
10. Deviny, J., M. Deshusses, and T. Webster, *Biofiltration for Air Pollution Control*. 1999: CRC Press. 51-81.
11. Sorial, G.A., et al., *Evaluation of trickle bed air biofilter performance for BTEX removal*. *Journal of environmental engineering* 1997. **123**(6): p. 530-538.
12. Jeong, G.-T., et al., *Application of Two-Stage Biofilter System for the Removal of Odorous Compounds*, in *Twenty-Seventh Symposium on Biotechnology for Fuels and Chemicals*, J.D. McMillan, et al., Editors. 2006, Humana Press. p. 1077-1088.
13. Ibrahim, M.A., et al., *Removal of mixtures of acetaldehyde and propionaldehyde from waste gas in packed column with immobilized activated sludge gel beads*. *Biochemical Engineering Journal*, 2001. **8**(1): p. 9-18.
14. Deviny, J.S. and D.S. Hodge, *Formation of acidic and toxic intermediates in overloaded ethanol biofilters*. *Journal of the Air & Waste Management Association*, 1995. **45**(2): p. 125-131.
15. Christen, P., et al., *Biofiltration of volatile ethanol using sugar cane bagasse inoculated with *Candida utilis**. *Journal of hazardous materials*, 2002. **89**(2): p. 253-265.
16. Vanek, T., et al., *A two-stage combined trickle bed reactor/biofilter for treatment of styrene/acetone vapor mixtures*. *Journal of Environmental Science and Health, Part A*, 2015. **50**(11): p. 1148-1159.
17. Raboni, M., V. Torretta, and P. Viotti, *Airborne toluene removal for minimizing occupational health exposure by means of a trickle-bed biofilter*. *Environmental Science and Pollution Research*, 2016. **23**(12): p. 11751-11758.
18. Prado, Ó.J., M.C. Veiga, and C. Kennes, *Biofiltration of waste gases containing a mixture of formaldehyde and methanol*. *Applied microbiology and biotechnology*, 2004. **65**(2): p. 235-242.
19. Maldonado-Díaz, G. and S. Arriaga, *Biofiltration of high formaldehyde loads with ozone additions in long-term operation*. *Applied Microbiology and Biotechnology*, 2015. **99**(1): p. 43-53.
20. Doronina, N.V., V.A. Ezhov, and Y.A. Trotsenko, *Aerobic biodegradation of formaldehyde, methanol, and methylamine by immobilized *Methylobacterium extorquens* cells*. *Applied Biochemistry and Microbiology*, 1997. **33**(2): p. 138-141.
21. Dragt, A.J., J.v. Ham, and L. Vereniging, *Biotechniques for air pollution abatement and odour control policies : proceedings of an international symposium, Maastricht, the Netherlands, 27-29 October, 1991*. 1992.

Spatial Variability of Streambed Hydraulic Conductivity across Multiple Stream Orders

Basic Information

Title:	Spatial Variability of Streambed Hydraulic Conductivity across Multiple Stream Orders
Project Number:	2017NE308B
Start Date:	3/1/2017
End Date:	2/28/2018
Funding Source:	104B
Congressional District:	NE-001
Research Category:	Climate and Hydrologic Processes
Focus Categories:	Water Quantity, Hydrology, Models
Descriptors:	None
Principal Investigators:	Aaron Mittelstet, Troy Edward Gilmore

Publication

1. Abimbola, O.P., A.R. Mittelstet, T.E. Gilmore and J.T. Korus. Spatial variability of streambed hydraulic conductivity across multiple stream orders. To be submitted to Hydrological Processes.

Spatial variability of streambed hydraulic conductivity across multiple stream orders

Olufemi P. Abimbola¹, Aaron R. Mittelstet¹, Troy E. Gilmore^{1,2}, Jesse T. Korus²

1. Department of Biological Systems Engineering, University of Nebraska-Lincoln, 223 L. W. Chase Hall, Lincoln, NE 68583-0726
2. Conservation and Survey Division, School of Natural Resources, University of Nebraska-Lincoln, 101 Hardin Hall, 3310 Holdrege Street, Lincoln, NE 68583-0996

Abstract

Streambed vertical hydraulic conductivity (K_v) is one of the significant parameters which control the movement of water from the stream to the aquifer and vice versa. Owing to the fact that streambed K_v may include a wide range of orders of magnitude for a given particle size group, modeling streambed K_v has remained conceptual and experimental. Although a wide variation in streambed K_v exists within a watershed, most modeling studies usually average out all values to determine a generalized streambed K_v . This often leads to under- or over-prediction of streamflow in channels. While some studies have measured streambed K_v at several sites in rivers across Nebraska and have discussed its spatial variability, they did not develop any empirical relationship between streambed K_v and watershed characteristics in order to capture the effect of this variability in watershed modeling. In this study, the statistical distribution and spatial variation of streambed K_v at 10 sites across different stream orders in Frenchman Creek watershed are presented. In-situ permeameter tests using the falling-head method were carried out to determine the streambed K_v values. Non-transformed streambed K_v values were found to be normally distributed at four sites for all six normality tests used. When the K_v values were log-transformed, values were found to be normally distributed for all the sites using the six normality tests. Normalized streambed K_v values were used to determine the pedo-transfer function relating streambed K_v to soil and sub-watershed characteristics.

Keywords: Streambed vertical hydraulic conductivity, Permeameter test, Normal distribution

1. Introduction

In the past 25 years, there have been significant changes in water resources in western Nebraska. This includes increases in irrigated acres and irrigation wells; decreases in streamflow, groundwater levels, and groundwater allocations; conversion from flood to pivot irrigation technologies and drip irrigation; moratoriums on new irrigation wells; and the encroachment of the eastern Red Cedar and other invasive species (Twidwell *et al.*, 2013). The Frenchman River watershed which is located in Nebraska has experienced each of these changes. In the last five decades, excess groundwater withdrawals in the Frenchman River watershed have led to groundwater declines ranging from 2 to 17 meters and decreased streamflow. In the 1960s, Frenchman River began several kilometers west of the Colorado border, yet today it begins 21 km east of the Colorado border (Traylor, 2012). These declines have led to reductions in groundwater allocations and a moratorium on new irrigation wells in the Upper Republican River Natural Resource District (NRD). Hence, there is a continued need for an integrated water resource assessment and management.

Water resources development and management in a watershed involve understanding the hydrological variations that are due to changes in watershed characteristics over long periods (Bhaduri *et al.*, 2000). This helps improve conceptualization of hydrological models, allow for quantitative analyses of runoff components and identify dominant hydrological processes, which are heterogeneous at all spatial and temporal scales (Abimbola *et al.*, 2017; Uhlenbrook *et al.*, 2008; Blöschl and Sivapalan, 1995). In order to assess and manage water resources in a better way that could lead to water policy changes in a watershed, it is important to understand the surface and groundwater interaction in the watershed. There is need for evaluation of the spatial variability of watershed characteristics that affect hydrological processes and phenomena. Often, modelling is required to infer what might happen under more extreme conditions as well as to understand complicated interacting phenomena of watersheds. Modelling and simulation lend support to providing such information. Hydrological models are often used to illustrate the impacts of water policy, land use change, climate change and irrigation management strategies (Wagener *et al.*, 2003). Such models can quantify the impact that watershed changes have on water resources as well as provide watershed managers with the research needed to make informed management decisions.

