

**Nebraska Water Center
Annual Technical Report
FY 2015**

Introduction

Dr. Chittaranjan Ray, P.E., professor in Civil Engineering Department at the University of Nebraska-Lincoln, took over as the interim director of the Nebraska Water Center as of August 1, 2013. Steve Ress and Tricia Liedle serve as the communications coordinator and program specialist, respectively. The Nebraska Water Center staff also includes Rachael Herpel as legislative liaison and outreach coordinator; and Craig Eiting as web developer and desktop publisher. The Nebraska Water Center also underwent a name change in February 2012 becoming the Nebraska Water Center, a part of the Daugherty Water for Food Institute at the University of Nebraska (formerly known as the University of Nebraska-Lincoln's UNL Water Center).

The Nebraska Water Center is currently housed with the Robert B. Daugherty Water for Food Global Institute, which is located at 2021 Transformation Dr., Ste. 3220, Lincoln, NE 68588-6204 U.S.A.

The Nebraska Water Center was the lead organizer for several events. First was a one-day science and policy symposium showcasing water-related research and programming in Nebraska on March 19, 2015. Its focus was on "High Plains Aquifer: Sustainability for Food Production and Water Supply." The event, was co-sponsored by USGS Nebraska Water Science Center and featured Donald Whittemore from the Kansas Geological Survey, University of Kansas speaking on "A Simple, First-Order Approach for Assessing Prospects for Sustainability of the High Plains Aquifer in Western Kansas." Directly following was a one-day water law conference on March 20, designed for practicing attorneys and water professionals, but open to the public. It was co-sponsored by University of Nebraska College of Law. In June the Nebraska Water Center hosted its 44th Annual Water Tour focusing on "The Republican River Watershed" from June 16-18. In October a faculty/stakeholders retreat was held on the University of Nebraska-Kearney campus.

Research Program Introduction

For the 2015 fiscal year, four research seed grants received funding through the USGS 104(b) program. These were: (1) Design of Multi-Scale Soil Moisture Monitoring Networks in Agricultural Systems Using Hydrogeophysics; and (2) Fate of Manure-Borne Antimicrobials Monensin, Lincomycin, and Sulfamethazine and Potential Effects to Nitrogen Transformation in Soil; and (3) Climate Variability and Decision Support Tool for Optimizing Yields with Limited Water Available for Irrigation; and (4) Development of Smart Alginate Hybrid Beads for Eco-Friendly Water Treatment.

Seed grants chosen for the upcoming year 2016 are: (1) Evaluation of Changing Irrigation Management on Ground Water Recharge and Quality; (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.

The Nebraska Water Sciences Laboratory (WSL) core facility, a part of the Nebraska Water Center, 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. Faculty, staff, and students have analyzed thousands of samples at the facility since it was established in 1990.

Fate of steroid hormone conjugates and E. coli from manure in soil: Potential sources of free hormones and pathogens in forages and the environment?

Basic Information

Title:	Fate of steroid hormone conjugates and E. coli from manure in soil: Potential sources of free hormones and pathogens in forages and the environment?
Project Number:	2014NE260B
Start Date:	3/1/2015
End Date:	2/29/2016
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Agriculture, Non Point Pollution, Solute Transport
Descriptors:	None
Principal Investigators:	Amy Millmier Schmidt, Shannon Bartelt-Hunt, Xu Li

Publications

There are no publications.

2015-16 Annual Report

Project #2104NEB260B

Fate of steroid hormone conjugates and *E. coli* from manure in soil: Potential sources of free hormones and pathogens in forages and the environment?

May 2016

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Co-Investigators: Daniel Snow, Director, Water Sciences Laboratory
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Reporting Period: March 1, 2014 through February 28, 2016

Financial Support: USGS

Participants:	<u>Undergraduate Students</u>	<u>Graduate Students</u>
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**Partially supported by this funding*

INTRODUCTION

Project Summary. The continued use of livestock manure for fertilization of agricultural land and the implications of manure-borne contaminants in the environment are important regionally and nationally. Among the compounds found in manure are pathogenic organisms, steroids, hormones, and other endocrine disrupting compounds (EDCs) (USEPA, 2004). Metabolites of steroid compounds administered to livestock are among the growing list of EDCs that are suspected as harmful to humans and animals for their ability to disrupt their natural hormone system. Endogenous (naturally occurring) steroidal hormones are commonly found in the manure and urine of livestock (Hoffmann *et al.*, 1997; Bartelt-Hunt *et al.*, 2012) and in runoff from cattle feedlots (Bartelt-Hunt *et al.*, 2012). Likewise, synthetic steroidal hormones used for beef cattle growth promotion can be found in the manure produced by beef cattle (Schiffer *et al.*, 2001).

Although “free” steroid hormones have been detected in surface waters at concentrations that are of concern (Kolpin *et al.*, 2002), there is question about what influences the deconjugation of steroids that are excreted in conjugated forms (glucuronides and sulfates) and are biologically less active than free steroids. Deconjugation, or hydrolysis, of steroid conjugates to their free form can be carried out by biological (enzymatic) or chemical (non-enzymatic) means (Gomes *et al.*, 2009). *Escherichia coli* (*E. coli*) has been suggested as a potential microorganism responsible for this process (D’Ascenzo *et al.*, 2003).

While *E. coli* O157:H7 is a very prevalent enterohemorrhagic *E. coli* (EHEC) associated with disease in humans, Shiga toxin-producing *E. coli* (STEC) O26 bacteria is recognized as an emerging pathogen of concern to both human and ruminant health. The World Health Organization has identified O26 STEC as the second most important serogroup of *E. coli* (WHO, 1998). While researchers have identified persistence of *E. coli* O157:H7 in soil (Looper et al., 2009), water (Chapman et al., 2000), and vegetable plant tissue (Solomon et al., 2002), the potential for internalization of *E. coli* in forage crops has been studied very little by comparison. Looper et al. (2009) reported that *E. coli* O157:H7 may become internalized in tall fescue plant tissue. The funding for this project allowed for the investigation of three phenomenon: the role of *E. coli* O26:H11 in the deconjugation of steroid hormones in beef cattle urine, the ability of tall fescue to internalize *E. coli* O26:H11, and the ability of tall fescue to internalize steroid hormones. The broad hypothesis was that the presence of *E. coli* O26:H11 in soils receiving applications of steroid hormones in cattle urine would increase the transformation of conjugated steroids to free steroids and facilitate the uptake of these compounds by tall fescue. Furthermore, we anticipated internalization of *E. coli* in the plant tissue of tall fescue grown on soil receiving application of the pathogen.

The project was completed in February 2016 and, as such, this represents the final report on this project.

Objectives. This research project was designed to quantify the effect of *E. coli* O26:H11 on deconjugation of steroids excreted in beef cattle urine and determine the ability of tall fescue to internalize steroid hormones and *E. coli* O26:H11 present in soil.

Specific objectives were to:

1. identify and quantify steroid conjugates in fresh beef cattle urine;
2. assess the effect of *E. coli* O26:H11 on deconjugation of steroid hormones, and
3. quantify the internal accumulation of steroid hormones and *E. coli* O26:H11 in soil and plant tissue of tall fescue receiving contaminated wastewater.

RESEARCH PROGRAM

Obj. 1: Identify and quantify steroid conjugates in fresh beef cattle urine.

Fresh urine (6 L) was collected from beef steers at the USDA-ARS U.S. Meat Animal Research Center near Clay Center, Nebraska, frozen, and transported to the University of Nebraska – Lincoln. Upon thawing, samples were pooled and processed at the UNL Water Sciences Lab for analysis to quantify concentrations of 21 steroid hormones in the fresh (conjugated) and enzyme treated (deconjugated) urine using the methods described by Gomes *et al.* (2009). Results of the analysis are summarized in Table 1.

Table 1. Concentrations of steroid hormones in fresh (as-excreted) and enzyme treated beef steer urine

Steroid Hormone	Concentration, ng/mL		Detection Limit, ng/mL
	<i>As-excreted</i>	<i>Enzyme Treated</i>	
17 α -Hydroxyprogesterone	0.000	0.000	0.010
4-Androstenedione	0.124	0.358	0.010
α -Estradiol	0.000	2.256	0.010

Androstanedienedione	5.677	5.601	0.010
Androsterone	0.000	0.000	0.010
α -Trenbolone	0.000	0.728	0.010
β -Trenbolone	0.000	0.000	0.010
Trendione	0.000	0.000	0.010
α -Zearalanol	0.000	0.000	0.010
α -Zearalenol	0.000	0.000	0.010
β -Zearalanol	0.000	0.000	0.010
β -Zearalenol	0.000	0.000	0.010
β -Estradiol	0.000	0.000	0.010
Estriol	0.000	0.000	0.010
Estrone	1.338	0.000	0.010
Epitestosterone	0.000	2.703	0.010
Ethynyl Estradiol	0.000	0.000	0.010
Melengesterol Acetate	0.000	0.000	0.010
Progesterone	0.000	0.508	0.010
Testosterone	0.000	0.000	0.010
Testolactone	0.000	0.000	0.010

Obj. 2/3: Assess the effect of *E. coli* O26:H11 on deconjugation of steroid hormones and Quantify the internal accumulation of steroid hormones and *E. coli* O26:H11 in soil and plant tissue of tall fescue receiving contaminated wastewater.

Endophyte-free tall fescue (*Festuca arundinacea*) was seeded (September 2015) into 24-compartment plastic inserts (Hummert International TRI-1204) containing a standard soil mix provided by the UNL Horticulture Greenhouse (1 part soil:1 part sand:1 part Vermiculite:2 parts Peat moss) and placed inside plastic flats (T.O. Plastics STF-1020-OPEN-NH). A total of 20 trays were established. Plants were grown in a greenhouse maintained at 21°C (70°F) and 60% relative humidity with lighting provided between 6:00 a.m. and 10:00 p.m. Plants received regular watering to a depth of 1.3 cm in trays as needed and were manually trimmed to 10 cm when needed.

Bacterial Transformation. *E. coli* O26:H11 strain EH1534 (ATCC BAA-1653) was obtained from the American Type Culture Collection (Manassas, VA, USA) and was cultivated in anoxic tryptic soy broth (TSB) medium (pH 6.7) at 37°C. Cells were transformed with light producing plasmid (pAK1-*lux*) following the methods described by Moulton *et al.* (2009b). Briefly, an ampicillin (AMP) resistance gene cassette was combined with the *lux* gene cassette for transformation with plasmid pAK1-*lux* (*E. coli*-pAK1-*lux*) for generation of photons and imaging. The plasmid (11,904 bp) is a broad-host-range cloning vector that is maintained at a medium copy number, is mobilizable, is compatible with numerous plasmid replicons, and contains the *lux* operon (Frackman *et al.*, 1990). The *lux* operon is a cluster of genes (*lux* CDABE) isolated from a nematode symbiont bacterium *Xenorhabdus luminescens* (luciferase) (Karsi *et al.*, 2006). This operon also encodes the biosynthetic enzymes for the proper substrate.

Colonies were grown overnight at 37°C on plates prepared with LB+AMP. The XR/MEGA-10Z™ camera with a 18 mm camera lens was positioned 250 mm above the imaging target (100 mm Petri dish) to confirm bioluminescence (Figure 1).

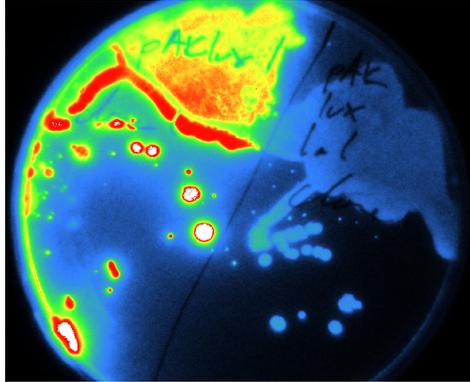


Figure 1. *E. coli*-pAK1-lux plate image illustrating plasmid luminescence

E. coli-pAK1-lux was grown overnight in Luria Bertani (LB) broth at 37°C on a shaking incubator to achieve an expected concentration of 10^9 CFU/mL. *E. coli*-pAK1-lux was diluted in LB broth to produce cell culture with the desired inoculation concentration of 1.0×10^6 CFU mL⁻¹ for treatment application .

Experimental Design. The study was conducted in a biosecurity level-2 (BSL-2) room in the Insectary Greenhouse on UNL East Campus. Room conditions were maintained at 21°C (70°F) and 60% relative humidity with lighting provided between 6:00 a.m. and 10:00 p.m. daily throughout the trial. Thirteen trays were randomly assigned to one of four treatment groups with the tray serving as the experimental unit as illustrated in Figure 2: UEC (n=3), URI (n=3), ECO (n=3) or CTL (n=1). One tray insert cell was removed from the corner of each treatment tray to allow for easy addition of water and treatment applications to the trays. For the URI treatment, urine (820 mL) and deionized water (820 mL) were applied to each tray beneath the inserts for uptake via plant roots. The UEC trays each received urine (820 mL) beneath the tray inserts and bacterial cell culture (820 mL) was irrigated on the soil by evenly distributing the culture among tray cells at the base of the plants to avoid splashing the liquid on the leaf blades. Soil in the ECO treatment trays was irrigated with bacterial culture (820 mL) in the same manner as it was applied to the UEC trays and deionized water (820 mL) was applied to each tray beneath the inserts for uptake via plant roots. The CTL treatment received 1640 mL of deionized water.

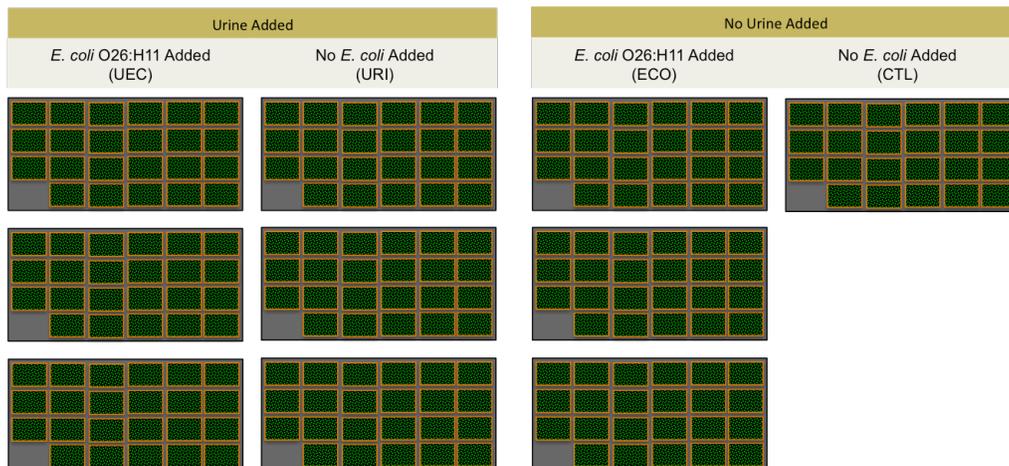


Figure 2. Experimental design

Four plants with soil intact were harvested from each tray on day 1, 4, 7, 14, 21 and 28 post-application of treatments. Collected plants were placed into individual sterile Whirl-pak bags and transported to the Schmidt Lab for processing. Upon removal from the bags, each plant was inverted and the top 10 to 13 cm of plant tissue submerged in 70% ethanol for approximately 20 s and then allowed to air dry in an upright position. Whole plants with intact soil around the roots were imaged with an XR/MEGA-10Z ICCD Camera System operated with Piper Control Software (Stanford Photonics, Inc., Palo Alto, CA).

Plant Tissue Microbial Analysis. The top 10 to 13 cm of plant tissue growth – beginning 3 cm above the soil surface – was removed from each sample using sterile methods. Plant tissue was minced into 2- to 3-mm pieces using sterile scalpels and a sub-sample (1 g) of each tissue sample was homogenized in sterile phosphate buffered solution (PBS). One milliliter samples of homogenate were serially diluted in 20-fold increments in PBS, plated on LB agar, and incubated for 24 h at 37°C. Dilution plates were counted for total colony-forming units (CFU) and photonic images of plates were taken utilizing an XR/MEGA-10Z ICCD Camera System operated with Piper Control Software (Stanford Photonics, Inc., Palo Alto, CA). *E. coli* O26:H11 log₁₀ values were determined based upon total CFU counted from LB agar minus non-emitting colonies (log₁₀ = Total CFU – non-emitting CFU).

Soil Microbial Analysis. Soil samples (1 g) were collected from the area around the roots of each plant and homogenized in sterile phosphate buffered solution (PBS). One milliliter samples of homogenate were serially diluted in 20-fold increments in PBS, plated on LB+AMP agar, and incubated for 24 h at 37°C. Dilution plates were counted for total colony-forming units (CFU) and photonic images of plates were taken utilizing an XR/MEGA-10Z ICCD Camera System operated with Piper Control Software (Stanford Photonics, Inc., Palo Alto, CA). *E. coli* O26:H11 log₁₀ values were determined based upon total CFU counted from LB agar minus non-emitting colonies (log₁₀ = Total CFU – non-emitting CFU).

Plant Tissue Chemical Analysis. The top 10 to 13 cm of plant tissue growth – beginning 3 cm above the soil surface – was removed from each sample using sterile methods. Plant tissue was minced into 2- to 3-mm pieces using sterile scalpels and a sub-sample (1 g) was collected and composited by experimental unit (tray) for each sample event. Samples were analyzed via microwave assisted solvent extraction followed by LC-MS/MS (Snow *et al.*, 2013) to quantify concentrations of free steroid hormones present in the tissue.

Soil Chemical Analysis. Soil samples (1 g) were collected from the area around the roots of each plant and composited by experimental unit (tray) for each sample event. Samples were analyzed via microwave assisted solvent extraction followed by LC-MS/MS (Snow *et al.*, 2013) to quantify concentrations of free steroid hormones present in the tissue.

Statistical Analysis. Concentrations of *E. coli*-pAK1-lux per g dry soil and plant tissue will be calculated for each collection period and used to determine the effect of length of time on concentration of the bacteria in soil and plant tissue. Concentrations of steroid hormones per g dry soil and plant tissue will be analyzed to determine the effects of time, *E. coli* treatment, and *E. coli* treatment x time. Statistical analysis procedures have not yet been completed at the time of this report submission but portions of raw data are presented to illustrate general results.

RESULTS

Obj. 1: Identify and quantify steroid conjugates in fresh beef cattle urine.

As illustrated previously in Table 1, fresh and enzyme treated steer urine were analyzed for the presence of 21 steroid hormones. Three steroid hormones were identified and quantified in the fresh urine: 4-androstenedione, androstenedione, and estrone at 0.12, 5.677, and 1.338 ng/L, respectively. Following enzyme treatment of the urine, six steroid hormones were identified and quantified: 4-androstenedione, α -estradiol, androstenedione, α -trenbolone, epitestosterone, and progesterone at concentrations of 0.358, 2.256, 5.601, 0.728, 2.703, and 0.508 ng/L, respectively. From this data, one would expect that the steroid hormones present in the enzyme treated urine would be identified in the soil and plant tissue of the UEC samples if *E. coli* were responsible for deconjugation of these compounds.

Obj. 2: Assess the effect of *E. coli* O26:H11 on deconjugation of steroid hormones

Analysis of soil and plant tissue samples from all treatments on days 1, 4 and 7 post-treatment application have been completed. Statistical analysis to determine the effects of time, *E. coli* treatment, and *E. coli* treatment x time on concentrations of steroid hormones in soil and plant tissue is underway at the time of this report submission.

Preliminary data on concentrations of the six steroid hormones quantified in enzyme treated steer urine (Table 1) in plant tissue and soil on days 1, 4, and 7 post-treatment are illustrated in Figure 2. All soil samples, regardless of treatment and time, contained measurable concentrations of 4-androstenedione, androstenedione, and progesterone. Greater concentrations of androstenedione were detected in soil from the UEC treatment on days 1 and 7 than URI soil while lesser concentrations of this compound were detected in ECO and CTL soil on all days compared to URI soil. Progesterone was detectable in plant tissue samples for each sample event and treatment, with α -estradiol and 4-androstenedione detected in the plant tissue in the UEC treatment on day 4 and the ECO treatment on day 1, respectively. While these results are interesting, little conclusive information can be gleaned prior to full statistical analysis of the data.

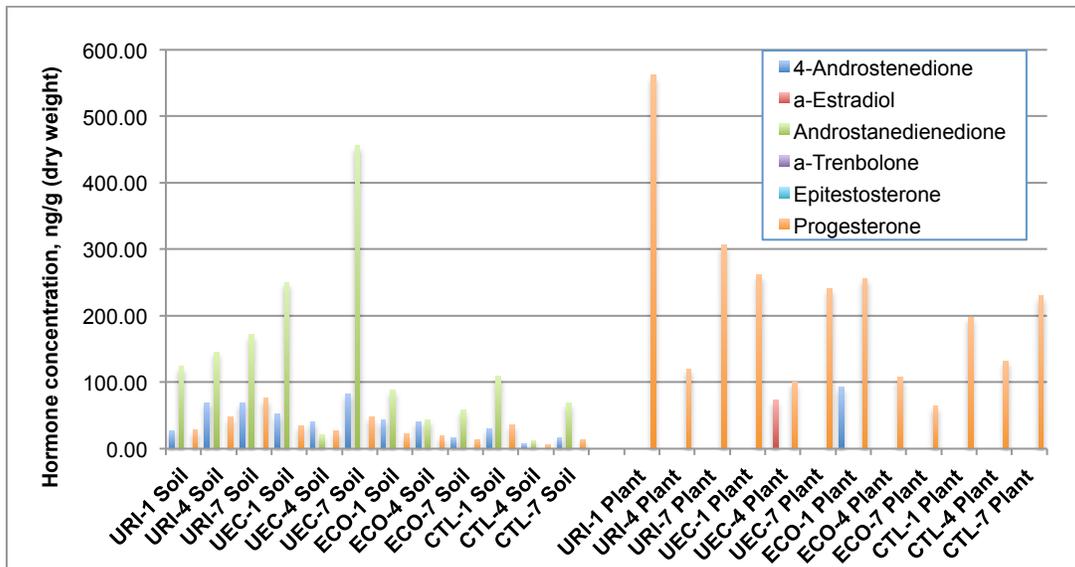


Figure 2. Mean steroid hormone concentration by treatment, day, and sample type for steroid hormone compounds identified in enzyme treated steer urine

Obj. 3: Quantify the internal accumulation of steroid hormones and *E. coli* O26:H11 in soil and plant tissue of tall fescue receiving contaminated wastewater.

Images of intact plants and microbial plates containing serial dilutions of plant tissue and soil have been obtained for all samples. Statistical analysis to determine the effects of time, treatment, and treatment x time on concentrations of *E. coli*-pAK1-lux in soil and plant tissue is underway at the time of this report submission.

However, the following figures (Figures 3 through 6) represent selected whole plant and microbial plate images collected during the duration of this project. These images illustrate the presence of the transformed *E. coli* O26:H11 (*E. coli*-pAK1-lux) in plant tissue and soil over time following application of treatments. Further data analysis is currently underway.

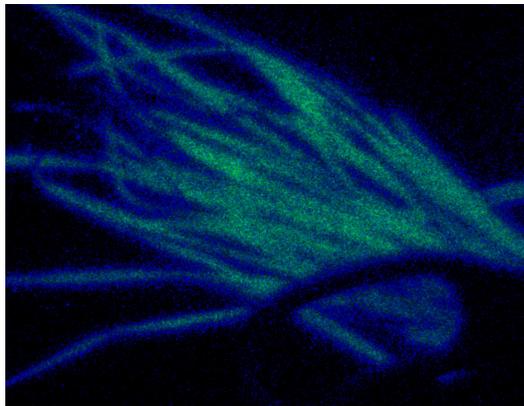


Figure 3. Whole plant image collected on day 14 from a plant sampled from the ECO treatment illustrating *E. coli*-pAK1-lux presence.

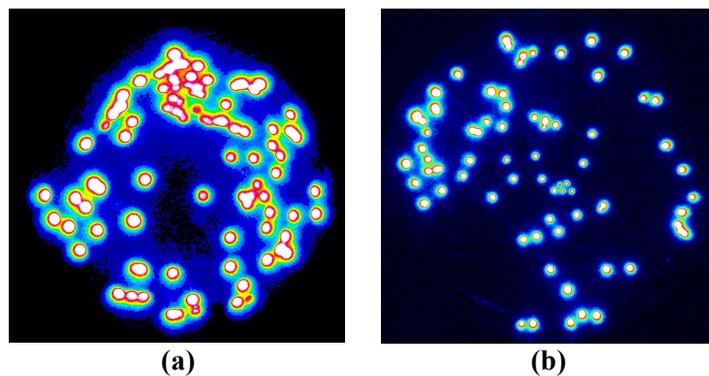


Figure 4 a-b. Microbial plate images for soil collected on (a) day 7 (10^{-5} dilution) and (b) day 21 (10^{-3} dilution) for soil samples from the ECO treatment illustrating *E. coli*-pAK1-lux presence.

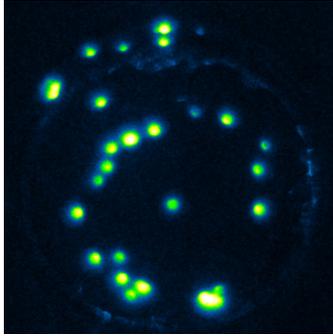


Figure 5. Microbial plate image for plant tissue collected on day 7 (10^{-1} dilution) from the ECO treatment illustrating *E. coli*-pAK1-lux presence.

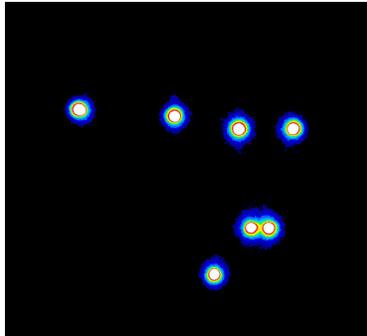


Figure 6. Microbial plate image for plant tissue collected on day 28 (10^{-1} dilution) from the UEC treatment illustrating *E. coli*-pAK1-lux presence.

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Hydroclimatic controls on the conjunctive use of surface and ground water in the Platte River Basin

Basic Information

Title:	Hydroclimatic controls on the conjunctive use of surface and ground water in the Platte River Basin
Project Number:	2014NE262B
Start Date:	3/1/2014
End Date:	10/31/2015
Funding Source:	104B
Congressional District:	1st
Research Category:	Climate and Hydrologic Processes
Focus Category:	Hydrology, Climatological Processes, Groundwater
Descriptors:	None
Principal Investigators:	Francisco MunozArriola

Publications

1. Livneh B., T.J. Bohn, D.S. Pierce, F. Munoz-Arriola, B. Nijssen, R. Vose, D. Cayan, and L.D. Brekke, 2015: A spatially comprehensive, hydrometeorological data set for Mexico, the U.S., and southern Canada 1950-2013, Nature Scientific Data (submitted).
2. Smith, K. B. Kimbal, M. Morton, and F. Munoz-Arriola. Soil Moisture and Evapotranspiration Responses to Extreme Hydrometeorological Events in the Platte River Basins (in progress).
3. Livneh B., T.J. Bohn, D.S. Pierce, F. Munoz-Arriola, B. Nijssen, R. Vose, D. Cayan, and L.D. Brekke, 2015: A spatially comprehensive, hydrometeorological data set for Mexico, the U.S., and southern Canada 1950-2013, Nature Scientific Data (submitted).
4. Smith, K. B. Kimbal, M. Morton, and F. Munoz-Arriola. Soil Moisture and Evapotranspiration Responses to Extreme Hydrometeorological Events in the Platte River Basins (in progress).

