Nebraska Water Resources Center
Annual Technical Report
FY 2013

Introduction

Dr. Chittaranjan Ray, 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 specialist 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. 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.

The Nebraska Water Center is currently housed in the School of Natural Resources, located in Hardin Hall (3310 Holdrege, Lincoln, NE 68583-0979). The Nebraska Water Center is part of the Robert B. Daugherty Water for Food Institute, which is located in Whittier Building in the Robert B. Daugherty Water for Food Institute, University of Nebraska, 234 Whittier Research Center, 2200 Vine Street, Lincoln, NE 68583-0857 U.S.A. Around August 1, 2014 the Robert B. Daugherty Water for Food Institute, along with the Nebraska Water Center, will move to the new Innovation Campus of the University of Nebraska.

The Nebraska Water Center was the lead organizer for two major events in the Fall of 2013. First was a one-day science and policy symposium showcasing water-related research and programming in Nebraska, with a focus on Changes: Climate, Water and Life on the Great Plains. The event, which was co-sponsored by the USGS Nebraska Water Science Center, featured David Yates from the National Center for Atmospheric Research and Stockholm Environment Institute speaking about Defining Robust Risk Management Strategies in Water Resources. The second event was a one-day water law conference, designed for practicing attorneys, but attended by many water policy makers and managers. It was co-sponsored by the University of Nebraska College of Law. The Nebraska Water Center also assisted the UNL Office of Research with the fifth annual Water for Food conference an event drawing international speakers and attendees. The conference is sponsored by, the University of Nebraska's Robert B. Daugherty Water for Food Institute at the University of Nebraska.

Research Program Introduction

For the 2013 fiscal year, two research seed grants received funding through the USGS 104(b) program. Seed grants chosen for funding in 2013 were: (1) Development of an Affinity-Based Concentrator-Detection Kit for Monitoring Emerging Contaminants in Recycled Water; and (2) An Innovative Graphene Oxide Filter for Drinking Water Contaminants Removal; in addition the Army Corps of Engineers awarded a supplemental grant through the Nebraska Water Center and USGS to study Development of a National Database of Depreciated Structure Replacement Values for Inclusinon with SimSuite/HAZUS and Flood Mitigation Reconnaissance Studies. Seed grants chosen for the upcoming year 2014 were: (1) Documenting Stream/Groundwater Interaction in the South Platte River; and (2) Hydroclimatic Controls on the Conjunctive Use of Surface and Ground Water in the Platte River Basin; and (3) Fate of Steroid Hormone Conjugates and E. coli From Manure in Soil: Potential Sources of Free Hormones and Pathogens in Forages and the Environment?

The Water Sciences Laboratory (WSL) core facility, a part of the Nebraska Water Center, is a state-of-the-art 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.

Direct Monitoring of Knickpoint Progression

Basic Information

Title:	Direct Monitoring of Knickpoint Progression
Project Number:	2012NE234B
Start Date:	3/1/2012
End Date:	11/30/2013
Funding Source:	104B
Congressional District:	1
Research Category:	Engineering
Focus Category:	Geomorphological Processes, Sediments, Water Quality
Descriptors:	
Principal Investigators:	David Mark Admiraal, David Mark Admiraal

Publication

1. Kephart, Clark, 2013, Flow and Geometry Measurements at an Active Knickpoint, "MS Dissertation," Civil Engineering Department, University of Nebraska - Lincoln, Lincoln, NE, 129 pp.

2013 Project Report: Direct Monitoring of Knickpoint Progression

MS Student: Clark Kephart[1]
PI: David Admiraal[1]

[1]Department of Civil Engineering, University of Nebraska, Lincoln, NE 68588-6105

Abstract

Channel degradation is of growing concern in areas of the Midwestern United States where there are large deposits of loess soils. Channel degradation occurs as a result of disturbances to the sediment load, bed soil configuration, and hydraulic characteristics of the stream (i.e. discharge, channel slope and geometry). These changes may occur suddenly or slowly over time. A given disturbance may be due to a large rain event, channel adjustments (i.e. dredging and straightening), and changes in land use around the stream (Chen et al. 1999).

A knickpoint is an abrupt drop in stream bed elevation over which water plunges and scours the downstream bed. The plunging water may lead to intense bed degradation and subsequent upstream migration of the knickpoint, often causing stream banks to become unstable and unsafe. Knickpoint migration problems have been particularly prevalent in the loess soil regions of western Iowa and eastern Nebraska as a result of wide spread channel straightening projects in the region. The goal of this project is to monitor the migration of an active knickpoint. Analysis of the knickpoint consists of: (1) acquiring time lapse images of the knickpoint every thirty minutes from a camera installed at the site, (2) periodically collecting detailed survey data of the stream channel and knickpoint, (3) collecting Large-scale Particle Image Velocimetry (LPIV) videos of the flow for a variety of high and low flow conditions, and (4) estimating discharges in the channel using the LPIV results.

The time lapse images provide a frame-by-frame depiction of the upstream movement of the knickpoint. The images allow us to assess when the knickpoint has migrated and if its migration is associated with a particular storm event. The less frequently collected survey data provide a more accurate assessment of knickpoint position and can also be used in conjunction with LPIV videos to establish velocity distributions and a rating curve for the knickpoint. LPIV videos have been converted to bitmaps and rectified for analysis using Particle Image Velocimetry (PIV) software. They are then used to examine depth, discharge, and velocity conditions for different flow events.

Background

Knickpoints are natural or man-induced formations that occur frequently in streams and rivers all over the world. A knickpoint is manifested as a sudden drop in channel bed elevation that may resemble a river rapid or (at a larger scale) a waterfall (Brush and Wolman, 1960). Knickpoints tend to induce large scale channel degradation that consequently causes headward (upstream) migration of the knickpoint. The headward migration of the knickpoint results in steepened side slopes, bank failures, and channel widening downstream of the knickpoint. These degradation processes introduce safety concerns for people and structures adjacent to the stream channels. It is important to develop a deeper understanding of the migration processes of knickpoints in order to properly assess the condition of a given stream channel and to insure the proper design of stream crossings and surrounding structures.

Objectives of Research

Extensive laboratory and flume studies concerning the behavior of knickpoints have been carried out over the years; however little research has been conducted on actively migrating knickpoints in the field. This study centers on an active knickpoint located within the deep loess area of western Iowa. The knickpoint has induced large amounts of channel degradation, and is approaching a bridge crossing upstream of the knickpoint. The end goal of this study is to acquire unique field measurements of the migration process of an active knickpoint that can help assess the condition of this and other streams containing headward progressing knickpoints. Analysis of the knickpoint consists of the following:

1.) Acquiring time lapse images of the knickpoint over an extended period of time. The goal is to create a unique two-dimensional depiction of the headward retreat of the knickpoint front. The images aid in the determination of when the knickpoint has moved, how far it has moved, and if the movement was related to a given storm event.
2.) Periodically collecting detailed survey data of the stream channel and the knickpoint. The elevation data are used to create a series of contour plots that can more accurately assess the position of the knickpoint and visually show the stream morphology over time as a result of the presence of the knickpoint. The surveyed data are also used in conjunction with Large-scale Particle Image Velocimetry (LPIV) to establish velocity distributions and discharge estimates.
3.) Collecting LPIV videos for a variety of high and low flow conditions. These videos are analyzed using Particle Image Velocimetry (PIV) or Particle Tracking Velocimetry (PTV) software that yield surface water velocity distributions. These velocity distributions are then used to estimate the discharge in the channel.

Site Description

The knickpoint selected for this study is in the deep loess area of the Midwestern United Sates, which has loess depths ranging from 50 to 75 feet. It is located on Mud Creek, a tributary stream of the West Nishnabotna River located in northeast Mills County, Iowa. Mills County is located in the Southwest corner of Iowa, and the study site is near the town of Henderson, Iowa. The site was selected because it was readily accessible, because it has a history of active knickpoints, and because it was a part of an ongoing study being conducted jointly with the University of Iowa. Mud Creek has a stream length of 25.75 km with a watershed area of 97.5 km^2.

This location of the Midwestern United States promotes a climate that is characterized by hot summers, cold winters, and wet springs. The average summer temperature in this area is 30^{0}C (86^{0}F) and is accompanied with periodic large thunderstorms. The winter average temperature is -4^{0}C (24.8^{0}F) with significant snow accumulation and periods of freeze and thaw. The average annual precipitation is approximately 846 mm/yr with the majority of the precipitation falling in the spring and summer months (April – September) (Papanicolaou, 2008). Over the course of this study the precipitation was recorded from the Iowa Environmental Mesonet (2013), which can be accessed at <mesonet.agron.iastate.edu>.

The knickpoint that was studied is active, but it is currently approaching a concrete grade stabilization structure just downstream of a bridge. The study site is surrounded by crop land and range land for cattle. Figure 1 shows the knickpoint and the study site.

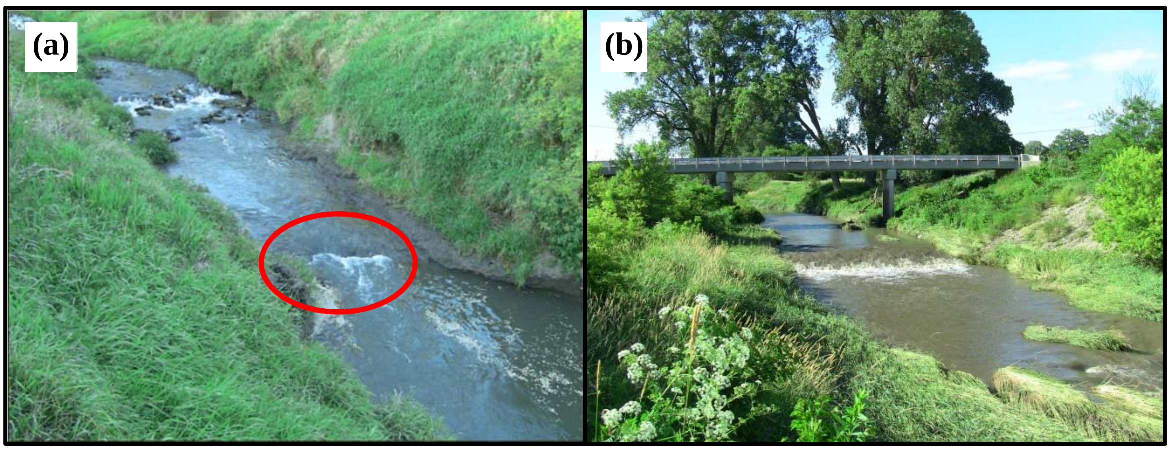

Figure 1: (a) Mud Creek knickpoint. (b) Upstream of the knickpoint showing the grade stabilization structure and bridge.

Methods

A time lapse camera was installed at the Mud Creek study site to continually monitor the headward progression of the knickpoint front over the study period. The images from the time lapse camera were used to create a two-dimensional overhead representation of the knickpoint migration. The camera was installed on the right descending bank of the channel and was programed to capture images of the knickpoint every thirty minutes. It was only possible to collect images during daylight hours. Though it was useful to gather images at 30 minute intervals to capture high-flow events and to allow selection of optimal images, one image per day was determined sufficient for monitoring knickpoint progression. Of the images collected, 499 images have been reviewed from July 14, 2011 to November 28, 2012.

To create an accurate representation of the knickpoint retreat, time-lapse images had to be processed to correct: (1) slight changes in the alignment of the camera when data were downloaded, (2) minor shifts in the camera position from day to day caused by temperature and humidity changes, and (3) the obliqueness of the images. First, the design of the camera made it difficult to return it to its exact previous position when images were downloaded. Slight rotations of the camera were corrected for by applying an oblique correction tool to align images collected after downloading data with those collected before downloading data. Second, minor shifts caused by thermal expansion of the camera mount and changes in moisture content of the soil supporting the camera were corrected by aligning fixed points within the images on consecutive days. The final adjustment that was necessary was to correct the images for obliqueness; that is, the camera was set up at an angle and not directly above the knickpoint. In order to properly determine knickpoint retreat distances, the images were rectified to make them appear as if they were being viewed from directly overhead. These processes are described in more detail by Kephart (2013).

As an example of the image rectification process; Figure 2 shows the oblique, unaligned images downloaded from the time lapse camera for the dates of September 15, 2011, December 3, 2011, and February 12, 2012. The corresponding rectified images are shown in Figure 3.

