5-2015

Effects of Landscape Disturbances on Autotrophic Processes Within Arkansas Ozark Streams

Bradley J. Austin
University of Arkansas, Fayetteville

Recommended Citation
Austin, Bradley J., "Effects of Landscape Disturbances on Autotrophic Processes Within Arkansas Ozark Streams" (2015). *Theses and Dissertations*. 22.
http://scholarworks.uark.edu/etd/22

Effects of Landscape Disturbances on Autotrophic Processes Within Arkansas Ozark Streams

Effects of Landscape Disturbances on Autotrophic Processes Within Arkansas Ozark Streams

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Biology

by

Bradley J. Austin
Ottawa University
Bachelor of Arts in Biology, 2005
Fort Hays State University
Master of Science in Biology, 2008

May 2015
University of Arkansas

This dissertation is approved for recommendation to the Graduate Council.

Dr. Michelle A. Evans-White
Dissertation Director

Dr. Daniel D. Magoulick
Committee Member

Dr. John D. Willson
Committee Member

Dr. J. Thad Scott
Committee Member

Abstract

Land-use change is one of the most widespread human impacts and can influence abiotic and biotic processes within surrounding streams. For example, streams in agricultural and urban watersheds receive greater light and nutrient inputs that can promote increased algal growth and primary production. Natural gas (NG) infrastructure development, a recent land use change in many regions, may also stimulate forested stream primary production, by reducing forest cover and increasing sediments and nutrient transport. I sampled streams across a NG activity gradient for algal biomass and gross primary production (GPP) to assess potential effects of this emerging land-use type. Algal biomass and GPP were positively associated with NG activity during winter, suggesting algal stimulation by nutrient enrichment of streams impacted by NG activity. To examine the nutrient limitation status of my study streams, I experimentally manipulated nitrogen (N) and phosphorus (P) in diffusing substrata and found that while P was not limiting, N-limitation was negatively related to NG activity (R^2= 0.57; p= 0.03). Best management practices (BMPs) have been implemented to help reduce sediment inputs, associated with NG activity on streams, though little has been done to assess their effectiveness. I used a before-after control-impact design to test the effectiveness of implemented BMPs at reducing impacts to autotrophic processes in headwater streams and the South Fork Little Red River. There were no differences between reference and impacted sites before and after the disturbance occurred for the autotrophic processes measured. These results suggest that BMPs were effective at mitigating effects of low levels of NG activity. However, NG activity in the study watersheds was less than in surrounding areas, potentially contributing to the absence of change. In my final study, I examined how human land-use affects recovery of algal communities and metabolic processes to flood disturbances. Biomass and metabolism recovered more rapidly in urban and agricultural

streams than forested streams likely due to increased nutrient availability. These findings highlight the defining role of increased nutrient availability as one main driver of effects of human land-use change on autotrophic processes in stream ecosystems.

Acknowledgements

I first and foremost thank Dr. Michelle Evans-White, for being an extremely influential part of my research, education and life for the last six years. Also, I thank my committee members Drs. Thad Scott, Dan Magoulick, J.D. Willson, and Gary Huxel for their advice and guidance throughout my research. I thank Dr. Sally Entrekin for the major role she played in the development of the natural gas project and her guidance and advice in the development of my own research questions within the broader project.

Many thanks go to the numerous undergraduate researchers and honors students including Phillip Bumpers, Joe Kanopsic, Stephanie Grise, Cymber Browder, Aaron Jackson, Kara Brick, Alyssa Bucci, Scott Hamby, Natalia Hardgrave, Delaney Hall, Andrew Sanders, Lindsey Able, and Jason Ramey for both assistance in the field and laboratory. I especially thank my fellow graduate students in the Evans-White lab Clay Prater, Hal Halvorson, Ayla Smartt, Katie Rose, Kayla Sayre, Allyn Fuell, and Brooke Parker for the great camaraderie and insightful conversations, comments, and suggestions in the preparation of my dissertation.

Finally, I thank my family, especially my parents Norman and Diana Austin for all their love and support throughout my entire academic career.

Preface

This dissertation was written in journal style and format and organized into four chapters intended for independent publication. Style and format may vary between chapters and some text may be repeated. These chapters are preceded by an introduction and conclusion chapter.

Table of Contents

Table of Contents Cont.

INTRODUCTION

Increases in the global human population over the past century have altered the Earth's surface and atmosphere in ways that may negatively impact all ecosystems including streams. Large expanses of forest have been cut down to build cities and create agricultural lands necessary to support a growing human population (Tilman et al. 2002). In addition to increased demand for living space and food production, acquiring fossil fuels for energy production may negatively influence the surrounding landscape and streams (Entrekin et al. 2011). Urbanization and agricultural practices result in the removal of riparian trees, increasing light availability and reducing inputs of terrestrial organic matter (OM) such as leaf litter to streams. Agricultural practices increase erosion of soils along with nutrient loading due to fertilization of crops and inputs from livestock manure (Nguyen et al. 1998; Paul and Meyer 2001; Allan 2004). Runoff from urbanized surfaces transports sediments, nutrients, metals, pesticides, road salts, and other contaminants to nearby streams (Paul and Meyer 2001; Vaze and Chiew 2002). Much like urban development and agricultural practices, the recent development of natural gas (NG) infrastructure may negatively influence the landscape and surrounding stream systems.

Advancements in drilling and hydraulic fracturing technologies have made the recovery of unconventional NG resources more economically feasible (Malakoff 2014). Additionally, these unconventional gas reserves are vast throughout North America and the world (U.S. EIA 2013; Rahm and Rhia 2014) and their harvest could meet 47-53% of the global energy demand by 2050 (Rahm and Rhia 2014; Malakoff 2014). In the US, one of the first unconventional NG plays to be developed using horizontal drilling and hydraulic fracturing was the Barnett shale in Texas, starting in 2003 (Powell Barnett Shale Newsletter 2008). Unconventional NG development expanded from there into surrounding states including the Fayetteville Shale play in Arkansas as early as 2005 (Entrekin et al. 2011). NG activity expanded rapidly in the Fayetteville shale and implementation of best management practices (BMPs) intended to protect freshwaters lagged several years behind the start of the expansion, with the U.S. Fish and Wildlife Service's 2007 release of "Best management practices for Fayetteville Shale natural gas activities". While NG development is expected to expand and NG stands to become a prominent component of energy use, little has been done to assess the potential impacts the development of this resource might have on the environment, specifically streams.

Disturbance from NG activity to the landscape and surrounding water resources can be of concern to ecosystem services of freshwater systems. The installation of well pads, pipelines and service roads require removal of terrestrial vegetation and exposure of bare land that can promote export of sediment from the landscape into surrounding water bodies (Williams et al. 2008, Entrekin et al. 2011). Sediments in the stream can negatively influence stream communities and functional processes through shading, burial, or scouring of the benthos. Alternatively, sediments entering streams may be a major source of nutrients that may alleviate nutrient- limitation of benthic algal growth. Given the suite of possible direct and indirect effects of sediments on primary producers, the impact of NG development on stream autotrophs may be complex. Chapter one focuses on the potential effects of increasing NG activities on stream nutrients, benthic algal biomass, and gross primary production (GPP) within streams in north central Arkansas.

Following the construction of well pads, for unconventional NG wells to produce, they must first be stimulated through hydraulic fracturing, which may introduce novel contaminants into nearby freshwaters. The hydraulic fracturing process utilizes a base brine solution which contains many proprietary chemicals and compounds that serve as preservatives and lubricants (Vidic et al. 2013). Improper fracturing practices can result in these chemicals and salts (along with NG) entering into ground water, which can make it to the surface (Osborne et al. 2011). Following the fracturing process a portion of the fracturing fluid returns to the surface along with the NG produced, this “produced” water needs to be stored on site until it can be disposed of. Improper handling, storage, and disposal of produced water on the surface can also result in these chemicals entering surrounding water bodies (Olmstead et al. 2013), increasing conductivity due to cations such as sodium (Na^+) and potassium (K^+). Conductivity is often positively related to algal production (Chételat et al. 1999; Dodds and Whiles 2010), likely due to a positive association between conductivity and nutrients (Dodds and Whiles 2010); however, cations could be confounding this relationship. While conductivity is relatively low throughout Ozark streams (Potapova and Charles 2003), increases in conductivity due to NG activity may have a positive effect on algal production. In chapter two nutrient diffusing substrates are utilized to tease apart potentially confounding effects of nutrient (nitrogen and phosphorus) and cation (sodium and potassium) enrichment on algal growth within streams influenced by NG activity in Arkansas.

State and Federal agencies have implemented BMPs to mitigate potential impacts arising from all stages of NG infrastructure development (well pads, pipelines and road ways; USFWS 2007; 2009). These BMPs include procedures to reduce sediment erosion from disturbed landscape. First they reduce the surface impact in high gradient regions, which are prone to increased sediment erosion, by avoiding such areas or using practices that minimally disturb the surface. After construction is complete, mulching of exposed surfaces is used to slow overland flow of rain runoff. Finally, hay bales and silt fences are installed to impede movement of sediment from the landscape to surrounding water bodies. Many of these BMPs have been found to be effective in the logging industry (Prud'homme and Greis 2002); however, their effectiveness has yet to be tested within areas impacted by NG development. Chapter three examines nutrients, algal biomass and GPP within both reference and impacted streams prior to and following the development of NG infrastructure to test the effectiveness of implemented BMPs at mitigating impacts from NG development.

Disturbance from land-use change on stream benthic communities may be compounded in the future due to modifications in natural flow regimes of streams as a result of global climate change (GCC). The frequency, magnitude, duration, rate of change, and timing of high and low flow events constitute the natural flow regime of a stream and regional scale parameters such as topography, geology, vegetation cover, and climate drive variability in flow regimes across different systems (Poff and Ward 1989; Poff et al. 1997). High flow events or flooding within these flow regimes constitute natural disturbances and they play an integral roles in maintaining stream community structure (Resh et al. 1988; Poff and Allan 1995) and function (Young and Huryn 1996; Acuña et al. 2004). Anthropogenic alteration of these regional factors, such as agricultural and urban land-use, can have adverse effects on the natural flow regime of streams, resulting in floods with greater intensity. Additionally, as noted earlier, both agriculture and urbanization can influence light and nutrient availability to the stream channel. Studies examining ecosystem responses to flood events within altered land-use are needed to provide the data necessary for forecasting the consequences of human-driven ecosystem change. Chapter 4 compares the variability in recovery response of algal biomass and metabolic processes to flooding within urban, agricultural and forested streams between spring and autumn. Together, this dissertation investigates multiple dimensions by which human land use affect structure and function of stream ecosystems.

LITERATURE CITED

Acuña, V., A. Giorgi, I. Muñoz, U. Uehlinger, and S. Sabater. 2004. Flow extremes and benthic organic matter shape the metabolism of a headwater Mediterranean stream. Freshwater Biology. 49: 960-971.

Allan, J.D. 2004. Landscapes and riverscapes: the influence of land use on stream ecosystems. Annual review of Ecology and Evolution 35:257-284.

Chételat, J., F.R. Pick, A. Morin, and P.B. Hamilton. 1999. Periphyton biomass and community composition in rivers of different nutrient status. Canadian Journal of Fisheries and Aquatic Sciences. 56: 560-569.

Dodds, W.K., and M.R. Whiles. 2010. *Freshwater Ecology: concepts and environmental applications of Limnology*. 2nd ed. Elsevier. Burlington, MA, U.S.A. 811pp.

EIA (Energy Information Administration). 2013. Annual Energy Outlook 2013: with projections to 2040. U.S. Department of Energy; Washington, D.C.

Entrekin, S., M. Evans-White, B. Johnson, and E. Hagenbuch. 2011. Rapid expansion of natural gas development poses a threat to surface waters. Frontiers in Ecology and the Environment. 9:503-511.

Malakoff, D. 2014. The Gas Surge. Science. 344: 1464-1467.

Nguyen, M.L., G.W. Sheath, C.M. Smith, and A.B. Cooper. 1998. Impact of cattle treading on hill land: 2. Soil physical properties and contaminant runoff. New Zealand Journal of Agricultural Research. 41: 279-290.

Olmstead, S.M., L.A. Muehlenbachs, J.S. Shih, Z. Chu, and A.J. Krupnick. 2013. Shale gas development impacts on surface water quality in Pennsylvania. Proceedings of the National Academy of Science. 110: 4962-4967.

Osborn, S.G., A. Vengosh, N.R. Warner, and R.B. Jackson. 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. Proceedings of the National Academy of Science. 108: 8172-8176.

Paul, M.J. and J.L. Meyer. 2001. Streams in the urban landscape. Annual Review of Ecology and Systematics 32:333-365.

Poff, N.L. and J.D. Allan. 1995. Functional organization of stream fish assemblages in relation to hydrological variability. Ecology. 76: 606-627.

Poff, N.L., J.D. Allan, M.B. Bain, J.R. Karr, K.L. Prestegaard, B.D. Richter, R.E. Sparks, and J.C. Stromberg. 1997. The natural flow regime: a paradigm for river conservation and restoration. Bioscience. 47: 769-784.

Poff, N.L., and J.V. Ward. 1989. Implications of stream flow variability and predictability for lotic community structure: a regional analysis of streamflow patterns. Canadian Journal of Fisheries and Aquatic Sciences. 46: 1805-1818.

Potapova, M., and D.F. Charles. 2003. Distribution of benthic diatoms in U.S. rives in relation to conductivity and ionic composition. Freshwater Biology. 48: 1311-1328.

Powell Barnett Shale Newsletter Research. 2008. www.barnettshalenews.com

Prud'Homme, B.A. and J.G. Greis. 2002. Best management practices in the South. Southern Forest Resource Assessment. 519-535.

Rahm, B.G. and S.J. Riha. 2014. Evolving shale gas management: Water resource risks, impacts, and lessons learned. Environmental Science: Processes Impacts. 16: 1400-1412.

Resh, V.H., A.V. Brown, A.P. Covich, M.E. Gurtz, H.W. Li, G.W. Minshall, S.R. Reice, A.L. Sheldon, J.B. Wallace, and R.C. Wissmar. 1988. The role of disturbance in stream ecology. Journal of the North American Benthological Society. 7: 433-455.

