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Arkansas Bulletin of Water Research

A publication of the Arkansas Water Resources Center

Issue 2018

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The Arkansas Bulletin of Water Research is a publication of the Arkansas Water Resources Center (AWRC). This bulletin is produced in an effort to share water research relevant to Arkansas water stakeholders in an easily searchable and aesthetically engaging way.

This is the second publication of the bulletin and will be published annually.

The submission of a paper to this bulletin is appropriate for topics at all related to water resources, by anyone conducting water research or investigations. This includes but is not limited to university researchers, consulting firms, watershed groups, and other agencies.

Prospective authors should read the "Introduction to the Arkanasas Bulletin of Water Research" contained within this publication and should refer to the AWRC website for additional infromation.

arkansas-water-resources-center.uark.edu

Cover Photo (left to right): Researchers conduct field work on rice evapotranspiration, courtesy of Benjamin Runkle, University of Arkansas professor; Southern Redbell Dace, courtesy of Dustin Lynch, Arkansas Natural Heritage Commission; Buffalo River, source unknown.

Arkansas Bulletin of Water Research

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Image caption: Brad Austin, postdoctoral research associate, conducts a sediment experiment using cores collected from a lake. Austin works under the guidance of Center director, Brian Haggard.

Introduction to the Arkansas Bulletin of Water Research (*reprint*)

Erin E. Scott* and Brian E. Haggard

Arkansas Water Resources Center, University of Arkansas
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Introduction

There is a lot of research being done in Arkansas that can provide valuable information to water stakeholders throughout the State. The research itself can come with a multitude of challenges, and sometimes what to do with that information can be even more difficult. But, sharing research results with the public is tantamount to the research itself.

The Arkansas Bulletin of Water Research was developed to provide an outlet for researchers to communicate project findings that might not be published in national or international journals, yet is extremely important to stakeholders in Arkansas. Further, this bulletin is designed to allow research to be disseminated in an easily searchable and aesthetically engaging way. The contents of this bulletin can be used to guide management decisions about water resources in Arkansas and the region.

Articles in this bulletin will inform the reader not only in the context of the research details, but especially in why such research is important to Arkansas. How can the research be used to address water problems for Arkansas? Can the research results be broadened to address water issues important in the region, and even the country?

Who Should Submit Articles?

The submission of papers to this bulletin is appropriate for topics related to water resources by anyone conducting water research or investigations in Arkansas. This includes but is not limited to university and student researchers, consulting firms, watershed groups, and other agencies.

Review Procedures

Papers will be reviewed by the editors of the Bulletin. The editors might send papers out for external reviews as needed; external reviews may become standard procedure for all papers in the future. The editors and or external reviewers will determine if the paper should be published with minor revisions, revised and resubmitted, or rejected. The editors will provide a written review with comments. The author will be expected to address comments in the paper and in a response to reviewer comments.

What Should the Paper Include?

The aim of this bulletin is to communicate applied research findings that people of various specialties can understand. Therefore, papers should be written in a relatively casual way, like a conversation with the reader.

"The most important rule: write for the busy reader who is easily distracted." This statement comes from a great reference on scientific writing,

Griffies, S.M., W.A. Perrie, and G. Hull. Elements of Style for Writing Scientific Journal Articles. 2013. Elsevier.

Another nice reference on scientific writing is,

Mackay, R.J. Writing Readable Papers: How to Tell a Good Story. Reprinted from the Bulletin of the North American Benthological Society 12(3):381-388; 1995.

Papers should be less than 2,500 words from the introduction through the conclusions and recommendations (not counting title, abstract, key points, references, or figure and table captions). Refer to the website arkansas-water-center.uark.edu to see style and formatting guidelines. The following sections should be included in submitted papers.

Title

Short Title
A title of 90 characters or less (including spaces).

Author Information
Include author first and last name, affiliation, and department of affiliation (if applicable). Also, identify the corresponding author if there is more than one author.

Abstract
In 250 words or less, summarize the report. Include the basic problem, why it's important to Arkansas, what's the research question, what's the objective(s) of the research, brief description of methods, specific results, and conclusions or recommendations to water managers.

Key Points
Include 3 to 5 bulleted statements of 25 words or less that concisely describe the overall importance, applicability, or impacts of the research.

Introduction
This is where you really get to capture the reader's attention and set up the story you're about to tell. The introduction should start fairly broadly by describing the general topic and problem. References to the literature should be used to describe what's already known about the topic, but also to show what the knowledge gap is that your research will address.

As you convey the basic facts and importance of the topic, the introduction should start to narrow focus to a more specific problem, location, or mechanism. This should then lead to specific objectives and hypotheses. This is also a great time to emphasize to the reader how the research can be applied by others…what's the big impact? How might this work be used by water resource specialists in Arkansas and perhaps around the region and country?

The introduction should be 3 to 5 paragraphs, each of 3 to 5 sentences.

Methods
The methods should provide adequate detail about the project such that someone else could repeat it. Include information about the study design, location or site description, sampling procedure, data collection, laboratory analyses, and statistical analyses.

Results and Discussion
What were the major or important findings that help to answer your research question? Be sure to include tables, figures, and statistical results. How do you interpret these findings, and how do they fit or not fit into the existing body of knowledge?

Conclusions
What do you want the reader to take away? What are your recommendations to water resource specialists? What are the benefits to Arkansas; also the region and the country, if applicable? This is the section where you should emphasize how your research can be applied by others to address pressing water problems in Arkansas.

Acknowledgements
This section allows you to recognize funding support and other assistance. It's also a place to include any disclaimers on behalf of your funding support if applicable.

References

Advice to Authors
Some scientists are great communicators, and some scientists struggle with how to convey information to the public. The goal of this bulletin is to provide information that's easy for people to understand who are from a range of disciplines. The writing should be interesting and conversational, and complex jargon should be left out.

This bulletin is designed to be a valuable resource to water specialists who have to make some tough decisions on how to address our most pressing water resource problems. It will also provide valuable reference material for current and future researchers focused on water issues in Arkansas. As you are writing the paper, frequently ask yourself, "how can results of this work help stakeholders in Arkansas."

Image caption: Dr. Matthew Covington observes a dye-trace study.

Comparative Microbial Community Dynamics in a Karst Aquifer System and Proximal Surface Stream in Northwest Arkansas

Matthew D. Covington[1*], Kristen E. Gibson[2], Josue Rodriguez[1]

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Abstract: Northern Arkansas is underlain largely by carbonate bedrock, with relatively well-developed karst flow systems. Much of this region is rapidly urbanizing, leading to a variety of potential threats to groundwater including increased and redirected runoff and the potential introduction of contaminants into the subsurface via septic systems, effluent wastewater discharge, and agricultural runoff. Here, Blowing Springs Cave (BSC) and Little Sugar Creek (LSC) were selected to serve as a model for how non-point source pollution may move through the subsurface and subsequently impact springs as well as receiving streams via contaminated water and resuspension of contaminated sediments. The objectives of the study were to: 1) explore structure, diversity, and temporal variability of microbial communities in BSC and LSC; 2) differentiate allochthonous bacteria from land surface runoff with bacteria in the sediments and water of the karst aquifer; 3) determine impact of sediment movement from karst springs to LSC through comparison of microbial communities; and 4) delineate the recharge area of BSC and constrain potential sources of *E. coli*. Water and sediment samples were collected routinely once per month for 9 months and during 2 rain events in a 3-day time series (1, 2, 4 d). During the study period, 92 water samples and 89 sediment samples were collected. Analysis of water samples for *E. coli* showed significantly higher median levels in LSC (120 MPN/100mL) when compared to BSC (56 MPN/100mL). Moreover, there was a strong correlation between discharge and levels of *E. coli* at BSC (Spearman's R=0.79, p<<0.05); however, this same relationship was not observed in LSC. It is evident that there are significant differences in the microorganisms present in water and sediment samples regardless of event type and sampling location. Last, dye tracing indicated a connection between Blowing Spring and a sinkhole located approximately 1 km to the NE. The average flow velocity of the tracer between the injection point and spring was approximately 40 m/day. The results of the study suggest that sources of *E. coli*, and microbial diversity in general, are different between the karst system and surface stream, even though LSC is under the influence of BSC.

Key Points:
- *Escherichia coli* concentrations were significantly higher in Little Sugar Creek (median=120 MPN/100 mL) than in Blowing Spring Cave (median=56 MPN/100 mL).
- *E. coli* concentrations at Blowing Spring Cave were strongly correlated with discharge (Spearman's R=0.79, p<<0.05), whereas concentrations at Little Sugar Creek showed no statistically significant correlation with discharge.
- There was significant dissimilarity in microbial composition among water and sediment samples regardless of location or event type.

Introduction

Northern Arkansas is underlain largely by carbonate bedrock, with relatively well-developed karst flow systems. Much of this region is rapidly urbanizing, leading to a variety of potential threats to groundwater including increased and redirected runoff and the potential introduction of contaminants into the subsurface via septic systems, effluent wastewater discharge, and agricultural runoff (Heinz et al., 2009; Katz et al., 2010). Impacts to groundwater can harm fragile karst ecosystems, but also pose direct threats to the public utilizing groundwater (Johnson et al., 2011). The karst systems within the Ozark Plateaus contain numerous linkages to surface water, with water often repeatedly entering and leaving the subsurface through karst sinking streams and springs. A large percentage of the population of Northern Arkansas utilizes decentralized wastewater treatment systems located within karst terrain. Consequently, threats to groundwater quality are also threats to surface water quality, which is used widely in the region for both drinking water and recreation.

The sites selected for the present study—Blowing Springs Cave (BSC) and downstream receiving surface water, Little Sugar Creek (LSC)—do not currently reside in an ANRC 319 Nonpoint Source Pollution Program priority watershed nor is the LSC or its tributaries listed on the ADEQ 303(d) list; however, there are several reasons for selecting these study sites. The Elk River Watershed (ERW), in which LSC resides, was identified in 1998 as impaired by the Missouri Department of Natural Resources due to excess nutrients primarily related to livestock and population growth. The ERW is bound in the east and west by the White River and Illinois River basins, respectively. Finally, Sugar Creek in Missouri has been listed on the 303(d) list for impairment related to low dissolved oxygen levels since 2006, though the source has yet to be identified.

Meanwhile, BSC is the site of several past and ongoing scientific studies. Specifically, Knierim et al. (2015) provided over six years of data on the presence of the *Escherichia coli* (*E. coli*) at the BSC discharge point as well as nitrate and chloride levels from 1992 to 2013. From 2007 to 2013, *E. coli* concentrations at BSC ranged from <1 to 2,420 most probable number (MPN) or colony forming units (CFU) per 100 mL. Median *E. coli* concentrations at base flow periods and during storm events were reported at 41 and 649 MPN or CFU per 100 mL, respectively, and storm event *E. coli* was significantly greater than base-flow concentrations. Based on the data, Knierim et al. (2015) hypothesized that septic tank effluents were a major contributor to chloride, nitrate, and *E. coli* levels in BSC. This hypothesis was largely based on the estimated recharge area for the spring, which was within a residential area that was known to have septic tanks present. Therefore, we selected the sites in the present study to serve as a possible model for how septic tank effluents may move through the subsurface and subsequently impact springs as well as receiving streams via contaminated water as well as resuspension of contaminated sediments.

The objectives of this study were to: 1) explore structure, diversity, and temporal variability of microbial communities in BSC and LSC; 2) differentiate allochthonous bacteria from land surface runoff with bacteria in the sediments and water of the karst aquifer; 3) determine impact of sediment movement from karst springs to LSC through comparison of microbial communities; and 4) delineate the recharge area of BS and constrain potential sources of *E. coli.*

Methods

Sample Collection

Routine sampling was conducted in BSC and LSC once per month from March to November of 2016. Samples were collected from three sites along the main stream of BSC and from LSC at four sites, one rural and three within the town of Bella Vista (Figure 1). Water samples consisted of 500 mL grab samples. Sediment samples (10 cm depth) were collected using a core sampler or scoop and placed in sterile Whirl-Pak® bags. Two storm events were also sampled at higher temporal resolution, with a threshold precipitation of 0.5 in in a 24-h period to trigger a storm sampling series. Storm sampling was conducted during the receding limb with samples taken approximately 1, 2, and 4 days following peak flow.

Dye Tracing

A dye tracing test was conducted to better constrain the recharge area of BSC. The hypothesized recharge area for BSC (Knierim et al. 2015) was searched for potential injection sites, and a single prominent sinkhole was identified within the basin. Fluorescein dye was chosen for the tracing experiment to minimize adsorption onto sediment within the sinkhole. Before introduction of dye into the sinkhole, approximately 50 gal of BSC water were dumped into the sinkhole. This was followed by 55 g of fluorescein dye dissolved in 500 mL of water, and then an additional 450 gal of spring water. Dye was detected using activated charcoal packets, which were deployed in the field to cumulatively absorb dye. Dye was extracted from the charcoal packets in the lab using an alcohol-potassium hydroxide eluent. Elutant was analyzed on a Shimadzu RF-5301 Spectrofluorophotometer. Before injection of dye, charcoal packets were placed in the field to determine any background fluorescence. Charcoal packets were placed in BSC, LSC, and all other nearby springs that were identified. To better determine the timing of the dye pulse, a GGUN-FL24 field fluorometer was deployed in the cave stream.

E. coli Analysis

For detection and enumeration of *E. coli* in water samples, Standard Method 9223B IDEXX Quanti-tray® 2000
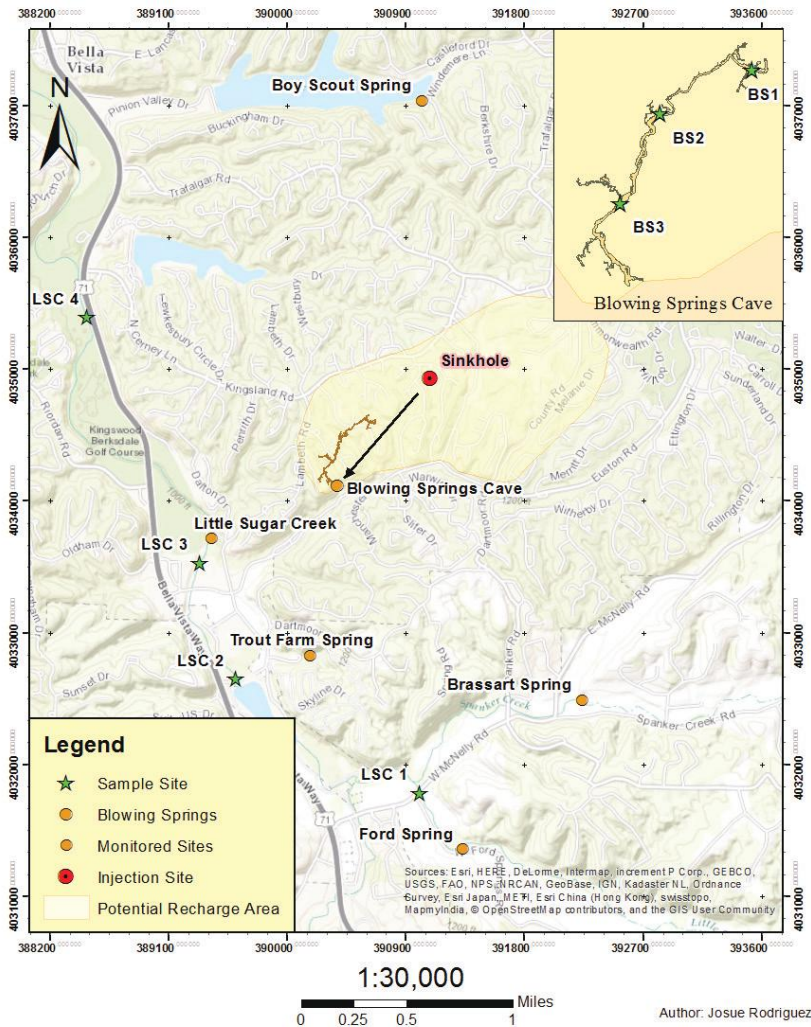
Dye Trace

Figure 1. Locations of the sampling points, dye injection, and charcoal packet deployment. A positive trace was detected from the sinkhole site to Blowing Spring Cave (indicated by arrow), but not at the other monitored sites.

16S rRNA Metagenomic Analysis

Extracted gDNA from water and sediment samples was used as template DNA for amplification of 16S ribosomal RNA (rRNA) gene by polymerase chain reaction (PCR) as described by Kozich (2013). The PCR analysis was completed through the service center at the University of Arkansas under the direction of Program Associate Dr. Si Hong Park. Briefly, forward and reverse primers targeting the 16S rRNA gene including the partial adapter overhang sequence, PCR master mix, and templated DNA were combined in a single PCR reaction well for each sample. The resulting PCR amplicons were verified by gel electrophoresis. 16S rRNA metagenomics for determination of bacterial community structures in water and sediment samples collected from the karst aquifer system (BSC) and receiving surface stream (LSC) over a 9-month period was completed at the University of Arkansas. The high quality sequence reads have been assembled. For data analysis, bioinformatics procedures using QIIME for operational taxonomic unit (OTU) assignment was applied as described by Kozich et al. (2013). Data are currently being analyzed to answer research questions.

Results

Both monthly and rain event water samples were collected at BSC (n=42) and LSC (n=56) (Tables 1 and 2). *E. coli* MPN/100 mL ranged from 0.9 to 921 at BSC and 4 to >2419.6 at LSC. *E coli.* concentrations were compared against discharge at both sites (Figure 2). Similar to Knierim et al. (2015), the highest *E. coli* concentrations at BSC in the present study were seen during and following high flow events. The correlation between discharge and *E coli.* was strong at BSC as quantified using Spearman's rank correlation coefficient (R_s=0.79, p<<0.05). In contrast, LSC showed no statistically significant correlation between discharge and *E coli.* concentrations (R_s=-0.1, p=0.33). Though *E. coli* concentrations generally increase at BSC during high discharge events, the relationship between discharge and *E. coli* displays some hysteresis, with peak concentrations occurring after peak discharge and during the time of flow recession (Figure 3). *E. coli* concentrations were statistically higher in LSC than in BSC as indicated by a nonparametric Mann-Whitney U test (p<0.005). The median *E. coli* concentration at BSC was 56 MPN/100 mL, whereas the median at LSC was 120 MPN/100 mL. While

system with Colilert™ reagent was used to determine the most probable number (MPN) in each sample. A negative control containing 100 ml of 0.1% peptone was analyzed by Colilert™ for each batch of samples.

DNA Extraction – Water and Sediments

For each sampling event, 200 mL of water from BSC and LSC was filtered through a 0.2-µm, 47-mm Supor-200 filter membrane to capture total bacterial cells. Filter membranes were placed at −80°C in 500 µl of guanidine isothiocyanate buffer. The total genomic DNA (gDNA) was extracted from prepared filters using the Fast DNA Spin Kit for Soil (MP Biomedicals). Genomic DNA was extracted from sediment samples as described by Gomes et al. (2007). Total gDNA was quantified using a NanoDrop UV spectrophotometer.

Table 1. *E. coli* concentrations (MPN/100 mL) and stream discharge at the Blowing Spring Cave sites.

Date	*E. coli*			Q_{bs} (cms)
	BSC1	BSC2	BSC3	
3/7/2016	1	0.9	0.9	0.038
4/4/2016	10.9	12.2	23.3	0.04
5/2/2016	435.2	285.1	290.9	0.097
5/25/2016	63.7	63.7	63.7	0.055
5/26/2016	165	165	165	0.093
5/27/2016	866.4	920.8	648.8	0.062
6/6/2016	143	165.8	117.8	0.041
7/11/2016	224.7	209.8	325.5	0.052
8/8/2016	161.6	88.2	88	0.052
9/8/2016	4.1	4.1	4.1	0.032
10/5/2016	48.7	48.7	48.7	0.015
10/6/2016	34.1	44.8	35.5	------
10/7/2016	18.3	18.9	24.3	------
11/10/2016	2	9.7	4.1	0.029

Table 2. *E. coli* concentrations (MPN/100 mL) and stream discharge at the Little Sugar Creek sites.

Date	*E. coli*				Q_{lsc} (cms)
	LSC1	LSC2	LSC3	LSC3	
3/7/2016	22.7	45.3	15.4	22.7	2.41
4/4/2016	22.8	116.2	4.1	12.2	4.08
5/2/2016	137.6	86	100.8	93.2	7.4
5/25/2016	920.8	2419.6	2419.6	2419.6	3.73
5/26/2016	78.9	2419.6	816.4	770.1	7
5/27/2016	275.5	1413.6	344.8	365.4	5.34
6/6/2016	61.3	23.5	73.8	124.6	4.79
7/11/2016	36.4	461.1	113.7	41.4	7.84
8/8/2016	30.5	58.3	75.4	13	4.34
9/8/2016	1413.6	106.1	125.9	31.5	1.06
10/5/2016	160.7	2419.6	816.4	488.4	1.74
10/6/2016	95.9	980.4	410.6	248.1	1.94
10/7/2016	114.5	920.8	579.4	547.5	2.07
11/10/2016	52.8	298.7	218.7	83.9	1.54

E. coli concentrations were typically similar at all of the cave sites (Figure 4a), the LSC site located just downstream from Bella Vista Lake (LSC2) frequently had higher concentrations (Figure 4b), with a median value of 380 MPN/100 mL.

Figures 5a and 5b show the genus level metagenomic results for water and sediment samples from the different sampling sites in BSC and LSC during a routine sampling
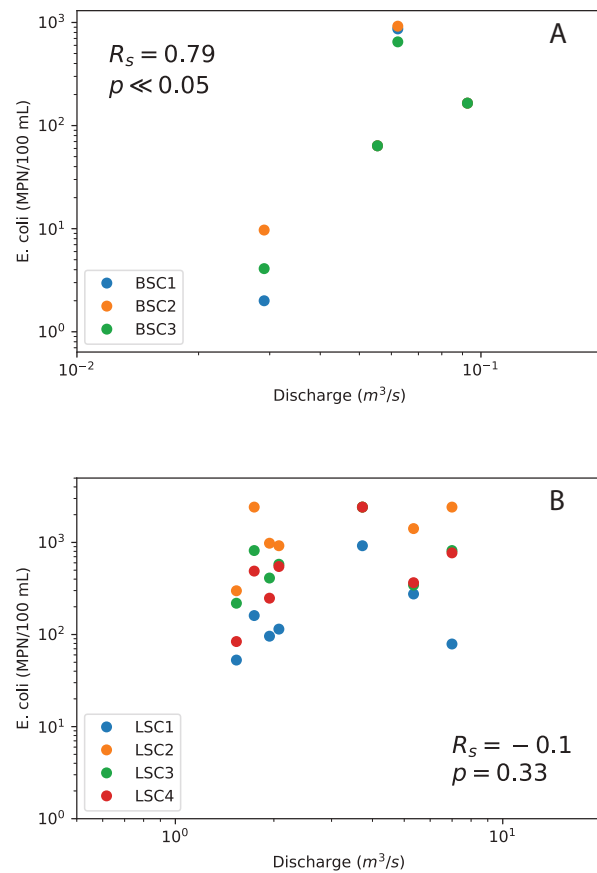
Figure 2. Discharge versus *E. coli* concentrations in Blowing Spring Cave (a) and Little Sugar Creek (b) during the study period. BSC1 is the site that is furthest downstream within the cave, and BSC3 is furthest upstream. LSC1 is the site that is furthest upstream, and LSC4 is furthest downstream. Spearman rank correlation coefficients (Rs) indicate that there is a strong positive correlation between *E coli*. and discharge at BSC, but there is no statistically significant correlation at LSC.

event on May 2, 2016. The most abundant bacterial genus in water samples was *Acinetobacter*--a gram negative bacteria commonly found in soil and water--followed by *Pseudomonas* and *Flavobacterium*, again both common to the soil and freshwater environments (Figure 5a). The family *Enterobacteriaceae* which includes *E. coli* is also represented at most water sampling locations though at lower percentages. With respect to sediment collected during the same routine sampling event, the microbial make up is quite different than paired water samples across all sampling sites (Figure 5b). The major bacterial families identified in sediment were *Bacillaceae* and *Enterobacteriaceae*, and one of the primary genera detected was *Clostridium*. The family *Bacillaceae* includes *Bacillus*, a microbe ubiquitous in nature. Meanwhile, *Clostridium* is also a soil microbe as well as an inhabitant of the intestinal tract of animals, including humans.

Samples were also analyzed by sample type for beta diversity which is the diversity of microbes between samples within a specific group. The weighted principal coordinate
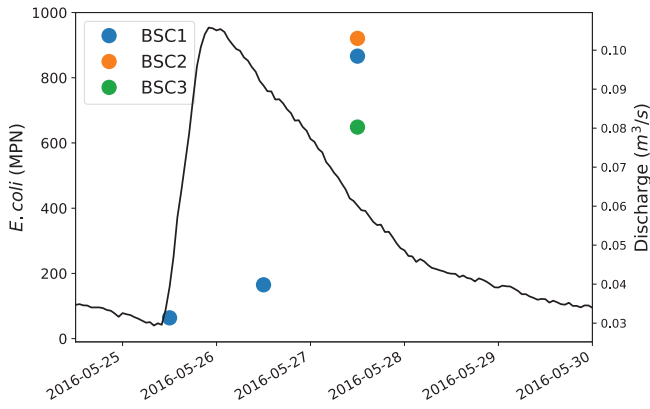
Figure 3. Hydrograph and *E. coli* concentrations at Blowing Spring Cave during a storm event. Peak *E. coli* concentrations occur after the time of peak discharge, during recession flow.
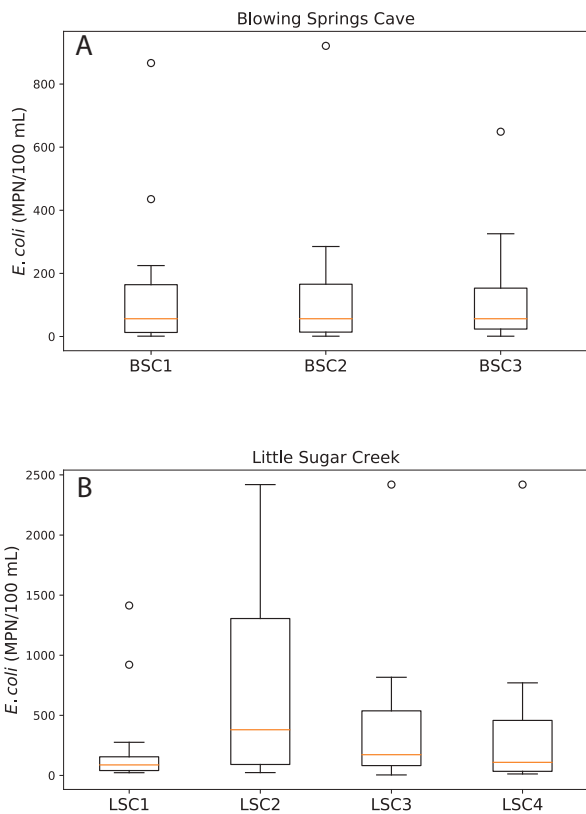
Figure 4. Boxplots of *E. coli* concentrations at: a) the three sites within Blowing Spring Cave from downstream (BSC1) to upstream (BSC3), and b) the four sites within Little Sugar Creek. Boxes indicate the median and quartile values and whiskers represent the range. Circles depict outliers, which are data points that lie outside of the box by more than 1.5 times the interquartile range. Note that the y-axis range on the Little Sugar Creek plot is much larger than on the Blowing Spring plot.

Figure 5. Relative abundance of major bacteria across the various sampling locations at the genus level in water (a) and sediment (b) collected on 5/2/2016. f in parenthesis indicates family, while f-C indicates family *Clostridiaceae* and f-L indicates family *Lachnospiraceae*--two families containing the genus *Clostridium*.

analysis (PCoA) UniFrac plot shown in Figure 6 illustrates the level of abundance of operational taxonomic units (OTUs) among sample types and their respective phylogenetic distances. In Figure 6, each data point representing an individual sample was aligned in parallel on the PC1 axis with 38.68%. An R value close to 1 was used to indicate that there was dissimilarity among sample type while an R value near 0 meant no separation. An R value from the weighted PCoA plot was 0.71 which implied a significant dissimilarity among water and sediment samples regardless of location or event type.

