Arkansas Bulletin of Water Research - Issue 2020

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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 third 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.

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Cover Photo: "The Twins and a Friend" by Mark Corder, of Twin Falls in the Ozarks of Arkansas.

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$^{\varphi}$*Denotes research that is part of the US Geological Survey's 104B Grant Program*

Image caption: Brina Smith, AWRC laboratory technician, analyzes turbidity.

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

Erin E. Scott* and Dr. Brian E. Haggard

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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of Water Research was developed to provide an outlet for researchers to communicate project findings that might not be published in national or international journals, yet is extremely important to stakeholders in Arkansas.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: A harmful algal bloom of *Microcystis* at Bryce Davis Park in West Fayetteville, Arkansas in August 2019. Photo from Dr. Brad Austin, Arkansas Water Resources Center.

An In Situ Approach to Harmful Algal Blooms: Simultaneous Treatment of Cyanobacteria and Cyanotoxins in Natural Water Sources Using Catalytic Nanoparticle-Fiber Nets

Dr. Lauren Greenlee[1*] and Dr. Wen Zhang[2]

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Abstract: Harmful algal blooms (HABs) and their associated cyanotoxins that are produced cause negative environmental, water quality, and human health impacts. Few treatment approaches currently exist that can treat both HAB cyanobacteria and cyanotoxins without a pump-and-treat requirement or negative environmental impacts. This research focuses on an innovative in situ approach based on the concept of a catalytic fishing net that is retrievable and reusable. Research results demonstrate that titanium dioxide (TiO_2) and iron oxide nanoparticle catalysts cause HAB cyanobacteria deactivation through a flocculation mechanism. The cyanotoxin microcystin-LR is removed by TiO_2 through UV light activated catalytic degradation.

Key Points:

- Harmful algal blooms (HABs) and the associated cyanotoxins occur in surface waters globally and in Arkansas.
- Current HAB and cyanotoxin treatment options involve significant disadvantages, including a pump-and-treat requirement, only addressing either HABs or the cyanotoxin(s), and possible environmental impacts.
- A fishing net concept is used as an in situ approach to simultaneously deactivate HAB cyanobacteria and degrade cyanotoxins.
- Non-toxic titanium dioxide (TiO_2) and iron oxide nanoparticle (NP) catalysts were tested for HAB cyanobacteria deactivation, with flocculation as the primary deactivation mechanism.
- TiO_2 NPs removed microcystin-LR cyanotoxin through UV-initiated catalytic degradation, where cyanotoxin adsorption plays a minimal role.

Introduction

Harmful algal blooms (HABs) are globally increasing in frequency and distribution due to excessive nutrient run-off from agriculture and worsening eutrophication of water sources (He et al., 2016; Marsalek et al., 2012). HABs are cyanobacteria that accumulate biomass and produce cyanotoxins such as microcystin-LR, and an estimated 25 to 75% of HABs are toxic (Blaha, Babica, & Marsalek, 2009; Meng, Savage, & Deng, 2015). Cyanobacteria and cyanotoxins are becoming more prevalent and are severely damaging ecosystems because of nutrient pollution; cyanobacteria have negative impacts on ecosystem functions, such as organism relationship disturbances, biodiversity changes, light conditions, and oxygen concentrations (Blaha et al., 2009). Several animal studies have shown evidence of microcystins exhibiting tumor promoting properties (Blaha et al., 2009).

Cyanobacteria and cyanotoxins adversely impact human health and promote negative health effects like liver damage, immunotoxicity, and neurotoxicity (Marsalek et al., 2012). Annually, the U.S. alone spends $2.2 to 4.6 billion on methods, including filtration, flocculation, coagulation, or sedimentation, to battle the effects of HABs (Marsalek et al., 2012; Meglic, Pecman, Rozina, Lestan, & Sedmak, 2017; Meng et al., 2015). However, these methods are only temporary solutions, and key disadvantages associated with these techniques include detrimental environmental impacts and inefficiency (Marsalek et al., 2012). To address these disadvantages, we posed the research question: Can an in situ treatment approach based on the concept of a retrievable fishing net be used to deactivate HABs in the source water, without the need to pump and treat the water and with minimal to no environmental impacts?

Our objectives for this project were to test commercially available and experimentally synthesized catalyst materials, immobilize nanoparticle (NP) catalysts on a polymer fiber net, and evaluate the NP-fiber net concept for in situ treatment of HAB cyanobacteria and cyanotoxin. Our approach specifically focused on non-toxic titanium dioxide (TiO_2) and iron oxide (Fe_2O_3) as the catalyst materials, and our preliminary results from this past year suggest that our approach works through a dual flocculation / catalytic degradation mechanism. Our initial studies over the past year focused on understanding the performance of the catalytic materials alone with future work to include and progress to catalyst-immobilized fiber materials.

As mentioned, HABs are a global phenomenon; therefore, Arkansas is also affected by the devastating consequences of HABs. One study showed the mortality event of certain types of catfish located in Mississippi, Alabama, Arkansas, and Louisiana ponds linked to microcystin-LR poisoning (Zimba et al., 2001). Microcystin-LR was detected in water samples and in catfish liver tissue, and fish were killed within 24 hours of being exposed to toxic bloom-infested pond water (Zimba et al., 2001). Given the prevalence and importance of surface waters in the state of Arkansas for human recreation, environmental health, fresh water supply, and municipal and industrial development, the occurrence of HABs has a direct impact on Arkansas state economic vibrancy and environmental health.

Methods

Microcystis aeruginosa *Growth and Preservation*

M. aeruginosa (strain #2386) in suspension was obtained from the UTEX algae center at the University of Texas, Austin, and maintained in autoclaved BG-11 medium as instructed. Flasks of *M. aeruginosa* were set near a window, allowing for adequate sunlight. The growth of *M. aeruginosa* was monitored by measuring the optical density at 680 nm. Fresh BG-11 medium was supplemented into existing culture every 21 days to maintain algal growth (UTEX Culture Collection of Algae, 2009).

Microcystin-LR Stock Preparation

A 500 μg film of microcystin-LR (MC-LR) was purchased from Cayman Chemical, and the film was dissolved in methanol to obtain a 500 mg/L concentration of MC-LR. Five mg/L MC-LR stock solutions were made by diluting with deionized water. From 5 mg/L stock solutions, 1 mg/L solutions were created, which minimize freezing and refreezing of MC-LR samples. All samples were frozen and stored at -20°C in a freezer.

Experimental Protocol for Microcystis aeruginosa

NP treatment impacts were discerned by adding different concentrations of TiO_2 and Fe_2O_3 to *M. aeruginosa* suspended cell solutions. Both NPs were prepared by Dr. Greenlee's lab at the University of Arkansas and the stock solutions of 1 mg/L concentration were used. Prior to each experiment, cell morphology and concentration were assessed using a Nikon NiE upright light microscope and a Beckman Multisizer 4 Coulter counter, respectively. Ten-mL samples were prepared in 15 mL centrifuge tubes with *M. aeruginosa* diluted in phosphate buffer saline (PBS) at a 1:10 ratio. After samples were prepared, centrifuge tubes were gently vortexed to encourage even cell distribution throughout the PBS. Samples of the supernatant were taken for cell concentration measurement prior to NP addition, measuring initial concentrations of *M. aeruginosa* in cells/mL with diameters ranging from 2.5 to 4 μm. All cell concentration measurements were taken using the Coulter counter, prepared in 20 mL accuvettes with 20 μL added of supernatant to 10 mL of Isoton III Diluent as the electrolyte. Prior to being added to the accuvette, the electrolyte was filtered using a 0.22 μm syringe filter. The 20 μm aperture tube was

used for Coulter counter readings, and the Coulter counter was operated using the volumetric operating mechanism. After initial cell concentrations were recorded in all samples, NPs were vortexed to evenly mix them. Treatment amounts of NPs were then added to each tube, with no NPs added to the two control tubes (Table 1). Cell concentration was again measured three hours following NP addition and once every 24 hours for three days after NP addition using the Coulter counter. Throughout the experiment, samples were left sitting upright in a 15 mL centrifuge holder near the window.

All experiments were conducted in duplicate. Results were analyzed using Z-score (Equation 1), which considers values greater than an absolute value of 2 to suggest significant differences (alpha=0.05); because this analysis involved decreasing concentrations over time, Z-scores less than -2 were considered significant cell removal. In the Z-score calculation, X represents the individual cell concentration of each tube, $\overline{X}$ represents the average cell concentration of all tubes prior to treatment, and S represents the sample standard deviation of all tubes prior to treatment.

Equation 1. Z-Score Calculation, $Z=(X - \overline{X})/S$

Finally, percent of cells removed was calculated by subtracting the final cell concentration of each tube from the initial average cell concentration of all tubes in the experiment. This value was then divided by the initial average cell concentration of all tubes in the experiment and multiplied by 100. Duplicates of percent cell removal were then averaged to gain percent cell removal of each treatment in each experiment.

Experimental Protocol for Microcystis-LR

The impacts of TiO_2 NP on MC-LR were investigated through water, MC-LR, and TiO_2 batch experiments. Commercial AEROXIDE TiO_2 P 90 NP with an average particle size of 14 nm were used due to high surface area and mixed crystal structure, which contribute to good photocatalytic activity. Concentrations of 0.5 or 1 g/L stock solutions of TiO_2 were made prior to each experiment and vortexed to ensure suspension of NPs. Before each experiment, 1 mg/L MC-LR stock solutions were thawed. Five-20 mL batches of water, MC-LR, and TiO_2 were added to quartz crystal Erlenmeyer flasks and capped with stoppers. Starting MC-LR and TiO_2 concentrations were 200 μg/L and 0.25 g/L, respectively. Batches were mixed with an orbital shaker at 100 rpm for a maximum of 60 minutes. Control experiments excluded TiO_2 NPs and/or ultraviolet (UV) light. For UV experiments, a UV lamp was the source of UV-A light with a wavelength of 365 nm and an intensity of 230 μW/cm^2 at 3 inches. Samples collected during experiments were centrifuged at 7500 rpm for roughly 20 minutes and added to vials for liquid chromatography–mass spectrometry (LC-MS) analysis. Standard concentration points of 200, 150, 100, 50, 10, and 0 μg/L MC-LR were made for each experimental sample set and standard curves were plotted.

Table 1. Experimental design for NP treatment on *M. aeruginosa*.

Treatment	Concentration NPs (mg/L)	Tube Number
Titanium Dioxide – low concentration	25	F1, F2
Iron (III) Oxide – low concentration	25	F3, F4
Titanium Dioxide – high concentration	50	F5, F6
Iron (III) Oxide – high concentration	50	F7, F8
Control	0	F9, F10

Initially, Amicon Ultra-4 regenerated cellulose centrifugal filter units with 3 and 10 KDa pore sizes were utilized to filter out NPs from samples prior to LC-MS analysis. Filtration ensured NP removal as a precaution for LC-MS instrumentation. Control experiments indicated that the concentration of MC-LR decreased significantly once MC-LR was centrifuged with the filter units. Syringe filters with 0.2 μm pore size made of PVDF also showed decreased MC-LR starting concentration after filtration of samples. The method for NP removal was modified due to filter unit complications. Samples were centrifuged in 15 mL centrifuge tubes for 20 minutes, and TiO_2 pellets accumulated on the side of the container. The supernatant was sampled.

Controls tested included no NPs, no UV light, UV light + no NPs, and no UV light + NPs. Adsorption of MC-LR to NPs was investigated by a constant 200 μg/L MC-LR concentration and varied TiO_2 concentrations.

Results and Discussion

Cell Morphology

M. aeruginosa cell morphology was confirmed using 100x oil emersion light microscopy (Figure 1). Cells were moving rapidly throughout the media; only *M. aeruginosa* cells were seen in the sample.

Flocculation

Preliminary experimentation revealed flocculation as the main method of algal removal. This is illustrated in Figure 2, which shows cells prior to treatment (left), after TiO_2 NP treatment (center), and after Fe_2O_3 NP treatment (right). The untreated sample showed cell movement, while the treated samples showed little movement of cells.

Flocculation was further evident in results through Coulter counter measurements, showing a decrease in cell concentration of the supernatant. When *M. aeruginosa* was treated with varying concentrations of NPs, it was revealed that increased concentrations lead to faster flocculation. All four high-concentration NP treatments showed significant reduction in cell concentration by 24 hours, while only

one replicate in the low-concentration iron NP treatment achieved the same (Table 2, Figure 3).

Concerning the effectiveness of the NP treatments, percent cells removed at 72 hours for each treatment is listed in Table 3. Despite these high removal rates, no samples achieved enough algae removal for the concentration to fall below 20,000 cells/mL, which is the threshold the EPA specifies as low probability of human health risk (D'Anglada, n.d.). Cell removal could likely be improved by increasing concentration or amount of time treated.

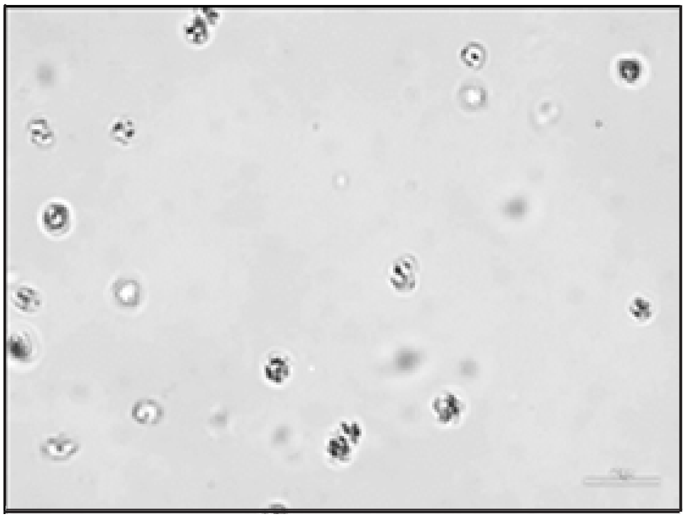

Figure 1. *M. aeruginosa* cell morphology, 10 µm scale bar.

LC-MS Analysis of MC-LR

The standard MC-LR concentration points 200, 150, 100, 50, 10, and 0 µg/L for Standards 1, 2, 3, and 4 from LC-MS analysis were used to calculate an average standard curve for experiments. Table 4 shows the multiple-reaction monitoring (MRM) LC-MS peak area data used to plot an average standard curve seen in Figure 4. Standard points are consistent between experimental runs.

MC-LR + water, MC-LR + water + 0.25 g/L TiO_2, MC-LR + water + UV light, and MC-LR + water + 0.25 g/L TiO_2 + UV light control experiments were tested over a 60 minute time period. Only MC-LR + water and MC-LR + water + UV light controls are shown in Table 5 since NP controls were tested with centrifugal filter units. Filter units affected MC-LR concentrations and produced inconclusive results. The microcystin-LR concentrations were reduced by 5.7% and 7.43% for the MC-LR + water and MC-LR + water + UV light controls, respectively. There is no significant evidence of MC-LR degradation by these control parameters.

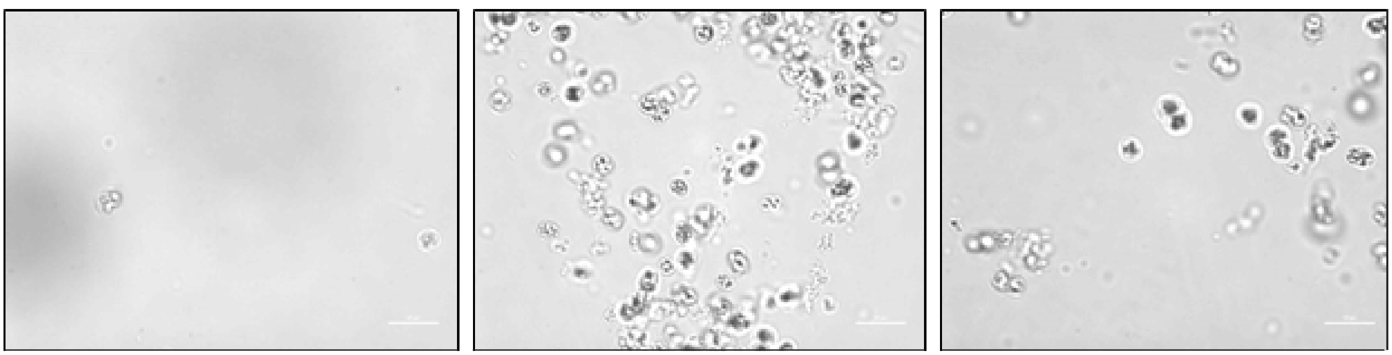

Figure 2. Images of *M. aeruginosa* prior to dilution in PBS and NP treatment (left), after TiO_2 NP treatment (center), and after Fe_2O_3 treatment (right). The scale bar is 10 µm.