Various rainfall-runoff models have been developed over the past decades. These models can mostly be classified based on the process description as physically based distributed models, empirical models, conceptual models and data-driven models (Beven, 2001). Physically based models are based on an understanding of the physical processes driving fluxes and stocks; empirical models based on the patterns observed in hydrological data, and conceptual models, which do not focus on the physics of the processes, but consists of a number of interconnected reservoirs in the form of cascading stores for water and fluxes. Some examples of physically based models include the SHE (System Hydrologique European) model (Abbott *et al.*, 1986); CSIRO TOPOG Model (Vertesy *et al.*, 1993); the IHDM model, (Claver and Wood, 1995); the HILLFLOW model, (Bronstert and Plate, 1997). Examples of conceptual models include Sacramento Soil Moisture Accounting model (Burnash *et al.*, 1973), TOPMODEL (Beven and Kirkby, 1979), HBV model (Bergström, 1995), HYMOD model (Boyle, 2000; Vrugt *et al.*, 2003), among others. Hydrological modelling techniques based on Geographical Information Systems (GIS) have also been reported in several studies as improving water modelling (Jain *et al.*, 2004; Zhan and Huang, 2004; Li and Zhang, 2008; Van Dijk and Renzullo, 2010). GIS tools are now commonly used in hydrological modelling for data preparation (Nageshwar *et al.*, 1992). The value of GIS in water quality modelling has also been demonstrated for various hydrological models including Soil and Water Assessment Tool (SWAT) (Arnold *et al.*, 1993). SWAT and MODFLOW (Harbaugh, 2005) are two popular models that have been used extensively to represent surface and groundwater processes, respectively. The newly coupled SWAT-MODFLOW is the ideal model to simulate the surface and groundwater.

Stream, rivers, and lakes are rarely isolated. They are usually connected to some extent with underlying groundwater reservoirs, and the water exchange or interaction pattern mostly dependent on rainfall inputs, water head changes, and substrate permeability (Castro and Hornberger, 1991). The travel time, length, and depth of the groundwater flow path vary significantly from the recharge areas to the discharge areas depending on the amplitude of topographic variations, geometric and hydraulic properties of the streambed (Tóth, 1962). Differences in streambed hydraulic conductivity are due to hydrologic position and scale, such as from higher gradient channels in the headwaters to low gradient valley rivers (Katsuyama *et al.*, 2010), as well as the variety of spatio-temporal factors such as the topography, the depth of

streambed, bed slope, landcover, and the hydrogeologic setting of the underlying aquifer (Woessner, 2000; Wang et al., 2016).

To understand the connectivity between surface water and groundwater, it is imperative to get a good estimate of K_v which is one of the most important parameters controlling the movement of water from the stream to the aquifer, and vice versa (Goswami *et al.* 2010; Genereux *et al.*, 2008; Sun and Zhan, 2007; Saenger *et al.*, 2005; Storey *et al.*, 2003; Chen and Shu, 2002). In addition, a better understanding of the stream-aquifer connectedness is required in order to prevent the transport of contaminants from the river to nearby well fields.

There has been an emerging interest in the estimation and modeling of streambed hydraulic conductivity (K_v) due to its connection to water quality, aquatic habitat, and groundwater recharge. Several studies have found ways to measure K_v in-situ and with laboratory tests. These methods of estimating K_v suggest challenges in determining representative samples and comparing results, considering the heterogeneity and anisotropy of streambed materials and geological conditions (Naganna, 2017). Acknowledging that the K_v for a given particle size group may include a wide range of orders of magnitude, the modeling of streambed K_v has remained conceptual and experimental. Since it is not practical to measure streambed K_v throughout the watershed for most studies, modelers often rely on literature values or limited measurements and assume streambed K_v does not vary across the watershed. Thus, assuming homogeneity of streambed K_v across a watershed often leads to under- or over-predicting streambed leakage and baseflow.

Several studies have reported field measurements of streambed K_v (e.g., Genereux *et al.*, 2008; Chen, 2000, 2004, 2005, 2007; Cardenas and Zlotnik, 2003; McMahon *et al.*, 1995; Hvorslev, 1951). While some studies focused on different measurement techniques (Kelly and Murdoch, 2003), others focused on only the spatial variability of streambed K_v along transects across a channel (Chen, 2004), both the spatial and temporal variability (Genereux *et al.*, 2008), statistical description (means, ranges, variances) for hydraulic conductivity data (Song *et al.*, 2007; Cardenas and Zlotnik, 2003), or spatial interpolation of streambed K_v (Kennedy *et al.*, 2008; Cardenas and Zlotnik, 2003). Advanced geostatistical techniques present a wide range of interpolation procedures that can be applied to these complex systems.

However, due to the complexity of hydrological systems, and also the variability across landscapes and stream systems, it is essential to find ways of determining K_v spatially as a function of watershed characteristics in order to capture the effect its variability in watershed modeling.

Based on the central hypothesis that streambed K_v will vary between the same and multiple stream orders as a function of soil properties and the contributing watershed characteristics, the aim of this study is to (i) measure the streambed K_v for multiple stream orders within the Frenchman River watershed, (ii) quantify the difference in the streambed K_v within the same stream order and between stream orders as a function of soil properties, and (iii) develop pedo-transfer functions to estimate K_v from soil properties and the contributing watershed characteristics.

2. Study Area and Test Sites

The Frenchman watershed is located in southwest Nebraska (Figure 1). It is a sub-watershed of the Republican River watershed located in the Upper Republican River NRD. The Frenchman River watershed drains over 7,600 km² of land located in both Nebraska (60%) and Colorado (40%), and it is composed predominantly of rangeland and cropland. The dominant soil series include Valent (70-100% sand) and Kuma (19-79% silt), and major tributaries include Stinking Water Creek, Spring Creek, and Sand Creek.

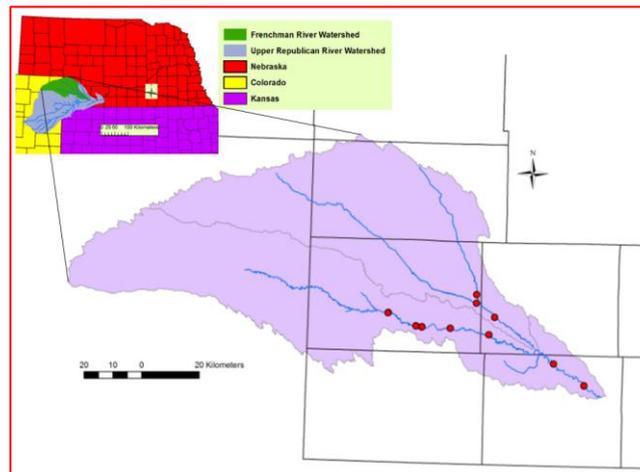


Figure 1. Map showing the study sites. *In situ* permeameter tests were performed at 10 test sites (from sites 1 to 10) in Frenchman Watershed

The primary land uses in the watershed consist of irrigated cropland, dry cropland, pastureland, and rangeland, with dense vegetation including trees, shrubs and grasses occurring in the riparian zones.

3. Methods

3.1. In situ Permeameter tests

In situ falling head permeameter test is one of several methods used to determine streambed K_v (Chen, 2000; Genereux et al., 2008; Chen et al., 2010; Dong et al., 2012). The falling head permeameter test usually involves inserting a tube into channel sediments (Figure 2). In this study, transparent tubes were used for 10 test sites within the Frenchman Creek watershed. Seven sites are on Frenchman Creek, two sites are on Stinking Water Creek and one site on Spring Creek. Other tributaries within the watershed were dry as at the time of the study. Each test site comprises of at least three transects and each transect comprises of at least three streambed K_v measurements. Figure 3 is a schematic diagram showing in-situ permeameter test installation at a test site. Transparent tubes (76 cm long and 8 cm inside diameter or 183 cm long and 6.8 cm inside diameter) are pressed vertically into the channel sediments. The thickness of the tube wall is about 10 mm, thus it has negligible disturbance on streambed sediments. The locations of permeameter stations were mapped with a global positioning system (GPS), which has a differential positioning measurement accuracy of 0.01 m. For each K_v measurement, after pressing the tube to a depth of 30 cm, the tube remained in the channel for a sufficient period of time in order to allow the hydraulic head inside the tube to equilibrate due to the slight compaction caused by the tube wall on the streambed sediments inside the tube (Chen *et al.* 2009). After the head inside the tube reached equilibrium, the surface water-level at the streambed surface was considered as the initial hydraulic head at the measurement point. Water was added slowly to fill up the tube from the top so as not to disturb the sediments inside the tube. As the hydraulic head in the tube began to fall, a series of hydraulic heads at given times were recorded for the derivation of the vertical hydraulic conductivity of the sediment column. K_v was calculated using the Hvorslev (1951) equation:

$$K_v = \frac{\frac{\pi D}{11m} + L_v}{(t_2 - t_1)} \ln \left(\frac{h_1}{h_2} \right) \quad (1)$$

where D is the inside diameter of the tube; L_v is the length of the sediment in the tube; t_1 and t_2 are the times between inside measurements of hydraulic heads h_1 and h_2 , respectively; and m is the isotropic transformation ratio $\sqrt{K_h/K_v}$ where K_h is the horizontal hydraulic conductivity of the sediment around the base of the tube. This study used the average of K_v values using $m = 1$ and $m = \infty$.