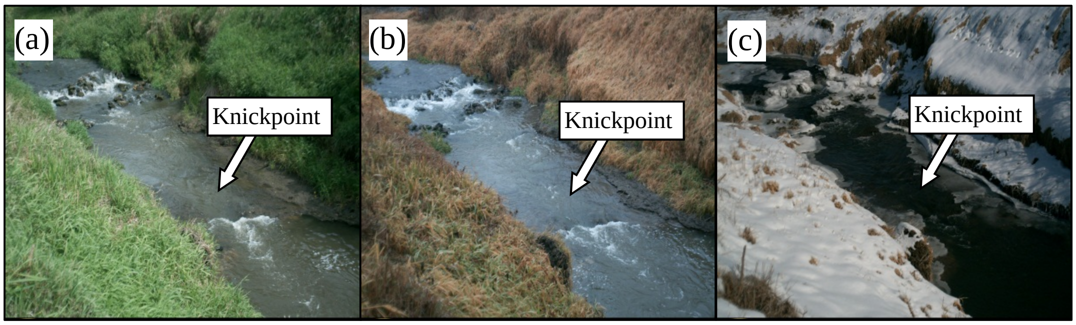

Figure 2: Time-lapse images collected on (a) September 15, 2011, (b) December 3, 2011, and (c) February 12, 2012

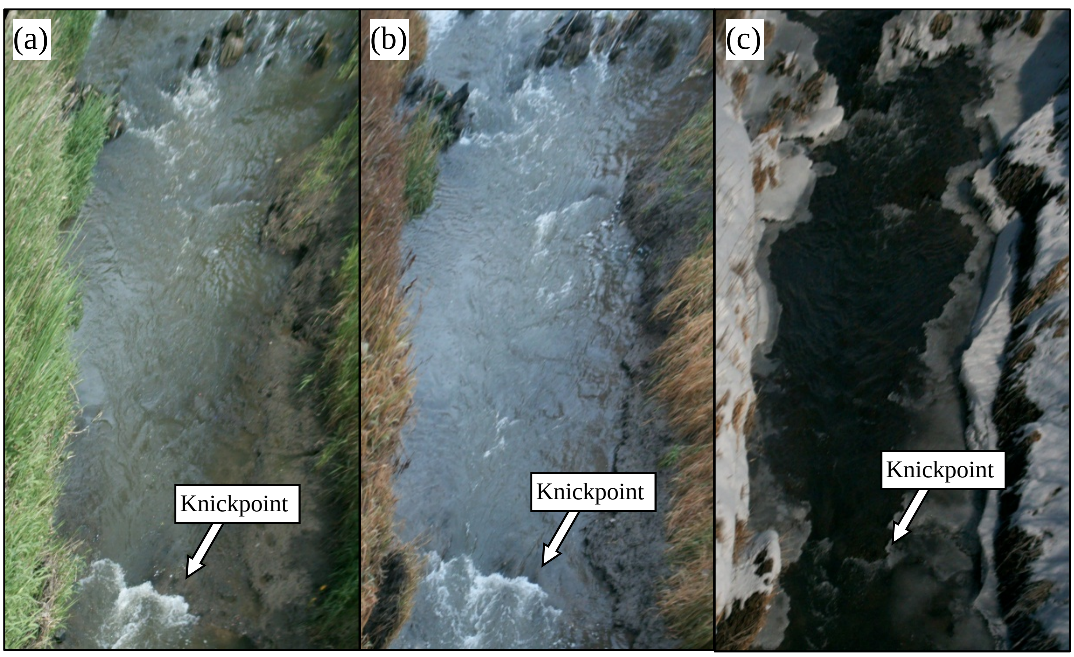

Figure 3: Rectified time-lapse images from (a) September 15, 2011, (b) December 3, 2011, and February 12, 2012

After the time-lapse images were aligned and rectified, the knickpoint front was identified and highlighted in each image. The exact location of the knickpoint front was not always easily identified due to variations in flow rate. The vertical face of the knickpoint is also somewhat three-dimensional, and what is actually observed in each time-lapse image is the location of the hydraulic jump above the knickpoint. However, at low flows, the hydraulic jump occurs at the crest of the knickpoint, and for the majority of the study period, the stream had relatively low flows, making the crest of the knickpoint face easy to identify.

Survey data of the banks and stream were collected during each site visit. The survey data were used to provide calibration points for rectifying Large-scale Particle Image Velocimetry (LPIV) videos and time lapse images. The surveys also provided bathymetric information of the channel. A series of detailed surveys were carried out on the dates of September 27, 2011, March 21, 2012, and September 25, 2012. These detailed surveys contained information about the changes in the stream bathymetry that occurred over the duration of the study.

Surface water velocity distributions upstream of the knickpoint were determined using Large-scale Particle Image Velocimetry (LPIV) techniques. During each visit to the site, a series of videos was taken of the flow. The videos were collected using a digital video camera that was placed on the right descending bank near the time lapse camera mount. Like the time lapse camera, the digital video camera was set up at an angle to the knickpoint and not directly above the knickpoint. The videos were converted into sequences of bitmaps with image separation times of 1/30th of a second. Using surveyed calibration points, the bitmaps were corrected for obliqueness (rectified) as shown in Figure 4.

Figure 4: LPIV images: (a) original image and (b) rectified image

Low flows were seeded with particles (slightly buoyant cereal) to aid in the LPIV analysis. High flows were left unseeded, as there was an abundance of highly visible bubbles present on the water surface. Surface velocities were calculated at a series of cross sections upstream of the knickpoint. The cross sections were developed where detailed elevation data of the stream were known from collected survey information. For each cross section, interrogation points were selected at regular intervals from bank to bank. The average velocities were calculated at each of the interrogation points using image analysis software developed for the project for 100 to 200 pairs of images (see Kephart 2013).

The results of the LPIV analysis in combination with bathymetric information were used to estimate discharges at multiple flow cross sections. Based on the $1/7^{th}$ power law, the depth averaged velocity for each velocity profile is $7/8^{th}$ of the surface velocity. The discharge at each cross section was then found using:

$$Q = \sum \frac{7}{8} U_{surf,i} A_i \quad (1)$$

Where Q is the discharge, $U_{surf,i}$ is the surface velocity found by applying LPIV analysis at each subsection of a transect of the channel, and A_i is the cross sectional area of the subsection based on bathymetric information. The total discharge is calculated by summing the subsection discharges over the entire cross section of the channel.

Results

For 499 days the position of the knickpoint front was continually observed using the time lapse images collected at the site. The images were collected between July 14, 2011 and November 28, 2012. The knickpoint fronts were identified and highlighted in each image. Nine of the front locations observed throughout the study period were overlain and placed on a rectified bitmap of the knickpoint (Figure 5). The time spacing between the front locations in Figure 5 was not uniform, but an effort was made to allow significant time between observations (approximately two months) and to present observations in each season of the year. Presenting the front position in this way offers a unique two dimensional representation of the headward retreat of the knickpoint over the observation period. Some of the front locations shown in the image overlap. The knickpoint crest is not always clearly identified because the depth of the water changes over time, and the knickpoint crest can erode downward as well as upstream – downward erosion of the crest can be perceived as downstream migration of the knickpoint due to the oblique angle of the camera.

Upon observing the movement of the knickpoint front over the duration of the study period (Figure 5), it is apparent that most of the time, the migration is very slow, moving only 2 meters over the 1.5-year study period. The data recorded thus far indicate that the migration upstream slows significantly in the fall and winter months, and increases during the spring and summer. Figure 6 graphically shows the progression of the knickpoint upstream over the duration of the study period.

Figure 6 was developed by recording the upstream-most point of the knickpoint lip in each of the time lapse images. There is uncertainty associated with the location of the knickpoint lip. In each of the time lapse images the lip of the knickpoint is submerged by the flow and what is actually observed is the position of the leading edge of the hydraulic jump. As the flow in the stream fluctuates, the position of the hydraulic jump changes slightly, causing positioning errors, and indicating that the knickpoint has migrated downstream in some cases. Nevertheless, Figure 6 clearly illustrates progression of the knickpoint throughout the study period.

Another possible reason for the apparently slower movement of the front may be a change in the mode of knickpoint erosion in combination with the time-lapse analysis technique. Only the upper surface of the knickpoint can be seen in the time-lapse images, and when the location of the knickpoint front is determined, it is the location of the crest. It is possible that the mode of knickpoint migration changes with the onset of the lower stream flows and freezing that take place during the winter months. The lower flows may cause the bulk of the erosion to shift from the knickpoint face to the knickpoint lip (i.e. causing the knickpoint to migrate in a rotating fashion). If this is the case, observing the movement of the knickpoint front in the way shown in Figure 5 does not completely capture the erosion behavior of the knickpoint front. The results may indicate that the knickpoint front is not eroding (or eroding slowly); when in reality the knickpoint front is being undercut during the winter months, and then retreating upstream in the spring and summer when higher flows are present in the channel to carry away loose sediment at the lip of the knickpoint.

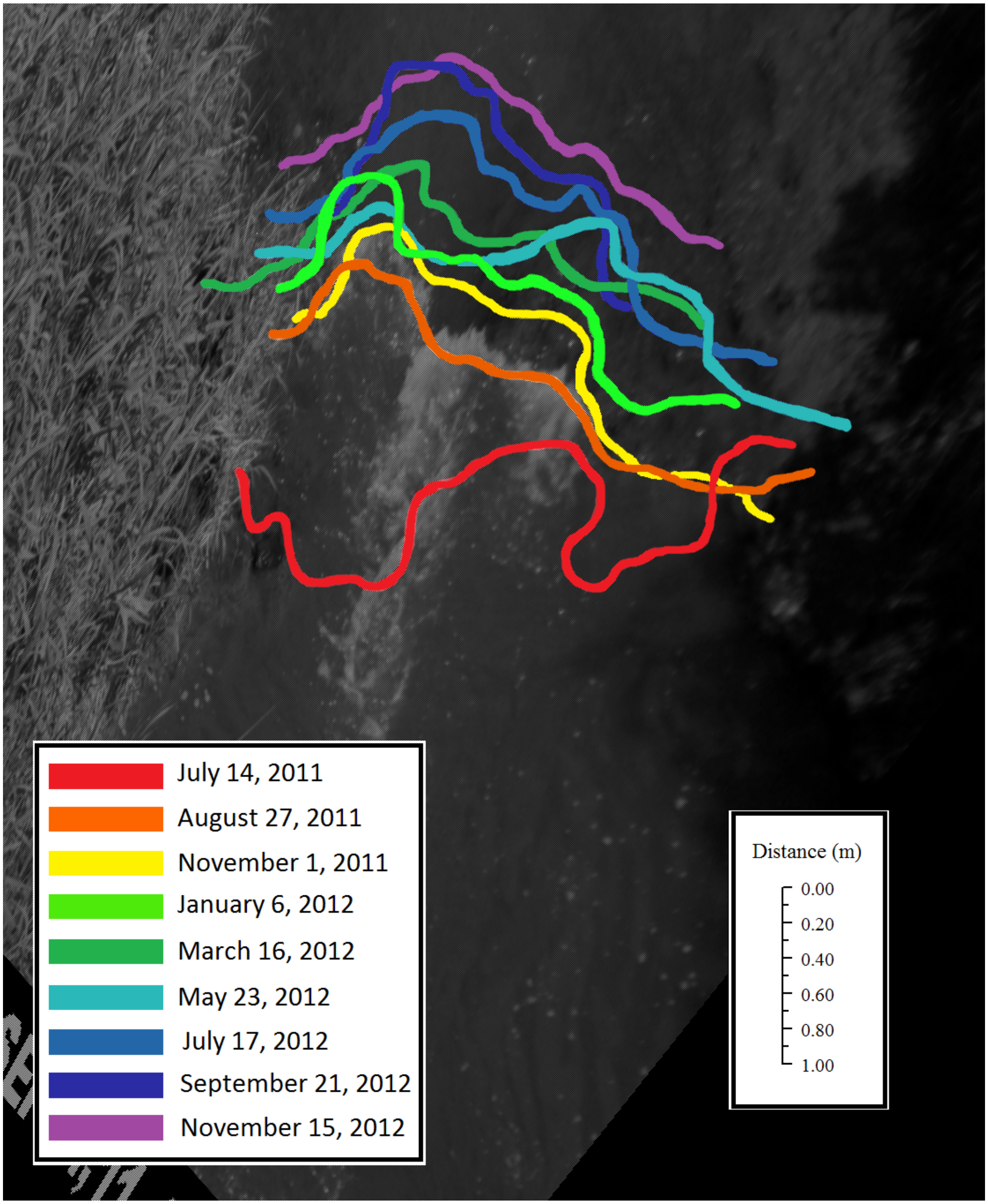

Figure 5: Knickpoint retreat over the duration of the study period.