Table 2. Z-score over cell concentration change after treatment of varying concentrations; significant reduction in cell concentration is represented in bold text.

Treatment	Hours Elapsed:	3	24	48	72
Titanium Dioxide – low concentration	Tube 1 z-score	0.49	-0.53	**-2.97**	**-3.11**
	Tube 2 z-score	0.69	0.32	0.47	**-3.11**
Iron (III) Oxide – low concentration	Tube 3 z-score	-0.35	**-2.1**	-1.89	**-2.68**
	Tube 4 z-score	**-6.46**	-0.8	-0.03	-1.84
Titanium Dioxide – high concentration	Tube 5 z-score	0.53	**-3.36**	**-2.17**	**-3.04**
	Tube 6 z-score	0.45	**-3.04**	**-2.1**	**-4.3**
Iron (III) Oxide – high concentration	Tube 7 z-score	1.02	**-3.36**	**-3.04**	**-4.11**
	Tube 8 z-score	0.69	**-3.81**	**-3.95**	**-4.3**
Control	Tube 9 z-score	0.45	0.81	0.19	-0.08
	Tube 10 z-score	0.47	6.68	0.26	0.42

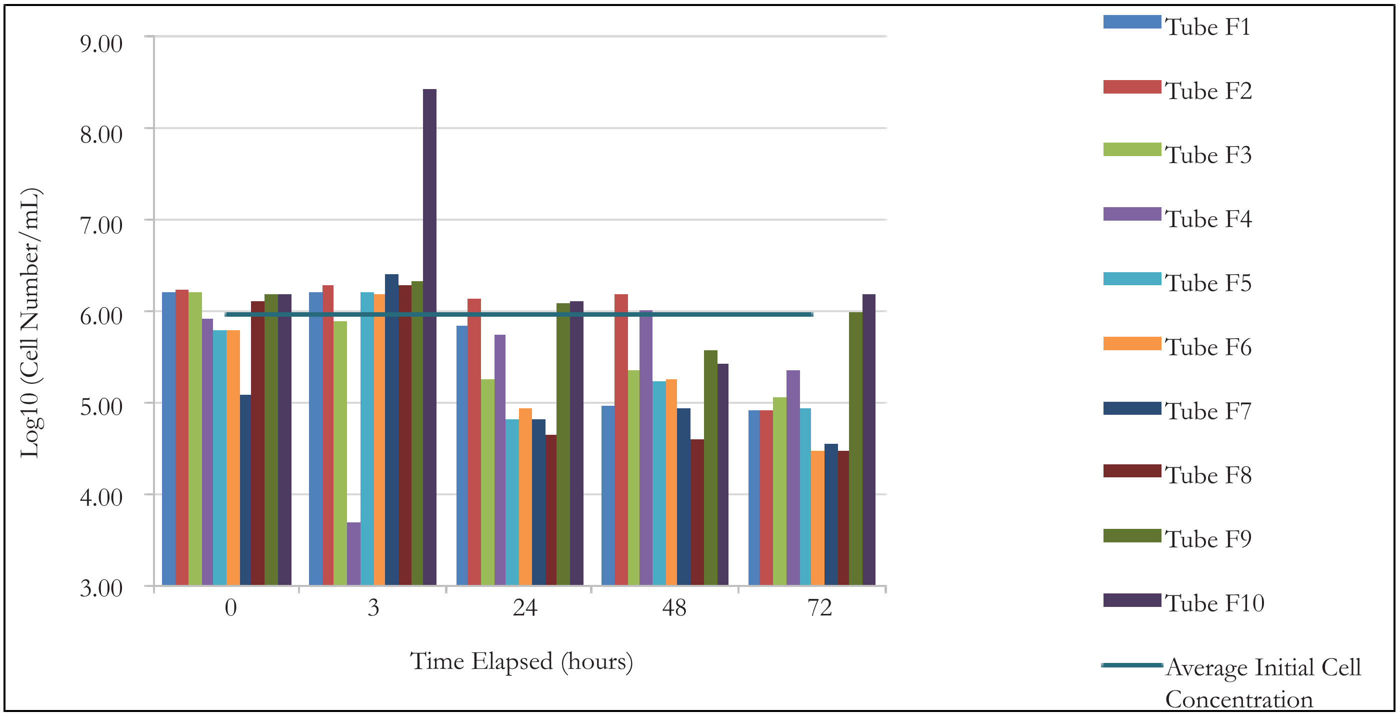

Figure 3. Cell concentration change over the treatment time. Tubes 1 and 2 were treated with the low concentration of TiO_2, tubes 3 and 4 were treated with the low concentration of Fe_2O_3, tubes 5 and 6 were treated with the high concentration of TiO_2, tubes 7 and 8 were treated with the low concentration of Fe_2O_3, and tubes 9 and 10 were the control.

Adsorption testing with varying TiO_2 concentrations and a constant 200 µg/L MC-LR concentration also produced inconclusive results due to centrifuge filtration units. Additional experiments have shown that MC-LR is not removed significantly by TiO_2 without UV light activation, suggesting adsorption is not a primary removal mechanism and that UV activation of catalytic activity is necessary for MC-LR removal.

Table 3. Percent algae removed from each treatment.

Treatment	Percent Algae Removed
Titanium Dioxide – low concentration	93.10%
Iron (III) Oxide – low concentration	85.10%
Titanium Dioxide – high concentration	95.00%
Iron (III) Oxide – high concentration	97.20%

Conclusions

Results this far have allowed us to discover that HAB cyanobacteria are deactivated even in the absence of light (i.e., no UV activation of catalyst activity), which suggests a flocculation mechanism for deactivation. Experiments on MC-LR have demonstrated repeatable quantitative standard curves, no adsorption of MC-LR onto TiO_2 NPs and significant adsorption of MC-LR onto some experimental materials, motivating changes in experimental procedure. Results also suggest that removal of MC-LR requires a catalytic function, in our system initiated by UV light. Based on our results thus far, we recommend further investigation of the catalyst-fiber composite for HAB-cyanotoxin mixed contaminant scenarios to evaluate the dual flocculation-catalytic degradation mechanism. We also recommend a focus on

Table 4. Multiple-Reaction Monitoring (MRM) Liquid Chromatography–Mass Spectrometry Peak Area for Standards 1, 2, 3, 4.

	Standard 1	Standard 2	Standard 3	Standard 4		
Microcystin-LR Concentration (µg/L)	Multiple-Reaction Monitoring (MRM) Chromatogram Peak Area				Average MRM Peak Area	Standard Deviation MRM Peak Area
10	4,734	6,269	5,451	5,990	5,611.03	585
50	28,220	33,134	26,979	30,467	29,700.04	2,344
100	59,339	68,557	52,398	59,936	60,057.45	5,733
150	86,055	101,592	78,510	90,531	89,172.00	8,359
200	110,275	138,010	102,819	124,187	118,822.80	13,473

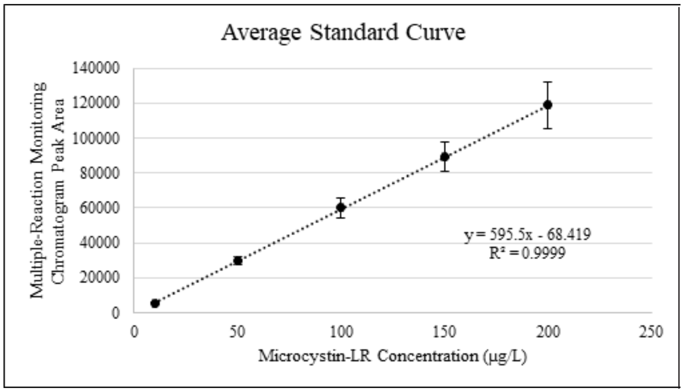

Figure 4. Microcystin-LR Average Standard Curve for Standards 1, 2, 3, and 4 with Standard Deviation Error.

Table 5. Microcystin-LR + water (no UV light + no TiO_2) and microcystin-LR + water + UV light (no TiO_2) control experiments.

	MC-LR Concentration (µg/L)	
Time (minutes)	**MC-LR + water**	**MC-LR + water + UV light**
0	193	202
5	186	191
10	183	190
15	181	193
20	187	185
40	189	182
60	182	187

catalyst-immobilized net configuration testing and optimization, as well as testing with real water samples that have been obtained from HAB-contaminated surface water sources. The State of Arkansas directly benefits from this research, where development of technologies based on our concept could enable HAB remediation in lakes without negative environmental impacts. This research also broadly benefits USGS, in that our focus and research will inform the agency on how HABs and associated cyanotoxins might be remediated throughout the US. The fishing net concept could be applied in a wide range of surface water scenarios, which would enable use across regions and general applicability.

Acknowledgements

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Image caption: Narrowwinged damselfly larva (Coenagrionidae) in an Arkansas stream. Photo from Dustin Lynch, Arkansas Natural Heritage Commission.

Legacy Sediment Bound Phosphorus and Low Macroinvertebrate Diversity in Agricultural Catchments Suggest a Long Road to Recovery

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Abstract: The extent of agriculture within stream catchments alters nutrient concentrations, phosphorus sorption dynamics, and macroinvertebrate communities. Pasture and row-crop production continues to grow in the Mississippi River watershed and water quality measured as chemical and biological condition continues to decline with unknown contributions from pasture versus row-crop. Therefore, we compared nutrient concentrations, sorption patterns, and macroinvertebrate communities between two locations with different forms of agriculture. We sampled 10 streams in Arkansas with more pasture and Michigan with more row-crop across an agricultural gradient for nitrate, ammonium, and soluble reactive phosphorus. We then measured the potential of benthic sediment to remove phosphorus from the water column using equilibrium phosphorus concentration (EPC_0) metrics. Finally, we sampled macroinvertebrates using both a benthic sampler and an artificial substrate sampler to understand the variable control of water quality, resources, and habitat on macroinvertebrate communities locally and regionally. We predicted greater nutrient concentrations and lower sorption capacity in streams with more row-crop agriculture and concomitant reductions in macroinvertebrate diversity. Nutrient concentrations were greater in stream catchments with a greater extent of agriculture. Phosphorus sorption rates were faster in Arkansas than Michigan and in catchments with less row-crop agriculture. The potential for phosphorus desorption was greater in Michigan and in catchments with a greater extent of agriculture in both locations. The aqueous phosphorus concentration at which sediment and water column concentrations are in equilibrium was greater in Michigan than Arkansas and greater in catchments with more agriculture in both locations. As predicted, macroinvertebrate density was greater in streams with more agriculture regardless of the location, but diversity was lower only in the more row-crop dominated catchments. In conclusion, the type and extent of agriculture within stream catchments affected headwater streams differently with Michigan row-crop agricultural affecting nutrient concentrations, sorption patterns and biodiversity more than Arkansas pasture.

Key Points:

- Nutrients from agriculture are transported by headwaters to rivers and estuaries that can result in algal blooms and hypoxia.
- Small catchments are being identified in the Mississippi River Basin (MRB) that could be most effective in reducing nutrient loads to downstream river networks.
- Small watersheds in Arkansas and Michigan contribute significant nutrients to the MRB despite different types of agriculture.
- The relative contribution of each agricultural type is not well known and the biological consequences have not been identified.
- A comparison between agricultural types in different regions of the MRB will guide targeted restoration efforts in small watersheds.

Introduction

Nutrient identity and concentrations vary from differences in geology and precipitation, but also from human activities that are resulting in impaired freshwaters around the world (Vitousek et al., 1997b). Agriculture, road deicers, water softeners, sewage, resource extraction effluent, fossil fuel combustion and weathering of rock formations exposed by mining and drilling contribute excess nutrients in historically unprecedented concentrations to freshwater (Vitousek et al., 1997a) . These rising concentrations interact with modified stream geomorphology and habitat changes to cause wide-spread species loss (Walsh et al., 2005). Globally, land cover modifications by humans are the single largest threat to species and ecosystems where 35% of Earth's ice-free land is devoted to agriculture (Foley et al., 2005). As nitrogen and phosphorus run-off modified landscapes into headwater streams, immobilized nutrients will eventually enter coastal waters where primary producers may be nutrient limited, bloom, die, and simulate microbial decomposition that results in hypoxia (Diaz and Rosenberg, 2008). There are currently over 400 hypoxic regions around the world caused by excess nutrients (Diaz and Rosenberg, 2008). The most recent available assessment of U.S. wadeable streams estimated poor biological condition of aquatic life in 49.1% caused by excessive nutrients, pathogen, sediment, and habitat degradation (USEPA, 2013).

Phosphorus can be measured as soluble reactive phosphorus (SRP), and total phosphorus (TP; Wetzel, 1975). The form of P determines its ability to be taken-up and incorporated into microbial biomass that includes algae, bacteria, and fungi. Total P from surface waters is the sum of assimilated, sorbed, and soluble P, while SRP generally represents the form readily assimilated by auto- and heterotrophic microbes (Wetzel, 1975). Monitoring sediment-P dynamics in streams can provide more information than stream concentration alone, given the possibility of sorption/desorption by sediments and ultimately whether sediments are a source or sink of P relative to the water column (Zhou et al., 2005). These conditions can be related to sediment composition, surface water chemistry, and upstream point or non-point sources of P and used to inform effective mitigation (Cormier et al., 2011).

We collected surface water nutrients as a way to assess very short-term (surface water chemistry), short-term biological processing and P immobilization (sediment P sorption), and longer term biological response to stream water quality (macroinvertebrate communities on Hester-Dendy plates) using methods comparable to an existing study near the Upper Mississippi River Basin (UMRB; Norton et al., 2000). We conducted the same analysis in streams at the edge of the UMRB with the overarching goal of comparing P transport and immobilization dynamics and the relationship with biological condition between the two regions where agricultural type, geology, and precipitation could result in variation in controls. Our aim is to improve understanding of nutrient export and biological impacts from human-dominated watersheds in the Mississippi River Basin.

Methods

Two baseflow samples were taken each season at each of our 10 sample locations in Michigan and in Arkansas. Samples were analyzed for several key parameters including total phosphorus, ortho-phosphorus (or SRP), nitrate-nitrogen, ammonia, total dissolved solids (TDS) and total suspended solids (TSS) using standard methods. Sediment P sorption/release assays and enzymatic activity were measured once in autumn and once in spring beginning spring 2018 through winter 2018. Sampling corresponded with surface water baseflow monitoring. For sediment sorption assays, methods from Haggard et al. (2004) were used. Three Hester-Dendy plates were deployed in late autumn in each of three streams along a 50-m reach. After one month, plates were retrieved, stored in ethanol, sieved through a 250 µm mesh, and identified to lowest practical taxonomic unit using Merritt, Cummins, and Berg (2008). Macroinvertebrates were counted and classified by trophic status and other traits (Poff et al., 2006) to determine stream biological condition and function.

Equilibrium phosphorus concentration (EPC_0) is a metric used to describe the ability of streambed sediment to act as a source or a sink for phosphorus. Sediment-EPC_0 was analyzed using methods derived from Haggard et al. (2004) and McDaniel et al. (2009). The top five centimeters of benthic sediment were collected along three transects in each stream along with unfiltered stream water. Primary phosphorus stock solution was prepared in the lab using KH_2PO_4 and ultra-pure water. The stock solution was diluted using the unfiltered stream water to create spiked solutions with concentrations of 0, 0.25, 0.5, 1.0, and 2.0 mg/L phosphorus. The spiked solutions were added to the collected benthic sediment in a centrifuge tube, shaken for 24 hours, then centrifuged to separate the supernatants. Water was decanted from the centrifuge tube, filtered, and analyzed for soluble reactive phosphorus (SRP) concentrations. The sediment from the corresponding centrifuge tube was dried in an oven and weighed to calculate the amount of phosphorus sorbed (mg P/kg dry sediment).