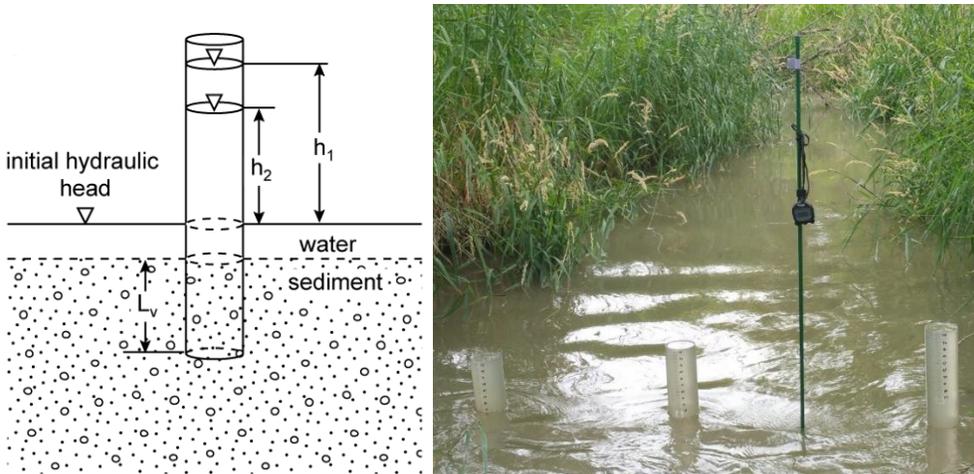


Figure 2. Basic design of falling-head permeameter. Left: Tube installation and definition of variables. Right: Photograph of permeameters. Each tube is installed to depth of 30 cm.

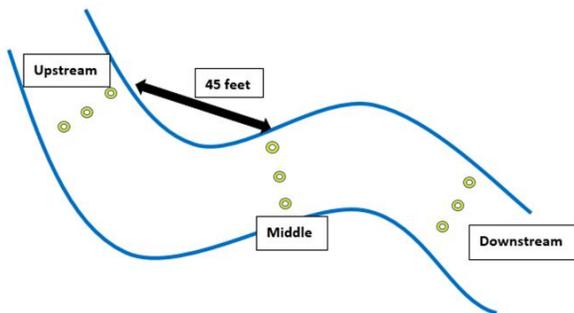


Figure 3. Layout of permeameter tubes along the streams

3.2. Normality Test and t -Test

To check whether the distributions of K_v are normal for the sites, graphical exploration ($Q-Q$ plots, histograms and box plots) and formal tests of normality were carried out. Six normality tests were chosen from among those detailed in D'Agostino and Stephens (1986). Anderson-Darling (AD), Cramer-von Mises (CVM), Lilliefors (LL), Pearson chi-square (CSQ), Shapiro-

Francia (SF), and Shapiro-Wilk (SW) tests were applied at 0.05 significance level. These normality tests can be categorized into tests based on correlation and regression (SW and SF tests), CSQ test, and empirical distribution test (such as LL, AD and CVM). Some of these tests are constructed to be applied under certain conditions or assumptions. The SW (Shapiro and Wilk, 1965) test is one of the most commonly used of the six tests. According to Royston (1982), it has requirements for the sample size N ($7 \leq N \leq 2000$), while the LL (Lilliefors, 1967) test is preferable to apply for a large sample size $N \geq 2000$ (Cheng *et al.*, 2011). The SF test is a simplified version of the SW test, which uses the squared normal probability plot correlation as a test statistic. The CVM and AD tests perform slightly worse than the Shapiro–Wilk test (Koning, 2015). Owing to the fact that there are still contradicting results as to which test is the optimal or best test (Yap and Sim, 2011, these six normality tests were compared in order to see how they performed for both non-transformed and log-transformed K_v values (Tables X and XX).

3.3. Soil datasets

The database used in this study includes soil datasets from the SSURGO database that consists of information about soil as collected by the National Cooperative Soil Survey over the course of a century (USDA-NRCS, 2018) in the United States. We selected the textural data (i.e., organic matter, sand, silt and clay contents) and erodibility index for all the counties covered by the study area in Nebraska State and Colorado State. The percentage of samples in each USDA soil texture class and the distribution of samples on the ternary diagram imply soils with different textures were used in this study as shown in Figure 4. Figure 5 shows the maps of percent organic matter (%OM), percent sand (%Sand), percent silt (%Silt), percent clay (%Clay) and erodibility index (K_{Erod}) values for the study area.

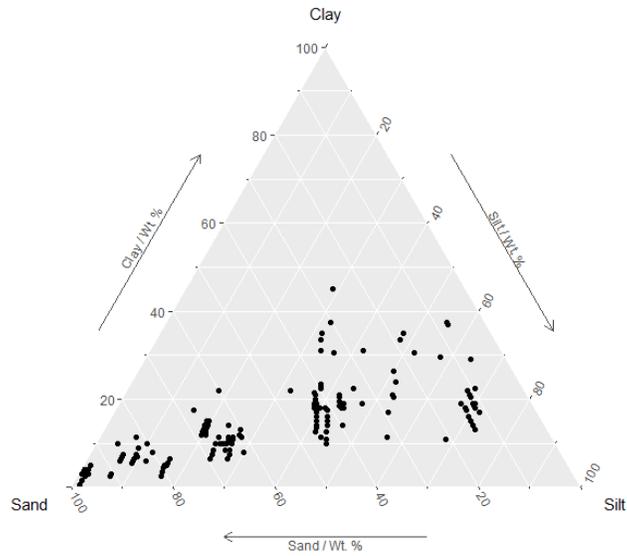
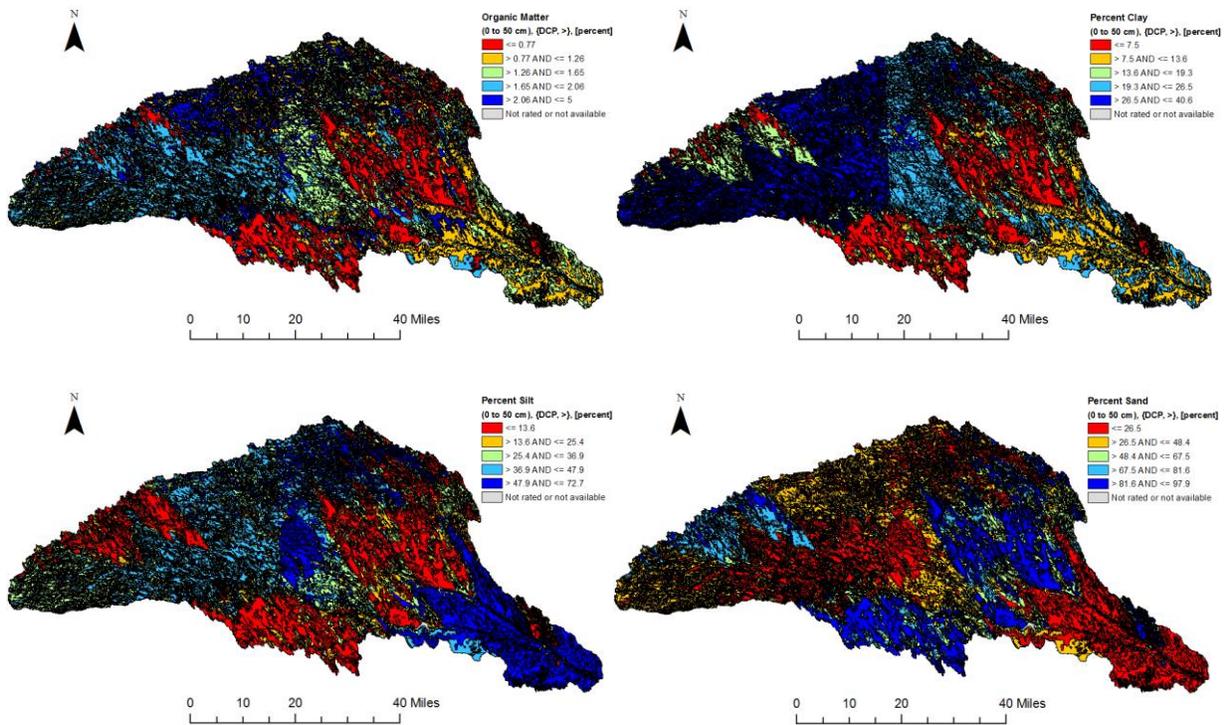