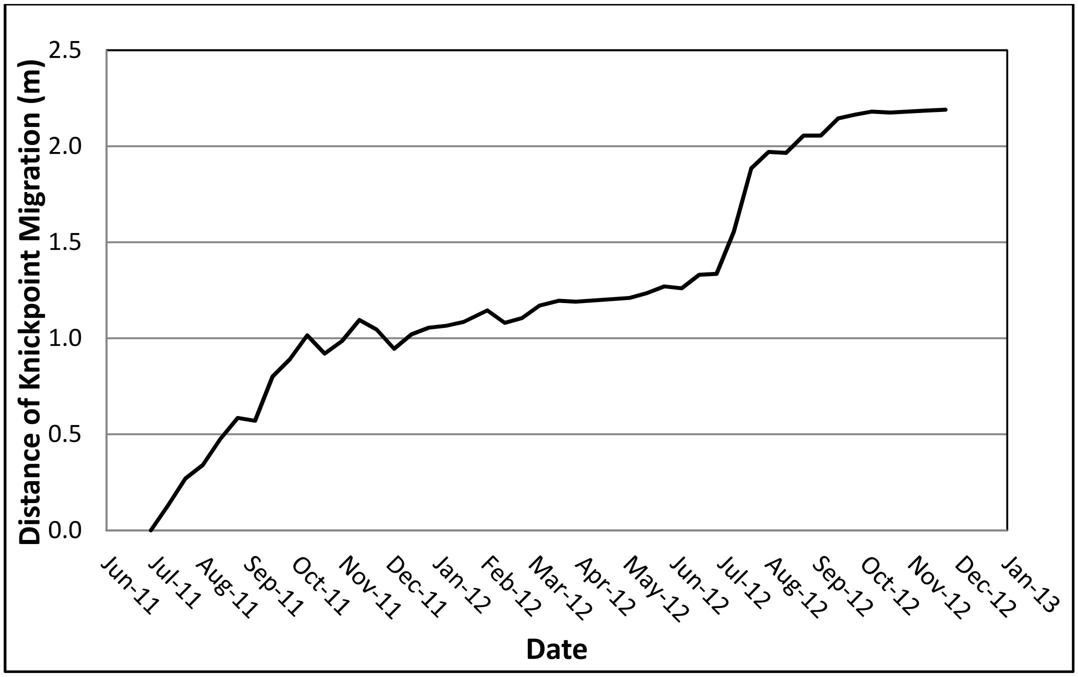

Figure 6: Knickpoint migration of upstream-most point of knickpoint over the study period.

Nevertheless, the knickpoint front has significantly migrated upstream over the course of the time lapse analysis. By examining the highlighted fronts in Figure 5 and the knickpoint progression in Figure 6, it is apparent that the knickpoint front has moved upstream approximately 2.2 meters over the 499 day study period. The most significant front movement appears to have occurred near the beginning of the study period migrating at 0.0102 m/day. The migration upstream then slowed in the winter months to 0.0009 m/day, and speeded up again in the spring and summer. The average migration rate over the duration of the study period was determined to be 0.0044 m/day. Table 1 provides a summary of the varied migration rate of the knickpoint throughout the 499 day study period.

Table 1: Summary of varied migration rates of the knickpoint

Season	**Time Period**	**Migration Rate (m/day)**
Summer and fall	July-Oct (2011) (100 days)	0.0102
Winter and spring	Nov - July (2012) (232 days)	0.0009
Summer and fall	June -Sept (2012) (99 days)	0.0089
Fall and early winter	Oct - Nov (2012) (68 days)	0.0007
All Seasons	Study Period (499 days)	0.0044

To further examine the morphology of the knickpoint front and the stream channel, extensive survey data were collected on the dates of September 27, 2011, March 21, 2012, and September 25, 2012. During the collection of the survey data, two separate sets of survey equipment were used. For the surveys collected on September 27, 2011 and March 21, 2012 a Sokkia Set 5A total station was used to gather the elevation data. For the September 25, 2012 survey a new TopCon GPS based survey system was acquired and used to gather the elevation data. There were some problems with the Set 5A system, and the data collected using the new TopCon system were assumed to be more accurate than those collected using the Set 5A. The inaccuracies in the Set 5A data were observed by comparing data collected at each of the bridge corners, which were points that should not change between surveys. The bridge corner elevations did not match up with the TopCon elevation points; they were considerable lower. To properly align the elevations of the three contour plots some adjustments to the Set 5A elevations were made. Comparison of fixed cross sections collected with the three surveys allowed us to accurately adjust the datums for the Set 5A surveys (see Kephart 2013 for details).

The elevation data collected during these surveys were used to create the series of contour plots presented in Figure 7. The east and north positions given on the x and y axes of the plots are relative to an arbitrary benchmark located at the southwest corner of the Elderberry Avenue Bridge set to (0,0). The elevations given in the contour plots are relative to the World Geodetic System 84 (WGS 84) datum. The same benchmarks were used for all of the contour plots so that the elevations could be directly compared with one another.

The three contour plots were able to illustrate the morphology of the stream channel and knickpoint throughout the period of analysis, as well as to highlight important features of the channel that may be affecting the migration of the knickpoint. To offer context to the three contour plots presented in Figure 7, the flow direction and the face of the knickpoint are shown.

As observed during the time lapse analysis (Figure 5), the contour plots confirm that measurable upstream migration of the knickpoint front has occurred over the duration of the study. However, the contour plots also show significant widening of the knickpoint face and that the downstream plunge pool is deepening and widening as well. Also, upstream of the primary knickpoint, on the left descending bank, a secondary scour hole is forming. Upon further examination of the contour plots, it was determined that the main channel itself is approximately 4.5 meters wide, but there also appears to be a deep, narrow trench forming at the center of the channel . This trench is approximately 1 meter wide and extends upstream from the primary knickpoint to the upstream scour hole. The trench has increased in depth over the study period and appears to have a significant impact on the morphology of the knickpoint and stream channel, as the knickpoint appears to be working its way upstream within the confines of the trench. The trench appears to be a mechanism by which knickpoint migration can occur much more rapidly than by direct erosion of the knickpoint face.

During each visit to the site, a series of videos were taken of the flow surface upstream of the knickpoint. The videos were converted into bitmap images. The Oblique images were then rectified using surveyed calibration points that were gathered at the edges of the water surface. A multi-file minimum quadratic difference algorithm was applied to determine average velocities at interrogation points spaced across a series of cross sections. The chosen cross section locations and processing information varied slightly for each data set. The cross section locations for each LPIV calculation are available in Tables 3, 4, and 5. These locations are relative to the location of the knickpoint.

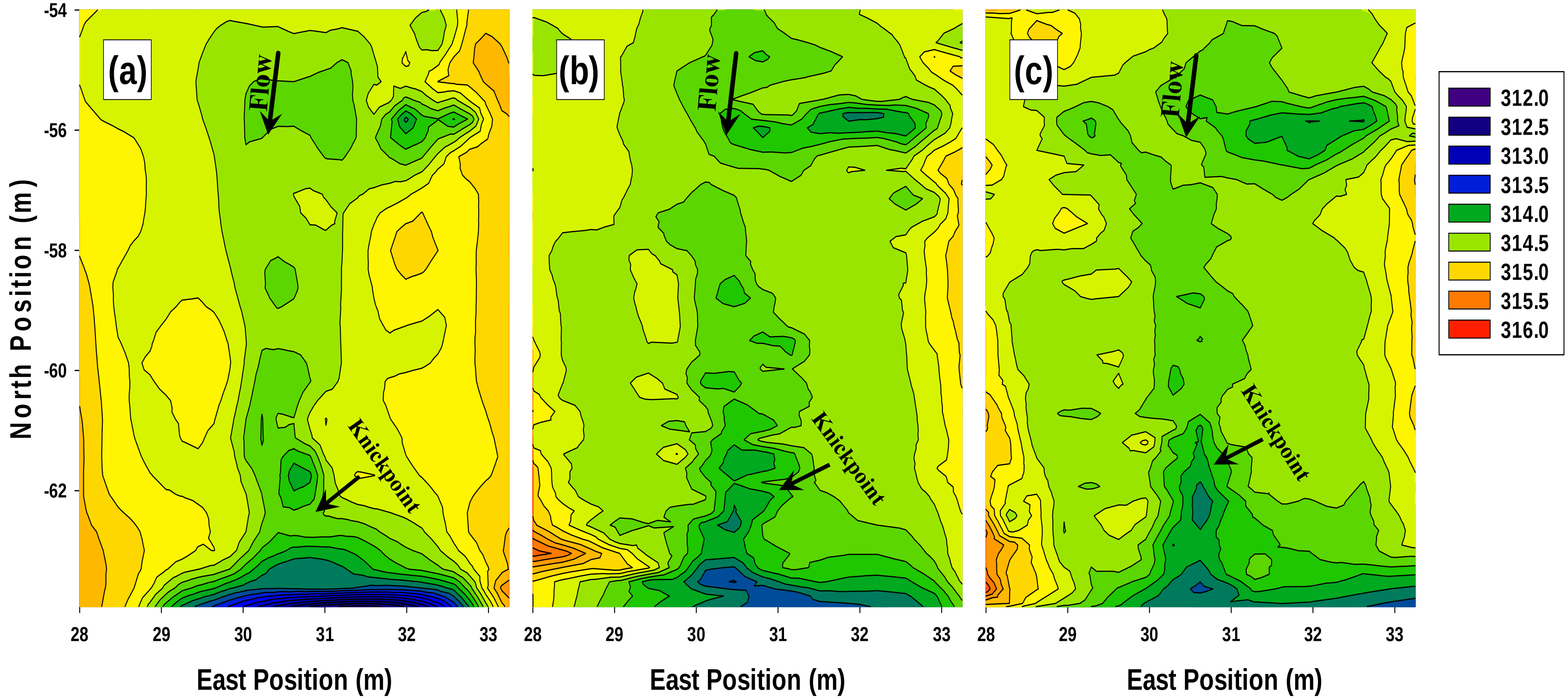

Figure 7: Contour plots of Mud Creek knickpoint: (a) September 27, 2011, (b) March 21, 2012, (c) September 25, 2012

The processing information for the LPIV data sets collected on September 27, 2011 and March 21, 2012 were nearly identical. The image scale was set at 2.0 pix/cm, the image separation time was 0.0333 s, the interrogation area was 16 pix by 16 pix, and the search bounds were set as 16 pix by 27 pix. 50 interrogation points were used across each cross section with a pixel spacing of 18 pix and 20 pix, respectively. For each of these two data sets, 100 pairs of images were used for processing. The processing information for the September 25, 2012 LPIV data set was slightly different than the previous two data sets. This was because the scale of the video taken at the site was considerably larger than for the previous two videos, as the water surface in the stream was very low due to drought conditions. For this reason the image scale for this data set was set to 3.0 pix/cm, providing higher resolution. The separation time remained at 0.0333 s, the interrogation area was set at 16 pix by 16 pix, and the search bounds were set to 16 pix by 27 pix. 100 interrogation points were used across each cross section with a pixel spacing of 7 pixels. For this data set, 200 image pairs were used for processing. Table 2 gives a summary of the LPIV processing information used for each data set collected at the site.

Table 2: Summary of LPIV Processing Information used for each data set

	Sept 27, 2011	**Mar 21, 2012**	**Sept 25, 2012**
Separation Time (s)	0.0333	0.0333	0.0333
Image Resolution (pix/cm)	2.0	2.0	3.0
Interrogation Area (pix^2)	16x16	16x16	16x16
Search Bounds (pix by pix)	16x27	16x27	16x27
Interrogation Points	50	50	100
Pixel Spacing (pix)	18	20	7
Image Pairs	100	100	200

A sample velocity distribution for the LPIV analysis is presented in Figure 8. Figure 8 corresponds to the March 21, 2012 site visit. Although the width of the water surface varies from observation to observation, the highest surface velocities are in the center of the channel. For the lower flows, there are areas of stagnation or flow rotation near the channel banks. This may be as a result of water being diverted into the deeper, narrower trench. The highest velocities for all flows were observed within the bounds of the 1 meter wide region directly above the trench that has developed upstream of the knickpoint. The higher velocities associated with this region result in an increase in shear stress within the trench. It is very likely that the concentrated flows will continue to deepen, lengthen, and widen the trench until a mass failure occurs; At this point the knickpoint front will likely quickly move upstream within the confines of the trench.

Figure 8: Surface water velocity distributions created from LPIV data collected on March 21, 2012 site visit.