2015 Annual Report

Project # 2014NE262B:

Hydroclimatic Controls on the Conjunctive use of Surface and Ground Water in the Platte River Basin

May 5, 2015

Principal Investigator: Francisco Munoz-Arriola, Assistant Professor
Department of Biological System Engineering and School of Natural Resources,
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Reporting Period: March 1, 2014 through February 28, 2015

Financial support: USGS

Participants:

Undergraduate students: Mallory Morton and Daniel Rico

Graduate students: Katherine Smith*

Postdocs: Carlos Carrillo-Cruz*

*Directly funded by this funding

I. INTRODUCTION

1. Project Summary: Problem and research objectives

A major challenge for global to local sustainable development of human activities and ecosystems is present and future availability of water. Water availability (by quantity and quality) is component of an environmental state in a particular time, forced by climate variability and change and regulated by human activities such as land-use changes and population growth. Water quantity and quality (components of a water state) are regulated by the interplay between water and agricultural management practices, which alter the transfer of water across the continuum from the atmosphere to the aquifer and the biogeochemical cycles of elements such as Nitrogen and Phosphorous, both modifying the natural availability of water. Also, resource management practices play a key role shaping the water, energy, and food security under a changing climate through (un)sustainable management practices of water and agricultural resources. Funding of the present project allow the Hydroinformatics and Integrated Hydrology research group to launch a number of activities aiming to improve our ability to predict future water states. Our broad hypothesis states that improved initial conditions and modeling capabilities will be reflected in better representations of future availability of water. Thus, we developed new datasets to force our land surface hydrology models, implement dynamical changes in land use (using remote sensing), and develop the foundation for model integration. Undergraduate, graduate, postdocs have been involved in this project, contributing and lead technologic developments as well as communicating or scientific progresses. We expect to complete this project by October of 2015, in the mean time we present the present (first) report.

2. Objective

To identify the most suitable integration mechanisms to integrate a land-surface hydrologic model and a conjunctive use of surface water-groundwater model through the use of hydroclimatic controls`.

2.1. Particular objectives

- a. Simulate the land surface hydrology of the Platte River Basin using Variable Infiltration Capacities model (VIC).
- b. Develop disaggregation techniques to increase the resolution of VIC forcings and parameters.
- c. Evaluate the sensitivity of land surface hydrology variables and state variables to gradual increments in spatial resolution.
- d. Identify the pertinence of daily to monthly time-steps in vadose zone hydrology simulations using HYDRUS2D (coupled off-line with VIC).

II. RESEARCH PROGRAM

1. The assessment of the hydroclimatology of the Platte River Basin

a. Land Surface Hydrology Model Implementation

At the first stage of the project we characterized the climatology of the Platte River Basin with focus on six sub-basins: Elkhorn, Loup, Lower Platte, Middle Platte, North Plate, and South Platte (Fig. 1). The Platte River Basin encompasses an approximate area of 220,000 km², and ranges from the eastern Rocky Mountains in Colorado and Wyoming to its outlet at the Missouri River in eastern Nebraska. The hydroclimatology across the basin varies, with the western basins receiving much less precipitation than the eastern basins (Fig. 2).

Nebraska relies heavily on the conjunctive use of groundwater and surface water to irrigate agricultural land. The state ranks first nationally in terms of irrigated acres, with about 8.5 million (Census of Agriculture, 2007). Over 565,000 of those acres are irrigated with surface water that has been diverted from streams or rivers. A major contributor to these streams is precipitation in the form of rainfall or snowmelt.

Using the Variable Infiltration Capacity (VIC) model, evapotranspiration (ET) and soil moisture (SM) were simulated. The forcings of the VIC model include precipitation, minimum and maximum temperature, and wind speed. Figure 3 shows the influence precipitation has on ET and SM in the Platte River Basin. These are monthly climatologies for the 2000-2013 period.

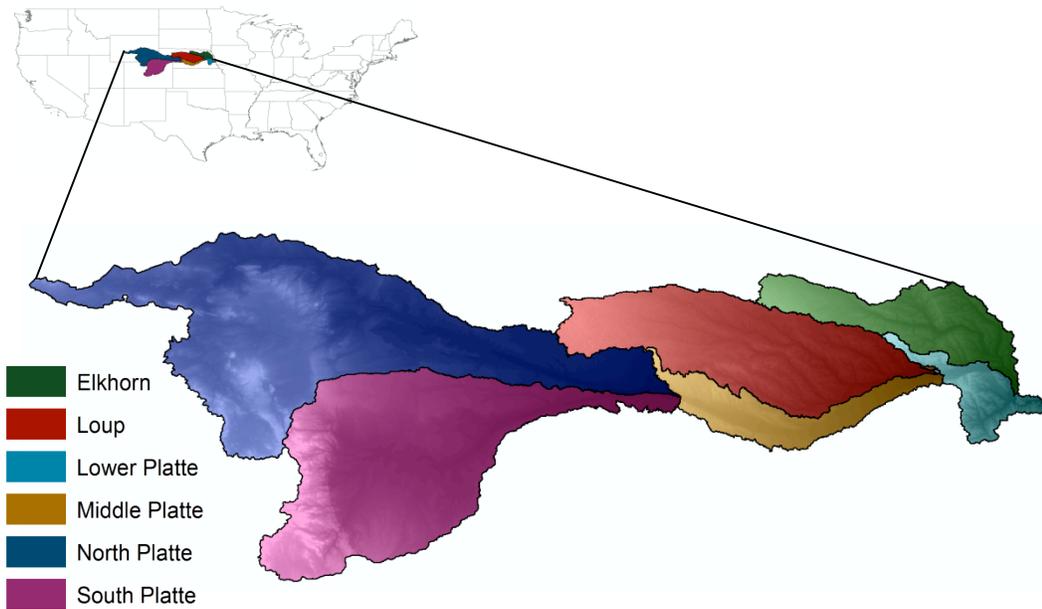


Figure 1: Location of the Platte River Basin with the sub-basins: Elkhorn, Loup, Lower Platte, Middle Platte, North Platte, and South Platte.

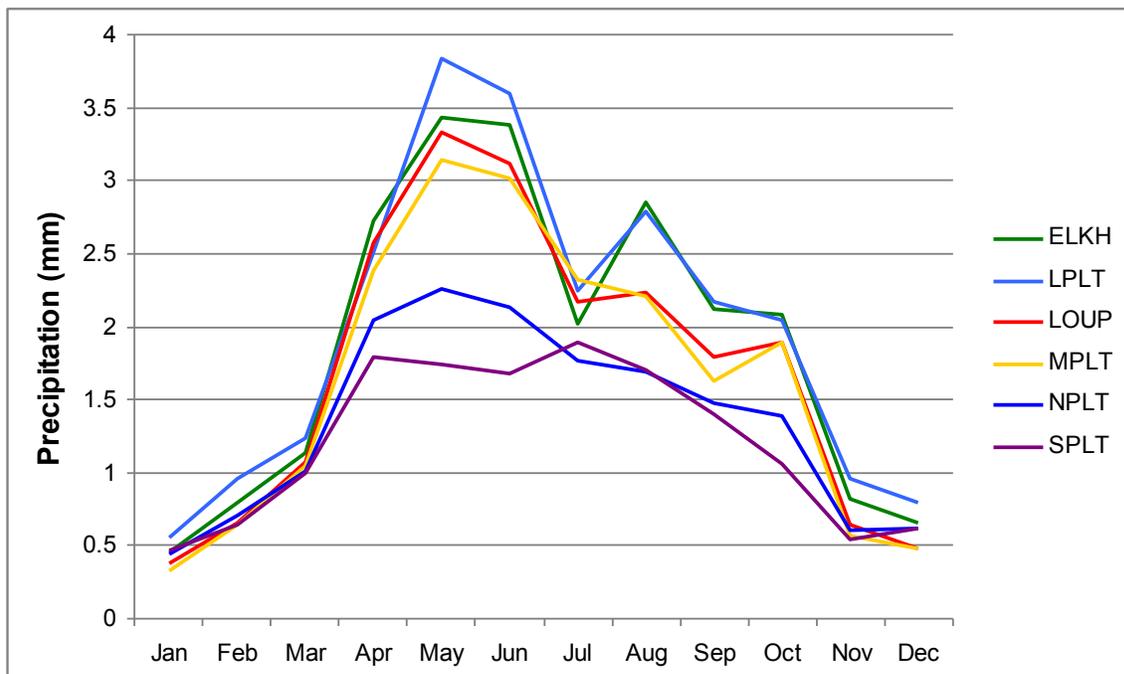


Figure 2: Annual cycle of average precipitation over the sub-basin indicated in Fig. 1.

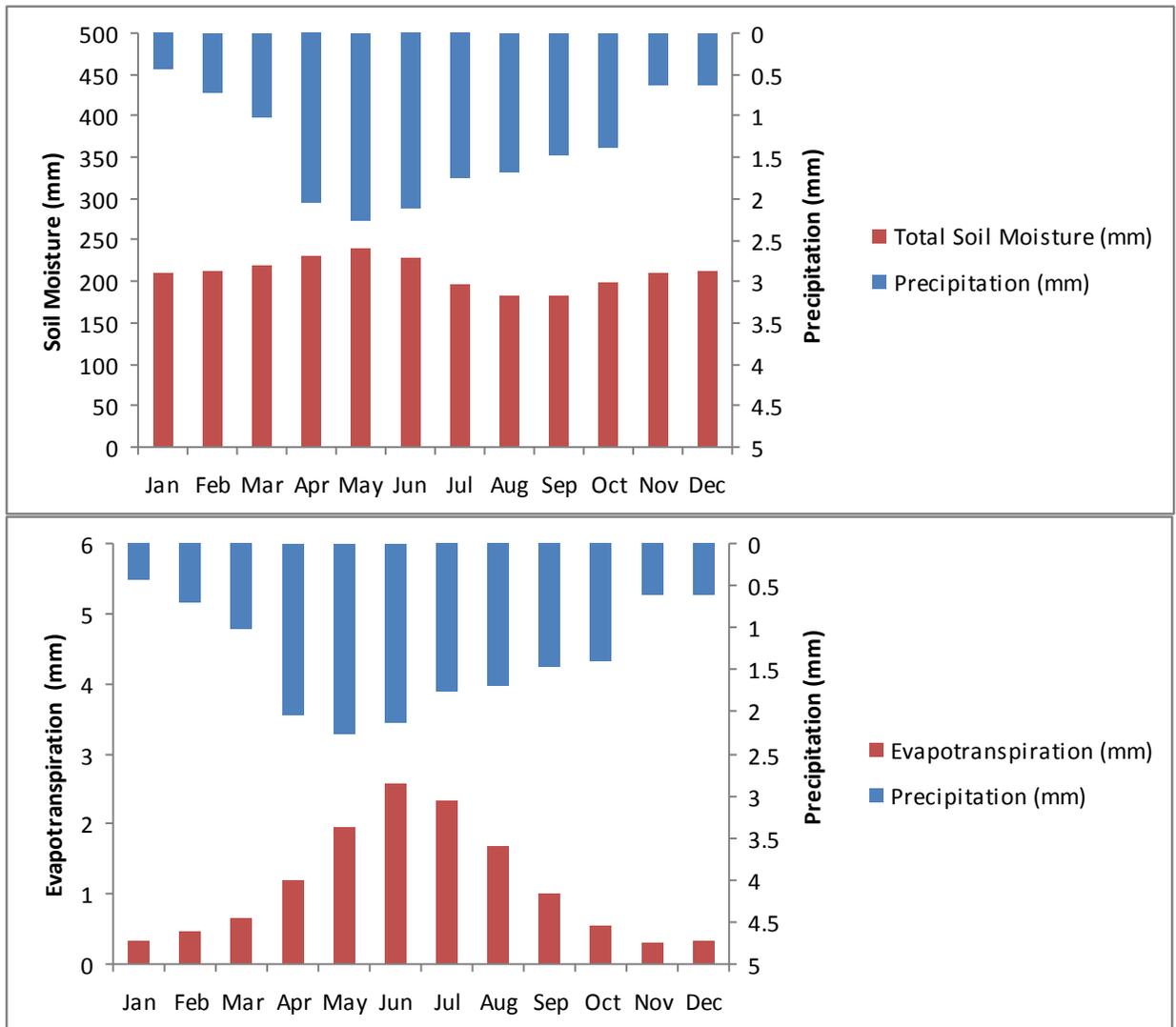


Figure 3: Annual cycle of simulated total soil moisture (top) and evapotranspiration (bottom) as simulated with VIC model over the Platte River Basin.

b. Hydroclimatic Controls

We implemented an experiment using the Land Surface Hydrology (LSH) Variable Infiltration Capacity (VIC) model, which was coupled with a routing model on the PRB to simulate streamflow. A streamflow sensitivity experiment with respect to precipitation and temperature was conducted over the Platte River Basin (PRB) during the years 1925-2005, to investigate if rising temperature or increase in changes in precipitation will be the main drivers of crop irrigation requirements in Nebraska. Our modeling simulation suggests that the PRB is sensitive to changes in precipitation and

temperature, with more conspicuous results for precipitation than temperature. For example, the north region of the PRB experienced a 0.02% (0.09%) change in streamflow value for every 1% change in temperature (precipitation) (Fig. 5). Similarly, the South PRB equaled a 0.02% (0.05%) change in streamflow for every 1% change in temperature (precipitation). The other two selected basins (Loup, and Elkhorn; Fig. 4) show a similar tendency. This work was presented in the 2015 American Meteorological Society annual meeting.

We also developed some tools to pre-process and post-process hydrologic and atmospheric data. In order to manipulate massive input and output files for VIC model, Python (a general purpose high level programming language) scripts were developed. Python codes were used to post process data as well as develop graphs from data in several formats such as ASCII and NetCDF. The advantage of converting VIC flux files into NetCDF format is compact and requiring very little overhead to store the ancillary data that makes the datasets self-describing. We expect to make these codes available to the public for our final report.

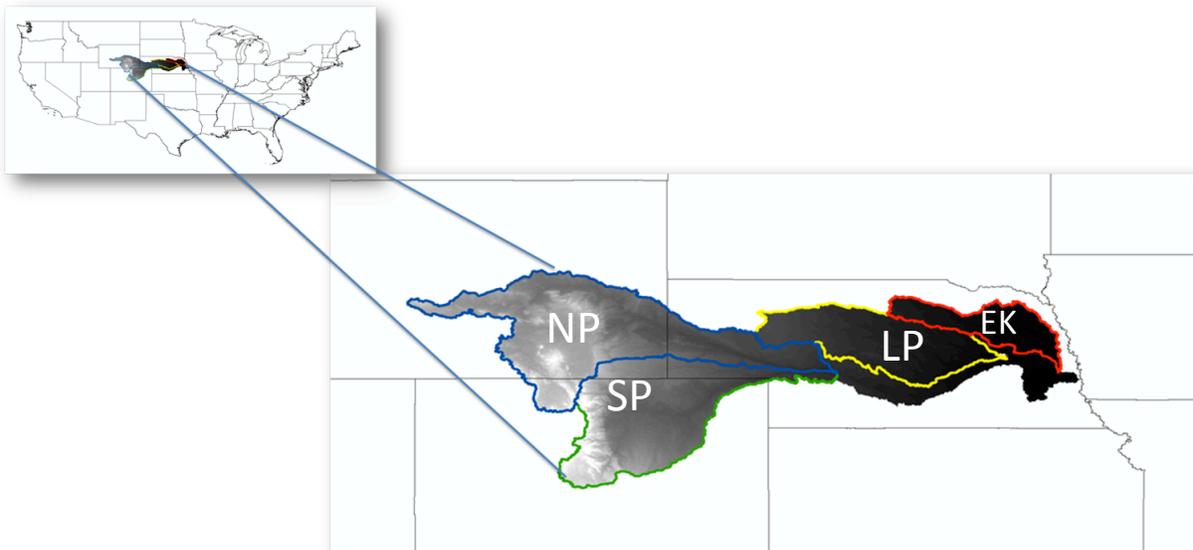


Figure 4: The PRB composed in ArcGIS delineating the four sub basins (North Platte, South Platte, Loup, and Elkhorn).

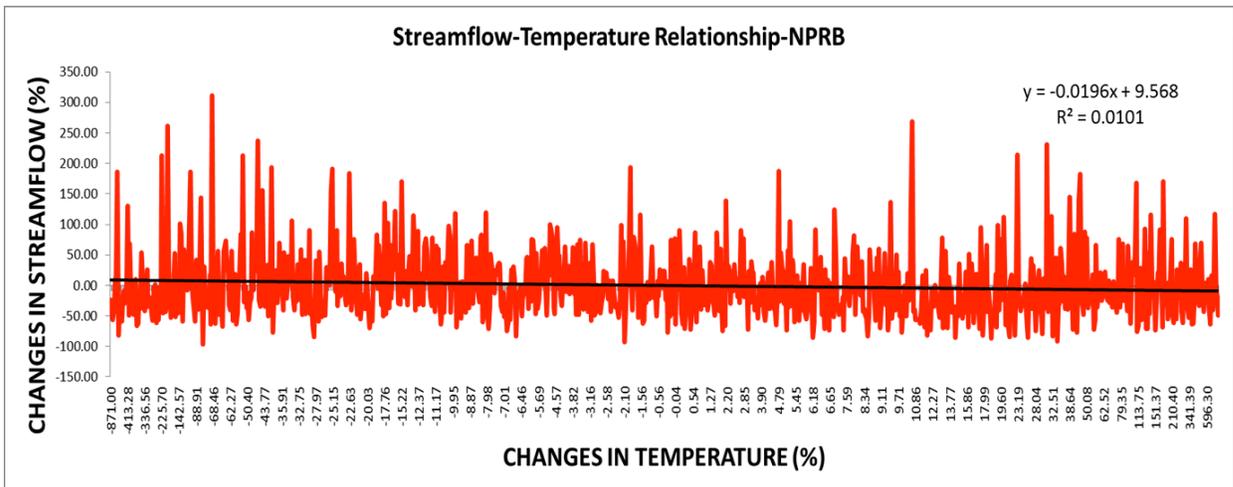
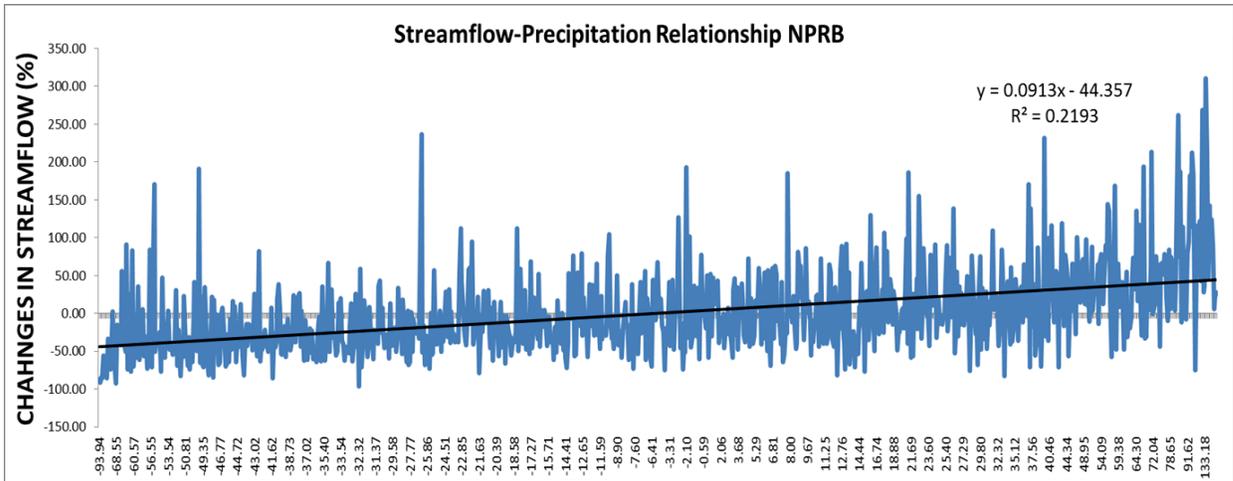


Figure 5: Sensitivity Analysis for the NPRB (additional representations of such analysis are just described) from 1925-2005

c. Crop Irrigation Requirements' responses to Climate Variability

A data set of leaf area index (LAI), evapotranspiration, soil moisture, and other hydroclimatic variables at one sixteenth degree resolution were produced from MODIS data and variable infiltration capacity model (VIC) simulations. LAI is used to characterize plant canopies. It is a vegetation parameter in VIC used to calculate water intercepted by the canopy, canopy resistance, root uptake rate, and evapotranspiration rate. In Figure 6 we evidence the role of dynamical changes in vegetation, through the use of MODIS's LAI. Some of those changes are more conspicuous during the summer, which is a critical season for plant growth and crop productivity. Changes in land use as a product of the influence of extreme Hydrometeorologic and climate events are part of our main interest. We have found that this dynamic LAI variability has an important impact

in extreme years (Fig. 8), which show the soil moisture variability for both a wet (2011) and a dry (2012) event. Thus, Soil moisture (SM) with dynamic LAI provides a comprehensive estimate of water availability for agricultural and ecosystem services' sustainability. Therefore, April-to-July SM and SM percentiles, representing the agricultural growing season, illustrate the effect of floods (i.e. 2011) and droughts (i.e. 2012). Two posters were presented at the American Geophysical Union 2014 Fall meeting and 2015 AMS conference, showing the hydrologic and crop irrigation responses to floods and droughts in the PRB, respectively. The latter was awarded as the best student poster in the Hydrology section.

Although is out of the scope of the present project, we are also exploring the suitability of LANDSAT-LAI to estimate crop evapotranspirative needs in regional hydrologic modeling (Fig. 7). LANDSAT- and MODIS-LAI are aimed to identify how dynamical changes in land-use influence the ET and its relationship with soil moisture. This is of the interest of our colleagues of the Nebraska and California Water Science Centers (Steve Peterson and Randall Hanson, respectively) whom we have started to identify areas of mutual interest and collaboration.

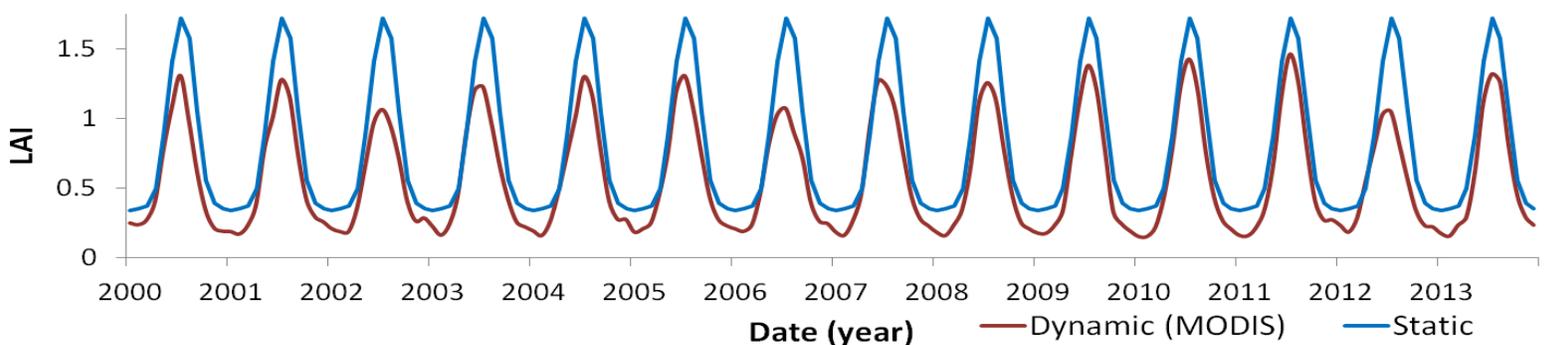


Figure 6: Static Leaf Area Index (LAI; in blue) as is described by default in the VIC model, and the obtained with MODIS dataset (in red) to incorporate interannual variation of greenness in the VIC simulation.

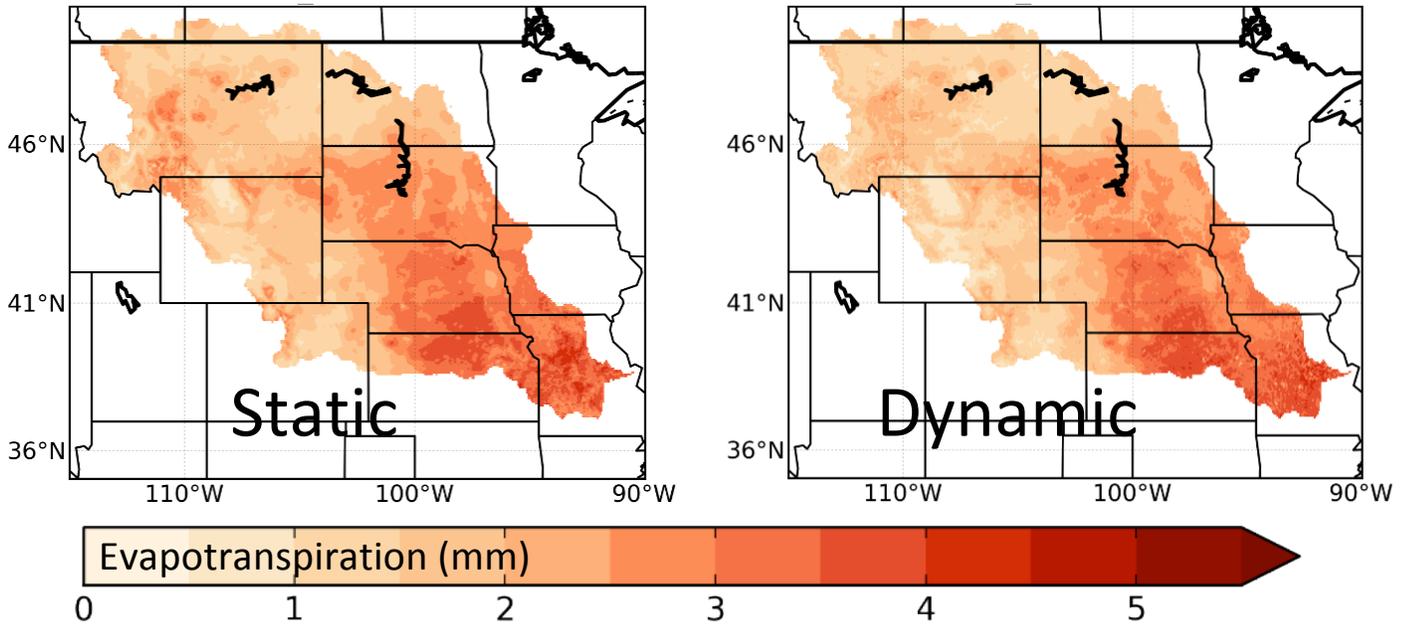


Figure 7: Evaporation simulated by VIC model under two scenarios: with static LAI (left) and dynamic LAI (right) as obtained by LANSDAT imagery.