Figure 4: Percentage of samples in each USDA soil texture class and distribution of samples on the soil texture triangle (n = 644).



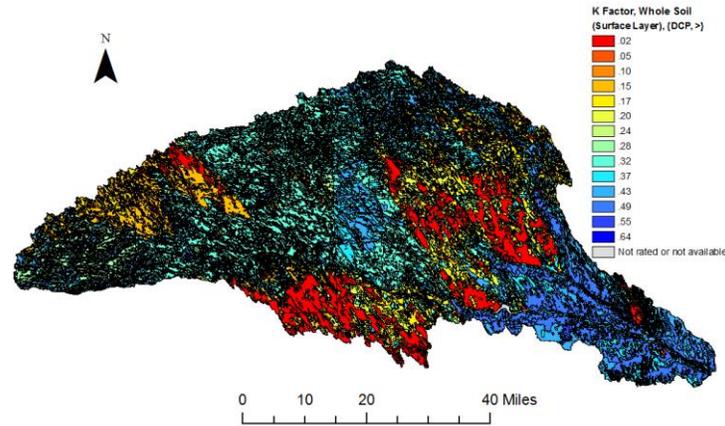


Figure 5. Spatial distributions of the soil physical properties

3.3. Development and Validation of Pedotransfer Functions (PTFs)

In the past five decades, there have been a lot of models developed for estimating the saturated hydraulic conductivity from other soil properties. These PTFs may not be applicable beyond the regions for which they were developed (Cornelis *et al.*, 2001). As such, we attempted to develop PTFs for single point estimation and van Genuchten parameter estimation using the basic soil properties measured in our study area. Similar to the majority of the previous studies, multiple linear regression (MLR) was used in assisting the development of the site-specific PTFs.

However, our study focused on developing PTF for estimating streambed vertical hydraulic conductivity K_v from frequently available watershed and soil characteristics, such as drainage area and reach slope as well as soil textural data i.e., organic matter, sand, silt, and clay content and soil erodibility in order to capture the spatial variability in the order of magnitude of K_v .

Owing to inherent spatial variability of K_v , large numbers of samples are required to properly characterize watersheds. However, these measurements are costly and time consuming. As an alternative, analysis of measured K_v data may result in PTFs. These functions fill the gap between the available soil data and the properties, which are more useful or required for a particular model or quality assessment. PTFs utilize various regression analysis and data mining techniques to extract rules associating basic soil properties with more difficult to measure properties. In practice, these functions often prove to be good predictors for missing hydraulic characteristics, since the

more readily available data from soil survey (e.g. field morphology, soil texture, and structure) can be translated into estimates of K_v .

The average of different watershed descriptors are summarized in Table X.

Add table with all the statistical descriptions

Spatial soil properties at surface, 0–50, 50–100, and 150–200 cm depth were extracted for each sub-watershed draining through each of the 10 test sites using Soil Map Viewer (**Add Reference**).

$$\text{MPE} = \frac{1}{n} \sum_{i=1}^n (\hat{y}_i - y_i) \quad (4)$$

$$\text{SDPE} = \sqrt{\frac{1}{n} \sum_{i=1}^n [(\hat{y}_i - y_i) - \text{MPE}]^2} \quad (5)$$

$$\text{RMSPE} = \sqrt{\frac{1}{n} \sum_{i=1}^n (\hat{y}_i - y_i)^2} \quad (6)$$

$$R^2 = \frac{[\text{cov}(\hat{y}_i, y_i)]^2}{\text{var}(\hat{y}_i) \cdot \text{var}(y_i)} \cdot 100, \quad (7)$$

where \hat{y}_i and y_i are the predicted and observed K_vA values, respectively, and n is the total number of observations. Each parameter fitting calculation and all statistical analyses were conducted using R version 3.3.2 (R Core Team, 2016).

4. Preliminary Results

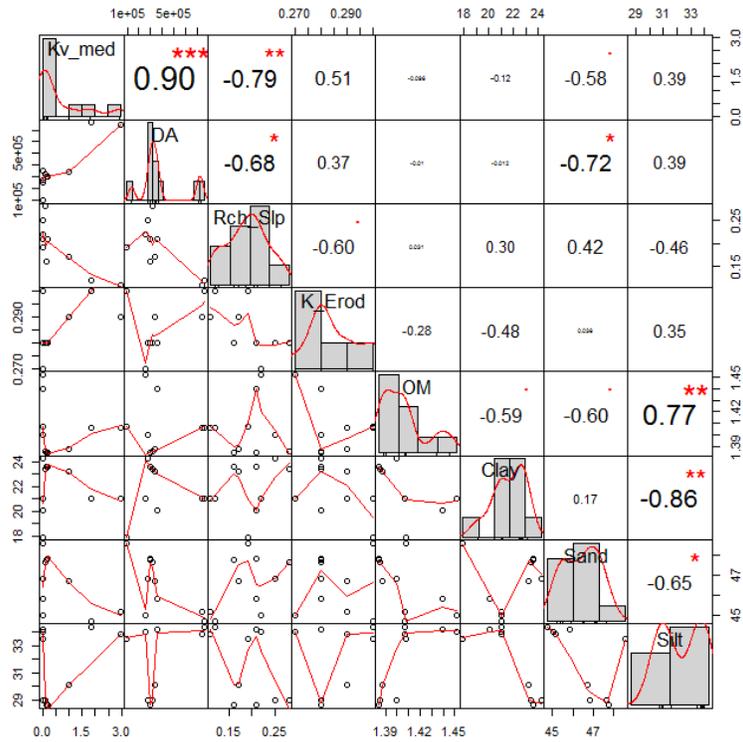


Figure 1: Correlation matrix of all variables

The correlation between streambed K_v and all selected variables are shown in Figure 1. There is a higher correlation between watershed and channel attributes when compared to soil textural properties. The correlation between streambed K_v and drainage area (DA) is highly positive while the correlation is negative for reach slope (Rch_Slp). To develop PTFs for predicting streambed K_v , regression analyses were performed to correlate the measured streambed K_v data with the soil properties including soil erodibility factor (K_Erod), OM, clay, sand, and silt, as well as watershed and channel attributes such as DA and Rch_Slp. The derived linear regression PTFs were formed by log-transforming all the aforementioned variables because non-transformed models often exhibit heteroscedasticity (Viglione et al., 2007; Vezza et al., 2010), and also to avoid heteroscedasticity and non-normality of the residuals of the regressions.