Using the average surface velocities obtained from the LPIV techniques, volumetric discharges through each cross section were estimated. The surface velocities were converted into mean velocities using the 1/7th power law. The mean velocities were then multiplied by the subarea associated with the velocity to obtain a discharge flux. Each flux was then summed to get a discharge for the entire cross section. A summary of cross section locations, flow areas, and volumetric discharges for the channel are presented in Tables 3, 4, and 5 for the three flow measurement tests. Transects where the uniform flow assumption is questionable and where discharge calculations are considered to be less accurate are highlighted in the tables.

Table 3 presents the discharge calculations determined from the LPIV data collected on September 27, 2011. The flow condition in the stream appeared to be a typical base flow condition for Mud Creek, since the water covered most of the non-vegetated bed. The discharge at cross section 1A was not calculated because of its proximity to the knickpoint; the hydraulic jump at the knickpoint face prevents accurate LPIV measurements in addition to the flow not being uniform in the vicinity of the face, meaning that the 1/7th power is not valid in this region. The remaining cross sections produced a consistent set of results, aside from the results at cross sections 1B and 1F, which seem a bit higher than the other measurements. Cross section 1B is still located quite close to the knickpoint and cross section 1F is located just downstream of a secondary scour hole. At these transects, rapid changes in the bathymetry make the assumption of uniform flow questionable. The average discharge for this first test was *0.306* m^3/s with a standard deviation of *0.036* m^3/s.

Table 3: LPIV Discharge Calculations and Cross Section Geometry: Sept 27, 2011

Cross Section	**Distance Upstream of Knickpoint (m)**	**Flow Area (m^2)**	**Discharge (m^3/s)**
1A	0.40	-	-
1B	1.60	0.705	0.351
1C	2.15	0.657	0.316
1D	2.85	0.582	0.244
1E	3.73	0.481	0.310
1F	4.45	0.776	0.342
1G	6.75	0.977	0.290
1H	8.85	0.679	0.293

Table 4: LPIV Discharge Calculations and Cross Section Geometry: March 21, 2012

Cross Section	**Distance Upstream of Knickpoint (m)**	**Flow Area (m^2)**	**Discharge (m^3/s)**
2A	0.15	-	-
2B	0.75	0.413	0.448
2C	1.45	0.472	0.332
2D	2.25	0.578	0.412
2E	2.95	0.505	0.401
2F	3.75	0.485	0.336
2G	4.45	0.613	0.396
2H	6.45	0.871	0.539

Table 5: LPIV Discharge Calculations and Cross Section Geometry: Sept 25, 2012

Cross Section	**Distance Upstream of Knickpoint (m)**	**Flow Area (m^2)**	**Discharge (m^3/s)**
3A	0.60	0.180	0.097
3B	1.20	0.237	0.081
3C	1.80	0.218	0.067
3D	2.20	0.224	0.088
3E	3.00	0.260	0.128
3F	3.42	0.302	0.130

Table 4 presents the results from the discharge calculations performed on the LPIV data collected on March 21, 2012. The flow condition in the stream on this date was slightly higher that than the flow calculated previously, as there was a light but consistent drizzle falling throughout the data collection period. Much like the previous calculation, Transect 2B appears to be a bit high because of its proximity to the knickpoint. Transect 2H is located just upstream of the secondary scour hole, and again may make the uniform flow assumption questionable. The average discharge is *0.387* m^3/s with a standard deviation of 0.045 m^3/s.

Table 5 shows the results from the discharge calculations carried out on September 25, 2012. On this date the observed flow in Mud Creek was very low, due to the increased drought conditions in the Midwest during the months leading up to the data collection. In an attempt to avoid inconsistencies in the LPIV data, cross sections that would not be affected by the knickpoint or by the secondary scour hole were selected for analysis. The average discharge for this flow was determined to be *0.098* m^3/s, with a standard deviation of 0.026 m^3/s. As can be seen in the discharge table, for this low flow, the irregular bathymetry of the channel plays a much larger role, resulting in increased relative error. However, as expected the discharge in the stream was significantly lower than the previous two flows because of the extreme drought conditions in the Midwest.

The three flows that were calculated represent a typical base flow, a small rainfall flow, and a low flow condition for Mud Creek. The discharges for the three flow events were 0.098, 0.306, and 0.387 m^3/s with corresponding stage elevation measurements upstream of the concrete weir of 316.17, 316.21, and 316.26 meters. By plotting the stage vs. discharge for these three flow conditions a rating curve for the site was created (Figure 9). The flows in Mud Creek during each data collection period were relatively low, with very little variation. More data should be collected to create a more reliable rating curve for the site. It will be important in the future to gather LPIV data for a high flow event and possibly a large storm event. With the collection of these data, a more accurate hydrologic record of Mud Creek can be created.

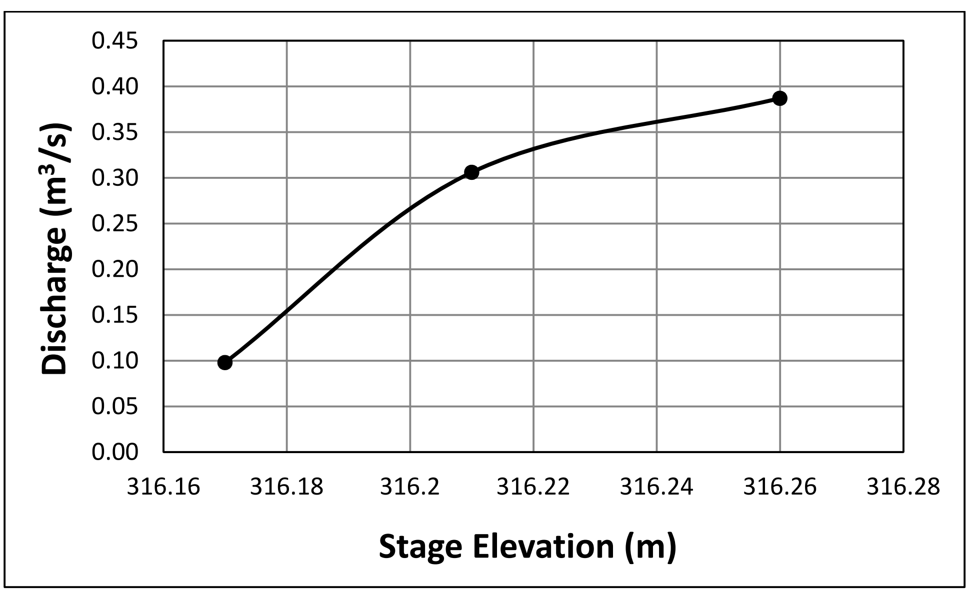

Figure 9: Grade control rating curve of discharge vs. stage for the three LPIV flows

Over the course of the study period precipitation records were continually monitored, but stage data for Mud Creek were available after March, 2012. With the use of stage information and the data in Figure 9, the discharge over the weir was calculated based on a standard weir equation. Discharge calculations performed well for the low flows when compared to the discharges found from the LPIV measurements. However the weir coefficient will need to be verified for higher flows, since the channel width increases at higher stages. A runoff hydrograph for the Mud Creek watershed was created and is shown in Figure 10 along with the relative position of the knickpoint. The hydrograph indicates that this watershed is quite flashy, meaning that with the onset of precipitation a sharp increase in flow occurs.

There were 6 significant flow events in March, April, and May of 2012; and a prolonged period of low stage in Mud Creek during the summer of 2012. The corresponding stage readings ranged from 316.12 m to 317.20 m. The period of low stage coincides with the extreme drought conditions that were documented in the Midwest during 2012; 2012 had only 692 mm of rainfall, which is 154 mm less than the annual average. The discharges in Mud Creek ranged from 0.1 m^3/s to 14.0 m^3/s, with the highest flows taking place in the late summer of 2011 and early spring of 2012 and the lowest flows taking place in mid-summer and winter of both years. Again prolonged drought conditions greatly influenced the stage records, meaning that observation of the stage in the stream will need to be continued for a more accurate assessment of typical knickpoint behavior.

Observing the recorded knickpoint front movement with the calculated flow as shown in Figure 10, the relationship between the migration of the knickpoint front and the discharge in the stream can be examined.

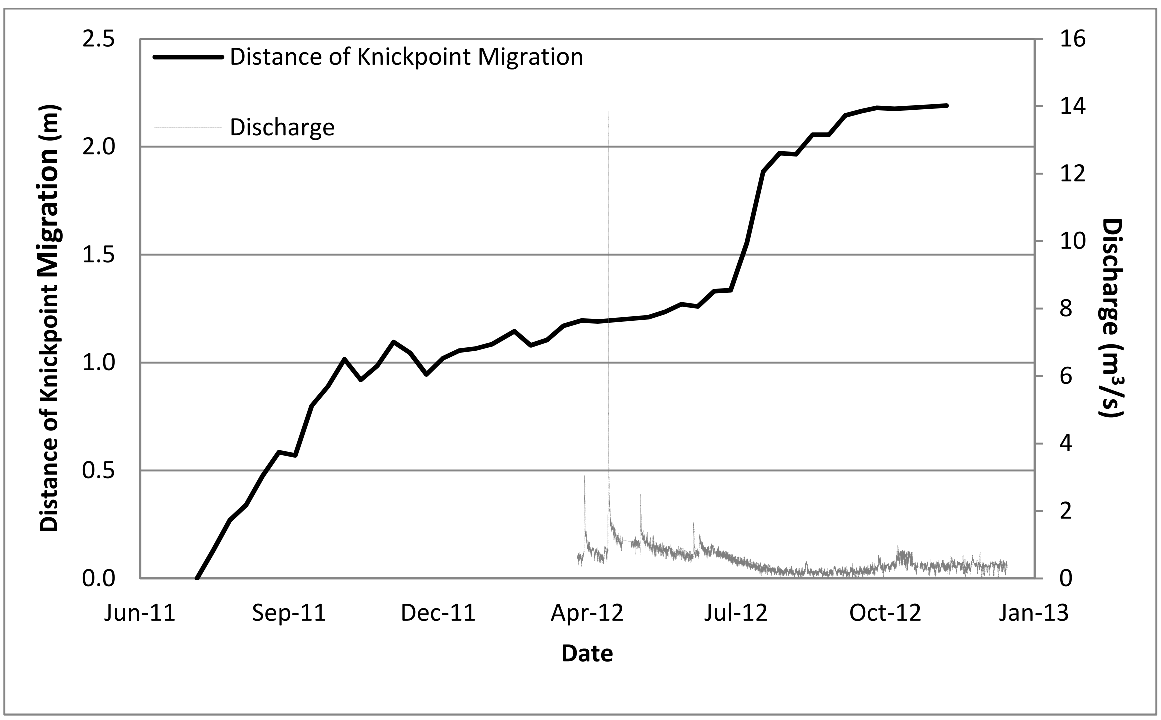

Figure 10: Knickpoint migration compared with the calculated discharge in Mud Creek

The main observation that can be made from Figure 10 is that knickpoint migration rates do not appear to be closely tied to large scale flow events. In general, bank failures occur more frequently following large storms, when saturated soils lose their cohesiveness. In the present case, the knickpoint is always submerged, so changes in the cohesiveness of the soils may be more likely to occur during dry periods, but the increase in erosion rate observed during the late summer in 2011 and 2012 during the driest periods was unexpected. A longer record of data, as is currently being collected at the site, will be helpful.

As mentioned previously, there was an extended period of low flow in Mud Creek during the summer of 2012. During these low flow conditions the majority of the flow was in the aforementioned trench, causing the majority of the erosive stresses from the flow to act within the confines of the trench and on a small portion of the knickpoint face. These concentrated low flows certainly influence the migration behavior of the knickpoint. Evidence of this can be seen as an increase in front moment during the extended period of low flow experienced during the summer of 2012. It is only during high flow conditions that the flow is more evenly distributed across the entire channel, and though the magnitude of the shear stresses acting on the channel may be larger for these high flows, they occur for such a brief period of time that they do not appear to be strongly correlated to the headward progression of the knickpoint. In March, April, and May of 2012 there were periods of increased flow events in Mud Creek, during which, the movement of the knickpoint front showed no increase in migration rate, and even appeared to retreat more slowly.

Conclusions

The results of the time lapse and survey analyses lend some insight into the mode of knickpoint migration. The mode of knickpoint migration changes with the change in season. Slowed headward retreat of the knickpoint front in the fall and winter months observed in this study may indicate that other forms of knickpoint erosion, not observed in the time-lapse photos, are taking place. It is also possible that the 2012 winter was too mild to provide a representative picture of knickpoint erosion. The 2013 winter will provide additional data for comparison with the previous year, but that will not be available for this report.