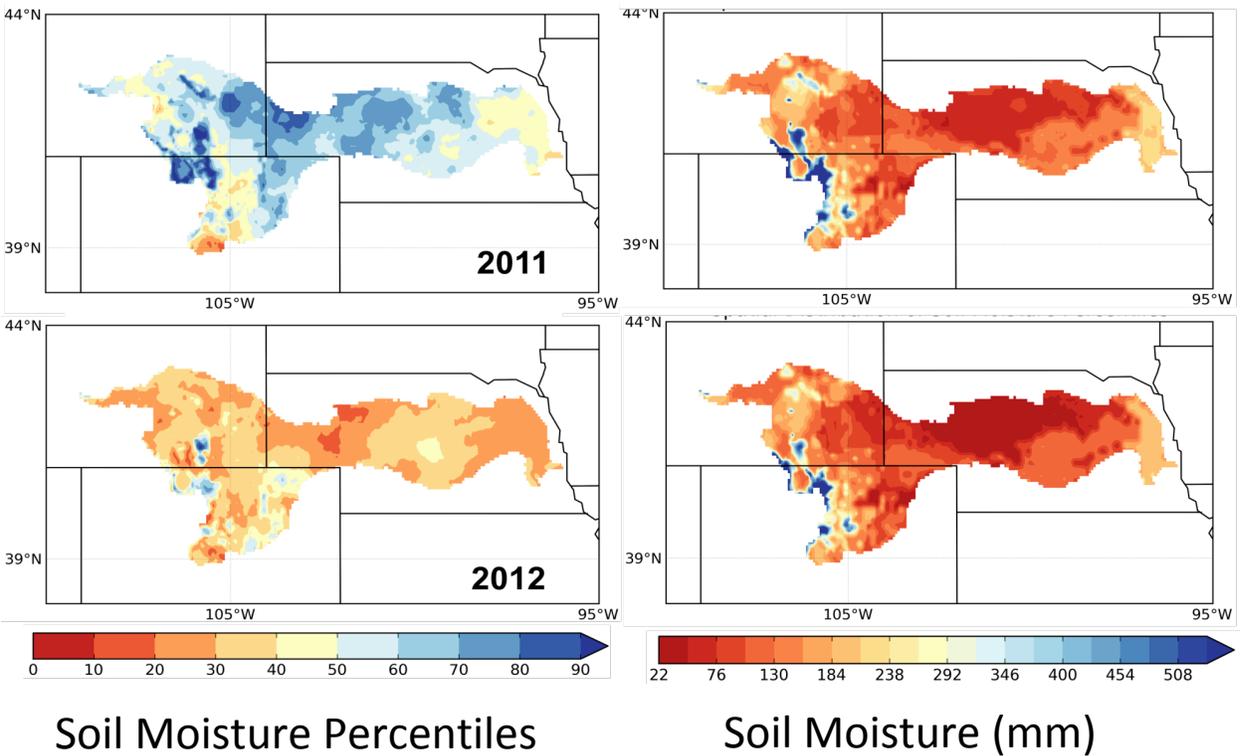


Figure 8: Response of the dynamic LAI variability on soil moisture described with percentiles (left panel) and absolute values (right) for two extreme years 2011 (wet) and 2012 (dry).

2. Resolution

With colleagues of the University of Colorado-Boulder, Arizona State University, NASA, and the US Army Corp of Engineers we developed and implemented a new precipitation, minimum and maximum temperatures, and wind speed daily dataset at 1/16th degree resolution for Southern Canada, the US, and Mexico (1950-2013). This dataset is unique because of the spatiotemporal resolution and the accountancy of topography along the subcontinent (Figure 8). Simulations in section 1 used this dataset and the previous version at 1/8th degree resolution. A paper submitted to Nature databases (Livneh et al., submitted) will describe the process, challenges, and opportunities. Currently we are automatizing the procedure in order to develop a test-bed for resolution-driven experiments but also to test uncertainties in estimations and interpolation techniques.

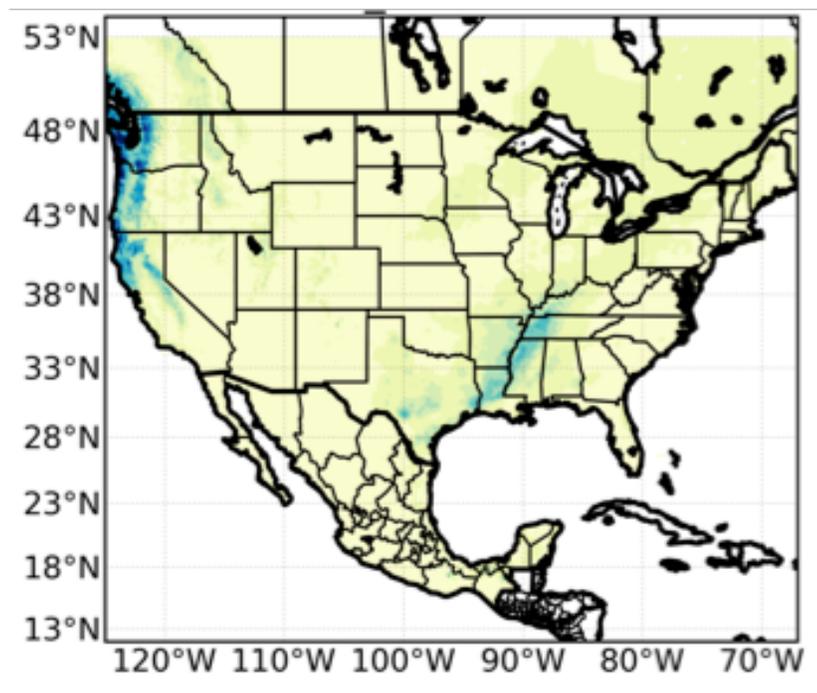


Figure 8. Sub continental precipitation historical average (mm/day) at 1/8th degree resolution from 1950-2013.

3. Pending work

Below is listed the pending work we are implementing in the following stage of the project:

- a. Our contribution to address the suitability of time-step and grid-size as a key step toward the improvement of Surface Water-Groundwater connections across spatiotemporal scales.
- b. Explore the integration of the Land Surface Hydrology (LSH) scheme to' MODFLOW-FMP (or the development of WATCOM).

Also, Dr. Carlos Carrillo was hired as Water Cycle modeler. His expertise in data analyses and model implementation will allow us to implement the pending tasks. Also, we have started our collaborations with USGS's Nebraska Water Science Center, which we expect will expedite our MODFLOW-FMP implementation.

III. INFORMATION TRANSFER PROGRAM

The present project provided training to undergraduate and graduate students as well as postdoctoral professionals. Two undergraduate students have contributed in the analyses of the hydrolimatology of the Platte River Basin. They focused on two aspects, soil moisture and snow water equivalent responses to large-scale phenomena and the streamflow and evapotranspiration sensitivity to changes in temperature. These two undergraduates, were awarded by the UCARE-program fellowship and have presented at International conferences such as the 2015 American Meteorological Society annual meeting. On the other hand, Katherine Smith, MSc student, funded by the present project contributed to (1) assess the hydroclimatology of extreme hydrometeorologic and climate events in the Platte River Basin; (2) document and run the first steps to implement MODFLOW in two locations in the state of Nebraska. Katherine Smith and Mallory Morton, also received the NASA received the "Recruitment Fellowship" award and has presented a preliminary report at the NASA Nebraska Space Grant, which also contributed to this project.

The information produced by the undergraduate and graduate students will contribute to elucidate the proper mechanisms to a fully integrated modeling system. The extreme-event assessment represents the diagnostic component of a predictability framework complemented by an assessment of VIC's integration into the Farming Process package. Future work will explore the integration of VIC and FMP from physical and computational perspectives.

Other information transfers include the possible transfer of Livneh et al. (submitted) dataset to NASA's Land Data Assimilation System, which is currently available upon request to the public. Also, codes for pre-processing and post-processing hydrologic data in multiple formats (ASCII, netCDF, HDF, among others) will be available for online access in our web page before the submission of our final report.

1. Participation in workshops and conferences:

Morton, F., K. Smith, A. Mohammad Abadi, I. Luna, and F. Munoz-Arriola. Assessing Land Surface Hydrologic Resilience to Extreme Hydrometeorological Events in Natural and Water-controlled Ecosystems. *American Meteorological Society*, Phoenix, AZ. January 9th 2015.

Smith, K., M. Morton, D. Rico, A. Mohamad Abadi, I. Luna, B. Livneh, and Francisco Munoz-Arriola. Hydroclimatology of Flood and Drought Events in the Northern High Plains, U.S. *American Geophysical Union, Fall Conference*, San Francisco, CA. December 16th 2014.

Munoz-Arriola, F. R. Walko, A. Mohamad Abadi, L. Castro-Garcia. Toward Improving Predictability of Extreme Hydrometeorological Events in the Northern High Plains. *American Geophysical Union, Fall Conference*, San Francisco, CA. December 18th 2014.

Morton, M., D. Rico, J. Abraham Torres, A. Mohammad Abadi, I. Luna, and F. Munoz-Arriola. Assessing Soil Moisture Response to Extreme Hydrometeorological Events in the Platte River Basin. *University of Nebraska-Lincoln Summer Research Symposium*, Lincoln, NE. August 6th 2014.

Rico, D.A., Abraham, J.T., Azar, M., Mallory, M., Francisco, M. (2014). *Determining Streamflow Sensitivity to Changes in Temperature on the Platte River Basin*. Poster presented at the *University of Nebraska-Lincoln Summer Research Symposium*, Lincoln, NE. August 6th 2014.

Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater

Basic Information

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Project Number:	2014NE265G
USGS Grant Number:	
Start Date:	9/1/2014
End Date:	8/31/2017
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Congressional District:	
Research Category:	Water Quality
Focus Category:	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)

United States Geological Survey 104(g) Report (2015)

Nitrate Mediated Mobilization of Naturally Occurring Uranium in Groundwater

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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 Assistant 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. 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 early career female investigators, this project has supported the research of two graduate students at (2 Ph.D. students in the Department of Earth and Atmospheric Sciences and includes one disabled veteran) and two undergraduate students, including one female through the Undergraduate Creative Activity and Research Experience Program (UCARE) at UNL.

Experimental research results have been disseminated by the PI and one graduate student 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 and state conferences, and the Department of Environmental Quality). One local presentation given the Nebraska Water Seminar Series is available on YouTube (<https://www.youtube.com/watch?v=e1jIU-qkBks>). Drs. Weber and Campbell-Hay are currently organizing a topical session entitled “Biogeochemical Redox Cycling of Metals and Radionuclides” at the annual Geological Society of America meeting to be held in Boulder, CO in late September 2016. This session will be sponsored by the GSA Mineralogy, Geochemistry, Petrology, and Volcanology Division. Dr. Campbell-Hay presented the Stout Lecture in the Department of Earth and Atmospheric Sciences at UNL in the Spring of 2015. To date one peer-reviewed publication (Nolan and Weber, 2015) has been published with an additional two

manuscripts currently in preparation resulting from data generated to date. Nolan and Weber (2015) received national and international press. This publication was also selected as a *Science* Editor's Choice in 2015.

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.

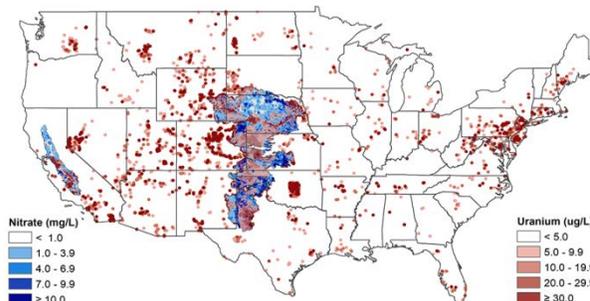


Fig. 1. Interpolated nitrate and U groundwater concentrations in the High Plains and Central Valley Aquifer from Nolan and Weber (2015).

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. Here we will experimentally determine the following:

- i. U(VI) reduction rates,
- ii. U(IV) oxidation rates in the presence of nitrate and oxygen,
- iii. U(IV) oxidation rates by abiotically and biogenically precipitated Fe(III) oxides,
- iv. Fe(III) reduction rates,
- v. Fe(II) oxidation rate by oxygen and nitrate.

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 ($30\mu\text{g/L}$) have little to no direct anthropogenic U activity suggesting geogenic U contamination in these aquifers that may be driven by nitrate. These results have been 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.

Uranium in groundwater can originate from reduced U deposited in sediments. We have identified a shallow aquifer in Nebraska where the groundwater U concentration ($302\mu\text{g/L}$) 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.

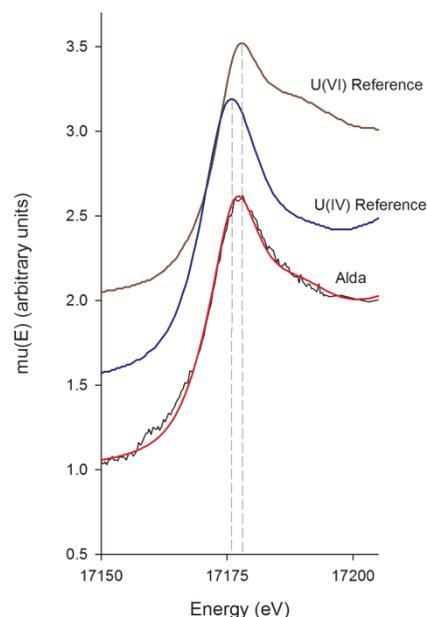


Figure 2. XANES data of natural sediments reveals U in both the reduced and oxidized state (50:50).

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). Following the initial 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



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

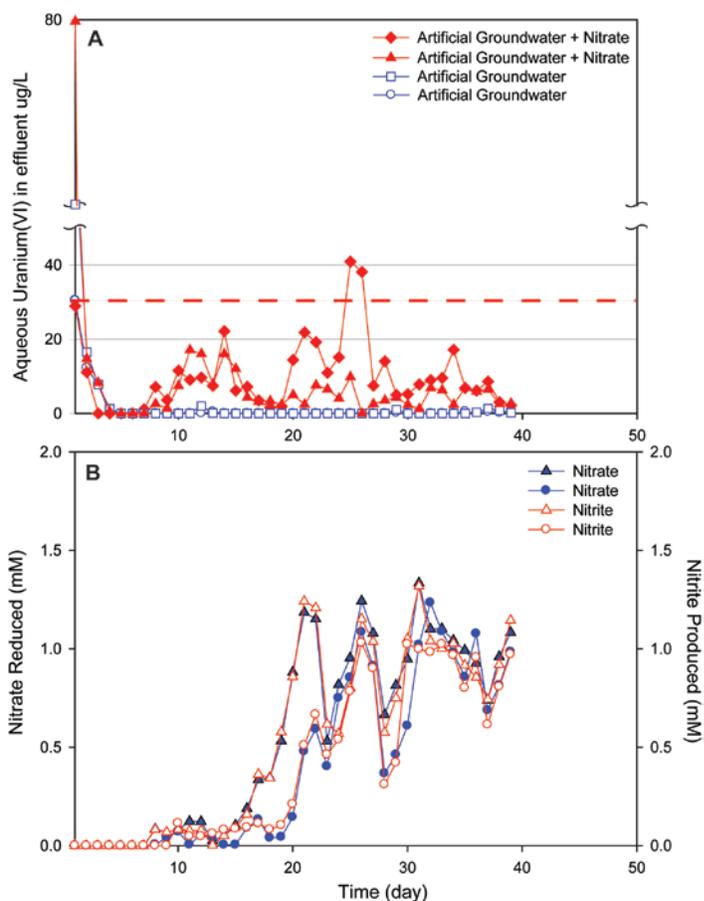


Figure 4. Upflow meso-scale column reactors packed with 50% sand and 50% sediment. Nitrate was amended into two column reactors and omitted from two reactors (A). Nitrate was reduced to nitrite in reactors receiving nitrate input (B).

production may be the 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. Experiments determining the quantity of U(VI) adsorbed to the sediments are underway and will be used to develop a surface complexation model.

Interestingly following the pulse of uranium released into solution around day 25, U(VI) concentrations began to decrease. This could be a result of

depletion of U(IV) in the sediments or the stimulation of the reduction of U(VI). We have observed the stimulation of reducing conditions with an influx of oxidant in a preliminary upflow meso-scale column experiment packed with subsurface sediments and amended with U(IV). Using subsurface sediments collected from a different region of the aquifer also high in organic matter resulted in U retention and Fe loss (data not shown). This result can be explained by metal/radionuclide reduction. The loss of iron would occur as Fe(III) oxides are reductively dissolved to soluble Fe(II) and thus lost via advective transport in the effluent. Uranium would be retained as a result of continued reduction which would yield an insoluble U(IV) mineral that would not be transported. These results are counterintuitive as we would expect the addition of nitrate directly into reduced sediments to stimulate metal/radionuclide oxidation and thus promote U mobility and retain Fe as an Fe(III) oxide. We hypothesize that organic carbon serves as a redox buffer in these reduced sediments and can control U mobility. A proposal was submitted to the Department of Energy, Subsurface Biogeochemistry Research program to further explore this hypothesis and investigate the link between carbon, nitrate, and uranium in natural and contaminated environments.

In order to understand the geochemical processes underpinning U stability in oxic subsurface sediments intact sediment cores (0-180ft) and groundwater (from later installed wells) from a deep aquifer were collected. Sample collection was obtained in collaboration with a local utility, Hastings Utilities, in Hastings Nebraska. Sediment consisted of mixed loess in the vadose zone (0 to ~110ft) and mixed sand and gravel alluvium in the saturated zone (~110 to 180ft) overlaying a clay aquitard, groundwater was oxic throughout (DO >7.0mg/L, Table 1). As nitrate concentrations increased (8.4 to 9.4mg/L; MCL=10mg/L) groundwater U(VI) concentrations (17.4 to 24.5mg/L) increased approaching the MCL (Table 1). The groundwater in the other core was suboxic (DO 0.1 to 2.1mg/L) with less nitrate (2.1 to 6.4mg/L) and lower U(VI) in groundwater (2.1 to 15.4 ug/L) (Table 1). Groundwater in both wells was saturated with calcium (78 to 90 mg/L) and had high levels of carbonate alkalinity (up to 291 and 416 mg/L as HCO_3^- , Table 1). Sediment associated U was highest in both cores (in the saturated zone) at the base of the aquifer (1.7mg kg^{-1}). Quantitative XRD of the ultra-fine sediment fraction (<20um) identified calcite (52.2% by mass) in sediment concurrent with highest levels sedimentary U(VI)

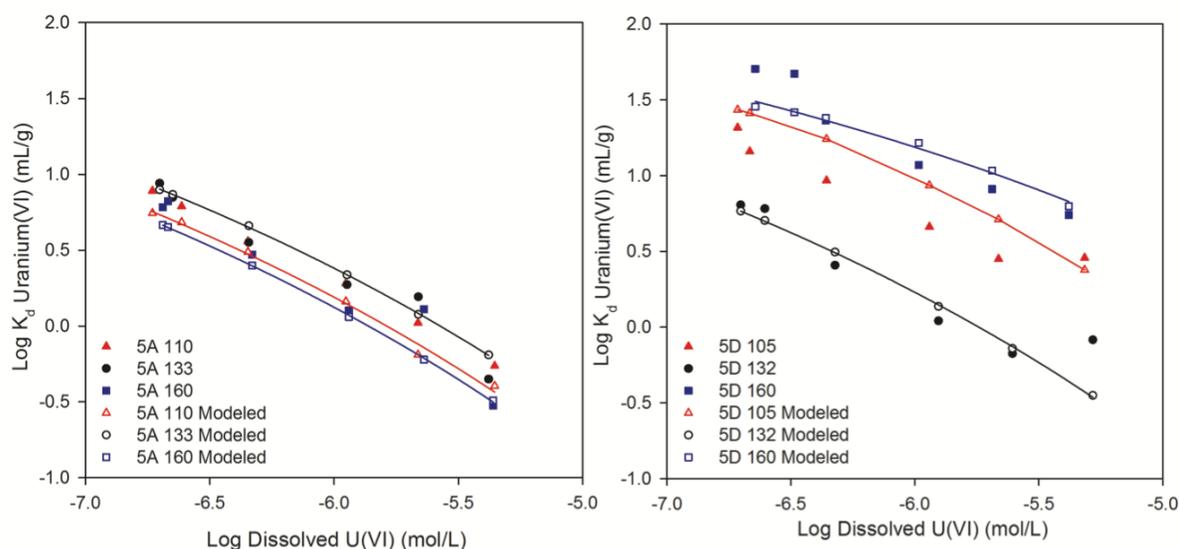


Figure 5. Equilibrium adsorption of U(VI) onto sediment (filled) in well MW-5D(left) and MW-5A(right) and modeled values with fitted surface complexation model curves (open).

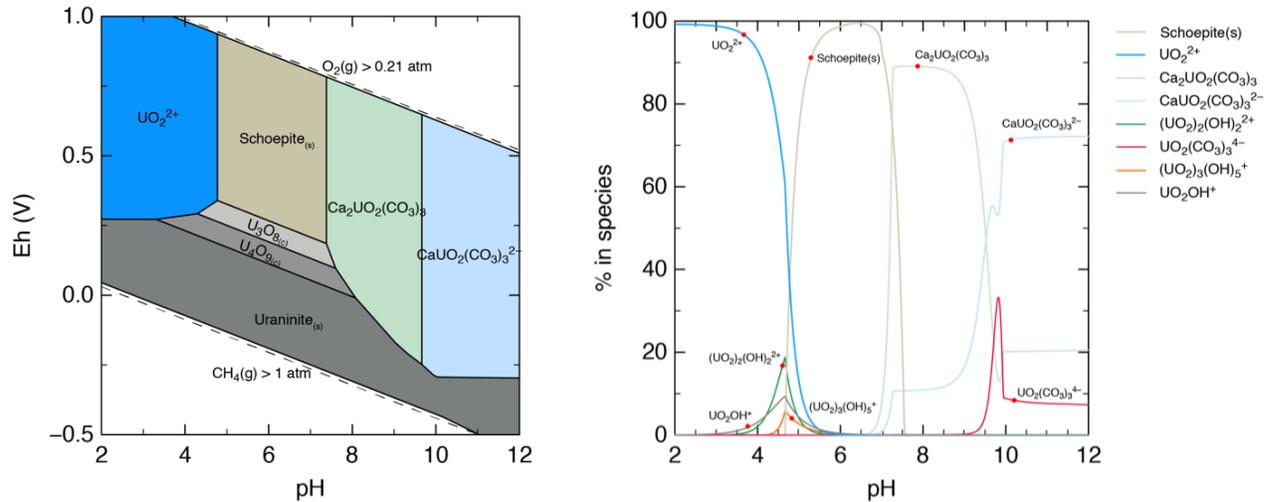


Figure 6 A&B. Pourbaix plot (a), indicating dominant phases at varying Eh and pH, and a speciation plot (b), of U in sample MW-5D-160 where XANES analysis was completed. Speciation plot indicates sample at the measured groundwater Eh (+252.4mV) and pH (7.0), Schoepite, a metastable solid-phase U(VI) was identified as the dominant U phase. Phreeplot (Kinniburgh and Cooper, 2011) using PhreeqC V.3.3 (Parkhurst and Appelo, 2013) with a hunt and track approach used for diagram creation.

(Table 2). While quantitative XRD did not identify U minerals, X-ray Adsorption Near Edge Structure (XANES), identified that the majority of sediment associated U was oxidized as U(VI) ($85\% \pm 10\%$) in this sample (data not shown). Surface Complexation Modeling (SCM) of equilibrium adsorption experiments, indicated that adsorptive mechanisms alone could not account for sediment retention of U(VI) ($<10\%$ total U) at observed levels using best fit reactions (Figure 5). Geochemical speciation modeling indicates that Schoepite, a meta-stable solid-phase U(VI) mineral, is likely the predominant ($>90\%$) U form in the sediments (Figure 6). The prediction of a solid-phase U(VI) mineral species is consistent with the results from XANES. Geochemical models further indicate the thermodynamically favorable precipitation of calcite due to supersaturation. $\delta^{13}C$ data further indicates that the carbon (inorganic carbon) associated with the carbonates is a product of abiotic origin ($0.57 \pm 0.15\%$). The co-occurrence of U(VI) solid-phase minerals with calcite has been well established in ore deposits and paleosols. Solid-phase U(VI) associated calcite may be a mechanism preventing U from exceeding the MCL. The formation of U(VI)-calcite likely occurs where increased alkalinity coincides with U(VI) contamination. Elevated dissolved U in this aquifer may be a result of calcite weathering rather than a mechanism of mobilization. However, continued influxes of oxidants such as nitrate into aquifers could directly/indirectly influence calcite kinetic weathering leading to the mobilization of U(VI) as well as nitrate-mediated oxidation of the U(IV) identified in the sediments which could lead to further groundwater contamination.

Table 1. Groundwater geochemical data from samples collected from two wells 5A and 5D in Hastings, NE.

Well Depth (ft)	Dissolved U(VI) ($\mu\text{g/L}$)	pH	Eh(mV)	Alkalinity (mg/L as HCO_3^-)	Dissolved Organic Carbon (mg/L)	Dissolved Oxygen (mg/L)	Nitrate (mg/L-N)	Dissolved Silica (mg/L)	Iron (II):Total Fe Ratio
5D-105	2.1 ± 0.2	8.4	+353.6	60	1.78	2.10	2.15	17.30	0.73
5D-132	13.4 ± 0.1	8.0	+412.6	175	1.59	2.02	3.02	24.40	0.70
5D-160	15.4 ± 0.4	7.0	+252.4	226	1.73	0.50	6.42	27.00	0.32
5A-110	24.5 ± 0.2	7.2	+377.2	416	2.21	7.70	9.24	28.10	0.74
5A-133	21.1 ± 0.8	7.2	+379.4	391	2.47	7.61	8.44	28.60	0.35

5A-160	17.4 ± 0.8	7.2	+385.6	371	2.43	7.55	8.95	23.50	0.21
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Table 2. Quantitative XRD results for <20µm fraction

Mineral	5A 133 Weight%	5D 160 Weight%
Quartz	34.0	18.0
Kspar¹	31.5	13.2
Plagioclase²	27.6	12.6
Amphibole³	6.3	4.0
Calcite	0.6	52.2

¹ Ordered Microcline; ² Albite, var. Cleavelandite; ³ Actinolite

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 models already in development will contribute to the model Dr. Campbell is currently developing in collaboration with a graduate student in the Weber laboratory. Kinetic data will be obtained from a series of upflow meso-scale column reactors (Figure 3) as outlined below.

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 the first column study 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. 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. UO_2 with varying isotopic composition will be prepared and used as standards for analysis of uranium minerals generated during reduction of ^{18}O -labelled NO_3 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 $\delta^{18}\text{O}$ of aqueous uranyl species which may be separated and concentrated using ion exchange and/or polymeric purification methods (Aly and Hamza, 2013).