Tilman, D., K.G. Cassman, P.A. Matson, R. Naylor, and S. Polasky. 2002. Agricultural sustainability and intensive production practices. Nature. 418: 671-677.

U.S. Fish and Wildlife Service. 2007. Best management practices for Fayetteville Shale natural gas activities. U.S. Fish and Wildlife Service. Conway, Arkansas. 30pp.

U. S. Fish and Wildlife Service. 2009. Arkansas best management practices for natural gas pipeline construction and maintenance activities in the Fayetteville Shale area, upper Little Red River watershed. U. S. Fish and Wildlife Service, Arkansas Ecological Services Field Office, Conway, Arkansas. 42 pp. + appendices.

Vaze, J., Chiew, F.H.S. 2004. Nutrient loads associated with different sediment sizes in urban storm water and surface pollutants. Journal of Environmental Engineering 130: 391-396.

Vidic, R.D., S.L. Brantley, J.M. Vandenbossche, D. Yoxtheimer, and J.D. Abad. 2013. Impacts of shale gas development on regional water quality. Science 340: DOI:10.1126/science.1235009.

Williams, H. F. L., Havens, D. L., Banks, K. E., and Wachal, D. J. 2008. Field-based monitoring of sediment runoff from natural gas well sites in Denton County, Texas, USA. Environmental Geology 55: 1463-1471.

Young, R.G., and Huryn, A.D. 1996. Interannual variation in discharge controls ecosystem metabolism along a grassland river continuum. Canadian Journal of Fisheries and Aquatic Sciences 53: 2199-2211.

Chapter I

Natural Gas Activity Measures Relate Positively to Primary Production Within North-Central Arkansas Streams

Bradley J. Austin

Department of Biological Sciences, University of Arkansas,
Fayetteville, AR 72701 USA

ABSTRACT

Construction of natural gas (NG) infrastructure (e.g., well pads, pipelines) is an increasingly common anthropogenic stressor that increases potential for habitat fragmentation and loss along with sediment erosion. Ten streams with varying catchment NG well densities (0-3.6 wells/km^2) were sampled during winter and spring of 2010 and 2011 to examine relationships between NG activity metrics and stream periphyton [chlorophyll *a* (Chl *a*)] and gross primary production (GPP). NG activity in the form of density of wells, well pad inverse flowpath length (IFPL), well rate of installation, and pipeline density were quantified for each catchment along with area, percent catchment slope and land use and cover variables percent pasture, urban and forest. Local scale variables including light availability and water column physicochemical variables were measured for each study site. A principal component analysis (PCA) was used to examine relationships among landscape scale variables and reduce variables by removing ones strongly correlated with one another. A second PCA was used to condense NG activity variables into a single NG activity metric, due to NG variables being strongly correlated with one another; both PCA analyses were repeated for the 2010 and 2011 sample years. Correlation analyses were used to examine the relationships of autotrophic processes and local scale variables with landscape scale variables. GPP and Chl *a* variability were primarily positively correlated with the NG activity metric during most sample periods. Catchment area exhibited similar correlations with GPP and Chl *a* as NG activity. At the local scale, both water column temperature and nutrients correlated better with NG activity, as opposed to catchment area. This suggests that Chl *a* and GPP variability, though related to catchment area, were most likely driven by NG activity variables through the mechanism of increased temperature and nutrients. Restricting NG activities from the riparian zone along with better enforcement of best

management practices should help reduce impacts of NG activities on stream autotrophic processes.

INTRODUCTION

As the United States (U.S.) strives to gain energy independence and find cleaner alternatives to coal and oil, exploration and recovery of natural gas (NG) has become more prominent. Additionally, technological advances in well installation, such as horizontal drilling and hydraulic fracturing, have made natural gas recovery from deep shale rock formations more feasible. In the U.S. there are 29 shale basins that span 20 states (Entrekin et al. 2011), including the Fayetteville shale in Arkansas, Barnett shale in Texas and Marcellus shale in Pennsylvania and surrounding states. These shale basins have been under intense development of natural gas infrastructure in the past decade, with more than 3,500 wells installed from 2005-2010 in the Fayetteville shale alone [Entrekin et al. 2011 (Figure 1)]. Combustion of natural gas is estimated to produce less carbon dioxide per unit energy gained relative to other fossil fuels (Shahidehpour et al. 2005), but the recovery of natural gas could have several negative environmental implications. Unfortunately, few studies exist that assess these potential impacts of NG production on terrestrial and aquatic ecosystems.

Construction of natural gas wells (NGW) and infrastructure increases potential for sediment erosion to surface waters (Entrekin et al. 2011, Williams et al. 2008). Several hectares of vegetation are cleared from the land prior to well pad construction. Additional infrastructure, such as roads and pipelines, is installed to facilitate the recovery and transport of the NG produced. Sediment from bare land associated with the well site and infrastructure construction can be transported in runoff to streams (Williams et al. 2008) and cause increased turbidity (Entrekin et al. 2011) and potentially sedimentation. After installation is complete, some vegetation may be allowed to grow back; however, gravel roads and the immediate vicinity of the well are usually kept cleared, which may cause a more lasting effect on sediment delivery to streams, as has been documented with logging roads (Beschta 1978).

Sedimentation is one of the major contributors to poor stream health among wadeable U.S. streams (USEPA 2006), having major direct and indirect influences on autotrophs. Increasing stream sediment load beyond natural levels might have direct negative effects on biotic communities (Allan and Castillo 2007, Owens et al. 2005). Specifically, suspended sediment attenuates light (Parkhill and Gulliver 2002), shading benthic algae (Brown and King 1987, Parkhill and Gulliver 2002, Wiley et al. 1990, Yamada and Nakamura 2002, Young and Huryn 1996) and reducing the fraction of periphyton that is algae. In addition, suspended sediments can scour rock surfaces removing periphyton (Horner et al. 1990). Decreasing discharge deposits sediment along the benthos, burying periphyton communities and reducing habitat quality for benthic algae (Waters 1995) due to the instability of finer sediments during spates (Biggs et al. 1999). Conversely, sediments entering into streams may have a positive, indirect influence on algal biomass due to increased sediment bound nutrients.

Landscape disturbances such as urbanization (Vaze and Chiew 2004) and pasture land use (Nguyen et al. 1998, Quinn and Stroud 2002, Vaze and Chiew 2004) can increase runoff of nutrients associated with sediments. Higher nutrient loads within streams that are nutrient limited can result in increased algal biomass (Tank and Dodds 2003), and an overall eutrophication of the system. Given the suite of possible direct and indirect effects of sediments on primary producers, the impact of NG development on stream periphyton may be complex.

Few studies have examined the impacts of NG drilling on stream processes even though NG activity has increased greatly in the past decade (Entrekin et al. 2011). Williams et al. (2008)

monitored sediment runoff from NGW sites and determined that well sites with a slope greater than 6% produced a substantial amount of sediment, but sediment runoff significantly decreased once well sites became naturally re-vegetated. Because streams in the Fayetteville Shale are high-gradient and NGW re-vegetation practices are rarely implemented, these streams might be strongly affected by sediment runoff from NGWs. For example, initial sampling of eight streams within the Fayetteville Shale region found a statistically significant positive relationship between well densities and turbidity during spring high flow; periphyton biomass measured as chlorophyll *a* (Chl *a*) and ash free dry mass (AFDM) were not related to well density (Entrekin et al. 2011). Higher flow associated with this preliminary sampling scoured rock surfaces and homogenized periphyton biomass across the sites, therefore it is important to know when to sample to better assess if NG activity is impacting stream processes.

Sediment erosion associated with NG activity might have both direct and indirect effects on in-stream autotrophic processes and the ability to detect these effects could vary seasonally due to spates. On one hand, increased in-stream sediments might have direct negative effects on benthic algal biomass and GPP through scour during spates (Horner et al. 1990) and burial following spates (Waters 1995). On the other hand, increased in-stream sediments might have an indirect positive effect on benthic algal biomass and gross primary production (GPP) through nutrient enrichment, following spates. Whether the effects of sediment erosion from NG activity on autotrophic processes are negative or positive may be variable seasonally. Spates, occurring most often during spring and autumn, scour the benthos regardless of increased sediment erosion, making it difficult to link landscape disturbances to changes in autotrophic processes. More stable flow conditions during summer and winter might allow for better detection of landscape disturbance effects on autotrophic processes. The objectives of this study are to determine how NG activity relates to algal biomass and GPP, and determine if those relationships are seasonally variable. We hypothesize that direct effects of sedimentation (scour and burial) associated with NG activity will outweigh the indirect effects (nutrient enrichment), negatively influencing algal biomass and GPP regardless of season. However, we predict flashy conditions during spring seasons will result in a reduced ability to detect landscape disturbances on algal biomass and GPP relative to winter seasons.

METHODS

Study Design

Algal biomass and GPP were measured in ten streams with varying NGW density located within north central Arkansas during the winter (February-March) and spring (May-June) of 2010 and 2011. Within each sample period, the association between the autotrophic variables, algal biomass and GPP, and NG activity were evaluated by testing for significant Pearson correlations ($P < 0.05$) between the measured autotrophic variables and NG activity. Additionally, the association between stream physical characteristics and NG activity were assessed by testing for significant Pearson correlations ($P < 0.05$) to examine the potential mechanisms driving relationships between autotrophic variables and NG activity.

Landscape Scale Variables

Well locations were downloaded from the Arkansas Oil and Gas Commission website (ftp://www.aogc.state.ar.us/GIS_Files/) and counted within each delineated catchment to estimate NGW densities (no./km^2). Additional NG activity variables were calculated for each stream to assess the potential impacts associated with NG infrastructure development that included rates of well installation (no./yr), pipeline density (m/km^2), unpaved road density (m/km^2), and the well pad inverse flowpath length (here further IFPL). Inverse flow path length provides an estimate of NG impact due to proximity of well pads to the stream channel within the catchment, where greater overall proximity of well pads relates to a higher IFPL value and greater impact. The IFPL was calculated in ArcGIS for all well pads upstream of each sampling location as follows: the flowpath length (FPL) from well pad to stream channel corrected for slope was determined using the flow length tool in the 'Spatial Analyst Tool' toolbox within ArcGIS. The inverse was taken of FPL estimates and then summed across all well pads for each catchment in the study. Ongoing NG infrastructure development throughout the duration of the study required recalculation of activity variables annually (Table 1). Non NG activity landscape scale variables that might be related to algal biomass and GPP, were also quantified for each site. Specifically, stream catchment variables (size and slope) were delineated and land use land cover variables (percent pasture, percent forest, and percent urban from the 2006 gap analysis program) were determined using Arc Map (Version 9.3.1; ESRI, Redlands, CA) for each of the streams in the study (Table 1).

Local Scale Variables

We measured stream physical characteristics at each site to assess differences in sample streams that might directly influence response variables. Habitat and stream physical characteristics (width and depth) were measured every 10 m along the length of a 200 m reach in each study stream. Sediment size was estimated following the Wentworth scale, classifying inorganic substrates as bedrock, boulder, cobble, gravel, pebble, sand and silt, and organic substrates as small and large woody debris, root wad, bryophyte and leaf litter were quantified at half meter intervals across the width of each 10 m transect. An overall percentage of each substrate type was then calculated for the entire 200 m reach.

All sites in the study were sampled over a one to two week time frame during each sample period to reduce any effect that might be associated with changing temperature or light availability, between weeks or months. Photosynthetic active radiation (PAR) was measured every 15 min, using an Odyssey light logger (Data flow systems, Christchurch, New Zealand) to monitor changing light availability across days and weeks. Light loggers were placed at a subset of sites in an area adjacent to the stream under similar light conditions as the stream channel. The percentage of shading from streamside trees at light logger stations was calculated and used to convert measured light to full sunlight and values across all sites were averaged to create estimates of regional daily PAR. Percent light transmittance was quantified along each stream by dividing the mean stream channel light availability by the ambient light availability outside of the stream in full sunlight. Percent light transmittance values for each stream were used to convert regional daily PAR into daily PAR reaching the stream channel. Daily PAR could not be determined for the winter 2010 sample period, due to programming errors.

Water temperature (ºC), specific conductance (µS/cm), base flow turbidity (NTU) and dissolved oxygen (mg/l) were measured every 15 min with a Hydrolab DS5X multiparameter sonde (Hach environmental, Loveland, CO). Dissolved oxygen data and water temperature were used in calculating GPP estimates, which are discussed later in this section. A mean value of turbidity over each day the sonde was deployed was used as the estimate of base flow turbidity.

Siphon samplers, constructed similarly to Graczyk et al. (2000), were used to collect water samples during storm flows. They were positioned next to the stream at 10 and 30 cm above base flow. Additionally, base flow unfiltered grab samples were collected from the thalweg of each stream during each sample period and stored on ice until returning to the laboratory. Subsets of both the storm and base flow grab water samples were stored at -20ºC until analysis for total nitrogen (TN) and total phosphorus (TP). Total nitrogen was analyzed using a Shimadzu TOC-V CSH equipped with the TNM-1 analyzer (Shimadzu Scientific Instruments, Columbia, MD). For TP analysis, water samples were digested using persulfate and then analyzed for SRP using the standard colorimetric molybdate/ascorbic acid method (APHA 2005). Geometric means were calculated for TN and TP annually from two base flow and two storm flow samples, due to the expectation that both base flow and storm flow conditions drive patterns of algal biomass and GPP. The geometric mean reduces the influence of extreme values and allows for a better estimation of annual nutrient concentrations than the arithmetic mean.

Algal Biomass

Two cobble samples from three sets of riffles and pools across each study reach were used to determine algal biomass. Each cobble was scraped and the resulting slurry was filtered through a pre-combusted and weighed filter (Pall GF/F) and then stored at -20 ºC until analysis for Chl *a*. Chlorophyll *a* was extracted by placing the filters in tubes with 10 mL of 95% ethanol, incubated in a water bath (78 ^{o}C, 5 min., Sartory and Grobbelaar 1984), and stored in the dark at 4 ^{o}C for 24 h, after extraction absorbance was measured on a Genesys 10 VIS spectrophotometer (Thermo Fischer Scientific inc., Waltham, MA) as described in APHA (2005). Rock surface area was estimated by wrapping each cobble with aluminum foil then a conversion factor based off of the mass of a 1cm^2 piece of foil was used to convert foil masses to area and divided by two to account for only the top surface of the cobbles (Lamberti et al. 1991). These values were used to quantify Chl *a* estimates as mass per unit area.