Fluorescein dye (55 g) was injected into the sinkhole site on February 27, 2017, during a relatively dry period. Following heavy rains, dye was detected at Blowing Spring within in a charcoal packet that was deployed from March 13-27, 2017. Additionally, a fluorescein pulse was detected on the field fluorometer on March 25, 2017. This suggests a travel time of approximately 26 days over a straight-line distance of 1100 m, giving an average velocity of roughly 40 m/day. There were no positive detections at the other monitored
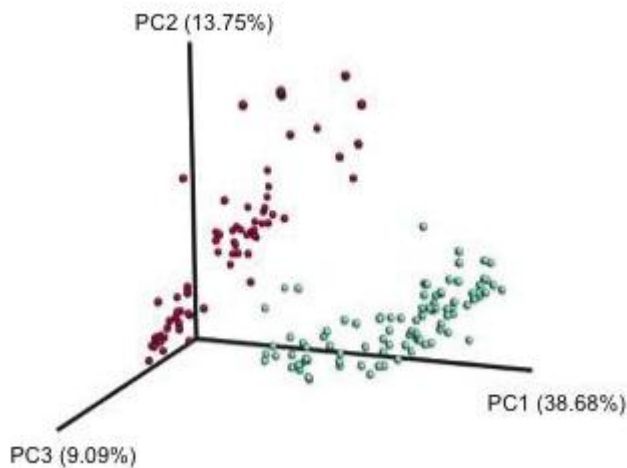
Figure 6. Beta diversity analysis among sample type, water (green) and sediment (red). Weighted principal coordinate analysis (PCoA) Unifrac plot of individual samples for each sample type.

sites. This trace confirms a positive connection between BSC and a portion of the recharge area hypothesized by Knierim et al. (2015) that lies within a residential area that contains some remaining septic tanks.

Conclusions, Recommendations, and Benefits

Even though Little Sugar Creek (LSC) receives contributions from numerous karst springs, such as Blowing Spring, the *E. coli* dynamics at the two sites are quite different, with concentrations at BSC displaying a strong positive correlation with discharge, and LSC showing no statistically significant correlation. *E. coli* concentrations at BSC peak during the recession period of storm events rather than during peak discharge. This could indicate that the contaminants are not mobilized from storage within the system but rather are delivered after recharging storm water has reached the spring. LSC frequently shows *E. coli* concentrations above the primary contact limit (410 CFU/100 mL) and sometimes above the secondary contact limit (2050 CFU/100 mL), indicating potential concerns for recreational users of the stream. The lack of correlation with discharge suggests that introduction of *E. coli* into the stream is not strongly linked with runoff, and that the sources are different than in BSC, where the contamination is hypothesized to result from septic tanks in the recharge area (Knierim et al. 2015). Concentrations just downstream of Bella Vista Lake (at LSC2) are particularly high, suggesting a source near that reach of the stream. Metagenomic analysis indicates that the microbial communities within the water and sediment are significantly different, and the cave and surface stream communities also display some differences. This study provides

insight into the microbial communities of karst spring and surface waters within a mixed urban and agricultural setting, where much of the population relies on decentralized wastewater treatment. This combination of geology and land use is common throughout the Ozark Plateaus and more widely throughout the southern and eastern United States. Therefore, insight gained here is likely to apply widely across the region.

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Image caption: Biofilms accumulate inside drinking water distribution pipes.

Accumulation of Lead by Biofilms in Water Distribution Systems

Kaleb Belcher and Wen Zhang*

Department of Civil Engineering, University of Arkansas
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Abstract: Lead accumulation in humans is detrimental at very low doses, especially in developing children. With millions of lead pipes and lead solder used in American homes before the 1980s, it is important to understand the interactions between lead pipes, their respective distribution systems, and the water flowing through them. This study examines the interaction between lead sources and biofilm, using a pipe loop system to determine how biofilms behave in the presence and subsequent absence of lead source. It also provides insight regarding lead activity in premise plumbing systems that have lead segments and how much of a threat these segments pose. A pipe loop with different pipe materials including lead was constructed to simulate water flows and stagnation periods of a typical household. Biofilms from the pipe loop were removed and analyzed for growth, lead concentration, and microbial community structure. In the presence of lead source, biofilms were shown to adsorb lead at concentrations as high as 48.39 $\mu g/cm^2$. This demonstrates that biofilms have the capability of accumulating lead in drinking water distribution systems. Lead levels in the biofilm ultimately decreased after the lead source was removed. No dissolved lead was observed releasing from the biofilm. The decrease of lead concentration within biofilm was likely due to detachment of the biofilm from the pipe. Biofilms can be a previously unrecognized source of lead following lead pipe removal. As the lead-laden biofilm detaches over time, a flushing regime and temporary avoidance of drinking tap water is recommended following pipe removal. This will ensure the safety of drinking water regarding lead concentration.

Key Points:
- Biofilm growth is ubiquitous in lead-containing water distribution systems.
- Biofilm grown within the water pipes accumulated lead at concentrations as high as 48.39 $\mu g/cm^2$ as well as other elements.
- No dissolved lead release was observed from biofilm after lead pipe was removed within the pipe loop system.

Introduction

Recently, lead (Pb) in the water supply has become a hot button issue following the early 2014 discovery of lead-contaminated drinking water in Flint, Michigan. Many scientists, government workers, and citizens nationwide now have serious concerns that other American communities may be at risk for potential lead contamination in drinking water. While the issue in Flint is believed to have been caused by a failure to use necessary corrosion control in the pipes, lead in distribution systems is a problem ranging across the United States.

Before the 1980's, many pipes used lead solder in order to connect lead pipes to copper pipes, and a number of lead pipes are still in use in distribution systems around the nation. This is a serious issue, as research has found that even small amounts of lead can be very hazardous to human health, especially young children in important developmental phases. Due to the severity of the effects of lead, the EPA has set a Maximum Contamination Level Goal (MCLG) at zero. Achieving this goal would essentially require removing all lead and lead containing parts in the entirety of a drinking water distribution system (DWDS). However, to perform such a removal would be a massive undertaking in economic terms as well as physical labor required. Thus, it is important to learn the consequences of slowly removing lead from DWDSs.

Disappointingly, a recent study found that replacing pipes in the system might actually exacerbate the problem due to the fact that in DWDSs, perceptible amounts of lead can be found within soft deposits and solids (St. Clair et al., 2016). We hypothesize another possible source of lead contamination is biofilm that develops throughout the DWDS. Biofilms are a group of cells that aggregate together and often adhere to an external surface by extracellular polymeric substances. In DWDSs biofilms have been shown to be ubiquitous (Berry et al., 2006). The goal of the present project is to discover the role biofilms play concerning lead contamination in DWDSs. It is very important not only to the state of Arkansas, but to society as a whole, to determine if trace amounts of lead are being accumulated and released into the water by biofilm in DWDSs.

Methods

Replaced Pipe Sampling

A 1-ft lead pipe was collected from 1023 Haskell St., Tulsa, OK 74106 on November 15, 2016. The pipe sample was preserved on ice and delivered to the University of Arkansas lab the next day. To access the biofilm and scale within the pipe, the pipe was cut open and into three equal pieces. Two of the pieces were used for lead analysis in scale and biofilm using ICP-MS. Pipe A was cut longitudinally to allow easy access to scraping the biofilm and scale with a metal spatula. Pipe B was left intact and the biofilm and scale was removed with a sponge that was pushed through the pipe and then sonicated. Then, metal analysis using ICP-MS was performed. The remaining piece was used for DNA analysis following the method below.

Pipe Loop Construction and Operation

Five types of pipe materials are included in the pipe loop: lead pipes (¾" ID × 1" OD), PEX-A (¾"), Copper Type K (¾" ID × 7/8" OD), galvanized steel (¾" ID × 1" OD), and PVC (¾" Schedule 40). Within each loop, 12 pieces of 6" long removable pipe sections were installed in the overall pipe loop. The total pipe length per train is 30-ft. The pipe loop configuration is shown in Figure 1, and the actual pipe loop is shown in Figures 2 and 3. After pipe loop construction, the entire system was flushed at high velocity for 30 min to ensure that there were no leaks in the system. During the initial operation, the pipe loop was placed in the A.B. Jewell plant, and water had a chloramine residual of 2.75 mg/L. Water in the pipe loop flowed in an intermittent mode at a flow rate of 1.0 gpm during the hours of 6:00am-9:00am, 11am–1:30pm, 4:00pm–6:30pm, and 9:30pm–10:30pm. The flow was designed to simulate a typical residential water usage pattern. There was no flow in other time periods and water was allowed to stagnate in the pipes during these times. The pipe loop was operated in two different stages. In Stage one, 2 ft of lead pipe in each train served as the initial source of lead contamination. This
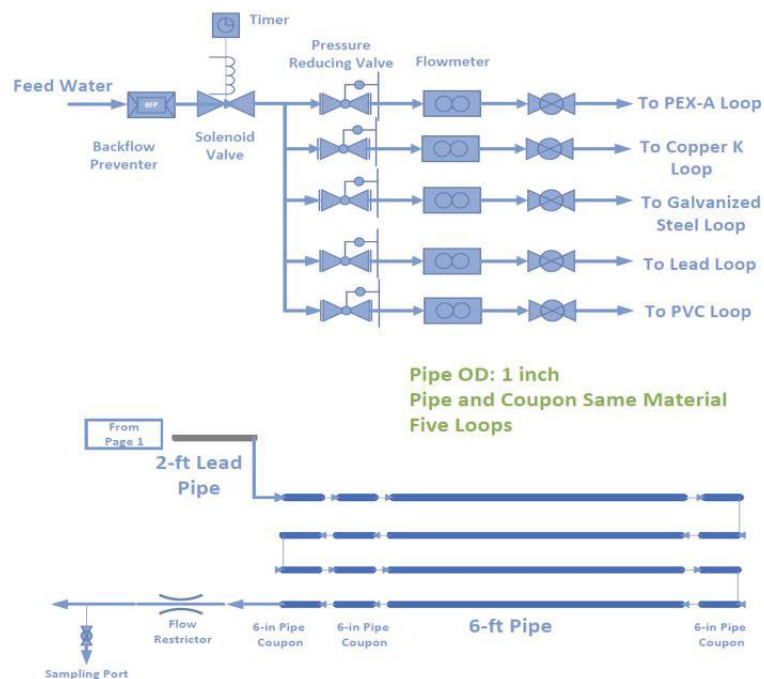

Figure 1: Pipe loop construction configuration.

Figure 2 (left) and 3 (right). On the left, a pipe loop displaying PEX-A train (on top of pipe loop), Galvanized Steel train (top of loop wall) and Copper-K train (bottom of loop wall). On the right, a pipe loop displaying Lead train (top of pipe wall) and PVC train (bottom of pipe wall).

Table 1: Elemental concentrations within deposits collected from the two pieces of removed pipe.

		Lead
Pipe Sample A	Conc. (μg/cm²)*	22.26
	Distribution (%)	38.71
Pipe Sample B	Conc. (μg/cm²)*	472.44
	Distribution (%)	70.27

*Surface area for pipe sample A and B is 49.98, and 24.47 cm², respectively.

stage lasted from January 23, 2017, to September 5, 2017. In Stage two, the 2 ft of lead pipes were removed from all trains and the system continued to operate until October 26, 2017.

Pipe Loop Sampling

Pipe loop samples were collected on February 17, March 22, April 21, July 11, October 6, and October 26, 2017. On each sampling day, two 6-in pipe coupons (duplicates) were collected from each train composed of different pipe materials. Each pipe sample was placed in a one gal ziploc bag with approximately 80 mL of water from its respective pipe train. The samples were then preserved on ice and transported to the University of Arkansas lab on the same day for processing. Each pipe coupon was sonicated using a Branson Sonifier 3800 (Emerson, Ferguson, MO) for 30 min within the collection bag to dislodge the biofilm from the pipe interior. Following the sonication step, the water from each gal Ziplock bag was filtered through separate 0.22 μm filters (Pall Corporation, Port Washington, NY). Each filter was then dried completely in the oven at 98°C. The filters were preserved in -20°C until subsequent processing.

Metal Analysis

Dried filters from the previous step were placed in 20 mL centrifuge tubes for storage and digestion. Five mL of deionized distilled (DDI) water from a Barnstead Gen pure Pro UV/UF 501311950 (Thermo Fisher Scientific, Waltham, Massachusetts) was added into the centrifuge tube and then sonicated for 30 min in a VWR Model 751 Sonicator (Radnor, PA). A solution of 1 mL of H_2O_2, 0.42 mL of HCl and 0.2 mL of HNO_3 was then added to each of the centrifuge tubes. That mixture was digested for 24-h in a Blue M model M01440A oven (Thermo Fisher Scientific, Waltham, Massachusetts) set at 50 °C. After 24-h, the mixture was diluted to 10 mL using DDI water. One mL was

then removed from the solution and 9 mL of 2% HNO_3 was added to that 1 mL for a final dilution of 10x. Elemental levels were calculated on the 10x dilution using a Thermo Sci. Icap Q (Bremen, Germany) Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

DNA Analysis

DNA was extracted for subsequent analyses from the filter containing the biofilm using a soil DNA extraction kit (Power Soil DNA Isolation Kit, Mo-Bio, Carlsbad, CA). The protocol recommended by the manufacturer was followed. DNA extracts were preserved in -20°C until subsequent processing. To quantify bacteria concentration, 16S rRNA was first amplified using PCR. PCR reactions were completed following the procedure used by Walden, Carbonero and Zhang, 2017. The presence of 16S rRNA genes was confirmed by gel electrophoresis. For bacteria community analysis, DNA extracts were submitted to the sequencing facility in Food Science at the University of Arkansas for next generation sequencing. Sequencing and data analysis was performed according to the procedure used by Walden, Carbonero and Zhang, 2017.

Results and Discussion

Replaced Pipe Scale Analysis

Lead concentrations were normalized by surface area (μg/cm²) as well as the percentage of lead compared to the overall total solids recovered. Results are shown in Table 1. For both pipe samples, lead was abundant in the deposit collected with concentrations going as high as 472.44 μg/cm². Notice that pipe A has a much lower lead concentration than B. We believe this was caused by the rinsing procedure after pipe A was cut open to remove the metal shavings.

Replaced Pipe Biofilm Growth

Figure 4 is the gel image showing the presence of universal bacteria genes (16S rRNA). It confirmed the biofilm

presence within pipelines from the DWDS in Tulsa, OK.

Biofilm Growth

PCR and Gel Electrophoresis showed positive bacterial genes from the pipe coupons, one example is shown from March 22, 2017, in Figure 5. This shows the biofilm growth within the pipe loops.

Biofilm Lead Adsorption

Results from ICP-MS showed each type of pipe in the pipe loop had biofilm that adsorbed lead. The metal concentrations are normalized in two ways – by surface area ($\mu g/cm^2$) and by dry weight ($\mu g/mg$). These are shown in Tables 2 and 3. The surface areas for the five pipe materials are 98.00 cm^2, 91.20 cm^2, 86.23 cm^2, 79.67 cm^2, and 112.70 cm^2 for PVC, galvanized steel, lead, PEX-A, and Copper Type K, respectively. The largest adsorption of lead for all materials occurred on October 6, 2017. We speculate this is due to the lead source that was removed in September which dislodged

Figure 4: Gel electrophoresis image showing the successful amplification of DNA extracted from lead pipe deposits in the City of Tulsa. The wells contain: ladder, triplicate DNA samples, negative control, and ladder (in vertical order).

Figure 5: Gel electrophoresis image showing the successful amplification of DNA extracted from biofilms in the pipe samples from the pipe loop on March 22, 2017. The wells contain: ladder, 5 DNA extracts from Galvanized Steel, Copper Type K, Lead, PEX-A and PVC pipes, negative control, and ladder (in vertical order).

particles of lead or lead scale were then able to attach to the biofilm. The highest reported adsorption of lead was in a lead pipe coupon at 40.18 $\mu g/cm^2$ and 738.10 $\mu g/mg$. The largest adsorption recorded for a non-lead pipe coupon was in galvanized steel at 42.77 $\mu g/cm^2$ and 98.76 $\mu g/mg$. However, the lead concentration found in the galvanized steel pipe biofilm may have been inflated. A recent study found that the zinc coating in galvanized steel pipes contained up to 2% of lead (Martin et al., 2015). In other pipe materials, the PEX coupon was shown to have adsorbed 11.75 $\mu g/cm^2$ and the Copper Type K coupon had adsorbed 70.02 $\mu g/mg$.

Lead Release

The lead concentration in biofilms initially increased after the lead source was removed. This data is shown in Tables 2 and 3. The largest change occurred in the Copper Type K with an increase of 21.44 $\mu g/cm^2$. We speculate that the removal of the lead source dislodged particulate lead or lead scale, which then attached to the biofilm. During the next sampling period the lead levels in each train decreased. However, dissolved lead levels in water did not increase during this time. This indicates that the lead may not have released from the biofilm into the water after the lead source pipes were removed; instead, particulate lead was released from biofilm and pipe deposits as biofilm detachment hap-

Table 2: Lead adsorbed by biofilms measured in $\mu g/cm^2$.

Date Collected	Pipe Material				
	Lead	PVC	PEX-A	Steel	Copper-K
17-Feb-17	3.01	0.07	0.04	0.05	0.04
22-Mar-17	5.25	0	0.02	0	0
21-Apr-17	9.16	0.05	0.05	0.02	0.32
11-Jul-17	7.26	0.08	0.03	0.04	0.02
6-Oct-17	23.05	7.57	11.75	10.87	21.44
26-Oct-17	23.5	1.3	0.07	1.41	0.45
26-Oct-17-Long	18.49	0.4	0.34	0.76	1.7

Table 3: Lead adsorbed by biofilms measure in $\mu g/mg$.

Date Collected	Pipe Material				
	Lead	PVC	PEX-A	Steel	Copper-K
17-Feb-17	117.94	0.31	0.16	0.7	0.3
22-Mar-17	1565.99	0.65	0.37	0	0.68
21-Apr-17	738.1	9.37	15.23	3.33	36.3
11-Jul-17	29.53	0.4	0.12	0.18	0.09
6-Oct-17	83.52	38.82	57.79	70.02	98.76
26-Oct-17	104.98	8.18	0.33	9.44	1.7
26-Oct-17-Long	54.52	2.08	0.63	2.52	3.24
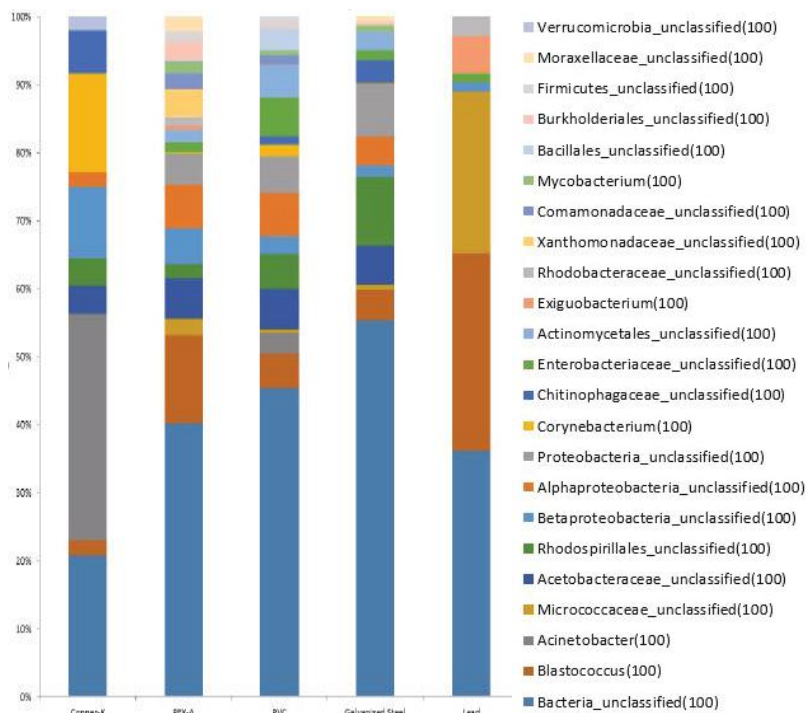
Figure 6: Stacked bar chart of the most abundant species of bacteria present in each pipe coupon from March 22, 2017.

pened. Ultimately, if this were a real system the particulate lead or dislodged biofilm would be consumed by human use or enter the sanitary sewer.

DNA Sequencing

DNA sequencing was performed on all pipe samples. Microbial communities were determined for each pipe loop material over time. An example of one microbial community is shown above in Figure 6. It shows different pipe material accumulated distinct microbial communities within the biofilm.

Conclusions

Scale pipe deposits in the replaced lead pipe from DWDS at the City had lead deposits with concentrations as high as 472.44 $\mu g/cm^2$. It also showed positive biofilm growth within the replaced pipe.

Biofilm formed within the pipe loop adsorbed lead at varying levels with concentrations as high as 48.39 $\mu g/cm^2$. Adsorption of lead occurred in all five pipe materials when there was a lead source pipe present. After the removal of the lead source, lead concentration in the biofilms rose on average by 13.45 $\mu g/cm^2$. Lead levels in biofilm then decreased in the next sampling period, however, no dissolved lead was observed releasing from the biofilm. We recommend continuing this research by conducting further pipe loop tests using other variables such as disinfectant, source

water, and treatment processes.

Lead is an ongoing problem at both regional and national level. The present research indicates that lead can be adsorbed into biofilms but no dissolved lead was released back into the water above detection limit. Additionally, a major finding is that when our lead source was removed in all five pipe trains, the lead concentration in the biofilm rose briefly. This indicates that when lead pipe is replaced in premise plumbing that a certain amount of lead released can be stored for a brief period by the biofilm. Our recommendation is that a flushing regime occurs following lead pipe removal to ensure that all stored lead is removed before continuing usage.

Acknowledgements

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Image caption: Big Creek, a tributary to the Buffalo National River. Photo courtesy of Tim Smith.

Characterization of Nutrient Sources, Transport Pathways, and Transformations Using Stable Isotope and Geochemical Tools in the Big Creek Watershed of Northwest Arkansas

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Abstract: The establishment of a concentrated animal-feeding operation (CAFO) near Big Creek, a tributary of the Buffalo National River, has raised concern over potential degradation of water quality in the watershed. In this study, isotopic tools were combined with standard geochemical approaches to characterize nutrient sources and dynamics in Big Creek. This study establishes an isotopic and geochemical reference library of potential nutrient sources in the Big Creek watershed by direct sampling of representative possible sources, including septic-system effluent, poultry, swine, and cattle manure, and CAFO waste lagoons. Representative nutrient sources and Big Creek stream samples were analyzed for $\delta 15N$-NO_3, $\delta 18O$-NO_3, and $\delta 18O$-PO_4, as well as a cation and anion suite. Big Creek stream samples were also analyzed for $\delta 18O$-H_2O and $\delta 2H$-H_2O. Similar chloride-bromide ratios for fresh cow manure, septic-system effluent, and Big Creek samples may indicate an influence on Big Creek water quality. Samples taken from the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit different $\delta 15N$ and $\delta 18O$ as compared to stream samples. Big Creek NO_3 isotope values are similar to NO_3 values expected from nitrification of N stored in soils sampled in the watershed. Discrimination of nutrient source input to Big Creek using $\delta 18O$-PO_4 is complicated by overlap between potential source $\delta 18O$ and stream $\delta 18O$. Stream equilibrium $\delta 18O$-PO_4 values indicate the biological processing of stream PO_4. The results of this study highlight the importance of effective agricultural, residential, and urban best management practices in protecting the quality of our waterways.

Key Points:
• Samples taken from the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit different $\delta 15N$-NO_3 and $\delta 18O$-NO_3 as compared to stream samples. The isotope data are most consistent with an interpretation of stream nitrate being derived from N stored in soils, or from manure or septic sources not represented by the limited number of samples collected for this study.
• Chloride to bromide ratios indicate human influence and may indicate an input to Big Creek from septic systems and cow manure.

Characterization of Nutrient Sources, Transport Pathways, and Transformations in Big Creek

Introduction

The Big Creek watershed has a history of mixed agricultural, "urban" (Mount Judea), and residential land use, and the recent establishment of a Concentrated Animal-Feeding Operation (CAFO) near Mt. Judea in Newton County, AR, has raised concerns over the potential for nutrient enrichment and degradation of water quality in Big Creek and the Buffalo National River (Figure 1). The complex distribution of land use and nutrient sources in the watershed, combined with the occurrence of karst terrain with rapid connection of groundwater and surface water, creates a challenging technical problem for understanding nutrient dynamics. Traditional methods of geochemical analysis often fall short of providing adequate characterization of watershed contamination. Stable isotope geochemical tools can augment traditional methods and improve our understanding of nutrient enrichment in aquatic environments and enable development of more effective management practices.

This project has applied a combined approach of traditional water-quality analysis and novel geochemical tools in characterizing nutrient dynamics in the Big Creek watershed. An isotopic reference database of representative nutrient sources for the Big Creek watershed was developed by sampling directly from nutrient sources. This database is essential for comparative analysis and characterizing pollutant sources in this study as well as for future projects. Stream samples were collected from Big Creek and related to nutrient sources using multi-parameter geochemical analysis. The specific objectives of the study are (1) to establish a database on isotopic compositions of potential nutrient sources; (2) to employ nitrate isotopes for characterizing sources, transport, and transformations; (3) to characterize stream phosphate oxygen isotopic compositions and identify potential sources and biological cycling; (4) to characterize water sources and pathways through the application of water isotopes.

Methods

Field Methods

Samples were taken from sites representative of potential sources based on dominant regional agricultural practices. Waste-holding ponds were sampled at C&H Farms and the University of Arkansas Swine Farm at Savoy, AR. Hog manure was sampled at the University of Arkansas Swine Farm due to sampling restrictions at C&H Farms. The University of Arkansas Broiler Research Unit provided a broiler-litter sample for analysis. Fresh and aged cattle manure samples were taken from a field near Mt. Judea. The manure and litter samples were extracted with deionized water for analysis. A residential septic-system sample was collected near Bella Vista, AR. Runoff samples from three fields (Field 1, Field 5A, and Field 12—all were used for cattle grazing and hay production, and fields 1 and 12 were amended with C&H Farms waste) near Mt. Judea were collected during a rainfall event from Big Creek Research and Extension Team (BCRET) sites (Figure 2). Parking-lot runoff was collected in Mt. Judea. Artificial fertilizer, 13-13-13 (13% nitrogen, 13% phosphorus, and 13% potassium), was dissolved and analyzed.

Four stream sites were chosen for base-flow and high-flow water and stream-bottom sediment sample collection (Tables 1 and 2, Figure 2). Table 3 depicts the samples collected and the analytes measured for individual samples.

Analytical Methods

Sample pH and conductivity values were measured in the field. Alkalinity titrations were performed using a Hach digital titrator, and alkalinity was calculated using the inflection point method (Rounds, 2006). Total nitrogen (TN), dissolved organic carbon (DOC), and cations were analyzed for all samples at the University of Arkansas Stable Isotope Laboratory (UASIL). Cations were analyzed using a Thermo Fisher iCapQ Quadrupole Mass Spectrometer with a CETAC ASX-560 Autosampler.

Samples were sent to the Arkansas Water Resources Center Water Quality Lab (AWRC) for analysis of anions, total phosphorous (TP), ammonia (NH_3), and nitrate+nitrite (NO_3+NO_2). Anions were measured with a Dionex ion chromatograph ICS-1600. Ammonia, TP, and NO_3+NO_2 were analyzed using a Lachat QuickChem 8500. Orthophosphate (PO_4) concentration was measured on a Seal AQ3 autoanalyzer at the University of Nebraska Water Sciences Laboratory (UNWSL) (Table 4).

Figure 1. Physiographic map of Arkansas with study area (Mt. Judea) denoted by red circle. Mt Judea lies on the edge of the Springfield Plateau and the Boston Mountains. Modified from Kresse et. al, 2014.
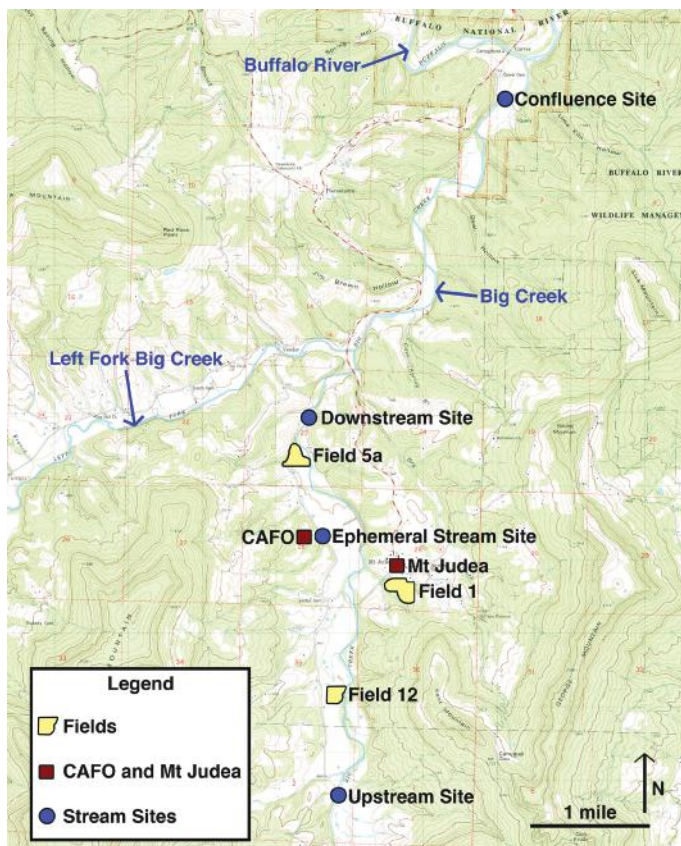
Figure 2. Map of stream sampling sites along Big Creek in Newton County, Arkansas. Storm runoff was collected from BCRET automatic samplers in fields depicted in yellow. Parking lot runoff was collected in Mt. Judea, and the CAFO waste lagoons were sampled. Modified from U.S. Geological Survey, 1980.