EPC_0 factors (EPC_0, slope, and y-intercept) were calculated by using linear or logarithmic equations based on the aqueous SRP concentrations related to the sediment SRP concentrations (Figure 1). Equilibrium phosphorus concentration at zero net sorption (EPC_0) defines the SRP concentration of the stream water when there is no SRP exchange between the sediment and the water column. The

slope describes the rate of sorption of phosphorus between the sediment and water column. The steeper the slope, the greater the rate of sorption. The absolute value of the y-intercept may indicate the amount of P that would be desorbed from the sediment if streamwater concentration was zero. If the streamwater SRP concentration is greater than the EPC_0, then the sediments would theoretically be a sink for P as water P moves into the sediment as EPC_0 is reached. On the other hand, if streamwater SRP is less than EPC_0, then the sediments would theoretically be a source of P as P moves from sediment into the water column until EPC_0 is reached.

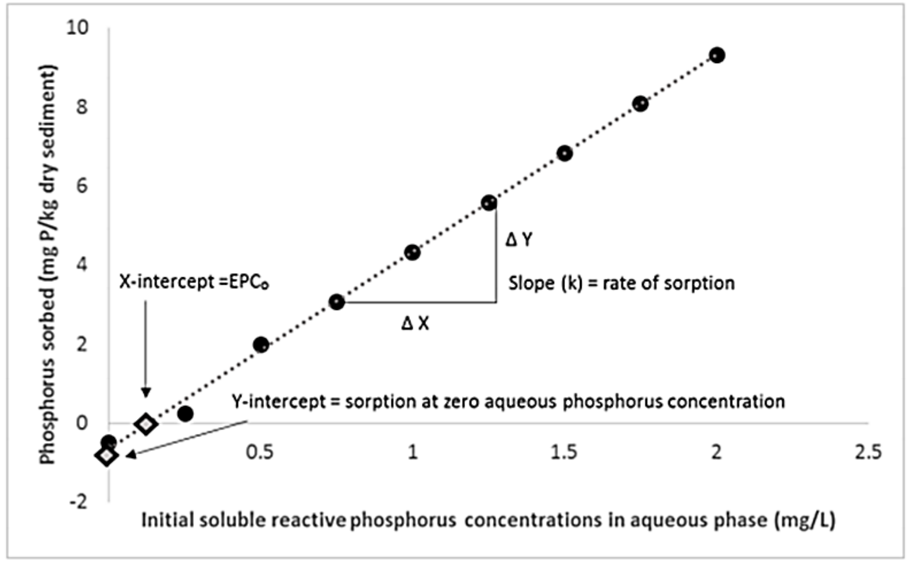

Figure 1. EPC_0 figure modified from Haggard et al., 2004. EPC_0 is the initial SRP concentrations in aqueous phase, slope (k) is the rate of sorption of SRP, and the y-intercept is the amount of SRP sorbed at aqueous SRP concentrations of zero.

An analysis of variance (ANOVA) was used to assess significant differences in nutrient concentrations, sorption dynamics and macroinvertebrate density, richness, and diversity. The alpha level was 0.05 and p-values that were less than the alpha level were deemed significant and p-values greater than the alpha level were considered insignificant. The ANOVAs were performed in R using the car package. Data were checked for parametric requirements by analyzing the distribution and variance of the data. Normal distribution was checked with the Shapiro-Wilk test and equal

Table 1. Arkansas and Michigan land cover categories calculated from the National Land Cover Dataset 2011 using Streamstats and Wikiwatershed.

Location	Study Site	Area (km^2)	Agriculture Group	Land Use Categories (%)							
				Developed	Deciduous Forest	Evergreen Forest	Mixed Forest	Pasture	Crop	Wetland	Other
Arkansas	EA2	3.39	More	4.3	3.4	12.4	2.9	74.2	0	0	2.8
	EA1	1.4	More	6.4	11.1	12.8	1.6	63.4	0	0	4.7
	WA2	1.66	More	11.5	14.9	15.1	5.2	48.7	2.6	0	2
	WA3	4.22	More	7.6	10.2	28.8	4.2	47.7	0	0	1.5
	WA1	5.23	More	4.3	28.8	17.4	4.3	40.8	0	0	4.4
	ER2	6.27	Less	6.4	35.6	25.2	6.6	23	0	0.5	2.7
	ER1	3.65	Less	5.3	60.2	16.5	2.7	9.5	0	0	5.8
	WR1	3.47	Less	4	87.2	4.9	2.1	0.2	0	0	1.6
	WR2	1.99	Less	1.6	23.8	70	4.6	0	0	0	0
	WR3	1.71	Less	4.8	37.6	46	4.5	0	0	0.3	6.8
Michigan	MI9	2.32	More	4	6.7	0	0.3	8.6	79.6	0.7	0.1
	MI6	6.61	More	5	8.6	0	0	5.5	74.4	4.6	1.9
	MI8	13.76	More	4.5	7.4	0.2	0.4	6	74	6	1.5
	MI7	16.34	More	5.3	7.7	0.1	0.4	5.4	73.2	6.5	1.4
	MI5	2.47	More	3.3	15.9	0	0.2	2.1	62.9	11.7	3.9
	MI1	12.82	Less	1.8	10.6	0	0.2	3.3	59.9	19.8	4.4
	MI4	2.23	Less	3.6	14.2	0	0	0.8	47.9	29.8	4
	MI2	10.12	Less	5.3	25.4	0	0.3	2.6	43.8	19.5	3.1
	MI3	9.5	Less	5.1	26.4	0	0.3	2.8	42.7	19.6	3.1

variation was checked with a Q-Q plot using the dyplr and ggpubr packages in R. If the data did not meet the parametric requirements, a log10 transformation or a square root transformation was performed. If the data still did not meet the parametric requirements, a non-parametric Friedman's test was run.

Results and Discussion

Land Use Differed between Locations and Amounts of Agriculture

Land use differed between Arkansas and Michigan and between amounts of agriculture (Table 1). Land use categories were associated with different locations and agriculture. For example, deciduous and evergreen forests represented Arkansas catchments with less agriculture, while mixed forest and pasture were associated with Arkansas streams with more agriculture.

Nutrient Dynamics in Arkansas versus Michigan

Nitrate concentrations differed between amounts of agriculture in both Arkansas and Michigan. Average nitrate concentrations in Arkansas ranged from 0.125 to 4.765 mg/L. As predicted, average nitrate concentrations were significantly greater in streams draining more agriculture in Arkansas (Table 2) and were two times greater in streams draining more agricultural land use than less agriculture (Figure 2).

Ammonium Concentrations Differed between Amounts of Agriculture in Arkansas but Not in Michigan

In Arkansas, ammonium ranged from 0.008-0.063 mg/L and tended to be greater in streams with a greater extent of agriculture within the catchment (Table 2). In Michigan, ammonium ranged from 0 to 0.514 mg/L. Contrary to our prediction, ammonium concentrations did not differ between amounts of agriculture in Michigan (Table 3). Average SRP concentrations differed between amounts of agriculture in Arkansas but not in Michigan. Average SRP con-

Table 2. Average nutrient concentrations from samples collected multiple times during baseflow in spring, summer, and autumn.

Location	Amount of Agriculture	Site	Nutrient Concentration (mg/L)		
			Nitrate	Ammonium	SRP
Arkansas	Less	WR1	0.125	0.025	0.007
		WR2	0.263	0.008	0.007
		WR3	0.667	0.008	0.004
		ER1	0.150	0.017	0.007
		ER2	1.75	0.008	0.009
	More	WA1	1.417	0.018	0.044
		WA2	4.765	0.086	0.054
		WA3	2.375	0.010	0.025
		EA1	2.733	0.021	0.024
		EA2	2.90	0.063	0.018
Michigan	Less	MI1	1.893	0.052	0.035
		MI2	0.688	0.022	0.011
		MI4	1.054	0.055	0.015
	More	MI6	2.607	0.017	0.013
		MI7	2.449	0.130	0.032
		MI8	1.76	0.070	0.033
		MI9	1.739	0.076	0.023

Table 3. Analysis of variance (ANOVA) results for average nutrient concentrations. Bolded p-values indicate significance (≤0.05) between less and more agriculture. Italicized values indicate a trend occurred (0.05<p-value<0.10).

Location	Nutrient	F	df	P-value	Transformation
Arkansas	Nitrate	12.9	1,8	**0.007**	None
	Ammonium	3.76	1,8	*0.089*	Log10
	SRP	39.14	1,8	**<0.001**	Log10
Michigan	Nitrate	5.33	1,5	*0.069*	None
	Ammonium	1.13	1,5	0.337	None
	SRP	0.33	1,5	0.588	None

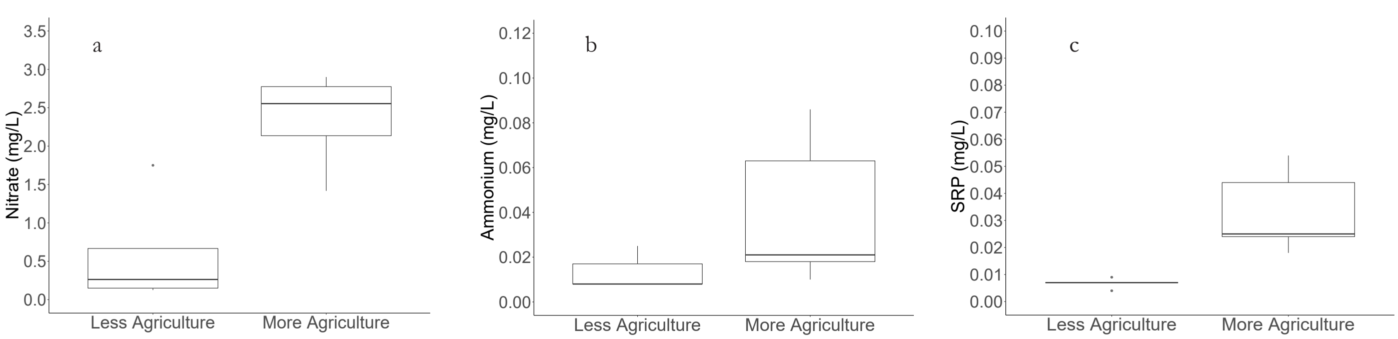

Figure 2. Nutrient concentrations for nitrate (a), ammonium (b), and SRP (c) in Arkansas were analyzed between amounts of agriculture using an ANOVA. 1a. Nitrate concentrations were significantly greater in more agriculture than less (F1,8 = 12.90, p = 0.007). 1b. Ammonium concentrations tended to be greater in more agriculture than less (F1,8 = 3.76, p = 0.089). 1c. SRP concentrations were significantly greater in more agriculture than less (F1,8 = 39.14, p < 0.001).

centrations in Arkansas ranged from 0.004 to 0.054 mg/L. As we predicted, SRP concentrations were five times greater in streams that drained more agriculture than less (Figure 2). In Michigan, concentrations ranged from 0.007 to 0.189 mg/L, but did not differ between amounts of agriculture (Figure 3, Table 2).

Overall sorption rates were an order of magnitude greater in Arkansas, but did not differ between amounts of agriculture (Figure 4). However, rates in Michigan had more among-site variation between amounts of agriculture (Figure 5). The proportion of agriculture within the stream catchments was not related to aqueous phosphorus binding rates. Linear regression between the rates of sorption values and substrate size also did not explain variation across sites (Table 4). SRP equilibrium constants also did not differ between land use amounts in Arkansas or Michigan (Table

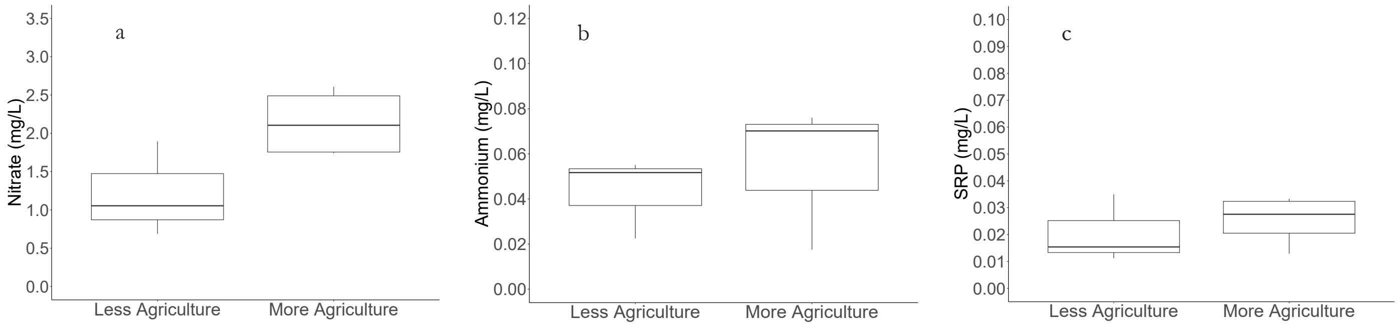

Figure 3. Nutrient concentrations for nitrate (a), ammonium (b), and SRP (c) in Michigan were analyzed between amounts of agriculture using an ANOVA. 2a. Nitrate concentrations tended to be greater in more agriculture than less (F1,5 = 5.33, p = 0.069). 2b. Ammonium concentrations did not differ between amounts of agriculture (F1,5 = 1.13, p = 0.337). 2c. SRP concentrations did not differ between amounts of agriculture (F1,5 = 0.33, p = 0.588).

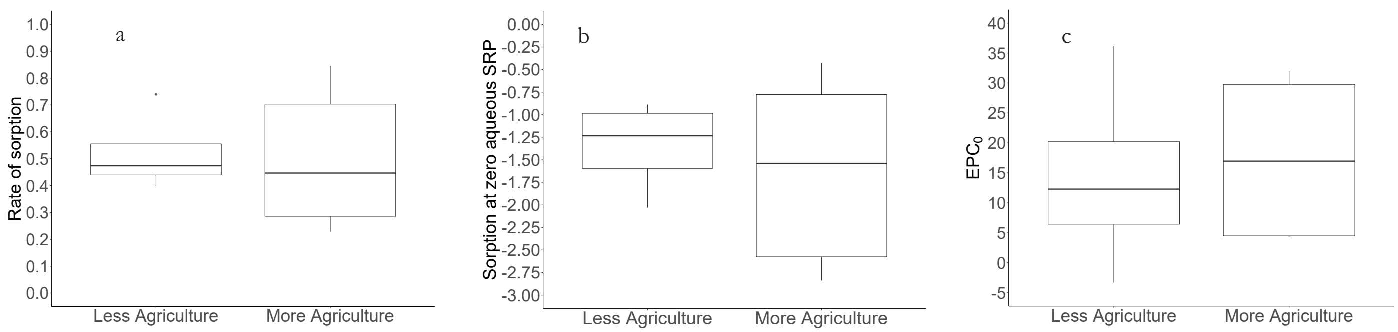

Figure 4. Equilibrium phosphorus concentrations (EPC) variables of rate of sorption, or slope (a), sorption at zero aqueous SRP, or y-intercept (b), and EPC_0 (c) in Arkansas between amounts of agriculture were analyzed using an ANOVA. 3a. Rates of sorption did not differ between amounts of agriculture (F1,7 = 0.001, p = 0.981). 3b. Sorption at zero aqueous SRP tented to be greater in less agriculture than more (F1,7 = 4.07, p = 0.083). 3c. EPC_0 values tended to be greater in more agriculture than less (F1,7 = 5.13, p = 0.058).