Interaction terms of soil textural properties were not added to the regression models since there were only ten sites, although they can greatly help in understanding the relationships among the variables in the models as well as allowing for more hypotheses to be tested. With seven

explanatory variables, all possible regression models with all possible combinations of the variables were analyzed. The performance of all PTFs was assessed by the values of thirteen selection criteria, namely: R-squared (R^2), Adjusted R-squared (Adj. R^2), Mallow's Cp, Akaike Information Criteria (AIC), corrected Akaike Information Criteria (AICc), Sawa's Bayesian Information Criteria (SBIC), Schwarz Bayesian Criteria (SBC), Mean Squared Error of Prediction (MSEP), Final Prediction Error (FPE), Hocking's Sp (HSP), Amemiya Prediction Criteria (APC), Leave-One-Out Cross-Validation (LOOCV), and Predicted Residual Error Sum of Squares (PRESS) as shown in Figure 2. The best subset regression models were selected for each variable-number ($k = 1, 2, \dots, 7$) category using these criteria. For instance in Model 1, of all the seven possible one-variable models ($k = 1$), the best performing model was selected (Figure 3). Also, since there is only one possible model with seven variables ($k = 7$), this implies that is the best Model 7 (Figures 2, 3).

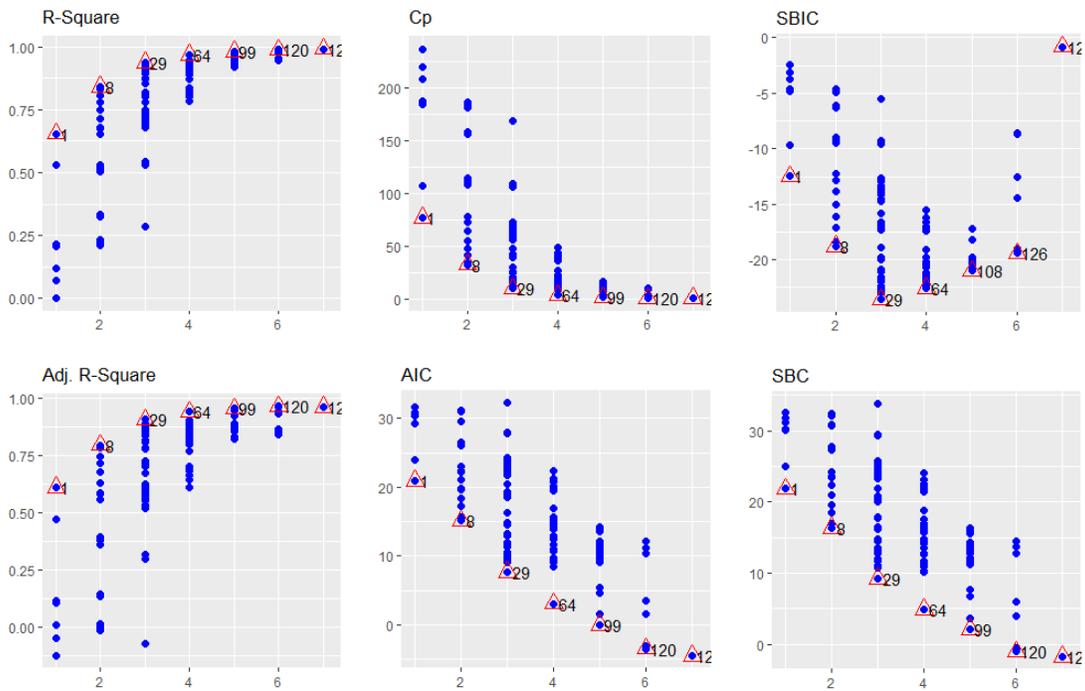


Figure 2: All possible regression models for predicting $\text{Log}K_v$

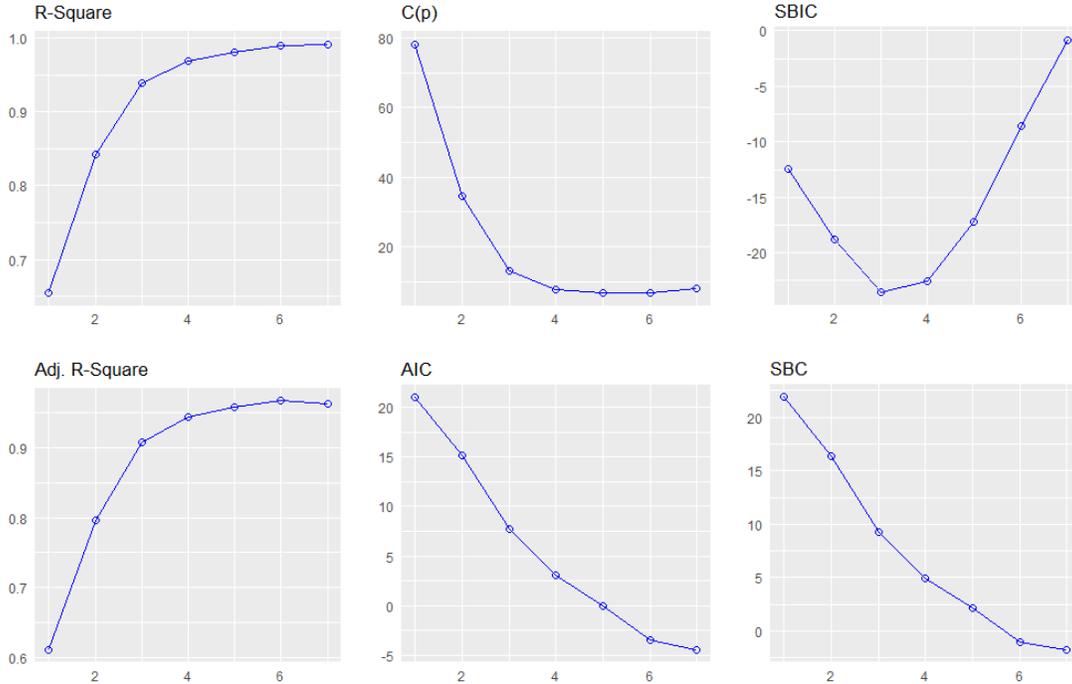


Figure 3: Selection criteria for the best subset regression models for predicting $LogK_v$

Except for the best Model 4 ($k = 4$), all the best subset PTFs consist of DA as a predictor and explains 65% of the variance in $LogK_v$ (Tables 1 and 2). The next most important variable is OM. Results shown in Table 2 indicated that there is no consistency in the selection of the overall best PTF based on these thirteen criteria, although Model 5 appeared to be the strongest candidate since more selection criteria chose Model 5 as the overall best PTF.

Table 1: Best subset regression for predicting $LogK_v$

Model Number	Predictors
1	$\log_{10}(\text{DA})$
2	$\log_{10}(\text{DA})$ $\log_{10}(\text{OM})$
3	$\log_{10}(\text{DA})$ $\log_{10}(\text{OM})$ $\log_{10}(\text{Silt})$
4	$\log_{10}(\text{OM})$ $\log_{10}(\text{Clay})$ $\log_{10}(\text{Sand})$ $\log_{10}(\text{Silt})$
5	$\log_{10}(\text{DA})$ $\log_{10}(\text{OM})$ $\log_{10}(\text{Clay})$ $\log_{10}(\text{Sand})$ $\log_{10}(\text{Silt})$
6	$\log_{10}(\text{DA})$ $\log_{10}(\text{Rch_Slp})$ $\log_{10}(\text{OM})$ $\log_{10}(\text{Clay})$ $\log_{10}(\text{Sand})$ $\log_{10}(\text{Silt})$
7	$\log_{10}(\text{DA})$ $\log_{10}(\text{Rch_Slp})$ $\log_{10}(\text{K_Erod})$ $\log_{10}(\text{OM})$ $\log_{10}(\text{Clay})$ $\log_{10}(\text{Sand})$ $\log_{10}(\text{Silt})$