Over the study period, the study area was in a severe drought, and stream flow was much lower than usual. The hydrographical data provided by the bridge-mounted sensor at the site showed that there were 6 large storms or increased flow events during 2012 that had estimated flow rates ranging from 0.50 m^3/s to 14.00 m^3/s. During the remainder of the year, the base flows were quite low, and ranged from 0.1 to 0.3 m^3/s. During the study time period, the knickpoint migrated 2.2 meters upstream, with the migration rate rising in the spring and summer and slowing in the fall and winter. The average migration rate observed for the 499 day study period was determined to be 0.0044 m/day. Though the migration rate varied from season to season, overall the rate of knickpoint migration was relatively steady over the study period with no large, punctuated knickpoint failures.

Compared with other related studies, the migration of the Mud Creek knickpoint appears to be quite slow. Daniels (1960), observed a headward progressing knickpoint in Willow Creek, IA over a 5-year period. The Willow Creek knickpoint migrated upstream 2,819 meters over the course of the 5-year study, which is much more than the Mud Creek knickpoint which migrated 2.2 meters upstream over a 2-year period. Simon and Thomas (2002) and Simon et.al., (2002) also observed larger migration rates for a series of knickpoints that had developed along the Yalobushaa River in Mississippi. They observed migration rates ranging from 0.4 m/yr (0.001m/day) to 11 m/yr (0.030 m/day), whereas the Mud Creek knickpoint exhibited migration rates ranging from 0.0007 m/day to 0.01 m/day.

Though the Mud Creek knickpoint study observed what appears to be a slowed rate of knickpoint migration, all three studies observed periods of varied migration rates. The Willow

Creek and Yalobussa River studies attributed the quick pulses of the knickpoint upstream to the onset of high flow events. In the case of the current Mud Creek study it appears as though the large flow events are not correlated to expedited movement of the knickpoint. As shown in Figure 10, during the onset of high flow events there was very little headward progression of the knickpoint. It was during the prolonged period of low flow that the larger migration rates were observed. This may be as a result of soil conditions in the area, as well as the dry weather patterns observed during the study period. However, the presence of the deeper narrower trench that has developed upstream of the Mud Creek knickpoint appears to be greatly affecting its migration behavior, by temporarily reducing headward migration at the knickpoint face, but potentially leading to rapid changes in the location of the knickpoint face in the future.

Throughout most of the year, especially during dry periods, the channel flow was mostly confined to a trench that progressed upstream from the knickpoint face. Low flows persisted most of the time, and the bulk of the flow traveled through the trench, causing an uneven distribution of erosion on the bed and on the face of the knickpoint, consequently slowing its headward progression. It was only during larger flow events that the flow was more evenly distributed within the channel and over the knickpoint face. The result was that low flows had a significant impact on the morphology of this particular channel (see Figure 10). The impact was observed as the development of the trench between surveyed contour plots. The trench appeared to be the mechanism that was driving the migration of the knickpoint. Comparing the contour plots in Figure 7, it appears that most of the erosion took place within the narrower region of the channel and in the location where the trench crosses the knickpoint face. Thus, the knickpoint is slowly migrating upstream within the confines of the trench, a process that is slowly deepening, widening, and lengthening the trench, but it is altogether possible that development of the trench will cause a rapid, punctuated mass failure of the knickpoint face to occur. If this happens, the knickpoint will quickly erode upstream until it reaches a location where the bed material is more stable.

This migration process will continue until the grade stabilization structure (the concrete weir upstream of the knickpoint) is reached. When the study began at the site in early 2011, evidence of the trench-based migration behavior of the knickpoint was present, though it was not recognized at the time. Figure 11*Figure* shows evidence of a trench and large plunge pool that existed downstream of the present knickpoint location, and through which the knickpoint had passed previously. It appears as though the knickpoint remained stationary for a long period as the previous plunge pool and trench developed. Then, a rapid mass failure occurred, and the knickpoint quickly retreated upstream within the confines of the trench until it reached more stable bed material. Other than photos like the one given in Figure 11, evidence of the previous trench and plunge pool of the knickpoint are now gone because of mass wasting of the downstream channel banks. The continuing upstream migration of the knickpoint and other knickpoints like it has resulted in a channel that is very incised, leading to extensive mass wasting of the channel banks.

Based on the current development of the secondary plunge pool and trench; we think that it is likely that when a mass failure of the knickpoint face occurs the knickpoint will quickly retreat upstream until it reaches the secondary scour hole. At this point the trench based migration process may begin again.

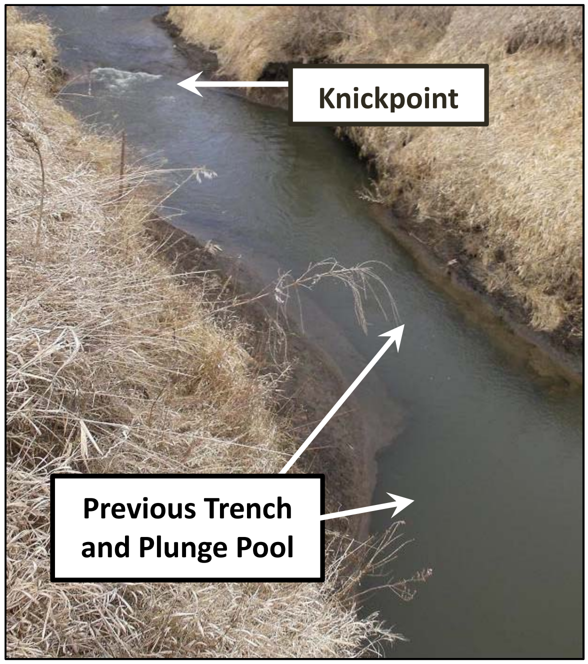

Figure 11: Image of knickpoint on March 18, 2011 with evidence of previous trench and plunge pool downstream of knickpoint.

References

Brush, Lucien M. Jr. and Wolman, M Gordon. "Knickpoint Behavior in Non-Cohesive Material: A Laboratory Study." The Geological Society of America Bulletin, Vol. 71, No. 1, January 1960, pp. 59-74

Chen, A.H., Rus, D.L., Stanton, C.P. "Trends in Channel Gradation in Nebraska Streams, 1913-95" USGS, Water Resources Investigations Report 99-4103, 1999

Daniels, R.B.. Entrenchment of the Willow Drainage Ditch, Harrison County, Iowa. *American Journal of Science*. 258:161-176, 1960

Daniels, R.B., and R.H. Jordan. Physiographic history and the soils, entrenched stream systems and gullies, Harrison County, Iowa. U.S. Department of Agriculture Technical Bulletin 1348, 1966

Gardner, Thomas W. "Experimental study of knickpoint and longitudinal profile evolution in cohesive, homogeneous material." The Geological Society of America Bulletin, Vol. 94, No 5, May 1983, pp. 664-672

Iowa Environmental Mesonet (2013) http://mesonet.agron.iastate.edu.

Kephart, C. (2013) Flow and Geometry Measurements at an Active Knickpoint, MS Thesis, University of Nebraska – Lincoln.

Papanicolaou, T. "The Effects of Headcut and Knickpoint Propagation on Bridges in Iowa" TR-541 Iowa Department of Transportation, October 2008

Rus, D.L. Dietsch, B.J. Simon, A. "Stream Adjustment and Channel Widening in Eastern Nebraska" USGS, Water Resources Investigations Report 03-4003, 2003

Simon, A. and R.E. Thomas, Processes and forms of an unstable alluvial system with resistant, cohesive streambeds. *Earth Surface Processes and Landforms*. 27:699-718, 2002.

Simon, A., R.E. Thomas, A.J.C. Collison, and W. Dickerson, Erodibility of cohesive streambeds in the Yalobusha River system. Research Report No. 26. USDA-ARS National Sedimentation Laboratory: Oxford, MS, 2002.

Development of an affinity-based concentrator-detection kit for monitoring emerging contaminants in recycled water

Basic Information

Title:	Development of an affinity-based concentrator-detection kit for monitoring emerging contaminants in recycled water
Project Number:	2013NE255B
Start Date:	3/1/2013
End Date:	8/31/2014
Funding Source:	104B
Congressional District:	NE-01
Research Category:	Water Quality
Focus Category:	Methods, Water Quality, Waste Water
Descriptors:	Emerging contaminants, water screening, analytical method development
Principal Investigators:	David Hage, Daniel Davidson Snow

Publications

1. Elliott Rodriguez, Ryan Matsuda, Christopher White II, Donald Jobe and David Hage*, “Development of a Displacement Assay for Screening Contaminants in Water”, 5th Annual Research Poster Session, Chemistry Dept., UNL, Lincoln, NE, August 2013.
2. Elliott Rodriguez, Ryan Matsuda, Christopher White II, Donald Jobe and David Hage*, “Development of a Displacement Assay for Screening Contaminants in Water”, Nebraska Summer Research Symposium, UNL, Lincoln, NE, August 2013.
3. Ryan Matsuda, So-Hwang Kye, Christopher White II, Elliott Rodriguez, Donald Jobe, Daniel Snow and David Hage*, “Detection of Emerging Contaminants in Water by a Displacement Assay through High-Performance Affinity Chromatography”, 2013 Nebraska Water Conference, Lincoln, NE, October 2013.

2013 Project Report: Development of a Displacement Assay for Emerging Contaminants in Water using High-Performance Affinity Chromatography

David S. Hage[1] (PI) and Daniel Snow[2]
[1] Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE
[2] Water Sciences Laboratory/Nebraska Water Center, Daugherty Water for Food Institute, University of Nebraska-Lincoln, Lincoln, NE

Project Summary: Problem & Research Objectives

Reuse of treated and untreated water is becoming increasingly common in countries and regions with limited water resources. Even in regions with abundant water resources, irrigation with recycled water is relatively common. For example, Nebraska ranks 2nd in the U.S. after California in the number of farms that use recycled or reclaimed water.[1] Though obviously beneficial from a water conservation perspective, reuse can lead to increasing concentrations and incidence of biologically-active contaminants occurring in water. For instance, recent evidence indicates that traces of pharmaceuticals and steroid hormones are present in surface and groundwater, and may even be found in drinking water supplies. Because of current treatment technologies and design limitations, treated municipal wastewater releases traces of steroids, pharmaceuticals, illicit drugs, and other chemicals into receiving waters.[2-3] Residues of antibiotics, other veterinary pharmaceuticals, and steroid hormones are also known to occur in livestock waste and wastewater.[4-6] Municipal wastewater discharge, run-off from feedlots, and crops fertilized with manure are all potential routes for releasing these compounds into aquatic environments. Many questions remain as to the relative importance of various contaminant sources, the feasibility and effectiveness of new treatment methods, and the potential health implications of increasing antibiotic resistance or direct toxicological effects of these compounds in reused water and resulting crops. The observed concentrations of these chemicals in water are typically quite low (i.e., ng/L-µg/L range) and these contaminants are often present in complex matrices. These factors have created a pressing demand for improved sampling and detection technologies for these biologically-active emerging contaminants in water.

Recent preliminary studies to develop new analytical approaches for examining these contaminants have been conducted by a multidisciplinary group in analytical and environmental chemistry at the University of Nebraska–Lincoln (UNL). This team has combined efforts to achieve a common goal of developing and testing innovative approaches for sampling and detecting emerging contaminants in environmental matrices. This initial work has led to the discovery that low-cost binding agents such as bovine serum albumin (BSA) can be used as affinity sorbents for the extraction of various pharmaceutical agents and steroid hormones in water. It has also been shown that these affinity sorbents can be used for the selective extraction of these contaminants and related compounds prior to identification and measurement by laboratory methods such as liquid chromatography-tandem mass spectrometry (LC/MS/MS). Continued refinement and expansion of these sorbents into new formats can lead to methods and technologies for both *in situ* contaminant detection and improved sample collection for emerging contaminants.

The overall goal of this research is to explore the development of novel, low-cost affinity sorbents for use in screening and concentrating indicator compounds for emerging contaminants in water. This work is expected to lead to the development of innovative, inexpensive, and rapid screening techniques for monitoring irrigation water quality and to help evaluate risk from water reuse. These techniques, in turn, should provide data that will lead to better tools for managing water quality for irrigation and both human and animal consumption. The specific objectives are to 1) explore the development and use of general binding agents such as BSA in low-cost, affinity-based assays for screening water samples for indicator compounds of biologically-active emerging contaminants and 2) examine such devices for collection of the same contaminants for analysis by LC/MS/MS.