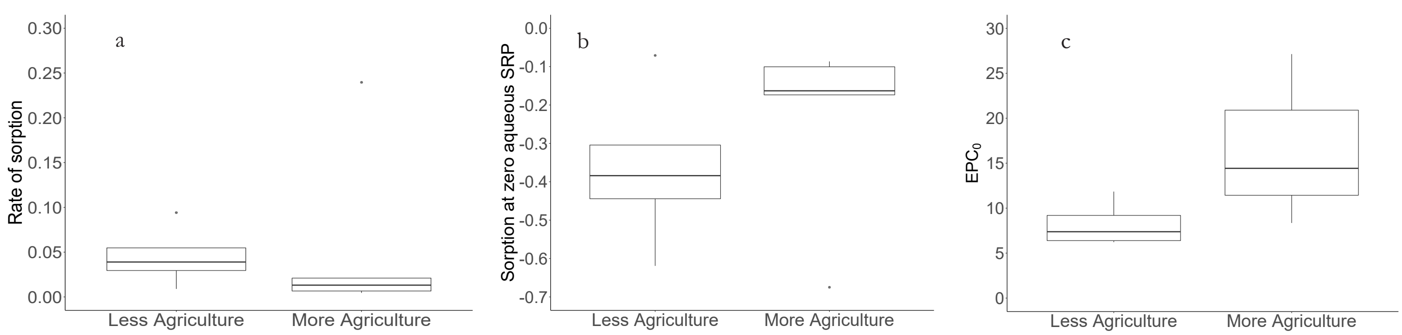

Figure 5. Equilibrium phosphorus concentrations (EPC) of rate of sorption, or slope (a), sorption at zero aqueous SRP, or y-intercept (b), and EPC_0 (c) in Michigan between amounts of agriculture were analyzed using an ANOVA. 4a. Rates of sorption did not differ between amounts of agriculture (F1,8 = 1.44, p = 0.264). 4b. Sorption at zero aqueous SRP did not differ between amounts of agriculture (F1,8 = 1.70, p = 0.229). 4c. EPC_0 values did not differ between amounts of agriculture (F1,8 = 0.15, p = 0.706).

4). All sites showed the potential for phosphorus release if SRP water column concentrations decline, indicating legacy phosphorus.

We found that SRP, a bioavailable phosphorus, was greater in streams with more agriculture within the catchment. SRP, a fractional component of TP, almost exceeded TP reference values in both Arkansas and Michigan, indicating SRP concentrations were elevated in both locations. Bio-available phosphorus concentrations have been found to increase with the land use conversions from forest to agriculture in stream catchments. We also found a greater increase in SRP concentrations from less to more agriculture in Arkansas, but Michigan SRP concentrations were more similar between less and more agriculture. Arkansas' Point Remove watershed is mostly pasture and the effluent runoff from cattle and chicken lots could contribute more SRP to streams than row crop in Michigan. Nutrient concentrations in Arkansas and Michigan exceeded eco-region-specific criteria. Nutrient reference values (<25th percentile) for the Arkansas ecoregion are 0.037 mg/L for TP and 0.69 mg/L for TN. Michigan nutrient reference values are 0.033 mg/L for TP and 0.54 mg/L for TN. Nitrate, a fractional component of TN, were four times greater than total TN reference concentrations in both. Average rate of SRP adsorption tended to be lower in more agricultural Michigan catchments.

Macroinvertebrates in Arkansas versus Michigan

Total density differed between amounts of agriculture in Arkansas but not in Michigan. Macroinvertebrate density averaged 1,523 (per stream) macroinvertebrates in Arkansas and 33 macroinvertebrates in Michigan. As predicted, total average density was 46 times greater in Arkansas than in Michigan (Table 5, 6); however, density was greater in catchments with more agriculture in Arkansas (Figure 6) but did not differ in Michigan (Figure 7). Density was more than seven times greater in streams with a greater extent of agriculture in Arkansas. Richness and diversity differed between amounts of agriculture in Michigan but not in Arkansas. As predicted, taxa richness responded to agriculture differently in each location (Table 5). However, richness was greater in catchments with less agricultural land use in Michigan (Figure 6) but did not differ between amounts of agriculture in Arkansas (Figure 6). Arkansas streams had an average of ten taxa, while Michigan streams had seven taxa. As predicted, diversity was greater in Arkansas than in Michigan (Table 5, 6); however, diversity was greater in catchments with less agriculture in Michigan (Figure 7) but did not differ between

Table 4. Analysis of variance (ANOVA) results for average equilibrium phosphorus concentration (EPC_0) variables. Bolded p-values indicate significance (≤0.05) between less and more agriculture. Italicized values indicate a trend occurred (0.05<p-value<0.10).

Location	Variable	F	df	P-value	Transformation
Arkansas	Rate of sorption (slope)	0.024	1,8	0.880	None
	Sorption at zero aqueous SRP (Y-intercept)	0.247	1,8	0.633	None
	EPC_0	0.570	1,8	0.472	None
Michigan	Rate of sorption (slope)	0.466	1,7	0.517	Log10
	Sorption at zero aqueous SRP (Y-intercept)	0.615	1,7	0.459	None
	EPC_0	4.245	1,7	*0.078*	None

Table 5. Macroinvertebrate metric results for analysis of variance (ANOVA) of Arkansas and Michigan artificial substrate samplers. Metrics were compared between amounts of agriculture in the two locations. Bolded p-values indicated significance (≤0.05) and italicized p-values indicated trends in the data (0.05<p-value<0.10).

Location	Metric	F	df	P-value	Transformation
Arkansas	Density	4.22	1,8	*0.074*	None
	Richness	2.13	1,8	0.182	None
	Diversity	0.17	1,8	0.691	None
Michigan	Density	0.46	1,7	0.520	None
	Richness	4.21	1,7	*0.079*	None
	Diversity	6.16	1,7	**0.042**	None

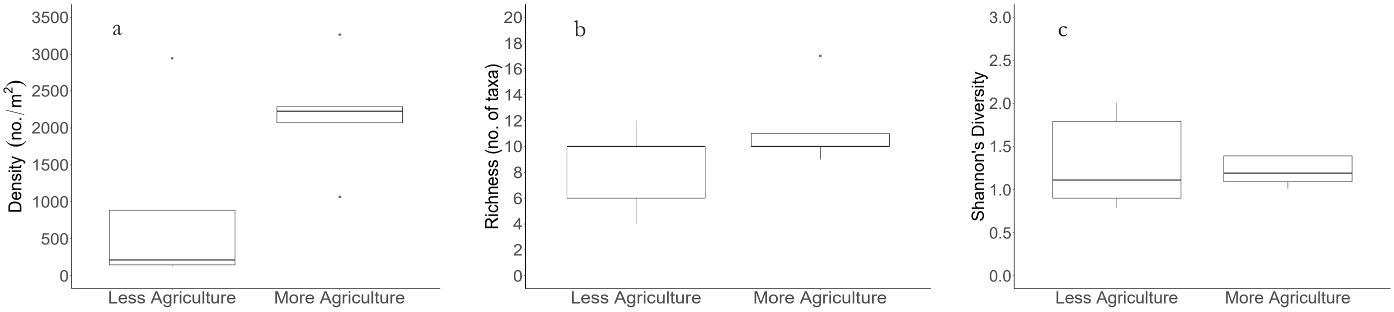

Figure 6. Macroinvertebrate metrics for density (a), richness (b), and diversity (c) in Arkansas were analyzed between amounts of agriculture using an ANOVA. 5a. Density tended to be greater in streams with a more agriculture than less ($F_{1,8} = 4.22$, $p = 0.074$). 5b. Richness did not differ between amounts of agriculture ($F_{1,8} = 2.13$, $p = 0.182$). 5c. Diversity did not differ between amounts of agriculture ($F_{1,8} = 0.17$, $p = 0.691$).

Table 6. Macroinvertebrate taxa abundance in Arkansas and Michigan sampled with Hester-Dendy artificial substrate samplers.

Order	Family	Genus	Location				Functional Feeding Group
			Arkansas		Michigan		
			Less Ag.	More Ag.	Less Ag.	More Ag.	
Acarina	Acari		13	51	-	-	Predator
Odonata	Aeshnidae	*Boyeria*	-	-	4	3	Predator
Isopoda	Asellidae	*Lirceus*	95	148	-	-	Collector-Gatherer
Ephemeroptera	Baetidae	*Acentrella*	2	-	-	-	Collector-Gatherer
Ephemeroptera	Baetidae	*Baetis*	2	8	-	-	Collector-Gatherer
Trichoptera	Brachycentridae	*Brachycentrus*	-	-	15	-	Collector-Gatherer
Odonata	Calopterygidae	*Calopteryx*	-	-	1	5	Predator
Plecoptera	Capniidae	*Allocapnia*	-	1	-	-	Shredder
Amphipoda	Crangonyctidae	*Crangonyx*	4	4	-	-	Collector-Gatherer
Megaloptera	Corydalidae	*Nigronia*	-	-	4	-	Predator
Coleoptera	Dryopidae	*Helichus*	-	1	-	-	Predator
Coleoptera	Dyticidae	*Hydoporus*	3	-	-	-	Predator
Coleoptera	Elmidae	*Stenelmis*	-	4	-	-	Scraper
Diptera	Empididae	*Hemerodromia*	-	-	-	1	Predator
Amphipoda	Gammaridae	*Gammarus*	-	-	34	54	Collector-Gatherer
Coleoptera	Gyrinidae	*Gyrinus*	2	5	-	-	Predator
Ephemeroptera	Heptageniidae	*Macdunnoa*	-	-	158	3	Scraper
Ephemeroptera	Heptageniidae	*Stenonoma*	195	157	-	-	Scraper
Trichoptera	Hydropsychidae	*Cheumatophsyche*	-	-	18	3	Collector-Filterer
Trichoptera	Hydropsychidae	*Potamyia*	-	-	1	-	Collector-Filterer
Ephemeroptera	Leptophlebidae	*Leptophlebia*	11	-	-	-	Collector-Gatherer
Diptera	Limoniidae	*Hexatoma*	-	-	1	-	Predator
Coleoptera	Lutrochidae	*Lutrochus*	-	-	6	5	Shredder
Nematomorpha			1	5	-	-	Predator
Plecoptera	Nemouridae	*Amphinemura*	3	-	-	-	Shredder
Diptera	Non-Tanypodinae		358	1195	203	328	Collector-Gatherer
Ostracoda			-	12	-	-	Collector-Gatherer
Plecoptera	Perlidae	*Anacroneuria*	1	14	-	-	Predator
Plecoptera	Perlidae	*Perlesta*	-	1	-	-	Predator
Plecoptera	Perlidae	*Perlinella*	3	5	-	-	Predator
Plecoptera	Perlodidae	*Isoperla*	-	1	-	-	Predator
Basommatophora	Physidae		-	2	-	-	Scraper
Basommatophora	Planorbidae		-	1	-	-	Scraper
Neotaenioglossa	Pleuroceridae		-	25	-	-	Scraper
Trichoptera	Polycentropidae	*Polycentropus*	-	1	-	-	Collector-Filterer
Lepidoptera	Pyralidae		-	-	-	2	Scraper
Trichoptera	Rhyacophilidae	*Rhyacophila*	-	-	4	2	Predator
Coleoptera	Scirtidae	*Cyphon*	-	1	-	-	Scraper
Diptera	Simulidae	*Simulium*	3	-	-	-	Collector-Filterer
Diptera	Tabanidae	*Tabanus*	-	1	-	-	Predator
Diptera	Tanypodinae		928	1330	13	18	Predator
Diptera	Tipulidae	*Tipula*	-	-	5	-	Shredder

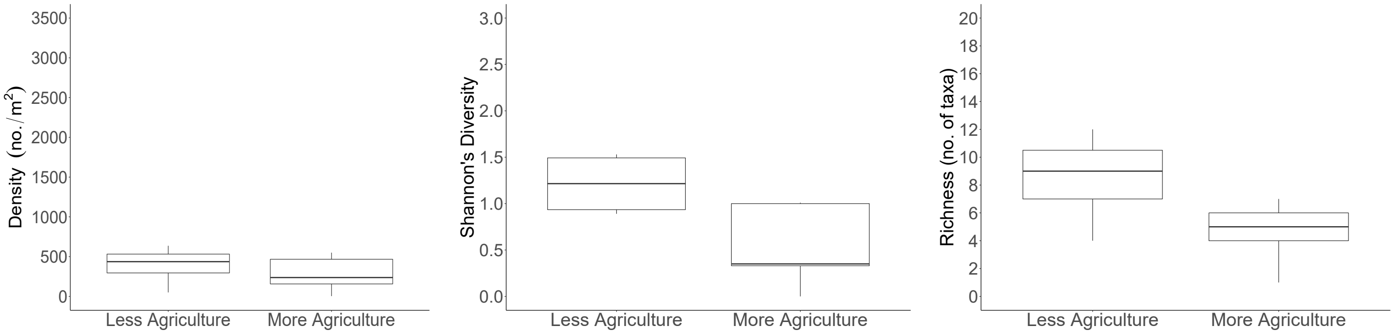

Figure 7. Macroinvertebrate metrics for density (a), diversity (b), and richness (c) in Michigan were analyzed between amounts of agriculture using an ANOVA. 6a. Density did not differ between amounts of agriculture (F1,7 = 0.46, p = 0.520). 6b. Richness tended to be greater in streams with less agriculture than more (F1,7 = 4.21, p = 0.079). 6c. Diversity was greater in streams with less agriculture than more (F1,7 = 6.16, p = 0.042).

amounts of agriculture in Arkansas (Figure 6).

Conclusions

We found that even if aqueous nutrient concentrations were reduced by mitigation efforts, phosphorus may remain elevated due to desorption of legacy phosphorus from the benthic sediment. Streams within Arkansas show potential for faster recovery from legacy land use effects due to lower water column nutrient concentrations, faster sorption rates and y-intercept values and a more diverse macroinvertebrate regional taxa pool. If nutrient concentrations from runoff were reduced, water quality and biological condition may recover some past characteristic freshwater biota. Michigan streams had the greatest potential for phosphorus release with greater EPC_0 values and lower y-intercepts and extremely low biological diversity and density compared to Arkansas streams. Regional species pools in Michigan may be depleted and sediments saturated with phosphorus making recovery from a legacy of intensive agriculture less feasible.

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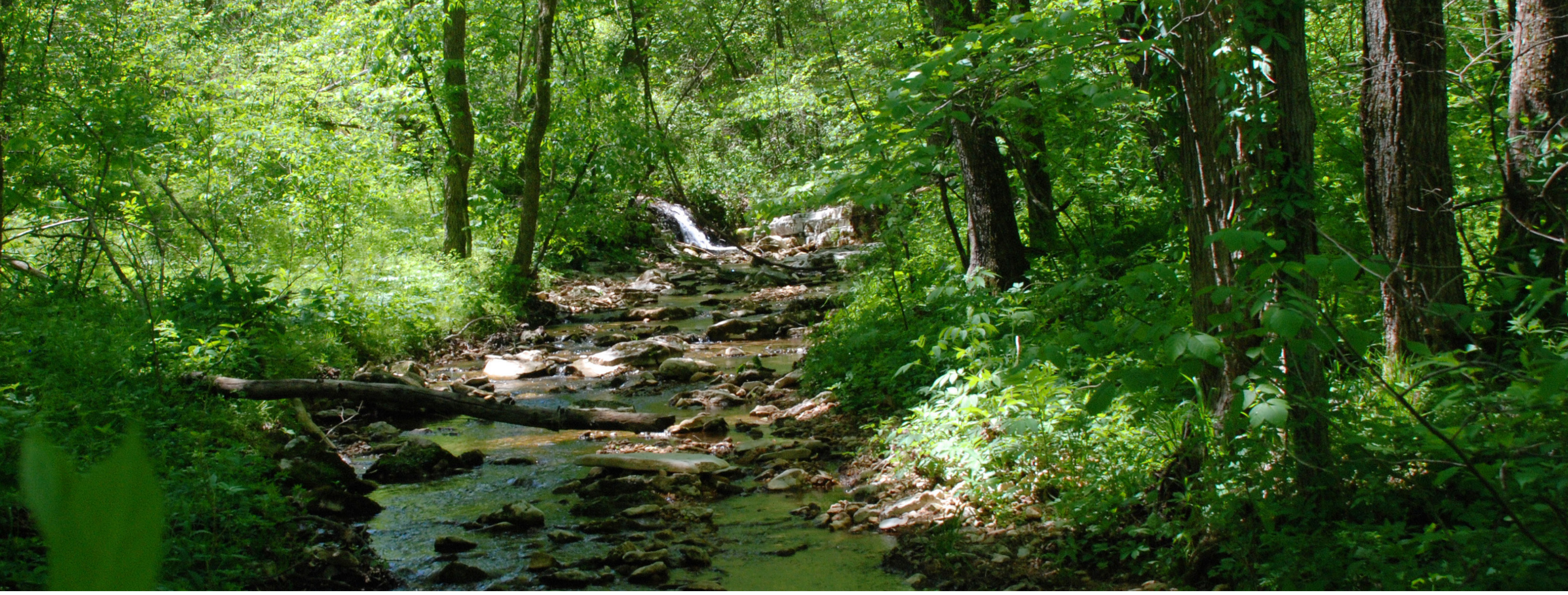

Image caption: A forested stream in the Ozarks of Arkansas. Photo from bioimages.vanderbilt.edu.