PUBLICATIONS

‡Undergraduate/Post-baccalaureate Student Contributing Author

§Graduate Student Contributing Author

Published

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.

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.* Uranium mobilization in groundwater and the role of nitrate. Little Blue Natural Resource District, Edgar, NE, December 1, 2015. (*invited conference presentation*)

Weber, K. A.* Life Beneath Our Feet: Influence on Water Quality, Department of Geography and Geology, University of Nebraska, Omaha, November 5, 2015. (*invited conference oral presentation*)

Weber, K. A.* Life Beneath Our Feet. Tri-Beta, Nebraska Wesleyan University (*BBB student invited oral seminar presentation*)

Weber, K. A.* Uranium mobilization in groundwater and the role of nitrate. Nebraska Association of Resource Districts Annual Conference. Kearney, NE, September 29, 2015. (*invited conference oral presentation*)

Weber, K. A.* Microbial oxidative dissolution of solid-phase minerals. Workshop of US NSF-China NNSF Collaborative Research on Microbe-Mineral Interaction: Microbial Extracellular Electron Transfer with Minerals as Electron Sources as Sinks, Peking University, Beijing, China, March 23-25, 2015. (*invited oral presentation*)

Weber, K. A.* Mobility of naturally occurring uranium in aquifers: lessons from the lab and the field. Nebraska Department of Environmental Quality, Mobilization of Uranium & Selenium in Aquifers Workshop, Lincoln, NE, December, 3, 2014 (*invited oral presentation*)

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August 18, 2015. “Researchers say High Plains Aquifer Contaminated with Uranium, TTU Researchers Weigh In” KAMC Lubbock, TX (TV Interview)

August 18, 2015. “Study suggests links between nitrate, uranium contamination” Associated Press, Numerous Print, TV, and Radio including but not limited to *The Washington Times, Sacramento Bee, Kansas City Star, Houston Chronicle, Business Insider, US News and World Report, Sioux City Journal, The Waco Tribune, News Sentinel, Central Valley Business Times, The Olympian, Bryan-College Station Eagle, The Wichita Eagle, The Baytown Sun, The State, Ventura County Star, Yankton Daily Press & Dakotan, Press Examiner, Charlotte Observer, McCook Daily Gazette, Lincoln Journal Star, Columbus Telegram, Tech Times* KLKNTv, NPR, KRQE News, KTVU, NTV, KAWL

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AWARDS AND ACHIEVEMENTS

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Design of Multi-Scale Soil Moisture Monitoring Networks in Agricultural Systems Using Hydrogeophysics

Basic Information

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End Date:	2/28/2016
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Principal Investigators:	Trenton Ellis Franz

Publications

1. Avery, William, 2016, The Cosmic-ray Neutron Probe Method for Estimating Field Scale Soil Water Content: Advances and Applications, "MS Thesis", School of Natural Resources, University of Nebraska-Lincoln, Lincoln, NE, 81 pages.
2. Avery, W., C. Finkenbiner, T. E. Franz, T. Wang, A. L. Nguy-Roberston, A. Suyker, T. Arkebauer, and F. Munoz-Arriola (2016), Incorporation of globally available datasets into the cosmic-ray neutron probe method for estimating field scale soil water content, Hess Discussions.
3. Franz, T. E., T. Wang, W. Avery, C. Finkenbiner, and L. Brocca (2015), Combined analysis of soil moisture measurements from roving and fixed cosmic ray neutron probes for multiscale real-time monitoring, Geophysical Research Letters, 42.
4. Wang, T., T. E. Franz, W. Yue, J. Szilagyi, V. A. Zlotnik, J. You, X. Chen, M. D. Shulski, and A. Young (2016), Feasibility analysis of using inverse modeling for estimating natural groundwater recharge from a large-scale soil moisture monitoring network, Journal of Hydrology, 533, 250-265.

2015 Annual Report

Project #2015NE266B

Design of multi-scale soil moisture monitoring networks in agricultural systems using hydrogeophysics

May 21, 2016

Principal Investigator: Trenton Franz, Assistant Professor
School of Natural Resources
University of Nebraska-Lincoln

Reporting Period: March 1, 2015 through February 28, 2016

Financial support: USGS

Participants:

Undergraduate students: Matthew Russell
Graduate students: William Avery

Publications:

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Conference Participation:

Franz, T., Avery, W., Finkenbiner, C., AGU, AGU, San Francisco, CA, "From the sprinkler to satellite: Combining fixed and mobile cosmic-ray neutron probes for realtime multiscale monitoring of soil moisture in agricultural systems". Accepted. (December 2015).

Finkenbiner, C., Avery, W., Kuzila, M. S., Munoz-Arriola, F., Franz, T., AGU, AGU, San Francisco, CA, "Improving the Operability of the Cosmic-ray Neutron Soil Moisture Method: An Estimation of Lattice Water using Global Datasets". Accepted. (December 2015).

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I. INTRODUCTION

1. Project Summary: Problem and research objectives

The Food and Agriculture Organization of the United Nations (FAO) (FAO 2009) estimates an increase of 70 percent in cereal grains production will be necessary to feed the projected nine billion people worldwide by 2050, placing great demand on dwindling agricultural water resources. Currently, 70 percent of global anthropogenic consumptive water use is for agriculture where irrigation agriculture accounts for 40 percent of global food production (Mekonnen and Hoekstra 2011). However, global trends in consumptive water use indicate a growing yet unsustainable reliance on groundwater resources (Mekonnen and Hoekstra 2011). Despite its critical importance in global food security, water paradoxically is wasted at an alarming rate. On the global scale, Clay (2004) estimates 60 percent of the 2,500 km³ used for agriculture each year is “wasted” through inadequate water conservation, losses in distribution, and inappropriate times and rates of irrigation. Given the massive time, labor, and economic costs of water application, a primary challenge is to better understand how much water in the soil is available for use by plants. The underlying difficulty when measuring soil moisture availability is its inherent heterogeneity in time and space in both natural (Western and Bloschl 1999) and agricultural settings (Hedley and Yule 2009), consequently requiring intensive time and labor sampling strategies in order to accurately quantify large areas. Thus, there is a *critical need* to quantify soil moisture storage at the application scales where water management decisions are made (Scott et al. 2014) with accurate and pragmatic techniques. In the absence of such techniques, the development of efficient water application strategies and agricultural production sustainability will likely remain difficult.

2. Objective

To develop effective strategies to improve the efficiency of water use in irrigated agriculture.

2.1 Particular objectives

- a. Identify hydrogeophysical techniques to quantify soil moisture storage of individual management sections within agricultural fields.
- b. Identify hydrogeophysical techniques to quantify soil moisture storage of many agricultural fields.

II. Research Program

In this work I will focus on agricultural production in the Central Great Plains (CGP), which uses the High Plains Aquifer (HPA) to complement surface water sources, although increasing blue water use for agriculture is a serious global concern (Mekonnen and Hoekstra 2011). To date, withdrawals from the HPA (mostly for agriculture) have resulted in the depletion of up to half of the water in some southern areas of the aquifer and an 8 percent depletion overall (Scanlon et al. 2012). Crop production within the HPA region accounts for 31 percent of sorghum, 24 percent of cotton, 15 percent of wheat, and 14 percent of corn production (NASS August 2013) in the United States; thus, the aquifer represents a significant contributor to this country's ability to meet its share of the increasing world demand for food, feed, fiber, and fuel.

The proposed research will take place at three locations along an east-west rainfall gradient in the state of Nebraska within the CGP. The rainfall gradient will capture the transitions from deficit irrigation to full irrigation to rainfed, making the research applicable to a wide-range of agricultural regions across the globe. The work will take in the Mead area (rainfed, field sites established in 2014), the York area (transition zone between rainfed and full irrigation, field sites established in 2014), and the Ogallala/Brule area (deficit irrigation, field sites will be established in 2015).

At each of the three sites I will install and calibrate with my research team two stationary cosmic-ray neutron probes for estimating hourly values of soil moisture storage integrated over a 28 ha area and vertical depths of 30 cm (Franz et al. 2012a; Franz et al. 2012b; Zreda et al. 2012; Desilets and Zreda 2013). Using the mobile cosmic-ray neutron rover (Chrisman and Zreda 2013; Dong et al. 2014) my team will survey an 11 by 11 km area, with 1.6 km transect spacing, twice a month over the primary growing season (May to September) at each of the three field sites. This survey strategy was established and implemented with success by my research team during the 2014 York field campaign. In addition, at 1 of the stationary cosmic-ray neutron probe sites in each study area my team will survey the entire field at a 50 m resolution by mounting the mobile sensor to an ATV or sprayer for in season mapping. The in-field mapping will be conducted five to seven times at each of the field sites. The Mead field site was selected based on existing infrastructure of point scale soil moisture sensors for cross comparison and validation. The site contains 10 profiles of Dynamax sensors distributed around the field, 5 of which have been operated by myself since 2014, and 5 of which have been operated by Todd Schimelfenig of the carbon sequestration project since 2001.

The other study sites in York and Ogallala will need to be instrumented with similar networks of point scale soil moisture sensors. At each of sites, my team will install four dataloggers with eight point sensors split into two paired profiles. The dataloggers will be placed in the four cardinal directions (N, E, S, W) and at a distance of 75 m from the centrally located cosmic-ray neutron probe. The point sensors will be placed at depths of 10, 20, 50, and 80 cm to

correspond to expected root zone activity. Some of the funds from this project will be used to purchase two networks of Watermark point sensors and dataloggers to be placed at the field sites. Watermark sensors are preferred given their low cost, ease of use, and wide spread use throughout the state for irrigation management (Irmak et al. 2010). As an additional benefit, the Watermark sensors measure soil tension and when spatially averaged and compared to the cosmic-ray neutron soil moisture measurements give an effective scale soil tension vs. soil moisture relationship. This relationship is 1 of 2 components of the difficult to measure soil hydraulic functions (Simunek et al. 2006) and is critical for accurately modeling water flux and velocity through the unsaturated zone (Vangenuchten 1980). Initial observations in 2014 from a network of twelve Watermark sensor profiles and a co-located cosmic-ray probe in the Central City, NE area are encouraging for describing part of the effective scale soil hydraulic function. Because of the fractal nature of soil texture fields (Rodriguez-Iturbe et al. 1995), upscaling of point measurements has been difficult and has limited the comparisons between watershed scale modeling grids and in-situ point sensors (Crow et al. 2012).

Following the conclusion of this project, I will provide three key products for advancing the use of hydrogeophysical sensors in quantifying soil moisture storage at two critical management scales. **First**, I will advance the calibration procedures for converting the measured geophysical properties of low-energy neutrons to relative changes in soil moisture storage. **Second**, I will develop a methodology combining in-situ point sensors with in field spatial cosmic-ray neutron mapping to provide realtime estimates of soil moisture storage for different management zones. A preliminary proof of concept of this method is provided elsewhere (Almeida et al. 2014). **Third**, I will develop a methodology combining stationary cosmic-ray neutron probes with watershed scale mobile cosmic-ray neutron mapping to provide realtime estimates of soil moisture storage for hundreds of agricultural fields. Preliminary results from the 2014 York field campaign are encouraging and corresponding manuscripts and extension publications are currently in preparation. Given the pragmatic nature of data collection and scale of measurements, the combined stationary and mobile cosmic-ray neutron probes would be a transformative technology for helping manage efficient irrigation systems around the globe. Preliminary discussions have taken place between myself and various industry partners and state agencies (i.e. pivot manufacturers, crop consultants, NRD managers, etc.) about technology development and transfer.

III. INFORMATION TRANSFER PROGRAM

The USGS104b funds were used primarily to purchase the two Watermark sensor networks as well as support travel by my research team between the three study sites across the state during the 2015 field campaign. An additional UNL internal grant was submitted along similar project lines to support the extensive travel, operation of the cosmic-ray neutron measurements, and setup and operation of the Watermark sensor networks. An undergraduate student was hired to support an existing MS and undergraduate student already working on related projects. Note, the MS and undergraduate students are currently being paid off federal grants and will not be used as match for this project. The undergraduate student was encouraged and successfully applied for a UCARE scholarship to provide partial support for the 2016 field campaign as well as during the 2016-2017 academic year. The undergraduate student will be trained on collecting and operating cosmic-ray neutron probes, calibrating cosmic-ray neutron

probes, and processing cosmic-ray neutron data. My university startup funds were used primarily to purchase the stationary and mobile cosmic-ray neutron probes used by this project. The USGS104b funds will provide this project with additional operating support for supplies, travel, and student labor. The lack of preliminary data and establishment of field sites with producers were the two main criticisms for an unsuccessful NSF EAR proposal submitted in December 2014 and an USDA AFRI proposal submitted in April 2015. The successful completion of this project will help fill the two main criticisms raised by reviewers.

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Development of Smart Alginate Hybrid Beads for Eco-Friendly Water Treatment

Basic Information

Title:	Development of Smart Alginate Hybrid Beads for Eco-Friendly Water Treatment
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End Date:	2/28/2016
Funding Source:	104B
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Research Category:	Water Quality
Focus Category:	Water Quality, Toxic Substances, Treatment
Descriptors:	None
Principal Investigators:	Jaehong Shim, Patrick John Shea

Publications

1. Shim J., B.-T. Oh, M. Rhoades, P.J. Shea, 2016. Development of a Novel Composite Adsorbent for Removal of Aromatic Odor and Antibiotic Compounds from Water. NRDs Legislative Conference, University of Nebraska, Lincoln, NE.
2. Shim J., M. Rhoades, P.J. Shea, 2015. Composite Alginate Beads for Heavy Metal(loid) Removal from Water, Research/Creative Activity, Workshop, State, Invited.” Water Center Retreat, University of Nebraska, Kearney, NE.
3. S.-N. Ma, J. Shim, M.G. Rhoades, P.J. Shea. 2015. Development and Testing of Novel Composite Alginate Beads for Removal of Aromatic Odor and Antibiotic Compounds from Water. EEU. University of Nebraska, USA.
4. Shim, J., P. Velmurugan, and B.-T. Oh. 2015. Extraction and physical characterization of amorphous silica made from corn cob ash at variable pH conditions via sol gel processing. *J Ind Eng Chem.* 30: 249-253.
5. Shim, J., J.-W. Kim, P.J. Shea, and B.-T. Oh. 2016. Novel use of corn cob silica to support silver nanoparticles for microbial inactivation. *J Mater Cycles Waste* (in review).
6. Shim, J., Y.-S. Seo, P.J. Shea, and B.-T. Oh. 2016. Calcined, amine-functionalized precipitate from urine as a support matrix for antimicrobial silver nanoparticles. *Water Environ Res* (submitted).
7. Shim, J., J.-M. Lim, B.-T. Oh, and P.J. Shea. 2016. Comparative removal of Cd from aqueous solution by alginate beads prepared under different drying conditions (in progress).
8. Shim, J., J.-M. Lim, B.-T. Oh, and P.J. Shea. 2016. Manganese dioxide-containing alginate adsorbent for simultaneous removal of p-cresol and heavy metal(loid)s from aqueous solution (in progress).
9. Shim, J., J.-M. Lim, B.-T. Oh, and P.J. Shea 2016. Removal of p-cresol and tylosin from aqueous solution by alginate beads containing MnO₂ (~85%) and activated carbon (in progress).

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Focus category	Water Quality, Fabrication, Recycled
Descriptors	None
Principal Investigators	Jaehong Shim (PI) and Patrick J. Shea (co-PI)

Publications

1. Shim, J., P. Velmurugan, and B.-T. Oh. 2015. Extraction and physical characterization of amorphous silica made from corn cob ash at variable pH conditions via sol gel processing. *J Ind Eng Chem.* 30: 249-253.
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2015 Project Report: Development of Smart Alginate Hybrid Beads for Eco-Friendly Water Treatment

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Abstract

Safe and efficient use and reuse of water is desirable globally and especially critical where water is scarce or availability is unpredictable. Environmentally benign, cost-effective, and practical alternatives are needed to mitigate contamination. We are developing and adapting eco-friendly technologies to remove contaminants from water and otherwise improve water quality. These technologies also have potential applications for extracting or reclaiming valuable metals from water and wastewater. One approach combines alginate with MnO₂ obtained from battery waste water, silica extracted from agricultural by-products, activated carbon (AC) and precipitate from urine to develop high performance, reactive beads for diverse applications. By varying the composition of the beads, removal (adsorption) capacity can be maximized for specific types of pollutants and targeted solutes, thus optimizing treatment and extraction processes. In this project, tests were conducted with composite alginate beads (CABs) containing MnO₂ and MnO₂ + AC. CABs with MnO₂ were evaluated for removal of heavy metals, metalloids and organic contaminants from water, and for inactivation of bacteria. Results show the CABs have enhanced removal capacity for most of the pollutants evaluated in this project. CABs containing MnO₂ and AC exhibited high adsorption/decomposition capacity for removing Cd and other heavy metals, As (metalloid), *p*-cresol (VOC), tylosin (antibiotic), and phosphorus from aqueous solutions. The CABs were not effective for nitrate-N removal. CABs exhibited faster removal kinetics and greater adsorption capacity than unmodified alginate gel beads. The CABs showed good reuse potential. The CABs were easily handled, with greater thermal stability and less dissolution in water than unmodified alginate gel beads. MnO₂ recovered from battery wastewater is a strong oxidizer and promoted VOC (*p*-cresol) decomposition, as well as inactivation of *E.coli*. Impurities in the recycled MnO₂ improved performance over pure MnO₂, likely acting as adsorption and reaction catalysts. Including AC in the CABs with MnO₂ provides a large surface area and hydrophobic sites for adsorption.

Research Problem and Objectives

Ground and surface waters are negatively impacted by contaminants at scales ranging from large superfund sites to industrial effluent to point and non-point agricultural sources. National water quality reports indicate that over 40% of the nation's rivers, more than 60% of lakes and 30% of estuaries show environmental distress. Safe and efficient use and reuse of water is essential and becomes especially critical in locations and instances where water is scarce or availability is unpredictable. Pollutants, from heavy metals and metalloids to volatile organic compounds (VOCs) compromise water quality, limiting water use efficiency. To mitigate contamination, alternative approaches are needed that are environmentally benign, cost-effective and practical, particularly when advanced technologies are not available or feasible. The primary focus of this research is mitigation of pollution to improve the quality of compromised water and increase

the efficient use of water resources, and to make optimum use of recycled and waste materials in reactive composite beads that can be targeted for specific contaminants. There is a large and increasing global demand for adsorbent/reactive materials for a wide range of industrial, municipal, agricultural and environmental applications. In 2012, the size of the North American market alone for environmentally friendly inorganic adsorbents exceeded \$2.4B, with ~4.3% annual growth projected (McWilliams, 2012).

We explored the development of novel composite alginate beads (CABs) for removal of contaminants from water using more “eco-friendly” materials. These materials include corn cob silica, MnO₂ from spent batteries, activated carbon (AC) in a matrix of alginate gel from seaweed. Our findings direct subsequent research and pilot-scale testing to maximize CAB use for remediation and mitigation applications, such as acid mine drainage, industrial waste water, agricultural runoff, and VOC control from feedlots.

This project investigated the removal of contaminants from water by CABs developed for these applications. Various potential applications of the composite materials were evaluated, with the aim to mitigate pollution from heavy metals such as Cd, Pb and others, metalloids such as As, phosphate, nitrate, antibiotics such as tylosin (TYL), bacteria such as *Escherichia coli* (*E.coli*) and VOCs such as *p*-cresol (feedlot VOC). We hypothesized that the inexpensive, biodegradable and nontoxic CABs can facilitate management of contaminants by removing them or decreasing their availability in water.

The overall research goal was to develop and adapt eco-friendly solidification technology to remove contaminants from water and improve water quality for diverse applications. Project objectives were to:

1. Prepare CABs containing silica (obtainable from corn cob), manganese oxide from spent batteries, activated carbon, and precipitate from urine.
2. Determine the effectiveness of CABs designed to remove heavy metal(loid)s, antibiotics (tylosin), VOCs (*p*-cresol), bacteria (*E.coli*), and agricultural pollutants (phosphate and nitrate) from water.

Project Results

Preparation of Materials for the Composite Alginate Beads

Silica extracted from corn cob. Silica was extracted from corn cob ash following our modification (Shim *et al.*, 2014, 2015) of the method of Kamath and Proctor (1998). Briefly, 1 N NaOH was added to the ash and boiled for 3 h with constant stirring to dissolve the silica and produce sodium silicate solution. The solution was then filtered, cooled to room temperature and pH lowered with 3 N HCl to 7.0, with constant stirring, to promote silica gel formation (wet gel). The gel was then dried at 80 °C for 24 h to produce silica xerogel (Fig. 1).



Fig. 1. Silica produced from corn cob by the sol-gel method.

Precipitate from urine. Precipitate was obtained from waste urine using urease-producing microbes to produce more efficient precipitation of calcium carbonate by initiating nucleation (Wei *et al.*, 2015). The urine was aerated for 3 d at room temperature. To maximize precipitate formation, 5×10^6 colony forming units (CFU) of urease-producing *Pseudomonas sp.* (isolated from soil) was added. The precipitate was separated by centrifuging at $1325 \times g$ and washed three times with distilled water. It was then freeze-dried at -80°C for 48 h, sieved (100 mesh) to obtain uniform particles, and calcined by heating at 800°C for 6 h to eliminate organic compounds and increase surface area and stability (Fig. 2). This was followed by several washings of the calcined precipitate, and separation by centrifuging at $1325 \times g$ for 15 min. The supernatant was discarded. This step was repeated several times to effectively remove residual N, P, and organic compounds from the matrix.

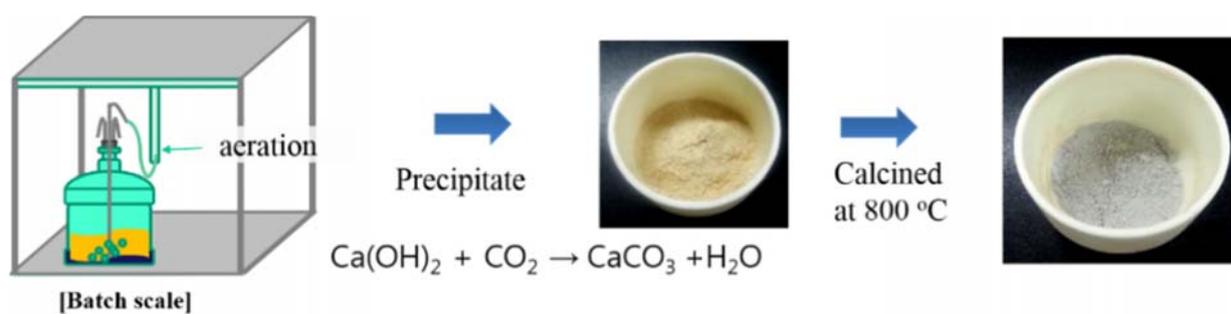
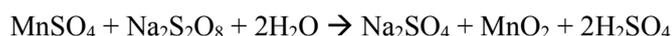


Fig. 2. Calcined precipitate produced from urine.

Manganese dioxide (MnO_2). The selective precipitation method (Bartolozzi *et al.*, 1994; Joo *et al.*, 2013) was used to obtain MnO_2 from lithium ion battery ternary cathodic material. The cathodic H_2SO_4 leachate (containing reduced Mn) was reacted with 0.1 M sodium persulfate as an oxidant to yield a MnO_2 precipitate:



The MnO_2 precipitate was recovered by centrifugation, washed multiple times with distilled water to eliminate water soluble ions, and dried for 24 h at 40°C (Fig. 3). The precipitate contained small amounts of Co, Ni and Li in addition to Mn.

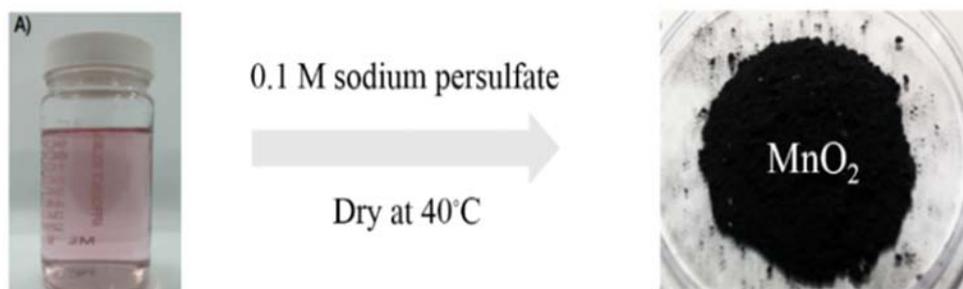


Fig. 3. Precipitation of MnO_2 from cathodic leachate by reacting with 0.1 M $\text{Na}_2\text{S}_2\text{O}_8$.

Characterization of CAB Component Materials

General methodology. For physical and chemical characterization, the raw and modified materials were washed in distilled water to remove water-soluble ions, dried at room temperature, and the powders were analyzed. Specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. Point of zero charge (pH_{PZC}) was determined (Bhaumik *et al.*, 2012). Morphology, crystalline structure and distribution, fine surface structure, and reactive functional groups of the materials were respectively characterized by field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR).

Silica. As shown in Fig. 1, Silica was extracted from corn cob using a modified “sol-gel” method (Kamath & Proctor, 1998; Shim *et al.*, 2015). SEM-EDS (Fig. 4A) showed that the silica nanoparticles were 98% Si, which was extracted with 0.1 M NaOH at pH 7. A broad XRD peak at $2\theta=30^\circ$, typical of amorphous solids (Kamath & Proctor, 1998), confirmed the absence of an ordered crystalline structure (Fig 4B). FTIR peaks at 802, 1100 and 1086 cm^{-1} confirmed siloxane (Si-O-Si) groups and the 3460 cm^{-1} band corresponded to germinal silanol groups (Si-OH) on the surface (data not shown) (Kamath & Proctor, 1998). TEM images (Fig. 4C) showed uniform, amorphous silica with an average particle size of ~ 50 nm.

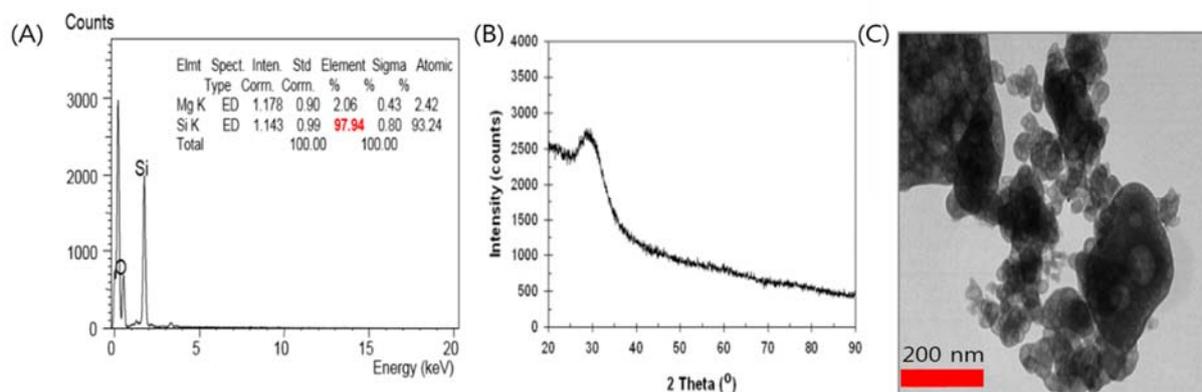


Fig. 4. (A) SEM-EDS, (B) XRD, and (C) TEM of corn cob silica.