Table 2: Best subset regression summary of selection criteria for predicting $LogK_v$

Model	R^2	Adj. R^2	C(p)	AIC	AICc	SBIC	SBC	MSEP	FPE	HSP	APC	LOOCV	PRESS
1	0.65	0.61	78.32	20.97	21.47	-12.49	21.88	0.41	0.39	0.05	0.52	NA	4.32
2	0.84	0.80	34.61	15.16	16.87	-18.76	16.37	0.25	0.22	0.03	0.29	0.28	2.76
3	0.94	0.91	13.02	7.72	11.72	-23.56	9.23	0.14	0.11	0.02	0.14	1.27	12.70
4	0.97	0.94	7.75	3.09	11.09	-22.54	4.91	0.11	0.07	0.01	0.10	0.24	2.38
5	0.98	0.96	6.66	0.01	15.01	-17.24	2.13	0.11	0.06	0.01	0.08	0.12	1.15

6	0.99	0.97	6.70	-3.45	24.55	-8.59	-1.03	0.12	0.05	0.01	0.06	0.12	1.16
7	0.99	0.96	8.00	-4.45	51.55	-0.82	-1.72	0.27	0.06	0.03	0.07	0.68	6.82

R²: R-squared
Adj. R²: Adjusted R-squared
C(p): Mallow's Cp
AIC: Akaike Information Criteria
AICc: Corrected Akaike Information Criteria
SBIC: Sawa's Bayesian Information Criteria
SBC: Schwarz Bayesian Criteria
MSEP: Mean Squared Error of Prediction, assuming multivariate normality
FPE: Final Prediction Error
HSP: Hocking's Sp
APC: Amemiya Prediction Criteria
LOOCV: Leave-One-Out Cross-Validation
PRESS: Predicted Residual Error Sum of Squares

In order to reduce this inconsistency and uncertainty in prediction, $\text{Log}(K_v \cdot DA)$ was used as the dependent variable.

Table 3: Best subset regression for predicting $\text{Log}(K_v \cdot DA)$

Model	Predictors
1	log10(Rch_Slp)
2	log10(OM) log10(Sand)
3	log10(OM) log10(Clay) log10(Silt)
4	log10(OM) log10(Clay) log10(Sand) log10(Silt)
5	log10(Rch_Slp) log10(OM) log10(Clay) log10(Sand) log10(Silt)
6	log10(Rch_Slp) log10(K_Erod) log10(OM) log10(Clay) log10(Sand) log10(Silt)

Table 4: Best subset regression summary of selection criteria for predicting $\text{Log}(K_v \cdot DA)$

Model	R ²	Adj. R ²	C(p)	AIC	AICc	SBIC	SBC	MSEP	FPE	HSP	APC	LOOCV	PRESS
1	0.52	0.46	42.25	28.38	28.88	-4.43	29.29	0.86	0.82	0.10	0.72	NA	8.28
2	0.87	0.83	9.44	17.60	19.31	-12.45	18.81	0.32	0.28	0.04	0.25	0.32	3.18
3	0.93	0.89	5.11	13.23	17.23	-12.22	14.74	0.24	0.19	0.03	0.16	0.93	9.33
4	0.96	0.93	3.91	9.26	17.26	-8.40	11.07	0.20	0.13	0.02	0.12	0.64	6.40
5	0.97	0.93	5.21	9.28	24.28	-2.66	11.40	0.27	0.15	0.03	0.13	0.59	5.92
6	0.97	0.91	7.00	10.60	38.60	4.00	13.03	0.50	0.19	0.06	0.17	0.86	8.63

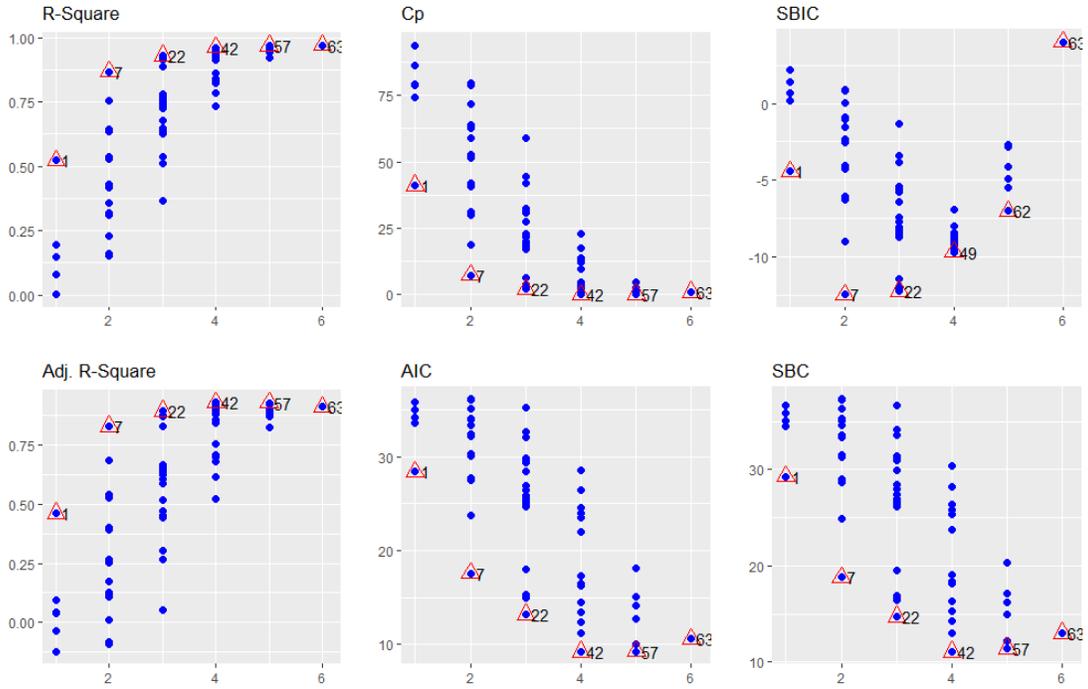


Figure 4: All possible regression models for predicting $\text{Log}(K_vDA)$

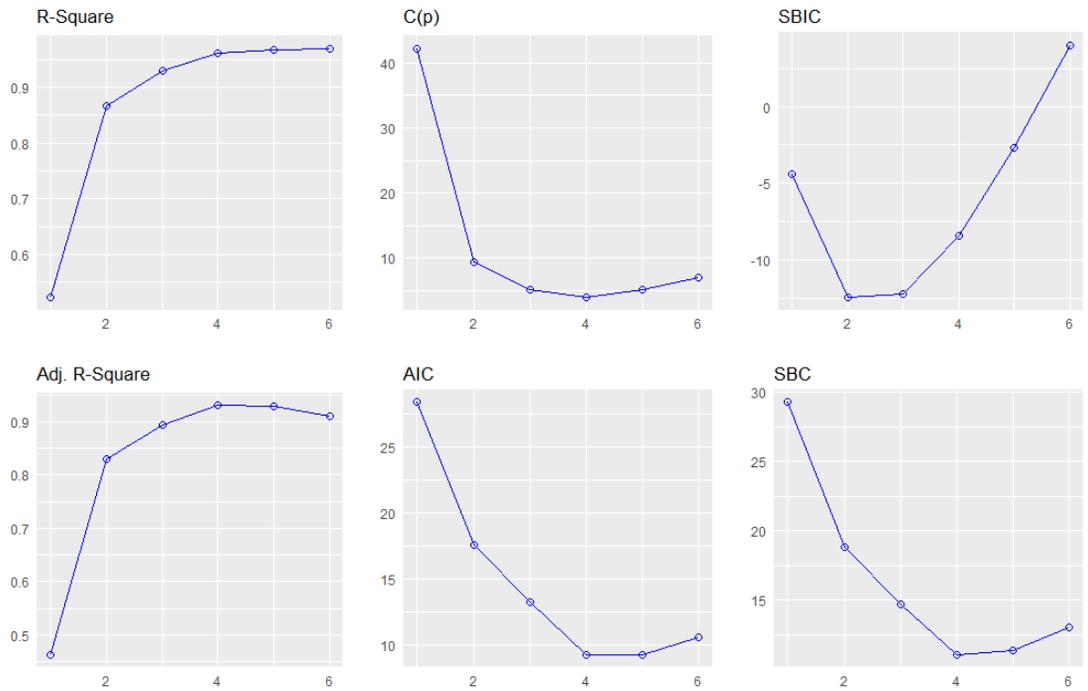


Figure 5: Selection criteria for the best subset regression models for predicting $\text{Log}(K_vDA)$