Table 1. Latitude and longitude of Big Creek stream sampling sites.

Site	Coordinate Location	
	Latitude	Longitude
Ephemeral Site	35° 55' 25.91"	93° 4' 15.24"
Upstream Site	35° 53' 31.9"	93° 4' 6.23"
Downstream Site	35° 56' 19"	93° 4' 21.6"
Confluence Site	35° 58' 39.38"	93° 2' 36.54"

Table 2. Hydrologic conditions and sampling dates for stream and run-off samples. Rainfall data is from the National Weather Service Harrison station. Rainfall values are totaled from the date of sampling plus the previous two days. Sample 5A was collected from the ephemeral stream site. Sample 5B was collected from a BCRET automatic sampler located at the ephemeral stream site.

	Date Sampled	Hydrologic Conditions
B1 Samples	7/17/2017	No rain for 7 days, discharge at base-flow conditions
B2 Samples	9/23/2017	No rain for 7 days, discharge at base-flow conditions
S1 Samples	3/30/2017	2.134 cm rainfall
S2 Samples	4/17/2017	1.778 cm rainfall
Samples 5A and 5B	5/2/2016	2.184 cm rainfall
Field Runoff Samples	5/1/2017	10.262 cm rainfall
Parking Lot Runoff	11/15/2017	1.473 cm rainfall

* B = baseflow; S = stormflow

The nitrogen and oxygen isotopic ratios of nitrate were measured at the UASIL. Nitrate $\delta15N$ and $\delta18O$ were analyzed simultaneously using the microbial denitrifier method (Sigman et al., 2001). After conversion to nitrous oxide, $\delta15N$ and $\delta18O$ were measured on a continuous flow Thermo Delta plus isotope ratio mass spectrometer (IRMS).

Phosphate oxygen isotopic ratios were prepared and measured at the UNWSL using the methods of McLaughlin et al. (2004) and McLaughlin et al. (2006). The $\delta18O$ of resultant silver phosphate was analyzed using high temperature pyrolysis on a Eurovector EA Isoprime continuous IRMS.

Hydrogen and oxygen stable isotope ratios of stream water were measured using a high temperature reduction unit interfaced to a continuous flow Thermo Delta plus XP IRMS at the UASIL. Nitrogen isotope ratios and %N of sediment were analyzed simultaneously at the UASIL on an EA IsoLink IRMS.

Results and Discussion

Geochemical Parameters

Data are presented in Table 4, and summary statistics are presented in Tables 5 and 6. The TN, DOC, and cation analyses contain values below the detection limit that could not be reliably estimated, known as left-censored data. Censored data means were computed using the Kaplan-Meier method.

Source sample NH_3 ranged from 0.11-1040 mg/L with little to no NO_3 (range: 0-0.38 mg/L), while stream samples contained little NH_3 (range: 0-0.06 mg/L) but slightly more NO_3 (range: 0.046-0.809 mg/L). Such results for relative N-species concentrations are expected because of the respective redox conditions of these media. The nitrogen in the possible nutrient sources is largely in the NH_3 (or NH_4^+) form. The NH_3 from various potential sources is being nitrified moving from source to stream. By way of example, the ephemeral S1 sample contained no discernable NH_3 and contained 0.77 mg/L NO_3. A Wilcoxon Rank Sum Test was conducted with a 95% confidence interval for nitrate and phosphate concentrations between the upstream and downstream sites. No statistically significant difference was observed, indicating that in-stream processes were not changing concentrations considerably—either very little processing was occurring or changes in nutrient inputs and removal were roughly balanced. Conductivity was consistently low in runoff samples. Base-flow stream samples

Characterization of Nutrient Sources, Transport Pathways, and Transformations in Big Creek

Table 3. List of samples collected and analytes. The waste-holding ponds at C&H Farms were sampled once early in the study; a second sample collection was attempted in order to remain within standard holding times for geochemical analyses but was denied. The waste-holding pond at the University of Arkansas Swine Farm at Savoy, AR was sampled on two separate dates. These two Savoy samples were used for comparison and to support the viability of the samples from the C&H holding ponds.

	Sample #	Sample Name	pH, Cond., Alk.	Anion Suite	Br	TP	TN, DOC	Cation Suite	$\delta^{15}N$ and $\delta^{18}O$ NO_3	$\delta^{18}O$ Phosphate and Ortho-phosphate Concentration	δ^2H, $\delta^{18}O$ Water	$\delta^{15}N$, %N
Stream Samples	5A	**Ephemeral In-Stream 5/2/16**						X	X	X		
	5B	**Ephemeral ISCO 5/2/16**	X	X	X			X	X	X		
	14, 15, 18, 19, 22, 23, 26, 27	**Storm-Flow Samples**	X	X	X	X	X	X	X	X	X	
	16, 17, 20, 21, 24, 25	**Base-Flow Samples**	X	X	X	X	X	X	X	X	X	
Possible Source Samples	1A	**Savoy Lagoon-Old**	X	X				X	X			
	1B	**Savoy Lagoon-Fresh**		X	X	X	X	X	X	X		
	2	**Hog Manure**	X	X	X	X	X	X	X	X		
	3	**Fresh Cow Manure**	X	X	X	X	X	X	X	X		
	4	**Chicken Litter**	X	X	X	X	X	X	X	X		
	6	**CAFO Solids Pond**	X	X	X	X	X	X	X	X		
	7	**CAFO Liquids Pond**	X	X	X	X	X	X	X	X		
	8	**Aged Cow Manure**	X	X	X	X	X	X	X	X		
	9	**Synthetic Fertilizer**	X	X	X	X	X	X	X	X		
	10	**Septic Effluent**	X	X	X	X	X	X	X	X		
	11	**Field 1 Runoff**	X	X		X	X	X	X	X		
	12	**Field 5A Runoff**	X	X	X	X	X	X	X	X		
	13	**Field 12 Runoff**	X	X	X	X	X	X	X	X		
	32	**Parking Lot Runoff**	X	X	X	X	X	X	X	X		
	28	**Upstream Sediment**								X		X
	29	**Downstream Sediment**								X		X
	30	**Confluence Sediment**								X		X
	31	**Ephemeral Sediment**								X		X

had higher conductance than storm-flow samples, indicating greater groundwater contribution to stream-flow during base-flow periods.

Chloride to bromide ratios were analyzed to determine potential anthropogenic influences in Big Creek (Table 7). A Cl/Br ratio of 400 is the theoretical maximum Cl/Br for natural waters; Cl/Br ratios of over 400 are indicative human-influenced waters (Thomas, 2000). The Cl/Br ratio of fresh cow manure was 827.04, and septic effluent had a Cl/Br ratio of 540.52. The stream samples that contained a Cl/Br ratio over 400 include upstream S1 (464.67), downstream S1 (747.5), and confluence S2 (449.8). Stream Cl/Br ratios indicate a human influence of stream sample chemistry

which could arise from any combination of the analyzed sources. Table 8 contains data from the analysis of cations.

Isotopic Parameters

Samples taken from the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit distinctly different $\delta^{15}N$ and $\delta^{18}O$ (Figure 3 and Table 8), and each of these sources is different as compared to stream samples. Big Creek NO_3 isotope values ($\delta^{15}N$ range: -7.59 to 9.10‰; $\delta^{18}O$ range: -3.41 to 6.71‰) are similar to NO_3 values expected from nitrification of N stored in soils sampled in the watershed ($\delta^{15}N$ range: 3.8 to 6.6; $\delta^{18}O$ range: 3.4 to 4.8‰). Chicken litter and old cow

Table 4. Concentrations of anions, NO$_3$+NO$_2$, TN, DOC, TP, pH, conductivity, and alkalinity.

	Sample #	Sample Name	NH$_3$ (mg/L)	Br (mg/L)	Cl (mg/L)	Fl (mg/L)	N+N (mg/L)	NO$_3$ (mg/L)	SO$_4$ (mg/L)	TN (mg/L)	DOC (mg/L)	TP (mg/L)	SRP (mg/L)	pH	Cond. (µS/cm)	Alk. (mg/L as CaCO$_3$)
Possible Source Samples	1A	Savoy Lagoon-Old	354	--	444.149	0*	0.16	0.105	24.704	--	--	--	--	7.77	6770	1187.8
	1B	Savoy Lagoon-Fresh	227	0*	542.874	0*	0.17	0*	43.057	<1	<2.14	52.95	16.8	--	--	--
	2	Hog Manure	491	0*	92.773	428.34	0.27	0*	61.951	219.66	819.57	455	319	6.08	5260	101.1
	3	Fresh Cow Manure	307	0.119	98.418	3.353	0.14	0*	0*	0.21*	<2.14	38.2	14.1	7.19	1732	490.3
	4	Chicken Litter	716	0*	1196.99	905.61	1.45	0*	4103.68	<1	<2.14	86.2	347	6.28	7310	535.8
	6	CAFO Solids Pond	1040	0*	586.68	0*	0.22	0*	43.622	<1	<2.14	75.2	122	8.16	4581	4134.5
	7	CAFO Liquids Pond	448	0*	472.332	0.627	0.12	0.108	6.175	<1	<2.14	110.4	91.3	7.96	3314	2987.2
	8	Aged Cow Manure	7.93	0*	16.248	0.242	0.05	0*	0*	<1	<2.14	37.9	21.4	7.06	297.7	272.9
	9	Synthetic Fertilizer	4.34	0.032	5.797	0.102	E 0.02	0*	2.807	9.79	3.45	5.079	6.15	6.95	63.6	--
	10	Septic Effluent	83.9	0.097	52.43	0*	0.06	0*	20.458	79.4	43.89	7.662	7.66	6.55	1313	278
	11	Field 1 Runoff	0.51	--	2.678	0.154	0.34	0.38	2.524	<1	<2.14	0.712	0.571	7.5	51	--
	12	Field 5A Runoff	0.39	0*	2.116	0.147	0.8	0.372	2.294	1.19	7.26	0.868	0.834	7.28	68	45.5
	13	Field 12 Runoff	0.14	0*	1.243	0.138	0.19	0.218	2.038	0.26*	4.69	0.368	0.248	7.35	60	15.2
	32	Parking Lot Runoff	0.11	0.006*	E 0.341	0*	0.08	0.181	1.416	<1	3.59	0.033	0.825	6.62	51.7	--
Stream Samples	14	Upstream S1	0*	0.006*	2.788	0.153	0.17	0.185	3.182	<1	1.46*	0.03	0.015*	7.82	84.7	53.6
	15	Upstream S2	E 0.01	0*	1.382	0.149	E 0.03	0.167	3.865	<1	1.01*	0.052	0.003*	7.89	95.8	55.6
	16	Upstream B1	E 0.04	0.01*	1.196	0*	0.2	0.18	3.876	<1	1.06*	0.024	0.439	8.05	119.1	25.3
	17	Upstream B2	E 0.02	0.011*	2.007	0.021*	0.09	0.046	4.261	<1	1.52*	E 0.01	6.29	7.64	235	55.6
	18	Downstream S1	E 0.01	0.002*	1.495	0.157	0.25	0.288	3.706	<1	1.90*	0.076	0.01*	7.63	114.5	23.3
	19	Downstream S2	0.06	0*	1.83	0.158	0.14	0.152	5.321	<1	1.49*	0.026	0*	7.75	162.9	53.6
	20	Downstream B1	E 0.02	0*	1.623	0.002*	0.18	0.152	4.295	<1	1.81*	0.02	0.157	7.57	180.7	65.7
	21	Downstream B2	E 0.02	0.019	2.595	0.007*	0.45	0.398	4.82	<1	2.53	0.004*	0.703	7.54	276	96
	22	Confluence S1	0.06	0*	1.919	0.155	0.29	0.305	4.852	<1	2.10*	0.03	0.01*	7.87	147.9	94
	23	Confluence S2	0*	0.005*	2.249	0.169	0.12	0.146	6.787	<1	1.37*	0.028	0.022*	8.1	200.7	69.8
	24	Confluence B1	E 0.04	0.008*	1.95	0.206	0.31	0.277	4.723	<1	1.14*	0*	0.185	8	217.7	65.7
	25	Confluence B2	0*	0.019	2.845	0.335	0.08	0.055	5.006	<1	1.63*	0*	0.031	7.44	263	85.9
	26	Ephemeral S1	0*	0.007*	2.649	0.149	0.77	0.809	2.168	0.28*	0.86*	0.062	0.002*	7.16	313	131.4
	27	Ephemeral S2	0*	0.015	3.93	0.146	0.65	0.692	3.127	0.10*	0.53*	0.03	0.016*	7.48	394	166.8
	5B	Ephemeral ISCO 5/2/16	E 0.03	0*	3.015	0.907	0.51	0.586	2.561	--	--	--	0	7.79	339	--

* = below method detection limit, should be viewed as an estimate

E = below reporting limit and above method detection limit, should be viewed as an estimate

-- = no data available

B = samples collected at base-flow conditions

S = samples collected after rainfall (storm-flow conditions)

< = censored data

EPA = Environmental Protection Agency

APHA = American Public Health Association

Samples 9, 32, and 5B were analyzed for alkalinity but did not yield any data

manure are most likely undergoing denitrification in-situ as indicated by their increased δ15N and δ18O compared to referenced manure and fertilizer ranges. Denitrification increases δ15N and δ18O by a 1:2 ratio. The chicken litter and old cow manure samples may also indicate nitrification involving waters that have been highly evaporated, resulting in relatively high δ18O values. All runoff samples and the Savoy lagoon sample have elevated δ18O, indicative of ei-

Characterization of Nutrient Sources, Transport Pathways, and Transformations in Big Creek

Table 5. Minimum and maximum of analytes for possible nutrient source samples.

Possible Nutrient Source Statistics	Minimum	Maximum
Ammonia (mg/L)	0.110	1040
Bromide (mg/L)	0.000	0.120
Chloride (mg/L)	0.340	197
Fluoride (mg/L)	0.000	906
Nitrate+Nitrite (mg/L)	0.020	1.450
Nitrate(mg/L)	0.000	0.380
Sulfate(mg/L)	0.000	4104
Dissolved Organic Carbon (ppm)	*	820
TN (ppm)	*	220
Total Phosphorous (ppm)	0.033	455
Orthophosphate (mg/L)	0.248	347
pH	6.1	8.2
Conductivity (μS/cm)	51	7310
Alkalinity (as $CaCO_3$) (mg/L)	15	4135
$\delta^{18}O$ Phosphate (‰)	-78.8	101.0
$\delta^{15}N$ Nitrate	-15.4	54.8
$\delta^{18}O$ Nitrate	-7.1	59.1
Lithium (ppm)	0.000	0.108
Boron (ppm)	0.004	8.710
Magnesium (ppm)	0.009	86.578
Potassium (ppm)	0.001	0.521
Calcium (ppm)	0.000	0.001
Gallium (ppm)	0.000	0.000
Vanadium (ppm)	0.000	0.000
Selenium (ppm)	0.000	0.011
Strontium (ppm)	0.000	0.000
Tin (ppm)	0.000	0.000
Antimony (ppm)	0.001	0.008
Barium (ppm)	0.000	0.159
Manganese (ppm)	0.001	0.212
Iron (ppm)	0.000	0.057
Rubidium (ppm)	0.000	0.000
Yttrium (ppm)	0.000	0.000
Dysprosium (ppm)	*	37.201
Sodium (ppm)	*	0.028
Aluminum (ppm)	*	0.001
Chromium (ppm)	*	0.001
Cobalt (ppm)	*	0.026
Nickel (ppm)	*	0.225
Copper (ppm)	*	0.001
Arsenic (ppm)	*	0.000

* = left-censored data

Table 6. Minimum, maximum, mean, and median of analytes for stream sources.

Stream Sample Statistics	Minimum	Maximum	Mean	Median
Ammonia (mg/L)	0.000	0.060	0.020	0.020
Bromide (mg/L)	0.000	0.019	0.007	0.006
Chloride (mg/L)	1.196	3.930	2.232	2.007
Fluoride (mg/L)	0.000	0.907	0.181	0.153
Nitrate+Nitrite (mg/L)	0.030	0.770	0.283	0.200
Nitrate(mg/L)	0.046	0.809	0.296	0.185
Sulfate(mg/L)	2.168	6.787	4.170	4.261
Dissolved Organic Carbon (ppm)	0.530	2.530	1.458	1.475
TN (ppm)	*	0.280	0.027	0.000
Total Phosphorous (ppm)	0.000	0.076	0.028	0.027
Orthophosphate (mg/L)	0.000	6.290	0.053	0.016
pH	7.160	8.100	7.720	7.750
Conductivity (μS/cm)	85	394	210	201
Alkalinity (as $CaCO_3$) (mg/L)	23	167	74	66
$\delta^{18}O$ Phosphate (‰)	-36.3	55.4	14.6	22.3
$\delta^{15}N$ Nitrate	-7.6	9.1	1.9	2.2
$\delta^{18}O$ Nitrate	-3.4	6.7	2.2	2.6
$\delta^{18}O$ Water	-6.7	-5.0	-5.6	-5.5
$\delta^{2}H$ Water	-41.8	-26.8	-33.4	-32.7
Lithium (ppm)	0.000	0.000	0.000	0.000
Boron (ppm)	0.000	0.001	0.000	0.000
Magnesium (ppm)	0.028	0.072	0.045	0.044
Potassium (ppm)	0.013	0.138	0.033	0.023
Calcium (ppm)	0.025	0.136	0.073	0.069
Gallium (ppm)	0.000	0.000	0.000	0.000
Vanadium (ppm)	0.000	0.000	0.000	0.000
Selenium (ppm)	0.000	0.000	0.000	0.000
Strontium (ppm)	0.001	0.002	0.002	0.001
Tin (ppm)	0.000	0.000	0.000	0.000
Antimony (ppm)	0.000	0.000	0.000	0.000
Barium (ppm)	0.001	0.002	0.001	0.001
Sodium (ppm)	0.022	0.062	0.035	0.033
Uranium (ppm)	0.000	0.000	0.000	0.000
Aluminum (ppm)	*	0.008	0.001	0.000
Chromium (ppm)	*	0.000	0.000	0.000
Manganese (ppm)	*	0.000	0.000	0.000
Iron (ppm)	*	0.005	0.001	0.000
Cobalt (ppm)	*	0.000	0.000	0.000
Arsenic (ppm)	*	0.000	0.000	0.000

* = left-censored data

Table 7. Chloride to bromide ratios of samples that contained bromide.

	Sample #	Sample Name	Br (mg/L)	Cl (mg/L)	Cl:Br
Possible Source Samples	3	Fresh Cow Manure	0.119	98.418	827.04
	9	Synthetic Fertilizer	0.032	5.797	181.16
	10	Septic Effluent	0.097	52.43	540.52
	14	Upstream S1	0.006	2.788	464.67
	16	Upstream B1	0.01	1.196	119.60
	17	Upstream B2	0.011	2.007	182.45
	18	Downstream S1	0.002	1.495	747.50
Stream Samples	21	Downstream B2	0.019	2.595	136.58
	23	Confluence S2	0.005	2.249	449.80
	24	Confluence B1	0.008	1.95	243.75
	25	Confluence B2	0.019	2.845	149.74
	26	Ephemeral S1	0.007	2.649	378.43
	27	Ephemeral S2	0.015	3.93	262.00

ther potential atmospheric deposition or oxygen-exchange effects. The hog manure exhibits a slightly elevated $\delta18O$. The septic system sample plots with a relatively heavy $\delta15N$, indicative of denitrification. Stream sample $\delta15N$ and $\delta18O$ overlap isotopic ranges documented in other studies for NO_3 in fertilizer and precipitation, soil NO_3, and manure and septic waste.

Stream samples show markedly different isotopic compositions as compared to potential local sources sampled—chicken litter, cow manure, field runoff, parking-lot runoff, and septic effluent; as such, stream NO_3 isotopic composition cannot be explained by simple, direct input of any one these potential sources into the stream. If these sources are responsible for a considerable part of the stream NO_3 load, then modification of isotopic composition by mixing or by fractionation/processing must be inferred.

The isotope data are most consistent with an interpretation of stream nitrate being derived from nitrate stored in soils or from manure or septic sources not represented by the limited number of samples collected for this study. The relatively heavy isotopic signature imposed on nitrate by denitrification is not apparent in stream samples (Figure 3), indicating little or no influence of in-stream denitrification and little direct input from these sources to Big Creek. A Wilcoxon Rank Sum Test was conducted with a 95% confidence interval for nitrate $\delta15N$ and $\delta18O$: $\delta15N$ was found to be statistically higher at the downstream site compared to the upstream site, while no difference was found between the sites for $\delta18O$. This implies that denitrification is not likely occurring in Big Creek between these sites and a source input with a more enriched $\delta15N$ is responsible for the elevated $\delta15N$ between sites. Sediment organic $\delta15N$ ranged

from -2.26 to 5.07‰ (Table 9), which overlaps the range for $\delta15N$ of stream samples. Nitrification of stream sediment N along the upstream to downstream reach of Big Creek may explain the decoupling of $\delta15N$ and $\delta18O$ signatures; such nitrification could obfuscate any isotopic indication of denitrification along the reach, making the assessment of denitrification there inconclusive.

Phosphate oxygen isotope ratios are shown in Figure 4 and documented in Table 10. Source $\delta18O-PO_4$ values were extremely variable: Sediment $\delta18O$ − -78.8 and 101‰, cow manure $\delta18O$ − 45.9 and 61.7‰, CAFO waste-holding ponds $\delta18O$ − 30.5 and 23.3‰, chicken litter $\delta18O$ − 21‰, septic effluent $\delta18O$ − 28.1‰, fertilizer $\delta18O$ − 19.9‰, runoff sample $\delta18O$ ranged from 8.47 to 38.6‰, and stream $\delta18O$ ranged from 36.3 to 55.4‰. This overlap between potential source $\delta18O$ values and stream $\delta18O$ values complicates discrimination of nutrient source input to the stream using phosphate oxygen isotopes. In addition, phosphate oxygen isotopic composition can be modified through biological mediation (Longinelli et al., 1976). Therefore, $\delta18O-PO_4$ values can indicate mixing of sources or biological oxygen exchange. Theoretical isotopic equilibrium values for $\delta18O-PO_4$ in stream samples were calculated by applying the following equation derived from Longinelli and Nuti, 1973:

$$\delta18O\text{-}PO_4 = [(T(°C)\text{-}111.4)/\text{-}4.3] + \delta18O\text{-}H_2O$$

where $T(°C)$ is the temperature of the water. Equilibrium
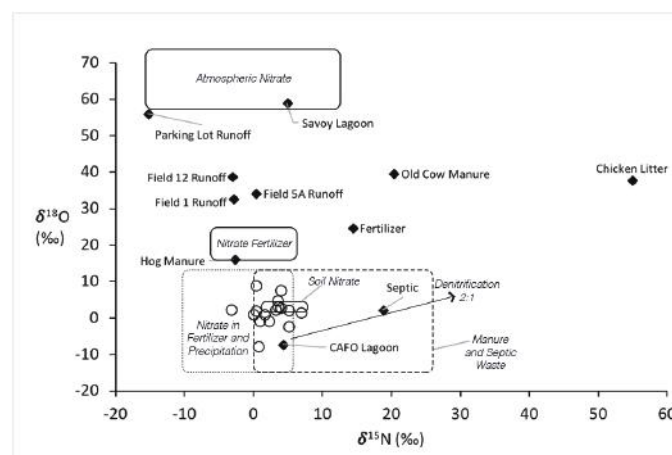
Figure 3. Nitrate isotope ratios. Possible source samples represented by diamonds, stream samples by circles. Boxes are representative of indicated nitrogen sources in italics, modified from Kendall and McDonnell, 1998. The range of $\delta15N$ and $\delta18O$ for the soil nitrate box is modified from Fields and Halihan, 2016. The range of $\delta18O$ for soil nitrate was derived from stream nitrate $\delta18O$ and estimated atmospheric nitrate $\delta18O$. Nitrate in soil is biologically nitrified from ammonia: during this process, one oxygen atom is taken from atmospheric O2, while two come from water (Hollocher, 1984). Possible $\delta15N$ fractionation in soil was accounted for by adding a 1‰ buffer to the range of $\delta15N$.

Table 8. Nitrate isotope ratios of possible source samples and stream samples. All values in permille (‰) notation.

	Sample #	Sample Name	$\delta^{15}N$ - Nitrate	$\delta^{18}O$ - Nitrate
Possible Source Samples	1A	Savoy Lagoon-Old	4.77	59.06
	2	Hog Manure	-2.78	16.09
	4	Chicken Litter	54.79	37.82
	6	CAFO Solids Pond	4.21	-7.15
	8	Aged Cow Manure	20.19	39.68
	9	Synthetic Fertilizer	13.28	30.80
	9D	Synthetic Fertilizer Duplicate	15.39	18.73
	10	Septic Effluent	18.66	2.21
	11	Field 1 Runoff	-3.18	33.37
	11D	Field 1 Runoff Duplicate	-2.82	32.14
	12	Field 5A Runoff	0.21	34.19
	13	Field 12 Runoff	-3.16	38.85
	32	Parking Lot Runoff	-15.40	56.07
Stream Samples	14	Upstream S1	-0.43	1.85
	14D	Upstream S1 Duplicate	0.11	0.28
	15	Upstream S2	0.20	9.10
	16	Upstream B1	0.17	2.15
	17	Upstream B2	3.76	7.07
	17D	Upstream B2 Duplicate	3.72	8.38
	18	Downstream S1	1.44	1.07
	19	Downstream S2	4.01	3.16
	19D	Downstream S2 Duplicate	2.89	3.33
	20	Downstream B1	4.98	2.25
	21	Downstream B2	6.41	-0.62
	21D	Downstream B2 Duplicate	7.02	3.75
	22	Confluence S1	3.07	2.39
	23	Confluence S2	3.42	4.87
	23D	Confluence S2 Duplicate	3.29	2.35
	23D	Confluence S2 Duplicate	2.66	6.90
	24	Confluence B1	3.80	2.95
	25	Confluence B2	4.90	-2.21
	25D	Confluence B2 Duplicate	5.27	-2.70
	25D	Confluence B2 Duplicate	3.84	4.50
	26	Ephemeral S1	0.72	-0.68
	27	Ephemeral S2	2.07	-0.66
	27D	Ephemeral S2 Duplicate	2.02	-0.61
	5A	Ephemeral In-Stream 5/2/16	-3.42	2.41
	5B	Ephemeral ISCO 5/2/16	0.54	-7.59

D = duplicate

The following samples were tested with no result: 1B Savoy Lagoon-Fresh, 3 Fresh Cow Manure, 7 CAFO Liquids Pond

Table 9. Nitrogen isotope ratios and %Nitrogen of sediment samples.

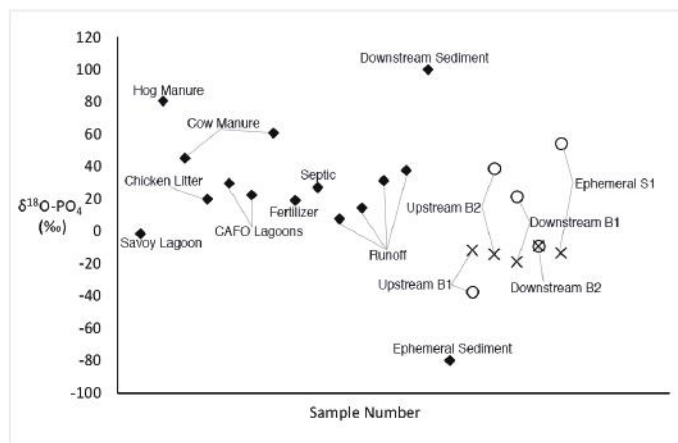| Sample Number	Sample Name	$\delta^{15}N$	%N
28	Upstream Sediment	4.572	0.023
28_d	Upstream Sediment Duplicate	2.612	0.025
29	Downstream Sediment	5.071	0.286
30	Confluence Sediment	2.180	0.154
31	Ephemeral Sediment	-2.258	0.053

Figure 4. Phosphate oxygen isotope ratios. Possible source samples represented by diamonds, stream samples by circles. Stream equilibrium phosphate oxygen isotope ratios represented by an X.