Project Results: Methodology & Principal Findings

The use of affinity sorbents and high-performance affinity chromatography (HPAC) can become a powerful tool for rapidly screening for common emerging contaminants found in water. HPAC is chromatographic technique that utilizes a biologically-related binding agent as the stationary phase to retain chemicals. A displacement assay based on HPAC was constructed in this project using a fluorescent labeled analog of the drug phenytoin and an affinity column containing immobilized bovine serum albumin (BSA). BSA is a serum transport protein found in cattle that has a series of sites that are capable of binding to various pharmaceuticals and hormones, as well as some pesticides (as shown in **Figure 1**).

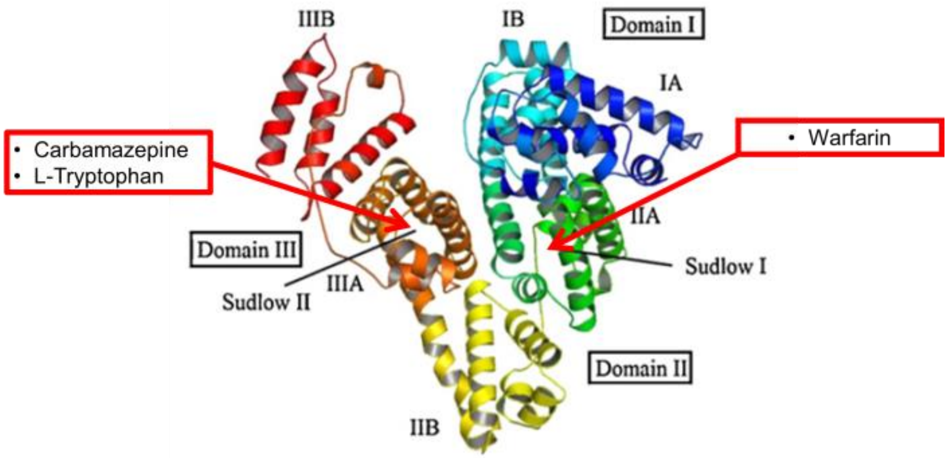

Figure 1. BSA and the binding sites to which carbamazepine, L-tryptophan and warfarin are bound during a displacement assay; phenytoin also interacts at each of these sites

Warfarin, carbamazepine (widely found in wastewater), and L-tryptophan were used as the model chemicals and binding probes to develop and test this assay. All of these compounds were found to displace labeled phenytoin when applied to the BSA column and provided a signal within a few minutes of sample application. This approach was examined in this study as a possible a screening tool that could be used for detection of emerging contaminants in reclaimed and recycled water.

Labeled phenytoin was synthesized by combining 20 µmol 3-amino-5,5-diphenylimidazolidine-2,4-dione (ADPH) with 9 µmol *N*-hydroxysuccinimide-fluorescein (NHS-fluorescein) in dimethyl sulfoxide (DMSO) and triethylamine. This reaction is shown in **Figure 2**. The mixture was allowed to react in the dark and in an ice bath for 4 hours. DMSO and triethylamine were then removed from the final product by using a vacuum oven at 60 ^{o}C and 25 mm Hg.

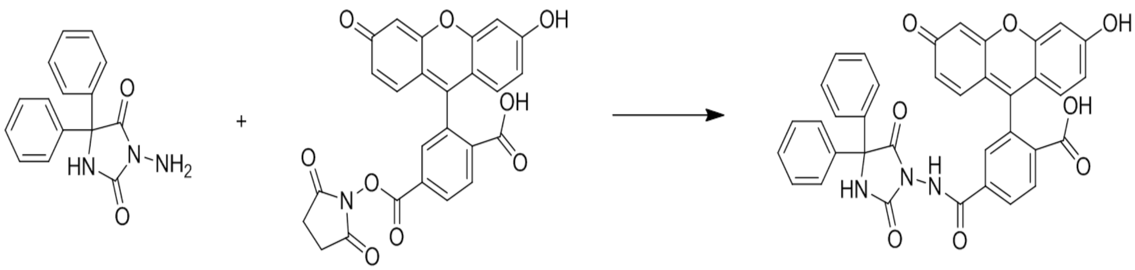

Figure 2. Reaction involved in synthesis of fluorescein labeled phenytoin.

Labeled phenytoin was first applied to a column containing immobilized BSA and allowed to bind to the BSA, as depicted in step 1 of **Figure 3**. Following the injection of the labeled phenytoin, the various model analytes were injected onto the column. This resulted in displacement of some of the labeled phenytoin, as depicted in step 2. Changes in the displaced peak area were found to be correlated with the concentration of the applied analyte, as shown in **Figure 4**.

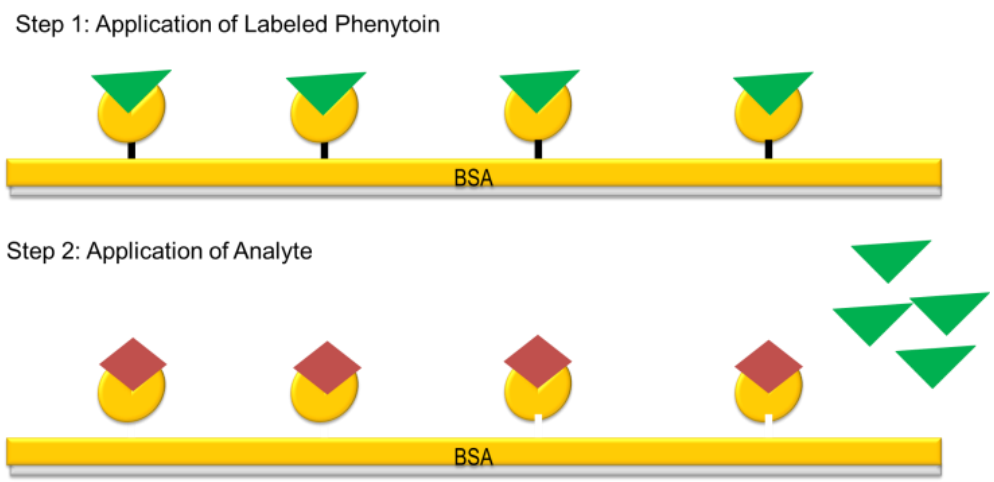

Figure 3. Scheme for displacement assay based on HPAC

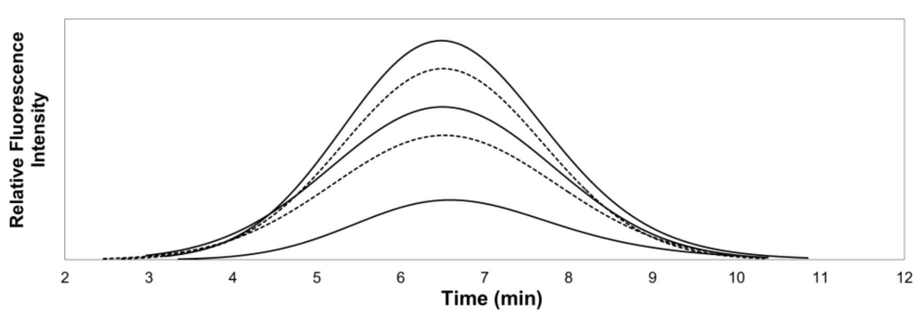

Figure 4. Example of a displacement assay using a BSA column (1 cm x 2.1 mm i.d.) and labeled phenytoin. These results were obtained for warfarin sample concentrations of 0-50 μM using a 20 μL sample injection at a flow rate of 0.25 mL/min.

Calibration curves were generated using a set of standards ranging from 0.01-1 µM for warfarin and carbamazepine, as shown in **Figure 5**. The linear ranges for the calibration curves are shown in the insets of these figures. A similar calibration curve was obtained for L-tryptophan. The estimated limits of detection for carbamazepine and warfarin were 11 nM and 6 nM, respectively.

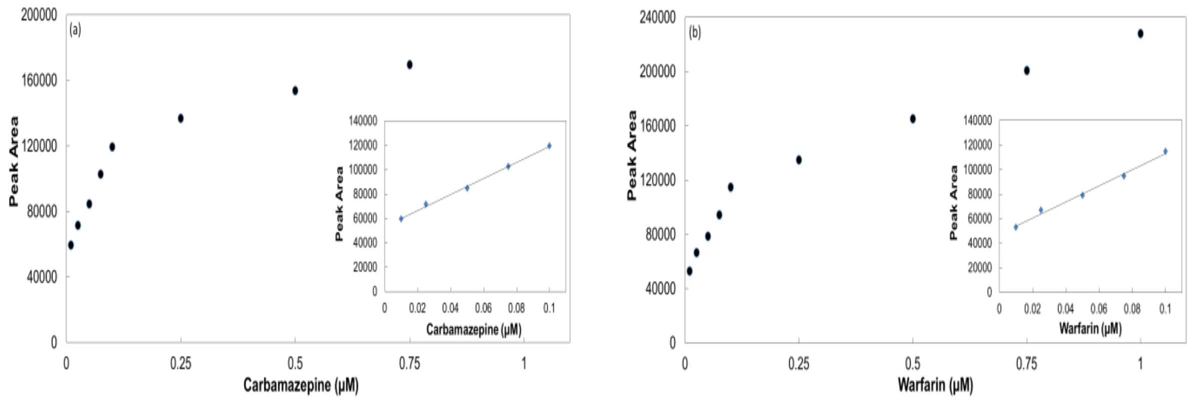

Figure 5. Calibration curves obtained for (a) carbamazepine and (b) warfarin

Spiked samples were also prepared by adding in a known concentration of either carbamazepine or warfarin to a 20 mL sample of tap water. The samples were then injected onto the BSA column containing the labeled phenytoin. The displayed peak area was used with the linear calibration plots to determine the concentration of the spiked samples, as shown in **Table 1**. There was a good correlation between the actual and detected concentration for both analytes.

Table 1. Results from spiked recovery experiments for carbamazepine and warfarin

Actual Conc. (µM)	Detected Carbamazepine Conc. (µM)	Detected Warfarin Conc. (µM)
0.10	0.10 (±0.03)	0.08 (±0.06)
0.25	0.25 (±0.08)	0.24 (±0.07)
0.49	0.49 (±0.15)	0.49 (±0.02)
0.73	0.75 (±0.21)	0.73 (±0.12)
1.0	1.04 (±0.12)	1.12 (±0.04)

Another portion of our work has begun to examine the use of BSA columns to capture emerging contaminant indicators. This was tested by using a 1 cm x 2.1 mm i.d. BSA column that contained 71 (± 5) mg BSA/g silica, or 1.1 mg BSA per column. The application of warfarin to this column indicated that this column had a binding capacity for such contaminants of 17 (± 1) nmol (or 5.2 µg for warfarin). A 5 cm x 4.6 mm i.d. BSA column of the same design was also coupled with LC/MS/MS, in preliminary work with NSF/EPSCoR and Teledyne-ISCO, and used to detect carbamazepine in water, giving a strong signal for 24 ng or 0.1 nmol of this drug.

Project Summary & Significance

Displacement assays can be developed into powerful tools for the detection of trace levels of pharmaceutical agents and other chemical contaminants and to help quickly evaluate the safety of reused water in the field and the laboratory. The detection range, using a standard fluorescence detector, was in the nM to µM range, with detection limits in the low nM range. The displacement assay also demonstrated comparable results to the actual concentrations for spiked samples containing warfarin or carbamazepine. Although this particular study looked at carbamazepine, warfarin and L-tryptophan as model analytes, the same approach could be extended to other compounds that bind to BSA. The next phase of this work will consider the use of this screening approach as a pre-concentration device for subsequent detection by LC/MS/MS. The information that has already been provided by this study indicates that this approach can be used as a potential screening tool to detect emerging contaminants in water and may thus be developed into a screening tool for irrigation water quality. Further studies will explore the use of this method in miniaturized systems, field-portable kits that can be used alone or in combination with LC/MS/MS.

References Cited

1. USDA, Census of Agriculture: Farm and Ranch Irrigation Survey, Vol. 3, Special Studies, Part 1, AC-07-SS-1, (2009).

2. Kolpin, DW, Skopec, M, Meyer, MT, Furlong, ET, Zaugg, SD. Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions. Sci Total Environ 328 (2004) 119-130.

3. Stackelberg, PE, Furlong, ET, Meyer, MT, Zaugg, SD, Henderson, AK, Reissman, DB. Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking-water-treatment plant. Sci Total Environ 329 (2004) 99-113.

4. Burkholder, J, Libra, B, Weyer, P, Heathcote, S, Kolpin, D, Thorne, PS, Wichman, M. Impacts of waste from concentrated animal feeding operations on water quality. Environ Health Perspect 115 (2007) 308-12.