Table 5: Rank totals of the best subset regression models for predicting $\text{Log}(K_vDA)$

Model	Adj. R^2	C(p)	AIC	AICc	SBIC	SBC	MSEP	FPE	HSP	APC	PRESS	Rank Total
1	6	6	6	5	4	6	6	6	6	6	6	64
2	5	5	5	3	1	5	4	5	4	5	1	45
3	4	2	4	1	2	4	2	3	2	3	5	35
4	1	1	1	2	3	1	1	1	1	1	3	20
5	2	3	2	4	5	2	3	2	3	2	2	35
6	3	4	3	6	6	3	5	4	5	4	4	53

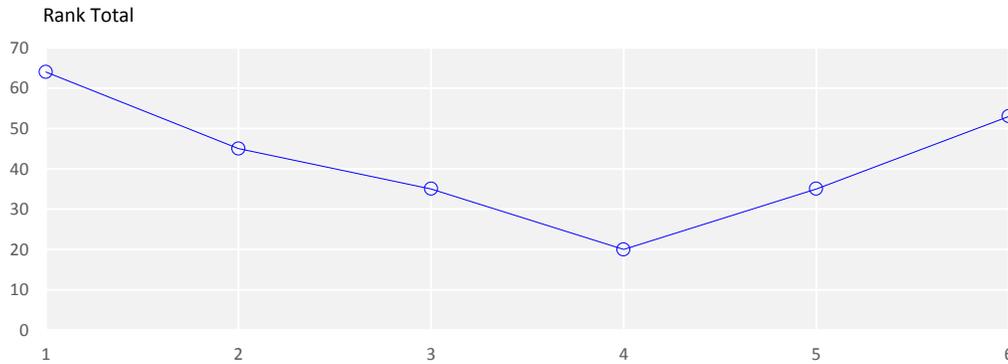


Figure 6: Rank totals of the best subset regression models for predicting $\text{Log}(K_vDA)$

References

- D'Agostino, R. B. and Stephens, M. A. (1986). *Goodness-of-fit Techniques*, New York: Marcel Dekker
- Yap, B. W. and C. H. Sim (2011). Comparisons of various types of normality tests. *Journal of Statistical Computation and Simulation*, 81:12, 2141-2155, doi: 10.1080/00949655.2010.520163
- Royston, J. P. 1982. An extension of Shapiro and Wilk's W test for normality to large samples. *Appl. Statist.*, 31: 115–124.
- Shapiro, S. S. and Wilk, M. B. (1965). An analysis of variance test for normality (complete samples). *Biometrika*, 52: 591–611.
- Lilliefors, H. W. (1967). On the Kolmogorov–Smirnov test for normality with mean and variance unknown. *J. Amer. Statist. Assoc.*, 62: 534–544.

- Cheng C., Song, J., Chen, X. and Wang, D. (2011). Statistical Distribution of Streambed Vertical Hydraulic Conductivity along the Platte River, Nebraska. *Water Resource Management* 25, pp. 265–285; doi: 10.1007/s11269-010-9698-5.
- Cramer, H. 1928. On the composition of elementary errors. *Skandinavisk Aktuarietidskrift*, 11: 13–74. 141–180
- von Mises, R. 1931. *Wahrscheinlichkeitsrechnung und Ihre Anwendung in der Statistik und Theoretischen Physik* Edited by: Deuticke, F. Vol. 6.1, Leipzig
- Smirnov, N.V. *Sui la distribution de w^2 (Criterium de M.R.v. Mises)*, C.R. (Paris) 202 (1936), pp. 449–452 (6.1)
- Koning, A. J. (2015). Normality Tests: Comparisons. In book: Wiley StatsRef: Statistics Reference Online, pp. 1-3. 10.1002/9781118445112.stat03893.pub2.
- USDA-NRCS (2018). Description of SSURGO Database. Natural Resources Conservation Service, United States Department of Agriculture. Web Soil Survey. Available online at <https://websoilsurvey.nrcs.usda.gov/>. Accessed (03/28/2018).
- USDA-NRCS (2015). Soil Data Viewer 6.2 User Guide. https://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs142p2_052432.pdf
- Goswami D., Kalita, P.K., and Mehnert, E. (2010). Modeling and simulation of baseflow to drainage ditches during low-flow periods. *Water Resour Manag* 24:173–191.
- Chen, X.H., Shu. L. (2002). Stream-aquifer interactions: Evaluation of depletion volume and residual effects from ground water pumping. *Ground Water* 40(3):284–290
- Sun, D., Zhan, H. (2007). Pumping induced depletion from two streams. *Adv Water Resour* 30:1016–1026
- Chen, X.H. (2000) Measurement of streambed hydraulic conductivity and its anisotropy. *Environ Geol* 39(12):1317–1324
- Chen, X.H. (2004) Streambed hydraulic conductivity for rivers in south-central Nebraska. *J Am-Water Resour Assoc* 40(3):561–574
- Chen, X.H. (2005) Statistical and geostatistical features of streambed hydraulic conductivities in the Platte River, Nebraska. *Environ Geol* 48(6):693–701
- Chen, X.H. (2007) Hydrologic connections of a stream-aquifer-vegetation zone in south-central Platte River valley, Nebraska. *J Hydrol* 333:554–568.doi:10.1016/j.jhydrol.2006.09.020

Information Transfer Program Introduction

The Nebraska Water Center has a long and proud tradition of actively pursuing a widely diverse information transfer program. USGS funding underwrites a range of public and professional information and educational efforts, including: (1) four quarterly issues of the Water Current newsletter, which are mailed to more than 2,800 subscribers and appears as an online pdf; (2) updating and reprinting Water Center fact sheets and informational brochures; (3) more than 20 press releases reporting on water-related research, education, event and outreach programming from across the University of Nebraska or promoting the NWC and WSL; (4) direct support for two internet web sites and Facebook, Twitter and YouTube accounts; (5) publicity and supporting materials for an annual water law conference, public lecture series, water symposium, and water and natural resources tour; (6) coordinating UNL Extension's largest public program and student recruitment event of the year at Farm Progress Co.'s Husker Harvest Days farm show; (7) other publications and events; and (8) publication and distribution of full-color annual reports.

Since 2012 NWC has been an integral part of the Daugherty Water for Food Global Institute, a global initiative involving all University of Nebraska water faculty and staff with a mission of greater global agricultural water management efficiency. NWC and DWFI are still co-located together at the University of Nebraska's new "Nebraska Innovation Campus" since September 2014. The two units continue serving unique clientele and missions, as well as cooperating closely in a number of areas.

Information Transfer Plan

Basic Information

Title:	Information Transfer Plan
Project Number:	2016NE289B
Start Date:	3/1/2017
End Date:	2/28/2018
Funding Source:	104B
Congressional District:	NE-001
Research Category:	Not Applicable
Focus Categories:	Education, None, None
Descriptors:	None
Principal Investigators:	Chittaranjan Ray, Steven W. Ress

Publication

1. Quarterly Newsletter "Water Current" (4 per year)

Other Print Resources (distributed free to clientele and public):

Brochures and pamphlets:

These are produced as needed to support Water Center programming and activities. They include, but are not limited to, mission and programming of the Nebraska Water Center, NU Water Sciences Laboratory, annual Water and Natural Resources Tour and for other programs affiliated with or sponsored by the Nebraska Water Center. All are posted online, as online PDFs as well.