Metabolism

GPP was determined through the measure of diel curves of dissolved oxygen (DO) at a single station following Owens (1974) and Bott (1996). The single station was chosen over the double to allow for more sites to be sampled within a shorter time frame. We measured DO for three days at 15 min intervals with a Hydrolab DS5X multiparameter sonde equipped with an LDO probe (Hach environmental, Loveland, CO). The sonde was deployed in a well-mixed area along the 200 m delineated section (Mulholland et al. 2005). Winkler titrations were conducted at the beginning and end of each sonde deployment to correct for drift in the DO measurements. Air to water gas exchange ($k\text{o}_2$) was estimated using a night time regression of the DO fluctuation, whereby the slope of the regression between the changes in DO concentration and the oxygen deficit, is equal to the reaeration coefficient (Wiley et al. 1990, Young and Huryn 1996). Dissolved oxygen, reaeration coefficients and mean depth were used to calculate an areal rate of change in DO as ($\text{gO}_2\ \text{m}^{-2}\ \text{min}^{-1}$) following calculations described in Bernot et al. (2010). Areal rates of oxygen change were then converted to rates of carbon change ($\text{gC m}^{-2}\ \text{min}^{-1}$) following equations described by Bott (1996). Rates of carbon change were then used to calculate GPP.

Data Analysis

Principal component analyses (PCAs) were used to visually examine how each of the landscape scale variables related to one another and to reduce the total number of landscape scale variables used in correlation analyses. Additionally, NG activity variables (well density, well pad IFPL, rate of well installation, and pipeline density) were used in a secondary PCA alone to reduce the different NG activity impacts into a single PC axis derived metric. This process was repeated for both the 2010 and 2011 sample years as NG activity variables changed between years. All PCAs were conducted in PC-Ord (PC-Ord version 6 mjm Software, Gleneden Beach, OR).

Pearson correlation analyses were used to examine directionality of the relationships between landscape scale variables, local scale variables and our response variables GPP and Chl *a*. Landscape scale factors of interest included the non-NG percent pasture, and percent urban along with the PCA metric derived from NG activities. Daily PAR, stream water conductivity, temperature, and nutrients (TN and TP) were the local scale factors included in correlation analyses along with response variables GPP and Chl *a*. Prior to analysis, visual inspection of box plots and scatter plot matrices were implemented to check that the data met the assumptions of independence, homoscedasticity, and normal distribution. Data not meeting the assumptions of the analysis were transformed and re-assessed to verify assumptions were met before conducting statistical analyses. All correlation analyses were performed in SAS (Version 9.3, SAS Institute, Cary, NC).

RESULTS

Landscape scale variable reduction:

The PCAs of landscape scale variables explained 84% of the variability in the first three axes for both the 2010 and 2011 sample years (Table 2). NG activity variables well density and rate and well installation along with watershed slope and the land cover variables percent pasture and percent forest loaded strongly on PC-axis 1, during the 2010 sample year. PC-axis 2 was explained by catchment area, well pad IFPL, and percent urban land; density of unpaved roads strongly correlated with PC-axis 3. The PCA of the landscape scale variables during the 2011 sample year was similar to the 2010 sample year, with a few exceptions. Rate of well installation and well pad IFPL were more strongly associated with PC-axis 2, and well density loaded strongly on both PC-axes 1 and 3 (Table 2). Pipeline density loaded on PC-axis 1, but only in 2011.

The secondary PCA used to reduce NG activity variables explained 61% and 54% of the variability in the first axis during the 2010 and 2011 sample years, respectively. Well density, well pad IFPL, and well rate of installation were all positively related to PC-axis 1 with $r > 0.70$ for all variables during both years (Table 3). Pipeline density was correlated with PC-axis 1 during both years but to a lesser extent than the other NG activity variables (Table 3). PC-axis 1 was also positively related to catchment area during both sample years ($r < 0.65$ for 2010 and 2011); in light of this relationship, partial correlations were used to remove the effect of catchment area so that the effects of the NG activity metric on local scale factors and response variables could be assessed.

Landscape Scale vs. Response Variables

Mean Chl *a* and variability were fairly consistent across all sample periods. Winter sample periods had greater mean values of Chl *a* and less variability (3.67 ± 0.35 and 3.61 ± 0.43 $\mu g/cm^2$ 2010 and 2011 respectively). During the spring 2010 sample period, mean Chl *a* was similar to the winter sample periods but had greater variability (3.20 ± 0.75 $\mu g/cm^2$). Finally, the spring 2011 sample period had the lowest mean value of Chl *a* with greatest variability (2.32 ± 0.83 $\mu g/cm^2$). Means and ranges of Chl *a* can be found in Table 4.

Chl *a* was correlated positively with both catchment area and NG activity during both winter sample periods (Table 5; Figure 2A&C); when the effect of catchment area was removed the partial correlations between Chl *a* and NG activity had reduced correlation coefficients but were still positive (Table 6; Figure 2E&G). Density of unpaved roads also correlated positively with Chl *a* during both winter sample periods (Table 5). Neither catchment area nor NG activity related strongly with Chl *a* during spring sample periods (Figure 2B&D), though Chl *a* correlated positively with catchment percent slope in spring 2010 and percent pasture land use in spring 2011 (Table 5).

The mean and variability of GPP values varied between sample periods. The lowest values of GPP were measured during the winter 2010 sample period (Mean±1SE; 0.15 ± 0.03 $gCm^{-2} d^{-1}$); while some of the greatest values of GPP were measured during the spring 2010 sample period (2.22 ± 0.83 $gCm^{-2} d^{-1}$). GPP values measured during the 2011 sample periods were intermediate to the values measured in 2010 (1.01 ± 0.23; 1.29 ± 0.18 $gCm^{-2} d^{-1}$; winter and spring respectively). Values from the spring 2010 and winter 2011 represent only 9 and 6 sites, respectively, due to problems associated with sonde malfunctions during these sample periods. GPP means and ranges can be found in Table 4.

Correlation analyses found GPP to be negatively related to catchment area in winter 2010 but positively related in winter 2011. Unlike Chl *a*, GPP was negatively related to NG activity in winter 2010, but exhibited a strong positive correlation during winter 2011 (Table 5; Figure 3A&C). When the effects of catchment area were removed with the partial correlation, the relationship between GPP and NG activity became positive in the winter 2010 sample period and the strength of the correlation for winter 2011 was reduced but remained positive (Table 6; Figure 3E&G). GPP was positively correlated with NG activity (Figure 3B) as well as with unpaved road density in spring 2010, but was not strongly correlated with any variable during spring 2011 (Table 5). Removing the effect of catchment area in the partial correlation between GPP and NG activity in spring 2010 reduced the strength of the relationship, but the correlation remained positive (Table 6; Figure 3G).

Landscape Scale vs. Local Scale Variables

Values for local scale variables, used in correlation analyses, were variable across both sites and seasons. Means and ranges for all local scale variables can be found in Table 4 organized by sample period for daily PAR, stream temperature, and stream conductivity and by year for TN and TP.

TP did not correlate with any of the landscape scale variables during the 2010 sample year, though it was positively related to percent pasture land use and negatively related percent catchment slope during the 2011 sample year (Table 5). TN had a weak positive correlation with NG activity during both sample years (Table 5; Figure 4A); however, when the effects of catchment area were removed from the relationship the correlations became stronger for both years (Table 6; Figure 4B). Daily PAR was positively related to NG activity in the three sample periods it was measured (Table 5); however, these relationships fell apart when catchment area was factored out with the partial correlation (Table 6). Turbidity correlated positively with NG activity and roads during both sample periods in 2010, but was primarily correlated positively with NG activity and catchment percent slope during the 2011 sample periods. Water temperature did not correlate well with any landscape variables in the spring 2010 sample period, but was correlated positively to NG activity during all other sample periods (Table 5). Only winter sample periods maintain their strong positive correlation between temperature and NG activity when partial correlations were used. Conductivity was primarily negatively correlated with percent catchment slope and positively with percent pasture land used during spring sample periods (Table 5).

DISCUSSION

NG activity was predicted to be negatively correlated to Chl *a* and GPP in streams due to increased sediment erosion which would scour the benthos during high flow events and bury the benthos during base flow conditions. NG activity was consistently important in explaining Chl *a* and GPP variability throughout the extent of the project. Turbidity was positively correlated with NG activity across all sample periods, which suggests that suspended sediments increased with NG activity. Instead of exhibiting negative relationships with NG activity due to the direct negative effects of sediments as hypothesized, Chl *a* and GPP were positively related to NG activity. This positive association between response variables and disturbance suggests NG activities within the catchments were alleviating one or more limiting factors on algal biomass and GPP.

NG Activity and Response Variables

NG activity was consistently positively correlated with GPP and Chl *a*, even across study reaches already impacted by pasture agriculture and urbanization. This suggests that NG activity produces a detectable effect on stream primary producers seen through GPP and Chl *a*, which are common bioassessment metrics. Chl *a* across all sample periods ranged from 0.25 – 9.37 µg/cm^2; these values place our stream reaches in all three of the distinct trophic groups set by Dodds et al. (1998). In comparison to other streams in the Ozarks, the Chl *a* measured was similar to low to moderately enriched streams (1.03 – 8.66 µg/cm^2), and lower than highly enriched streams (4.68 – 21.67 µg/cm^2) (Lohman et al. 1992). This range in Chl *a*, in addition to the positive relationships with NG activity, clearly suggests that neither scour nor burial of the benthos played a strong role on algal biomass within streams at the time of my sampling; this range can also be seen with GPP.

The range of GPP measured in our study (0.03 – 8.20 gC m^{-2} d^{-1}) exceeded the higher limits of GPP measured within the minimally impacted streams of the Lotic Intersite Nitrogen eXperiment (LINX) I (0.03 – 4.29 gC m^{-2} d^{-1}, Mulholland et al. 2001) and urban and agriculturally influenced streams of LINX II (0.03 – 4.63 gC m^{-2} d^{-1}, Bernot et al. 2010). Similarly, streams influenced by agricultural practices in the Little Tennessee River watershed on average had lower measured GPP (0.03 – 0.29 gC m^{-2} d^{-1}, McTammany et al. 2007). Surprisingly, GPP measured in this study more closely approached values measured across prairie streams impacted by row-crop agriculture in central Illinois (0.03 – >15 gC m^{-2} d^{-1}, Wiley et al. 1990). As with algal biomass, the relationship between NG activity and GPP does not support a direct negative effect of sediments on primary production at the time of sampling. However, these relationships suggest that NG activity may be directly or indirectly affecting other local scale factors such as water temperature and nutrient availability.

Water temperature was consistently positively correlated to NG activity during winter sample periods (Table 6), which might have been promoted through removal of riparian vegetation upstream of our sampling reaches due to infrastructure construction. Exposed sections of stream channel upstream of study reaches would increase water column temperatures without resulting in increased light availability within the sample reach. In addition to increasing water temperatures, NG activity might have driven TN variability during both 2010 and 2011 (153.19 – 759.73 µg/l and 661.66 – 2500.10 µg/l respectively; Table 4) as seen by the strong positive correlations between NG activity and TN during both years (Table 6; Figure 4). Increased temperature and TN have been found to promote greater algal biomass and GPP in previous studies (Wiley et al. 1990, Bernot et al. 2010), supporting these two local scale variables as the mechanism through which NG activity promoted greater Chl *a* and GPP.

Alternative Models

Catchment area also frequently correlated with both GPP and Chl *a* during several sample periods (Table 5). In general, catchment area provides the same relationship and explains a similar amount of variability as NG activity (Table 5), likely due to the high level of correlation between these two variables (r= 0.669 and 0.677 in 2010 and 2011 respectively). This correlation might be driven by larger watersheds having greater space for infrastructure development. However, we did not expect a positive relationship between catchment area and autotrophic metrics given relatively small range in catchment area of study streams (12-84 km^2; Table 1). Studies that have found positive relationships between catchment area and primary production have done so over an order of magnitude greater range in catchment area (e.g., 1-1000 km^2; Lamberti and Steinman 1997). Further, the river continuum concept primarily predicts changes across broad categories of stream order (1^{st}-3^{rd}, 4^{th}-6^{th}, 7^{th} and larger; Vannote et al. 1980). All of our sites were 4^{th}-6^{th} order streams. Therefore, we do not think catchment area alone is responsible for the positive correlations observed between NG and autotrophic variables.

With the high range in percent pasture land use across study reaches it is apparent our streams were not only impacted by NG activity. Increased nutrient inputs into streams are commonly associated with pasture land use (Justus et al. 2010), which can have a positive effect on GPP (Wiley et al. 1990) and Chl *a* if light is not limiting to the system. TP ranged from 11.95 – 151.95 µg/l in 2010 and 13.22 – 85.92 µg/l in 2011 (Table 4) and was positively related to pasture land use during the 2011 sample year (Table 5), providing a possible mechanism through which pasture land use might have influenced GPP during the spring 2011 sample period. Additionally, molar ratios of total N:P calculated from geometric means each year ranged from 10.96 – 77.59 in 2010 and 17.03 – 167.95 in 2011, suggesting that the streams were primarily P limited. However, in general pasture land use correlated poorly with GPP. During the sample period where GPP variability was best explained by pasture, the relationship was negative, which is opposite of what would be expected if P was limiting to the system. This negative relationship suggests that pasture land use was not confounding the positive relationship between natural gas activity and autotrophic variables in the study streams.

Seasonality and Flow Variability

We predicted that flow variability during different seasons might influence our ability to detect an impact with flashy flow conditions in the spring resulting in a reduced ability to detect landscape disturbance impacts on Chl *a* and GPP. There was an apparent effect of seasonality and flow variability on the degree to which landscape scale variables correlated with response variables. The strongest correlations throughout the study occurred during the winter sample periods. Extended periods of base flow conditions during the winter sample periods allowed for streams to recover for more than one month following high flow events, whereas spring samplings occurred within less than one month of flood disturbances, with the spring 2011 sampling occurring only one week post flood (Figure 5). The stream benthos might require up to a month to fully recover following flood disturbances in Ozark streams (Lohmann et al. 1992) and sampling prior to recovery of the system from flood events reduced our ability to detect landscape scale effects. Though flooding transports sediments and nutrients from the disturbed landscape to the streams, it is possible that flooding also disconnects the response of Chl *a* and GPP to the landscape scale disturbances.