$\delta18O$ ranged from -17.75 to -8.44‰. The equilibrium $\delta18O$-PO_4 for the upstream B2, downstream B1, and ephemeral S1 samples was depleted compared the measured stream $\delta18O$. Phosphate sorbed onto sediment in the ephemeral stream (-78.8‰) is likely influencing $\delta18O$ in the ephemeral stream. The enriched $\delta18O$ values seen in all source samples other than ephemeral sediment may imply a source input to Big Creek is influencing $\delta18O$. Stream water $\delta18O$ and $\delta2H$ are presented in Table 11. Figure 5 illustrates that stream water $\delta18O$ and $\delta2H$ lie slightly but consistently above the local meteoric water line.

Conclusions

Big Creek water quality and isotopic data show the CAFO waste lagoon, a septic system, field and parking-lot runoff, fertilizer, and hog manure exhibit different $\delta15N$ and $\delta18O$ as compared to stream samples. Big Creek NO_3 isotope values are similar to NO_3 values expected from nitrification of N stored in soils sampled in the watershed. Similar chloride-bromide ratios for fresh cow manure, septic-system effluent, and Big Creek samples may indicate an influence on Big Creek water quality. We recommend that monitoring continues on Big Creek to ensure potential future effects on water quality are recognized. The database of compositions

Table 10. Phosphate oxygen isotope ratios for possible source samples and stream samples, along with water temperature and phosphate oxygen isotope equilibrium ratios for stream samples.

	Sample #	Sample Name	δ^{18}O - Phosphate (‰)	Water Temp (°C)	Equilibrium δ^{18}O - Phosphate (‰)
Possible Source Samples	1B	Savoy Lagoon-Fresh	-0.652	--	
	2	Hog Manure	81.6	--	
	3	Fresh Cow Manure	45.9	--	
	4	Chicken Litter	21	--	
	6	CAFO Solids Pond	30.5	--	
	7	CAFO Liquids Pond	23.3	--	
	8	Aged Cow Manure	61.7	--	
	9	Synthetic Fertilizer	19.9	--	
	10	Septic Effluent	28.1	--	
	11	Field 1 Runoff	8.47	--	
	12	Field 5A Runoff	15.2	--	
	13	Field 12 Runoff	32	--	
	32	Parking Lot Runoff	38.6	--	
	29	Downstream Sediment	101	--	
	31	Ephemeral Sediment	-78.8	--	
Stream Samples	16	Upstream B1	-36.3	24	-10.6
	17	Upstream B2	39.6	28.6	-13.2
	20	Downstream B1	22.3	24.3	-17.7
	21	Downstream B2	-8.08	24.4	-8.4
	26	Ephemeral S1	55.4	14	-12.5

-- = No Data

The following samples did not contain enough phosphate to measure the oxygen isotope ratio: Upstream S1 and S2 (14 and 15), Downstream S1 and S2 (18 and 19), All Confluence Samples (22, 23, 24, 25), Ephemeral S2 (27), Ephemeral 5/2/16 (5A and 5B), Upstream Sediment, Confluence Sediment.
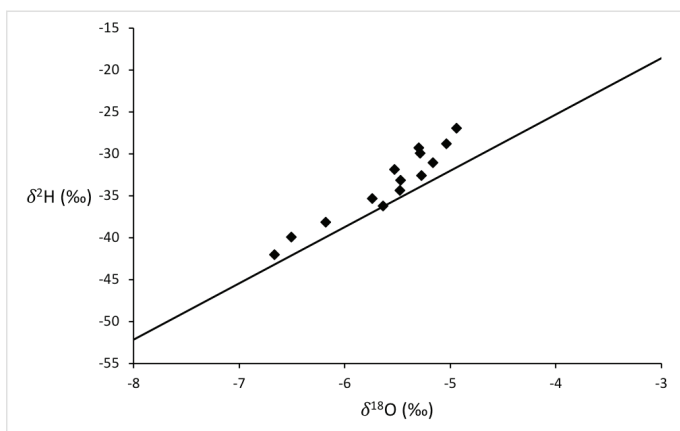

Figure 5. Stream water isotope ratios. Stream samples are represented by diamonds. Black line is a local meteoric water line modified from Knierim, 2015.

Table 11. Hydrogen and oxygen isotope ratios of stream water samples. All values in permille (‰) notation.

Sample #	Sample Name	δ^{18}O - Water	δ^2H - Water
14	Upstream S1	-4.96	-26.83
15	Upstream S2	-5.31	-29.11
16	Upstream B1	-5.18	-30.93
17	Upstream B2	-5.28	-32.44
18	Downstream S1	-5.54	-31.71
19	Downstream S2	-6.52	-39.73
20	Downstream B1	-6.19	-38.00
21	Downstream B2	-5.05	-28.68
22	Confluence S1	-6.68	-41.82
23	Confluence S2	-5.30	-29.74
24	Confluence B1	-5.49	-34.18
25	Confluence B2	-5.65	-36.06
26	Ephemeral S1	-5.75	-35.16
27	Ephemeral S2	-5.48	-33.03

of potential nutrient sources developed in this study will assist in addressing nutrient enrichment in other watersheds. The results of this study highlight the importance of effective agricultural, residential, and urban best management practices in protecting the quality of our waterways.

Acknowledgements

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Image caption: Algal bloom in a fisheries farm pond.

Mitigating Cyanobacterial Blooms and Cyanotoxins in Hypereutrophic Ponds Following the Application of a Granular Hydrogen Peroxide-Based Algaecide

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Abstract: To control cyanobacterial blooms and their toxins, the efficacy of a newly developed granular compound (sodium carbonate peroxyhydrate 'SCP', trade name 'PAK® 27') containing hydrogen peroxide (H_2O_2) as the active ingredient was investigated. First, the dose efficacy of the SCP that corresponded to 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 and 8.0 mg/L H_2O_2 was tested for 10 days in small-scale tanks installed in 0.1-acre experimental hypereutrophic ponds dominated by blooms of the toxic cyanobacterium *Planktothrix sp.* SCP ranging from 2.5- 4.0 mg/L H_2O_2 selectively killed *Planktothrix sp.* without major impacts on either eukaryotic phytoplankton (e.g., diatom *Synedra sp.*, green algae *Spirogyra sp.* and *Cladophora sp.*) or zooplankton (e.g., rotifers *Brachionus sp.* and cladocerans *Daphnia sp.*). Based on these results, SCP at 2.5 mg/L and 4.0 mg/L H_2O_2 were homogeneously introduced into entire water volume of the experimental ponds in parallel with untreated control ponds. Temporal analysis indicated that *Planktothrix sp.* blooms collapsed remarkably in both 2.5 mg/L and 4.0 mg/L H_2O_2 treatments. Both treatments also were accompanied by an overall reduction in the total microcystin concentration. At 2.5 mg/L H_2O_2, the growth of eukaryotic phytoplankton (*Synedra* and *Cladophora sp.*) increased, but these populations along with zooplankton (*Brachionus* and *Daphnia sp.*) were suppressed at 4.0 mg/L H_2O_2. The longevity of 2.5 and 4.0 mg/L H_2O_2 treatment effects were up to 5 weeks. In addition, the added granular algaecide degraded within a few days, thereby leaving no long-term traces of H_2O_2 in the environment.

Key Points:
- Cyanobacterial blooms and their toxins are potential threat to aquatic animals.
- Granular H_2O_2 based sodium carbonate peroxyhydrate (SCP) compound was investigated.
- SCP at 2.5 and 4.0 mg/L H_2O_2 effectively suppressed cyanobacterial bloom and toxin.
- SCP left no footprint of H_2O_2 in water; hence, SCP is an eco-friendly compound.

Introduction

Cyanobacterial blooms have been increasingly reported and are progressively becoming a major water quality issue in pond, lakes, and river ecosystems throughout Arkansas, thus impacting their fisheries resources. There are several strategies suggested to remove cyanobacterial blooms. Reducing nutrient loads (typically phosphorus) to prevent eutrophication is probably the best strategy (Conley et al., 2009; Matthijs et al., 2012; Smith and Schindler, 2009), though it often requires several years for the effect to be realized. Dredging of nutrient-rich sediments from pond bottoms followed by a phosphorus-binding clay treatment is the simplest remedial approach to eliminate phosphorus loads. However, these practices are associated with high operating costs, slow action, and the outcomes are not always predictable or effective (Robb et al., 2003; Van Oosterhout and Lurling, 2011). Additional strategies such as artificial pond mixing also may restrain cyanobacterial populations (Huisman et al., 2004; Visser et al., 1996), but is economically infeasible in most cases. Chemical alternatives including herbicides (e.g., diuron), copper-based compounds (e.g., copper sulfate), and alum have been used for many decades. However, there are concerns with lengthy environmental persistence and risks of ecotoxicity to other non-target aquatic biota, including green algae, zooplankton, and fishes (Jancula and Marsalek, 2011). High-frequency sonication is a newer method of selectively bursting gas vesicles and vacuoles in cyanobacteria, which disrupts cell membranes and retards photosynthetic activity (Rajasekhar et al., 2012). Although this technique kills the cyanobacterial blooms by lysing their cells, it has no effect on the toxins. Consequently, following mass cell ruptures, large amounts of cyanotoxins are released into surrounding waters, which often deteriorates rather than resolves the water-quality issues.

In light of the well-documented problems associated with cyanobacterial blooms and their toxins, there is a corresponding need for an environmentally-benign treatment that rapidly restrains the cyanobacterial populations while also destroying their toxins. Recently, hydrogen peroxide (H_2O_2) has been proven useful in selectively reducing cyanobacteria in mixed phytoplankton communities (Barrington et al., 2013; Bauza et al., 2014; Drabkova et al., 2007; Matthijs et al., 2012; Wang et al., 2012). The algaecidal action of H_2O_2 occurs via the formation of free hydroxyl radicals (OH^-) in the solution, which in turn, inhibit electron transport and photosynthetic activity by rendering photosystem II inactive, and thus causing cellular death. Nevertheless, adding large volumes of pure H_2O_2 solution directly into water bodies poses safety concerns, and also is likely to spill during broadcasting, transportation, and storage. An attractive alternative to traditional H_2O_2 solution is sodium carbonate peroxyhydrate (SCP), which is a relatively new, dry granulated H_2O_2-based algaecide (USEPA, 2004). When added to water, SCP decomposes rapidly and liberates H_2O_2 and sodium carbonate.

In the present study, our primary goal was to examine the use of this granulated H_2O_2-based algaecide (SCP) for treating cyanobacterial blooms in ponds. We hypothesized that adding SCP to hypereutrophic experimental ponds would selectively suppress cyanobacterial overgrowth and destroy the associated toxins. We also proposed that SCP added to ponds would degrade within a few days, and that no long-term traces of H_2O_2 would remain. Findings of this study will provide insights into the current knowledge base of effective, rapid, and safe technologies to successfully control cyanobacterial blooms in Arkansas water resources and beyond.

Methods

Experimental Site and Algal Bloom Culture

Experimental trials using the granular SCP-based algaecide were performed in a series of ponds located at the Aquaculture Research Station on the campus of the University of Arkansas at Pine Bluff (UAPB). The experiments were performed at two different scales: small-scale trials done in outdoor tanks and full-scale trials conducted in experimental ponds. A total of six experimental ponds (0.1-acre each with average depth of 1.2 m) were filled with shallow well water, and fertilized with an inorganic fertilizer and commercially available de-oiled rice bran to stimulate phytoplankton growth. In early July 2017, water from a nearby hypereutrophic pond (i.e., 'seed stock') was used to inoculate each of the six experimental ponds. Nutrients (inorganic fertilizer and de-oiled rice bran) were added, as needed, throughout the culture phase until hypereutrophic, cyanobacteria-dominated conditions were obtained. Average values and range of the various physico-chemical parameters measured in experimental ponds prior to the SCP treatments are provided in Table 1.

Preparation of SCP Dilutions

The SCP-based algaecide used in this study is marketed as SePRO 'PAK® 27' (active ingredient ~ 27% H_2O_2; USEPA Registration number, 67690-76, SePRO Corporation, Carmel, IN, U.S.A.). The physical properties and characteristics of PAK® 27 are outlined in Table 2.

Small-Scale Outdoor Tank Experiment

Small-scale tank experiments were performed first to screen for the most appropriate dose of SCP (quantified as H_2O_2 concentrations) for the full-scale pond application. Three circular 75-L tanks were installed in each of the six hypereutrophic algal bloom ponds in early August 2017. Each tank was filled with water (up to 65 L) from the respective algal bloom ponds. SCP (as PAK® 27) at 5.56,

Table 1. Mean values ± S.E of the physico-chemical and biological parameters of control and the treatment ponds prior to the SCP (PAK® 27) application.

	Control	SCP (2.5 mg/L H$_2$O$_2$)	SCP (4.0 mg/L H$_2$O$_2$)
Water temperature (°C)	24.4 ± 0.6	25.8 ± 0.5	24.2 ± 0.4
Transparency (cm)	19.92 ± 1.12	20.94 ± 0.94	18.86 ± 1.24
pH	8.62 ± 0.20	8.48 ± 0.11	8.82 ± 0.14
Dissolved oxygen (mg/L)	2.84 ± 0.34	2.76 ± 0.29	3.04 ± 0.26
Total hardness (mg/L as CaCO$_3$)	187 ± 12	182 ± 13	196 ± 17
Total alkalinity (mg/L as CaCO$_3$)	119 ± 9	102 ± 12	121 ± 10
Conductivity (μS/cm)	385 ± 18	371 ± 10	405 ± 21
Ammonia – N (mg/L)	0.92 ± 0.08	0.96 ± 0.12	0.89 ± 0.14
Nitrite – N (μg/L)	35.0 ± 4.2	41.0 ± 3.8	39.0 ± 4.2
Nitrate – N (mg/L)	0.37 ± 0.03	0.43 ± 0.03	0.39 ± 0.03
Total Nitrogen (TN, mg/L)	8.06 ± 0.34	7.96 ± 0.29	7.79 ± 0.31
Total Phosphorus (TP, mg/L)	1.71 ± 0.09	1.76 ± 0.10	1.72 ± 0.14
TN:TP	4.71 ± 0.17	4.52 ± 0.19	4.53 ± 0.14
Chlorophyll a (μg/L)	1002 ± 84	989 ± 72	1112 ± 81
Planktothrix sp. (10^6 cells per mL)	1.09 ± 0.10	1.11 ± 0.12	1.08 ± 0.09

Table 2. Physical and chemical properties of PAK® 27 (Source: Pak® 27 Technical Data Sheet).

Ingredient	Property
Sodium Carbonate Peroxyhydrate (active ingredient)	> = 85.0 %
Carbonic acid sodium salt	< =13.0 %
Sodium silicate SiO$_2$/Na$_2$O	< =1.5 %
EPA Registration no.	68660-9-67690
CAS No.	15630-89-4
Physical state	Free flowing white granules
Mean Particle Size	350 – 650 (μm)
Alkalinity (%Na$_2$CO$_3$)	67
Solubility	150 g/L
pH	10.4-10.6 (10.1 g/L)
Bulk density	900-1200 kg/m^3

7.41, 9.26, 11.11, 12.96, 14.81, 18.52 and 29.63 mg/L was mixed into each tank to achieve final concentrations of 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 and 8.0 mg/L H$_2$O$_2$ respectively. This design also included one control to which no SCP was added. Each of the eight treatments and the control were conducted in duplicate.

Full-Scale Pond Experiment and Sampling

Based on the results of the small-scale tank experiments, which are reported in the Results and Discussion section, concentrations of 2.5 mg/L (low dose) and 4.0 mg/L (high dose) H$_2$O$_2$ as SCP were chosen for further study in full-scale ponds. Two ponds were treated with 2.5 mg/L H$_2$O$_2$, two ponds were treated with 4.0 mg/L H$_2$O$_2$, and the remaining two ponds received no treatments and served as control ponds. The experimental design consisted of first sampling the water on day 1 following the initiation of SCP treatments followed by daily sampling for the next 10 days. This was followed by weekly sampling from week 2 through week 6.

Sampling Protocols and Analytical Techniques

All phytoplankton were identified to the lowest practical taxonomic level via 200X, 400X, 600X (oil), or 1000X (oil) magnifications by using a 0.1-mm hemocytometer under an optical microscope (Axiostar plus, Zeiss, USA). Zooplankton composition and numbers was determined using Sedgewick Rafter counting cell and viewed at either 100X or 150X. Total microcystin concentrations were determined

using Abraxis microcystins assay kit (product No. 520011). Standard water quality parameters were determined through a portable multi-probe field meter (HQ40D portable multi meter, HACH) and HACH assay kits (method details are provided in the Table 3 legends).

Statistical Analysis

All data are presented as mean ± standard error (S.E.). For comparisons among treatment and control groups, one-way completely randomized analyses of variance (ANOVA) were performed; if significant differences were detected, among-treatment differences were assessed using Dunnett's test. Student's two-tailed t-test was used for single comparisons. A probability level of 0.05 was used for rejection of all null hypotheses.

Results and Discussion

Selective Toxicity and Dose Optimization of Granular H$_2$O$_2$ Algaecide (SCP) Towards Cyanobacterial Blooms

The present study tested the feasibility of a commercially available SCP granular algaecide (PAK® 27) that would release H$_2$O$_2$ when added to the water as a means of selectively eliminating cyanobacteria from mixed phytoplankton communities. In this study, determination of the correct dosage through a small-scale tank experiment was a critical step for the effective application at the full-scale pond level. The tank experiments suggested that the addition of the SCP corresponding to 2.5 mg/L H$_2$O$_2$ and greater sig-

nificantly reduced the dominating cyanobacterium *Planktothrix sp.* population (Figure 1). However, concentrations of 5 mg/L H_2O_2 and greater would not be feasible, as non-targeted eukaryotic phytoplankton communities (e.g., green algae *Spirogyra sp.*, *Cladophora sp.* and the diatom *Synedra sp.*) and herbivorous zooplankton (e.g., the rotifer *Brachionus sp.* and cladoceran *Daphnia sp.*) appeared sensitive to these elevated levels (Figures 2 and 3). On the basis of these findings, SCP corresponding to 2.5 mg/L and 4.0 mg/L H_2O_2 were selected for application in experimental ponds to investigate optimal suppression of cyanobacteria without affecting the remaining, non-target plankton community.

Plankton Dynamics in the SCP Treated Ponds

The application of 2.5 mg/L H_2O_2, in the form of SCP in the full-scale experimental ponds reduced the abundance of cyanobacterium *Planktothrix sp.* (Figure 4), whereby other phytoplankton classes (e.g., green algae *Cladophora sp.* and the diatom *Synedra sp.*) exhibited a conspicuous increase in abundance (Figures 5A,5B). This finding suggested that eukaryotic phytoplankton species in the 2.5 mg/L H_2O_2 -SCP treated ponds exploited the cyanobacterial collapse and mobilized the available nutrients, which would otherwise have been rapidly exhausted by the cyanobacteria bloom. This was supported by an initial significant increase in ammonia (Table 3). Another possibility could include the presence of nitrifying bacteria (i.e., oxidizing ammonia to nitrite and to nitrate), based on a gradual increase in nitrite and nitrate in all treated ponds after 3 weeks (Table 3). Furthermore, comparatively greater total phosphorus content in the treated ponds relative to controls was consistent with the reduction in cyanobacterial blooms in treatment ponds, which rendered phosphorus more bioavailable in the water column (Table 3). We also observed that the abundance of herbivorous zooplankton (*Brachionus* and *Daphnia sp.*) strongly declined in the 4.0 mg/L H_2O_2 -SCP applied ponds in contrast to those that received 2.5 mg/L H_2O_2 (Figures 6A,6B). It is very likely that the oxidative damage induced by a higher dose of 4.0 mg/L H_2O_2 is beyond the tolerance range
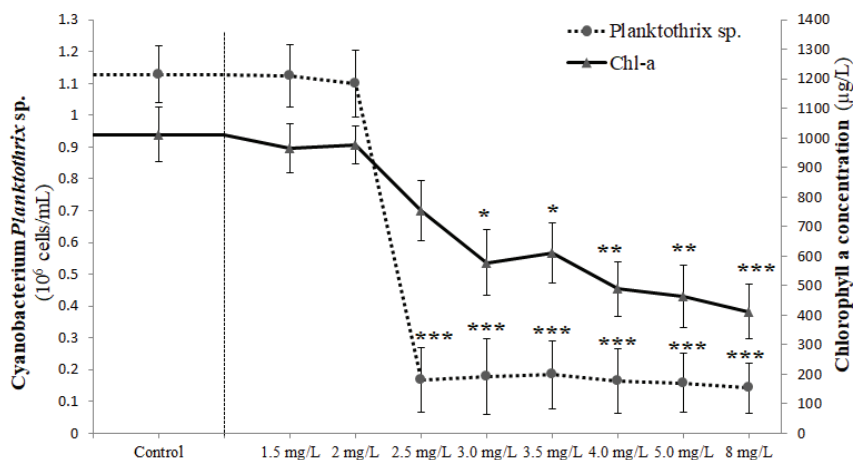

Figure 1. Changes in the cyanobacterium *Planktothrix sp.* abundance (dotted line) and chlorophyll a concentrations (solid line) in tanks after 10 days with different concentrations of H_2O_2 as SCP (PAK® 27). Values are means ± S.E. Asterisks (*) indicates a significant difference between the exposure groups (n=6) and the respective control (n=6) (*P < 0.05; **P < 0.01; ***P < 0.001).
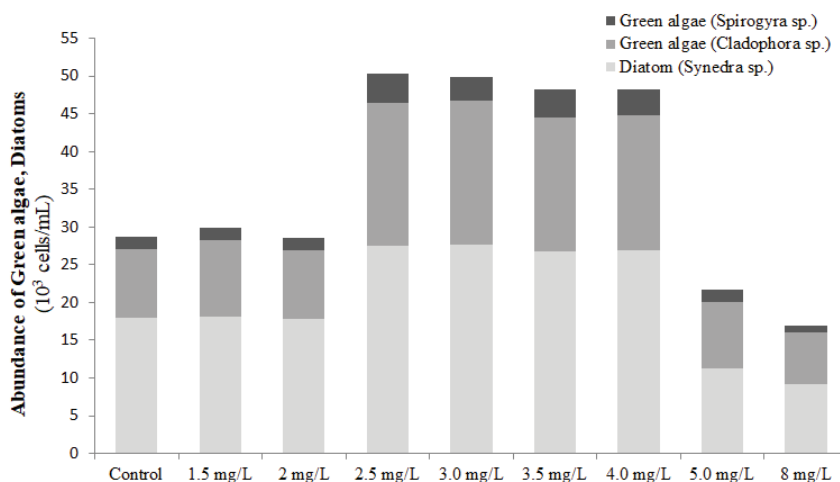
Figure 2. Abundance of green algae (*Spirogyra sp.* and *Cladophora sp.*) and diatom (*Synedra sp.*) in the tanks after 10 days with different concentrations of H_2O_2 as SCP (PAK® 27). Data show the means (n=6) of two duplicate tanks per treatment.
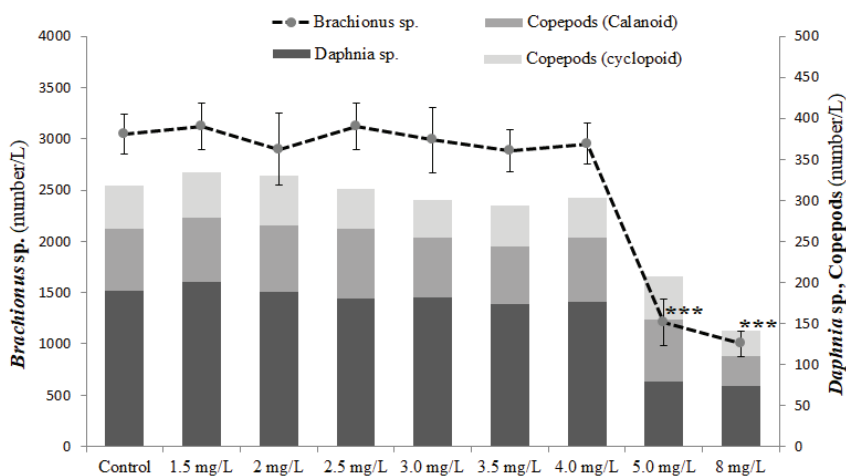
Figure 3. Abundance of zooplankton in the tanks after 10 days with different concentrations of H_2O_2 as SCP (PAK® 27). Line graph represents the population dynamics of rotifers (*Brachionus sp.*) while cladocerans (*Daphnia sp.*) and copepods (calanoid, cyclopoid) are illustrated as bar graphs. Data show the means (n=6) of two duplicate tanks per treatment.

Table 3. Temporal dynamics of water quality parameters of experimental ponds over the duration of 6 weeks following application with 2.5 mg/L and 4.0 mg/L H$_2$O$_2$ as SCP (PAK® 27).

| Parameter	Treatment	Days						
		1	2	3	4	5	6	7
Chlorophyll a (µg/L)	Control	1048 ± 89	1086 ± 89	1025 ± 105	1000 ± 86	938 ± 114	942 ± 88	929 ± 84
	2.5 mg/L	1070 ± 89	1030 ± 78.4	1023 ± 85	966 ± 157	740 ± 112	790 ± 85	725 ± 82
	4.0 mg/L	1115 ± 86	1060 ± 87	1078 ± 86	944 ± 157	680 ± 132	713 ± 81	621 ± 115*
Water Temperature (°C)	Control	25.8 ± 0.8	25.2 ± 0.4	23.1 ± 1.1	23.1 ± 1.1	19.5± 1.2	19.1 ± 0.7	22.8 ± 0.9
	2.5 mg/L	26.2 ± 1.0	25.2 ± 0.7	25.5 ± 0.7	25.5 ± 0.7	20.5 ± 0.8	19.0 ± 1.1	21.3 ± 0.7
	4.0 mg/L	26.1 ± 0.8	25.8 ± 0.9	23.9 ± 1.1	23.9 ± 1.1	20.9 ± 1.4	18.6 ± 0.6	22.6 ± 0.9
pH	Control	8.62 ± 0.33	8.61 ± 0.11	8.62± 0.24	8.68± 0.27	8.67± 0.23	8.64± 0.21	8.62± 0.23
	2.5 mg/L	8.51 ± 0.41	8.53± 0.32	8.62± 0.16	8.64± 0.16	8.62± 0.09	8.66± 0.31	8.52± 0.16
	4.0 mg/L	8.81± 0.21	8.80± 0.25	9.16 ± 0.27	9.18± 0.21	9.4± 0.20*	9.41± 0.22 *	9.39± 0.21 *
Transparency (cm)	Control	19.87 ± 1.23	18.83 ± 1.33	19.01 ± 1.12	21.11 ± 1.12	22.22 ± 1.89	23.34 ± 1.67	22.22 ± 1.21
	2.5 mg/L	20.88 ± 1.11	17.99 ± 2.00	20.02 ± 1.11	20.12 ± 1.32	21.01 ± 1.09	22.09 ± 1.75	22.0 ± 1.89
	4.0 mg/L	18.86 ± 1.09	19.09 ± 2.01	21.11 ± 1.06	22.00 ± 1.44	20.09 ± 1.90	19.98 ± 1.82	21.00 ± 1.92
Total alkalinity (mg/L as CaCO$_3$)	Control	119 ± 9	112 ± 9	119 ± 8	110 ± 8	120 ± 13	121 ± 12	111 ± 12
	2.5 mg/L	102 ± 8	117 ± 12	109 ± 8	116 ± 9	111 ± 8	118 ± 12	122 ± 13
	4.0 mg/L	121 ± 9	127 ± 14	131 ± 7	128 ± 10	127 ± 13	134 ± 13	139 ± 13
Conductivity (µS/cm)	Control	384 ± 24	376 ± 22	365 ± 24	381 ± 16	389 ± 24	387 ± 26	377 ± 23
	2.5 mg/L	376 ± 22	368 ± 24	389 ± 26	378 ± 18	389 ± 15	375 ± 24	376 ± 26
	4.0 mg/L	401 ± 17	378 ± 25	399 ± 27	376 ± 20	408 ± 27	410 ± 25	424 ± 27
Dissolved oxygen (mg/L)	Control	2.84 ± 0.21	3.01 ± 0.26	2.38 ± 0.19	2.46 ± 0.23	3.04 ± 0.16	3.41 ± 0.17	2.88 ± 0.28
	2.5 mg/L	2.76 ± 0.31	3.02 ± 0.32	2.67 ± 0.33	2.33 ± 0.33	2.90 ± 0.33	3.13 ± 0.35	2.81 ± 0.32
	4.0 mg/L	3.01 ± 0.24	2.89 ± 0.30	2.99 ± 0.23	2.01 ± 0.23	3.19 ± 0.26	3.21 ± 0.29	2.89 ± 0.30
Total hardness (mg/L as CaCO$_3$)	Control	182 ± 7.8	190 ± 7.8	178 ± 13.2	181 ± 11.7	180 ± 12.9	189 ± 11.5	190 ± 12.2
	2.5 mg/L	187 ± 7.7	186 ± 9.2	180 ± 7.6	182 ± 12.3	190 ± 8.2	192 ± 13.2	188 ± 15.8
	4.0 mg/L	196 ± 7.1	192 ± 10.1	189 ± 13.3	190 ± 12.7	183 ± 14.3	190 ± 13.7	185 ± 14.8
Ammonia – N (mg/L)	Control	0.92 ± 0.11	0.91 ± 0.08	0.88 ± 0.11	0.97 ± 0.11	0.91 ± 0.10	0.89 ± 0.14	0.92 ± 0.12
	2.5 mg/L	0.96 ± 0.12	0.90 ± 0.12	0.91 ± 0.12	0.88 ± 0.10	0.82 ± 0.11	0.88 ± 0.10	0.90 ± 0.09
	4.0 mg/L	0.89 ± 0.12	0.88 ± 0.12	0.79 ± 0.09	0.91 ± 0.12	0.94 ± 0.07	1.02 ± 0.11	0.89 ± 0.07
Nitrite – N (µg/L)	Control	39.2 ± 5.80	41.1 ± 5.61	43.7 ± 5.80	39.5 ± 5.67	37.2 ± 5.67	40.2 ± 6.18	45.5 ± 5.61
	2.5 µg/L	38.6 ± 5.73	37.4 ± 5.61	41.3 ± 5.22	33.5 ± 5.61	28.7 ± 5.73	29.5 ± 5.61	30.3 ± 5.80
	4.0 mg/L	40.2 ± 5.03	40.1 ± 5.80	39.6 ± 5.99	30.2 ± 6.50	29.4 ± 5.80	30.1 ± 5.73	28.2 ± 5.86*
Nitrate – N (mg/L)	Control	0.43 ± 0.05	0.44 ± 0.05	0.44 ± 0.05	0.45 ± 0.04	0.49 ± 0.04	0.48 ± 0.04	0.47 ± 0.04
	2.5 mg/L	0.41 ± 0.02	0.41 ± 0.02	0.39 ± 0.01	0.38 ± 0.03	0.46 ± 0.03	0.34 ± 0.04*	0.41 ± 0.03
	4.0 mg/L	0.39 ± 0.02	0.37 ± 0.03	0.38 ± 0.03	0.37 ± 0.02	0.28 ± 0.03	0.32 ± 0.03**	0.40 ± 0.03
Total Nitrogen (mg/L)	Control	8.04 ± 0.39	7.77 ± 0.38	8.11 ± 0.46	7.97 ± 0.34	7.76 ± 0.41	7.87 ± 0.28	8.02 ± 0.31
	2.5 mg/L	7.10 ± 0.41	6.96 ± 0.41	8.78 ± 0.43	8.63 ± 0.44	7.48 ± 0.44	8.27 ± 0.45	8.51 ± 0.49
	4.0 mg/L	7.79 ± 0.39	7.29 ± 0.37	8.44 ± 0.38	8.46 ± 0.37	6.97 ± 0.28	8.09 ± 0.32	8.95 ± 0.40
Total Phosphorus (mg/L)	Control	1.72 ± 0.13	1.75 ± 0.13	1.78 ± 0.13	1.69 ± 0.13	1.70 ± 0.15	1.70 ± 0.14	1.58 ± 0.14
	2.5 mg/L	1.88 ± 0.13	1.84 ± 0.12	1.89 ± 0.12	1.80 ± 0.11	1.82 ± 0.14	1.81 ± 0.11	1.87 ± 0.13
	4.0 mg/L	1.73 ± 0.12	2.03 ± 0.14	2.09 ± 0.14	1.72 ± 0.12	1.92 ± 0.09	1.99 ± 0.10	1.80 ± 0.12

Table 3 continued. Temporal dynamics of water quality parameters of experimental ponds over the duration of 6 weeks following application with 2.5 mg/L and 4.0 mg/L H_2O_2 as SCP (PAK® 27).