Precipitate from urine. The SEM image for the powdered precipitate showed the presence of irregular granular-shaped particles (Fig. 5A). EDS analysis (Fig. 5B) showed the precipitate contained 22.8% N, 1.8% Mg, 5.6% P, 6.6% Ca and 63.2% other elements (C and O). XRD (Fig. 5C) shows that the raw precipitate primarily contained struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$; JCPDS 15-0762), as well as dolomite ($\text{CaMg}(\text{CO}_3)_2$; JCPDS 01-079-1344), and calcite (CaCO_3 ; JCPDS 00-024-0030). The predominance of struvite is consistent with precipitate formed in urea or ammonium carbonate solution containing the urease-active bacterium *Proteus mirabilis* (Chen *et al.*, 2010).

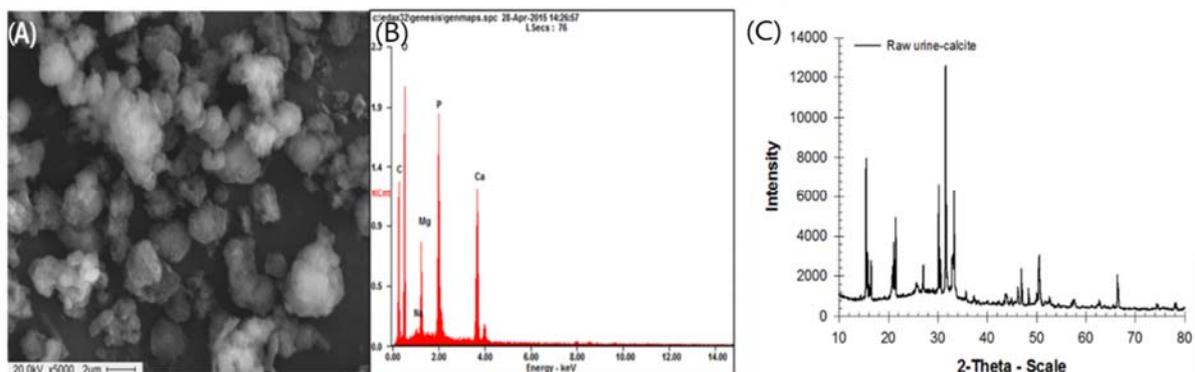


Fig. 5. (A) SEM-image, (B) EDS spectrum, and (C) XRD of the calcined precipitate from urine.

MnO₂ particles. The selective precipitation method (Bartolozzi et al., 1994; Joo et al., 2013) was used to obtain high purity MnO₂ from lithium ion battery ternary cathodic material. The cathodic H₂SO₄ leachate (containing reduced Mn) was reacted with 0.1 M sodium persulfate (oxidant) to produce MnO₂ (>87% pure, with a crystal purity of ≥98%). The MnO₂ was quite stable and little Mn was released after four washings with deionized water. The recovered precipitate contained 87% MnO, 3.40% Co₃O₄, 1.2% Fe₂O₃, 2.1% Na₂O, 0.05% NiO, 0.17% Al₂O₃, ~ 6% oxides of other elements (SiO, ZnO, and CaO, etc.). According to Joo et al., (2013), the Co, Fe, and Na impurities can be removed by washing with a 4M sulfuric acid solution. As observed in Fig. 6A, the MnO₂ displayed the high crystallinity of a β-MnO₂ phase (JCPDS 44-0141). The FTIR peak at ~3485 cm⁻¹ corresponds to -OH stretching, and the peaks at 1650, 1473 and 1128 cm⁻¹ can be attributed to OH groups in association with Mn–O bonds (Fig. 6B). These results demonstrate recovery of MnO₂ in high purity form ternary battery cathodic waste.

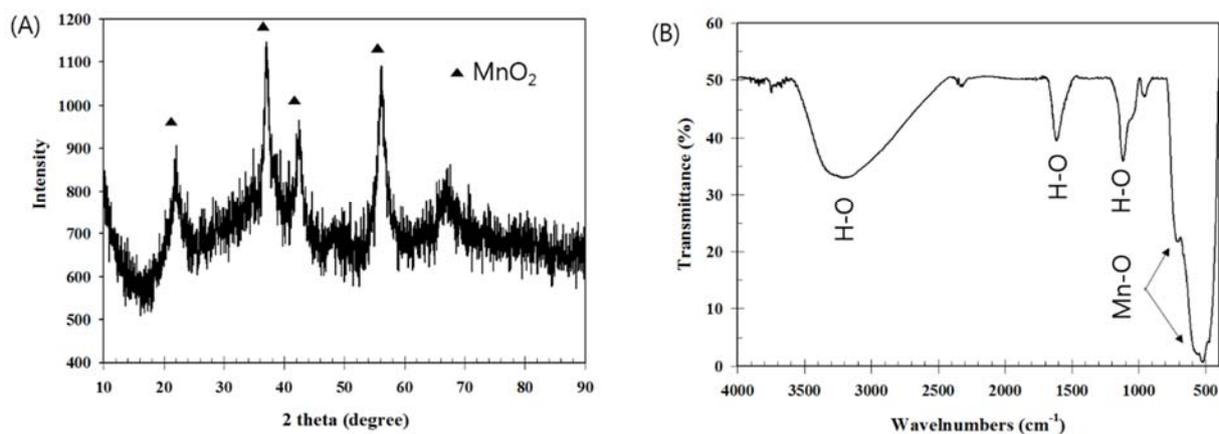


Fig. 6. (A) XRD pattern and (B) FTIR spectrum of the MnO₂ recovered by 0.1 M sodium persulfate.

Pollutant Removal by the Adsorbent and Reactive Materials

Corn cob silica (CCS). Our previous research showed that treating Pb-contaminated soil with CCS reduced its availability and phytotoxicity (Shim *et al.*, 2014). The TEM image (Fig. 7) indicated formation of insoluble lead silicate, confirmed by XRD (data not shown). Adding CCS also increased soil pH, which further promoted Pb binding and precipitation. Results showed CCS promotes Pb stabilization and decreases its mobility in soil and water. The study suggested that CCS is a very suitable material for removal of Pb ions from aqueous solution.

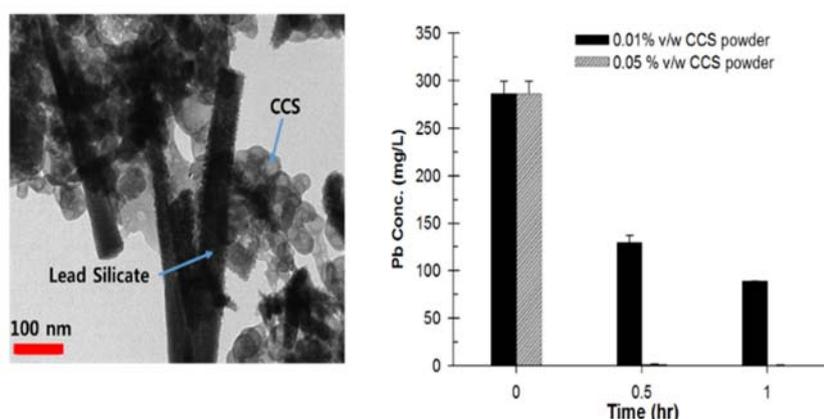


Fig. 7. (A) TEM image of CCS after reaction with Pb and (B) removal efficiency of Pb.

Precipitate from urine. The raw and calcined precipitate obtained from urine were evaluated for removal of the heavy metal(loid)s Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and As^{3+} from aqueous solution (Fig. 8). Results showed that the raw precipitate effectively removed heavy metals such as Cd, Cu and Zn. Removal efficiency for As, Ni and Pb using the calcined precipitate was better than with the raw precipitate. The maximum adsorption capacity (q_{max}) of the material was approximately 204 mg Pb, 111 mg Cd, 96 mg Zn, 104 mg As, 149 mg Cu and 163 mg Ni per g. SEM-EDS spectra and XRD (Fig. 9) confirmed removal of the heavy metal(loid)s. Results suggest that the precipitate obtained from the urine is a suitable adsorbent for heavy metal(loid) removal from aqueous solution.

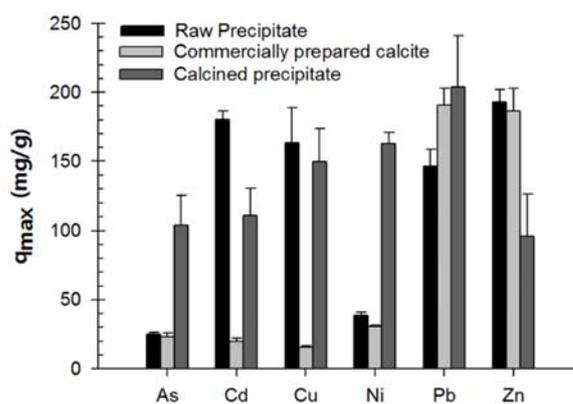


Fig. 8. Maximum adsorption capacity of various heavy metal(loid)s by raw precipitate, chemically prepared calcite, and calcined precipitate.

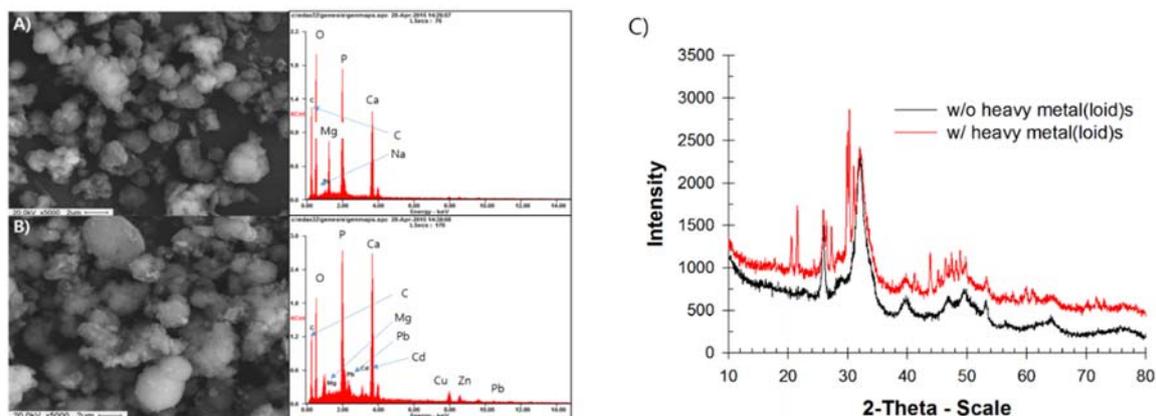


Fig. 9. SEM image and EDS spectrum of the precipitate (A) before and (B) after heavy metal(loid) removal. (C) XRD patterns before (red) and after (black) after heavy metal(loid) removal.

Removal of *p*-cresol and TYL using various Mn oxides. Physical and chemical properties of *p*-cresol and TYL are given in Table 1. Removal of *p*-cresol and TYL from aqueous solution was determined using manganese oxide varying in Mn oxidation state and purity. FTIR spectra suggested more reactive sites on Mn(IV) oxide (85% pure) than less oxidized forms (Fig. 10A). Removal of *p*-cresol and TYL were greater using MnO₂ recycled from batteries compared to the other Mn oxides (Fig. 10B). Aside from differences in reaction sites, trace metals in the less pure Mn(IV) oxide may enhance adsorption and catalyze oxidation reactions.

Table 1. Physical and chemical properties of *p*-cresol and tylosin (TYL).

Compound	Formula	Structure	Molecular Weight (g/mol)	pKa at 20 °C
<i>p</i> -cresol	CH ₃ C ₆ H ₄ OH		108	9.6
tylosin (TYL)	C ₅₀ H ₈₃ NO ₂₃		1066	7.73

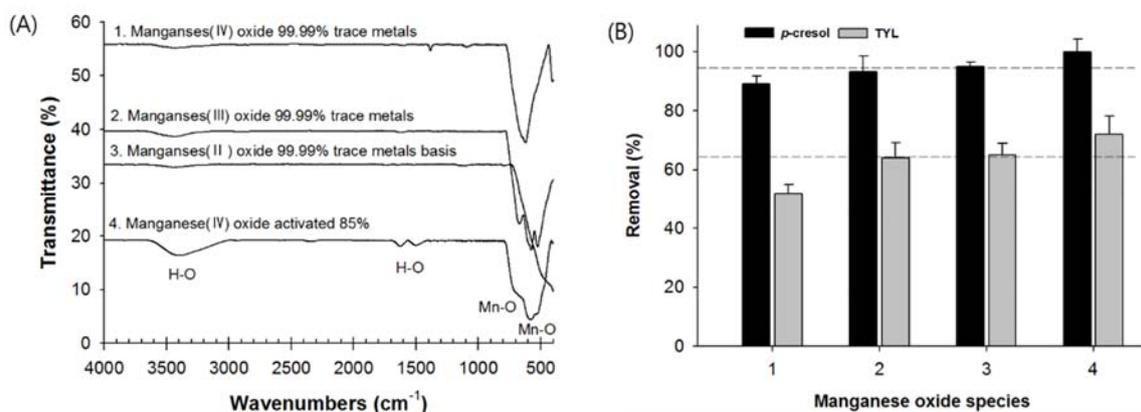


Fig. 10. (A) FTIR spectra of various Mn oxides and (B) removal of *p*-cresol and TYL by the Mn oxides.

Removal of phenol using the recovered MnO₂. A batch test for removal of phenol from aqueous solution showed that MnO₂ (~85%) significantly accelerated the oxidation kinetics of *p*-cresol compared to other Mn oxides and higher purity MnO₂. More than 95% of the phenol was removed from water containing 98.3 mg phenol/L (Fig. 11A). The oxidation product was identified as benzoquinone by UV/VIS spectra (Fig. 11B). Benzoquinone is a major oxidation product of phenol (Zhang *et al.*, 2006). These observations suggest that oxidation is the major mechanism of degradation by MnO₂.

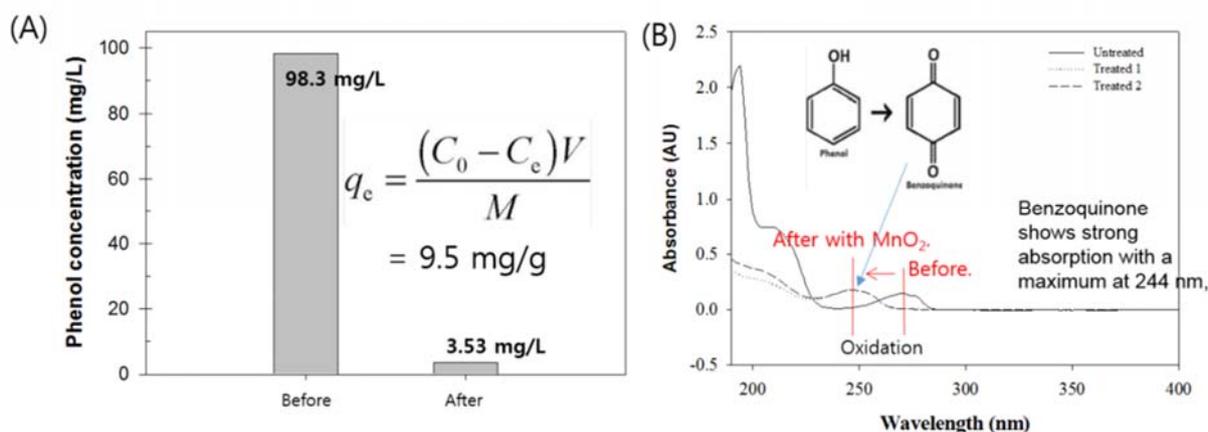
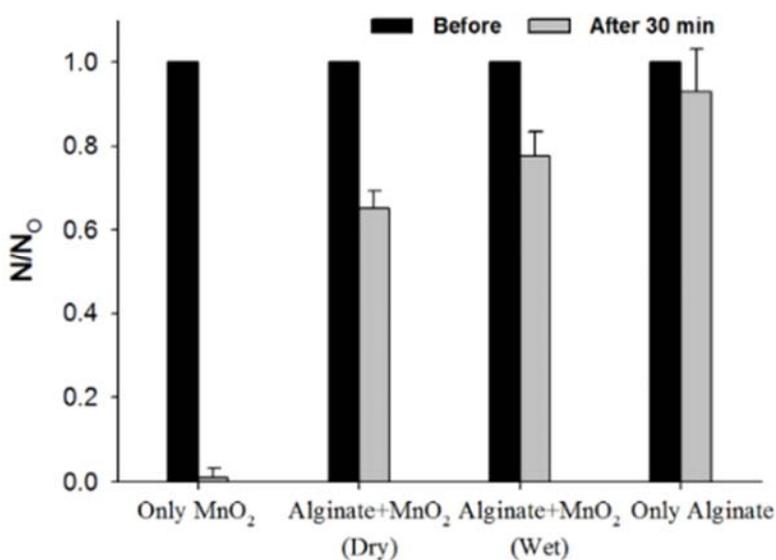


Fig. 11. (A) Removal (q_e) of phenol and (B) UV/VIS spectra before and after reaction of phenol with MnO₂, showing formation of benzoquinone.

Inactivation of *E. coli* by MnO_2 The microbial inactivation capacity of the recycled MnO_2 was evaluated in PBS using *E. coli* (12×10^6). The MnO_2 inactivated 99% of the *E. coli* within 30 min (Fig. 16). The inactivation mechanism likely involves free radical reactions at MnO_2 surfaces. *P*-cresol oxidation was inhibited by bisphenol A (BPA), a well-known $\bullet OH$ scavenger. MnO_2 has shown oxidative capacity for phenolic compounds (Lin *et al.*, 2009). Metal oxides (e.g. TiO_2 , MnO_2 , and Al_2O_3) generate free radicals. Watts (1998) reported manganese oxides produced transient oxygen species, such as hydroxyl radicals ($OH\bullet$) and superoxide radical anion ($O_2^{\bullet -}$). Formation of intermediate radicals can activate and trigger a series of subsequent radical reactions.

Fig. 12. Inactivation of *E. coli* by MnO_2 , alginate, and alginate + MnO_2 .



Fabrication of Composite Alginate Beads (CABs)

Approach. CABs (Fig. 13) can be used as a filter to remove pollutants from solution. The composite is prepared in an alginate matrix. Alginate (alginic acid) is a polysaccharide abundant in brown marine algae (*Sargassum and Ascophyllum*). It is relatively inert in aqueous media, and can be used to create a matrix for entrapment of organic and inorganic compounds. Alginate reacts with Ca^{2+} to form an insoluble gel (Braccini & Pérez, 2001), providing a desirable matrix for the CABs. CABs can be prepared in sizes ranging from nano- to macro-, are usable over a wide pH range, and have reuse potential (Nayak & Lahiri, 2005). Advantages of composite alginate beads (CABs) over conventional treatment methods include low cost, high efficiency, high potential for regeneration and reuse, and generation of secondary pollutants is low. As no specialized facility or technology is required, use of the CABs is straightforward.

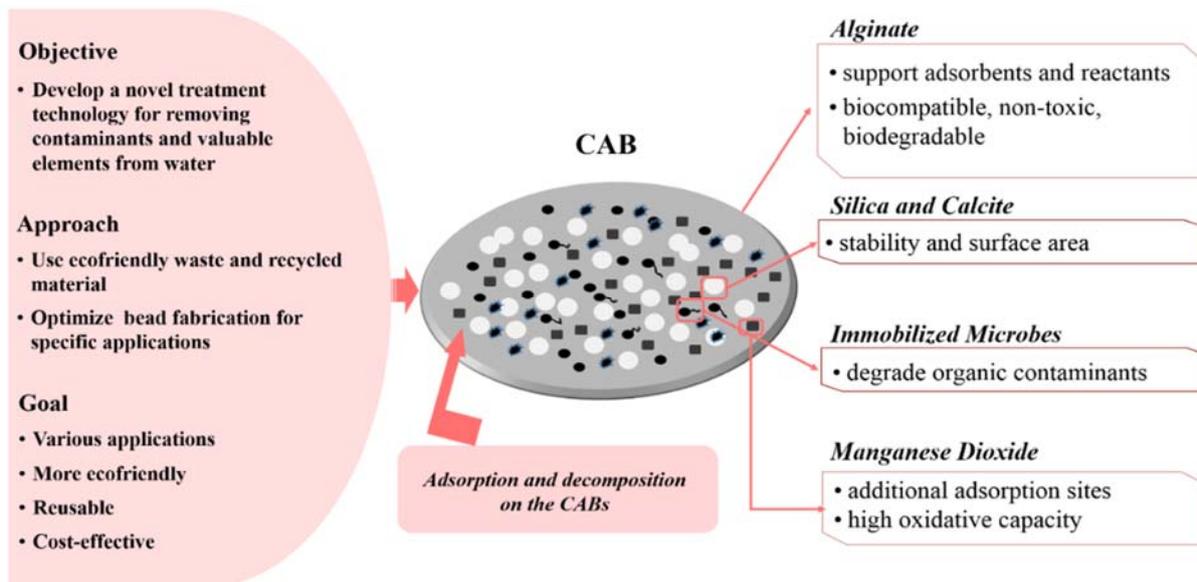


Fig. 13. Fabrication of CABs with various adsorbents and reactive materials.

CAB preparation. CABs were prepared, incorporating MnO₂ recycled from spent lithium batteries, precipitate from urine, and activated carbon (AC) (Fig. 14). The CABs were prepared by mixing sodium alginate solution with the reactive material (ultra-sonication and pulsing) and adding dropwise to 0.2 M CaCl₂ solution. The CABs were then hardened at 4 °C for 12 h, washed with distilled water, filtered, air-dried at room temperature or freeze dried at -80 °C, and stored at 4 °C.



Fig. 14. Scheme showing CAB fabrication with the prepared adsorbent and reactive materials.

CABs stability and reuse. Dried CABs were stable in aqueous solution containing *p*-cresol and TYL at pH 6-8 (room temperature) for over 6 months. CABs containing AC and MnO₂ were stable at pH 2-12. Swelling was less in beads containing AC and MnO₂.

Mechanical stability is necessary for practical use of the CABs. Stability was evaluated after freeze-drying, room temperature drying and drying at 70 °C). CABs dried at room temperature were most stable (not easily broken and integrity was maintained in water) (Fig. 15). However, freeze-dried CABs had the highest adsorption capacity for *p*-cresol, As, and Cd, primarily attributable to surface area differences (BET surface area: freeze-dried > 70 °C > room temperature) (Table 2).

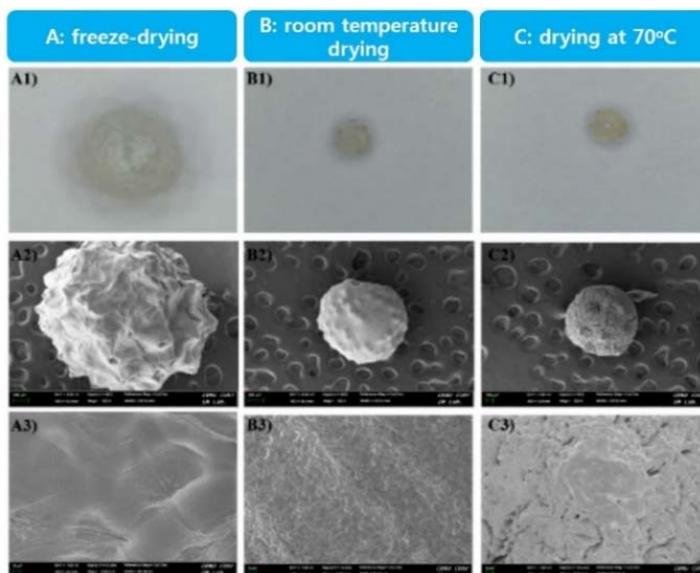


Fig. 15. SEM images of alginate beads dried under different conditions (1: granular, 2 and 3: surface morphologies)

Table 2. Brunauer Emmett Teller (BET) analysis of three types of beads.

Dying process	Freeze-dried	Room temp. dried	70 °C dried
Surface area (m ² /g)	3.045	0.544	1.687

Another desirable attribute for commercially viable adsorbents is the capacity for reuse. To evaluate reuse potential, multiple contaminant removal and washing cycles were conducted in a batch system. Washing with 0.1 M HCl was more effective than with distilled water. Dried alginate beads washed with 0.1 M HCl solution could be reused for five cycles without a significant decrease in Cd removal capacity (Fig. 16).

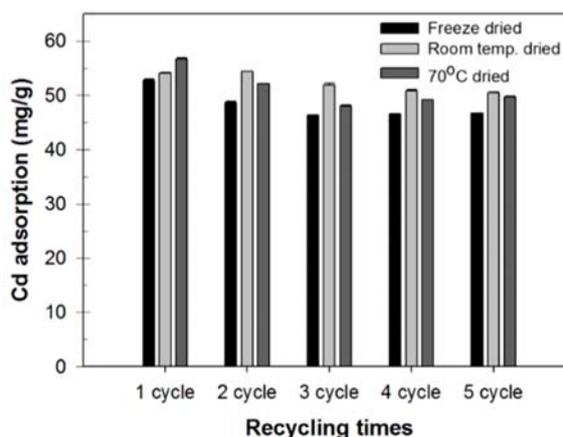


Fig. 16. Multiple cycles of Cd adsorption on alginate beads dried by different methods.

Characterization of the CAB with MnO₂ or MnO₂ and Activated Carbon.

CABs containing the recycled MnO₂.

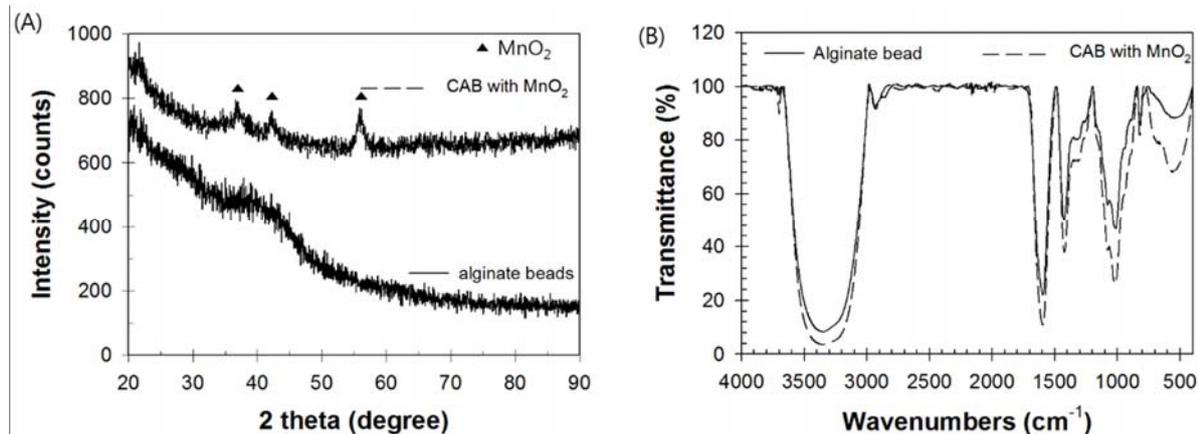


Fig. 17. (A) XRD analysis and (B) FTIR spectra of alginate beads alone and CABs containing 0.5%, (w/w) MnO₂.