CONCLUSIONS

To our knowledge, this study and Jensen et al. (unpublished data) are the first studies examining implications of NG activity in catchments on stream biota, algal biomass and GPP within streams. Contrary to our hypothesis, NG activity generally stimulated algal biomass and GPP. Therefore, indirect effects associated with increases in sediment-bound nutrients or increases in light and temperature associated with NG infrastructure might promote autotrophic processes. Additionally, stable flow conditions associated with the winter sample periods provided an increased ability to detect landscape scale disturbances on autotrophic processes. Based on this, monitoring programs examining impacts to autotrophic processes should focus their efforts during seasons with stable base flow conditions.

Site selection provided a wide variability in NG activity, but some variation in catchment area and land use land cover (e.g., pasture) did occur. Variability in non-experimental factors and the regression design of this natural experiment reduce our ability to establish mechanisms. Additionally, low sample size during all sample periods reduced our statistical power. However, the consistency with which Chl *a* and GPP responded to NG activity variables suggests that they are both useful bio-assessment metrics for detecting impact due to NG activity. Further the relationships between NG activities and TN and stream temperature suggest that NG activity across the landscape can result in increased sediment bound nutrients entering the surrounding streams; additionally, NG development within the riparian zone of streams may increase stream temperatures (Entrekin et al. 2011). Restricting well pads and other NG construction activities to areas away from the riparian zone should help reduce issues with increased stream temperature. Furthermore, keeping riparian zones intact along with better enforcement of best management practices that impede the flow of sediments from the landscape should help reduce sediment-bound nutrients associated with NG and pasture activities entering surrounding streams.

ACKNOWLEDGEMENTS

We thank Lindsey Abel, Phillip Bumpers, Chris Fuller, Jessie Green, Jordan Johnson, Julie Kelso, Lindsey Martindale, Chelsea Miller, Adam Musto, Clay Prater, Jason Ramey, Andrew Sanders, Katie Rose, Loren Stearman, and Richard Walker for their assistance in the field. The NSF BIO REU (0755331 and 1063067) funded several undergraduate researchers, Aaron Jackson, Kara Brick, Jordon Patterson, and Zach Eldrige who assisted with the collection and processing of data. We also thank co-authors Sally Entrekin, Michelle A. Evans-White, Ethan Inlander, and Cory Gallipeau as well as project collaborators Ginny Adams, Reid Adams, Brian Haggard, Steve Filipek, and Lindsey Lewis. Additionally, we thank Leslie Massey, Hal Halvorson and Ayla Smartt for providing valuable discussion and advice on the writing of the manuscript. This research was funded by State Wildlife Grants Program (Grant#T-31-R) from the US Fish and Wildlife Service through an agreement with the Arkansas Game and Fish Commission. Additionally, valuable comments and guidance were provided by my dissertation committee that included Michelle Evans-White, Thad Scott, Dan Magoulick, J.D. Willson, and Gary Huxel.

LITERATURE CITED

Allan, J.D., Castillo, M.M. 2007. *Stream Ecology: Structure and Function of Running Waters*. (2nd edn.). Springer. Dordrecht, the Netherlands. 436 pp.

APHA (American Public Health Association). 2005. *Standard Methods for the Examination of Water and Wastewater*. (21st edn.). American Public Health Association: Washington D.C. 1368 pp.

Bernot, M.J., D.J. Sobota, R.O. Hall, JR., P.J. Mulholland, W.K. Dodds, J.R. Webster, J.L. Tank, L.R. Ashkenas, L.W. Cooper, C.N. Dahm, S.V. Gregory, N.B. Grimm, S.K. Hamilton, S.L. Johnson, W.H. McDowell, J.L. Meyer, B. Peterson, G.C. Poole, H.M. Valett, C. Arango, J.L. Beaulieu, A.J. Burgin, C. Crenshaw, A.M. Helton, L. Johnson, J. Merriam, B.R. Niederlehner, J.M. O'Brien, J.D. Potter, R.W. Sheibley, S.M. Thomas, and K. Wilson. 2010. Inter-regional comparison of land-use effects on stream metabolism. Freshwater Biology 55:1874-1890.

Beschta, R.L. 1978. Long-term patterns of sediment production following road construction and logging in the Oregon coast range. Water Resources Research. 14:1011-1016.

Biggs, B.J.F., Smith, R.A., and Duncan, M.J. 1999. Velocity and sediment disturbance of periphyton in headwater streams: biomass and metabolism. Journal of the North American Benthological Society 18: 222-241.

Bott, T.L. 1996. Primary productivity and community respiration. Pages 533-556 *in* Methods in Stream Ecology, F. Richard Hauer and G.A. Lamberti (eds), Academic Press, New York, NY, USA.

Brown, S.S., and King, D.K. 1987. Community metabolism in natural and agriculturally disturbed riffle sections of the Chippewa River, Isabella County, Michigan. Journal of Freshwater Ecology 4: 39-51.

Dodds, W.K., J.R. Jones, and E.B. Welch. 1998. Suggested classification of stream trophic state: distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus. Water Resources. 32: 1455-1462.

Entrekin, S., M. Evans-White, B. Johnson, and E. Hagenbuch. 2011. Rapid expansion of natural gas development poses a threat to surface waters. Frontiers in Ecology and the Environment. 9:503-511.

Graczyk, D., D. Robertson, W. Rose, and J. Steuer 2000. Comparison of water-quality samples collected by siphon samplers and automatic samplers in Wisconsin. United States Geological Survey, United States Geological Survey Fact Sheet FS-067-00. USGS, Middleton, WI.

Horner, R.R., Welch, E.B., Seeley, M.R., and Jacoby, J.M. 1990. Responses of periphyton to changes in current velocity, suspended sediments and phosphorous concentration. Freshwater Biology 24: 215-232.

Justus, B.G., J.C. Petersen, S.R. Femmer, J.V. Davis, and J.E. Wallace. 2010. A comparison of algal, macroinvertebrate, and fish assemblage indices for assessing low-level nutrient enrichment in wadeable Ozark streams. Ecological Indices. 10: 627-638.

Lamberti, G.A., S.V. Gregory, L.R. Ashkenas, R.C. Wildman, and K.M.S. Moore. 1991. Stream ecosystem recovery following a catastrophic debris flow. Canadian Journal of Fisheries and Aquatic Sciences. 48:196-208.

Lamberti, G.A. and A.D. Steinman. 1997. A comparison of primary production in stream ecosystems. Journal of the North American Benthological Society. 16: 95-104.

Lohman, K., J.R. Jones and B.D. Perkins. 1992. Effects of nutrient enrichment and flood frequency on periphyton biomass in Northern Ozark streams. Canadian Journal of Fisheries and Aquatic Sciences. 49: 1198-1205.

McTammany, M.E., E.F. Benfield, and J.R. Webster. 2007. Recovery of stream ecosystem metabolism from historical agriculture. Journal of the North American Benthological Society 26: 532-545.

Mulholland, P.J., C.S. Fellows, J.L. Tank, N.B. Grimm, J.R. Webster, S.K. Hamilton, E. Martí, L. Ashkenas, W.B. Bowden, W.K. Dodds, W.H. McDowell, M.J. Paul, and B.J. Peterson. 2001. Inter-biome comparison of factors controlling stream metabolism. Freshwater Biology. 46: 1503-1517.

Mulholland, P.J., J.N. Houser, and K.O. Maloney. 2005. Stream diurnal dissolved oxygen profiles as indicators of in-stream metabolism and disturbance effects: Fort Benning asa case study. Ecological Indicators 5: 243-252.

Nguyen, M.L., G.W. Sheath, C.M. Smith, and A.B. Cooper. 1998. Impact of cattle treading on hill land: 2. Soil physical properties and contaminant runoff. New Zealand Journal of Agricultural Research. 41: 279-290.

Owens, M. 1974. Measurements on non-isolated natural communities in running waters. Pages 111-119 *in* R.A. Vollenweider (editor). A manual on methods for measuring primary production in aquatic environments. Blackwell Scientific Publications, Oxford, UK.

Owens, P.N., Batalla, R.J., Collins, A.J., Gomez, B., Hicks, D.M. Horowitz, A.J., Kondolf, G.M., Marden, M., Page, M.J., Peacock, D.H., Petticrew, E.L., Salomons, W., Trustrum, N.A. 2005. Fine-grained sediment in river systems: Environmental significance and management issues. River Research and Applications 21: 693-717.

Parkhill, K. L. and J.S. Gulliver. 2002. Effect of inorganic sediment on whole-stream productivity. Hydrobiologia 472: 5-17.

Quinn, J.M., and M.J. Stroud. 2002. Water quality and sediment and nutrient export from New Zealand hill-land catchments of contrasting land use. New Zealand Journal of Marine and Freshwater Research. 36: 409-429.

Sartory, D. P. and J.U. Grobbelaar. 1984. Extraction of chlorophyll a from freshwater phytoplankton for spectrophotometric analysis. Hydrobiologia 114: 177-187.

Shahidehpour, M., Y. Fu, and T. Wiedman. 2005. Impact of natural gas infrastructure on electric power systems. Proceedings of the IEEE. 93:1042-1056.

Tank, J. L. and Dodds, W. K. 2003. Nutrient limitation of epilithic and epixylic biofilms in ten North American streams. Freshwater Biology 48: 1031-1049.

U.S. Environmental Protection Agency (2006) *Wadeable streams assessment, a collective survey of the nation's streams.* Washington 841-B-06-002.

Vannote, R.L., G.W. Minshall, K.W. Cummins, J.R. Sedell, and C.E. Cushing. 1980. The river continuum concept. Canadian Journal of Fisheries and Aquatic Sciences. 37: 130-137.

Vaze, J., and F.H.S. Chiew. 2004. Nutrient loads associated with different sediment sizes in urban storm water and surface pollutants. Journal of Environmental Engineering 130: 391-396.

Waters, T.F. 1995. Sediment in streams. Sources, biological effects and control. American Fisheries Society Monongraph.

Wiley, M.J., L.L. Osbourne, and R.W. Larimore. 1990. Longitudinal structure of an agricultural prairie river system and its relationship to current stream ecosystem theory. Canadian Journal of Fisheries and Aquatic Sciences 47: 373-384.

Williams, H. F. L., D.L. Havens, K.E. Banks, and D.J. Wachal. 2008. Field-based monitoring of sediment runoff from natural gas well sites in Denton County, Texas, USA. Environmental Geology 55: 1463-1471.

Yamada, H. and F. Nakamura. 2002. Effect of fine sediment deposition and channel works on periphyton biomass in the Makomanai River, northern Japan. River Research and Applications 47: 481-493.

Young, R.G., and A.D. Huryn. 1996. Interannual variation in discharge controls ecosystem metabolism along a grassland river continuum. Canadian Journal of Fisheries and Aquatic Sciences 53: 2199-2211.

Table 1: Landscape scale variables for each site in the study. Separate data are provided for 2010 and 2011 for variables that changed between sample periods, namely variables associated with natural gas activity (well density, IFPL[a], well rate of installation, and pipeline density).

Site	Area (km^2)	Slope (%)	PAST[b] (%)	URB[c] (%)	FOR[d] (%)	Well Density (no./km^2)		IFPL[a]		Installation rate (no./yr)		Pipeline (km/km^2)	Road (km/km^2)
						2010	2011	2010	2011	2010	2011		
BFK[e]	32	6	50	2	39	0.41	0.69	0.01	1.26	2.02	3.35	0.20	0.75
CLR[f]	19	6	38	2	51	0.21	0.79	0.04	0.06	0.65	1.928	1.69	0.61
CLF[g]	58	6	47	1	43	0.57	0.97	1.18	1.21	7.08	9.17	0.00	1.05
EPR[h]	68	8	24	2	64	1.62	2.32	2.04	2.08	23.2	25.92	0.89	1.07
FOR[i]	37	8	42	2	51	0.54	0.89	0.41	0.84	3.77	5.32	0.08	0.72
HOG[j]	55	8	23	3	63	1.44	1.78	1.48	1.48	16.6	17.28	1.22	0.97
LOB[k]	12	10	13	1	66	0.67	0.67	0.02	0.03	1.51	1.57	0.63	0.57
PMN[l]	84	7	39	5	45	1.15	1.60	3.75	3.98	21.08	23.1	0.85	0.72
SUN[m]	14	6	40	1	49	2.29	3.64	0.27	0.28	7.6	8.4	1.46	1.31
TEN[n]	29	5	48	5	43	0.34	0.59	0.25	0.80	2.05	2.78	0.00	0.63

[a] IFPL = well pad inverse flowpath length; [b] PAST= Pasture land use; [c] URB= Urban land use; [d] FOR= Forest land use; [e] BFK= Black fork creek; [f] CLR= Clear creek; [g] CLF= Clifty creek; [h] EPR= East Fork Point Remove; [i] FOR= Fourteenmile creek; [j] HOG= Hogan creek; [k] LOB= Long branch creek; [l] PMN= Pine mountain creek; [m] SUN= Sunny Side creek; [n] TEN= Tenmile creek

Table 2: Principal Component Analysis correlation coefficients of landscape scale variables from the 2010 and 2011 sample years.

	2010			2011		
Independent Variable	Axis 1 (39%)	Axis 2 (28%)	Axis 3 (17%)	Axis 1 (35%)	Axis 2 (30%)	Axis 3 (19%)
Catchment Area (km^2)	0.45	-0.80	-0.20	0.25	-0.89	-0.19
Watershed Slope (%)	0.73	0.50	-0.36	0.81	0.29	-0.43
Well Density (no./km^2)	0.75	-0.09	0.57	0.61	-0.20	0.71
Inverse Flowpath Length	0.56	-0.75	-0.20	0.14	-0.93	-0.22
Rate of Well Installation (no./yr)	0.81	-0.57	0.02	0.64	-0.76	-0.01
Pipeline Density (m/km^2)	0.54	0.23	-0.25	0.60	-0.31	0.28
Road Density (m/km^2)	0.46	-0.12	-0.84	0.45	0.14	0.28
Pasture Land use (%)	-0.76	-0.51	-0.38	-0.84	-0.31	0.43
Urban Land use (%)	-0.10	-0.71	0.44	-0.28	-0.66	-0.38
Forest Land use (%)	0.75	0.53	0.29	0.84	-0.19	-0.34

Table 3: Principal Component Analysis (PCA) correlation coefficients of NG activity variables from the 2010 and 2011 sample years for only Axis 1.