Quantifying Flow Sources and Their Impacts on Water Quality in Forested Ozark Streams

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Abstract: Stream water sources play a key role in nutrient and water budgets. Current hydrologic models predict two dominant flow regimes in northern Arkansas, each characterized by differing dominant flow sources: groundwater and runoff from precipitation. Current model estimates of groundwater input were generated at catchment- and kilometer-level scales using probability estimates. Direct measurements of water chemistry from flow sources (i.e. groundwater and precipitation) provide more refined estimates of instream source apportionment, especially in small headwater systems. Water samples were collected in three, primarily-forested Runoff and three Groundwater streams twelve times from March 2018 to November 2018. Nine samples were taken at base or near-base flow while three samples were taken during storm flow. In addition to determining discharge, nutrient concentrations, and conductivity, hydrochemical tracers and end-member mixing analysis (EMMA) were used to apportion streamflow originating from precipitation or groundwater. Results showed that all Runoff streams were driven primarily by rain, which accounted for approximately 89% of channel flow across sites and sampling dates. Median Groundwater stream flow was comprised of 79% groundwater over the study period. Total phosphorus (TP) and nitrogen (TN) concentrations were both greater in Groundwater streams. However, Runoff stream TN was driven by groundwater nitrogen addition and discharge, while no such relationships were found in Groundwater streams. This study validates hydrologic model prediction of flow regime sources while revealing an important yet overlooked source of nitrogen in precipitation-driven streams. Given that this work took place in forested streams, further work is needed in agricultural systems, as Runoff streams may be more susceptible to nitrogen enrichment from nutrient migration through soils to groundwater.

Key Points:

- Groundwater streams were driven primarily by groundwater inputs, except during storm events, when precipitation became the dominant flow source.
- Runoff streams were driven by precipitation inputs during base and storm flows.
- Nitrogen concentrations in Runoff streams increased with groundwater contributions high in nitrogen.
- Runoff stream nitrogen decreased with discharge.
- Groundwater inputs were important nutrient sources in forested precipitation-driven systems.

Introduction

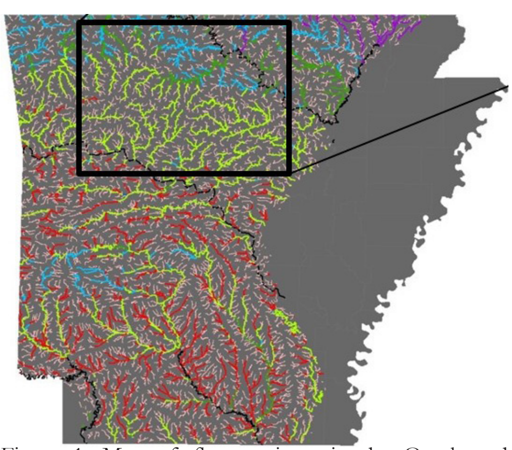
The relative input of groundwater versus surface water varies temporally and spatially across lotic systems. These waters have differing chemistries and nutrient dynamics; however, data quantifying the source and amounts of water entering headwater streams are lacking, even though such data would provide critical insight into potential impacts of nutrient pollution, particularly in streams with low nutrient buffering. Importantly, data revealing the relative contributions of various water sources to headwater streams and how these sources may vary in time and space also provides a decision-making tool for managers to address nutrient mitigation measures across ecoregions and flow classifications. Several natural flow categories exist for streams within the Ozark and Ouachita Interior Highlands (Leasure et al., 2016). Previous work has shown that these classifications influence variation in ecosystem function, discharge, conductivity, and nutrient concentrations, even among minimally-impacted forested systems (Dodd et al., unpublished data). One possible mechanism for these differences in function and water quality is the dominant channel flow source. Further, Leasure et al. (2016) revealed distinct hydroecological areas defined by two dominant flow classifications in the Ozark Highlands and Boston Mountains ecoregions that are likely differentially impacted by pollutants due to differing nutrient buffering capacities and other water quality parameters. These two dominant flow classifications are Runoff Flashy (hereafter Runoff) systems, which dominate the Boston Mountains ecoregion, and Groundwater Flashy (hereafter Groundwater) streams, which dominate the Ozark Highlands.

Currently, little information is available to address the influence of flow regime on the spatial and temporal extent that pollutants may be mitigated by dilution with groundwater inputs. This is critical for freshwater conservation, as understanding the nutrient buffering capacity of streams and variation in water quality lays the foundation for better water resource management (Jarvie et al., 2014). It is especially important to determine these parameters in streams that experience high traffic by the public for recreation, such as forested streams, as pollution in these areas can lead to the closing of campgrounds and swimming areas during the summer months. Source-related nutrient enrichment in forested streams would signal a need for additional focused efforts in agricultural systems. Differences in flow sources and, in turn, potential avenues for enrichment allow managers to focus on streams that are most susceptible to water quality degradation.

Our study objective was to use water chemistry and hydrologic field data to confirm distinctions between groundwater and surface water-dominated modeled flow regime classifications. We investigated whether actual stream water sources align with predicted flow types and how nutrient concentration in source waters affected instream nutrients. We also examined conductivity, gross primary production, and community respiration. We predicted that groundwater would contribute 70 to 95% of the flow in Groundwater streams and less than 50% of flow in Runoff streams based on previous studies in this region (Jarvie et al., 2014).

Methods

This study took place in six minimally-impacted forested streams (Figure 1). Three streams classified as Runoff systems were located in the Boston Mountains ecoregion, while three Groundwater streams were nested within the Ozark Highlands ecoregion. All streams were nested with-



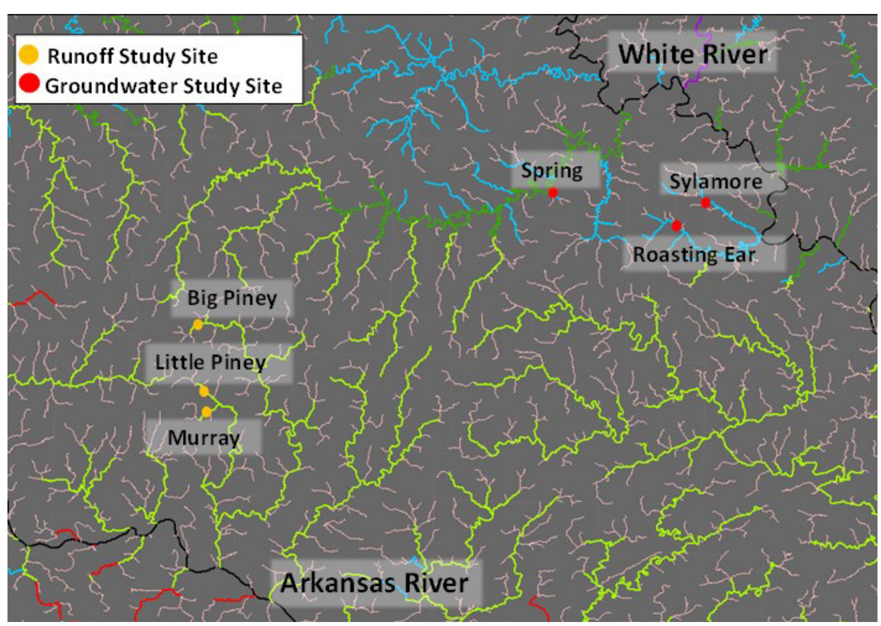


Figure 1. Map of flow regimes in the Ozark and Ouachita Interior Highlands based on Leasure et al. (2016). Highlighted area shows individual study sites sampled from 2018 to 2019 across northern Arkansas. Teal streams in map represent groundwater streams. Light green streams in map represent runoff streams.

in watersheds that consisted of 84-97% forested land cover and 1-8% pastoral land use, with existing datasets showing strong relationships with downstream USGS gage discharges (R^2 values from 0.70 to 0.94).

Water samples were taken roughly every two weeks as well as during storm flow for total nitrogen (TN), total phosphorus (TP), conductivity, and trace and rare earth elements from March 27th to May 19th, then from July 31st to November 2nd, 2018. Flow in study reaches was monitored using established relationships between discharge in the reach and discharge at a downstream USGS gage or a nearby proxy gage within the watershed. Groundwater sources were directly sampled from a well at least monthly and deposition samples were collected directly after precipitation events using a rain sampler placed near the stream in an area of little to no canopy cover. Nutrient concentrations of source waters (rain and groundwater) were measured on the six sampling dates from August 1st to October 30th.

Persulfate digests of unfiltered water samples followed by colorimetric benchtop SRP analyses using the ascorbic acid method yielded TP concentrations. TN was determined using a Shimadzu TOC-L analyzer (Shimadzu Corporation, Kyoto, Japan). Samples for trace elements and metals (aluminum, arsenic, barium, beryllium, boron, cadmium, cesium, cobalt, chromium, copper, iron, potassium, lithium, lutetium, manganese, mercury, molybdenum, phosphorus, nickel, lead, samarium, selenium, titanium, uranium, vanadium, and zinc) were measured on an inductively-coupled plasma mass spectrometer (Thermo Fisher Scientific, Waltham, MA) on source (groundwater and precipitation) and stream water samples to estimate relative surfacewater:groundwater contributions.

End-member mixing analysis (EMMA) was employed to apportion water sources. Conservative tracers were identified and confirmed using pairwise comparisons of all tracer combinations (Hooper 2003). Mixing ratios (m) were determined according to the equation

$$m = \frac{[\text{Tracer}]_{\text{sample}} - [\text{Tracer}]_{\text{groundwater}}}{[\text{Tracer}]_{\text{precipitation}} - [\text{Tracer}]_{\text{groundwater}}}$$

(Rueedi et al., 2005)

Nutrient concentrations, conductivity, discharge, and mixing fractions were compared across flow regimes and sampling dates using repeated-measures ANOVA (RM-ANOVA). Linear regressions were used to investigate relationships between mixing fractions and discharge as well as nutrient concentrations and discharge. Unless otherwise specified, data are reported as median ± standard error of the median.

Results and Discussion

Groundwater accounted for 70% or more of channel flow in Groundwater streams on eight out of twelve (67%) of sampling events. During base flow, median groundwater contribution to channel flow in Groundwater streams was 82 (±3.4)%. Groundwater made up 35 (±14.3)% of channel flow during storm events. Two out of three Groundwater streams were not diluted by precipitation inputs during one storm event in late August, which accounted for the high variation in storm sample groundwater fractions.

In Runoff streams, groundwater contributed less than 25% of channel flow on all but one sampling date (Figure 2). On April 6th, 2018, Runoff streams consisted of 60 (±17.0)% groundwater. Median base flow groundwater contribution was 10 (±6.0)%, while median storm flow contribution was 14 (±3.9)%. These findings align with model-predicted flow sources, though these data reveal a degree of temporal variation in dominant sources, especially in Groundwater streams when inundated by storm runoff.

Discharge differed between flow regimes on three sampling dates, two of which were storm events (Flow: $F(1,25)= 0.17$, $p=0.68$; Date: $F(11,25)$: 11.62, $p<0.0001$; Flow*Date: $F(11,25)$: 2.20, $p=0.05$). Groundwater site discharge increased with percent flow derived from precipitation ($R^2= 0.48$, $p=0.01$). However, Runoff sites did not exhibit any relationship between mixing fractions and discharge ($R^2= 0.08$, $p=0.38$). Median base flow in Runoff streams was 0.40 (±0.38) m^3/s, while discharge in Groundwater streams was 0.66 (±0.76) m^3/s. Storm flow in Runoff streams was 6.48 (±3.14) m^3/s, while median storm flow in Groundwater streams was 4.52 (±2.63) m^3/s. Hydrographs showing median flows within each flow regime are shown in Figure 3.

Conductivity was greater in Groundwater streams (Flow: $F(1,25)=926.77$, $p<0.0001$) and was greatest during the summer/early fall when discharge was low (Date: $F(11,25)$: 5.33, $p<0.0001$; Flow*Date: $F(11,25)$: 0.92, $p=0.52$). Con-

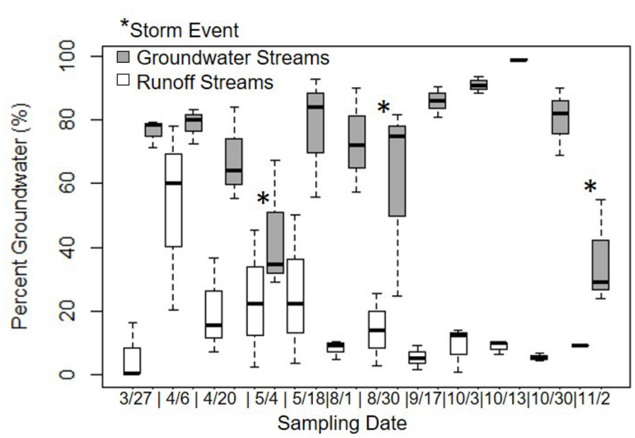


Figure 2. Median groundwater contribution to Runoff and Groundwater streams on each sampling date. Whiskers represent ± 1 SE of median.

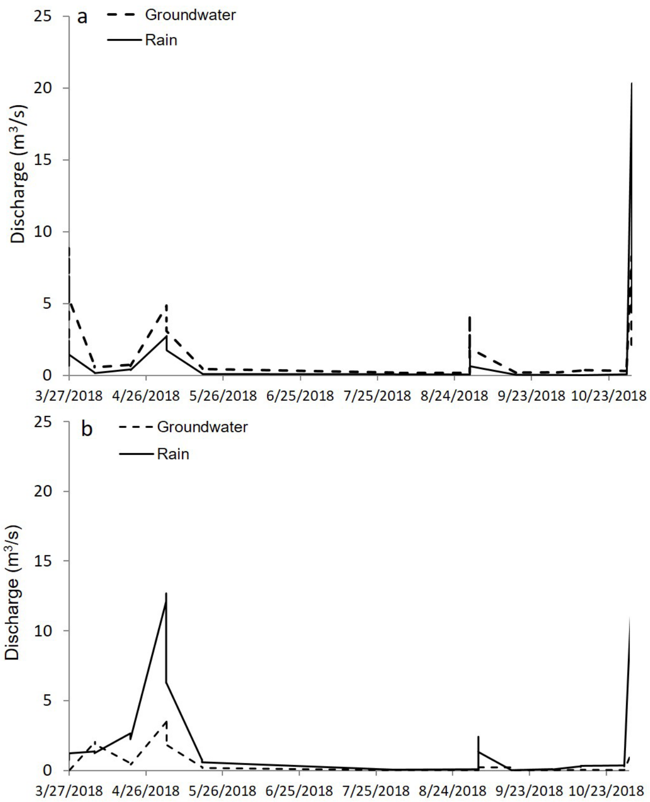


Figure 3. Median hydrographs for (a) Groundwater and (b) Runoff streams, illustrating groundwater and precipitation contributions to channel flow over the study period.

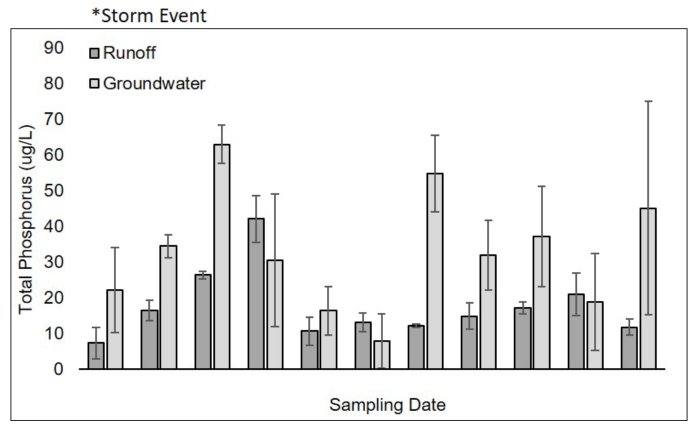


Figure 4. Median instream total phosphorus concentrations on each sampling date. Whiskers= 25th and 75th percentiles.