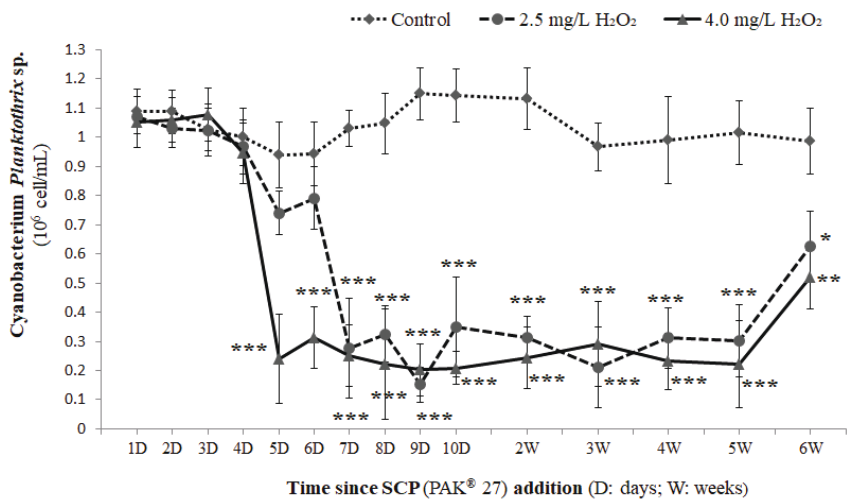|				Weeks			
8	**9**	**10**	**2**	**3**	**4**	**5**	**6**
917 ± 84	1148 ± 62	1142 ± 115	1130 ± 127	966 ± 126	889 ± 116	807 ± 149	987 ± 90
698 ± 87	651 ± 110**	649 ± 77**	614 ± 170*	510 ± 142*	311 ± 139**	394 ± 122*	678 ± 69*
622 ± 78*	602 ± 135**	569 ± 175**	544 ± 191*	571 ± 157*	231 ± 153**	389 ± 147*	601 ± 73**
21.1 ± 0.3	22.4 ± 0.5	23.4 ± 0.6	21.4 ± 0.8	20.1 ± 0.9	18.4 ± 0.2	15.4 ± 0.6	14.4 ± 0.5
21.7 ± 0.7	21.3 ± 0.9	22.0 ± 1.1	21.0 ± 0.7	18.9 ± 0.7	19.2 ± 0.6	16.2 ± 0.7	15.1 ± 0.8
21.2 ± 0.7	21.6 ± 0.8	22.1 ± 0.3	20.8 ± 0.7	20.8 ± 0.7	18.8 ± 0.5	15.8 ± 0.6	14.0 ± 0.6
8.59 ± 0.21	8.62 ± 0.23	8.71 ± 0.25	8.73 ± 0.22	8.71 ± 0.27	8.71 ± 0.27	8.67 ± 0.31	8.64 ± 0.21
8.59 ± 0.22	8.54 ± 0.42	8.57 ± 0.22	8.62 ± 0.22	8.52 ± 0.21	8.52 ± 0.21	8.61 ± 0.20	8.59 ± 0.24
8.96 ± 0.25	8.97 ± 0.24	8.86 ± 0.21	8.91 ± 0.29	9.02 ± 0.22	9.16 ± 0.22	8.94 ± 0.21	9.06 ± 0.18
20.09 ± 2.02	21.0 ± 2.21	20.09 ± 2.26	22.09 ± 1.90	20.09 ± 1.65	21.21 ± 1.56	22.99 ± 1.45	21.90 ± 2.10
21.20 ± 1.89	23.78 ± 1.78	24.02 ± 2.12	23.98 ± 1.90	22.89 ± 1.91	23.33 ± 1.88	22.45 ± 2.12	22.34 ± 2.09
22.32 ± 1.67	20.01 ± 2.12	19.05 ± 1.23	21.39 ± 1.78	21.08 ± 1.78	22.98 ± 1.90	19.01 ± 1.91	20.98 ± 2.14
115 ± 12	131 ± 15	111 ± 16	121 ± 13	112 ± 12	124 ± 11	121 ± 10	119 ± 15
124 ± 13	121 ± 12	112 ± 15	112 ± 13	103 ± 13	111 ± 13	125 ± 15	129 ± 15
148 ± 12*	140 ± 12	138 ± 9	130 ± 12	132 ± 12	139 ± 13	136 ± 13	130 ± 15
392 ± 24	378 ± 31	397 ± 32	378 ± 27	378 ± 23	381 ± 22	390 ± 20	382 ± 24
389 ± 26	391 ± 25	369 ± 30	381 ± 27	375 ± 27	391 ± 26	366 ± 30	362 ± 24
412 ± 23	432 ± 24	429 ± 17	398 ± 25	390 ± 25	401 ± 27	410 ± 27	405 ± 27
2.31 ± 0.28	2.34 ± 0.22	2.64 ± 0.22	1.65 ± 0.26	2.01 ± 0.21	2.38 ± 0.16	2.26 ± 0.27	2.04 ± 0.26
2.32 ± 0.31	2.21 ± 0.31	2.48 ± 0.38	1.75 ± 0.29	2.12 ± 0.28	2.61 ± 0.36	2.78 ± 0.35	2.58 ± 0.35
2.67 ± 0.29	2.52 ± 0.29	2.42 ± 0.35	2.27 ± 0.36	2.32 ± 0.29	2.72 ± 0.36	2.88 ± 0.37	2.70 ± 0.38
191 ± 11.9	185 ± 15.1	191 ± 12.5	190 ± 13.0	196 ± 11.3	182 ± 14.7	190 ± 9.9	201 ± 10.2
184 ± 13.3	188 ± 11.6	201 ± 13.2	200 ± 14.4	190 ± 14.4	186 ± 14.6	192 ± 16.0	189 ± 14.9
189 ± 13.3	186 ± 13.3	188 ± 12.9	201 ± 13.5	204 ± 12.9	190 ± 14.9	201 ± 14.4	205 ± 13.4
0.88 ± 0.12	0.89 ± 0.11	0.9 ± 0.11	0.92 ± 0.08	0.91 ± 0.10	0.91 ± 0.11	0.86 ± 0.12	0.89 ± 0.11
0.90 ± 0.11	1.31 ± 0.11**	1.34 ± 0.14**	1.21 ± 0.11*	1.27 ± 0.12*	0.98 ± 0.13	1.09 ± 0.12	1.04 ± 0.12
1.22 ± 0.11*	1.32 ± 0.11**	1.29 ± 0.13*	1.23 ± 0.12*	1.30 ± 0.12*	1.08 ± 0.12	1.07 ± 0.11	1.01 ± 0.08
46.4 ± 5.73	44.6 ± 8.34	47.1 ± 8.54	52.3 ± 7.71	51.9 ± 5.80	49.4 ± 8.28	47.3 ± 5.67	50.4 ± 6.82
28.4 ± 5.47*	31.1 ± 8.41	28.3 ± 8.22	29.6 ± 7.83*	30.7 ± 6.24*	47.6 ± 5.48	42.4 ± 6.62	48.5 ± 6.11
29.8 ± 5.77*	28.5 ± 5.86	31.1 ± 5.86	33.2 ± 8.09	29.3 ± 6.88*	42.5 ± 6.94	48.3 ± 6.43	46.8 ± 5.67
0.49 ± 0.05	0.46 ± 0.03	0.46 ± 0.04	0.46 ± 0.03	0.47 ± 0.05	0.47 ± 0.05	0.49 ± 0.04	0.48 ± 0.05
0.28 ± 0.03***	0.31 ± 0.03**	0.39 ± 0.03	0.39 ± 0.03	0.41 ± 0.03	0.48 ± 0.03	0.50 ± 0.03	0.47 ± 0.03
0.31 ± 0.05**	0.31 ± 0.04 **	0.35 ± 0.03 *	0.38 ± 0.031	0.39 ± 0.029	0.47 ± 0.035	0.51 ± 0.026	0.48 ± 0.032
8.26 ± 0.39	7.97 ± 0.39	8.13 ± 0.41	7.63 ± 0.48	8.03 ± 0.50	8.28 ± 0.47	8.50 ± 0.47	8.16 ± 0.49
9.22 ± 0.48	9.30 ± 0.47*	9.82 ± 0.50*	9.75 ± 0.46**	9.19 ± 0.46	8.99 ± 0.47	8.67 ± 0.47	8.16 ± 0.48
9.15 ± 0.31	9.87 ± 0.31**	9.76 ± 0.35*	9.96 ± 0.38**	8.97 ± 0.46	8.16 ± 0.39	8.33 ± 0.51	7.99 ± 0.48
1.59 ± 0.15	1.59 ± 0.14	1.33 ± 0.14	1.21 ± 0.14	1.17 ± 0.15	1.22 ± 0.15	1.18 ± 0.15	1.08 ± 0.15
1.71 ± 0.19	1.67 ± 0.09	1.58 ± 0.12	1.53 ± 0.15	1.32 ± 0.13	1.46 ± 0.15	1.35 ± 0.16	1.33 ± 0.15
1.99 ± 0.19	1.84 ± 0.09	1.59 ± 0.14	1.51 ± 0.16	1.45 ± 0.12	1.53 ± 0.15	1.51 ± 0.16	1.42 ± 0.15

Figure 4. Temporal changes in the cyanobacterial *Planktothrix sp.* abundance in ponds over 6 weeks of treatments with 2.5 mg/L and 4.0 mg/L H_2O_2 as SCP (PAK® 27). Values are means ± S.E. Asterisks (*) indicate a significant difference between the treatment groups (n=8) and control (n=8) at the same sampling period (*P < 0.05; **P < 0.01; ***P < 0.001).
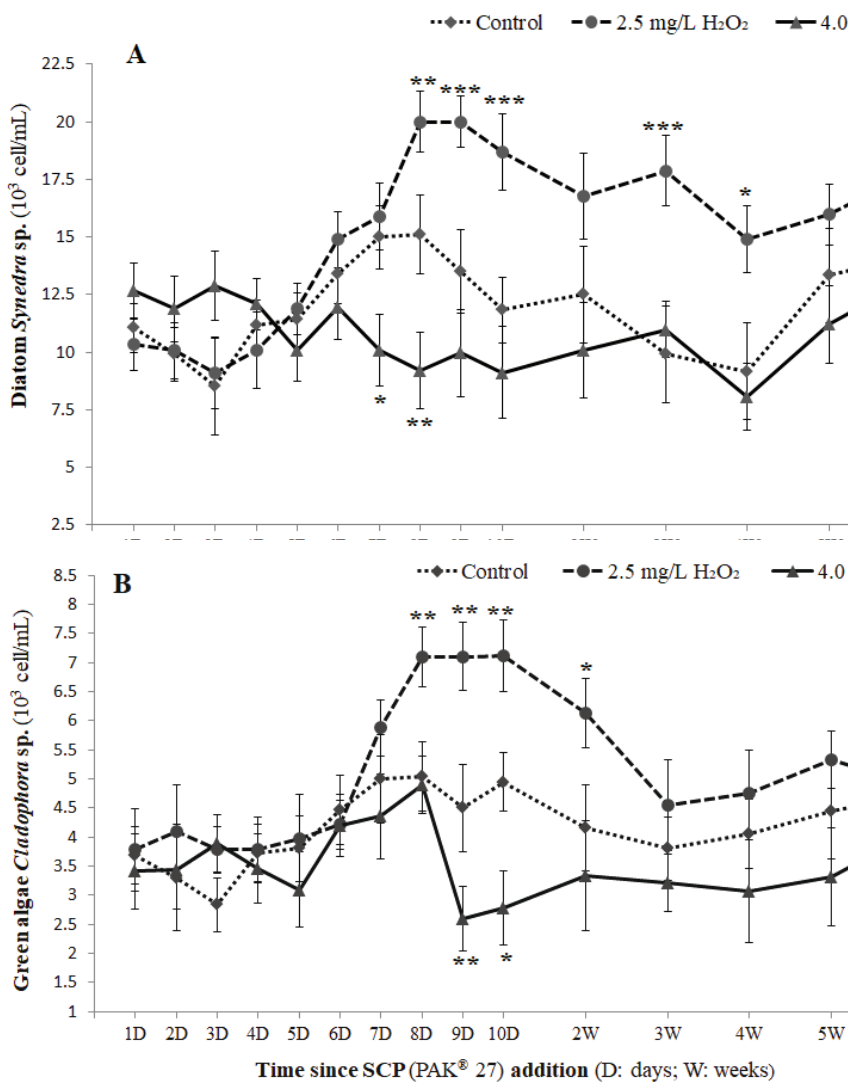

Figure 5. Temporal variations in the dynamics of eukaryotic phytoplankton (A) diatoms *Synedra sp.* and (B) green algae *Cladophora sp.* populations in ponds over 6 weeks of treatments with 2.5 mg/L and 4.0 mg/L H_2O_2 as SCP (PAK® 27). Values are means ± S.E. Asterisks (*) indicate a significant difference between the treatment groups (n=8) and control (n=8) at the same sampling period (*P < 0.05; **P < 0.01; ***P < 0.001).

of these zooplankton groups. This reduction in herbivorous zooplankton might have also been potentially coupled with the reduction of eukaryotic phytoplankton richness that limits the supply of phytoplankton as a food source.

Cyanotoxin Degradation and Environmental Feasibility of SCP-Based Algaecide

A potential risk associated with the massive cyanobacterial lysis is the copious release of internally produced cyanotoxins into the surrounding water (Westrick et al., 2010). For instance, the persistence of cyanotoxins has the potency to kill food fish, cause food safety issues, or adversely affect product quality (Sinden and Sinang, 2016). Hence, the timely control of not merely the cyanobacterial blooms, but also their associated toxins from the culture system is essential. Copper-containing algaecides (e.g., Captain and K-Tea) are effective in controlling cyanobacterial populations; however, evidence suggests that these chemicals cannot mitigate cyanotoxins or microcystin concentrations (Greenfield et al., 2014; Jones and Orr, 1994; Kenefick et al., 1993). This study provides strong evidence that the total microcystin concentrations are dramatically reduced by H_2O_2 applications in the form of SCP-based algaecide (Figure 7). The oxidation of the H_2O_2 fraction of the SCP granules may have catalyzed the production of hydroxyl and hydroperoxyl radicals that induced the oxidative cleavage of microcystins. This process, in effect, degrades microcystins into peptide residues by either modifying the Adda-moiety or breaking the amino-acid ring structure of the microcystins (Antoniou et al., 2008; Liu et al., 2003).

Aquaculturists, water resource managers, and water authorities should consider not only the efficiency, but also the ecological consequences of cyanobacteria bloom prevention and control approaches. In this study, the H_2O_2 added in the form of SCP-'PAK® 27' rapidly degraded in the water column, usually within 3 to 4 days (Figure 8), which suggests that this product is unlikely to leave any significant environmental footprint. Consequently, the SCP-based algaecide seems to exert minimal detrimental consequences on aquatic food webs compared to

other algaecides (e.g., copper-based compounds) that have a more lengthy environmental persistence.

Conclusions

With the current scenario of increased frequencies of cyanobacterial blooms worldwide, largely due to anthropogenic activities, an environmentally compatible management strategy is crucial that not only controls the blooms, but also their toxins. To address this issue, the efficacy of a newly developed granular H_2O_2 based SCP algaecide (PAK® 27) application for full-scale hypereutrophic ponds was assessed following a dose range-finding test in outdoor tanks. The applications of SCP at both 2.5 and 4.0 mg/L H_2O_2 substantially reduced cyanobacteria *Planktothrix sp.* cell numbers. However, given the minimal effects on non-target eukaryotic algae and zooplankton, the 2.5 mg/L H_2O_2 concentration as SCP had practical advantages over the 4.0 mg/L H_2O_2 concentration for reducing cyanobacteria and diminishing the likelihood of recurring cyanobacteria blooms. Furthermore, the present study also revealed that the added H_2O_2 as PAK® 27 degrades within a few days, and thus leaves no long-term traces in the environment. Overall, these results suggest that SCP based PAK® 27 algaecide is effective at both removing cyanobacterium Planktothrix and microcystins, while also being environmentally benign. However, the optimal dosage may also depend on the species composition of the cyanobacteria. In the future, conducting similar experiments with other genera of dominating cyanobacterial blooms (e.g., *Microcystis* or *Anabaena sp.*) will be crucial.
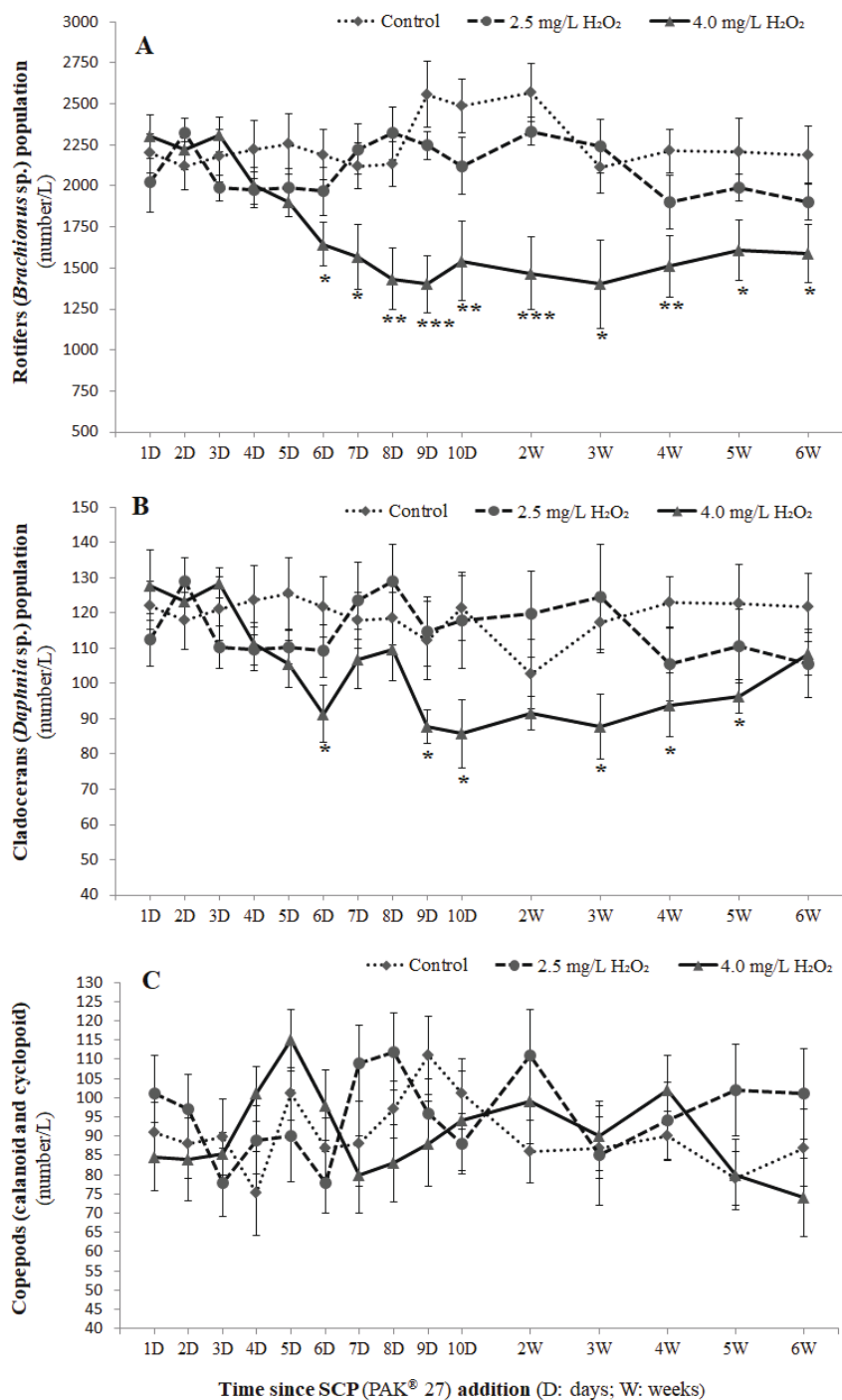
Acknowledgements

Figure 6. Abundance patterns of zooplankton (A) *Brachionus sp.*, (B) *Daphnia sp.* and (C) copepods in ponds over 6 weeks of treatments with 2.5 mg/L and 4.0 mg/L H_2O_2 as SCP (PAK® 27). Values are means ± S.E. Asterisks (*) indicate a significant difference between the treatment groups (n=8) and control (n=8) at the same sampling period (*$P < 0.05$; **$P < 0.01$; ***$P < 0.001$).

Figure 7. Changes in microcystin concentrations (ppb) in ponds over 6 weeks of treatments with 2.5 mg/L and 4.0 mg/L H_2O_2 as SCP (PAK® 27). Values are means ± S.E. Asterisks (*) indicate a significant difference between the treatment groups (n=8) and control (n=8) at the same sampling period (*P < 0.05; **P < 0.01; ***P < 0.001).
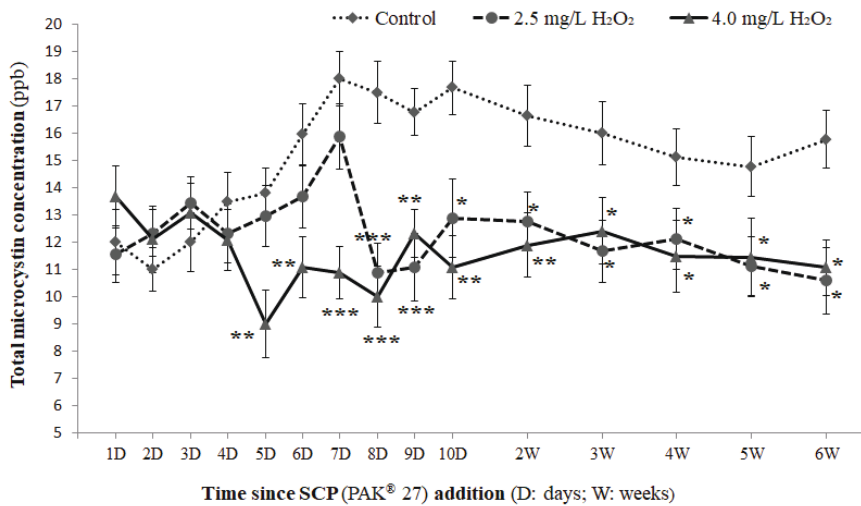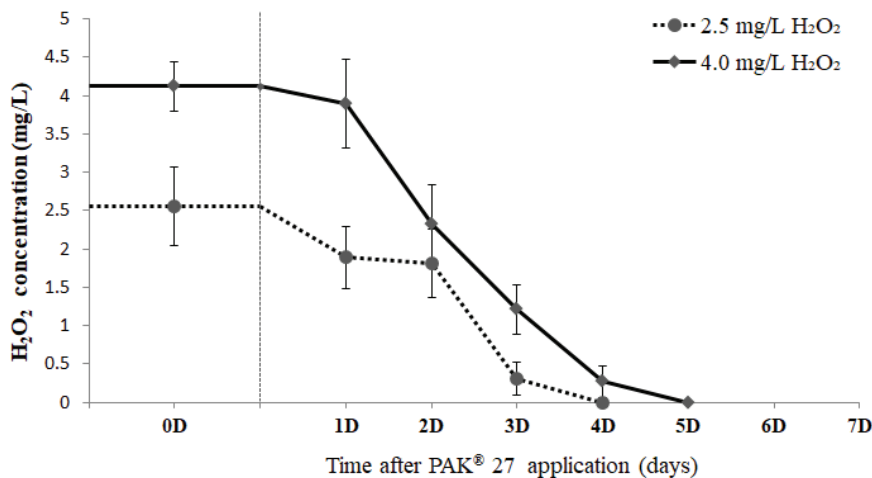

Figure 8. Degradation profile of 2.5 mg/L and 4.0 mg/L H_2O_2 applied as SCP (PAK® 27) in ponds. Values are means ± S.E (n=8).

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Image caption: A water sample is being collected from an on-farm tailwater recovery reservoir.

Herbicide Mitigation Potential of Tailwater Recovery Systems in the Cache River Critical Groundwater Area

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Abstract: Unsustainable water level decline in Arkansas aquifers has led agricultural producers to incorporate ditches and reservoirs into irrigation systems to recover tailwater and store winter-spring precipitation. These tailwater recovery systems offer water-saving benefits, but little is known about how they affect herbicide fate and transport, or the potential implications of these effects on the surrounding landscape. This study initiated a herbicide monitoring record for tailwater recovery systems in the Cache Critical Groundwater Area. Grab samples were collected weekly from April – August 2017 from seven tailwater recovery systems in Craighead and Poinsett counties. Samples were processed by filtration and concentration using solid phase extraction on reverse-phase polymer columns in preparation for analysis by high performance liquid chromatography with photodiode array detection. Target analytes were 2,4-D, clomazone, dicamba, metolachlor, propanil, and quinclorac. Clomazone, metolachlor, and quinclorac were frequently detected in the monitored systems, while 2,4-D, dicamba, and propanil were rarely or never detected. Across compounds, concentrations in ditches were higher, on average, and more variable than in reservoirs. Peak clomazone concentrations were observed in April, with few remaining detections by August. Quinclorac and metolachlor concentrations peaked in June, and these compounds were more persistent, with frequent low-level detections continuing through August. These findings were consistent with expectations that the majority of herbicide transport from fields occurs in a "spring flush" and that relatively large water volumes in reservoirs will "treat" elevated residual herbicide concentrations leaving fields in tailwater and runoff through dilution.