XRD patterns of alginate beads (Fig. 17A) and CABs containing MnO₂ (Fig. 17B) shows characteristic MnO₂ peaks at 36°, 42°, and 55.5°. The FTIR spectra (Fig. 20B) of both alginate beads and CABs with MnO₂ show alginate matrix bands at 3450-3400 cm⁻¹ (OH stretching) and peaks at 2930 cm⁻¹ (CH stretching), 1597 cm⁻¹ (COO⁻ asymmetric stretching), 1415 cm⁻¹ (COO⁻ symmetric stretching), 1095 cm⁻¹ (CO stretching of ether group), and 1065 cm⁻¹ (CO stretching of alcohol group) (Gok and Aytas, 2009). Peaks at 510 and 689 cm⁻¹ in the spectrum of CABs containing MnO₂ are attributed to the Mn-O groups, similar to the spectrum of recycled MnO₂ (Fig. 6B).

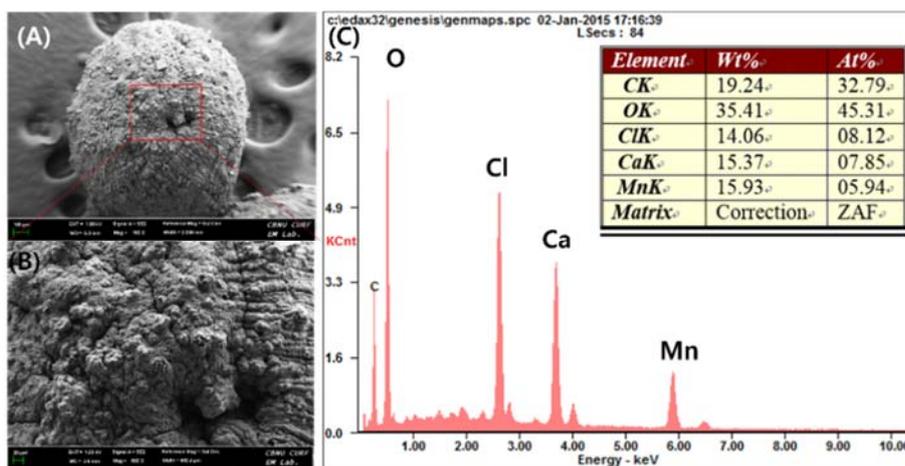


Fig. 18. (A) FE-SEM image, (B) surface morphology, and (C) EDS analysis of CABs containing 0.5% (w/w) MnO₂.

The average size of the CABs was ~ 0.3 mm after drying at room temperature (Fig 18A). Figure 18B shows the CAB surface and EDS analysis confirmed the presence of Mn (Fig. 18C). CABs containing MnO_2 could be dried without losing their original shape and were easily handled in the dried state. Stability and handling are essential for application of the materials, allowing the CABs to be easily packed, transported, and stored. Without the MnO_2 , dried alginate beads formed much smaller, irregular particles, with little re-swelling in water.

CABs with MnO_2 and activated carbon (AC).

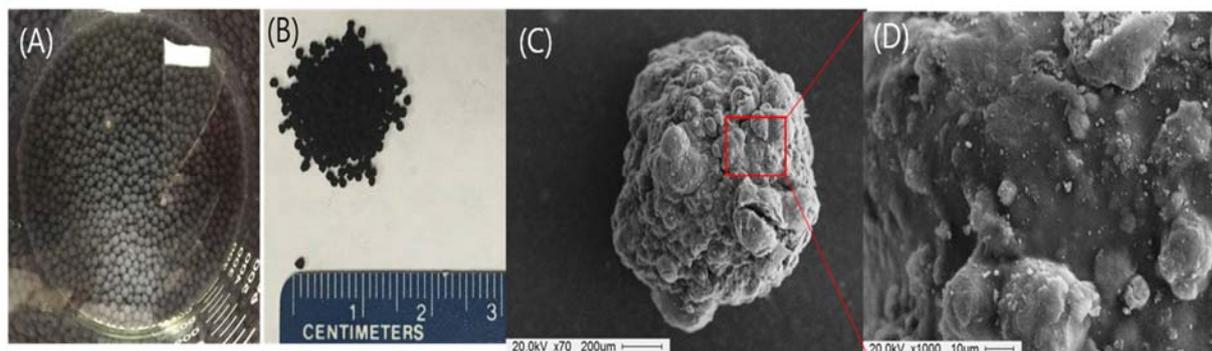


Fig. 19. Morphologies of (A) the wet CABs in aqueous solution, (B) the dried CABs at room temperature, (C) and (D) FE-SEM image of CABs containing 0.25% (w/w) MnO_2 and 0.25% (w/w) AC.

Figures 19 and 20 show that AC was successfully combined with MnO_2 and the alginate matrix. The average size of the CABs with AC and MnO_2 was 0.4 mm. The surface morphology of dry CABs was observed by SEM (Figs. 19C and D) and shows a large surface area for adsorption of contaminants. XRD and FTIR results strongly support physical and/or chemical interactions between Mn oxide, AC, and alginate (Figs. 20A and B).

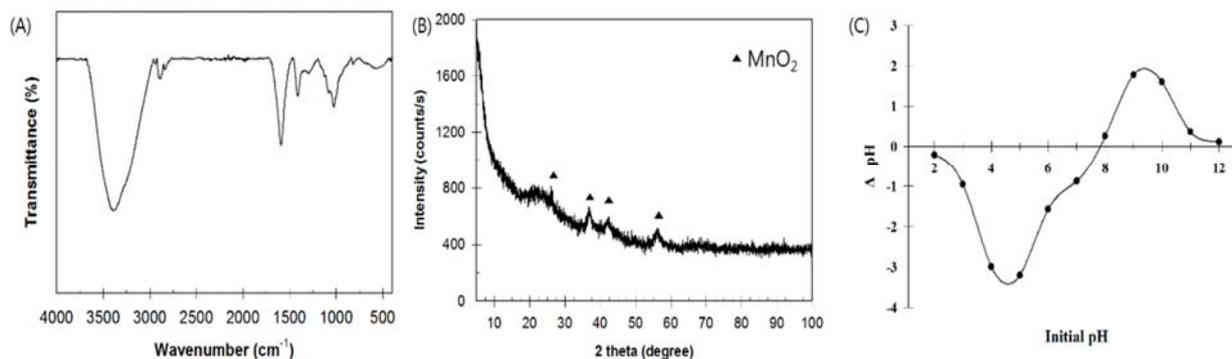


Fig. 20. (A) FTIR spectrum, (B) XRD analysis, and (C) pH_{PZC} of CABs containing 0.25% (w/w) MnO_2 and 0.25% (w/w) AC.

The point of zero charge (pH_{PZC}) is an important property identifying the surface electrical neutrality of the adsorbent. CAB pH_{PZC} was determined at pH 2–12 (Fig. 20C). The CAB pH_{PZC} was estimated at 7.8. At $\text{pH} > \text{pH}_{\text{PZC}}$, the surface of is negatively charged and at $\text{pH} < \text{pH}_{\text{PZC}}$, the surface is positively charged. Thus, the adsorption of cationic pollutants is favored when the pH of solution is above the pH_{PZC} of the material (Srivastava et al., 2005). The CABs showed high *p*-cresol and TYL adsorption and decomposition of *p*-cresol was observed. Incorporation of AC enhanced removal of both the VOC (*p*-cresol) and antibiotic (TYL) from solution. CABs containing both MnO_2 and AC were more efficient for removal of *p*-cresol and TYL in aqueous solution than beads containing only immobilized MnO_2 .

BET and Langmuir surface area analyses were used to measure pore structure and surface area for alginate beads alone and CABs containing MnO_2 and or both MnO_2 and AC. CABs containing MnO_2 and AC had significantly higher surface areas than beads containing alginate alone (Table 3). The surface area of the alginate beads was $0.117 \text{ m}^2/\text{g}$ and the respective surface areas of CABs containing MnO_2 alone and both MnO_2 and AC were 2.043 and $31.784 \text{ m}^2/\text{g}$. The increase in adsorption capacity may be correlated with the increase in specific surface area.

Table 3. Surface area of CABs with MnO_2 and $\text{MnO}_2 + \text{AC}$ (dried at room temperature).

Types	BET surface area (m^2/g)	Langmuir surface area (m^2/g)
Beads with alginate only	0.117	0.156
CABs with MnO_2	2.043	2.842
CABs with MnO_2 and AC	31.784	45.581

Contaminant Removal by the CABs

Batch reactor experiments. Laboratory batch reactors were conducted to evaluate solute removal and, in the case of the organics, degradation/decomposition by the CABs. Selected representative analytes were obtained commercially. Quantitative and confirmation analyses were by HPLC, GC/MS, and ICP/AES.

The basic batch reactor procedure involved adding the prepared CABs to solution at various mass to volume and mass to analyte concentration ratios. Analyte concentrations were monitored by periodically removing aliquots from reaction vessels at selected times and intervals appropriate to establish pseudo-equilibrium or within a desired treatment/holding time.

For *heavy metal(loid)s*, removal/adsorption experiments were carried out using prepared stock solutions of analytical grade reagents (e.g., Cd(II) as $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ and As(III) as NaAsO_2). The initial pH of the solutions (buffered as required) was adjusted with 1 M HCl or NaOH, based on previous determinations of optimum metal binding capacity. The effect of pH on removal by the CABs was examined, ranging from acidic to highly basic (pH 2-12).

For the *VOCs*, removal/degradation experiments were carried out using prepared stock solutions of analytical grade *p*-cresol. Aqueous solutions of the desired analyte were mixed with prepared CABs at various ratios in a stoppered conical flask. This mixture was agitated on a shaker with temperature control

(~15-50 °C). Samples were removed periodically, filtered and refrigerated or frozen until analysis.

The amount of the analyte removed at time t , Q_t (%), is $Q_t = (C_0 - C_t / C_0) \times 100\%$, where C_0 (mg/L) and C_t (mg/L) were initial and time = t solute concentrations. Removal capacity was calculated as $q_e = (C_0 - C_e)(V/m)$, where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium solute concentrations, m (g) is adsorbent mass, and V (L) is solution volume.

Adsorption of As, Cd, p -cresol and TYL by the CABs was described using kinetic and isotherm models. The adsorption process was characterized by fitting first- and second-order expressions to the data. The pseudo-first order rate equation is represented as: $dq_t/dt = k_1(q_e - q_t)$, where q_t , q_e and k_1 are the amount of As, Cd, p -cresol and TYL adsorbed at time t (mg/g), the amount adsorbed at equilibrium (mg/g), and the pseudo first-order rate constant (1/min), respectively. The pseudo-second order rate equation is expressed as: $dqt/dt = k_2(q_e - q_t)^2$, where k_2 is the pseudo second-order rate constant (g/mg min). Adsorption isotherms were used to describe the relationship between the mass of As, Cd, p -cresol and TYL adsorbed per unit mass of adsorbent and the aqueous phase metal concentration at equilibrium and constant temperature. The Langmuir model, which is frequently used to describe the adsorption of cations, is: $q_e = q_{max}K_L C_e / (1 + K_L C_e)$, where q_{max} , C_e and K_L are the maximum adsorption capacity (mg/g), concentration of the metal in solution at equilibrium (mg/L), and the Langmuir adsorption constant (L/mg), respectively. The Freundlich isotherm, often used to describe the adsorption of a broad range of adsorbates, is expressed as: $q_e = K_F C_e^{1/n}$, where K_F is the Freundlich adsorption constant (L/mg) and $1/n$ is the adsorption intensity.

The potential to reuse the composite beads was determined in multiple cycles. Aqueous solutions (100 mL) containing compounds such as As, Cd, p -cresol and TYL were first equilibrated with CABs (adsorption/decomposition). The beads were then separated from the solution by filtration and washed with distilled water until the pH of wash solution was neutral. The CABs after adsorbed compounds were then added to 50 mL of distilled water or 0.1 M HCl and mixed by shaking at 25 °C for more than 2 h. The regenerated beads were reused in a subsequent removal experiments and the process was repeated.

Removal experiments included (i) simultaneous removal of p -cresol, As, and Cd with CABs containing MnO₂ recycled from spent batteries, (ii) simultaneous removal of p -cresol and TYL using CABs with MnO₂ and activated carbon into alginate beads, (iii) removal of nitrogen and phosphate from aqueous solution by CABs containing MnO₂ and AC, and (iv) simultaneous removal of p -cresol, As and Cd by CABs containing recycled MnO₂ recovered from spent batteries.

CABs containing immobilized MnO₂ (0.5% w/w) resulted in significantly greater removal of As and greater sorption and decomposition of p -cresol (Fig. 21). Equilibrium was achieved within 48 h, with optimum adsorption at pH 7, and the maximum capacities for adsorption of As and Cd were 2.1 and 63.6 mg/g, respectively. The potential for reuse, after regenerating with 0.1 M HCl, was excellent for three consecutive reuse cycles.

Figure 22 shows simultaneous removal of p -cresol, TYL with the fabricated CABs containing MnO₂ and AC. CABs containing both MnO₂ (0.25% w/w) and AC (0.25% w/w) had a high capacity for the adsorption/decomposition of p -cresol and TYL. Solution pH had little effect on removal (Fig. 22A). Removal of both compounds was dependent on initial concentration and contact time (Fig. 22B). Removal efficiency remained high after five regeneration cycles (Fig. 22C). The Langmuir model provided a good

fit to the adsorption data for both As and Cd (Table 4). Removal kinetics were well-described by first- or pseudo-second order models (Table 4).

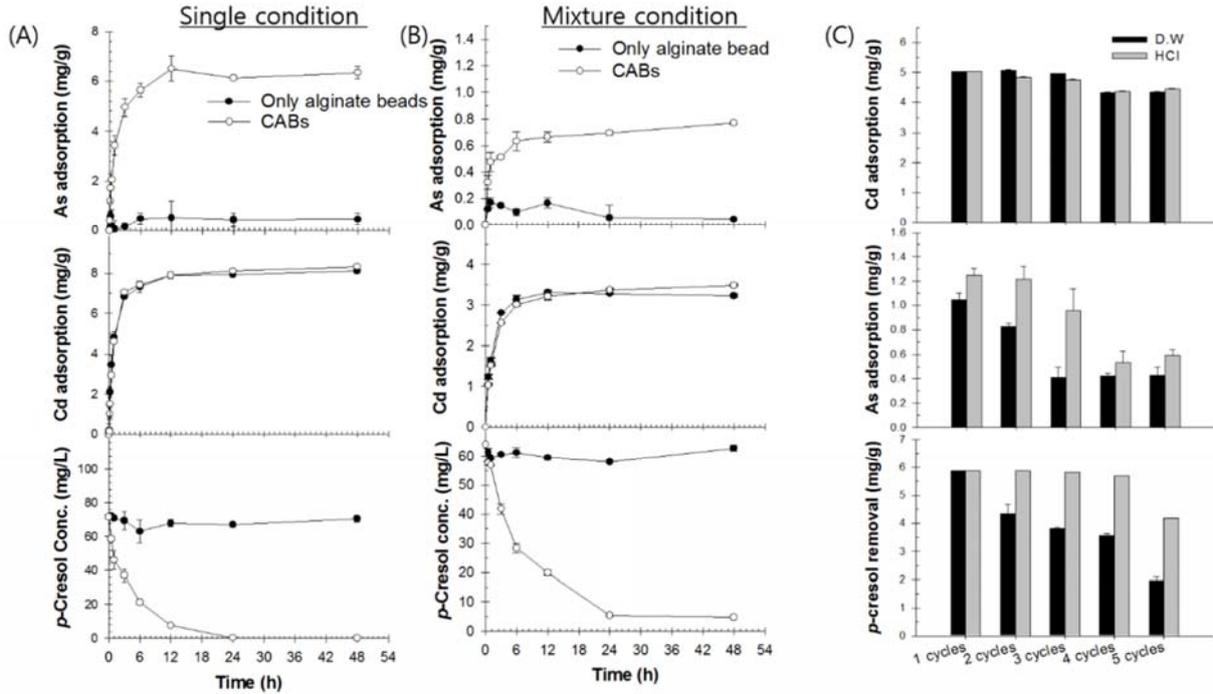


Fig. 21. (A) Single and (B) mixed contaminant experiments for removal of *p*-cresol, As, and Cd using CABs with 0.25% (w/w) MnO₂ and 0.25% (w/w) AC, and (C) adsorption capacity of CABs containing 0.5% (w/w) MnO₂ after multiple regeneration cycles by desorption.

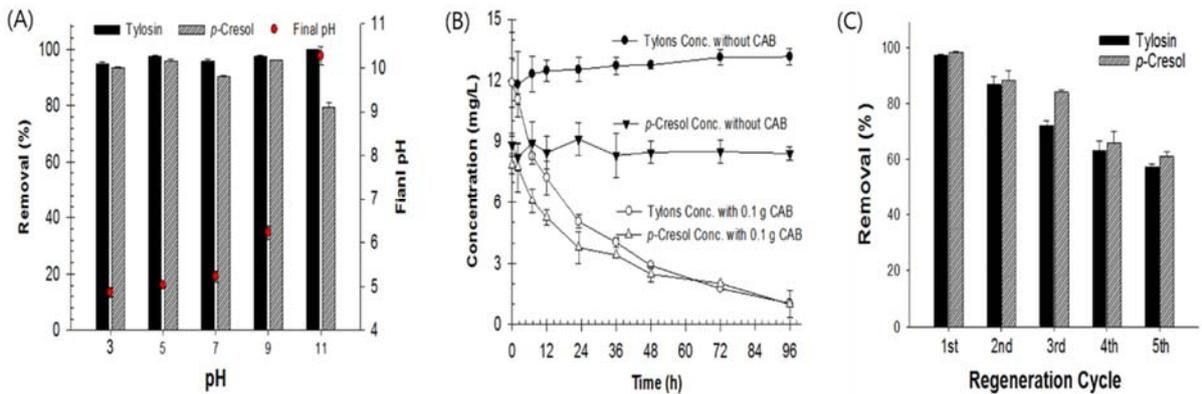


Fig. 22. (A) Effect of initial pH, (B) removal efficiency, and (C) regeneration of removal *p*-cresol and TYL using CABs containing 0.25% (w/w) MnO₂ and 0.25% (w/w) AC.

Table 4. Parameters for pseudo first- and second-order kinetic models and parameters for Langmuir and Freundlich isotherms for the adsorption of total arsenic (As) and cadmium (Cd) by CAB during agitation at 180 rpm and 30 °C.

Model and parameter	Arsenic			Cadmium		
Pseudo-first order	q ₁ (mg/g)	k ₁ (1/min)	R ²	q ₁ (mg/g)	k ₁ (1/min)	R ²
	5.96	0.87	0.989	7.80	0.87	0.997
Pseudo-second order	q ₂ (mg/g)	k ₂ (g/mg min)	R ²	q ₂ (mg/g)	k ₂ (g/mg min)	R ²
	6.59	0.16	0.996	8.66	0.12	0.996
Langmuir	q _{max} (mg/g)	k _L (L/mg)	R ²	q _{max} (mg/g)	k _L (L/mg)	R ²
	2.09	0.02	0.967	63.62	0.01	0.9997
Freundlich	K _F	n	R ²	K _F	n	R ²
	0.18	2.36	0.933	0.15	1.20	0.995

As Table 5 shows, the kinetics of *p*-cresol and TYL removal using CABs follows the pseudo second-order rate model. A higher K₂ value indicated that *p*-cresol will likely be more rapidly adsorbed/decomposed than TYL by the CABs containing 0.25% (w/w) MnO₂ and 0.25% (w/w) AC. Equilibrium was reached within 48-120 h, depending on initial concentration. The Langmuir isotherm gave a better fit to the *p*-cresol and TYL adsorption data than the Freundlich model (Fig. 23). The adsorption of *p*-cresol and TYL was found to fit the Langmuir isotherm model, which suggests monolayer coverage of the adsorbent surface. Langmuir adsorption constants (K_L) indicated similar affinities of *p*-cresol and TYL for the CABs; maximum adsorption capacities (q_{max}) were 76.14 mg *p*-cresol and 129.24 mg TYL.

Table 5. Parameters for pseudo first- and second-order kinetic models and for Langmuir and Freundlich isotherms for the adsorption of *p*-cresol and tylosin (TYL) by CABs (initial pH = 7, 0.5 g CABs in 100 ml solution, and agitation for 120 h at 200 rpm).

Model and Parameter	<i>p</i> -cresol			tylosin (TYL)		
Pseudo-first order kinetic	q ₁ (mg/g)	k ₁ (1/min)	R ²	q ₁ (mg/g)	k ₁ (1/min)	R ²
	1.512	0.542	0.959	2.35	0.381	0.996
Pseudo-second order kinetic	q ₂ (mg/g)	k ₂ (g/mg min)	R ²	q ₂ (mg/g)	k ₂ (g/mg min)	R ²
	1.591	0.533	0.989	2.48	0.258	0.996
Langmuir adsorption	q _{max} (mg/g)	k _L (L/mg)	R ²	q _{max} (mg/g)	k _L (L/mg)	R ²
	76.14	0.004	0.988	129.24	0.003	0.954
Freundlich adsorption	K _F	N	R ²	K _F	N	R ²
	1.24	1.68	0.966	2.47	2.067	0.877

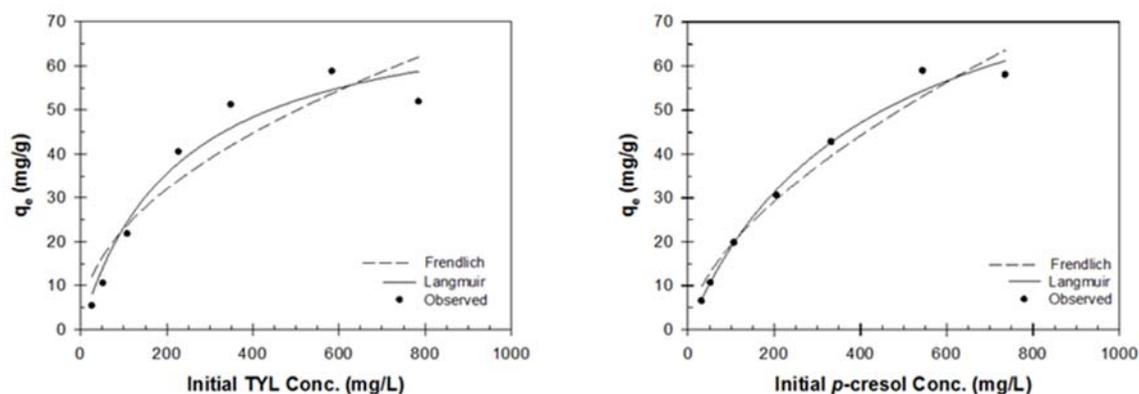


Fig. 23. Adsorption isotherms for (A) TYL and (B) *p*-cresol on CABs containing both MnO₂ and AC (0.25% each, w/w; 0.5 g CABs/100 mL at pH 7, 25 °C and 120 h contact time).

CABs containing only alginate and MnO₂ were not effective for phosphate and nitrate ions removal (Fig. 24). However, CABs containing both MnO₂ and AC removed ~100% of the P (initial concentration = 3.8 mg P/L) within 120 h. CABs containing AC could be an effective alternative material for removing phosphate ions from contaminated water. Adsorption of phosphate is likely via electrostatic attraction, ion exchange, and/or Lewis acid–base interactions with the adsorbents (Zhang *et al.* 2011).

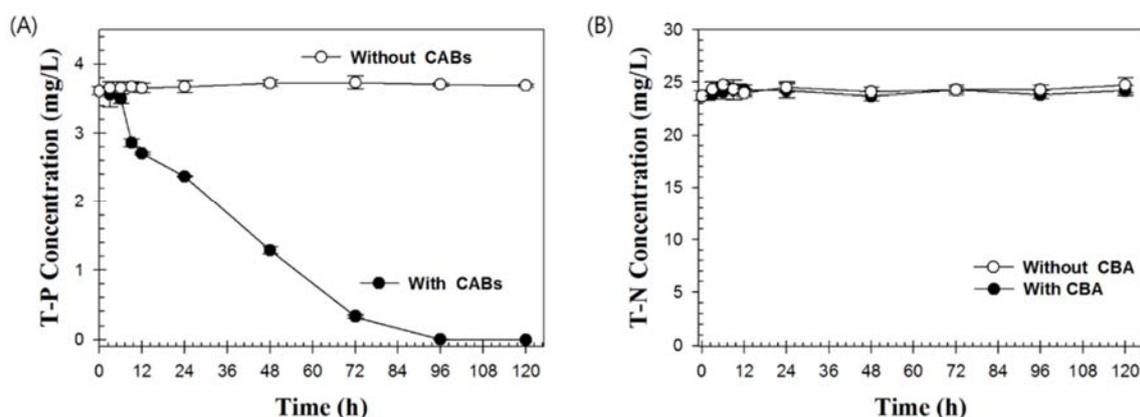


Fig. 24. Removal total (A) phosphate and (B) nitrate ions using CABs containing MnO₂ and AC for 120 h.

Identification of transformation products. GC/MS was used to identify transformation products resulting from reaction of *p*-cresol with the CABs containing MnO₂. The CABs removed ~100% of the *p*-cresol (initial concentration = 50 mg/L) within 48 h (Fig. 25A). Figure 25B shows a decrease in *p*-cresol, and a new *p*-benzoquinone peak following removal by CABs containing MnO₂. Decomposition of *p*-cresol can be attributed to reaction with oxygen radicals at MnO₂ surfaces.

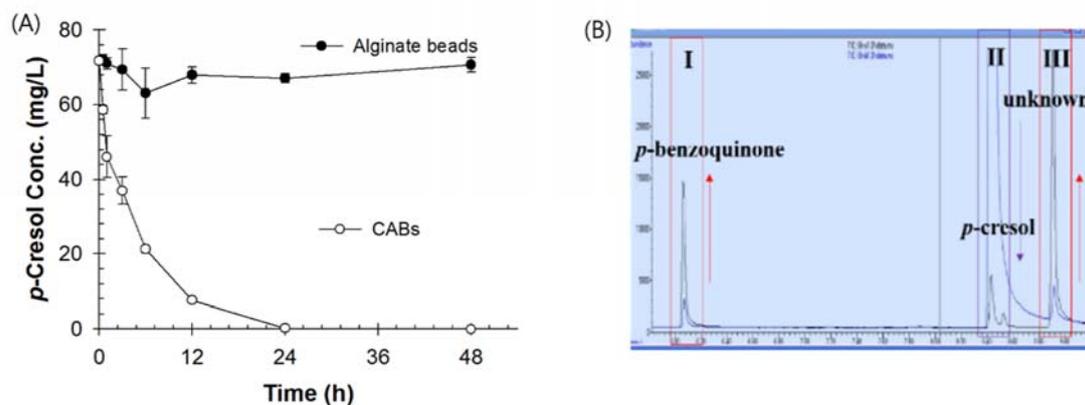


Fig. 25. (A) *P*-cresol removal and (B) transformation by CABs containing MnO₂ in aqueous solution.