Water Center fact sheets:

Generally, two pages, front-to-back, full color, produced as needed. Used to inform and promote general mission areas, or for specific programs, seminars, conferences, tour, etc.

Electronic Resources:

Nebraska Water Center:

<http://watercenter.unl.edu/>

Water Sciences Laboratory:

<http://waterscience.unl.edu>

Facebook:

<facebook.com/NebraskaWaterCenter>

Twitter:

<twitter.com/NebrWaterCenter>

YouTube:

<Youtube.com/NebraskaWaterCenter>

Conferences, Seminars, Tours, Workshops, Other Outreach:

Water Law Conference:

This one-day event was planned and hosted by the University of Nebraska College of Law at the College of Law. The conference focuses on current Nebraska water law in such areas as water right transfers, drainage issues, Clean Water Act enforcement, etc. and is primarily used as an annual updating of Nebraska water law primarily for practicing attorneys and water professionals, but is open to all. Continuing Legal Education (CLEs) credits are typically available in Nebraska, Iowa and Colorado. The event was last held in October 2017 and will be held again in October 2018. It generally attracts 120 to 150 participants.

Water Symposium:

The annual water symposium was a two-day event in 2017 with the theme focusing on "Managing Impacts to Water Quality in Production Agriculture" and other Nebraska water issues of current importance. Both panel discussions and individual speakers are featured. The event is co-sponsored by UNL's Institute of Agriculture and Natural Resources, The Robert B. Daugherty Water for Food Global Institute and the USGS Nebraska Water Science Center. The event was last held in October 2017 and will be held again in October 2018.

Water and Natural Resources Seminars:

An annual series of seven or eight free lectures conducted roughly every other week from January to April. The series dates to the early 1970's. It covers a broad range of water and natural resource-related topics and is often themed to a particular area of research or interest. Individual lectures attract a broad public audience of 60 to 100. Normally 20-25 students enroll in the seminar as a one credit hour course, offered through the University of Nebraska-Lincoln's School of Natural Resources. News releases, Internet and social media postings support the lectures. Most lectures are taped and posted online at the Nebraska Water Center's YouTube account for public viewing.

Water and Natural Resources Tour:

The tour is in its 46th year, dating to UNL Extension "Irrigation tours" first conducted in the early 1970's. The 2017 tour explored Nebraska's central Platte River basin and the many uses and users associated with what is arguably Nebraska's most important surface water resource. Tour attendees include state legislators, congressional staff, faculty, students, agricultural producers and water-related professionals. Young water professionals in the Nebraska State Irrigation Association's "Water Leaders Academy" are encouraged to attend through the offer of a reduced registration rate. Sponsorships and registration fees pay all tour expenses. The event is jointly sponsored with The Central Nebraska Public Power and Irrigation District, UNL's Institute of Agriculture and Natural Resources and Robert B. Daugherty Water for Food Global Institute and many other entities.

Faculty Mentoring:

The Nebraska Water Center helps mentor new water faculty, as well as graduate students and post-doctoral researchers, to help them establish successful careers. Newer faculty from the many academic units within the University of Nebraska, particularly those doing water-related research, teaching or outreach work, can attend Nebraska Water Center-sponsored brown bag sessions during the year where they get acquainted and receive advice from senior faculty and external partners on topics such as working with stakeholders, multidisciplinary research, and managing large data sets over their careers. In addition to helping link individual faculty members to groups, Nebraska Water Center faculty and staff meet with faculty individually as needed on an ongoing basis.

Research faculty retreats, for all University of Nebraska water-related faculty, are held typically twice per year to facilitate interdisciplinary cooperation for the purposes of grant writing and research collaborations. These retreats have been notably successful in getting faculty to work together on successful grant applications. These retreats have been held at NU campuses statewide and attendance has grown to oftentimes up to 100 faculty in attendance.

Other Outreach:

Nebraska Water Center staff routinely provides talks for groups and responds to requests for information. These include requests for water-related presentations from the public schools, the media, non-profit organizations, government organizations dealing with water issues and many others.

The Water Sciences Laboratory, established in 1990, is part of the Nebraska Water Center. It is a unique, state of the art analytical laboratory focused on teaching student researchers and developing new methodologies for the detection of trace contaminants such as explosives; pesticides and their metabolites; pharmaceuticals; steroid hormones in water, tissues, sediments and wastewater; cyanotoxins in lake environments; and new tools for isotope fingerprinting and

geochemical tracers. Publicity, media relations, Internet visibility, marketing and other communications requirements of the laboratory are handled by the Nebraska Water Center.

The University of Nebraska-Lincoln's Pesticide Safety Education Office, tasked with educating licensed pesticide applicators on proper use of restricted and non-restricted use pesticides of all types, also relies on the Nebraska Water Center for much of its media support, as well as helping publicize a statewide series of educational seminars for applicators preparing to take state license examinations. The unit has no dedicated communications staff. Due to its essential water quality-related mission, the Nebraska Water Center helps fulfill those needs.

Educational Displays:

The Nebraska Water Center makes public exhibits in association with conferences, symposiums, trade shows, educational open houses and water and environmental education festivals. Nebraska Water Center staff make presentations and sit on steering committees for such annual educational and informational festivals as "Earth Wellness Festival" and others. For the past 10 years, the Nebraska Water Center's communicator has led UNL research and Nebraska Extension exhibits at Penton Industries' "Husker Harvest Days," the nation's largest irrigated farm exposition, which has more than 600 commercial exhibitors. During the three-day agricultural show, more than 25,000 attendees typically tour UNL research and Nebraska Extension exhibits.

Primary Information Dissemination Clientele:

U.S. Department of Agriculture
U.S. Environmental Protection Agency
U.S. Geological Survey
U.S. Bureau of Reclamation
U.S. Army Corps of Engineers
U.S. Bureau of Land Management
Nebraska Department of Natural Resources
Nebraska Department of Agriculture
Nebraska Health and Human Services System
Nebraska Department of Environmental Quality
Nebraska Environmental Trust Fund
Nebraska Association of Resources Districts (and 23 individual NRDs)
Nebraska Congressional delegation
Nebraska State Senators
Public and private power and irrigation districts
The Audubon Society
The Nature Conservancy
Nebraska Alliance for Environmental Education
Nebraska Earth Science Education Network
Other state Water Resources Research Institutes
University and college researchers and educators
NU students Public and parochial science teachers
Farmers
Irrigators
Irrigation districts and ditch companies
Private citizens

Cooperating Entities:

In addition to primary support from the USGS, the following agencies and entities have helped fund communications activities by the UNL Water Center during the past year.

U.S. Environmental Protection Agency
U.S. Department of Agriculture
Nebraska Department of Environmental Quality
Nebraska Research Initiative
Nebraska Game and Parks Commission
Nebraska Environmental Trust
Nebraska Department of Environmental Quality
National Water Research Institute
Nebraska Public Power District
Central Nebraska Public Power and Irrigation District
Farm Credit Services of America
Kearney Area Chamber of Commerce
Nebraska Association of Resources Districts
UNL Institute of Agriculture and Natural Resources
UNL Agricultural Research Division
UNL College of Agricultural Sciences and Natural Resources
UNL School of Natural Resources
University of Nebraska Robert B. Daugherty Water for Food Institute
NU College of Law
USGS Nebraska Water Science Center
Nebraska Center for Energy Sciences Research
Nebraska Water Balance Alliance

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	1	2	0	0	3
Masters	1	0	0	0	1
Ph.D.	0	3	0	0	3
Post-Doc.	0	2	0	0	2
Total	2	7	0	0	9

Notable Awards and Achievements

Jeff Westrop, Ph.D. student, working on the 104(g) project submitted supplemental funding to the Geological Society of America. He was selected as one of the top ten applicants and received the ExxonMobil Geological Society of America Geoscience Grant.