	2010	2011
	Axis 1 (61%)	Axis 1 (54%)
Well Density (no./km^2)	0.795	0.743
Inverse Flowpath Length	0.813	0.701
Rate of Well Installation (no./yr)	0.942	0.926
Pipeline Density (m/km^2)	0.510	0.503

Table 4: Local scale variable mean and ranges for each sample year for TN and TP and for each sample period for GPP, Chl *a*, turbidity, daily PAR, stream temperature and stream conductivity.

Variable	2010		2011	
Total Nitrogen (µg/l)	450.21 (153.19 - 759.73)		1279.00 (661.66 - 2500.10)	
Total Phosphorus (µg/l)	53.25 (11.95 - 151.95)		44.23 (13.22 - 85.92)	
	Winter	Spring	Winter	Spring
GPP (gC/m^2/d)	0.15 (0.03 – 0.27)	2.22 (0.53 – 8.20)	1.01 (0.49 – 2.03)	1.29 (0.45 – 2.26)
Chl *a* (µg/cm^2)	3.66 (2.45 – 5.59)	3.20 (1.01 – 8.80)	3.61 (1.71 – 6.13)	2.32 (0.25 – 9.37)
Turbidity (NTU[a])	4.27 (0.29 – 19.86)	5.92 (0.97 – 10.38)	3.34 (1.23 – 6.17)	4.66 (0.83 – 17.96)
PAR[a] (mol quanta/d)	NA	3.03 (0.29 - 11.11)	17.70 (1.77 - 59.65)	3.66 (0.42 - 7.83)
Temperature (°C)	5.38 (4.61 - 6.68)	22.87 (19.22 - 29.16)	13.05 (9.98 - 16.77)	16.87 (15.44 - 19.46)
Conductivity (µS/cm)	37.45 (30.57 - 46.99)	40.74 (29.29 - 51.95)	50.79 (42.03 - 59.62)	44.22 (33.21 - 60.94)

[a] NTU = Nephlometric turbidity units; [b] PAR= Photosynthetically active radiation

Table 5: Pearson's correlations between local scale response variables and landscape scale variables. Values with an r> 0.550 are underlined.

	Chl *a*[a]	GPP[b]	TP[c]	TN[d]	PAR[e]	NTU[f]	Temp[g]	Cond[h]
Winter 2010			*			*		
Area	0.832	-0.718	-0.310	-0.101	NA	0.401	-0.040	-0.165
NG Activity	0.850	-0.309	-0.140	0.353	NA	0.588	0.542	0.033
Slope	0.162	0.308	-0.342	-0.242	NA	0.094	-0.009	-0.560
Roads	0.467	-0.002	-0.284	0.280	NA	0.439	0.617	0.145
Pasture	-0.125	-0.248	0.162	-0.021	NA	-0.235	-0.146	0.497
Spring 2010		*	*		*		*	
Area	0.060	0.350	-0.310	-0.102	0.100	0.180	0.193	-0.155
NG Activity	-0.232	0.495	-0.140	0.353	0.088	0.742	0.329	-0.158
Slope	0.408	0.275	-0.342	-0.242	-0.232	0.071	-0.258	-0.517
Roads	-0.221	0.658	-0.285	0.280	-0.161	0.507	0.225	-0.271
Pasture	0.010	-0.398	0.162	-0.021	0.061	-0.288	0.016	0.333
Winter 2011	*	*		*				
Area	0.698	0.648	-0.345	-0.041	0.693	0.324	0.833	0.202
NG Activity	0.664	0.830	-0.448	0.420	0.558	0.379	0.983	0.155
Slope	-0.296	0.552	-0.614	-0.414	-0.032	0.620	0.852	-0.276
Roads	0.744	0.602	-0.117	0.572	-0.084	-0.076	0.344	-0.491
Pasture	0.182	-0.592	0.786	0.267	0.070	-0.199	-0.688	0.320
Spring 2011	*			*	*	*	*	
Area	0.460	0.023	-0.345	-0.041	0.448	0.446	0.656	-0.239
NG Activity	0.112	0.019	-0.448	0.420	0.141	0.494	0.611	0.058
Slope	-0.224	-0.337	-0.614	-0.414	-0.236	0.393	-0.137	-0.591
Roads	-0.107	0.118	-0.117	0.572	-0.221	0.169	0.033	0.263
Pasture	0.473	0.348	0.786	0.267	0.264	-0.479	0.185	0.540

* Denotes $\log_{10}$ transformed response variables during particular sample periods.

[a] Chl *a*= Chlorophyll *a*; [b] GPP= Gross primary production; [c] TP= Total phosphorus; [d] TN= Total nitrogen; [e] PAR= Photosynthetically Active Radiation; [f] NTU= Nephelometric Turbidity Units [g] Temp= Temperature; [h] Cond= Specific conductance

Table 6: Pearson’s partial correlations between natural gas activity (PC-Axis 1) and local scale variables with catchment area held constant. Values with r>0.550 are underlined

	Chl *a*[a]	GPP[b]	TP[c]	TN[d]	PAR[e]	NTU[f]	Temp[g]	Cond[h]
			*			*		
Winter 2010	0.711	0.386	0.096	0.569	NA	0.470	0.767	0.196
		*	*		*		*	
Spring 2010	-0.367	0.400	0.096	0.569	0.029	0.850	0.318	-0.051
	*	*		*				
Winter 2011	0.362	0.683	-0.311	0.610	0.167	0.208	0.943	-0.031
	*			*	*	*	*	
Spring 2011	-0.305	0.007	-0.311	0.610	-0.247	0.291	0.301	0.308

* Denotes logarithmically transformed response variable during a particular sample period.
[a]Chl *a*= Chlorophyll *a*; [b]GPP= Gross primary production; [c]TP= Total phosphorus; [d]TN= Total nitrogen; [e]PAR= Photosynthetically Active Radiation; [f]NTU= Nephelometric Turbidity Units [g]Temp= Temperature; [h]Cond= Specific conductance

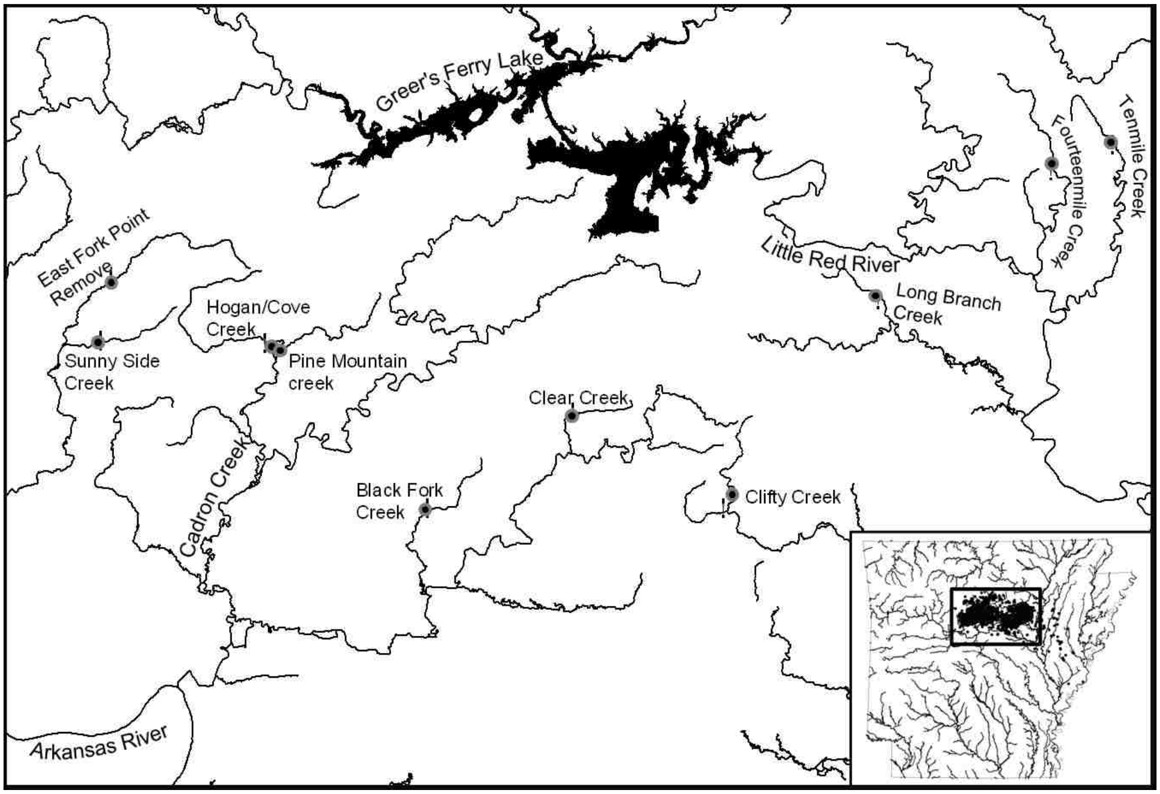


Figure 1. Study reaches in north central Arkansas within the Fayetteville Shale play.

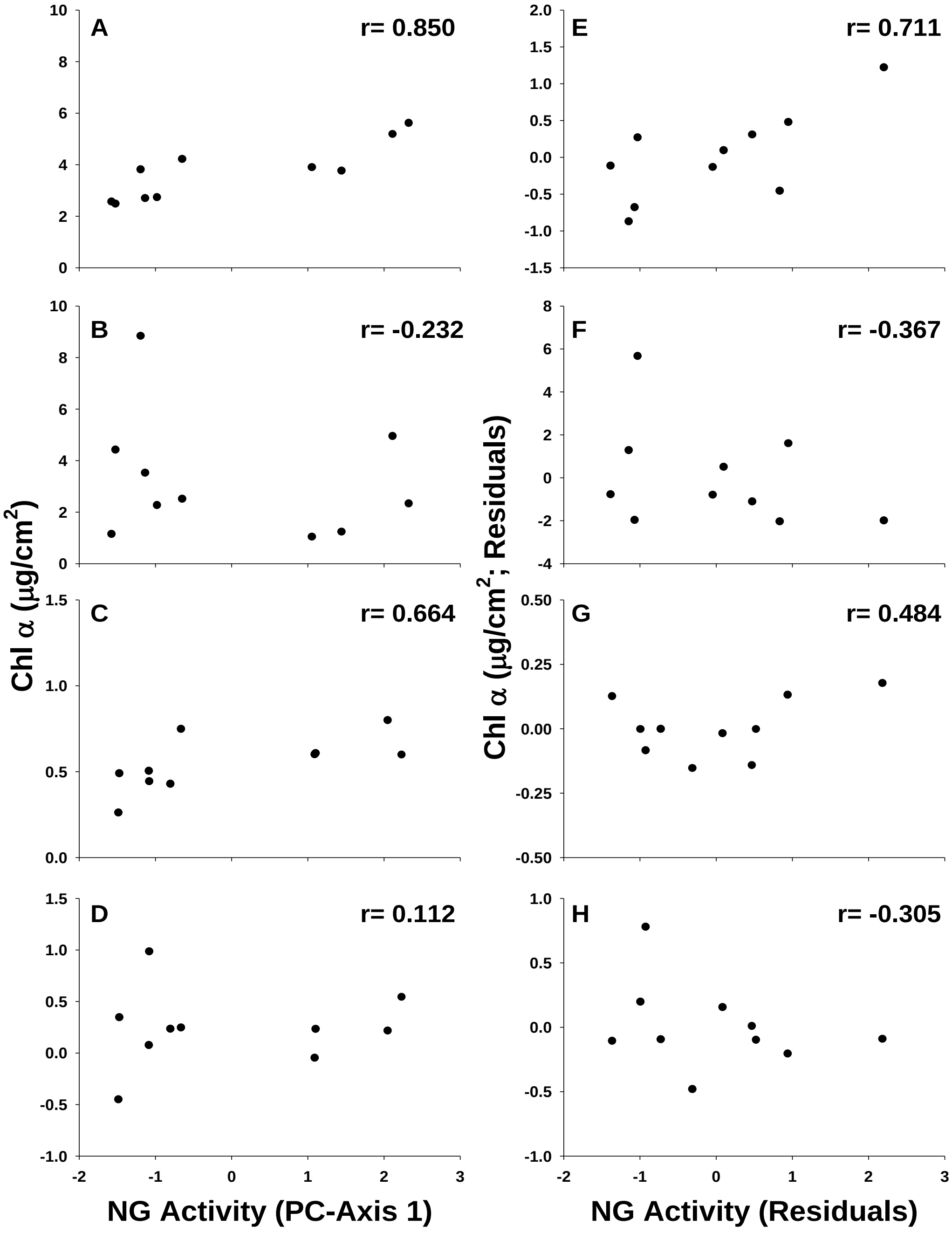


Figure 2. Scatter plots depicting the correlations between Chl *a* and NG activity metric (A-D) and partial correlations between Chl *a* and NG activity metric with effects of catchment area removed (E-H). With A&E depicting the correlation and partial correlation for winter 2010, B&D depicting the correlation and partial correlation for spring 2010, C&G depicting the correlation and partial correlation for winter 2011, and D&H depicting the correlation and partial correlation for spring 2011. Chl *a* data in panels C and D are logarithmically transformed.