Key Points:
- Herbicide concentrations were higher and more variable in tailwater ditches than in reservoirs.
- The concentrations of herbicides peaked in May-June following a "spring flush".
- Recycling irrigation from reservoirs will minimize risk of off-target cross-crop contaminations.
- Strategies to use on-farm reservoir water for artificial groundwater recharge should focus on non-growing season.

Introduction

Current agricultural groundwater use rates in Arkansas are unsustainable, demonstrated by the drawdown of agriculturally important aquifers, such as the Mississippi River Valley Alluvial, in recent decades (Schrader, 2015; Reba et al. ,2017). Continued groundwater decline is predicted as long as irrigation demand exceeds aquifer recharge. In addition to problems of water quantity, agricultural field runoff of sediment, nutrients, and pesticides contributes to impaired surface water quality (USEPA, 2009). Herbicide usage in Arkansas and the Midsouth is only anticipated to intensify in the age of herbicide-resistant weeds (Norsworthy et al., 2013; Riar et al., 2013), increasing the risk of elevated herbicide concentrations in surface and ground waters. These water quality and quantity challenges will limit options for safe and appropriate water use in regions of intensive agriculture without effective mitigation strategies.

In zones of groundwater depletion, such as the Cache Critical Groundwater Area, agricultural producers have begun incorporating tailwater recovery into their irrigation systems by constructing networks of ditches and storage reservoirs (Fugitt et al., 2011; Yaeger et al., 2017). Ditches recapture runoff and tailwater leaving fields, while reservoirs provide capacity to store recaptured tailwater and

winter-spring precipitation long-term for growing season irrigation supply. The water-saving benefits of on-farm reservoirs have been established, potentially replacing 25-50% of groundwater irrigation (Sullivan and Delp, 2012). But, little is known about how these systems affect water quality in the surrounding landscape or about the persistence and accumulation of herbicides within them. Beyond the primary objective to reduce reliance on groundwater, tailwater recovery systems offer the potential benefit of conserving water quality in adjacent surface waters by preventing off-site movement of nutrients, sediment, and herbicides through retention and transformation processes. Further, water stored in reservoirs has been proposed as suitable supply water for managed artificial aquifer recharge using structures such as injection galleries (Reba et al., 2015; Reba et al., 2017). But these systems also pose potential risks of cross-crop impacts if residual herbicides are present at levels that could injure non-target crops when applied as irrigation water, and any artificial recharge supply must meet water quality and human health safety standards.

The objective of this study was to initiate a herbicide monitoring data record for tailwater recovery systems located in the Cache Critical Groundwater Area (Figure 1). Data from this study can be used to screen recovered tailwater

Figure 1. Map showing the location of the 7 monitored tailwater recovery systems (A-G) in Poinsett and Craighead counties in Arkansas.

for herbicide concentrations that could lead to cross-crop injuries during the growing season, characterize quality of water stored in tailwater systems in terms of suitability for artificial groundwater recharge, and estimate herbicide loads intercepted by tailwater recovery systems.

Methods

Seven tailwater systems were selected for herbicide monitoring from across the Cache Critical Groundwater Area in Craighead and Poinsett counties (Figure 1). Meteorological data were collected from a weather station on the campus of Arkansas State University. Herbicide application records were collected from producers in early April 2017 and were updated throughout the growing season. Based on this information, broad frequency of use in the region, and anticipated future use, seven herbicides were selected as target analytes: 2,4-dichlorophenoxyacetic acid (2,4-D), 2-[(2-chlorophenyl) methyl]-4,4-dimethyl-1,2-oxazolidin-3-one (clomazone), 3,6-dichloro-2-methoxybenzoic acid (dicamba), 2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl)acetamide (metolachlor), N-(3,4-dichlorophenyl) propanamide (propanil), and 3,7-dichloroquinoline-8-carboxylic acid (quinclorac). The herbicides 2,4-D and dicamba were selected for monitoring based on anticipated future use with the release of dicamba- and 2,4-D-tolerant soybean and cotton cultivars.

Tailwater ditch and reservoir grab samples were collected weekly (April – August 2017) in high density polyethylene bottles. Samples were stored on ice and shipped overnight for processing by the Residue Lab at the University of Arkansas. Upon receipt, samples were stored at 4°C until filtration through a 0.45 μm nylon membrane within 48 hours. Filtered samples were preserved by freezing until analysis by high performance liquid chromatography with photodiode array detection (HPLC-DAD) following concentration by solid phase extraction (SPE). During SPE, samples were concentrated from 200 mL (aqueous) to 8 mL 50:50 acetonitrile:methanol using Strata-X reverse-phase polymer columns. Columns were conditioned with 10 mL 100% methanol, equilibrated with 0.5% phosphoric acid in ultrapure water, and rinsed with a 20% methanol and 0.5% phosphoric acid solution in ultrapure water prior to elution. Eluates were spiked with 100 mg L^{-1} metazachlor to a known concentration to correct for volumetric variability. Eluates were analyzed for concentrations of the remaining target herbicides using HPLC-DAD with a mobile phase gradient of acetonitrile in 0.1% phosphoric acid ranging from 34-64% over 20 minutes. Clomazone, metolachlor, and metazachlor absorbances were monitored at 195 nm, 2,4-D and dicamba were monitored at 200 nm, propanil was monitored at 210 nm, and quinclorac was monitored at 226 nm. Wavelengths were selected to maximize each compound's absorption intensity. Bulk water sample herbicide concentrations were

calculated by multiplying the concentration measured using HPLC by the ratio of the eluate and beginning sample volumes after correcting eluate volume for differences in the measured and expected metazachlor concentration.

Results and Discussion

Clomazone, metolachlor, and quinclorac were frequently detected in tailwater ditches and reservoirs during April – August 2017 (Table 1). The herbicides 2,4-D, dicamba, and propanil were rarely detected or not detected in any of the monitored systems (data not shown). These findings were consistent with producer herbicide application reports. The majority of producers reported applying rice herbicides containing clomazone and/or quinclorac in mid-April 2017, as well as residual herbicides containing metolachlor as late as mid-June. No producers reported applying 2,4-D or dicamba. One producer reported propanil use, though the compound was not detected in that tailwater system. Propanil is known to rapidly degrade in the environment (Kanawi et al. 2016), and these findings suggest that the sampling intensity of the current scheme may not be sufficient to track propanil transport in these systems.

For clomazone, metolachlor, and quinclorac, concentrations were consistently more variable and higher, on average, in tailwater recovery ditches than in reservoirs. This trend was observed both across all monitored systems, and for each paired ditch and reservoir, with the exception of Ditch 2 at Site C, where mean quinclorac concentration was low and comparable with the reservoir, and site F, where the average metolachlor concentration was 2 times greater in the reservoir. At Site C, low concentrations of quinclorac and clomazone in Ditch 2 suggest few or no rice production acres in the drainage. However, the reservoir at Site C also aggregates tailwater from Ditches 3 and 5, where quinclorac was detected at high concentrations. At Site F, the ditch has substantial forested riparian land cover that may accelerate or change retention and transformation processes for metolachlor when compared to other ditches. Further, in several of the monitored reservoirs, metolachlor concentrations were more variable than quinclorac and clomazone, with maximum concentrations that were comparable with ditches. This finding suggests that the factors controlling transport and transformation may be affected differently in tailwater recovery systems for metolachlor than for quinclorac and clomazone.

The finding that residual herbicide concentrations were higher in tailwater ditches than in reservoirs is congruent with the concept that residues are diluted along the flow path by mixing with increasingly large volumes of water with lower residual concentrations, as well as break down over time. While herbicide concentrations in tailwater systems have not been extensively monitored, Mattice et al. (2010) found a similar pattern for clomazone and quinclorac residues with-

Table 1. Summary statistics by site for clomazone, metolachlor, and quinclorac concentrations measured in ditches and reservoirs during April – August 2017 in the monitored tailwater recovery systems in the Cache Critical Groundwater Area. "ND" indicates that the herbicide was not detectable.

Site	Structure	Compound	n	Median (µg/L)	Mean (µg/L)	Standard Deviation (µg/L)	Range (µg/L)
A	Ditch	Clomazone	17	ND	3.40	5.75	17.62
A	Reservoir	Clomazone	15	0.66	0.48	0.46	1.33
B	Ditch	Clomazone	16	0.69	1.35	3.00	12.38
B	Reservoir	Clomazone	18	ND	0.08	0.23	0.91
C	Ditch 2	Clomazone	17	ND	0.04	0.16	0.64
C	Ditch 3	Clomazone	16	ND	0.50	1.00	3.00
C	Ditch 5	Clomazone	20	ND	0.53	1.26	5.29
C	Reservoir	Clomazone	20	ND	ND	ND	ND
D	Ditch	Clomazone	15	1.16	7.77	15.96	60.39
D	Reservoir	Clomazone	15	0.25	0.36	0.40	0.98
E	Ditch	Clomazone	16	0.39	1.36	2.58	10.30
E	Reservoir	Clomazone	18	ND	0.03	0.11	0.33
F	Ditch	Clomazone	14	1.57	2.30	3.32	12.88
F	Reservoir	Clomazone	16	1.35	1.35	1.20	3.49
G	Ditch	Clomazone	15	1.52	2.67	3.82	12.34
G	Reservoir	Clomazone	14	1.13	1.34	1.73	7.11
A	Ditch	Metolachlor	17	0.83	1.67	2.36	9.75
A	Reservoir	Metolachlor	15	ND	0.58	1.31	4.30
B	Ditch	Metolachlor	16	ND	0.23	0.65	2.55
B	Reservoir	Metolachlor	18	ND	0.02	0.07	0.32
C	Ditch 2	Metolachlor	17	ND	2.96	5.65	21.90
C	Ditch 3	Metolachlor	16	0.51	2.34	4.39	17.45
C	Ditch 5	Metolachlor	20	ND	1.54	3.85	15.01
C	Reservoir	Metolachlor	20	ND	0.57	0.85	2.10
D	Ditch	Metolachlor	15	1.35	4.61	6.01	19.51
D	Reservoir	Metolachlor	15	0.84	2.50	3.73	10.23
E	Ditch	Metolachlor	16	0.57	2.57	5.40	20.80
E	Reservoir	Metolachlor	18	ND	1.72	5.15	22.06
F	Ditch	Metolachlor	14	ND	0.69	1.25	4.59
F	Reservoir	Metolachlor	16	ND	1.40	2.72	10.17
G	Ditch	Metolachlor	15	1.18	2.35	5.00	20.08
G	Reservoir	Metolachlor	14	0.00	1.06	1.65	3.86
A	Ditch	Quinclorac	17	3.93	5.33	8.81	37.36
A	Reservoir	Quinclorac	15	0.38	0.49	0.58	1.38
B	Ditch	Quinclorac	16	0.65	3.10	6.69	27.08
B	Reservoir	Quinclorac	18	0.43	0.53	0.88	3.91
C	Ditch 2	Quinclorac	17	0.75	0.70	0.52	2.00
C	Ditch 3	Quinclorac	16	1.44	2.29	2.99	12.72
C	Ditch 5	Quinclorac	20	1.22	2.89	4.95	21.94
C	Reservoir	Quinclorac	20	0.94	0.94	0.13	0.61
D	Ditch	Quinclorac	15	0.98	3.13	5.86	18.73
D	Reservoir	Quinclorac	15	0.58	0.83	0.95	2.33
E	Ditch	Quinclorac	16	5.21	10.54	15.87	63.07
E	Reservoir	Quinclorac	19	0.84	1.70	1.63	6.26
F	Ditch	Quinclorac	14	2.94	7.54	13.42	43.35
F	Reservoir	Quinclorac	16	0.59	0.76	0.85	2.06
G	Ditch	Quinclorac	15	7.14	10.19	15.50	59.67
G	Reservoir	Quinclorac	14	1.43	1.43	0.87	2.37

in 4 river networks in the region, including the Cache. In that study, concentrations decreased moving downstream, with increasing flow in the rivers. However, the finding that ditches and reservoirs have different magnitudes of herbicide concentrations is in contrast with previous findings for nutrient concentrations and other water quality parameters (Moore et al., 2015). In a 13-month study of another tailwater recovery system in the region, no difference in water quality was observed between ditches and reservoirs.

Clomazone, metolachlor, and quinclorac all exhibited a spring flush trend in the monitored tailwater recovery systems, with concentrations peaking in April – June across all sites (Figure 2). This period coincides with heavy precipitation in the region (Figure 3), immediately following or overlapping the bulk of annual herbicide application. Peak clomazone concentrations were observed in April, with few remaining detections by August. Quinclorac and metolachlor concentrations peaked in June, and these compounds were more persistent, with frequent low-level detections continuing through August.

Conclusions

Herbicides applied to fields adjacent to tailwater recovery systems were readily detectable in ditches and reservoirs during the 2017 growing season. The highest concentrations were detected during the "spring flush" when precipitation events immediately follow or overlap herbicide application. Concentrations were consistently higher in ditches than in reservoirs, up to an order of magnitude for single events. These findings support the following recommendations to minimize risk of cross-crop contamination when using recovered tailwater for irrigation: 1) source irrigation water only out of reservoirs and 2) always cycle recovered tailwater through the reservoir for treatment of residual herbicides. Before it can be determined if any of the concentrations detected represent high-risk events for cross-crop contaminations, more information is needed about how common crops like soybean, rice, or cotton respond to off-target exposure to residual herbicides in irrigation water across a range of concentrations. Further, study findings support the current non-growing season focus of proposals to use on-farm reservoirs as supply water for artificial groundwater recharge, as the periodically elevated concentrations of herbicide residues during the growing season may be deemed hazardous by regulatory bodies.

Continued work on the project will assess the non-growing season residual herbicide concentrations in the monitored on-farm storage reservoirs. This study initiated a herbicide monitoring record that provides data needed to assess costs and benefits of tailwater recovery systems, a best management practice with the potential to preserve Arkansas' groundwater resources into the future. The United States Geological Survey and others can use this dataset to
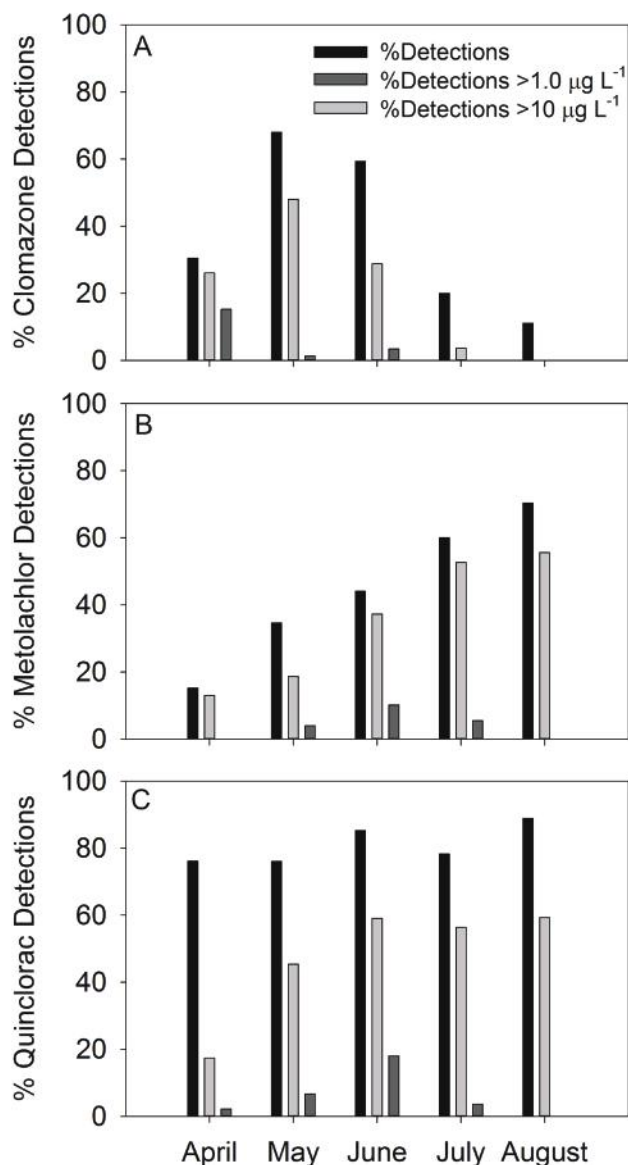
Figure 2. Frequency of all detections, detections > 1.0 ug L^{-1}, and detections > 10 ug L^{-1}, expressed as a percentage of the total number of samples for the month, during the period April – August 2017 for A) clomazone, B) metolachlor, and C) quinclorac.
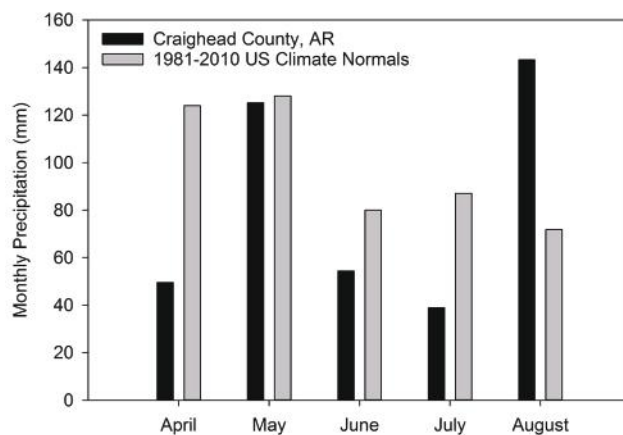

Figure 3. Monthly precipitation measured in Craighead County, Arkansas during April – August 2017 and U.S. precipitation normals for the region averaged over 30 years between 1981-2010 (NOAA, 2018).

improve models of herbicide fate and transport to include the mitigation potential of tailwater recovery systems to reduce herbicide loads from agricultural lands to the Mississippi River Basin.

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Image caption: Rice field in Arkansas. Photo from Valley Irrigation.

Assessment of Strategies to Address Future Irrigation Water Shortage in the Arkansas Delta

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Abstract: Conversion to surface water irrigation has been identified as one of the critical initiatives to address the decline in groundwater supply in Arkansas. Using the Arkansas Irrigation Use Survey conducted by the PIs with collaborators, this study uses statistical analysis to estimate Arkansas agricultural producers' willingness to pay (WTP) for off-farm surface water and examine which factors have predictive powers of producers' WTP for irrigation water. The estimated mean WTP for irrigation water is $33.21/acre-foot. Comparison indicates a significant share of producers are likely to have higher WTPs for surface water than the average pumping cost in the study area. Producers located in areas with less groundwater resources have higher WTPs. Producers that are more concerned with a water shortage occurring in the state in the next 10 years have higher WTPs. A somewhat unexpected result is that participation in the Conservation Reserve Program predicts lower WTPs. One possible explanation is that farmers see the transfer of land out of crop production as a more viable financial decision when groundwater supply decreases.

Key Points:
- More than 70% of sampled producers in Arkansas are likely to be willing to pay more than the average pumping cost of groundwater to purchase surface water from an irrigation district.
- The level of willingness to pay for surface water is positively correlated with the extent of groundwater shortage as perceived by producers.
- The existence of other conservation programs may lower the level of willingness to pay for surface water.

Assessment of Strategies to Address Future Irrigation Water Shortage in the Arkansas Delta

Introduction

Irrigation is the most important input in Arkansas's crop production. Nearly 86% of irrigation water in Arkansas in 2013 was sourced from groundwater in the Mississippi River Valley alluvial aquifer (MRVAA, NASS, 2014; Schrader 2008). However, the continuous and unsustainable pumping has put the MRVAA in danger by withdrawing at rates greater than the natural rate of recharge. In the 2014 Arkansas Water Plan by the Arkansas Natural Resources Commission (ANRC), an annual gap in groundwater as large as 8.6 billion cubic meters (7 million acre-feet) is projected for 2050 and most of the expected shortfall is attributed to agriculture (ANRC, 2015). To combat growing projected scarcity, two critical initiatives have been identified: conservation measures to improve on-farm irrigation efficiency and infrastructure-based solutions to convert to surface water (ANRC, 2015). Surface water in Arkansas is relatively abundant and is allocated to farmers based on riparian water rights. The ANRC (2015) estimates that average annual excess surface water available for interbasin transfer and non-riparian use is about 7.6 million acre-feet. Currently, the purchase of off-farm surface water is relatively rare in Arkansas. In the Farm and Ranch Irrigation survey conducted by the National Agricultural Statistics Service (NASS) of the USDA, only 4.82% of all farms reported utilization of off-farm surface water in Arkansas in 2012 (NASS, 2014).

In total, ANRC (2015) estimates that the construction of needed infrastructure to shift groundwater irrigation to surface water irrigation in the nine major river basins of eastern Arkansas will cost between $3.4 and $7.7 billion. Financing these projects has grown increasingly difficult because of decreases in the availability of federal grants, cost-share and loans (ANRC, 2015). As such, understanding the nature of water use and quantifying the full value of irrigation water to agricultural producers in the Delta will be critical for continued funding and long-run success of irrigation district projects, as well as the long-run viability of agricultural production in Arkansas.

This study has two objectives: 1). to estimate Arkansas agricultural producers' willingness to pay (WTP) for off-farm surface water; 2). to examine which factors have predictive powers of producers' WTP for irrigation water. This study is the first to provide estimates of Arkansas producers' WTP for irrigation water. In areas where infrastructure needs to be constructed to deliver surface water, estimates of the economic value of irrigation water to producers would be needed to conduct cost-benefit analysis of such projects as well as assess the financial viability of surface water irrigation systems. Our research findings also help water policy makers design polices to facility infrastructure projects that bring surface water to farming communities in Arkansas.

Methods

The data set comes from the Arkansas Irrigation Use Survey conducted by the PIs with collaborators from Mississippi State University. The survey was completed in October 2016 via telephone interviews. Potential survey respondents come from the water user database managed by the ANRC and all commercial crop growers identified by Dun & Bradstreet records for the state of Arkansas. The final sample size is 199 producers that completed the survey in its entirety.

The key information used in this study comes from the WTP section. Each producer first answered an initial question "Would you be willing to pay $___ per acre-foot of water to purchase water from an irrigation district?" When a respondent answered "yes" ("no"), the question was repeated at a higher (lower) bid value with a 50% increment; by increasing the interval between the first and second bid as the initial bid level increase we control for acquiescence bias (Alhassan et al., 2013; Lee et al. 2015). For respondents who answered "no" to the initial bid and "no" to the following lower bid, a third WTP question with a nominal bid amount of 50¢/acre-foot was used to determine whether true WTP was zero or if the respondent was offering a protest bid. To reduce starting point bias, when a respondent was interviewed, one out of the six values in the unit of $/acre-foot (10, 20, 30, 40, 50, 60) was randomly selected to ask the producer (Aprahamian, Chanel and Luchini 2007; Flachaire and Hollard 2006). This range of values was tested in a pilot survey and confirmed as appropriate. The responses to the questions are summarized in Table 1.

The mean WTP, E(WTP), is related to the cumulative density function, F(·) as

$$E(\text{WTP}) = \int [1 - F(b)] \mathrm{d}b \qquad (1)$$

where b is any positive amount of money and F(b) is Prob(WTP≤b). With the assumption of a logistic distribution,

$$\text{Prob}(\text{WTP} \leq b) = 1/[1 + \exp(-\alpha - \beta b - z'\delta)] \qquad (2)$$

where z is the vector of variables that measure farm and producer characteristics such as farm location, total irrigated acres, crop mix, year of farming, gross income, education, producers' awareness of and past participation in conservation programs and producers' rating of the severity of water shortage in Arkansas. Using equations (1) and (2), the mean WTP can be imputed as (Koss and Khawaja, 2001):

$$E(\text{WTP}) = -\ln[1 + \exp(\alpha + z'\delta)]/\beta \qquad (3)$$

The parameters needed to calculate WTP, α, β and δ, are estimated using the method of maximum likelihood estimation

Table 1. Number of Yes and No Responses at Each Bid Level.

		Bid	Yes	(%)	No	(%)	Total Responses
Bid Set 1	**Lower bid:**	0.4¢/m³ ($5/aft)	2	(0.33)	4	(0.67)	
	Initial bid:	0.8¢/m³ ($10/aft)	14	(0.70)	6	(0.30)	20
	Upper bid:	1.2¢/m³ ($15/aft)	10	(0.71)	4	(0.29)	
Bid Set 2	**Lower bid:**	0.8¢/m³ ($10/aft)	5	(0.63)	3	(0.38)	
	Initial bid:	1.6¢/m³ ($20/aft)	5	(0.38)	8	(0.62)	13
	Upper bid:	2.4¢/m³ ($30/aft)	4	(0.80)	1	(0.20)	
Bid Set 3	**Lower bid:**	1.2¢/m³ ($15/aft)	5	(0.56)	4	(0.44)	
	Initial bid:	2.4¢/m³ ($30/aft)	9	(0.50)	9	(0.50)	18
	Upper bid:	3.6¢/m³ ($45/aft)	5	0.56	4	(0.44)	
Bid Set 4	**Lower bid:**	1.6¢/m³ ($20/aft)	7	(0.44)	9	(0.56)	
	Initial bid:	3.2¢/m³ ($40/aft)	9	(0.36)	16	(0.64)	25
	Upper bid:	4.9¢/m³ ($60/aft)	6	(0.67)	3	(0.33)	
Bid Set 5	**Lower bid:**	2.0¢/m³ ($25/aft)	5	(0.38)	8	(0.62)	
	Initial bid:	4.1¢/m³ ($50/aft)	5	(0.28)	13	(0.72)	18
	Upper bid:	6.1¢/m³ ($75/aft)	2	(0.40)	3	(0.60)	
Bid Set 6	**Lower bid:**	2.4¢/m³ ($30/aft)	3	(0.23)	10	(0.77)	
	Initial bid:	4.9¢/m³ ($60/aft)	7	(0.35)	13	(0.65)	20
	Upper bid:	7.3¢/m³ ($90/aft)	1	(0.14)	6	(0.86)	

*Out of the 199 producers that completed survey, 6 respondents refused to answer both WTP questions and 1 refused to answer the second bid level. Twenty-four respondents answered "no" to this third question. Of the remaining 169 respondents, 54 registered "don't know" responses to one or more of the proposed bid levels. All three groups of respondents were excluded from analysis. In total, 114 respondents were retained for final analysis.

(MLE). In MLE, the log likelihood function, the sum of the probabilities of observing each data point in the log form, is maximized. For each observation, a "yes" response to the question "Would you be willing to pay $___ per acre-foot of water to purchase water from an irrigation district?" means a respondent's WTP is greater than or equals the amount listed in the question (Hanemann, Loomis and Kanninen, 1991; Koss and Khawaja, 2001). The estimation is done using the STATA statistic software package. Summary statistics of variables are reported in Table 2.

Results and Discussion

Table 3 reports the results of the MLE estimation. If the sign of the estimated coefficient of a variable is positive, it means the variable has a positive effect on the level of WTP. The size of the effect of a variable on WTP is determined by the size of its coefficient as well as the coefficients of other variables. The coefficient of the bid variable is negative and statistically significant at the 1% level, indicating that respondents are more likely to say no to a large bid. A producer located east of Crowley's Ridge is less likely to say yes to any bid. This is probably because

groundwater resources are more abundant in areas east of Crowley's Ridge and so producers are likely to exhibit lower WTP. The coefficient of respondent's rating of groundwater shortage in the state is positive and statistically significant at the 5% level, indicating greater willingness to pay for irrigation water when groundwater resources are perceived as scarce. Respondents who indicated awareness of Arkansas' tax credit program for construction of on-farm surface water infrastructure display a greater likelihood to answer yes to a higher bid. These results highlight the importance of increasing extension efforts to raise awareness of growing and long-term groundwater scarcity in the Delta as well as providing information that explains financial or technical assistance available to farmers who wish to transition to surface water irrigation.

A somewhat unexpected result is that Arkansas producers' WTP for irrigation water from irrigation districts decreases if they have participated in or are currently enrolled in the CRP. Previous studies have shown that producers who participate in conservation programs, such as the CRP, have better access to conservation information and make production decisions based on the impact of their choices

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Table 2. Variable Definitions and Summary Statistics.