Characterizations of CABs after reaction with As, Cd, and p-cresol. FTIR spectra suggested that As, Cu, and *p*-cresol can be adsorbed onto the surface of CABs with MnO₂ through carboxyl and hydroxyl groups (Fig. 26). Major peaks were observed at 3418, 1607, 1421 and 500 to 700 cm⁻¹. Peaks at 500 to 700 cm⁻¹ are assigned to the stretching vibration of the Mn-O bond in manganese oxide. The MnO₂ is bound to alginate via the interaction between the carboxylic groups of alginate and the surface hydroxyl groups of metal oxide (Finotelli *et al.*, 2004, Soni *et al.*, 2012). The -OH stretching band at 1100 and 1540 cm⁻¹ suggests binding of As, Cu, and *p*-cresol on the surface of CABs.

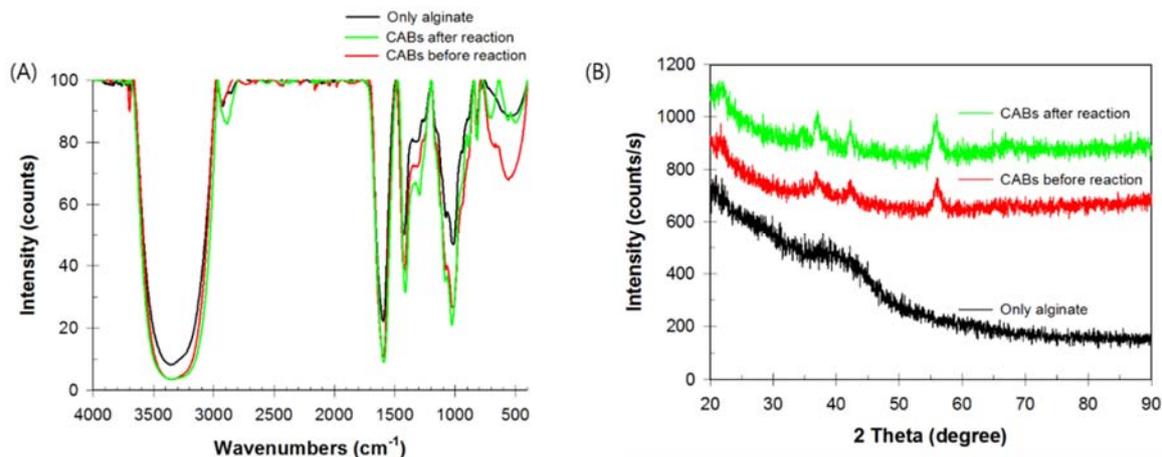


Fig. 26. (A) FTIR spectra and (B) XRD of alginate alone and alginate containing recovered MnO₂ before and after equilibrating with aqueous solution containing 100 mg/L each of arsenic, cadmium and *p*-cresol.

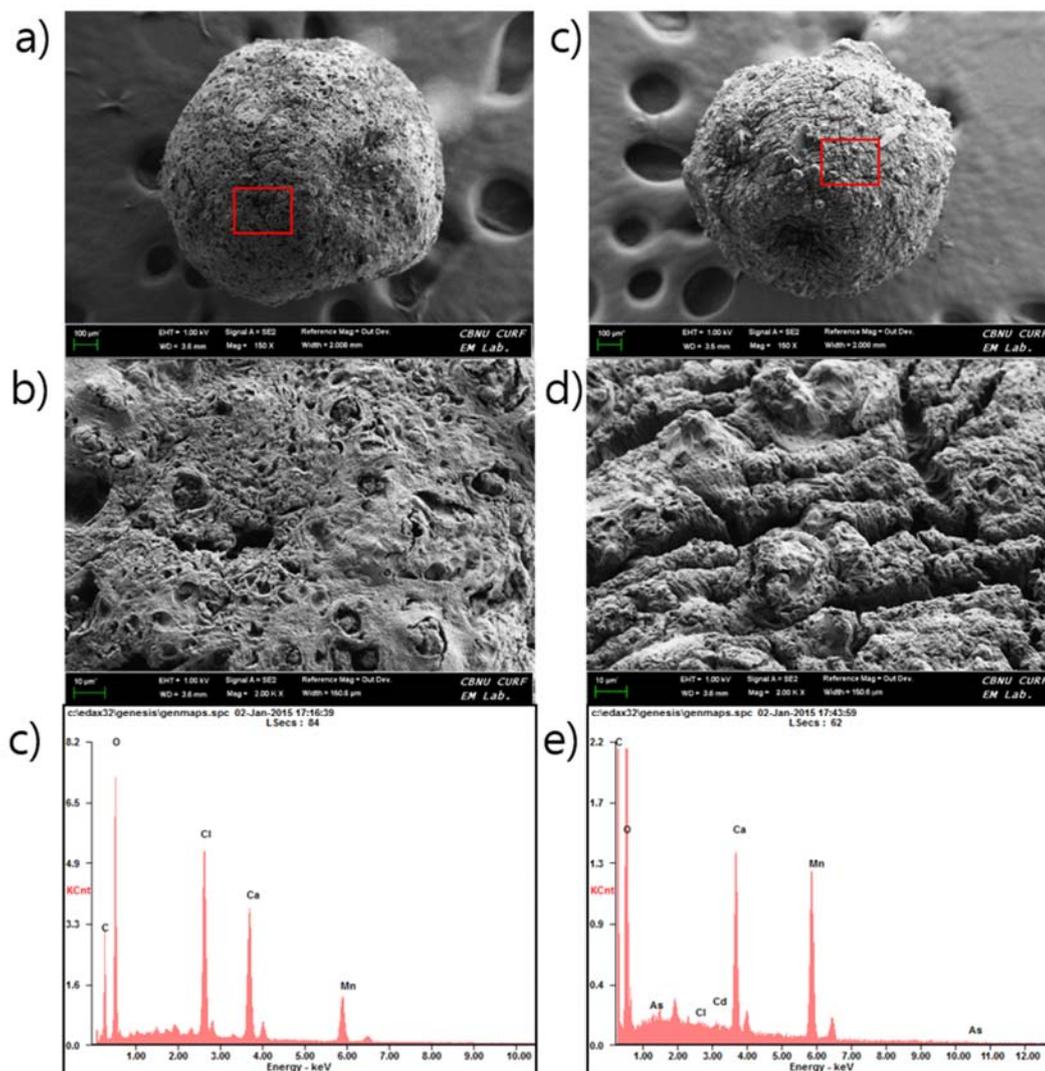


Fig. 27. SEM micrographs and EDS analysis of CABs containing recycled MnO_2 before (A, B, C) and after (D, E, F) equilibrating with aqueous solution containing 100 mg/L of arsenic, cadmium and *p*-cresol.

The SEM image shows the rough and heterogeneous, relatively spherical shape and narrow size distribution of the manganese dioxide in alginate (Fig. 27). Sharp XRD peaks at 37, 42, and 56 ° suggest impregnation of MnO_2 into alginate beads. The crystallinity of MnO_2 -loaded alginate beads was calculated as ~15-20%. Addition of AC and MnO_2 also increased mechanical and chemical stability, making the CABs more amenable to regeneration for multiple reuse cycles than beads containing alginate alone (data not shown).

Summary and Significant Findings

This project showed that CABs containing recycled MnO₂ and AC in an alginate matrix can be used to mitigate pollution and improve water quality of water. The fabricated CABs were tested for removal of As, Cd, *p*-cresol, TYL, phosphate and nitrate ions from aqueous solution and for inactivation of bacteria. Significant findings were as follows:

- Characterizations of CABs with MnO₂ (0.5% w/w) and both MnO₂ and AC (0.25% w/w each) showed MnO₂ and AC homogeneously distributed within the alginate gel beads.
- CABs containing MnO₂ and AC exhibited a high capacity for removing Cd and other heavy metals, As (metalloid), *p*-cresol (VOC), TYL (antibiotic), and phosphate ions from aqueous solutions.
- The CABs showed potential use over a wide solution pH range (from 2 to 12).
- Adding AC to the CABs with MnO₂ improved *p*-cresol and TYL removal.
- The CABs containing MnO₂ and/or AC were not effective for nitrate-N removal.
- CABs exhibited faster removal kinetics and greater adsorption capacity than unmodified alginate gel beads.
- The CABs showed good reuse potential.
- The CABs were easily handled, with greater thermal stability and less dissolution in water than unmodified alginate gel beads.
- MnO₂ recovered from battery wastewater is a strong oxidizer and promoted VOC (*p*-cresol) decomposition, as well as inactivation of *E.coli*.
- Impurities in the recycled MnO₂ improved performance over pure MnO₂, likely acting as adsorption and reaction catalysts.
- Including AC in the CABs with MnO₂ provides a large surface area and hydrophobic sites for adsorption.

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Climate Variability and a Decision Support Tool for Optimizing Yields with Limited Water Available for Irrigation

Basic Information

Title:	Climate Variability and a Decision Support Tool for Optimizing Yields with Limited Water Available for Irrigation
Project Number:	2015NE270B
Start Date:	3/1/2015
End Date:	2/29/2016
Funding Source:	104B
Congressional District:	NE 01
Research Category:	Climate and Hydrologic Processes
Focus Category:	Climatological Processes, Irrigation, Management and Planning
Descriptors:	None
Principal Investigators:	Jane Asiyu Okalebo, Kenneth G Hubbard

Publications

There are no publications.

Project #: 2015NE270B
Funding Period: March 1, 2015 through February 29, 2016
Title: Climate Variability and Decision Support Tool for Optimizing Yields with Limited Water Available for Irrigation
PI(s): Jane Okalebo and Kenneth Hubbard

Introduction

The grant is intended to fund the development of an online decision support tool that will assist farmers to select the most crucial time to irrigate by taking into account:

- Climate variability
- Amount of irrigation water available
- Crop water use sensitivity at different phenological growth stages.
- Short term weather forecasts.

Progress

The Robinson-Hubbard Model was used for the purposes of this work that incorporated the evapotranspiration yield sensitivity computations. Irrigation combinations for 1 to 6 irrigation events have been generated and tested for 2005 (Figure 1) below. It is evident that the ratio of actual yield to yield potential (Y/Y_p) can remain as low as about 0.53 despite an increase of irrigation events (blue dots). Optimized timing of irrigation events increases yield potentials with as few as 3 irrigation events over the season yielding a high Y/Y_p ratio of greater than 0.9.

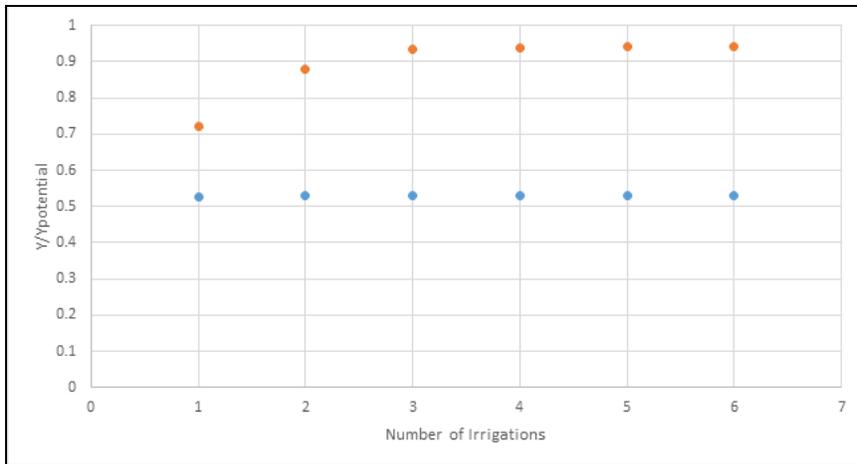


Figure 1: The impact of irrigation events on the he ratio of actual to potential corn grain yield. The blue dots depict the lowest ratio while the orange dots represent the highest ratio based on the combination of irrigation dates.

Since the irrigation combinations increased exponentially, we utilized the Holland Computing Center services to conduct the runs/simulations. Further modification of the code by adding a new subroutine CombolRR; were also conducted.

Hybrid Maize: A Simulation Model for Corn Growth and Yield.

Since debugging and getting the software to work has been time consuming, consideration using the Hybrid Maize Model have been discussed and some results are presented.

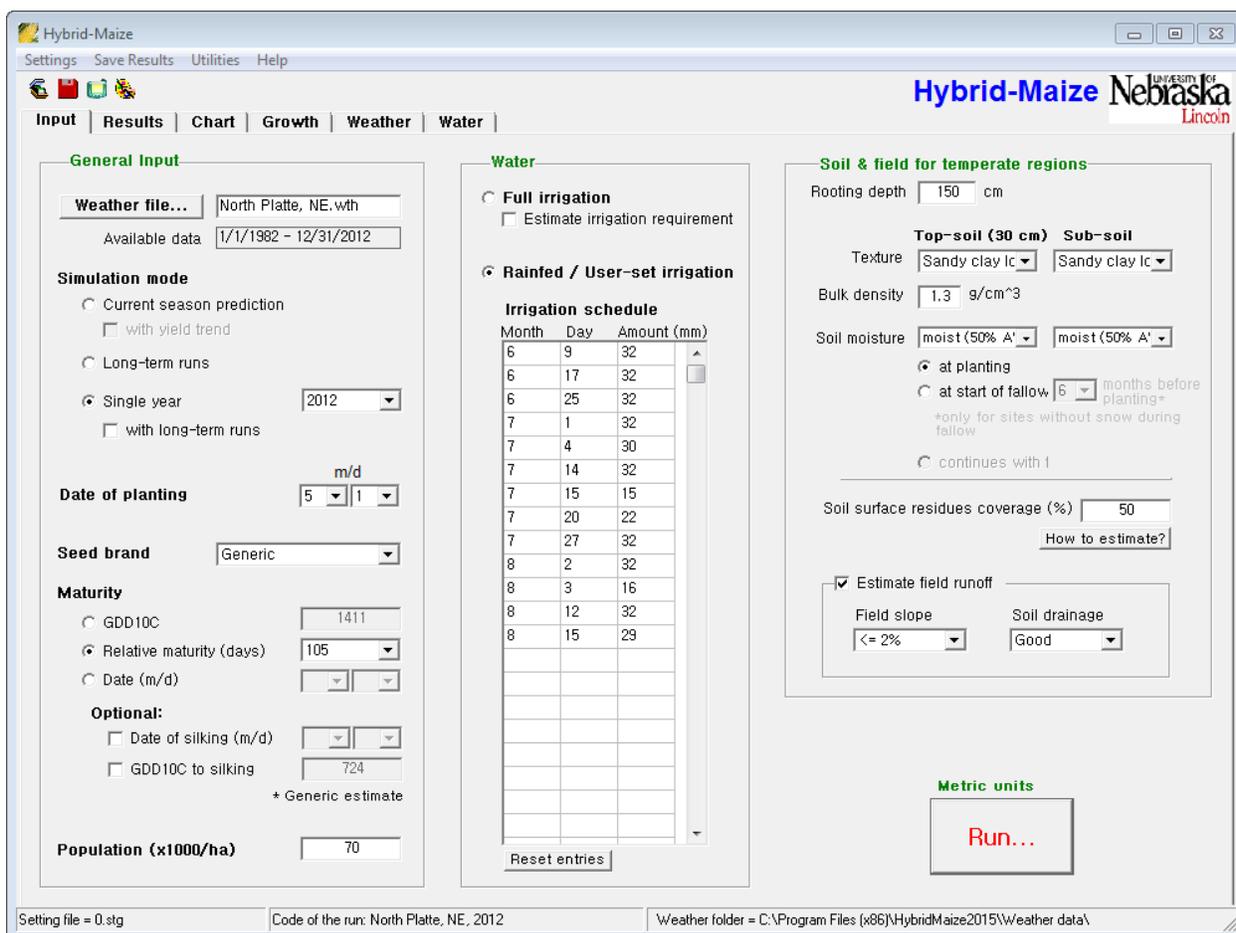
Scenario	Date that Irrigation Event Omitted	Grain yield at 15.5% (Mg/ha)	Grain Dry Matter (Mg/ha)	stover dry matter (Mg/ha)	Total above ground dry matter (Mg/ha)	Harvest Index	Kernel Setting Rate %	% of Potential Yield
1	9-Jun	10.40	8.80	14.00	22.80	0.38	70.00	0.98
2	17-Jun	10.30	8.70	13.70	22.20	0.39	69.00	0.97
3	25-Jun	9.50	8.10	15.50	23.60	0.34	64.00	0.90
4	1-Jul	9.80	8.30	15.30	23.60	0.35	66.00	0.92
5	4-Jul	10.00	8.50	15.00	23.40	0.36	67.00	0.94
6	14-Jul	10.40	8.80	14.00	22.80	0.39	70.00	0.98
7	15-Jul	10.60	9.00	15.00	24.00	0.37	71.00	1.00
8	20-Jul	10.60	9.00	13.30	22.30	0.40	71.00	1.00
9	27-Jul	10.60	9.00	10.60	19.60	0.46	71.00	1.00
10	2-Aug	10.60	9.00	11.60	20.60	0.44	71.00	1.00
11	3-Aug	10.60	9.00	14.40	23.40	0.38	71.00	1.00
12	12-Aug	10.60	9.00	14.00	23.00	0.39	71.00	1.00
13	15-Aug	10.60	9.00	14.80	23.80	0.38	71.00	1.00
0	0	10.60	9.00	16.10	25.10	0.36	71.00	1.00

Table 1: The impact of omitting a single irrigation event on maize grain yield, grain dry matter, stover dry matter, total above ground dry matter and potential yield. Simulations conducted using Hybrid Maize (Version 2015.6.1).

The model that is currently being tested and used alongside the Robinson-Hubbard Model is called: Hybrid-Maize (Version 2015.6.1) that was designed by: H.S. Yang, A. Dobermann, K.G. Cassman, D. Walters and P. Grassini of the Department of Agronomy & Horticulture. University of Nebraska-Lincoln.

Using North Platte (41.08 N, 107.77 W) as a test site together with weather files from the HPRCC, a total of 13 irrigation events were recommended by the program on the days shown. Runs were conducted to determine how the omission of any one of the irrigation events would impact the grain yield, grain dry matter, stover dry matter, total above ground dry matter and potential yield. From the runs/simulations, it was noticeable that any omission of an irrigation event after the 15th of July, did not reduce grain yield. Kernel setting rates were affected by water stress early in the vegetative development of the corn (e.g. irrigation omission on the 25th of June) which indicates that irrigation should be conducted early in the season to prevent water stress and yield losses.

This model will utilize 72 hour - short term weather forecasts (Source: Wang et al, Atmospheric Sciences, UNL) which will be incorporated into the model. Thereafter both water and economic savings can be calculated following results of simulations.



“HYBRID-MAIZE IS A PROGRAM (the ‘Software’), DEVELOPED AND OFFERED BY THE UNIVERSITY OF NEBRASKA-LINCOLN (UNL), DESIGNED TO PROVIDE INFORMATION THAT CONTRIBUTES TO BETTER UNDERSTANDING OF CORN YIELD POTENTIAL AND THE INTERACTIVE EFFECTS OF CROP MANAGEMENT PRACTICES AND CLIMATE ON CORN YIELDS. ALTHOUGH THE MODEL HAS BEEN VALIDATED UNDER A NUMBER OF ENVIRONMENTS AND CROP MANAGEMENT REGIMES, THE AUTHORS MAKE NO CLAIM THAT THE MODEL PREDICTIONS ARE ACCURATE OR REALISTIC FOR ALL ENVIRONMENTS OR MANAGEMENT REGIMES. THEREFORE, MODEL PREDICTIONS SHOULD BE CONSIDERED AS ONLY ONE SOURCE OF INFORMATION THAT CAN BE USED TO HELP GUIDE DECISIONS ABOUT CROP MANAGEMENT PRACTICES AND GRAIN MARKETING IN COMBINATION WITH OTHER SOURCES OF INFORMATION, COMMON SENSE, AND PAST EXPERIENCE.” Yang et al, 2015).

Presentations

Jane Okalebo presented and shared results through generous project funding at the AWRA conference in June, 2015.

**American Water Resources Association
2015 SUMMER SPECIALTY CONFERENCE
Climate Change Adaptation
June 15 - 17, 2015
New Orleans, LA
Wednesday, June 17
3:30 PM – 5:00 PM**

SESSION 21: Dealing with Agriculture and Vegetation Changes

An Evaluation of in Season Water Stress Sensitivity Using a Multiplicative Evapotranspiration- Grain Yield Model for *Zea mays* L. Growing in Mead, Nebraska, USA -
Jane Okalebo, University of Nebraska-Lincoln, Lincoln, NE (co-authors: K. G. Hubbard, A. Kilic, R. Oglesby, M.Hayes.)

An empirical crop growth model was developed using long term corn (*Zea mays* L.) experimental data from the University of Nebraska-Lincoln's Carbon Sequestration Project (CSP) at the Agricultural Research and Development Center near Lincoln NE. The model utilized the multiplicative approach to evaluating water demands expressed as the ratio of actual and potential evaporation at different periods of corn development. Total evapotranspiration measurements derived from eddy covariance measurements (EC), represented actual evapotranspiration while potential evapotranspiration (ET_{rp}) was based on a modified Penman equation for Nebraska's climatic conditions. Several combinations of corn development periods were formulated where a period was comprised of more than one growth stage. The study herein tested the ET-yield model using several period combinations also known as models (A-E).

Due to the nature of the evapotranspiration measurements made and the available data, the EC/ET_{rp} was tested using 15 site-years. Model B which was comprised of three periods; VE-9, V10- V19 and V20-R3; resulted in a robust EC/ET_{rp} relationship (RMSE= 1.067 Mg/ha) and was found to be reliable in estimating actual yields. The crop water sensitivity coefficients (λ_i) generated using Model B were: 0.138, -0.048, and 0.935. The large value of λ_3 of 0.935 in the V20-R3 stages is proof that the reproductive stages of growth including pollination are most sensitive to water stress during the growth and development of the plants. As suggested from the dataset and models tested, the characteristically small and negative sensitivity coefficients at the mid vegetative growth stages were proof that yield increased with water stress. This concurs with the underlying theory that promotes deficit irrigation practices through the extension of roots to lower lying depths, lateral root development, crop water productivity and water use efficiency. The study examined only water use sensitivity and did not address other stresses such as heat, insect and/or pest stresses and their impacts on the overall yield of crops. Improved estimations of both actual and reference evapotranspiration will prove useful in enhancing the efficiency of empirical crop-weather models in estimating crop yields and scheduling irrigation events.

Student Worker: A student worker assisted through the summer with data inputs and simulations.

Significance of the work: The preliminary results demonstrate that producers can maintain and/or increase their yields with fewer irrigation events. Corn producers can apply this model to support their irrigation strategies.

Future work: This project can be extended for soybeans and other crops after water use sensitivities have been determined.

Fate of Manure-Borne Antimicrobials Monensin, Lincomycin, and Sulfamethazine and Potential Effects to Nitrogen Transformation in Soil

Basic Information

Title:	Fate of Manure-Borne Antimicrobials Monensin, Lincomycin, and Sulfamethazine and Potential Effects to Nitrogen Transformation in Soil
Project Number:	2015NE283B
Start Date:	3/1/2015
End Date:	2/28/2016
Funding Source:	104B
Congressional District:	1
Research Category:	Water Quality
Focus Category:	Agriculture, Toxic Substances, Nitrate Contamination
Descriptors:	None
Principal Investigators:	Daniel Davidson Snow, Matteo DAlessio

Publication

1. Aga, D.S., M. Lenczewski, D.D. Snow, J. Muurinen, J. B. Sallach, and J.S. Wallace. 2016. Measurement of Antibiotics and Assessment of their Impacts in Agroecosystems: State of the science. Journal of Environmental Quality (Special Issue). 45, Issue 2, 10.2134/jeq2015.07.0393.

2016 Project Report: Fate of Manure-Borne Antimicrobials Monensin, Lincomycin, and Sulfamethazine and Potential Effects to Nitrogen Transformation in Soil

Daniel D. Snow¹, Matteo D'Alessio² and Daniel Miller³

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²Nebraska Water Center and Water for Food Institute, University of Nebraska, Lincoln

³USDA Agricultural Research Service, Agroecosystems Management Unit, Lincoln, NE

Project Summary

Excretion of incompletely metabolized pharmaceutical compounds used to treat livestock is well known, though it was not until the last decade that concerns were raised about their environmental occurrence and potential ecological effects. Antibiotics and other biologically active compounds have been detected in a wide variety of agricultural sources including livestock wastewater, manure and crops fertilized with manure¹. A national survey by the U.S. Geological Survey reported that multiple pharmaceuticals and steroids occur in surface waters across the U.S.². On-going work at the University of Nebraska has found a variety of veterinary pharmaceuticals in agricultural settings at both the field and watershed scale. Residues of monensin, erythromycin, sulfamerazine, and other antibiotics were found in lagoon wastewater and associated groundwater at livestock feeding operations in Nebraska³⁻⁴. A “spring flush” of antibiotics was observed in passive sampler extracts with relatively high time weighted average concentrations of monensin, lincomycin and sulfamethazine in a central Nebraska watershed with a density of livestock feeding operations⁵.

A recent study in collaboration with scientists from the USDA Agricultural Research Service examined antimicrobials and steroids in runoff from cattle feedlots that was applied to a vegetative treatment system designed to remove runoff nutrients. A variety of antimicrobial compounds were detected in runoff and after soil application (McGhee et al., in preparation). Monensin was the most abundant antimicrobial and showed potential for transport across the vegetative treatment system. A study in California⁶ reported persistent levels of monensin in wastewater and in groundwater at levels ranging from 0.04 to 0.39 µg/L near the production area of a dairy. Due to its mobility and relative persistence, monensin may be a good indicator compound of livestock waste contamination in ground and surface water. Because of their biological activity, residues of any antibiotic compound may impact microbial respiration in soil and aquatic systems, including processes that affect nutrient transformation and availability.

Nitrate is a very common contaminant in groundwater beneath agricultural areas⁷⁻⁸. A long residence time and difficulty in treatment or remediation impact drinking water supplies, particularly in the shallow aquifers of Nebraska. Sources of nitrate may be related to excessive soil nitrogen from manure and chemical fertilizer application beyond crop needs. Unless used by crops or converted to other forms, excess nitrate from any source in soil can leach below the crop root zone, through the vadose zone and eventually into groundwater. While generally applied as ammonia or organic nitrogen, reduced forms of nitrogen in manure (urea, organic N, and ammonium) are usually mineralized in soil and subsequently oxidized to nitrate. Under aerobic (oxygen rich) conditions, nitrate is the most mobile and persistent form of nitrogen thus leading to its widespread occurrence in groundwater.