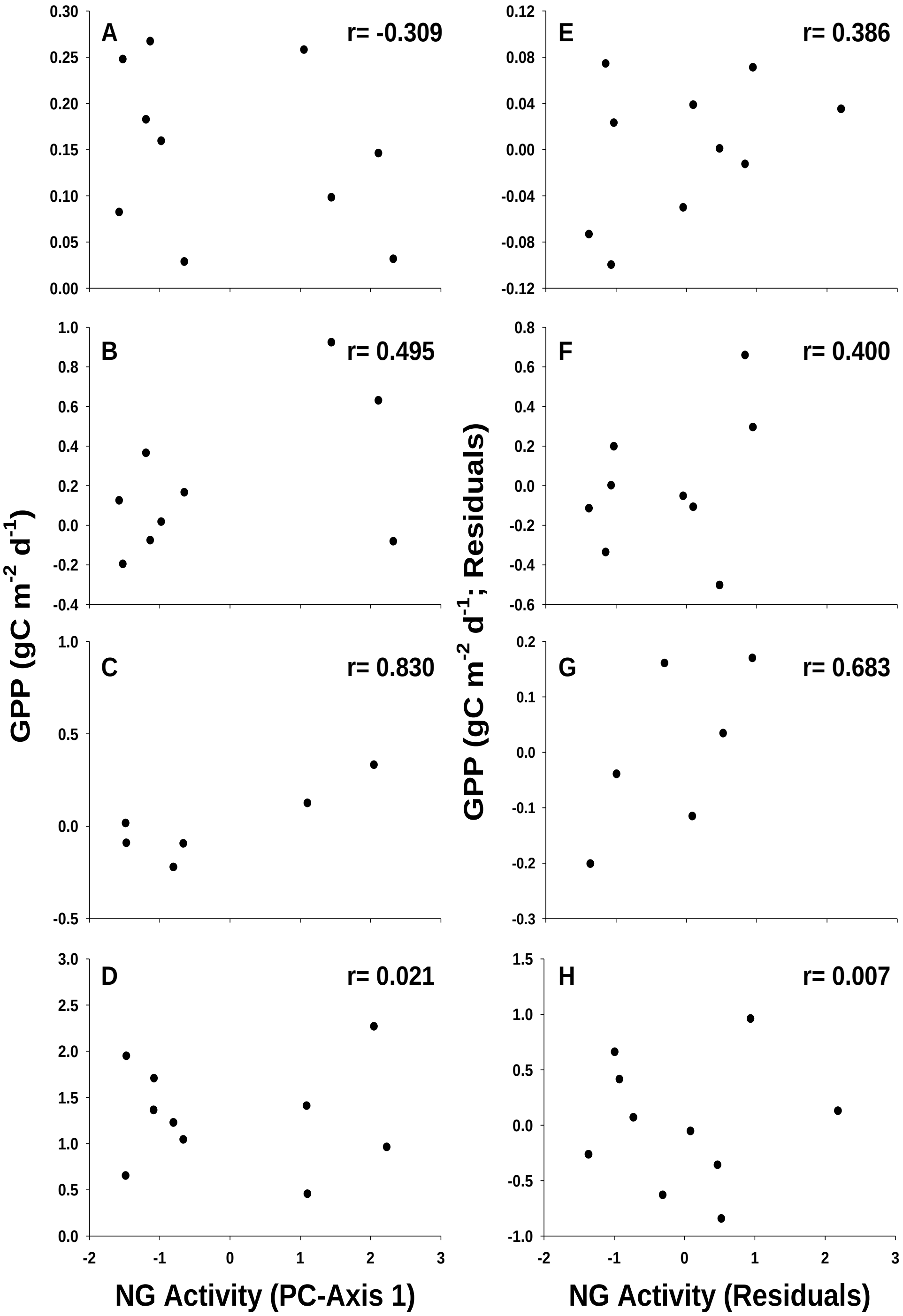


Figure 3. Scatter plots depicting the correlations between GPP and NG Activity metric (A-D) and partial correlations between GPP and NG activity metric with effects of catchment area removed (E-H). With A&E depicting the correlation and partial correlation for winter 2010, B&D depicting the correlation and partial correlation for spring 2010, C&G depicting the correlation and partial correlation for winter 2011, and D&H depicting the correlation and partial correlation for spring 2011. GPP data in panels B and C are logarithmically transformed.

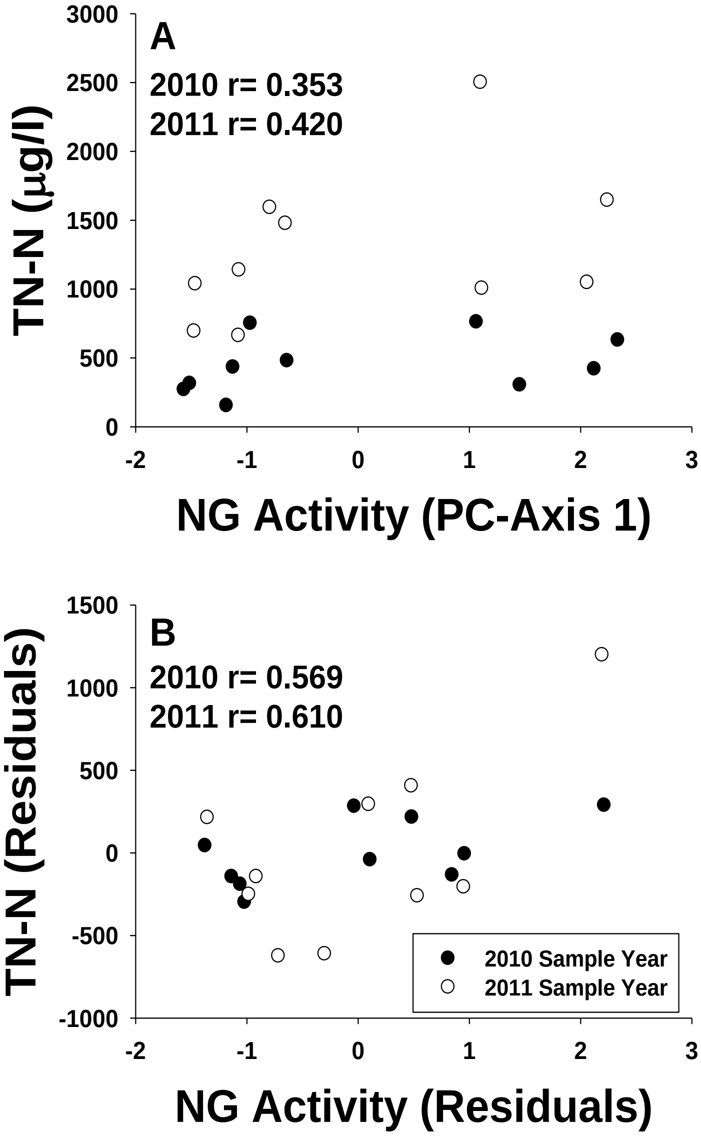


Figure 4. Scatter plot showing the correlations between the PC-axis defining NG activity and total nitrogen (TN) for both 2010 (●) and 2011 (○) sample periods (A) and residuals plots showing the correlations between the PC-axis defining NG activity and TN with the effects of catchment area removed for both 2010 (●) and 2011 (○) sample periods (B).

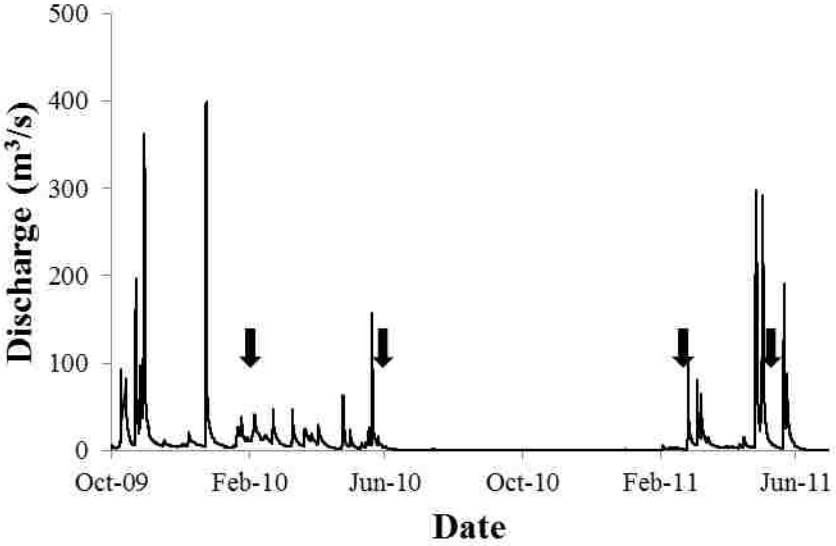


Figure 5. Hydrograph of Cadron Creek near Guy, Arkansas for the water years Oct 1st 2009-September 30th 2011. Black arrows indicate sample periods.

Chapter II:

Assessment of Nutrient and Cation Limitation of Algal Growth Across a Gradient of Natural Gas Impacted Streams

Bradley J. Austin

Department of Biological Sciences, University of Arkansas,
Fayetteville, AR 72701 USA

ABSTRACT

Construction of natural gas (NG) infrastructure (well pads, pipelines, and roads) may negatively influence streams by clearing watershed vegetation and increasing inputs of sediments, sediment-bound nutrients, and ions. Additionally, produced water, a brine solution that flows up the well bore with NG, can contribute cations (Na^+ and K^+) to nearby streams if improperly stored or disposed of. Nutrients and cations from the landscape may alleviate nutrient limitation of benthic algal communities promoting the increased algal growth and primary production observed in prior correlative studies. With positive relationships between both nutrients and cations, it is impossible to determine which variables were driving increased algal biomass. Nutrient diffusing substrates (NDSs) were used to separate out potential effects of increased nutrients, nitrogen (N) and phosphorus (P) along with cations, Na^+ and K^+, on algal biomass within 8 streams in north central Arkansas impacted by NG activity. Cation enrichment of algal biomass revealed neither Na^+ nor K^+ limitation across the sites sampled. Minimally impacted streams were found to be N-limited and one was co-limited by both N and P, while streams with high levels of NG activity were neither N- nor P-limited. In addition, algal biomass values from the +N treatments were negatively related to well density within the catchment (R^2= 0.57; p= 0.03) as well as to background total N (R^2= 0.52; p= 0.04). This suggests that as NG activity increases N-limitation of algal biomass is alleviated. These data provide evidence that the mechanism by which NG activity stimulates the primary production of Fayetteville shale streams is via alleviation of N- or P- rather than cation limitation.

INTRODUCTION

In the past decade, extraction and combustion of natural gas (NG) from unconventional shale formations has become a prominent component of the U.S. energy budget (Malakoff 2014). Currently the U.S. is a world leader in unconventional NG extraction and use, but an increase in global extraction is expected due to vast unconventional gas reserves (Malakoff 2014). By the year 2050, unconventional NG is expected to meet 47 – 53% of global energy demands (Rahm and Rhia 2014; Malakoff 2014). While NG combustion is considered less environmentally detrimental than oil and coal due to decreased output of atmospheric CO_2 (Shahidehpour et al. 2005; Kintisch 2014), the development of NG infrastructure and extraction of NG from unconventional sources can have potential negative effects on the landscape and nearby streams.

Recent work suggests that soil erosion resulting from the construction of NG infrastructure (Williams et al. 2008) directly increases stream turbidity via allochthonous sediment inputs (Entrekin et al. 2011). Sedimentation is one of the major contributors to poor stream health among wadeable U.S. streams (USEPA 2006). Increased sediments can also be a major source of nutrients to aquatic systems (Nguyen et al. 1998, Quinn and Stroud 2002, Vaze and Chiew 2004). Additionally, disturbance to the landscape, such as vegetation removal, promotes leaching of nutrients and cations from the soils into nearby streams (Likens et al. 1970). Increased inputs of sediment-bound and dissolved nutrients into streams may alleviate nutrient limitations of algal communities, promoting increased algal growth.

Nutrient limitation studies have provided an understanding of what nutrients, generally nitrogen (N) and phosphorus (P), are limiting to autotrophs in streams throughout different regions of the U.S. (Grimm and Fisher 1986; Hill and Knight 1988; Lohman et al. 1991; Tank and Dodds 2003). Ozark streams tend to be N-limited (Lohman et al. 1991; Borchardt 1996);

however, NG activity in the Fayetteville shale of north central Arkansas may alleviate this nutrient limitation. Previously, we found NG activity to have a positive relationship with total nitrogen (TN) in streams (Austin, Chapter 1). While NG activity was also positively related to algal biomass during each winter sampling, there were no significant relationships between TN and algal biomass in the same season (Austin, Chapter 1). This correlative evidence provides some indication that NG activity may stimulate primary production by increasing N availability in these study streams. Experimentally increasing N and P availability to stream autotrophs across a gradient of NG activity would provide a further test of the hypothesis that Fayetteville shale streams with relatively little human impacts in their watershed are nutrient limited and that NG activity may be alleviating nutrient limitation of benthic algal production.

Following well pad construction, wells are drilled and then must go through hydraulic fracturing "fracking" before they will produce NG (Entrekin et al. 2011). This process injects large volumes of water (2-7 million gallons) along with salts, and proprietary chemicals and compounds into the well to fracture the shale formation freeing the NG stored within (Vidic et al. 2013). Following the fracturing process a portion of the fracturing fluid returns to the surface along with the NG produced, this "produced" water needs to be stored on site until it can be disposed of (Vidic et al. 2013). Improper handling, storage, and disposal of produced water on the surface can also result in these chemicals entering surrounding water bodies (Olmstead et al. 2013). Roughly half of over 1400 drilling violations within Pennsylvania from January 2008 to October 2010 involved surface-water contamination (Entrekin et al. 2011). A previous correlative study found that measures of conductivity, and cations potassium (K^+) and sodium (Na^+) were all positively related with well density across 10 streams within the Fayetteville shale region of north central Arkansas in late winter of 2011 (Table 1). This increase in K^+

corresponded with an increase in algal biomass as well as increased TN (Table 1). Therefore, it is not clear whether K^+ or TN is stimulating algal production.

Studies examining nutrient requirements of cyanobacteria have found both Na^+ and K^+ to be important for growth (Allan 1952; Kratz and Meyrs 1955). However, no known studies have examined the effects of Na^+ and K^+ on stream algal community growth and activity, though previous efforts have addressed the relationship between conductivity and algae. Low to moderate increases in conductivity have resulted in a range of outcomes from no effect when increasing conductivity from 1609 to 4428 μs cm^{-1} (Cook and Francoeur 2013) to a strong positive relationship across a conductivity range of 65 – 723 μs cm^{-1}(Chételat et al. 1999). Increasing conductivity from 1609 – 35320 μs cm^{-1} resulted in a decrease in photosynthetic activity (Cook and Francoeur 2013); this decrease in photosynthetic activity over extended periods of time could result in decreased algal growth. Conductivity across Ozark streams is relatively low in comparison to streams in other regions of the U.S. (Potapova and Charles 2003). In a previous study of NG activity influenced streams with the Fayetteville shale region of Arkansas, conductivity ranged from 29.29 – 60.94 μS cm^{-1} (Austin, Chapter 1). While conductivity across these streams was positively associated with NG activity, it did not relate to algal biomass (Table 1). Further increases in conductivity associated with NG activity may promote increased algal growth as seen by Chételat and others (1999); however, since both TN and cations are positively associated with conductivity it is necessary to separate out the effects of both nutrients and cations on algal growth.