Variable	Description	Mean	St. Dev.	Min.	Max.
Crowley's Ridge	Binary variable where 1 = lives in a county to the east (in part or fully) of Crowley's Ridge, 0 = not	0.342	0.477	0	1
Years Farming	Total years of farming experience	30.91	14.41	1	60
Years Farming, Squared	The square of total years of farming experience	1161.35	909.89	0	3,600
Gross Income	Binary variable where 1 = gross income from all sources is greater than $75,000 and less than or equal to $150,000, 0=not	0.412	0.494	0	1
Percent Farm Income	Percent of gross income from farming	81.69	26.23	0	100
Bachelor's or Higher	Binary variable where 1 = education greater than or equal to a Bachelor's degree, 0 = not	0.561	0.498	0	1
Total Hectares	Total irrigated in 2015	939.2	774.5	0	4,046.80
Percent Rice	Percent irrigated rice production of total hectares in 2015	27.51	26.42	0	100
Percent Soybean	Percent irrigated soybean production of total hectares in 2015	53.93	27.37	0	100
Awareness of State Tax Credit	Binary variable where 1 = is aware of state tax credit program, 0 = not	0.483	0.502	0	1
Conservation, CRP	Binary variable where 1 = has participated in the Conservation Reserve Program, 0 = not	0.491	0.502	0	1
Groundwater Shortage	Respondent rating of the severity of water shortage in Arkansas, from 0=no shortage to 5=severe shortage, in the state	2.66	1.96	0	5

in future periods (Lubbell et al., 2013). One possible explanation for this finding is that farmers see the transfer of land out of crop production as a more viable financial decision when groundwater supply decreases. The squared term of years of farming experience is added to investigate if it has a nonlinear effect on WTP. The estimated coefficients are both statistically significant at 1%. The coefficient of years of farming experience is positive and that of the squared term is negative, revealing an inverted U-shaped relationship between years of farming experience and WTP. The values of estimated coefficients indicate that the turning point is 38. That is, in contrast to findings from previous studies that age is strictly negatively correlated with WTP for irrigation water (Mesa-Jurado et al., 2012), we find that WTP for water from irrigation districts increases with years of farming experience until approximately 38 years of experience, after which, WTP decreases with years of farming experience.

The estimation results are used to derive the willingness to pay for each observation. Of producers sampled, the minimum WTP is $3.09/acre-foot and the maximum WTP was $78.98/acre-foot. The mean WTP is $33.21/acre-foot (Table 4). One important finding is that for a significant share of the producers, the estimated WTP for surface water is likely to be greater than the energy cost they are currently paying to pump groundwater from the Aquifer. The Arkansas Irrigation Use Survey did not collect information on pumping cost by producer. Using the data on the depth-to-groundwater from the Natural Resources Con-

Table 3. Maximum Likelihood Estimation Results.

	Coefficient	Standard Error
Intercept	-1.684	1.382
Bid	-0.0615***	0.008
Crowley's Ridge	-1.0586**	0.436
Years Farming	0.2124***	0.066
Years Farming, Squared	-0.0029***	0.001
Gross Income	0.460	0.399
Percent Farm Income	-0.193	0.764
Bachelor's or Higher	0.504	0.424
Total Irrigated Hectares	-0.0001**	4.05E-5
Percent Rice	-0.101	0.942
Percent Soybean	0.820	0.942
Awareness of State Tax Credit	1.1214***	0.418
Conservation, CRP	-1.1974***	0.419
Groundwater Shortage	0.2044**	0.099

***significant at 1%, **significant at 5%, and * significant at 10%

servation Service (Swaim et al., 2016) and energy prices, we calculate the pumping cost producers are currently paying to pump groundwater out. About 72% of our sample producers use both electric and diesel pumps, 12% uses electric pumps and 13% uses diesel pumps. For most producers, it is more expensive to pump using diesel fuel. The price of diesel used for the calculations is $3.77/gallon, which is about

Table 4. Willingness to Pay (WTP) and Average Groundwater Pumping Cost.

Region	Average Depth-to-groundwater [a]	Estimated Cost of Pumping [b]	Estimated WTP	Percentile in the Distribution of Estimated WTPs
Arkansas Delta	12.3m (40.49 ft)	1.8¢/m^3 ($22.17/acft)	2.7¢/m^3 ($33.21/acft) [c]	29th
Lonoke County (greatest average depth-to-groundwater in Arkansas)	25.6m (83.35 ft)	3.7¢/m^3 ($45.62/acft)	3.4¢/m^3 ($42.03/acft) [d]	72nd
Mississippi County (lowest average depth-to-groundwater in Arkansas)	4.9m (16.22 ft)	0.7¢/m^3 ($8.9/acft)	2.0¢/m^3 ($24.81/acft) [d]	5th

a. Data on the depth-to-groundwater are obtained from Arkansas Natural Resources Commission (Swaim et al. 2016).
b. Pumping cost is computed using the average depth-to-groundwater and the cost of diesel fuel reported by the Energy Information Administration.
c. Mean WTP is reported.
d. Due to small sample size in each of the two counties, median WTP is reported.

the 80th percentile of the weekly diesel prices between 1994 and 2016 reported by the US Energy Information Administration. Thus our estimates of pumping cost are on the high end of the distribution of pumping costs. The estimated pumping cost for the Arkansas Delta is $22.17/acre-foot, which is about the 29th percentile using the distribution of the estimated WTPs. This means 71% of the sample producers have estimated WTPs higher than the estimated average pumping cost.

The comparison is also carried out for Lonoke County, which is located to the west of Crowley's Ridge and has the greatest average depth-to-groundwater in Arkansas. Although the median WTP is lower than the average pumping cost ($42.03/acre-foot versus $45.62/acre-foot), 28% of the sample producers have estimated WTPs higher than the estimated average pumping cost in the county with the greatest average depth-to-groundwater. Mississippi County is located east of Crowley's Ridge, where the average depth-to-ground water is as shallow as 16 feet and pumping costs rarely exceed $9/acre-foot. The estimated median WTP is $24.81/acre-foot, much higher than the average pumping cost of $8.9/acre-foot. Thus, even in areas of the state where groundwater is most abundant, producers' WTP for surface water is likely to exceed the energy cost paid to pump groundwater from the aquifer.

Conclusions

The most significant finding of this study is that for the majority of the sample producers, their estimated WTPs for surface water are likely to be greater than the average pumping cost of groundwater producers are currently paying. Our study also identifies a set of factors that influence producers' WTP. For example, higher awareness of water shortage problems seems to predict increases in producers' WTP for irrigation water. This finding highlights the importance of continued outreach by the extension service to increase awareness of water problems in Arkansas. While producers are aware of growing state-level groundwater

scarcity, few producers believe that scarcity is a problem which directly impacts their farm operations.

The finding that participation in the CRP decreases WTP could have important policy implications. While large water savings could be achieved by increasing producers' awareness of the CRP, such practices may also decrease the level of producers' WTP for water from irrigation districts. If the downward influence on the WTPs of such programs is to the extent that irrigation districts cannot set the price of surface water to a level that allows them to recover the cost of delivering water, then the financial viability of such projects may be hampered. Similar conflict may also arise between conservation programs that focus on improving irrigation efficiency and programs that focus on conversions to surface water. Both types of programs would positively impact the health of the Aquifer by reducing groundwater use or moving producers towards surface water resources. However, the effectiveness or viability of one program may be negatively influenced by the existence of the other program. If such changes limit the revenue earned by irrigation districts, the financial viability of such projects may also be limited. Policymakers and extension need to take such unintended consequences into account when promoting these programs. For example, conservation programs that focus on improving irrigation efficiency may be more fruitful in areas where conversion to surface water is not an option (e.g., due to lack of infrastructure).

Acknowledgements

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Image caption: On-farm water storage ponds can be used for irrigation. Photo from Open Rivers.

Tracking the Growth of On-Site Irrigation Infrastructure in the Arkansas Delta with Remote Sensing Analysis

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Abstract: Surface water impoundments built on farms to store water in the wet season for irrigation later in the year are one approach to reduce groundwater pumping and to sustain aquifers. However, there is limited information on where and how many of these reservoirs are present in Eastern Arkansas. This information would be useful to formulate effective policies to encourage the construction of more surface water systems. Analysis of Landsat imagery from 1995 to 2015 provides evidence for where and when reservoirs and tail-water recovery systems are present, doing so with annual resolution. Comparing our analysis – which extends the Dynamic Surface Water Extent (DSWE) algorithm for Landsat to identify irrigation storage reservoirs in Arkansas County – to the verified locations of these surface water impoundments, the analysis identifies 98% of all reservoirs in the verified study area.

Key Points:
- Publicly available imagery can identify on-farm surface water storage in Eastern Arkansas.
- The algorithm developed to identify the facilities for surface water storage identifies more than 98% of verified reservoirs.

Introduction

The sustainability of the Mississippi River Valley Alluvial Aquifer (MRVAA) is vital to maintaining long-term agricultural profitability in Arkansas (Maupin and Barber, 2005; Konikow, 2013). The extent of the aquifer includes seven states, and Arkansas is the largest consumer of water from the aquifer (Maupin and Barber, 2005). Although Arkansas has often been considered an area rich in water resources with annual precipitation amounts ranging from approximately 50 to 57 inches (NOAA, 2014), there are several key constraints to maintaining agricultural profitability in the region. The first is lack of timely rainfall, and the second is the increasing need for irrigation. The number of irrigated acres continues to increase in Arkansas in order to maintain and increase yields and mitigate risk as a result of recurring drought conditions (Vories and Evett, 2010). Moreover, most irrigated acres result from producers privately funding the installation of irrigation wells that draw groundwater from the MRVAA. It is known that the current rate of withdrawals from the aquifer is not sustainable, especially as the number of irrigated acres continues to increase each year (Barlow and Clark, 2011; ANRC, 2012; Evett et al., 2003).

The Agricultural Act of 2014 (or 2014 U.S. Farm Bill) introduced the Regional Conservation Partnership Program (RCPP) which consolidated several programs including the Mississippi River Basin Healthy Watersheds Initiative, Environmental Quality Incentives Program (EQIP) and the Conservation Stewardship Program (CSP), in order to promote coordination between Natural Resources Conservation Service (NRCS) and its partners and provide technical and financial assistance to producers and landowners. These federal and state programs encourage more efficient and effective irrigation and have contributed to the voluntary implementation of water conservation practices such as tail-water recovery ditches, on-farm storage reservoirs, and use of sensor technologies, to name a few. Despite the prevalence of programs that are targeted to help farmers sustainably manage agro-ecosystems in Arkansas, the level of information about the use of these management practices and technologies is less than ideal and can be improved significantly. We do not yet know how much adoption of water conservation measures has already occurred and to what extent these various water conservation measures reduce pumping pressure on the MRVAA. This lack of knowledge is a pressing problem, especially as federal incentive programs face increased public scrutiny. We need to determine if conservation practices are effective at reducing groundwater declines in the MRVAA and also which practices are most frequently adopted and retained by farmers.

While the National Agricultural Statistic Service (NASS) does collect some data on water conservation practices, they depend on problematic sampling techniques when only a small proportion of producers use a practice, which is the case for on-site water storage and tail-water recovery. Further, NASS data do not disclose the location of the producer adopting a practice, and this prevents a full assessment of available surface water and what spatial features of the landscape might have caused the producer to adopt the practice. The objective of this research is to understand the construction of on-site water storage and tail-water recovery systems over time in the critical groundwater area of Arkansas County. Using various sources of multispectral imagery and aerial photography, we aim to identify and map the spatial extents of on-site water storage in the area and to attribute construction dates in a GIS database layer.

Methods

Data

Because of its continuous operation over the last several decades and its frequent return times, Landsat satellite imagery was used to track the construction of on-site irrigation storage reservoirs. Using the United States Geological Survey (USGS) EarthExplorer tool, we acquired all Landsat scenes overlying a study area of Arkansas County, Arkansas between January 1995 and December 2015. Landsat data are multispectral images with a spatial resolution of 30 meters and a return time of 16 days. Landsat-based methods for identifying on-site water storage are cost-effective, time-efficient, reliable, and easily repeatable.

Water Identification

In order to make the initial classification of all surface water we use the Provisional Dynamic Surface Water Extent (DSWE) algorithm developed by USGS (Jones and Starbuck, 2015; Jones, 2015). The identified scenes were pre-processed using the provisional DSWE algorithm which classifies water and non-water pixels in the Landsat imagery according to their surface reflectance and slope characteristics. Primary inputs to the algorithm are a Digital Elevation Model (DEM) and the Landsat reflectance bands for Blue, Green, Red, NIR, SWIR1, and SWIR2, along with the CFMASK band used to filter cloud and cloud shadow (Jones and Starbuck, 2015).

Extending the Algorithm for Reservoir Identification

Using Python and the arcpy library, all non-water pixels, including cloud and shadow, were reclassified to a value of "0" while all pixels identified as water were assigned a value of "1". This was done for each scene between 1995 and 2015. With only surface water pixels containing values, we use TerrSet Geospatial Monitoring and Modeling software in combination with Python to apply filters based upon size and shape characteristics. Using TerrSet's Group function, clusters of water pixels were identified as bodies of water and all pixels in a water body were assigned an ID value for

that body of water. The Area and Perim functions calculated the area and perimeter of each grouped and identified water body, assigning these values to each pixel in a group. We characterize shape using a measure for compactness ratio and TerrSet's cratio function. Using the area and perimeter layers as inputs, the cratio function calculates the square root of the ratio of the area of the polygon to the area of a circle having the same perimeter as that of the polygon. This value is assigned to each pixel in a group.

We use Python and the arcpy library to filter out bodies of water with size and shape traits that are uncharacteristic of on-site irrigation storage reservoirs. Data on the characteristic size of reservoirs were obtained from both a 2016 survey (Edwards, 2016) and communication with Charolette Bowie of the USDA Natural Resources Conservation Service (NRCS) in Lonoke, Arkansas. The USDA-NRCS administers the EQIP program and maintains records on the construction of irrigation reservoirs under the cost-share program. Based on the information obtained from these sources, bodies of water smaller than 2.5 acres and larger than 600 acres were removed from all scenes.

Features with a high compactness ratio have a high likelihood of being man-made (McKeown and Denlinger, 1984). Because some of the constructed reservoirs do have organic, natural, shape qualities, we apply a minimal level of filtering based upon compactness. We do this primarily to eliminate streams and rivers with the lowest compactness ratios. Bodies of water with a compactness ratio less than .005 were removed from all scenes. For each scene, we executed a BooleanAnd operation, keeping surface-water pixels that satisfied both the area and compactness criteria. The results of this operation represent potential reservoirs in each individual scene.

The three-month period of March, April, and May is the wettest period of the year, and being prior to the growing season, irrigation storage reservoirs are likely to be most full. Interpreting Landsat scenes in these months is complicated by the presence of cloud cover (Kaufman, 1987; Ju and Roy, 2008). Due to this, we created a composite of probable reservoirs for the period (March – May) by taking the union of all algorithm-processed scenes within the calendar period, doing this for each year (1995 – 2015). Compositing of Landsat images provides a method for addressing data gaps resulting from cloud cover (Roy et al., 2010; Wulder et al., 2011). Probable reservoirs missing in one scene due to cloud cover are likely to be captured in the composite by another scene. Figure 1 summarizes the extended algorithm, while supplemental material reports the Landsat scenes used in constructing each of the annual composites.

Verification and Construction of Annualized Reservoir Data Layer

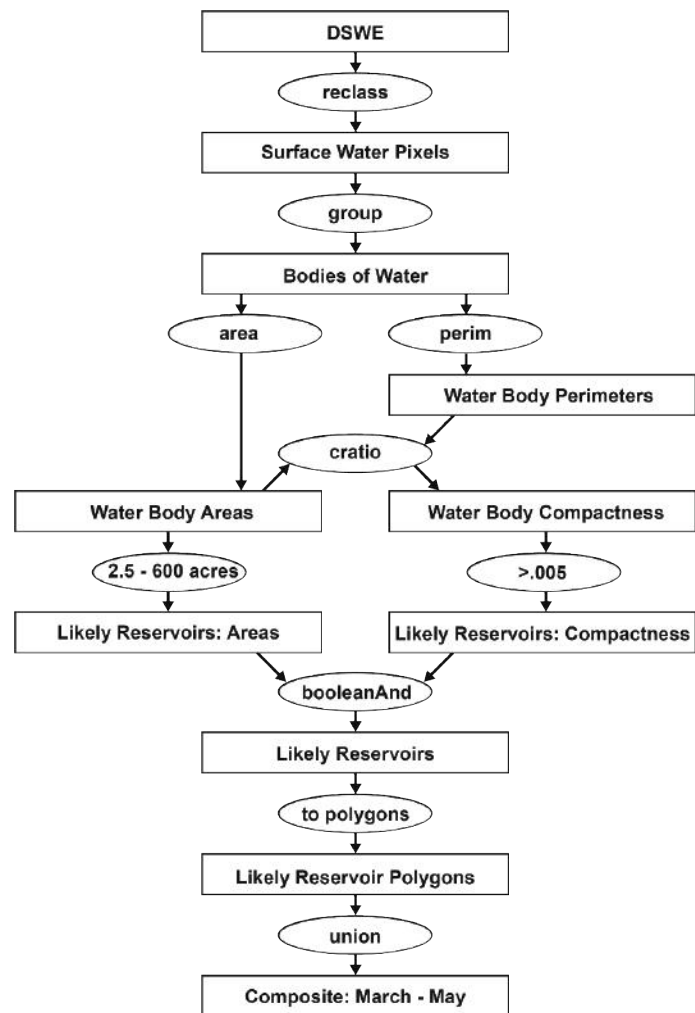High-resolution imagery from the National Agriculture

Figure 1. This summarizes the algorithm used to process Landsat scenes for identifying irrigation storage reservoirs. It takes scenes processed using the U.S. Geological Survey's Provisional Dynamic Surface Water Extent (DSWE) algorithm and extends that using spatial and temporal constraints (Jones and Starbuck, 2015; Jones, 2015). Rectangles in the figure represent data layers used or created in the algorithm, while ovals represent operations applied using Python and GIS.

Imagery Program (NAIP) and Google Earth were necessary to identify tail-water recovery ditches and verify the presence of irrigation storage reservoirs. Mary Yeager and Michele Reba with USDA Agricultural Research Service (USDA-ARS) recently used these imagery sources and manual methods to identify and map irrigation storage reservoirs with tail-water recovery ditches for 2015 in the Cache and Grand Prairie areas, including Arkansas County. Though Yeager and Reba were not able to produce an annualized data layer, they do use NAIP imagery and historical imagery from Google Earth to verify reservoirs for each of the years 1996, 2000, 2006, 2009, 2010, and 2013, in addition to 2015.

We use this layer to assess the accuracy of reservoir identification for our extension of the DSWE algorithm and to aid in verifying annual reservoir locations. For each year verified manually, reservoir extents were compared to annual composites from the matching year. We also construct an

annualized reservoir data layer using the annual composites, verified years, and some cases of deductive reasoning. We create Boolean identifiers in a GIS data layer to indicate the presence of a reservoir in a given year from 1995 to 2015.

Results

We compare probable reservoirs from the conceptual model (annual composites) to available years of verified reservoir locations. Table 1 reports the results of the algorithm accuracy assessment using manually verified years. The percentage of the manually verified reservoirs that were identified by matching annual composites ranged from 95.7% to 99.1% for the seven years included in the assessment. The most accurate composite was 2013 where 221 of 223 reservoirs were identified by the algorithm. The composite for 1996 failed to identify the largest number of reservoirs, missing seven, and was the least accurate by percentage identified. Between 2000 and 2006, the number of reservoirs increased by 30 which is the largest increase between verified years. It is also the longest period without available high-resolution imagery.

Table 2 reports the percentage of water bodies from the outputs of the conceptual model that positively identify verified reservoirs. On average, approximately 10% of probable reservoirs detected by the model proved to be actual reservoirs in the verified layer. The least accurate model year was 2006 (5.1% positive identification), while 2015 was more than twice as accurate as the average (20.3% positive identification). We construct an annualized GIS reservoir data layer for Arkansas County (Figure 2) using annual composites and verified years. Between 2000 and 2001 and between 2002 and 2003 there were 10 new reservoirs constructed, making these the most significant single years for growth in on-site irrigation storage infrastructure. In total, 69 storage reservoirs were constructed in Arkansas County from 1995 to 2015, with a majority built during the first 10 years of that period.

Conclusions, Recommendations and Benefits

We develop an algorithm using Landsat imagery that is more than 98% accurate at identifying verified surface water reservoirs. This algorithm is useful for application to future imagery without undertaking expensive travel to verify the presence of the reservoirs or to identify the presence of a reservoir not readily visible from public roadways. The ability to employ an accurate algorithm with Landsat imagery enables manual verification using high-resolution imagery to be much more feasible. In addition, the algorithm works with public Landsat imagery that is available at high frequencies. This could allow a temporally more granular investigation of the water levels at these storage systems to help irrigation specialists understand how these systems are in use throughout the year. The information gathered about the storage systems is useful for tailoring programs and policies to encourage more surface water use for irrigation and to help stabilize the aquifer levels in Eastern Arkansas.

We note that feedback obtained about the characteristic size of reservoirs indicated substantial variability in the depth and constructed dimensions of reservoirs. This fact, along with the prevalence of organically shaped reservoirs, meant that Landsat-based methods were inadequate for estimating reservoir storage volumes. Furthermore, the algorithm is only roughly accurate at the reservoir scale for identifying the presence of reservoirs. This fact decreases confidence that estimated reservoir areas are accurate enough to report. Future research to complement the imagery information is to collect data on the groundwater levels, weather patterns, and producer characteristics near the farms where the storage systems are present. This should help us to identify which of the factors that potentially drives the adoption of these systems plays the greatest role. A pilot survey or a series of focus groups might provide this information for the areas where clusters of the storage systems are present and built with greater frequency over the past few years.

Table 1. Accuracy Assessment, Percentage of Verified Reservoirs Identified. This summarizes the results of the accuracy assessment comparing annual composites to years with verified reservoir layers (Type II error).

NAIP-verified years	Number of verified reservoirs	Number identified by matching composite	Percentage Identified by composite
1996	164	157	95.70%
2000	176	171	97.20%
2006	206	204	99.00%
2009	215	212	98.60%
2010	219	215	98.20%
2013	223	221	99.10%
2015	229	225	98.30%

Table 2. Accuracy Assessment, Percentage of Model Water Bodies Identifying Verified Reservoirs. This summarizes the results of the accuracy assessment comparing annual composites to years with verified reservoir layers (Type I error).

NAIP-verified years	Total water bodies identified by model	Number positively identifying verified reservoirs	Percentage identifying verified reservoirs
1996	2476	150	6.10%
2000	1862	152	8.20%
2006	3763	193	5.10%
2009	2031	207	10.20%
2010	2597	201	7.70%
2013	2358	208	8.80%
2015	1115	226	20.30%

NUMBER OF RESERVOIRS
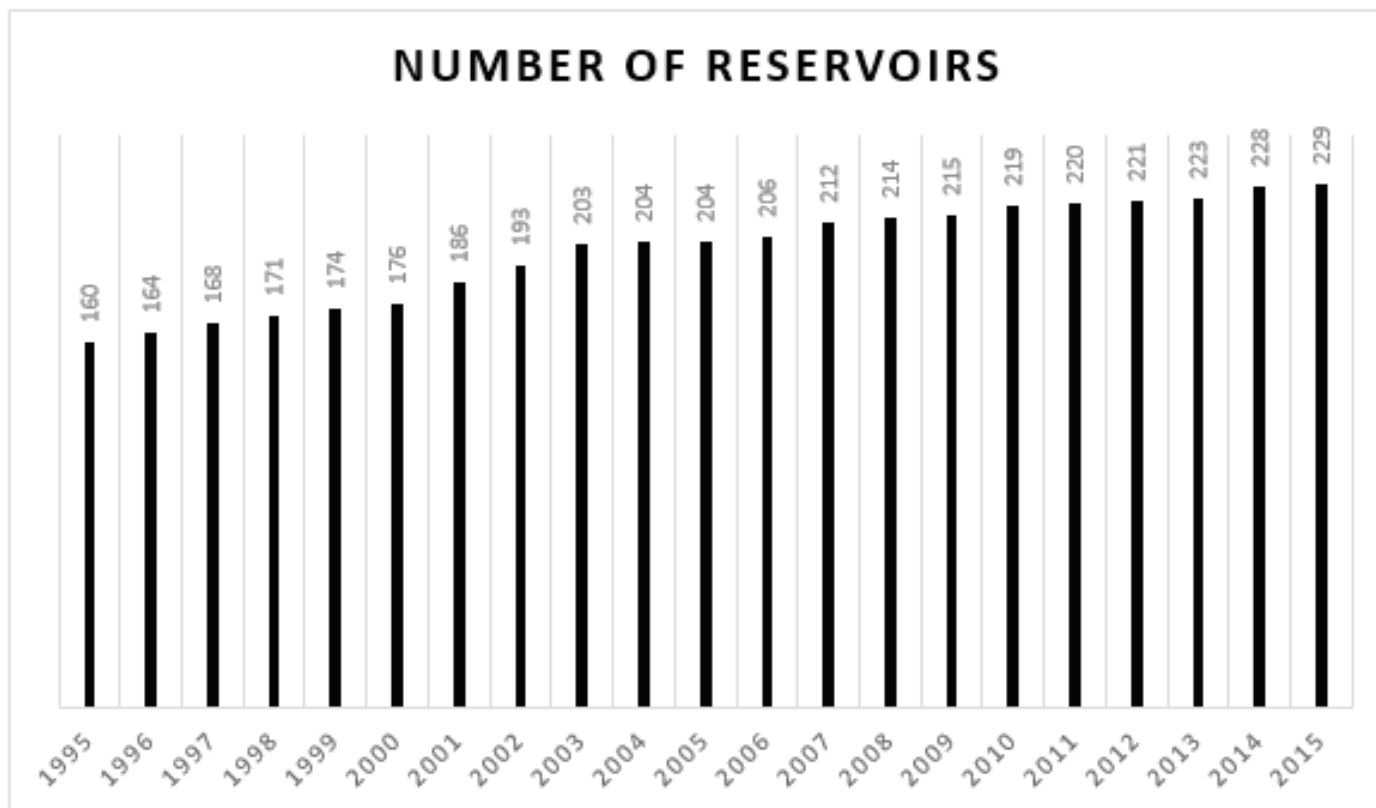
Figure 2. Reservoirs in Annualized GIS Data Layer.

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Supplement: Annual Composite Scene Lists

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LC80240362015148LGN00_b1
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Image caption: Post-doctoral research associate, Beatriz Moreno Garcia, works with the Eddy Covariance equipment in a rice field in the Arkansas Delta. Garcia works for Dr. Benjamin Runkle, University of Arkansas professor of Biological and Agricultural Engineering.

Regionalizing Agricultural Field Evapotranspiration Observations

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Abstract: This project aimed to quantify evapotranspiration (ET) estimates in different agricultural production systems in Arkansas as part of a broader strategy to understand and improve upon the over-consumption of groundwater in the state. The project team directly observes ET in a cotton and several rice fields over different growing seasons. These measurements are taken with the eddy covariance method, compared to the Penman-Monteith model, and are also taken with a more experimental method called "surface renewal". Growing season ET is determined to be 567-636 mm in the rice fields and 555-615 mm in the cotton field. The Penman-Monteith model over-estimated ET, with estimates ranging from 752-835 mm. The surface renewal method was within 10-20% of eddy covariance estimates, encouraging its broader adaptation as a more cost-effective ET observation method. Quantifying ET will be helpful to quantify the dynamics of the crop water use. By knowing the water use dynamics we can follow up with questions about how to save water and associated pumping costs. The project findings are contextualized through inclusion in a growing, multi-institution network named Delta-Flux, which will be used to develop climate-smart and water-saving agricultural production.

Key Points:
- Growing season evapotranspiration estimates of between 67-636 mm have been made for production-scale rice fields in Lonoke County, Arkansas, for the years 2016-17.
- Growing season evapotranspiration estimates of 555-615 mm have been made for production-scale cotton production fields in Mississippi County, Arkansas.
- The surface renewal method, a potentially cheaper and more adaptable strategy of providing direct observations of the evapotranspiration flux, is within 10-20% of more standardized eddy covariance estimates.
- The surface renewal method performs better after the canopy cover develops, guiding future research directions.

Introduction

Rice and cotton agriculture together use approximately 50% of Arkansas's irrigation water; unfortunately Arkansas's groundwater supplies are being unsustainably applied to irrigate fields (Reba et al., 2013; ANRC, 2014). To understand this water use better and to create targeted water management solutions that preserve both food and water security, estimates of evapotranspiration (ET) are necessary for different Arkansas row crops. ET is the dominant part of the growing season water balance and is directly tied to plant primary production and growth. ET is therefore also an indicator of the landscape's cycling of water, carbon, and energy and a key link between field function and performance. Over-application of irrigation water contributes to groundwater depletion, changing surface water base flow regimes, and has real energy costs due to its pumping requirement. ET is difficult to directly observe, and to determine constrained state-wide estimates of water use. Thus, we need to improve and reduce costs in ET measurement systems in order to have better measurement resolution across different crops and across the whole aquifer-withdrawing region. Using additional and/or alternative observations of ET allows researchers to make predictions of irrigation scheduling that have a scientific basis in how they represent expected crop dynamics.