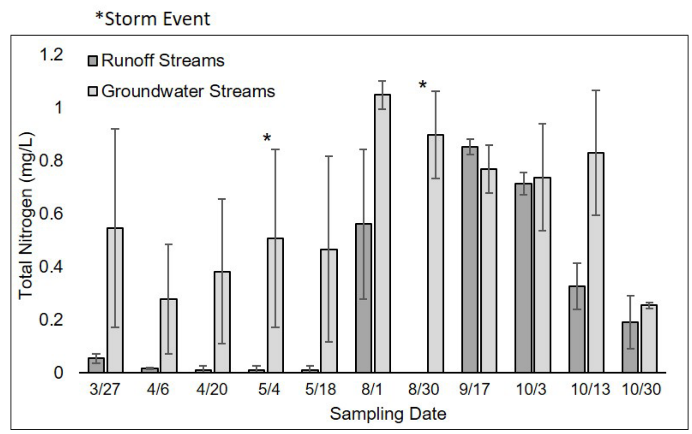


Figure 5. Median instream total nitrogen concentrations on each sampling date. Whiskers= 25th and 75th percentiles.

ductivity varied from 123 to 294 µS/cm in Groundwater streams, while conductivity in Runoff streams ranged from 11 to 47 µS/cm. Runoff stream conductivity was not related to discharge or source mixing fractions; however, Groundwater stream conductivity increased with greater groundwater contributions (R^2=0.64, p=0.03). Groundwater sources across flow regimes exhibited high conductivity (Groundwater=183±81 µS/cm, Runoff=199±33 µS/cm), while precipitation samples had low conductivity across flow regimes (Groundwater=14±6 µS/cm, Runoff=3±0.89 µS/cm).

Total phosphorus concentrations differed by flow regime on four out of twelve sampling dates (RM-ANOVA; Flow: F(1,25)=10.61; p=0.003; Date: F(11,25): 3.34, p= 0.002; Flow*Date: F(11,25): 48.0, p<0.0001) (Figure 4). Specifically, Groundwater streams held greater phosphorus concentrations on three sampling dates (April 6, April 20, and August 30), while Runoff streams exhibited greater P during the final storm sampling event on November 1. Runoff stream P concentrations ranged from 7.33 to 26.38 µg/L P under base flow conditions, while Groundwater stream P ranged from 7.9 to 63 µg/L P. Storm event P levels ranged from 12.19 to 42.09 µg/L P in Runoff streams and 0.94 to 54.81 µg/L P in Groundwater streams. Rain and groundwater P concentrations were not related to instream P concentrations in either flow regime (Table 1). We observed greater variation in Groundwater stream P, which may be due to pastoral land use in the surrounding area around Roasting Ear Creek. Regardless, P from groundwater and precipitation inputs did not drive instream P concentrations.

Total nitrogen concentrations were greater in Groundwater streams (RM-ANOVA: Flow: F(1,21)=9.43; p=0.004) (Figure 5). Nitrogen did not differ significantly across sampling dates (Date: F(11,21): 1.73, p=0.10; Flow*Date: F(11,21): 0.90, p=0.54). However, we observed that nitrogen levels across flow regimes were consistently low during the spring, reached their maximum levels between August 30th and October 3rd, then declined to their lowest concentrations at the end of the study. Runoff stream nitrogen levels ranged from below detection (<0.01) to 0.85 mg/L N, while Groundwater stream nitrogen varied from 0.25 to 1.05 mg/L N. We found a strong positive relationship between Runoff stream nitrogen and groundwater source N concentrations (R^2=0.93, p=0.007) (Figure 6), though no other relationships between instream and source nitrogen concentrations were observed (Table 1). Additionally, instream nitrogen levels decreased with greater discharge (R^2=

Table 1. Results of linear regression analyses between stream and source water nutrient values. Asterisks denote significant relationships.

Total Phosphorus	R^2	p-value
Runoff		
Stream v. Groundwater	0.05	0.92
Stream v. Rain	0.49	0.32
Groundwater		
Stream v. Groundwater	0.88	0.08
Stream v. Rain	0.4	0.45
Total Nitrogen	R^2	**p-value**
Runoff		
Stream v. Groundwater	0.93	0.007**
Stream v. Rain	0.54	0.26
Groundwater		
Stream v. Groundwater	0.51	0.3
Stream v. Rain	0.27	0.61
Total Organic Carbon	R^2	**p-value**
Runoff		
Stream v. Groundwater	0.37	0.47
Stream v. Rain	0.51	0.3
Groundwater		
Stream v. Groundwater	0.44	0.38
Stream v. Rain	0.36	0.48

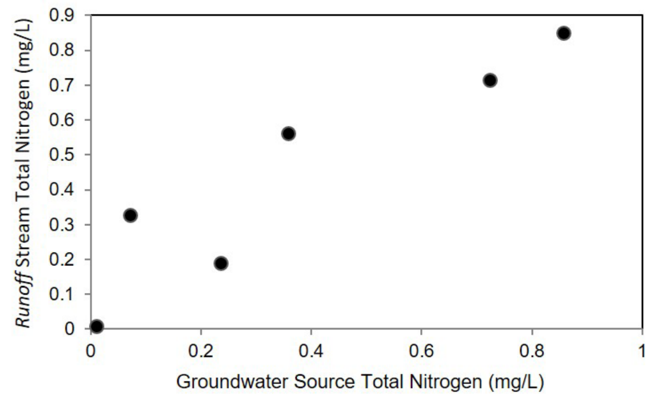


Figure 6. Runoff stream total nitrogen versus groundwater source nitrogen concentrations.

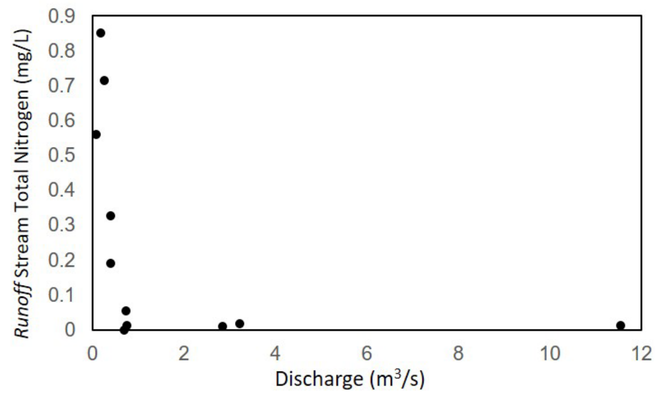


Figure 7. Relationship between Runoff stream discharge and total nitrogen concentrations.

0.86, p=0.03) (Figure 7). These data suggests that groundwater rather than runoff from precipitation is the primary source of instream nitrogen in Runoff systems. Further, precipitation events that increase stream discharge may be diluting nitrogen inputs from groundwater sources. This is of interest given that other Runoff streams in the ecoregion experience greater pressure from anthropogenic activities, and groundwater enrichment exerts a greater influence on instream nitrogen regimes than previously expected.

Total organic carbon (TOC) tended to be greater in Groundwater streams, though TOC levels were not significantly different between flow regimes across sampling dates (Flow: $F(1,25)=0.07$; $p=0.79$; Date: $F(11,25)$: 1.23, $p=0.30$; Flow*Date: $F(11,25)$: 0.32, $p=0.97$). Additionally, instream TOC concentrations were not related to groundwater or rain source TOC in either flow regime (Table 1).

Gross primary production did not differ across flow regimes and sampling dates (Flow: $F(1,16)=0.38$; $p=0.55$; Date: $F(3,16)$: 1.73, $p=0.20$; Flow*Date: $F(3,16)$: 0.09, $p=0.96$). However, ecosystem respiration was greater in Groundwater streams (Flow: $F(1,16)=4.48$; $p=0.05$), though respiration was similar across sampling dates (Date: $F(3,16)$: 1.05, $p=0.40$; Flow*Date: $F(3,16)$: 0.19, $p=0.90$). Stream metabolism was measured only in the late summer and fall portion of the study; three out of four sampling days took place in September and October, which may account for the similarity in production and respiration across dates. Groundwater stream primary production and respiration were both greatest during late August; Runoff stream respiration was also greatest in August, though primary production was similar between August and late October. Stream temperature peaked in August, which likely drove higher rates of production and respiration on that sampling date. Table 2 contains metabolism values for each flow regime across the four days sampled.

Table 2. Gross primary production (GPP) and ecosystem respiration (ER) estimates on four days during summer/fall portion of the study. All values reported in g $O_2/m^2/d$.

	Runoff		*Groundwater*	
Date	GPP	ER	GPP	ER
8/31/2018	1.47	-7.53	2.14	-7.85
10/2/2018	0.52	-1.62	1.35	-5.85
10/18/2018	0.52	-1.67	1.06	-5.12
10/30/2018	1.67	-1.95	1.93	-3.61

Chloride concentrations were consistently greater in Runoff streams (Flow: $F(1,16)=1.67$; $p=0.04$; Date: $F(3,16)$: 0.72, $p=0.25$; Flow*Date: $F(3,16)$: 0.12, $p=0.60$), though chloride concentrations were low across all stream on all sampling dates. Chloride concentrations in Runoff streams averaged 2.83 (±0.25) mg/L Cl, while chloride in Groundwater streams averaged 2.05 (±0.27) mg/L Cl.

Sulfate concentrations were also greater in Runoff streams (Flow: $F(1,16)=1.01$; $p=0.05$; Date: $F(3,16)$: 0.24, $p=0.62$; Flow*Date: $F(3,16)$: 0.12, $p=0.64$). However, similar to chloride, concentrations were low across flow regimes and sampling dates. Sulfate in Runoff streams ranged from 1.03 to 4.67 mg/L SO_4^{2-}, while Groundwater streams exhibited sulfate concentrations of 1.36 to 6.31 mg/L SO_4^{2-}.

Conclusions

This study confirms previous probability models of primary water sources in the two dominant flow classifications across northern Arkansas while revealing temporal variation in rain and groundwater contributions. Even during base flow, streams occasionally exhibited source contributions that departed from predictions- further work to determine the cause of these events would provide greater insight into drivers of channel flow in these systems. Importantly, we discovered a significant link between Runoff stream and groundwater source nitrogen. In the forested, nutrient-limited systems we sampled, this nitrogen provides a subsidy; however, in other areas of the Boston Mountains, encroachment by pastoral and urban land use will necessitate focused attention on potential effects of groundwater enrichment given that streams in this ecoregion are more influenced by groundwater than previously considered.

Acknowledgements

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Image caption: On-farm water storage pond. Photo from Mississippi State Extension.

Herbicide Mitigation Potential of Tailwater Recovery Systems in the Cache River Critical Groundwater Area [updated from 2018]

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Abstract: This study initiated an herbicide monitoring record (April 2017 through March 2018) for seven Arkansas tailwater recovery systems. Four herbicides (clomazone, glyphosate, metolachlor, and quinclorac) were readily detectable and peaked seasonally, reflecting interplay of application timing and precipitation. Clomazone and quinclorac, common spring-applied rice herbicides, were elevated in spring (Apr il 1 through June 15) and summer (June 16 through September 15). Metolachlor was elevated in summer only, reflecting mid-season applications to soybean acres. Glyphosate concentrations peaked in summer, but were also elevated in spring and fall (Septempber 16 through December 15), reflecting frequent, broad spectrum glyphosate use. Herbicide concentrations were otherwise low in off-season months and mostly below detection. During the growing season, clomazone, glyphosate, and quinclorac concentrations were higher in ditches than in the linked reservoir. Metolachlor concentrations were similar in magnitude between linked ditches and reservoirs. The observed spatial and temporal patterns in residual herbicide concentrations will inform best management practices for tailwater recovery systems to preserve Arkansas' water resources into the future. Recovered tailwater should be cycled through and sourced from the reservoir before reapplication to minimize the risk of sensitive crop exposure to residual herbicides. Artificial groundwater recharge strategies should source water from reservoirs and only during winter months to minimize the risk to groundwater. Further, the United States Geological Survey and others can use this dataset to 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.

Key Points:
- Select herbicide concentrations in on-farm reservoir - tailwater recovery systems were frequently detected during the growing season.
- The greatest herbicide concentrations were detected in drainage ditches during the growing season.
- Irrigation from on-farm reservoirs compared to ditches will minimize the risk of off-target cross-crop contamination.
- Strategies to use on-farm reservoir water for managed aquifer recharge should focus on non-growing season.

Introduction

Current agricultural groundwater usage rates in Arkansas are unsustainable, demonstrated by the drawdown of agriculturally important aquifers, such as the Mississippi River Valley Alluvial Aquifer, in recent decades (Konikow, 2013; Schrader, 2015; Reba et al., 2017). Continued groundwater decline is predicted as long as irrigation demand exceeds aquifer recharge (Reed, 2003; Clark et al., 2011; Clark et al., 2013). 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 the Midsouth is anticipated to intensify in the age of herbicide-resistant weeds (Norsworthy et al., 2013; Riar et al., 2013), increasing the likelihood herbicide residues will be found 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 water conservation strategies.

In areas with groundwater decline, such as the Cache River Critical Groundwater Area (CRCGA), agricultural producers have incorporated on-farm storage - tailwater recovery systems into their irrigation practices by constructing a network of ditches paired with a storage reservoir (Fugitt et al., 2011; Yaeger et al., 2017; Yaeger et al., 2018). Ditches capture field runoff, while reservoirs provide capacity to store tailwater and winter-spring precipitation long-term for an irrigation source during the growing season. 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, on-farm storage - 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 on-farm reservoirs has been proposed as a suitable water supply during the non-growing season for managed aquifer recharge (MAR) strategies (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 irrigation water is applied. Further, any MAR water supply source must meet water quality and human health safety standards, since enhanced groundwater recharge will enter a municipal water source.

The objective of this study was to initiate a herbicide monitoring data record for tailwater recovery systems located in the CRCGA (Figure 1). Data from this study can be

Figure 1. Sample location map of the seven monitored tailwater recovery systems (A-G) west of Crowley's Ridge in Poinsett and Craighead counties, Arkansas.

used to screen recovered tailwater for herbicide concentrations that could lead to cross-crop injuries during the growing season, characterize water quality in tailwater systems in terms of suitability for MAR, and estimate herbicide loads in tailwater recovery systems.

Methods

Seven tailwater systems were selected for herbicide monitoring from the CRCGA in Craighead and Poinsett counties west of Crowley's Ridge (Figure 1). Herbicide application records were collected from producers in early April 2017 and updated throughout the growing season. Based on these records, as well as regional frequency of use and anticipated future use, seven target herbicides were selected: 2,4-D, clomazone (e.g. Command®), dicamba (e.g. Clarity®), glyphosate (e.g. RoundUp®), metolachlor (e.g. Dual®), propanil (e.g. Stam®), and quinclorac (e.g. Facet®) (Table 1). Dicamba and 2,4-D were selected based on anticipated future use with the release of tolerant soybean and cotton cultivars.

Tailwater ditch and reservoir grab samples were collected weekly (April 2017 through March 2018) 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) or by enzyme-linked immunosorbent assay with photometric detection (ELISA; glyphosate only). 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 metazachlor to a known concentration to correct for volumetric variability. Eluates were analyzed for concentrations of the target herbicides using HPLC-DAD with a mobile phase gradient of acetonitrile in 0.1% phosphoric acid ranging from 34-64% over 20 minutes. Herbicides were monitored at wavelengths maximizing each compound's absorption intensity (Table 1). Bulk water sample herbicide concentrations were calculated by multiplying the measured concentration in the eluate by the ratio of the eluate and beginning sample volumes after correcting eluate volume for differences in the measured and expected metazachlor concentration. Non-detections or concentrations estimated below reporting limits were censored at the appropriate reporting threshold (Table 1).

Median, mean, and standard deviation of herbicide concentrations were calculated seasonally for all sites combined. Seasons were defined as spring (SPR; March 16 through June 15), summer (SUM; June 16 through September 15), fall (FALL; September 16 through December 15), and winter (WIN; December 16 through March 15). Summary statistics were calculated for ditches and reservoirs across seasons and during the growing season (GS; March 16 through September 15) and off-season (OS; September 16 through March 15). Summary statistics were calculated using analyses adapted for censored datasets (Helsel, 2012). For datasets that were <50% censored, Kaplan Meier survival analysis was used, while robust regression order statistics were used for sites with ≥50-80% censored data. For sites with >80% censored observations, summary statistics could not be calculated. Herbicide concentrations were analyzed for differences in ranks and median concentrations between seasons and between ditch and reservoir subsites using generalized Wilcoxon tests, where increasingly negative or positive score statistics indicate higher and lower median concentration, respectively. Further comparisons were conducted on adja-

Table 1. Chemical name and analysis details for the seven herbicides selected for monitoring in this study. Six herbicides were analyzed using high performance liquid chromatography with diode array detection (HPLC-DAD). Glyphosate was analyzed using enzyme-linked immunosorbent assay (ELISA) with photometric detection. Compounds were measured at wavelengths that maximized absorbance. Reporting limits were set at 10 times the method quantification limit.