The purpose of this study was to determine the extent of nutrient- or cation- limitation on algal biomass within streams varying in levels of NG activity. No known manipulative studies to date have investigated the effects of cation enrichment of algal biomass in natural settings.

Given the potential for NG activity to increase inputs of cations as well as nutrients and the prior positive relationship between NG activity and algal measures, it is important to determine the relative importance of nutrient and cation enrichment to algal responses to help guide management options. We hypothesized that sites minimally impacted by NG activity would express N-limitation as described in Lohman et al. (1991), while N-limitation would be alleviated at sites with higher NG activity, due to increased availability of N in NG impacted streams. Natural gas activity also influences Na^+ and K^+ concentrations in streams (Table 1). A positive correlation between K^+ and algal metrics previously observed in our study streams, suggests that increased cations from NG activity may be driving the algal biomass in streams. However, due to the strong correlation between TN and cations (Table 1), it was predicted that this relationship was spurious and that N, P, or both are the main dissolved components limiting algal biomass in the Fayetteville shale study streams.

METHODS

Experimental Design

Nutrient limitation (specifically, N and P) and cation (specifically, Na^+ and K^+) limitation of algal growth were examined during June and July of 2014 at 8 sites within the north central Arkansas Fayetteville shale play. The study sites represented varying levels of NG activity in their watersheds. A fully factorial cross of N and P amendments was used to examine the extent of nutrient limitation at each site resulting in the following N and P treatments: no nutrients (control), +N only, +P only and +N+P. Additionally, Na^+ and K^+ were examined in independent fully factorial crosses with N and P with treatments including: no nutrients (control), +N+P only, +cation (Na^+ or K^+), and +N+P+cation. With each analysis for ions the +N+P treatment contained the opposite cation (Figure 2). This resulted in 6 distinct nutrient and cation amendments and the control, of which, each were replicated 5 times at each site for an n=35. The 8 sites used in the experiment were divided into 3 groups, high NG activity (2 sites), low NG activity (3 sites), and no NG activity (3 sites). NG activity was quantified based on well density calculated as the total number of wells in the catchment divided by total catchment area upstream of the sampling reach (no./km^2). Well locations were downloaded from the Arkansas Oil and Gas Commission database (ftp://www.aogc.state.ar.us) and stream catchment sizes and predominant land-use land-covers (Table 2) delineated using ArcMap (Version 9.3.1; ESRI, Redlands, CA).

Local Site Characteristics

At each stream, discharge was measured at the base of the sample reach via the midsection method (Gore 2006); water velocity values for the equation were collected using a Marsh McBirnery Flo-mate 2000 (Hach Co. Loveland, CO). As a proxy for light availability, canopy cover was measured using a concave spherical densiomenter at 6 sites (3 left bank and 3 right bank and measurements averaged) within each reach following USGS stream reach characterization methods (Fitzpatrick et al. 1998). A 1L whole water grab sample was collected from the thalweg of each stream for the determination of the water chemistry parameters: TN, TP, conductivity, turbidity, K^+, and Na^+. Water samples were stored on ice and taken to the Arkansas Water Resource Center for analysis.

Nutrient Diffusing Substrata

Agar solutions amended with nutrients for the nutrient limitation experiment were produced following similar methods described by Tank and Dodds (2003). The control consisted of a 2% (by weight) agar solution amended with no nutrients, NH_4Cl and $NaNO_3$ were both added for treatments containing N (0.5M-N as 0.25M from each N source), and NaH_2PO_4 was added for treatments containing P (0.5M-P). Controls and +N+P experimental units were used also in the analysis of the cation enrichment studies. Sodium chloride was added to a 2% agar solution to create the +Na treatment (0.75M-Na) and KCl was used to create the +K treatment (0.75M-K). A second +N+P treatment was created by substituting $NaNO_3$ and NaH_2PO_4 with KNO_3 and KH_2PO_4. A 3% (by weight) agar solution was used for the treatment containing both N and P to ensure the agar solution solidified. Cation only treatments were 0.75M so that they would have the same molar concentrations of Na^+ and K^+ as in the +N+P treatments. Agar solutions were heated to dissolve agar and nutrients and then pre-labeled 50ml centrifuge tubes were filled with 40ml of the corresponding agar solutions. Tubes were capped and inverted and allowed to cool so that agar would solidify at the top of the centrifuge tube.

Upon deployment of NDSs at each sampling location, caps were replaced with 2.6cm porous porcelain crucible covers, from here further referred to as glass frits (Leco Corporation, St. Joseph, MI) and re-capped with caps containing a 2.2cm diameter opening. Centrifuge tubes were placed into holding racks and secured to the stream bed with rebar. Holding racks were oriented perpendicular to stream flow to prevent nutrients leaching from one experimental unit affecting other experimental units within the holding rack. All units were placed into the same 20m reach, which was selected for homogeneous light conditions and relatively deep flowing water.

Algal Biomass

Algae were allowed to colonize NDSs for 14-18 days before units were retrieved. Glass frits were removed from centrifuge tube and placed into individual pre-labeled Whirl-Pak (Nasco, Modesto, CA). Samples were stored on ice until returning to the laboratory where they were kept at -20^0C until analyzed for Chlorophyll *a* (Chl *a*).

Chlorophyll *a* was extracted from glass frits by adding 10ml of 95% ethanol to each Whirl-Pak then incubated in a water bath (78^{o}C, 5 min., Sartory and Grobbelaar 1984), and stored in the dark at 4^{o}C for 24h. The absorbance of the extract was measured on a Genesys 10 VIS spectrophotometer (Thermo Fischer Scientific inc., Waltham, MA) as described in APHA (2005). Chlorophyll *a* estimates were standardized to the area of the glass frit exposed to light defined by the open area of the caps (3.8cm^2).

Statistical Analysis

Two-way ANOVAs were used to examine the individual and interactive effects of N and P limitation on algal growth, as well as the effects of Na^+ and K^+ in relation to N and P on algal growth. In the event of a significant interactive effect between factors a *post hoc* Tukey's honestly significant difference (HSD) test was performed to determine where significant differences occurred. To assess changes in nutrient and cation limitations across sites with variable NG activity, Chl *a* estimates for each nutrient and cation treatment were normalized to the control. Normalized Chl *a* values for each treatment were then regressed against well density and the in-stream background concentration of the respective nutrient or cation (i.e. +N treatment regressed against TN). Prior to all analyses visual inspection of box plots and scatter plot matrices were implemented to check that the data met the assumptions of independence, homoscedasticity, and normal distribution. Data not fitting the assumptions of the analysis were transformed and re-assessed to verify assumptions were met before conducting statistical analyses. All statistical analyses were performed in SAS (Version 9.3, SAS Institute, Cary, NC).

RESULTS

Local Site Characteristics

Local site characteristics varied across study sites. Canopy cover was greater than 50% at all of the sites except for one, which had 19% canopy cover (Table 3). All sites had measureable discharge, though it was low. Total nitrogen was low at the all sites with either no or low NG activity (0.02 – 0.17mg/l); while TN was 2 – 73 times higher at the high NG activity sites. A similar trend was found for TP, though the variability across sites was lower with TP at the highest impacted site only 3 times higher than TP at the lowest impacted sites. Conductivity and both Na^+ and K^+, like TN and TP were highest at the high NG activity sites and lowest at the minimally impacted sites. Turbidity was relatively low and consistent across all sites, though was slightly higher at Point Remove (Table 3).

Nutrient Limitation Experiment

There were only a few statistically significant differences across all sites for the nutrient limitation experiment. There was a statistically significant difference between treatments with N added (+N and +NP) and treatments without N (Control and +P) at the minimally impacted sites Point Remove and Powerline (p= 0.011 and p= 0.001 respectively; Table 4; Figure 3D & E) indicating N-limitation at these two sites. Low cedar also showed a trend of N-limitation (Figure 3C); however, loss of sampling equipment resulted in too few replicates to analyze the data properly. Driver was the only site with algal biomass co-limited by both N and P as indicated by significant interaction between the N and P factors (F= 6.82; p= 0.0189; Table 4; Figure 3B). While there were no differences between treatments for Black Fork, Rock, Sis Hollow and Sunny Side (Table 4), visual inspection of the figures suggests mild N-limitation at Rock, Sis Hollow and Low Cedar (Figure 3C, F, & G)

At the landscape scale there was a significant negative relationship between logarithmically transformed well density and normalized +N values (R^2= 0.57; p= 0.03; Figure

4). At the local scale, normalized +N values were also negatively related to TN (R^2= 0.52; p= 0.04; Figure 5). Similar relationships were found for the +NP treatment when the normalized Chl *a* values were compared to logarithmically transformed well density (R^2= 0.53; p= 0.04), but was not related to logarithmically transformed TN and TP (R^2= 0.45; p= 0.07 and R^2= 0.49; p= 0.05 respectively). For P enrichment, when normalized Chl *a* values were compared to logarithmically transformed well density and TP there were no significant relationships (R^2= 0.24; p= 0.21 and R^2= 0.15; p= 0.34 respectively).

Sodium and Potassium Limitation Experiment

There were no significant differences across all sites due to the addition of Na^+ or K^+ (Table 4). There was a significant difference between treatments with N and P and those without at Driver and Powerline for both the Na^+ and K^+ analyses, and Sis hollow for only the Na^+ analysis (Table 4; Figure 6 & 7). This indicates that N and P promoted increased algal growth at these sites regardless of the cation (Na^+ or K^+) associated with the nutrients. There was a statistically significant interaction between the NP and K^+ factors at Driver and post hoc Tukey's HSD test found that the addition of N and P significantly increased algal biomass relative to the control. This confirms the findings from the nutrient enrichment experiments for this site. Additionally, the +K treatment had statistically significantly lower algal biomass than the control treatment (Table 4; Figure 7B), suggesting possible inhibition of algal growth.

Cation enrichment treatments were further examined by comparing the normalized Chl *a* values to logarithmically transformed well density at the landscape scale and in stream concentrations of Na^+ for the +Na treatment and K^+ for the +K treatment. Plus Na treatment normalized Chl *a* values were not related to well density or in stream Na^+ (R^2= 0.35; p= 0.12 and R^2= 0.18; p= 0.29 respectively). Similar to the +Na treatment, +K treatment normalized Chl *a* values were not related to well density or in stream K^+ concentration (R^2= 0.16; p= 0.33 and R^2= 0.17; p= 0.31 respectively).

DISCUSSION

In a previous study, NG activity was positively related to stream algal measures and to TN and cation concentrations during some sample periods suggesting that NG activity alleviates nutrient- or cation-limitation of algal growth in Fayetteville shale streams. The present study provides manipulative evidence, based on NDSs, that nutrients rather than cations limited primary production in the streams with relatively low NG activity. Further, as NG activity increased, responses to nutrient additions declined suggesting that nutrient limitation of algal growth was alleviated in streams with high NG activity.

Streams with high NG activity had greater TN and TP than sites with minimal NG activity (Table 3). The elevated nutrients at the two sites with high NG activity, Black Fork and Sunny Side, resulted in an alleviation of nutrient limitation at both streams (Table 4; Figure 3A & H). Three of the six sites with minimal NG activity were limited by N availability; an additional site, Driver, was co-limited by both N and P (Table 4, Figure 3B, C, D, & E). Two of the minimally impacted streams, Rock and Sis Hollow, appeared to be N-limited but were not statistically significant (p= 0.100 and p= 0.062 respectively; Table 4, Figure 3F & G). While Rock was only minimally impacted by NG activity, it had the third highest TN concentration (0.17 mg/l; Table 3), which likely resulted in a decreased response of algal growth to added nutrients. Higher sample size may have allowed for better detection of N-limitation in both cases (Francoeur 2001); however, due to the design of this study greater replication of treatments was not feasible. The overall N-limitation of the minimally impacted streams is similar to what was found previously across Ozark streams in Missouri (Lohman et al. 1991).

We found no evidence that Na^+ or K^+ were limiting algal production in any of the streams tested. Cations never resulted in a positive effect on algal biomass. In one case, a negative effect on biomass was observed (Driver; Table 4, Figure 7B). Based on these results, the positive relationships between K^+ and algal biomass in the previous study was likely spurious. Laboratory studies have provided some evidence that primary producers can respond positively when amended with Na^+ and K^+ (Allan 1952; Kratz and Meyrs 1955). However, these previous efforts utilized pure cyanobacteria cultures, which may have vastly different nutritional requirements from *in situ* algal communities in Fayetteville shale streams. Further studies examining possible negative effects of possible leaks from storage tanks or ponds and improper waste disposal of high-salinity produced waters (Olmstead et al. 2013) on benthic algae may be warranted.

CONCLUSIONS

NG activity may be increasing N availability in streams resulting in greater primary production. Previous correlative studies have found positive relationships between NG activity and TN and between NG activity and primary producers (Austin, Chapter 1). The present study indicates that algal growth in minimally impacted Fayetteville shale streams was primarily N-limited. Additionally, when the algal biomass on the +N treatment is normalized to the control for each site and then plotted against well density and TN we find negative relationships (Figures 4 & 5 respectively) providing additional evidence that NG activity is associated with greater N availability. These findings represent a snapshot in time and might vary seasonally (Francouer et al. 1999). Therefore, further NDS experiments across winter and spring seasons would improve confidence in the nutrient limitation status of these streams. Increased NG activity has the potential to further reduce nutrient limitations in nearby Fayetteville shale streams, transforming these systems from nutrient sinks into sources of nutrients for adjacent downstream habitats.