5. Dolliver, HAS, Gupta, SC. Antibiotic losses from unprotected manure stockpiles. J Environ Qual 37 (2008) 1238-1244.

6. Shappell, NW, Billey, LO, Forbes, D, Matheny, TA, Poach, ME, Reddy, GB, Hunt, PG. Estrogenic activity and steroid hormones in swine wastewater through a lagoon constructed-wetland system. Environ Sci Technol 41 (2007) 444-450.

An Innovative Graphene Oxide Filter for Drinking Water Contaminants Removal

Basic Information

Title:	An Innovative Graphene Oxide Filter for Drinking Water Contaminants Removal
Project Number:	2013NE256B
Start Date:	3/1/2013
End Date:	12/31/2014
Funding Source:	104B
Congressional District:	1
Research Category:	Engineering
Focus Category:	Water Quality, Treatment, Methods
Descriptors:	
Principal Investigators:	Yusong Li, Yongfeng Lu, Daniel Davidson Snow

Publications

There are no publications.

2013 Project Report: An Innovative Graphene Oxide Filter for Drinking Water Contaminants Removal

Yusong Li[1], Daniel Snow[2] and Yongfeng Lu[3]

[1] Department of Civil Engineering, [2] School of Natural Resources, [3] Department of Electrical Engineering, University of Nebraska-Lincoln

PROJECT SUMMARY

According to a World Bank estimate, nearly 1.1 billion individuals lack access to safe drinking water, resulting in millions of deaths annually by waterborne disease in developing countries. In agricultural areas such as Nebraska, nitrate and pesticide contamination of drinking water supplies is also a concern, as are contaminants such as uranium and arsenic that may be mobilized by pumping. In the rural or remote areas, portable water purification devices, or point-of-use water treatment systems, can be extremely helpful for people to obtain drinking water from untreated or natural sources. Only a few point-of-use technologies are available providing economical and efficient removal of a wide range of contaminants. Therefore, there is a critical need to develop technologies for effective, practical and robust treatment of drinking water.

Dr. Andre Geim, the winner of 2010 Nobel Prize in Physics, recently (January 2012) published in *Science* an innovative membrane made from graphene oxide (GO) nanomaterials, which possess extremely rapid permeation of water, but can be completely impermeable to liquids, vapors, and gases, including helium one of the most difficult to contain elements in nature. The article reported that water permeates through the membranes 10^{10} times faster than helium gas. This unusual property was explained by the unique structure of GO sheets, which arrange in such a way that between them there is room for exactly one layer of water molecules. A low friction flow of a monolayer of water is possible through two-dimensional capillaries. When a solution is exposed to a GO membrane, water molecules will rush into the capillaries and form a highly ordered monolayer. As such, pore space will be clogged with water molecules so that other chemicals cannot get through.

The overall goal of this research is to evaluate the possibility to apply GO nanomaterial membrane for use in water purification. Objectives of this proposal include:

- Fabricate and characterize GO membranes suitable for water purification.
- Produce preliminary data to assess the ability of GO membranes to remove contaminants in drinking water.

The original project period was March 1 2013 to February 29, 2014. The project was granted non-cost extension to until December 2014.

PROJECT RESULTS

1. Fabrication of GO membrane

Two different methods were evaluated to develop GO membrane. The first method is based on vacuum filtration approach, and the second one is based on a layer by layer deposition approach.

Vacuum Filtration Method:

As purchased GO need to be modified to make it more hydrophobic. The modified GO suspension will then be vacuum filtered to make GO film membrane. Steps are as illustrated in Figure 1.

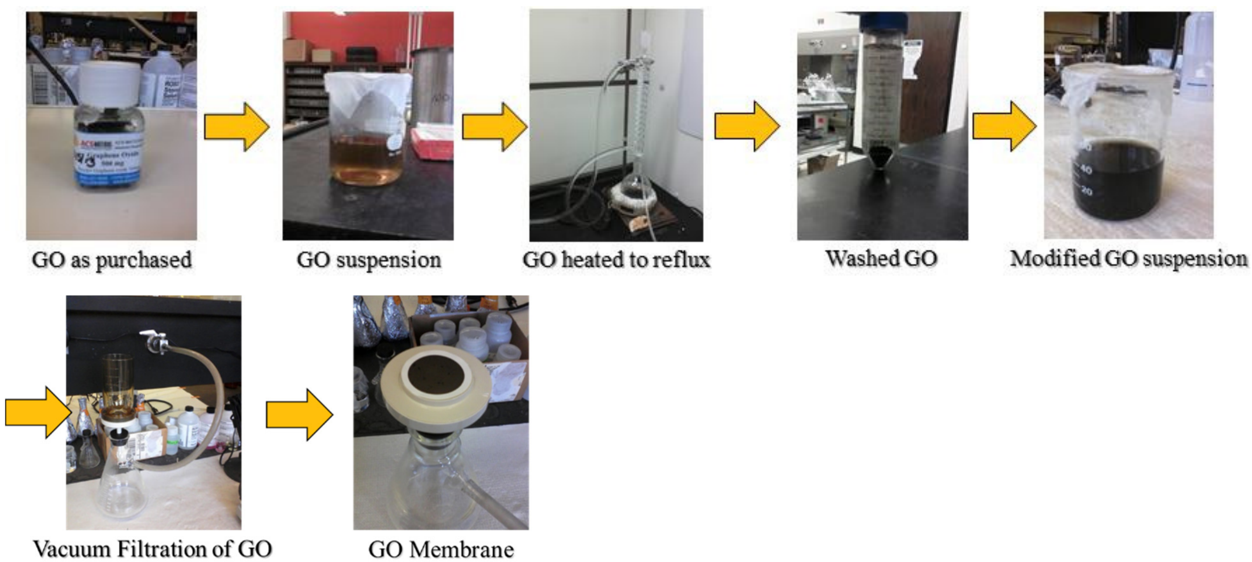

Figure 1 Procedure of making GO membrane

- Graphene Oxide single layered flakes were sonicated in ultrapure water and subsequently centrifuged
- The sediment obtained following the centrifuging process was re-dispersed in ultrapure water and the process was repeated four more times
- Sodium hydroxide was added to the suspension in order to create a more hydrophobic membrane
- The suspension was then stirred under the flow of nitrogen
- The suspension was heated to reflux for one hour

- The suspension was centrifuged again and the sediment was re-dispersed in ultrapure water and repeated 3 times in order to wash the GO
- Small amounts of the modified GO suspension were sonicated in ultrapure water and then vacuum filtrated onto a polyethersulfone membrane

Layer by Layer Deposition Method:

This method is currently under evaluation. Following is a list of steps:

- Membrane soaked in GO solution that was sonicated in Isopar
- Membrane then rinsed with Isopar to remove excessive GOs
- Membrane then dipped in TMC and GO solutions a designated amount of times
- The synthesized GO membrane was boiled in a 95 ^{o}C water bath for 2h to remove residual Isopar

2. Characterization of GO membrane

We have characterized the GO suspension and GO membrane produced using the vacuum filtration method. Zeta Potential of modified GO suspension is measured around -38mV for pH varied from 3 to 10. A negative zeta potential indicates that the modified GO suspension is very stable. GO flakes vary greatly in size, ranged from 500nm-2µm.

Contact angle was measured to evaluate the hydrophobicity of the GO. As shown in Figure 2. The contact angle of unmodified GO suspension was 28^{o}, and the contact angle of modified GO was 59^{o}. The increase of contact angle is a direct indicator that the modified GO was more hydrophobic.

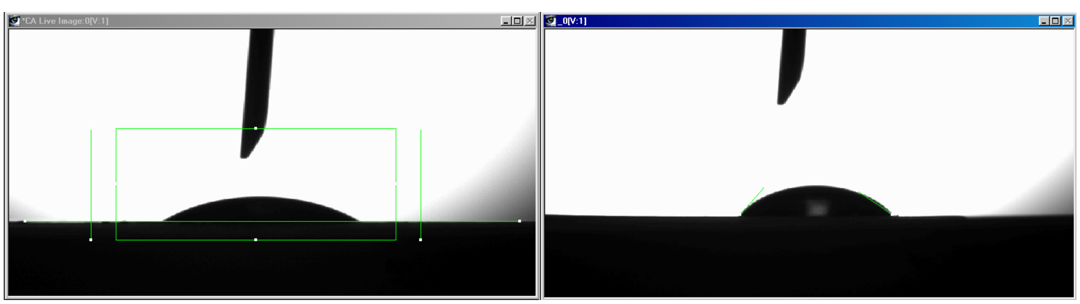

Figure 2. Contact angle measurement for GO suspension before (left) and after (right) modification

Figure 3 is an AFM image of the GO suspension. AFM shows height profiles on the left and the surface roughness on the right. The thickness of GO flakes in the suspension was determined as 1 nm per flack.

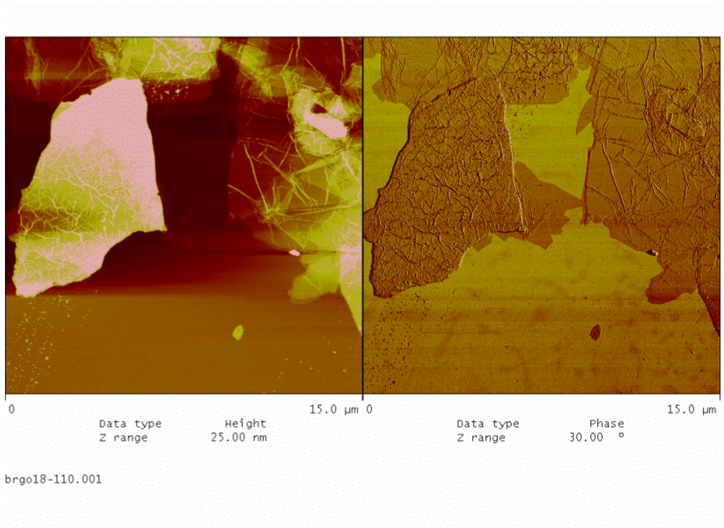

Figure 3. AFM image of GO suspension

3. Evaluate the Water Flux of GO membrane

We investigated water flux of the GO membrane using a dead end membrane filtration system (Figure 4).

Figure 4 Dead-end Filtration System

This system consists of a feed tank pressurized with a nitrogen cylinder, a stirred cell from Millipore (Billerica, MA), and a digital balance to monitor the permeate of water flux. DI water was used to test the pure water flux of the membrane. The membranes was placed in a stirred cell filter holder. The cell was connected to a pressure tank where water (clean or contaminated) was stored in order to pass through the GO membrane. Figure 5 is a typical water flux curve under a pressure of 1 bar. The steady state water flux at the end of the curve was recorded as water flux for GO membrane. Pure water flux values dropping quickly immediately is common in filters.

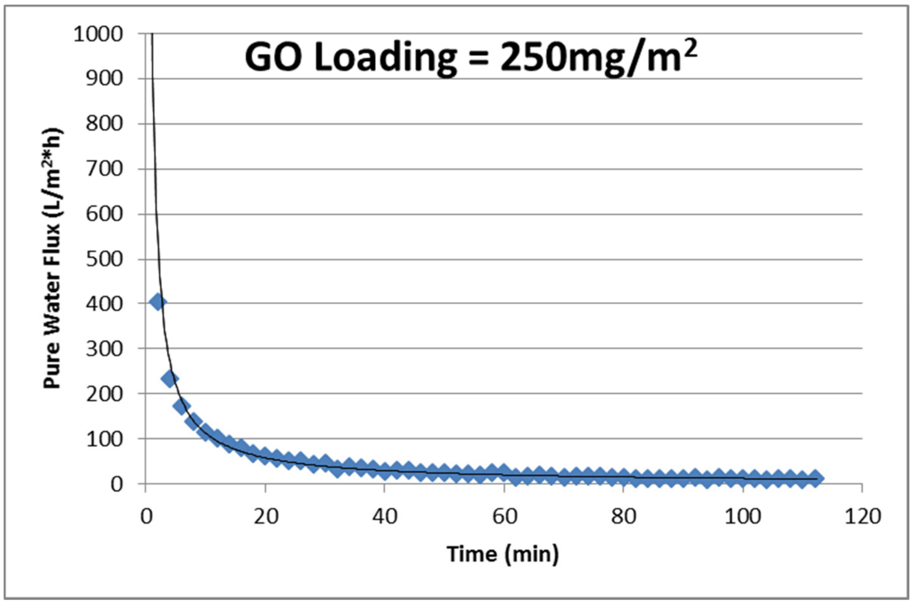

Figure 5 Pure water flux measurement curve for a GO membrane with load of 250 mg/m^2.