Herbicide	Chemical Name	Analysis	Wavelength (nm)	Reporting Limit (µg/L)
2,4-D	2,4-dichlorophenoxyacetic acid	HPLC-DAD	200	0.50
Clomazone	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-1,2-oxazolidin-3-one	HPLC-DAD	195	0.80
Dicamba	3,6-dichloro-2-methoxybenzoic acid	HPLC-DAD	200	0.80
Glyphosate	N-(phosphonomethyl)glycine	ELISA	450	0.50
Metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl)acetamide	HPLC-DAD	195	2.0
Propanil	N-(3,4-dichlorophenyl) propanamide	HPLC-DAD	210	0.40
Quinclorac	3,7-dichloroquinoline-8-carboxylic acid	HPLC-DAD	226	0.40

cent ditch and reservoir subsites using paired Prentice-Wilcoxon tests. For all analyses, differences were considered significant when p<0.05. Summary statistic calculations and generalized Wilcoxon tests were carried out in R 3.1.6 using the NADA and interval packages. Paired Prentice-Wilcoxon tests were conducted in Minitab® 19.

Results and Discussion

Clomazone, glyphosate, metolachlor, and quinclorac were frequently detected in the monitored tailwater ditches and reservoirs (Figure 2A-D). Dicamba, 2,4-D, 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 in mid-June through early July. No producers reported applying 2,4-D or dicamba. One producer reported propanil use, but 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 detect propanil transport in these systems.

Herbicide concentrations peaked during the growing season (Figure 2A-D; Table 2), with different temporal patterns between herbicides likely reflecting an interplay of application timing and precipitation. Clomazone and quinclorac are common spring-applied rice herbicides (Barber et al., 2019), and generalized Wilcoxon tests indicated that concentrations were higher in the monitored tailwater recovery systems in spring and summer (p-value 0.001). Metolachlor concentrations were higher in summer only (p-value 0.001), likely reflecting mid-season applications to soybean acres. Glyphosate concentrations peaked in the summer but were also higher in spring and fall relative to winter (p-value 0.001), likely reflecting the frequent, broad spectrum use of glyphosate. Herbicide concentrations were lowest (p-value 0.001) and usually below detection in off-season months. Clomazone and metolachlor were rarely detected in the tailwater recovery systems outside of the growing season, such that summary statistic calculations were not possible. Glyphosate and quinclorac detections were frequent in fall and winter, but concentrations were low in magnitude compared to peak summer months.

Differences in herbicide concentrations between ditches and reservoirs were also observed (Table 3) and were most apparent when data were partitioned into growing season and off-season datasets and when ditches and reservoirs were paired within sites. During the growing season, the paired Prentice-Wilcoxon tests indicated that concentrations of clomazone, glyphosate, and quinclorac were

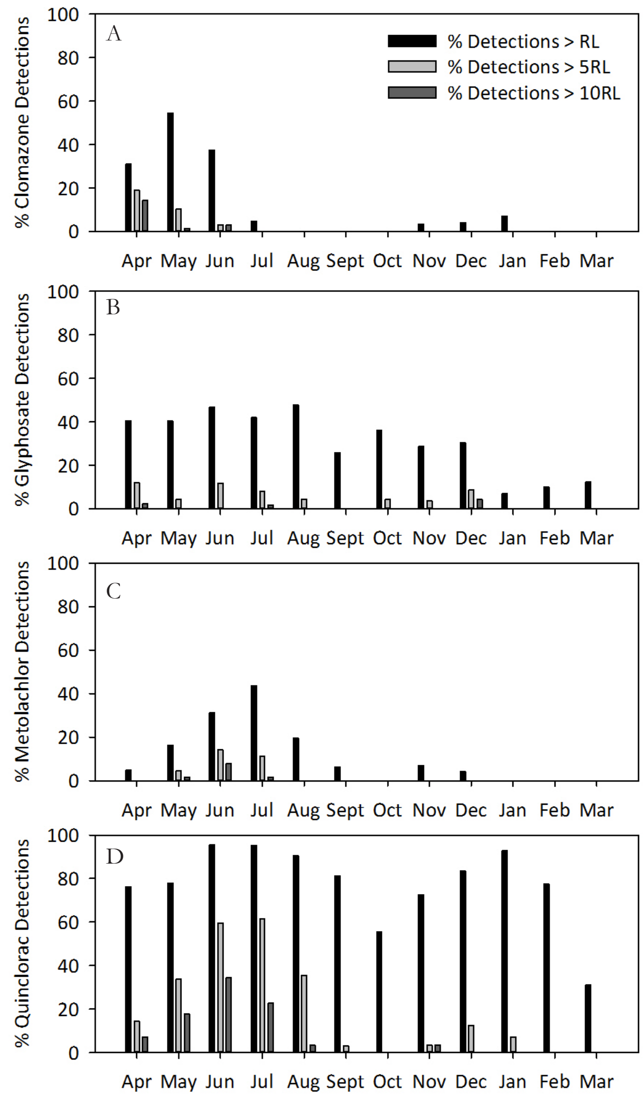

Figure 2. Frequency of herbicide detections: detections greater than the reporting limit (RL), detections > 5 times the reporting limit (5RL), and detections > 10 times the reporting limit (10RL). These values are expressed as a percentage of the total number of samples for the month, during the period April 2017 through March 2018 for A) clomazone, B) glyphosate, C) metolachlor, and D) quinclorac.

higher in the ditches than in the adjacent reservoirs (p-value <0.001). The trend of higher concentration in ditches than reservoirs was clearest for glyphosate, with results from all seasons and both paired and unpaired subsites supporting this interpretation. In contrast, no differences were found between metolachlor concentrations in ditch and reservoir subsites during the growing season for either analysis (p-value>0.05), with the concentration maxima in a similar range for ditches and reservoirs (Table 2).

For both metolachlor and quinclorac, generalized Wilcoxon test results indicated that reservoir concentrations exceeded ditch concentrations during the off-season (p-value 0.002). For quinclorac, paired Prentice-Wilcoxon test results substantiated this finding for linked reservoirs and ditches (p-value<0.001). Higher reservoir concentrations could reflect more frequent flushing in ditches during the wetter

Table 2. Summary statistics of herbicide concentrations by season for the four herbicides that were frequently detected in the tailwater recovery systems. For datasets with >80% censored observations, mean and standard deviation (StDev) could not be estimated, and median was known only to be below the reporting limit. Results of generalized Wilcoxon tests comparing concentration ranks and medians between seasons are reported for spring (SPR; March 16 through June 15), summer (SUM; June 16 through Septempter 15), fall (FALL; September 16 through December 15), and winter (WIN; December 16 through March 15). Increasingly negative score statistics indicate higher median herbicide concentration; while increasingly positive score statistics indicate lower median herbicide concentration. Seasonal differences were considered significant when p<0.05, with lower case letters indicating seasons or season groupings that were statistically different.

	n				Median (µg/L)				Wilcoxon Score Statistic				
Compound	SPR	SUM	FALL	WIN	SPR	SUM	FALL	WIN	SPR	SUM	FALL	WIN	Wilcoxon p
Clomazone	142	141	106	71	0.57	<0.80	<0.80	<0.80	-43.91 a	1.08 b	26.62 c	16.21 c	0.001
Glyphosate	141	129	103	71	0.45	0.57	0.20	<0.50	-6.57 ab	-16.99 a	6.483 b	17.08 c	0.001
Metolachlor	142	141	106	71	<2.0	1.06	<2.0	<2.0	14.34 b	-42.47 a	16.73 b	11.4 b	0.001
Quinclorac	142	141	106	71	0.90	2.0	0.6	0.50	-1.09 b	-49.15 a	27.89 c	22.36 c	0.001

	Mean (µg/L)				StDev (µg/L)				Maximum (µg/L)			
Compound	SPR	SUM	FALL	WIN	SPR	SUM	FALL	WIN	SPR	SUM	FALL	WIN
Clomazone	2.2	-	-	-	6.5	-	-	-	67	2.0	3.0	2.0
Glyphosate	0.86	0.96	1.4	<0.50	1.1	1.0	9.3	-	5.2	6.2	95	3.4
Metolachlor	-	3.2	-	-	-	5.6	-	-	20	32	2.0	<2.0
Quinclorac	3.4	2.7	0.84	0.66	8.5	4.5	1.9	0.39	62	37	20	3.0

winter months, but the herbicide concentrations and detected differences between reservoirs and ditches during this period were small in magnitude relative to the growing season. For metolachlor, this finding appears to have been driven by a few low-level detections in reservoirs during fall months and was not substantiated when concentrations were compared only between linked ditches and reservoirs.

Residual concentrations of three of the seven monitored herbicides were higher in ditches than in reservoirs during the months surrounding herbicide application. This finding is congruent with the concept that herbicide residues are diluted along the flow path by mixing with increasingly large water volumes with lower residual concentrations, as well as degradation 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 within four river networks in the region, including the Cache River. In that study, concentrations decreased moving downstream, as basin flow increased. However, a previous 13-month study comparing herbicide and nutrient concentrations in the ditches and reservoirs of a tailwater recovery system in the region found no water quality differences (Moore et al., 2015).

Conclusions

Herbicides applied to fields adjacent to tailwater recovery systems were frequently detected in the monitored ditches and reservoirs during the 2017 growing season, with higher concentrations in ditches than in reservoirs for clomazone, glyphosate, and quinclorac. Study findings support the following recommendations to minimize risk of cross-crop contamination when recycling tailwater: 1) use reservoir water for surface irrigation and 2) cycle tailwater through the reservoir for treatment of residual herbicides before reuse. The lowest herbicide concentrations occurred in the winter or fall-winter for all herbicides. During the off-season, metolachlor and quinclorac concentrations were higher in reservoirs than in ditches, but concentrations were low and subsite differences were minor compared to the growing season. These findings support targeting winter months (mid-December to mid-March) to use on-farm reservoirs as source water for MAR strategies in order to protect groundwater quality. The herbicide residue monitoring record initiated in this study and the observed patterns between seasons and subsites will inform best management practices for tailwater recovery systems to preserve Arkansas' water resources into the future. Further, the United States Geological Survey and others can use this dataset to 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.

Acknowledgements

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Table 3. Summary statistics of herbicide concentrations by subsites for the four herbicides that were frequently detected in the tailwater recovery systems. Summary statistics were calculated both across seasons and for the growing season (GS) and off- season (OS). For datasets with >80% censored observations, mean and standard deviation (StDev) could not be estimated, and median was known only to be below the reporting limit. Results of generalized Wilcoxon tests comparing concentration ranks and medians between ditches and reservoirs (Rsvr) are reported, with increasingly negative or positive score statistics indicating higher or lower median herbicide concentrations, respectively. Results of paired Prentice-Wilcoxon test comparing herbicide concentrations between linked ditches and reservoirs are reported, with a positive median difference indicating higher concentrations in ditches and a negative median difference indicating higher concentrations in reservoirs. Differences between ditches and reservoirs were considered significant when p<0.05 for both tests.

		n		Median (µg/L)		Wilcoxon Score Statistic		
Herbicide	**Dataset**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**	**Wilcoxon p**
Clomazone	All	251	209	0.13	<0.80	-8.43	8.43	0.088
Clomazone	GS	156	127	0.29	<0.80	-8.36	8.36	0.056
Clomazone	OS	95	82	<0.80	<0.80	-1.33	1.33	0.27
Glyphosate	All	244	200	0.55	0.18	-51.04	51.04	0.002
Glyphosate	GS	150	120	0.71	0.28	-29.9	29.9	0.002
Glyphosate	OS	94	80	0.28	<0.50	-18.78	18.78	0.002
Metolachlor	All	251	209	<2.0	<2.0	8.92	-8.92	0.082
Metolachlor	GS	156	127	0.48	0.78	-0.57	0.57	0.9
Metolachlor	OS	95	82	<2.0	<2.0	10.66	-10.66	0.002
Quinclorac	All	251	209	0.80	0.90	1.34	-1.34	0.828
Quinclorac	GS	156	127	2.0	0.90	-20.78	20.78	0.002
Quinclorac	OS	95	82	0.40	0.70	21.89	-21.89	0.002

	Paired Prentice-Wilcoxon test		Median (µg/L)		StDev (µg/L)		Maximum (µg/L)	
Herbicide	**Median Difference**	**p**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**	**Ditch**	**Rsvr**
Clomazone	-0.078	<0.001	1.2	-	5.0	-	67	6.0
Clomazone	0.078	<0.001	1.9	-	6.2	-	67	6
Clomazone	0.08	0.083	-	-	-	-	3.0	<0.80
Glyphosate	0.50	<0.001	1.4	0.36	6.1	0.52	95	4.1
Glyphosate	0.50	<0.001	1.3	0.47	1.2	0.56	6.2	4.1
Glyphosate	0.50	<0.001	1.6	-	9.8	-	95	3.0
Metolachlor	0.20	0.83	-	-	-	-	32	22
Metolachlor	0.20	0.39	2.4	1.8	5.3	3.1	32	22
Metolachlor	0.072	0.056	-	-	-	-	2.0	2.0
Quinclorac	-0.019	0.67	3.2	1.0	7.3	0.74	62	6.0
Quinclorac	0.44	<0.001	4.6	1.2	8.8	0.89	62	6.0
Quinclorac	-0.34	<0.001	0.77	0.77	2.0	0.3	20	2.0

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Image caption: Irrigated cropland in the Arkansas Delta.

Groundwater and Time Preference Elicitation: Estimating the Value of Market and Non-Market Groundwater Services Over Time

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Abstract: Limited evidence exists about the public's willingness to pay (WTP) and time preferences for sustainable groundwater management policies. Evidence is also limited for how WTP and time preferences relate to market versus non-market groundwater services. We conducted a choice experiment survey in Arkansas, the largest consumer of groundwater in the Lower Mississippi River Basin (LMRB), to jointly estimate the public's WTP and rate of time preference for groundwater preservation in the Mississippi River Valley Alluvial Aquifer (MRVA). Marginal WTP is estimated for groundwater services (certainty of irrigation supply known as buffer value, jobs in agriculture, groundwater quality, wildlife habitat, and avoidance of subsidence) and for two distinct management policies (surface water infrastructure and a cap and trade program for groundwater trading) relative to the status quo of subsidies for best management practices. Results show a significant and positive marginal WTP for buffer value and for jobs from irrigated agriculture, while there is a clear preference for surface water infrastructure investment over a cap and trade groundwater market.

Key Points:

- A choice experiment elicits time preferences for groundwater service values in Eastern Arkansas.
- The largest public values of groundwater relate to agricultural production and water quality, and the policy preference is for surface water infrastructure investment over a cap-and-trade groundwater market.
- Time preferences indicate that the present value of future groundwater services diminishes at an annual exponential discount rate of about 35%.

Introduction

Current policies to mitigate groundwater scarcity mostly involve voluntary incentive programs that target agricultural users because they hold long-term financial interests linked to groundwater availability. However, aquifer depletion continues and even accelerates in many agricultural production regions despite current management efforts (Konikow, 2015; Schaible and Aillery, 2012), warranting deeper policy consideration. Efficient policies consider values to society rather than only to the marketplace. The benefits of groundwater cannot be appropriately valued solely on market forces, and a better framework considers the importance of groundwater across all of its values to society.

This study focuses on the Mississippi River Valley Alluvial Aquifer (MRVA), a valuable water resource asset economically and strategically that supports intensive irrigated crop production in the Lower Mississippi River Basin (LMRB). High levels of groundwater use and expanding irrigated acreage have drawn down groundwater levels in the MRVA, and the current rate of withdrawal threatens the long-term viability of irrigated agriculture in the region. More than 98% of water use from the MRVA goes to support agricultural irrigation (USDA, 2013), and current valuation and management of the groundwater focuses on its extractive uses.