This work builds on USGS 104B grants in both FY2015 and FY2016 to study the hydrological implications of increased water use efficiency – with a focus in rice production. These projects have generated the intriguing finding (from the FY2015 award) that total evapotranspiration (ET) from an AWD field is similar or even slightly greater than a reference, continuously flooded field. This response may be due to the strong ability of rice roots to pull water from the soil matrix and from the relatively short length of the dry down period (approximately 11 days). The FY2016 award demonstrated the potential of the FAO-56 version of the Penman-Monteith equation for ET to adequately and accurately simulate observed ET. This equation seems to significantly outperform the relatively simpler Hargreaves model currently used in Arkansas's irrigation scheduling tools. We recognized a need to work beyond rice, as it represents less than half the irrigation water used in Arkansas and any solution to water withdrawal issues will come from a concerted, multi-crop effort.

In this work, we therefore measure ET in production-scale rice and cotton fields in Arkansas. We observe and model ET rates, partition ET into its two constituent parts (evaporation and transpiration), and compare ET measured in different years. We also test a novel ET measurement strategy as a step toward implementing a potentially cheaper and more scalable method to observe ET under many different land management regimes. This new strategy is a micrometeorological method called "surface renewal" (Paw U et al., 1995) and is based on detecting and quantifying ramp-like structures seen in the turbulent transport of H_2O or other scalars into the atmosphere. It is compared to the more common and expensive, eddy covariance method (Baldocchi, 2003) whose observations we have presented in the previous years' reports.

We focus on fields already under potentially water-saving irrigation practices. In cotton, pivot irrigation has been shown to halve irrigation water use while increasing yield, relative to more traditional furrow irrigation practices (Reba et al., 2014). In rice, the Alternate Wetting and Drying (AWD) style of irrigation (Lampayan et al., 2015), especially when applied on zero-grade fields, can save 40% of water applications (Hardke, 2015; Henry et al., 2016). AWD can also serve as a carbon-offset credit option (ACR, 2014), and its implementation expenses may partially be paid for through the Natural Resources Conservation Service's Environmental Quality Incentives Program (EQIP).

Methods

We measured water vapor fluxes as observations of evapotranspiration by the eddy covariance (EC) method (Baldocchi, 2003) of deriving the turbulent transport from landscape to atmosphere. These flux terms are then modeled by the Penman-Monteith equation (Monteith, 1981) as implemented in FAO document 56 (Allen et al., 1998). In brief, the measurement procedure uses a sonic anemometer to measure the wind vector components and an infrared gas analyzer (IRGA) to measure CO_2 and H_2O concentrations. We then derive an observational data-stream and gap-filling it using an artificial neural network, as documented in our previous report (Runkle, 2017). As before, the dual crop coefficient method within the FAO56 procedure is used to calculate separate crop coefficients used to convert reference evapotranspiration (ET_o) into transpiration and evaporation: $ET=(K_b+K_e)*ET_o$. The part modified by K_b is the estimated transpiration and the part modified by K_e is the estimated evaporation. These coefficients are adjusted for the higher relative humidity conditions present in the US Mid-South following the FAO56 protocol. The reference evapotranspiration rate was calculated using methods also outlined in FAO56 as part of the Penman-Monteith method.

Surface renewal (SR) estimates of ET were generated using the IRGA's time series of H_2O concentration to detect recurrent ramp structures. The ramp characteristics were detected by structure function analysis (van Atta, 1977). These characteristics are then processed with horizontal wind speed in a calibration-free approach (Castellví, 2004) that iterates a solution by deriving friction velocity, H_2O flux, and atmospheric stability parameters. These ET estimates are gap-filled using the same neural network strategy applied to the EC observations.

Site Description

This research is performed at two privately farmed, adjacent rice fields (34° 35' 8.58" N, 91° 44' 51.07" W) outside of Humnoke, Arkansas, and a cotton field near Manila, Arkansas (35° 53' 14" N, 90° 8' 15" W). The rice fields are zero-graded and their size is approximately 350 m wide from north to south and 750 m long from east to west (i.e., 26 ha each). One field was managed with continuous flooding (CF) during the rice growing season and the other with AWD management practice, facilitating a direct comparison of the two types of systems with minimal spatial separation. The sites are not tilled and are flooded for two months in winter for duck habitat and hunting. The dominant soil mapping unit in this area is a poorly-drained Perry silty clay. In 2016 the fields were drill-seed planted 23 April and harvested 13 September. In 2017 the fields were drill-seed planted on 9-10 April and harvested 26-27 August. The fields are surface irrigated through perimeter ditches; in 2016 an Alternate Wetting and Drying irrigation strategy was used on both fields; in 2017 a continuous flood was established in both fields on 17 May and held until 4 August.

The pivot-irrigated, 63 ha cotton field had a cover crop eliminated by a mixture of Glyphosphate, Dicamba and Firstshot approximately three weeks before planting. The DeltaPine 1518B2XF cotton variety was planted at a rate of 118,610 seeds ha^{-1} (48,000 seeds ac^{-1}). In 2016, cotton was planted on 8 May and harvested 10 October while in 2017, cotton was planted on 19 May and harvested 30 October.

Results and Discussion

The observed ET by eddy covariance (EC) in rice was relatively consistent across the measurement fields and growing seasons (Figure 1; Figure 2). In the northern field at Humnoke, ET ranged from 567-608 mm and in the southern field ET at Humnoke, ranged from 594-636 mm. In all cases, the Penman-Montieth FAO56 model over-estimated ET, with estimates ranging from 752-835 mm. This over-estimation was consistent across the growing season. This over-estimation may result from higher crop coefficients – derived from their global synthesis – than necessary in Arkansas under water-efficient or higher humidity conditions. Following the FAO56 method of partitioning growing season ET into its constituent parts, evaporation and transpiration, transpiration represented 23-35% of the seasonal total ET flux. The partition between these terms follows the seasonal growth cycle, with more transpiration during later vegetative and early reproductive stages.

The cotton field evapotranspiration rates were similar to the rice fields, with measured values of 555-615 mm (Figure 3). ET increased after emergence likely due to higher
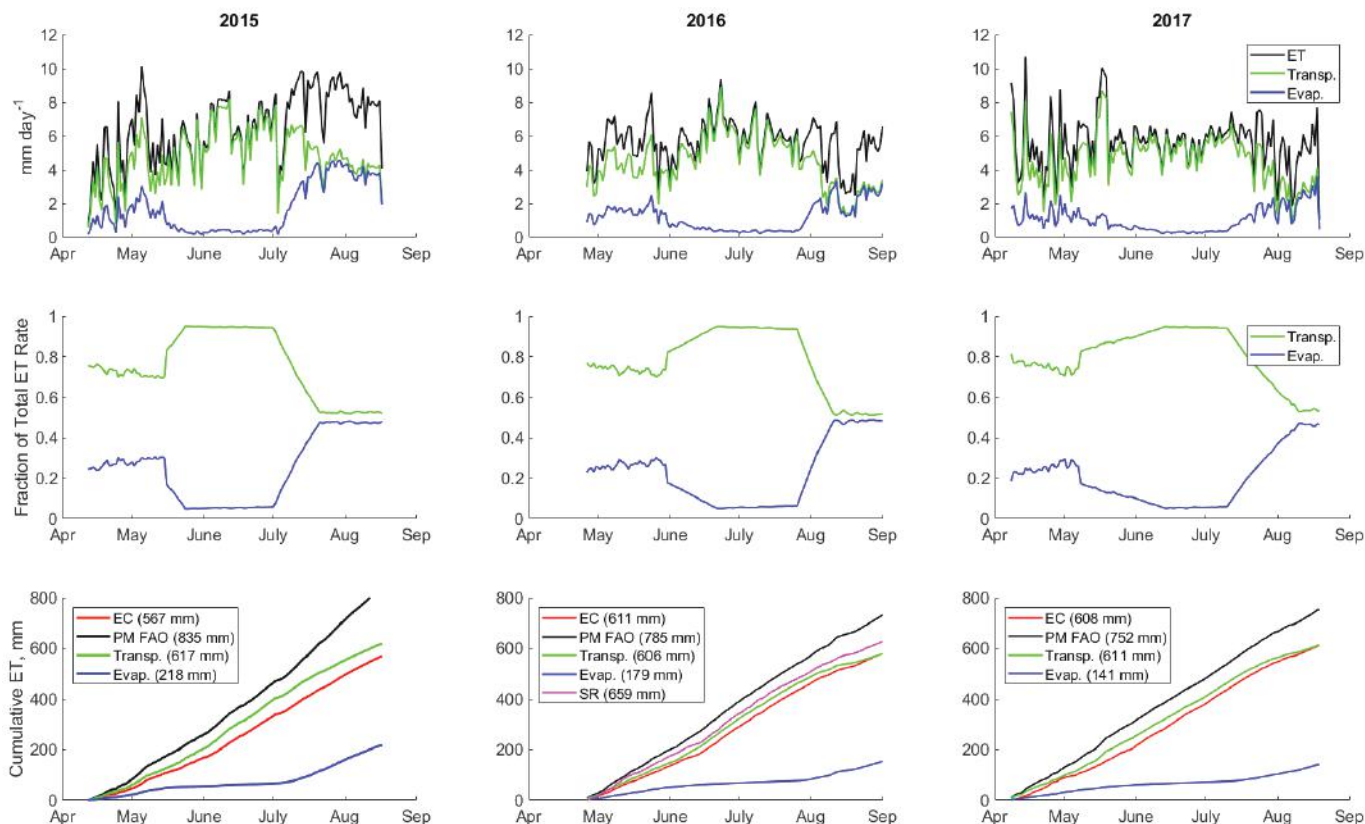

Figure 1: ET measured and modeled at the northern rice field in Humnoke (2015-17). The top six figures use the Penman Monteith model (PM FAO) to estimate ET and its partition into evaporation and transpiration components. Note the surface renewal observations are presented in for 2016 in the lower panels.
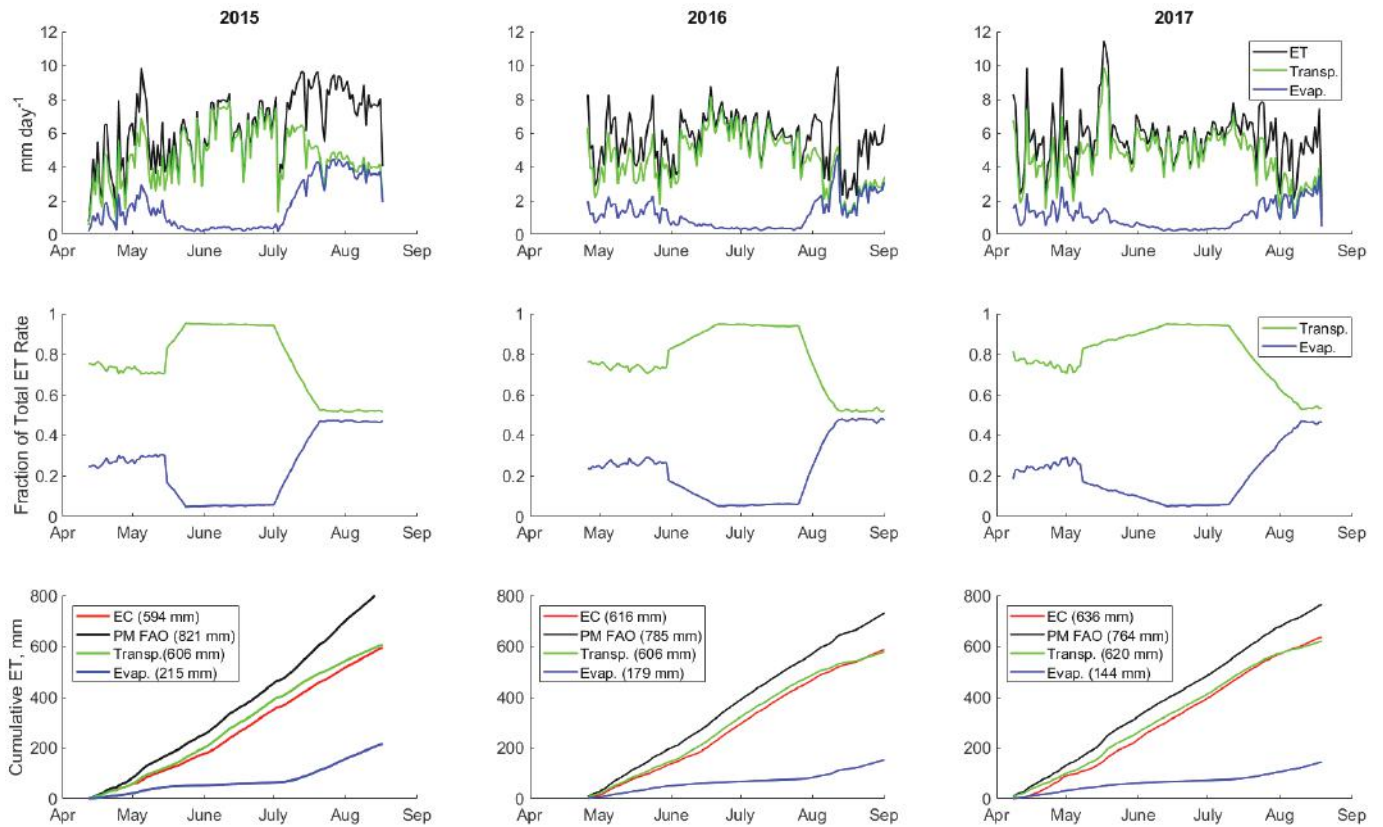
Figure 2: ET measured and modeled at the southern field in Humnoke (2015-17), and otherwise similar to Figure 1, though for this field we do not present the surface renewal data in 2016.
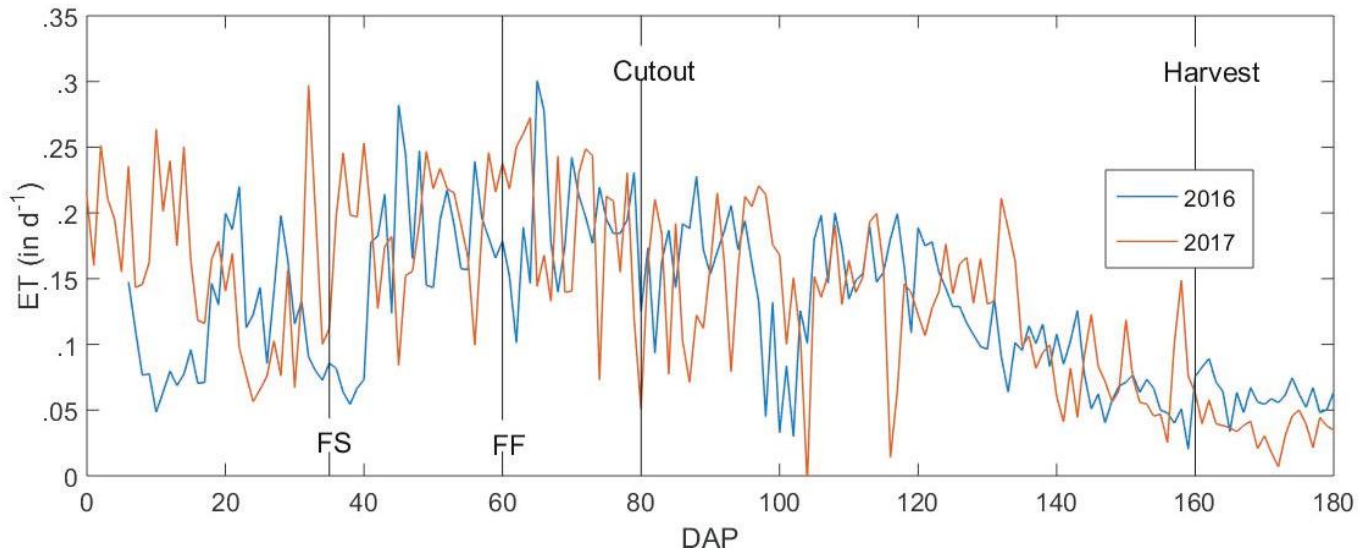

Figure 3: Daily crop evapotranspiration (ET) during 2016 and 2017 cotton growing seasons presented against days after planting (DAP). FS is first week of squaring, FF is first week of flowering, and cutout is physiological cutout or nodes above white flower equal to 5.

transpiration activity, greater water applications or rainfall, and higher air temperatures. ET later decreased after physiological cutout during boll maturation, likely due to lower plant water needs. Likely due to the higher relative humidity and greater cloud cover (reducing incoming solar radiation), these ET estimates are lower than in other regions. For example, a two-year study in Texas using weighing lysimeters found ET of 739-775 mm in full irrigation conditions; compared to 578-622 mm under a deficit irrigation strategy that also reduced field yields by 10-50% (Howell et al., 2004).

The surface renewal estimates are presented for the northern rice field for 2016 as these were the most complete
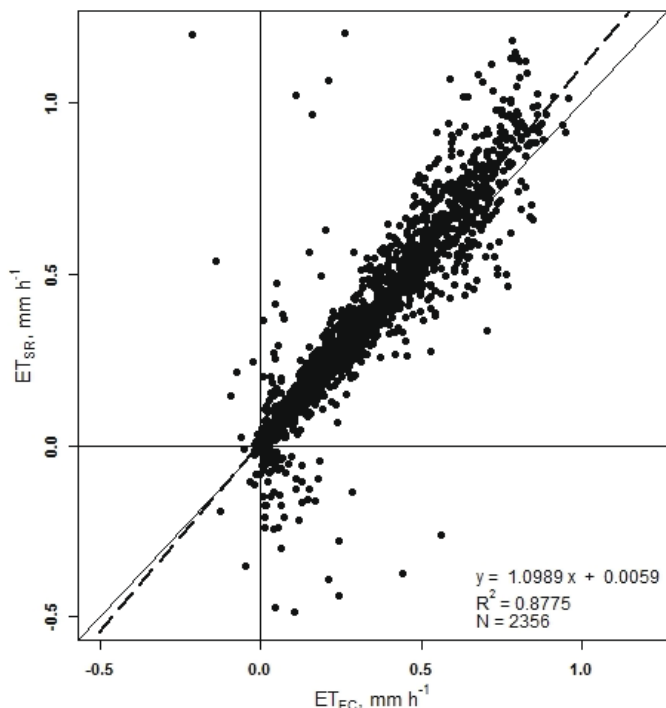
Figure 4: EC measured by surface renewal (SR) as compared to eddy covariance (EC) methods, in the northern rice field in Humnoke (2016).

time series (Figure 4). This method performed well – when gap-filled, its cumulative estimate of ET was very similar to the EC method (660 mm vs. 616 mm). On a one-to-one comparison, the methods agree well. Most of the over-estimation of SR relative to EC is largest earlier in the season, prior to full canopy development. Reasons may include the larger effective measurement height (with less surface roughness and greater effective eddies) and changes in canopy interference with turbulent structures. While corrected for density fluctuations, it may be that the concentration signals under high evaporative fluxes are challenging to interpret with the structure functions that have been more rigorously tested under temperature, rather than water vapor, time series.

Conclusions

The project finds good agreement between methods for estimating ET and more carefully partitions ET between transpiration and evaporation. Total ET shows less year-to-year variability. Similar to our previous work, we find that ET is largely controlled by transpiration during the peak growing season. We see little impact from irrigation style on the magnitude of ET fluxes, indicating minimal potential reduction to crop yield (due to the link between the carbon and water cycles through stomatal transfer of both CO_2 and H_2O). Work is ongoing to enhance the ability of the Penman-Monteith method to adequately represent ET in these land cover types. We will work to determine crop co-efficients for rice derived from local measurements rather

than the global values found in the FAO56 handbook. The ET measurements from the Arkansas cotton fields support this approach, as these measurements also indicated lower ET than in Texas, in part due to the greater cloudiness and higher humidity of the mid-south vs. other cotton-growing regions.

Local, regional, and national benefits

The site-based data is helpful to guide farmer decisions on water application to their fields. It is also contextualized through inclusion in the growing network named Delta-Flux (Runkle et al., 2017) for climate-smart agriculture. This multi-institution network, is composed of a suite of eddy covariance measurement towers on multiple crop and land cover types. The most representative crops and landscapes of the Lower Mississippi Alluvial Plain will be monitored for their water use, potentials for the decrease in water applications to the fields and carbon sequestration possibilities.

The scientists involved represent the USGS, USDA, and higher education institutions. The group is beginning to work with USGS partners on the MERAS groundwater model to contribute our ET datasets to their regional modeling initiatives. Additionally the locally-calibrated mechanistic relationships we are working to develop will offer predictive strategies upon which to strengthen irrigation planning tools. Being part of the Ameriflux and Fluxnet network, our measurements contribute to the global database for landscape types that have historically not been represented for their ET rates and CO_2 fluxes.

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Image caption: Grass clippings on roads can be washed into the stormdrain when it rains, and can cause pollution in receiving streams.

Educating the Masses Using Mass Media for Stormwater Pollution Prevention

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University of Arkansas System Division of Agriculture Cooperative Extension Service

Abstract: Trying to educate the largest number possible of the general population is always difficult. In the rapidly growing population of Northwest Arkansas, can paid advertising still influence people? Using electronic media developed for a neighboring state, commercials aimed at increasing awareness for pollution prevention activities were utilized. The message platforms were cable television and social media. After several weeks, voluntary electronic survey data demonstrated raised awareness and a behavioral influence on pollution prevention practices. Small budgets did not mean small impact.

Key Points:
- Effective media outreach can be accomplished on a limited budget.
- Commercials increase knowledge.
- Behavioral changes toward pollution prevention can occur from educational media.

Introduction

The University Of Arkansas System Division of Agriculture Cooperative Extension Service (UACES) is always interested in trying something new and innovative, and there was a project presented at a regional conference that deserved further investigation. The commercials for the City of Tulsa's outreach campaign to mediate runoff and prevent urban water pollution sources seemed well-designed. The City had already focus-group-tested the animated characters and commercials, so adapting the materials for the neighboring Northwest Arkansas area seemed logical.

An electronic media campaign like this one was new territory for UACES, especially using animated characters. While Tulsa was very happy with their campaign, the commercials ran mostly on public access channels with limited estimates on viewing by the general public. The electronic media avenues in Northwest Arkansas would include cable television and social media. Survey data would look at behavior change.

Contracts were established with Red Water Watch, a division of Grasshorse Productions. This company did the original design for the City of Tulsa's outreach campaign. Three separate commercials would be rebranded for the Northwest Arkansas area. The commercial series consisted of scenarios involving a turtle and a fish discussing best management practices (BMPs) with other characters who were about to pollute the storm drainage system. The animated commercials could be tailored for a fraction of the original production costs in a reasonable time frame. In essence, the project hoped to demonstrate that effective television commercials could be utilized in a cost effective manner, educating the public and result in actual behavioral changes.

Methods

The final products included three 30-second commercials and their short 15-second condensed spots for distribution (see UASDA, 2017). The videos were redesigned by having the original production company replace logos and contact information on the animated sign to reflect the Northwest Arkansas project information. Each piece focused on a different topic: (1) illicit discharge because of dumping into drains, (2) dead zones caused by improper lawn waste management, and (3) erosion issues as part of construction.

Cox Communication would be the avenue for distribution to the public. Cox Communication advertising regions were very similar to county geographical lines allowing the commercials to be seen by mainly residents within the Beaver Lake, Elk River, and Illinois River watersheds. Social media promotion via Facebook and Twitter would be a secondary outlet for the developed media and used for evaluation distribution.

The educational commercials ran from November 28, 2016 through April 9, 2017. The commercials ran on 8 different networks, 4 times a week. For cost saving, no particular shows were selected, just the networks. No spots aired between the hours of 11 pm – 5 am. Networks that aired the commercials were The Weather Channel, TBS, ESPN, FreeForm (Previously ABC Family), Food Network, HGTV, History, and Nickelodeon. FreeForm was left out of rotation from Christmas thru mid-January as spots were shown on the Hallmark Network instead. The networks were chosen because of demographic information provided by Cox. This line up allowed for a mix of children to adult viewers, male and female audiences to be exposed to the messages. A total of 608 commercials were shown for the 19 week period for an average of 32 commercials a week. Cox data showed that nearly 65 thousand households were reached.

For the social media side of the campaign, Facebook was the primary outlet. Closed captions were added to the different pieces for those who view without sound. All six videos (15-second and 30-second spots) were posted throughout winter beginning in December 2016, with the last post on March 22, 2017. Each video was shared an average of three times with views growing from 46 on the first post to 1,520 views on the later posts.

To determine effectiveness of the media campaign a voluntary evaluation piece was utilized. The survey materials and questions were reviewed for validity by an extension specialist and the survey was submitted and approved by the University of Arkansas Internal Review Board. The 12 question survey (Table 1) was developed and analyzed using Qualtrics software. The survey was emailed to over 600 individuals via two different list serves of stormwater, erosion, and educational contacts that have voluntarily signed up to receive information on workshops and trainings. The survey was also posted to Facebook (paid promotions) and Twitter. Initial recipients were asked to share the survey among their contact lists.

Results and Discussion

There were no anticipated results for the survey since there was a not a similar media campaign in this region previously conducted. Any received feedback would be valuable. Overall, 167 individuals responded to the survey with only 34% saying they subscribed to Cox Cable. When asked if they recognized the characters in the photo - the main characters in the commercials (Figure 1), 17% said that they did. Of those respondents, 38.5% said they had seen the characters on cable television but 73% had seen them on social media as well. When given a Likert scale to determine how well individuals liked the characters in the commercials, 77% reported they either somewhat liked or liked the characters a great deal. Only 23% of the respondents said that they neither liked nor disliked the characters. No one reported disliking the characters. Demographic information

Table 1. List of questions asked in the participant survey.

Do you subscribe to Cox Cable?
Check ALL method(s) you use to watch television (TV). (or NA if you do not watch)
Have you seen these characters on commercials or videos on television, social media, or a website?
Where have you seen these characters?
How well do you like the characters in the commercials/videos?
After viewing the commercials (or video), do you understand the actions you need to take to prevent pollution from entering the water?
Please describe how you dispose of the following household waste.
Would you like to see more educational videos like this to help you learn how to reduce water pollution?
Are there other places we should share messages like this? Please share your ideas and/or other comments.

* 3 other questions asked for demographic information according to age, sex, and location.

Figure 1. Image of two of the main characters in the commercials.

showed an equal distribution of respondents by age and sex.

Although the goal of distributing information to the masses seemed accomplished, was it impactful and cost effective? Questions were asked to see if a change in behavior occurred because of the messages in the commercials. The question asked about the primary messages of dumping chemicals in storm drainage ways and putting leaves and grasses in ditches or down the drain. The responses were quite surprising. Of those who recognized the characters in the commercials, almost 8% said they stopped dumping chemicals because of what they learned in the videos; 19% said they stopped putting leaves and grass in ditches because of the videos. When asked "after viewing the commercials, do you understand the actions you need to take to prevent pollution from entering the water?", 38.5% said yes, 0% said no, 3.8% were unsure, while 57.7% said they already knew how to prevent pollution. An overwhelming 100% of respondents wanted to see more videos like these to help learn how to reduce water pollution.

The cost to produce and air these commercials was minimal. Having the commercials rebranded, viewed on cable, posted to social media, and evaluations submitted and data analyzed was accomplished for less than $4,800. However, this amount does not include the time and salary of the project coordinator.

Conclusions

Overall, the outreach methods and commercial messaging was a success. Because the Northwest Arkansas areas of Benton and Washington County are similar geographically and demographically to the Tulsa area for which the commercials were originally produced, there was no surprise in the positive receipt of the characters and messages. Raising awareness and invoking change primarily through

paid advertising was a new and worthwhile venture. The likability of the characters lets us know that the investment was a positive one and that social change can occur from well-structured media methods without completely recreating the wheel. The rebranding of the materials was also extremely cost effective demonstrating that effective media outreach can be accomplished on a limited budget. Total costs in relationship to household reaches is about 7 cents per home, much less than the cost of a stamp.

The geographical and demographical similarities of the outreach areas made the commercials logical to modify and use. This campaign could potentially be used in many different areas of the state and region with only minor modifications. The production company was eager to work with new clients, which made the project enjoyable to organize. Other groups looking at behavioral changes to reduce water pollution might benefit from these commercials.

If there was an opportunity to repeat this project, some changes might be beneficial. Survey results showed 41% of respondents watched television through an online format so online advertising would need to be explored. National surveys following the 2016 elections showed that many people received news information primarily from social media foretelling the need for more budgetary allotments to social media expenditures. The electronic formatting of educational messages needs to be utilized more frequently, which is why this type of project should be repeated.

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