Residues of monensin or other antibiotics applied with livestock wastewater or manure may interfere with mineralization and subsequent nitrification or denitrification in soils or in the vadose zone. Mobilized antibiotic residues in soil will likely encounter a variety of redox environments (aerobic, anaerobic, and denitrifying) all of which will affect persistence of both the antibiotic and potentially transformation of nitrate. Previously published studies have suggested that denitrification can be inhibited by a variety of antibiotic compounds including sulfamethazine⁹, erythromycin, clarithromycin, and amoxicillin¹⁰. In spite of the increasing evidence for co-occurrence of these compounds with nutrients, few studies have been focused on understanding how commonly-used antibiotics, such as monensin, lincomycin, and sulfamethazine are mobilized and persist in the environment and how traces of these residues may affect fate and transport of nitrate-nitrogen.

The objective of this study was to determine the persistence and mobility of three antibiotics (monensin, lincomycin and sulfamethazine) combined with nitrate after application to soil, and to determine whether the occurrence of these antibiotics affects nitrate biotransformation rates and pathways. These experiments were conducted to simulate the conditions observed in a vegetative treatment system receiving feedlot runoff.

Methods

Soil samples used in the microcosms and column experiments were collected at a vegetative treatment area (VTA) adjacent to a 6,000-animal capacity, open-air cattle feedlot at the USDA Meat Animal Research Center located in south-central Nebraska. Feed water was collected from a run-off holding pond on the facility. Serum bottle incubations were prepared as previously described¹¹ in triplicate at concentrations of 0, 5, 500 and 5000 ng/L. Nitrate was added at 100 mg NO₃-N/L and incubated anaerobically, and gas and water samples were collected and analyzed over several weeks. Four simultaneously-operated vertical flow-through columns (5 cm inner diameter; 16 cm height) were constructed, packed with VTA soil and outfitted with in-line sampling ports and effluent sensors. Feed water was metered at a flow rate of 0.2 mL/min at the column head using a 4-head peristaltic pump and acclimated for 14 days using a 10:90 mixture of diluted holding pond wastewater prior to introduction of the antibiotics, nitrate and inert tracer (Table 1). Each column received the diluted wastewater, antibiotics, tracer and additional amendments for 7 days, and then was flushed for an additional 30 days with diluted wastewater. A control column received sodium azide to inhibit microbial activity. Water samples were analyzed for pH, ORP, conductivity, dissolved ions using ion chromatography and antibiotic concentrations measured using liquid chromatography tandem mass spectrometry.

Table 1. Conditions used in the vertical flow columns

Experimental condition	Achieved by.....	Feed Water	Packing material	Antibiotics added
Aerobic	Open to the atmosphere and bubbling air	10% runoff + 90% DI water & autoclaved 1x at 120°C for 30min	Disturbed soil (# 10-#200)	Mix 20 µg L ⁻¹ monensin, lincomycin, sulfamethazine + 100 mg L ⁻¹ of Br tracer
Anaerobic (DO reduced)	Bubbling nitrogen	10% runoff + 90% DI water & autoclaved 1x at 120°C for 30min	Disturbed soil (# 10-#200)	Mix 20 µg L ⁻¹ monensin, lincomycin, sulfamethazine + 100 mg L ⁻¹ of Br tracer
N_reduced	Bubbling nitrogen Add 10 mmoles KNO ₃	10% runoff + 90% DI water & autoclaved 1x at 120°C for 30min	Disturbed soil (# 10-#200)	Mix 20 µg L ⁻¹ monensin, lincomycin, sulfamethazine + 100 mg L ⁻¹ of Br tracer
Control	Open to the atm Add 1 ppm NaN ₃	10% runoff + 90% DI water & autoclaved 1x at 120°C for 30min	Disturbed soil (# 10-#200) & autoclaved 3x at 120°C for 30min	Mix 20 µg L ⁻¹ monensin, lincomycin, sulfamethazine + 100 mg L ⁻¹ of Br tracer

Project Results

Serum Bottle Incubations:

Microbial respiration, as indicated by carbon dioxide production, was inhibited under aerobic and anaerobic conditions at the highest concentrations (5,000 ng/L) of antibiotic used (Fig 1). Monensin had the greatest effect under anaerobic (denitrifying and methanogenic) conditions. Lincomycin and sulfamethazine had a lower inhibitory effect, and was only evident in the aerobic microcosms. Methane was detected after 14 days of incubation in all but the highest concentration of monensin treatment.

Nitrous oxide production, from either nitrification or denitrification, was indicated by detectable N_2O concentrations in days 1-5 of the incubations, and then again between 20 and 28 days in the aerated microcosms with very low concentrations of antibiotic. In the denitrifying incubations, there was a clear inhibitory effect of antimicrobials on N_2O production. Monensin concentrations at 500 and 5000 ng/L inhibited N_2O production, sulfamethazine at 5000 ng/L also inhibited N_2O production, while lincomycin had little effect at any of the dosages.

Column Experiments: Conductivity, dissolved chloride, sulfate and orthophosphate concentrations increased rapidly due to leaching of these anions from the soil during the acclimation period. Bromide concentrations peaked within 1 pore volume after injection coupled with symmetrical breakthrough curve (BTC) suggested no preferential flow and/or adsorption to the packing material. Nitrate and nitrite were detected only under denitrifying conditions (where

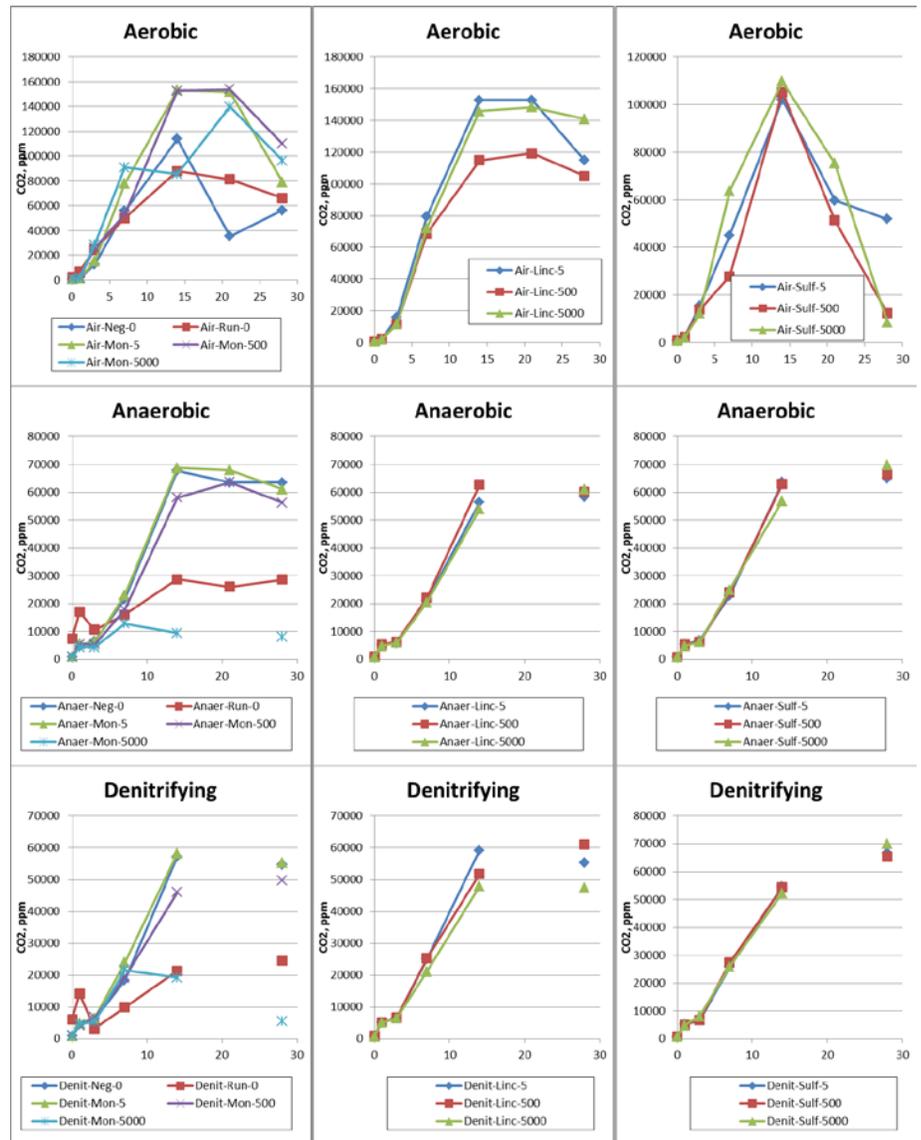


Fig 1. Changes in CO₂ concentrations in the headspace of soil slurry serum bottle incubations with monensin (MON), lincomycin (LINC), or sulfamethazine (SULF) at 0, 5, 500, and 5000 ng/L. Incubation conditions included aerobic, anaerobic, and denitrifying conditions (top, middle, bottom row, respectively).

feed water was spiked with nitrate), and the presence of antibiotic residues impacted the transformation and occurrence of each anion. After 6d of antibiotics' injection, NO_3 concentrations resumed to pre-dosage levels and NO_2 concentrations also increased. After switching to feed water without antibiotics, NO_3 increased while NO_2 decreased. This overall trend was most pronounced in the upper portion of the column (Fig 2).

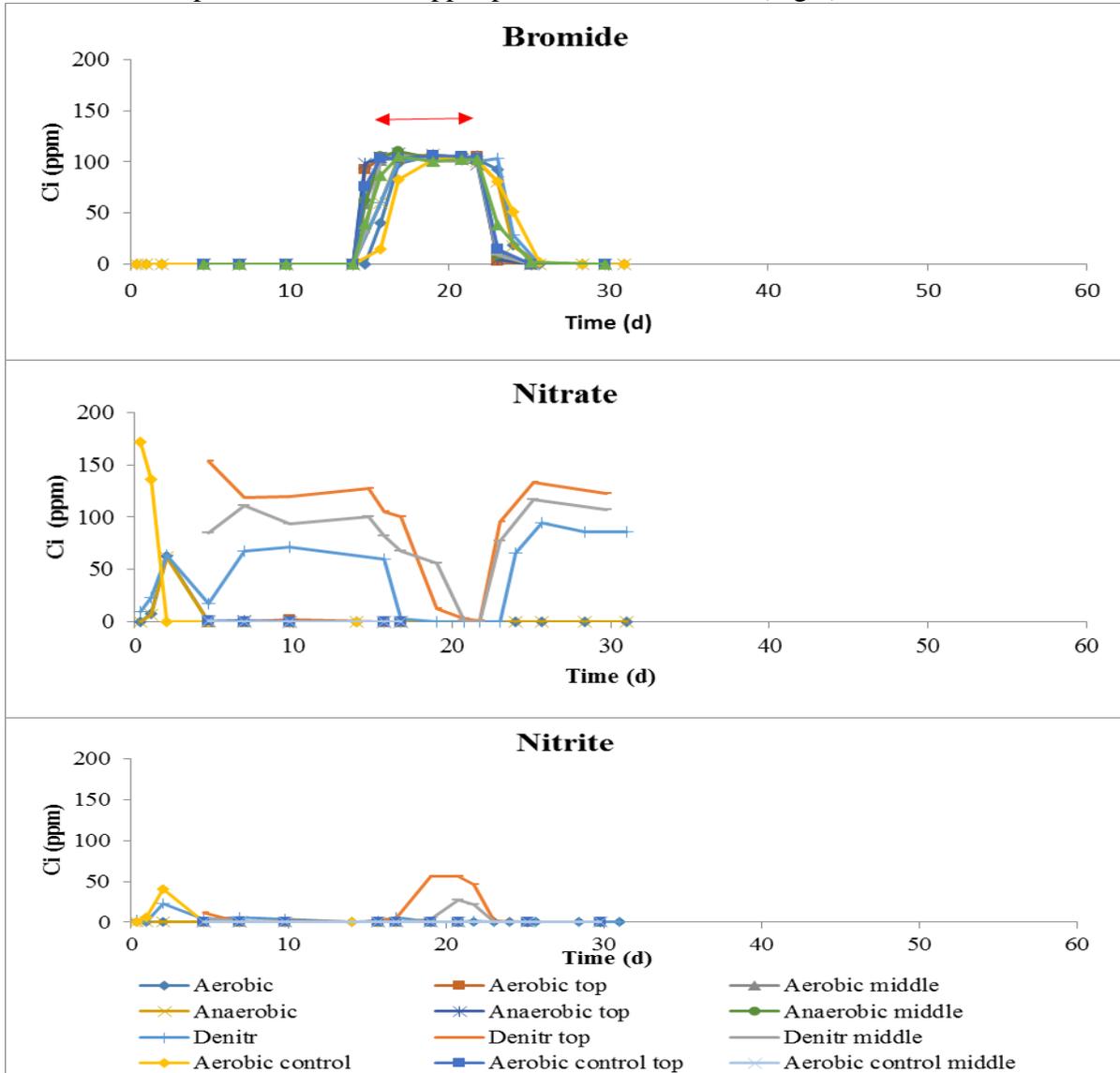


Fig 2. Changes in bromide tracer, nitrate and nitrite concentrations in soil column effluent (Aerobic/Anaerobic, Denitr) and sampling ports near the top and middle of each column. The red arrow indicates when a mixture of antibiotics (dosed @ 20 $\mu\text{g/L}$) and bromide tracer was introduced at day 14 and continued until day 21. Note reduction in nitrate effluent concentrations as denitrification developed and eliminated nitrate in effluent until day 21 after antibiotics were introduced.

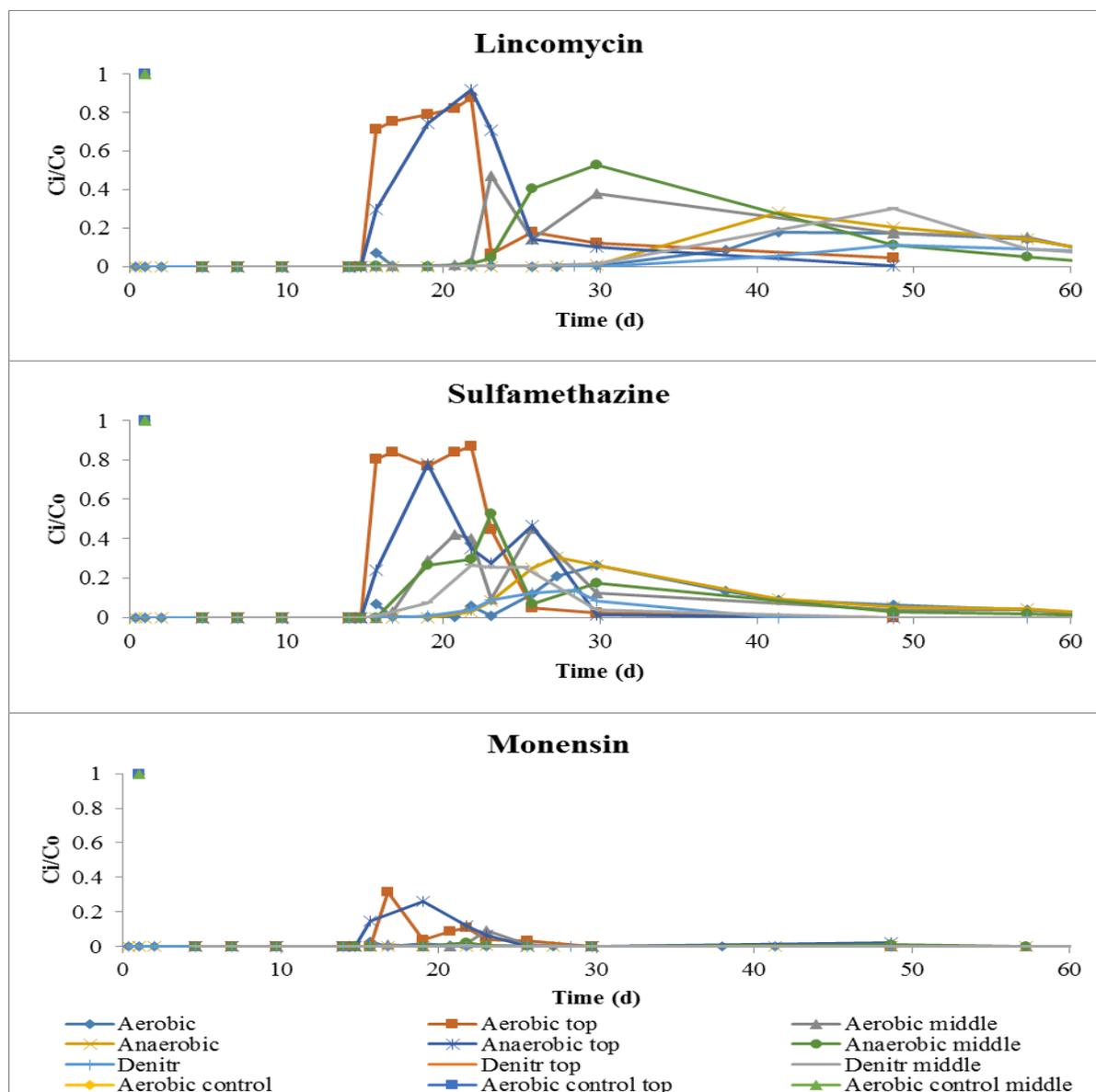


Fig 3. Effluent (Aerobic/Anaerobic/Denitr) and sampling port breakthrough curves for lincomycin, sulfamethazine, and monensin in the vertical soil columns. C_i/C_0 = measured concentration divided by spiking concentration (20 $\mu\text{g/L}$).

Surprisingly, monensin was only detected in pore water samples collected in the upper portion of the columns regardless of environmental (aerobic vs. anaerobic vs. denitrifying conditions). The asymmetric shape of the breakthrough curves and the much lower effluent concentrations compared to the inflow concentrations showed that retention and quite likely degradation, of all three antibiotics occurred during transport through the soil columns. Results from the sampling ports, regardless of the environmental conditions, showed that the concentrations of the three antibiotics decreased throughout the columns suggesting enhanced removal during the soil passage (Fig 2).

Mass recovery from each sampling port and effluent was estimated by multiplying the measured concentration times the volume pumped and dividing by the volume applied. The highest overall estimated mass recovery was observed for lincomycin and sulfamethazine in the top and middle sampling port samples. Effluent recovery was lowest for monensin in all three treatments (Table 2). The lowest overall recovery for all three antibiotics was observed in the induced denitrification column (Denitr).

Scholarly Outputs

This project provided 1) preliminary results describing the potential inhibitory effect of specific antibiotics on nitrate transformation, 2) the fate of monensin, lincomycin and sulfamethazine in soils collected from a vegetative treatment area, 4) the effect of monensin and other antimicrobial concentrations on denitrifying activity in the soil, 5) enrichments of microorganisms capable of monensin degradation, and 6) information on the potential leaching rate of these antimicrobics relative to nitrate in soil cores.

Future research to address the fate of other antimicrobial compounds in manure-impacted environments will be developed based on the results of this study. Two manuscripts have been prepared and will be submitted in peer-reviewed journals.

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Lincomycin (%)			
	AS	Top	Middle
Aerobic	53	106	110
Anaerobic	68	100	118
Denitr	28	112	64
Sulfamethazine (%)			
	AS	Top	Middle
Aerobic	61	92	73
Anaerobic	59	73	64
Denitr	18	63	32
Monensin (%)			
	AS	Top	Middle
Aerobic	3	14	3
Anaerobic	1	22	2
Denitr	0	8	0

Table 2. Estimated recovery (%) of each antibiotic from effluent (AS), top and middle sampling ports of the vertical soil columns.

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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 Nebraska Water Center and its affiliated NU Water Sciences Laboratory; (4) direct support for two internet web sites and several 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, public 2013-14 annual report.

The Nebraska Water Center is part of the Robert B. 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 WFI co-located to offices at the University of Nebraska's new "Nebraska Innovation Campus" in September 2014. The two units continue serving unique clientele and missions, as well as cooperating closely in a number of areas.

Information Transfer Plan/Water Education

Basic Information

Title:	Information Transfer Plan/Water Education
Project Number:	2008NE173B
Start Date:	3/1/2015
End Date:	2/28/2016
Funding Source:	104B
Congressional District:	1
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	None
Principal Investigators:	Chittaranjan Ray, Steven W. Ress

Publications

1. Newsletter: The Water Current newsletter has a free, subscriber-based distribution of approximately 3,100 copies per issue, more than 95% of which are requested subscriptions. It is published quarterly in a full-color magazine format, and is available online. Water-related research, engagement, education and outreach faculty and water-related professional staff are featured in each issue. Guest columns and articles are encouraged. A director's column is published in each issue. News Releases: The Water Center produces about 30 press releases annually focused on research results or progress, extension programming, educational opportunities, public tours, seminars, lectures, symposiums and conferences, awarding of major research grants and other matters of public impact involving the Water Center and other natural resource-focused UNL entities. These releases support a wide variety of UNL water-related research and outreach that cross departmental and academic disciplines. They focus on public impacts of UNL-sponsored research and programming. The UNL Water Center writes these for many UNL environmental science-related departments and faculty members who do not have a staff communicator available to them. The Water Center coordinates public media requests for information and interviews with sources on any water-related topic of interest to them and devotes significant attention to cultivating long-term relationships with members of the working media. The Water Center has a long reputation as a willing and reliable "source" among local, state and regional media for water and natural resources news. Media calls are frequent and water-related faculty and staff are accustomed to fielding questions from the media, doing radio and television interviews, etc. The Water Center makes wide use of electronic and broadcast journalism sources, as well as more traditional print (newspaper) sources.
2. Brochures and pamphlets: All full color. Produced as needed. These include, but are not limited to, mission and programming of the UNL Water Center, UNL Water Sciences Laboratory, Tern and Plover Conservation Partnership, annual Water and Natural Resources Tour and for other units or programs affiliated with or sponsored by the Water Center. All have online versions, as well.
3. Water Center fact sheets: All full-color, generally one sheet. Used to inform and promote both general themes, such as the Water Center itself, or to announce specific programs, seminars, courses, etc. There are various editions, designed for specific internal and external audiences.
4. Nebraska Water Map: A 24 x 36" full-color map of Nebraska surface and groundwater resources. Includes inset maps, diagrams and photos that describe the basics of water quantity, quality and use in Nebraska. The map is used for educational purposes across the state, and is available online. More than 65,000 have been distributed statewide. A range of publications produced outside the UNL

Information Transfer Plan/Water Education

Water Center, particularly fact sheets, research project results and other print materials from USGS, Nebraska Department of Environmental Quality, U.S. Environmental Protection Agency, U.S. Army Corps of Engineers, local Natural Resources Districts and University of Nebraska-Lincoln Extension, are available through Water Center and School of Natural Resources web sites or in print form. UNL Water Center assists with content, design, editing and production for many of these publications.

5. Electronic Resources: Print materials produced by the UNL Water Center, and other information, are available online. The Water Center co-sponsors, designs and maintains the following related Internet web sites: UNL Water: <http://water.unl.edu> UNL Water Center: <http://watercenter.unl.edu/> Water Sciences Laboratory: <http://waterscience.unl.edu> UNL School of Natural Resources: <http://snr.unl.edu/water/index.asp>
6. Full color, 2013-2014 annual report. 35 pages. Mailed to “Water Current” newsletter subscribers and distributed at NWC-sponsored events.
7. NWC also frequently responds to media requests for information and interviews and devotes significant attention to cultivating long-term relationships with members of the working press. NWC has a well-earned reputation for being a reliable “source” for water and natural resources news. Media calls are frequent and water-related faculty and staff are accustomed to fielding media questions.
8. The Water Current newsletter, now in its 47th consecutive year of publication, has a free distribution of more than 2,800 subscriber copies per issue. Subscriptions are by request. The newsletter publishes quarterly in full-color and is available online. One or two water-related faculty and/or professional staff are featured in each issue. Guest columns and articles are encouraged. Research, outreach and extension programming involving the NWC and DWFI are featured. A director’s column/report is included in each issue.
9. News Releases: NWC publishes about 20 press releases annually focused on water-related research, outreach, extension programming, educational opportunities, public tours, seminars, lectures, symposiums and conferences, major research grants and other matters of public interest. They support the activities of many water faculty and staff and cross many academic disciplines. NWC frequently writes and distributes these for many water-related programs and faculty members who do not have their own communications staff.
10. NWC also frequently responds to media requests for information and interviews and devotes significant attention to cultivating long-term relationships with members of the working press. NWC has a well-earned reputation for being a reliable “source” for water and natural resources news. Media calls are frequent and water-related faculty and staff are accustomed to fielding media questions.
11. Full color, 2015 annual report. 48 pages. Mailed to Water Current subscribers and distributed at NWC-sponsored events.

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

Brochures and pamphlets:

Produced as needed to support Water Center programming and activities. These 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 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.

A range of publications produced outside the Nebraska Water Center, particularly fact sheets, research project results and other print materials from U.S. Geological Survey, Nebraska Department of Environmental Quality, U.S. Environmental Protection Agency, U.S. Army Corps of Engineers, local Natural Resources Districts and University of Nebraska-Lincoln Extension, are available via the Nebraska Water Center web site.

Electronic Resources:

Nebraska Water Center:

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

NU 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 and Natural Resources Seminars:

An annual series of 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. 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. News releases, Internet and social media postings and posters support the lectures. Most lectures are taped and posted online for viewing.

Water and Natural Resources Tour:

The tour is in its 44th year, dating to UNL Extension “Irrigation tours” first conducted in the 1970’s. The 2015 tour examined a variety of current issues in the Republican River basin in Nebraska, Kansas and Colorado. 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. 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 Global Water for Food Institute.

Water Law Conference:

A one-day event focused on current Nebraska water law issues such as water right transfers, drainage issues, Clean Water Act enforcement, etc. It is targeted to practicing attorneys and water professionals, but is open to all. The event is co-sponsored by the University of Nebraska College of Law. Continuing Legal Education (CLEs) credits are available in Nebraska, Iowa and Colorado. The event was held in March 2015.

Water Symposium:

A one-day event preceding the water law conference focusing on 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 Global Water for Food Institute and the USGS Nebraska Water Science Center. The event was held in March 2015.

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 associated with the Nebraska Water Center attend 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.

Two University of Nebraska system-wide water faculty retreats were held by the Nebraska Water Center to foster interdisciplinary collaboration on research grant applications. One of these retreats was held on the flagship UNL campus in Lincoln, the other at the University of Nebraska at Kearney. They are typically attended by 50-70 research faculty members.

Other Outreach:

Nebraska Water Center staff routinely provides talks for groups and respond to requests for information. These include requests for water-related presentations from the public schools.

The Nebraska 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 frequent public displays 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. Water Center staff superintends UNL research and extension exhibits at "Husker Harvest Days," the nation's largest irrigated farm expo. More than 25,000 tour UNL Extension exhibits during this three-day, mid-September event.

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	2	0	0	2
Post-Doc.	1	0	0	0	1
Total	3	4	0	0	7

Notable Awards and Achievements

Nolan and Weber (2015) has received significant attention since it's publication. Of note are the following

- i) This publication was also highlighted as an Editor's Choice in Science
- ii) This publication received, TV, radio and print press coverage and is detailed in the report.
- iii) This publication was the most downloaded or read in ES&T Letters in August 2015 and remains the 2nd most read in last 12 Months at the time of submission of this report.

Nolan, Jason P., Karrie A. Weber. 2015. Natural uranium contamination in major US aquifers linked to nitrate. Environmental Science and Technology Letters. 2: 215-220. doi:10.1021/acs.estlett.5b00174