Consideration for the total economic value (TEV) of groundwater is crucial for estimating the net benefits of potential policies and management actions. Furthermore, policymakers would benefit from greater knowledge about how groundwater's social value disaggregates among its constituent components: market and non-market values, or direct use values (i.e., extractive uses), passive use values (e.g., subsidence avoidance), non-use values (i.e., use by others or by future generations), and option values (i.e., ensuring the option to use in the future). Identifying all groundwater services within a region and then estimating the public's WTP for preserving each of those services provides a detailed starting point for estimating these component values. There is however limited empirical evidence about the public's WTP for preserving groundwater in aquifers facing depletion due to irrigated agriculture. Beyond TEV, even less is known about the relative values placed on the existing flows of groundwater services.

The dynamics of aquifer depletion and recharge are complex, and meaningful resource change occurs over decadal timescales, which complicates valuation and policy deliberation. This makes understanding the time preferences for the flow of groundwater services vital for appropriately managing them. Hence, joint modeling of the annual flow of groundwater services and time preferences is important. This also allows policymakers to calculate the TEV with social discount rates. The literature has widely observed that individuals have high rates of discounting (Meier and Springer, 2010; Frederick, 2002). But social investments are typically made with social discount rates rather than individual discount rates. By separating the value of annual groundwater services from individual time preferences, a recalculation of the TEV with social discount rates is possible. This provides policymakers with a social TEV to weigh against the policy costs when evaluating social projects.

The optimal framework for valuing groundwater considers not only hydrologic factors and the aggregation of all existing flows of groundwater services, but also temporal and policy contexts. The value of groundwater is affected by circumstances, and only a limited number of studies explore groundwater valuation across alternative policy contexts or in contexts that incorporate realistic environmental timescales and time discounting. Potential policy initiatives for addressing groundwater decline include improved irrigation efficiency, surface-water infrastructure projects, managed aquifer recharge (MAR), and the establishment of groundwater marketplaces to facilitate regional pumping caps and efficient trading of allocated pumping permits (Reba et al., 2017; Chong and Sunding, 2006).

The objective of this research is to conduct a choice experiment (CE) in order to estimate total WTP for groundwater preservation under different policy alternatives, as well as marginal WTP for existing groundwater services and rates of time preference. We conducted the CE survey in Arkansas, the largest consumer of MRVA groundwater, and then estimated the marginal WTP values for groundwater services (certainty of irrigation supply known as buffer value, jobs in agriculture, groundwater quality, wildlife habitat, and avoidance of subsidence) and for two distinct management policies (surface water infrastructure and a cap and trade program for groundwater trading) relative to the status quo of subsidies for best management practices. We also estimated time preference parameters associated with the costs and benefits of long-term groundwater management.

Methods

Intertemporal Utility and Time Preference Functions

Public goods policies such as those for the long-term management of groundwater resources exemplify choices that realize benefits and costs at different points in time. Money invested today in groundwater savings can produce benefits that continue into the future. In fact, meaningful benefits from groundwater savings may not accrue or begin to be realized until a policy has been underway for some years. Individuals typically discount the utility they receive from future outcomes relative to the utility of current outcomes. Samuelson (1937) developed the first discounted utility model for intertemporal choice commonly known as the exponential discounting model, estimating a single dis-

count rate parameter. This is the standard model for intertemporal utility, largely because of its simplicity (Meyer, 2013a; Frederick, 2002). The exponential discounting function takes the form of

$$U(c_0, c_1, \ldots, c_T) = \sum_{t=0}^{T} \psi_t u(c_t),$$

where the discount factor for year t is $\psi_t = \left[\frac{1}{1+\rho}\right]^t$ and ρ is the discount rate.

We integrate this time preference function into a discounted utility model similar to Meyer (2013a; 2013b).

Empirical Model

To analyze discrete choice data involving intertemporal goods, let the instantaneous utility for individual *i* alternative *j* in choice situation *k* and period *t* be given by

$$u_{ijkt} = v_{ijkt} + \xi_{ijkt}.$$

The term, u_{ijkt}, contains a vector of fixed coefficients and a vector of observed variables, while ξ_{ijkt} is the instantaneous error draw. The additively separable utility through time period *T* is given by

$$U_{ijk} = \sum_{t=0}^{T} \psi_t u_{ijkt} = \sum_{t=0}^{T} \psi_t v_{ijkt} + \varepsilon_{ijk},$$

where ψ_t is the discount factor for year *t* and $\varepsilon_{ijk} = \sum_{t=0}^{T} \psi_t \xi_{ijkt}$ is the weighted sum of all instantaneous error draws, weighted each period by the discount factor, ψ_t. We assume that v_{ijkt} depends upon a bundle of alternative-specific groundwater service attribute levels in time period *t*, including benefits, x_{ijkt}, and the cost, p_{ijkt}. The multinomial logit (MNL) specification is then

$$U_{ijk} = \sum_{t=0}^{T} \psi_t \left(-\lambda p_{ijkt} + \boldsymbol{\beta}' \ \boldsymbol{x_{ijkt}}\right) + \varepsilon_{ijk},$$

where ε_{ijk} is distributed i.i.d. Type I Extreme Value.

Respondent *i* chooses alternative *j* in choice situation *k* if $U_{ijk} > U_{imk} \ \forall m \neq j.$. The probability that individual *i* chooses alternative *j* in choice situation *k* is given by,

$$\boldsymbol{P}_{in_{ik}kt} = \frac{\exp(\sum_{t=0}^{T} \psi_t \left(-\lambda p_{ijkt} + \boldsymbol{\beta}' \ \boldsymbol{x_{in_{ik}kt}}\right)}{\sum_{j=1}^{J} \exp(\sum_{t=0}^{T} \psi_t \left(-\lambda p_{ijkt} + \boldsymbol{\beta}' \ \boldsymbol{x_{ijkt}}\right)}$$

The Log-likelihood function is then,

$$LL(\boldsymbol{\beta}, \lambda) = \sum_{k=1}^{K} \sum_{i=1}^{I} \ln \left(\frac{\exp(\sum_{t=0}^{T} \psi_t \left(-\lambda p_{ijkt} + \boldsymbol{\beta}' \ \boldsymbol{x_{in_{ik}kt}}\right)}{\sum_{j=1}^{J} \exp(\sum_{t=0}^{T} \psi_t \left(-\lambda p_{ijkt} + \boldsymbol{\beta}' \ \boldsymbol{x_{ijkt}}\right)} \right)$$

We estimate the model using Maximum Likelihood Estimation (MLE) and a version of the GMNL package in R that has been modified to include the joint estimation of time preference. We include alternative-specific constants (ASCs) that represent choice alternatives different from the reference status quo. To avoid imposing the unrealistic data requirements necessary for estimating ψ_t, structure can be placed on the type of discounting using the exponential discounting formula described in the section above so that we can estimate ψ_t at any time *t* (Meyer, 2013a).

Questionnaire and Experimental Design

For eliciting groundwater and time preferences, we chose to conduct a CE involving MRVA outcomes. Respondents choose among three groundwater management policy alternatives, including a surface water infrastructure (SWI) alternative, a cap and trade (CAT) alternative, and a status quo (SQ) alternative involving no change to current MRVA groundwater management. Information about each alternative is clearly provided to survey respondents, and each respondent must successfully answer comprehension questions about each alternative before advancing in the survey.

To determine the most appropriate attributes for the CE design, we conduct a focus group and collect information about the socio-environmental services people value from MRVA groundwater. Focus group participants reviewed survey questionnaire sections related to the MRVA and potential policy alternatives, discussing clarity, comprehension, and difficulty. This feedback, together with existing conceptual frameworks for groundwater valuation (NRC, 1997), guide the selection of the CE attributes. There are five main groundwater services, or attributes, that we identify contributing to the MRVA's TEV. These are water quality for irrigated agriculture, the provision of jobs in the agricultural economy, the provision of habitat for maintaining wildlife, especially fish and waterfowl for local tourism, the avoidance of subsidence and its associated infrastructure costs, and the certainty of adequate water supply in case of drought (buffer). We rely on existing hydrologic (Clark et al., 2013) and economic (Kovacs et al., 2015) simulation models to help in setting realistic attribute levels for the SQ alternative. The attributes and levels in our CE are shown in Table 1.

We express all attribute levels as percentage values in order to lessen the difficulty of comparing alternatives across multiple attributes. Levels indicate outcomes for the year 2050 and appear in terms of a percentage of current levels, so that 100% indicates no change from current levels. We include a cost attribute using an increase to state income taxes for the household as the payment mechanism.

To identify time preferences, we employ a split-sample design and vary the timing of the expenses associated with the cost attribute. There are treatments for the cost attribute that include perpetual annual payments beginning in the current tax year, perpetual annual payments beginning in the following tax year, a single lump payment for the current tax year, and a single lump payment for the following tax year. By varying the onset and duration of the payment mechanism in the choice sets, estimation of the time preference parameters within the discount factor for the exponential, hyperbolic, and quasi-hyperbolic functional forms is possible (Meyer, 2013a; 2013b). The range of the lump payment

Table 1. Experiment attributes and definitions.

Attribute	Definition	Levels[a,b]
Buffer Quantity	The percentage of current acres with adequate groundwater for 5 consecutive drought years	25%, 40%, 55%, 70%
Water Quality	The percentage of current acres with adequate groundwater quality for irrigation	75%, 80%, 85%, 90%
Jobs from Irrigated Agriculture	The percentage of current (120,000) jobs	80%, 90%, 100%, 110%
Wildlife Diversity & Abundance	The percentage of current wildlife diversity and abundance	75%, 80%, 85%, 90%
Infrastructure Integrity	The percentage of current infrastructure integrity	75%, 80%, 85%, 90%
Cost to Household (lump)	The dollar increase in state income taxes	$0, $30, $90, $150, $210, $270
Cost to Household (perpetual)	The dollar increase in state income taxes	$0, $12, $24, $36, $48, $60

[a] The status quo levels are indicated in bold

[b] Levels indicate outcomes for the year 2050 and 100% indicates no change from current levels

cost attribute levels is similar to Meyer (2013a; 2013b) and Viscusi et al. (2008). Following Egan et al. (2015), we convert lump payment levels to perpetual payment levels using a 25% discount rate and rounding to equal-interval dollar amounts.

This study elicits preferences for long-term groundwater management policies implemented at the state level. We concentrate on sampling voting-aged residents of Arkansas, where the dominant portion of the MRVA is located and the most groundwater use occurs. Between August 27th and October 17th of 2018, we administered a stated preference survey regarding long-term MRVA groundwater management and outcomes using the survey research firm, Qualtrics. Approximately 2000 adult residents of Arkansas voluntarily accessed the four versions of the internet-based survey from proprietary research panels and other internet sources. The survey is designed to be compatible with both traditional and mobile internet platforms. Individuals receive financial incentive for participating in Qualtrics surveys. Qualtrics pre-filters responses to remove any potential duplicate from a single individual or any observation with a total response time less than one-third the median total response time. Observations that are incomplete are dropped from the analysis, leaving 782 usable survey responses and data for 3,910 choice occasions.

Results and Discussion

Overall, the sample is a close representation of the target population. Relative to the general population of Arkansas residents, our sample shares characteristics for median income and unemployment rate while being slightly older (median age 42 compared to 38), more female (66% to 51.5%), and more educated (30.3% with bachelor's degree to 23.4%) (US Census Bureau, 2018). Statistics on voters and registered voters in the US suggest that the voting electorate shares these same biases relative to the general population (File, 2018), supplying added confidence in the validity of the stated preferences for groundwater policies. Table 2 provides summary statistics for sample demographics. The spatial distribution of the sample also closely represents Arkansas's actual population density. Comparing sample proportions across Arkansas's 75 counties to the Census population proportions using the Mann-Whitney test shows no significant difference (p-value=0.247).

Table 3 shows the results from the joint estimation of the MNL model, including the estimated annual discount rate, preference coefficients for market and non-market groundwater services, and the ASCs for each policy alternative. Marginal WTP present values are computed and reported in Table 4. Results indicate significant and positive preferences for buffer, water quality, and jobs from irrigated agriculture. The policy preference is clearly for current sub-

Table 2. Sample demographics.

Characteristic	MRVA Survey Sample	Arkansas Population
Median Age	42	38
(standard deviation)	-15.29	
Percent Female	66	51.5
(standard error)	-0.017	
Mean persons per household	2.85	2.53
(standard deviation)	-1.27	
Median household income	$ 40,000 - $ 49,000	$45,869
Percent high school degree or higher	95.3	86.7
(standard error)	-0.008	
Percent bachelor's degree or higher	30.3	23.4
(standard error)	-0.016	
Percent married	57.9	49.2
(standard error)	-0.018	
Percent Unemployed	6.3	5.6
(standard error)	-0.009	

Table 3. Model results.

Parameter	Estimate	P-value
Exponential-r	0.353	< 0.001***
	-0.050	
ASC.SW	-0.085	0.465
	-0.117	
ASC.CAP	-0.249	0.0350**
	-0.118	
Buffer	0.070	0.0009***
	-0.021	
Quality	0.122	0.0148**
	-0.050	
Jobs	0.072	0.0155**
	-0.030	
Wlife	0.042	0.288
	-0.040	
Infra	0.039	0.329
	-0.040	
Cost	-0.010	< 0.001***
	-0.001	
LogLiklihood		-4212.5

Table 4. Marginal willingness to pay (WTP) results.

Marginal WTP	
ASC.SW	-8.714
ASC.CAP*	-25.357
Buffer*	7.122
Quality*	12.490
Jobs*	7.306
Wlife	4.316
Infra	3.959

*Computed from significant MNL estimates

sidy programs over the initiation of a cap-and-trade groundwater market. Any differences in preference between the status quo and new investments in surface water infrastructure are not indicated to be significant. The greatest marginal WTP is for the provision of the water quality service (about $12 per 1% increase over 30 years), while buffer and jobs are valued similarly (about $7 per 1% increase over 30 years). The joint estimation indicates an annual exponential discount rate of 35%.

Conclusions

We conduct a choice experiment in Arkansas to estimate preferences for groundwater services in the MRVA. The results of the MNL estimation support the conclusion that Arkansas residents value groundwater in the alluvial aquifer primarily for its provision of services related to agricultural production. These constitute use values of the groundwater, and current policies are aimed at maintaining the groundwater's use values. The lack of any significant preference for wildlife service provision or subsidence avoidance shows there is no evidence for any desired shift in current policies.

The same conclusion is supported by the ASCs for alternative policies. The ASC for a cap-and-trade groundwater alternative is significant and negative, indicating a strong preference for the status quo. The ASC for additional investment in surface water infrastructure is not significant. It may be that close similarities between the surface water infrastructure alternative and the status quo explain this similarity in policy preference between them, as surface water infrastructure impoundments are an important component of current best management practices.

Water quality provision that is adequate for agricultural irrigation has the highest marginal WTP valuation among the groundwater services. This compares predictably to other literature that shows very high preferences for attributes related to food safety (Bazzani et al., 2018), which may be a driving concern when considering water quality for agricultural irrigation.

Relative to similar studies that use stated preference methods to empirically estimate a social discount rate for environmental improvements, we estimate an annual exponential discount rate with a similar, but slightly larger magnitude. Meyer (2013a) and Meyer (2013b) find annual discount rates that range from about 10% to about 13%. Viscusi et al. (2008) finds an annual discount rate that ranges from about 8% to over 14%. They observe a discount rate as high as 22.9% for people who make no use of the environmental area in question. Though lower than our estimated annual discount rate of 35%, the differences are not large and could reflect systematic differences between target populations of the respective studies. Meyer targets residents of Minnesota and Viscusi a nationwide sample, while we examine preferences of Arkansas residents. Compared to Minnesotans and the nation at large, Arkansas residents in our study demonstrate a higher rate of time preference, meaning they place greater weight on present benefits relative to future ones.

A higher rate of time preference theoretically translates to lower social investment in future benefit streams. The results of our survey indicate that current groundwater policies in the state of Arkansas, though perhaps insufficient to reverse the trend of groundwater depletion present in the MRVA, are well aligned with the overall policy preferences of Arkansas residents. There is no evidence of any preference either for a paradigmatic shift in policy (i.e., cap-and-trade groundwater market) or a significant increase in investments for surface water infrastructure projects. Continuing research should seek to better understand segments of the population that possess significantly different groundwater preferences and examine the spatial or socio-demographic characteristics that might be driving those differences. These differences could have meaningful implications for indicating the most appropriate scale or policy arena in which to advance new long-term groundwater management policies.

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