Water flux was tested for GO membrane with GO loading ranged from 100 to 300 mg/m^2. Figure 6 presents the influence of GO loading on the membrane water flux. In general, water flux of GO membrane is in the decreasing with the increase of GO loading. The water flux was about 275 L/m^2 h for a GO loading of 100 mg/m^2, and can be as low as about 25 mg/m^2. Typical values for nano-filtration are between 20-50 L/m^2 h. Flux decreasing with increasing loading rate makes sense, however one similar study found no trend between thickness and flux through the GO membrane.

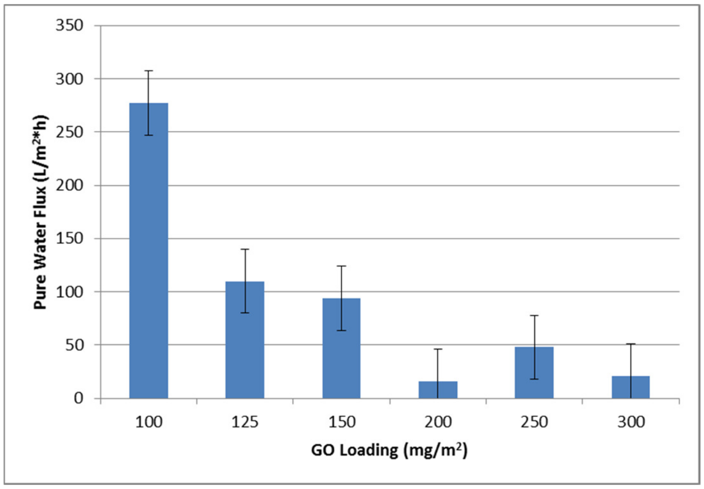

Figure 6 Measured water flux with different GO loading

4. Summary of the findings and plan for the next step.

In summary, due to the small amount of GO needed, GO membrane will be cost effective. GO suspensions are very stable even for a wide range of pH values. A high pure water flux reveals GO membrane's ability to pass water quickly even with high loading rates. Removal efficiencies have been found to be high in similar research studies with dissolved contaminants. It is hoped that this research will have similar results and make GO membranes a more viable option for water purification in the future.

The project was granted non-cost extension to until December of 2014. In the next several months, we will evaluate GO membrane developed using layer by layer deposition method. Both types of GO membranes will be tested and compared for their removal efficiency of various contaminants that are common to drinking water. Possible contaminants to be tested are: salts, nitrates, uranium, arsenic, atrazine, strontium, manganese and copper. It is expected that the GO membranes will be able to achieve a high removal rate, and will be especially useful for separating dissolved contaminants that are otherwise very difficult to remove. The efficiency of the GO filters over time will also be monitored in order to determine the practical life expectancy of individual filters.

References:

Dreyer, Daniel R., Sungjin Park, Christopher W. Bielawski, and Rodney S. Ruoff. "The Chemistry of Graphene Oxide." *Chemical Society Reviews* 39 (2010): 228-40. *RSC.* The Royal Society of Chemistry, 3 Nov. 2009. Web. 13 Nov. 2013.

Yi Han, Zhen Xu, and Chao Gao. "Ultrathin Graphene Nanofiltration Membrane for Water Purification." *Advanced Functional Materials* (2012): 1-8. *Wiley Online Library*. 13 Dec. 2012. Web. 13 Nov. 2013.

Hu, Meng, and Baoxia Mi. "Enabling Graphene Oxide Nanosheets as Water Separation Membranes." *Environmental Science & Technology* 47 (2013): 3715-723. Print.

Rourke, Jonathan P., Priyanka A. Pandey, Joseph J. Moore, Matthew Bates, Ian A. Kinloch, Robert J. Young, and Neil R. Wilson. "The Real Graphene Oxide Revealed: Stripping the Oxidative Debris from the Graphene-like Sheets." *Angewandte Chemie* 50 (2011): 3173-177. *Wiley Online Library*. 25 Feb. 2011. Web. 20 Nov. 2013.

Sun, Pengzhan, Miao Zhu, Kunlin Wang, Minlin Zhong, Jinquan Wei, Dehai Wu, Zhiping Xu, and Hongwei Zhu. "Selective Ion Penetration of Graphene Oxide Membranes." *ACS Nano* 7 (2012): 428-37. *ACS Nano*. American Chemical Society, 7 Dec. 2012. Web. 20 Nov. 2013.

Award--Development of a National Database of Depreciated Structure Replacement Values for Inclusion with SimSuite/HAZUS and Flood Mitigation Reconnaissance Studies

Basic Information

Title:	Award--Development of a National Database of Depreciated Structure Replacement Values for Inclusion with SimSuite/HAZUS and Flood Mitigation Reconnaissance Studies
Project Number:	2013NE257S
Start Date:	1/1/2013
End Date:	7/31/2014
Funding Source:	Supplemental
Congressional District:	
Research Category:	Social Sciences
Focus Category:	Floods, Economics, Management and Planning
Descriptors:	
Principal Investigators:	Suat Irmak, Steven Shultz

Publication

1. None

Shultz NIWR-IWR Project Report

‘Development of a National Database of Depreciated Structure Replacement Values for Inclusion with SimSuite/HAZUS and Flood Mitigation Reconnaissance Studies’

Progress Report

GIS coverages of census geography (block groups and tracts) for were obtained for three study site locations Fargo/Moorhead (ND/MN), Minot, ND, and Sarpy County, NE.

Then both residential and non-residential DSRVs (from existing USACE feasibility studies) for these same three study areas were aggregate and summarize within both census block group and tract levels of geography This required GIS database development, quality control, and the merging of various database files from the USACE and sub-contractors who collected the original DSRV values.

Hazus points collected and modified by the USACE-IWR(HEC) staff were also obtained and integrated within the GIS database and assigned to specific floodplain and DSRV inventory areas.

Spatial analyses of census geography with both 100 and 500-year regulatory floodplain boundaries were then performed. Of particular interest was the relationship between census geography and floodplain areas (or how well block groups and tracts spatially overlap with floodplains and DSRVs).

Database development from multiple regression models is almost complete. These models will be used to predict residential DSRVs will be estimated for non-residential properties.

Information Transfer Program Introduction

The Nebraska Water Center continued active pursuit of its traditional diverse information transfer program in 2012. USGS funding continues to help underwrite a wide variety of public and professional information, public relations and education 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) updated and reprinted Water Center fact sheets and online UNL water faculty directories database; (3) more than 20 press releases reporting on water-related research and outreach programming or promoting Nebraska Water Center and University of Nebraska water-related educational activities; (4) helping to support four internet web sites; (5) publicity and supporting materials for an annual water law conference, public lecture series, water symposium, brown bag lectures, water and natural resources tour; (6) coordinating UNL Extension’s largest public display and student recruitment event of the year at the Husker Harvest Days farm show; (7) publication via U.S. Environmental Protection Agency grant funds of a full-color book detailing the Nebraska Department of Environmental Quality’s “CLEAR” community lake restoration program; and (8) publication of a full-color University of Nebraska “Water Faculty and Staff Directory” book.

The Nebraska Water Center continues as part of the Robert B. Daugherty Water for Food Institute, a global imitative involving all University of Nebraska water-related faculty and staff with a mission of greater global agricultural water management efficiency.

Information Transfer Plan/Water Education

Basic Information

Title:	Information Transfer Plan/Water Education
Project Number:	2008NE173B
Start Date:	3/1/2013
End Date:	2/28/2014
Funding Source:	104B
Congressional District:	1
Research Category:	Not Applicable
Focus Category:	Education, None, None
Descriptors:	
Principal Investigators:	Steven W. Ress, 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

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

Publication

Newsletter: The *Water Current* newsletter has a free, subscriber-based distribution of approximately 2,800 copies per issue, more than 95 percent of which are requested subscriptions. Published quarterly in full-color magazine format and available online as a pdf. One or two water-related faculty and/or professional staff are featured in each issue. Guest columns and articles are encouraged. A director's column/report publishes in each issue. News Releases: The Nebraska Water Center produces, on average, more than 20 press releases annually focused on water-related research results, extension programming, educational opportunities, public tours, seminars, lectures, symposiums and conferences, major research grants and other matters of public impact. These releases support and cross many departmental and academic discipline lines within the University of Nebraska system. The Nebraska Water Center writes these for many faculty members who do not have a staff communicator available to them. The Nebraska Water Center also coordinates many working media requests for information and interviews and devotes significant attention to cultivating long-term relationships with members of the media, locally and nationally. Within media communities, the Nebraska Water Center has a long reputation as being a willing and reliable "source" for water and natural resources news. Media calls are frequent and water-related faculty and staff are accustomed to fielding media questions.

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

Brochures and pamphlets: Produced on an as-needed basis. These include, but are not limited to, mission and programming of the Nebraska Water Center, UNL Water Sciences Laboratory, annual Water and Natural Resources Tour and for other units or programs affiliated with or sponsored by the Nebraska Water Center. All have electronic versions, as well.

Water Center fact sheets: Generally one sheet and produced as needed. Used to inform and promote general themes, such as the Nebraska Water Center and UNL Water Sciences Laboratory, or to announce specific programs, seminars, courses, etc. Used for both specific internal and external audiences.

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. An updated version is pending.

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 or in print form. Nebraska Water Center assists with content, design, editing and production for many of these publications.

Electronic Resources:
The Nebraska Water Center co-sponsors, designs and maintains the following related Internet web sites:

UNL Water:
http://water.unl.edu
Nebraska Water Center:
http://watercenter.unl.edu/
Water Sciences Laboratory:
http://waterscience.unl.edu
Robert B. Daugherty Water for Food Institute:
http://waterforfood.nebraska.edu/

Conferences, Seminars, Tours, Workshops, Other Outreach:

Water and Natural Resources Seminars: A longstanding annual series of 12 to 14 free weekly public lectures conducted January to April. The series dates to the early 1970's and includes a broad range of water and natural resource-related topics, including the latest research and programming on irrigation and other agriculture topics, fish and wildlife, drinking water and wastewater, watershed management, modeling, energy, climate change, law, economics, and political science. Individual lectures attract an audience of 60 to 100, including approximately 15 to 20 graduate and undergraduate students enrolled for a one-credit-hour course. Other audience members include faculty, government and organizational employees, policy makers and interested members of the public. News releases, mailings, brochures, posters and web-based information are produced supporting this series. Most lectures are taped and then posted online for viewing.

Water and Natural Resources Tour: The tour is another long-standing Nebraska Water Center activity, dating to UNL "Irrigation tours" first conducted in the 1970's. The 2012 tour explored water and agricultural issues arising from the 2011 flooding of the Missouri River lowlands. Attendees include state legislators, congressional staff, faculty, and water scientists and managers from a wide variety of public and private entities. The event is co-sponsored and co-planned with the Kearney Area Chamber of Commerce, Nebraska Public Power District, Central Nebraska Public Power and Irrigation District, USGS Nebraska Water Science Center and others.

Water Law Conference: A one-day event focused on Nebraska water law issues such as water rights transfers, drainage issues, Clean Water Act enforcement, etc. It is targeted to practicing attorneys but open to all. Typically half those attending are water managers and policy-makers. The program is developed by a committee that includes Nebraska's top water lawyers, and is co-sponsored by the University of Nebraska College of Law. Continuing Legal Education (CLEs) credits are made available in Nebraska, Iowa and Colorado.

Great Plains Climate, Water and Ecosystems Symposium: A one-day event following the water law conference focusing on Great Plains climate, water and ecosystems and showcasing impacts at the intersection of climate change or variability, water and all other disciplines, including infrastructure, design, hydropower, agriculture, ecosystem services, drinking water and many others. Geographic focus was centered on the Great Plains, including research or programming transferrable to the Great Plains.

Mentoring: The Nebraska Water Center prioritizes mentoring newer assistant professors to help them establish successful careers. Newer faculty from the many academic units associated with the Nebraska Water Center attended several brown bag sessions during the year where they could get acquainted and get 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 upon their arrival and as needed afterwards. This is an ongoing effort. Weekly funding opportunity emails are sent to all water-related faculty and staff.

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 and special "Sunday with a Scientist" displays at the Nebraska State Museum.

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," one of the largest commercial agricultural expos in the country. More than 50,000 tour UNL exhibits during this three-day 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

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	3	0	0	1	4
Masters	2	0	0	2	4
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	7	0	0	3	10

Notable Awards and Achievements

Presentation at the 2013 NE Water Center Confernce. Titled Estimating Flood Damage Estimates Using Public Data Sources. S Shultz.

Publications from Prior Years