ACKNOWLEDGEMENTS

This research was in funded in part through the National Science Foundation (BIO REU 1359188) for funding undergraduate researchers. I would like to thank REU undergraduate researchers, Natalia Hardgrave and Scott Hamby as well as honors undergraduate researcher William Carman who assisted in the sampling and processing of data for this project. We thank Brian Haggard and the Arkansas Water Resource Center for processing water samples for nutrient and cation data. I would also like to thank the members of the Evans-White lab, Hal Halvorson, Ayla Smartt, Allyn Fuell, Kayla Sayre, and Brooke Parker along with Lindsey Bruckerhoff and Matthew Jennings for providing valuable comments and suggestions in the editing of this manuscript. We also thank co-authors Sally Entrekin and Michelle A. Evans-White as well as project collaborators Ginny Adams, Reid Adams, Brian Haggard, Steve Filipek, Lindsey Lewis, Ethan Inlander, and Cory Gallipeau. Additionally, valuable comments and guidance were provided by my dissertation committee that included Michelle Evans-White, Thad Scott, Dan Magoulick, J.D. Willson, and Gary Huxel.

LITERATURE CITED

Allen, M.B. 1952. The cultivation of Myxophyceae. Arch. Mikrobiol. 17: 34-53.

APHA (American Public Health Association). 2005. *Standard Methods for the Examination of Water and Wastewater*. (21st edn.). American Public Health Association: Washington D.C. 1368 pp.

Borchardt, M.A. 1996. Nutrients. Pages 183-227 in R.J. Stevenson, R. Lowe, and M. Bothwell (editors). Algal ecology: freshwater benthic ecosystems. Academic Press, New York.

Chételat, J., F.R. Pick, A. Morin, and P.B. Hamilton. 1999. Periphyton biomass and community composition in rivers of different nutrient status. Canadian Journal of Fisheries and Aquatic Sciences. 56: 560-569.

Cook, L.J., and S.N. Francoeur. 2013 Effects of stimulated short-term road salt exposure on lotic periphyton function. Journal of Freshwater Ecology. 28: 211-223.

Entrekin, S., M. Evans-White, B. Johnson, and E. Hagenbuch. 2011. Rapid expansion of natural gas development poses a threat to surface waters. Frontiers in Ecology and the Environment. 9:503-511.

Fitzpatrick, F.A., I.R. Waite, P.J. D'Arconte, M.R. Meador, M.A. Maupin, and M.E. Gurtz. 1998. Revised methods for characterizing stream habitat in the National Water-Quality Assessment program. U.S. Geological Survey. Water-Resources Investigations Report 98-4052.

Francoeur, S.N. 2001. Meta-analysis of lotic nutrient amendment experiments: detecting and quantifying subtle responses. Journal of the North American Benthological Society. 20: 358-368.

Francoeur, S.N., B.J.F. Biggs, R.A. Smith, and R.L. Lowe. 1999. Nutrient limitation of algal biomass accrual in stream: seasonal patterns and a comparison of methods. Journal of the North America Benthological Society. 18: 242-260.

Gore, J.A. 2006. Discharge measurements and streamflow analysis. Pages 51-77 *in* Methods in Stream Ecology (2nd edn.), F. Richard Hauer and G.A. Lamberti (eds), Academic Press, New York, NY, USA.

Grimm, N.B., and S.G. Fisher. 1986. Nitrogen limitation in a Sonoran desert stream. Journal of the North American Benthological Society. 5: 2-15.

Hill, W.R., and A.W. Knight. 1988. Nutrient and light limitation of algae in two Northern California streams. Journal of Phycology. 24: 125-132.

Kintisch, E. 2014. A bold baby step on emissions. Science. 344: 1070-1071.

Kratz, W.A., and J. Myers. 1955. Nutrition and growth of several blue-green algae. American Journal of Botany. 42: 282-287.

Likens, G.E., F.H. Bormann, N.M. Johnson, D.W. Fisher, and R.S. Pierce. 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. Ecological Monographs. 40: 23-47.

Lohman, K., J.R. Jones, and C. Baysinger-Daniel. 1991. Experimental evidence for nitrogen limitation in a Northern Ozark stream. 1991. Journal of the North American Benthological Society. 10: 14-23.

Malakoff, D. 2014. The Gas Surge. Science. 344: 1464-1467.

Nguyen, M.L., G.W. Sheath, C.M. Smith, and A.B. Cooper. 1998. Impact of cattle treading on hill land: 2. Soil physical properties and contaminant runoff. New Zealand Journal of Agricultural Research. 41: 279-290.

Olmstead, S.M., L.A. Muehlenbachs, J.S. Shih, Z. Chu, and A.J. Krupnick. 2013. Shale gas development impacts on surface water quality in Pennsylvania. Proceedings of the National Academy of Science. 110: 4962-4967.

Potapova, M., and D.F. Charles. 2003. Distribution of benthic diatoms in U.S. rivers in relation to conductivity and ionic composition. Freshwater Biology. 48: 1311-1328.

Quinn, J.M., and M.J. Stroud. 2002. Water quality and sediment and nutrient export from New Zealand hill-land catchments of contrasting land use. New Zealand Journal of Marine and Freshwater Research. 36: 409-429.

Rahm, B.G. and S.J. Riha. 2014. Evolving shale gas management: Water resource risks, impacts, and lessons learned. Environmental Science: Processes Impacts. 16: 1400-1412.

Sartory, D. P. and J.U. Grobbelaar. 1984. Extraction of chlorophyll a from freshwater phytoplankton for spectrophotometric analysis. Hydrobiologia 114: 177-187.

Shahidehpour, M., Y. and Fu, T. Wiedman. 2005. Impact of natural gas infrastructure on electric power systems. Proceedings of the IEEE. 93:1042-1056.

Tank, J. L. and W.K. Dodds. 2003. Nutrient limitation of epilithic and epixylic biofilms in ten North American streams. Freshwater Biology 48: 1031-1049.

U.S. Environmental Protection Agency (2006) *Wadeable streams assessment, a collective survey of the nation's streams.* Washington 841-B-06-002.

Vaze, J., and F.H.S. Chiew. 2004. Nutrient loads associated with different sediment sizes in urban storm water and surface pollutants. Journal of Environmental Engineering 130: 391-396.

Vidic, R.D., S.L. Brantley, J.M. Vandenbossche, D. Yoxtheimer, and J.D. Abad. 2013. Impacts of shale gas development on regional water quality. Science 340: DOI:10.1126/science.1235009.

Williams, H. F. L., D.L. Havens, K.E. Banks, and D.J. Wachal. 2008. Field-based monitoring of sediment runoff from natural gas well sites in Denton County, Texas, USA. Environmental Geology 55: 1463-1471.

Table 1: Pearson correlation coefficients [r and (p-values)] comparing potential contaminants from NG activity (Cond.[a], K^{+b}, Na^{+c}, TN[d], and TP[e]) with NG activity, quantified as well density, and algal biomass as Chl *a*[f].

	Cond.[a]	K^{+b}	Na^{+c}	TN[d]	TP[e]	Well Density
K^+	0.746 (0.013)					
Na^+	0.763 (0.010)	0.525 (0.119)				
TN	0.612 (0.060)	0.891 (0.001)	0.597 (0.068)			
TP	-0.156 (0.661)	-0.245 (0.495)	-0.060 (0.870)	-0.389 (0.267)		
Well Density	0.599 (0.093)	0.736 (0.015)	0.679 (0.031)	0.783 (0.007)	-0.477 (0.164)	
Chl *a*[f]	0.278 (0.436)	0.617 (0.058)	0.233 (0.517)	0.417 (0.231)	-0.021 (0.942)	0.493 (0.148)

[a]Cond.= Specific conductance; [b]K^+= Potassium; [c]Na^+= Sodium; [d]TN= Total nitrogen; [e]TP= Total phosphorus; [f]Chl *a*= Chlorophyll *a*

Table 2: Landscape scale data for sites sampled

Site	Lat[a]	Long[b]	Catchment (km^2)	Well Density ($\#/km^2$)	For[c] (%)	Past[d] (%)	Urb[e] (%)
Black Fork	35.25	-92.31	32.16	0.69	39	50	2
Driver	35.50	-92.73	12.28	0.00	96	2	2
Low Cedar	35.57	-92.67	27.18	0.04	89	6	1
Point Remove	35.52	-92.65	3.45	0.00	99	1	0
Powerline	35.50	-92.63	6.18	0.17	92	2	0
Rock	35.45	-92.80	16.11	0.12	94	4	1
Sis Hollow	35.59	-92.70	6.67	0.00	81	12	0
Sunnyside	35.39	-92.62	14.41	3.64	49	40	1

a: Lat= latitude; b: Long= longitude; c: For = Forest; d: Past= Pasture; e: Urb= Urban

Table 3: Reach scale characteristics of study sites sampled

Site	CC[a] (%)	Discharge (m^3/s)	TN[b] (mg/l)	TP[c] (mg/l)	K[d] (mg/l)	Na[e] (mg/l)	Cond.[f] (µs/cm)	Turbidity (NTU[g])
Black Fork	82.4	0.090	0.35	0.038	1.37	2.42	38.6	5.6
Driver	63.7	0.014	0.05	0.014	0.64	0.97	19.3	5.1
Low Cedar	55.9	0.059	0.02	0.014	0.76	1.01	28.5	4.7
Point Remove	86.3	0.003	0.03	0.016	0.84	1.03	24.8	10.4
Powerline	18.6	0.003	0.08	0.016	0.64	1.35	27.8	6.3
Rock	68.6	0.017	0.17	0.014	0.92	1.52	27.0	6.8
Sis Hollow	72.5	0.011	0.04	0.016	0.78	1.09	31.4	6.0
Sunny Side	73.5	0.024	1.47	0.046	2.67	4.16	71.0	6.3

a: CC= Canopy Cover; b: TN= Total Nitrogen; c: TP= Total Phosphorus; d: K= Potassium
e: Na= Sodium; f: Cond= Specific conductance; g: NTU= Nephlometric Turbidity Units

Table 4: 2-way ANOVA results for nutrient (N x P) and cation (NP x Na; NP x K) limitation for the 8 study sites. A loss of half of the sampling racks at Low Cedar resulted in too low of replication for a 2-way ANOVA (n= 3), so only main effects were examined using a 1-way ANOVA.

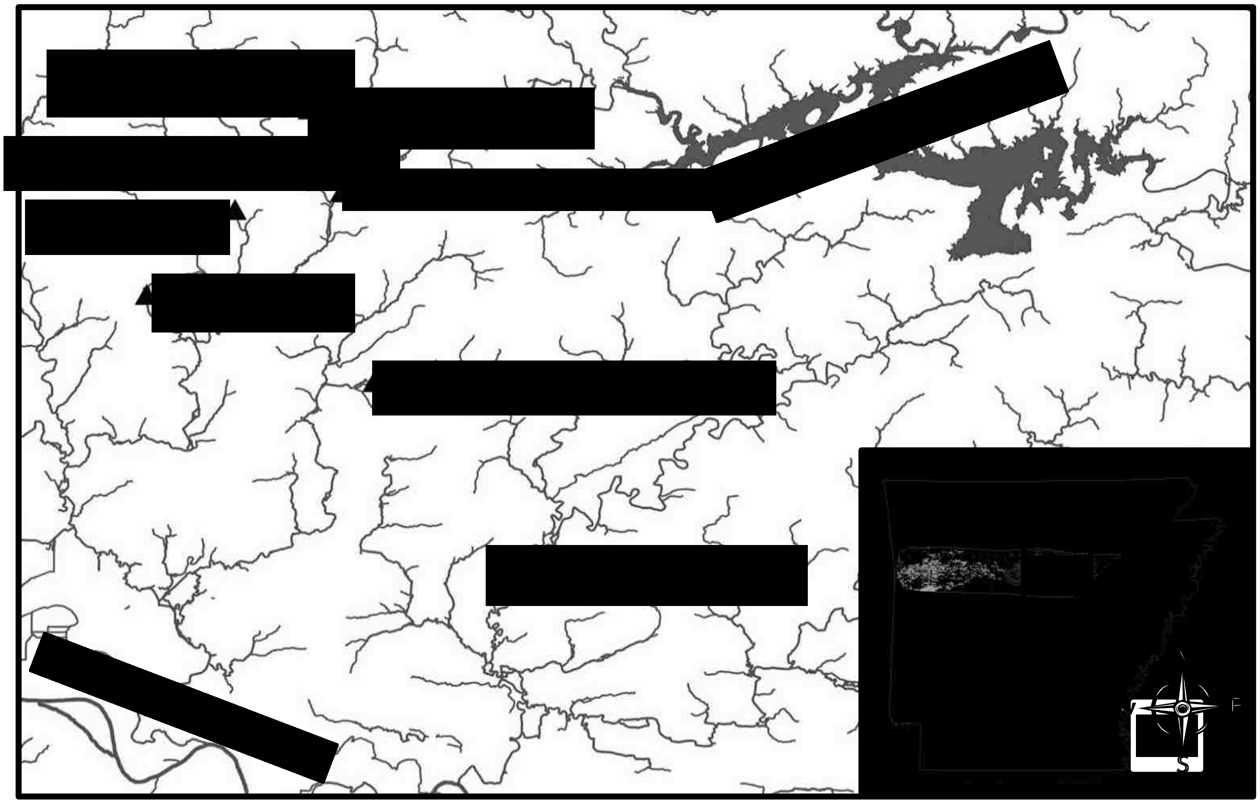
Site		N x P	NP x Na	NP x K
BF[a]	Limitation	(*) -	-	-
	Factor 1	F(n)= 1.27; p= 0.277	F(np)<0.01; p= 0.945	F(np)< 0.01; p= 0.978
	Factor 2	F(p)= 2.86; p= 0.110	F(na)= 0.75; p= 0.400	F(k)= 0.28; p= 0.069
	Interaction	F= 1.02; p= 0.3267	F= 0.46; p= 0.508	F= 0.40; P= 0.538
DR[b]	Limitation	(*) Co-limitation	(*) NP	(*) NP
	Factor 1	F(n)= 4.00; p= 0.063	F(np)= 120.62; p< 0.001	F(np)= 112.32; p< 0.001
	Factor 2	F(p)= 6.07; p= 0.025	F(na)= 1.48; p= 0.241	F(k)= 3.21; p= 0.093
	Interaction	F= 6.82; p= 0.019	F= 0.53; p= 0.478	F= 4.90; p= 0.043
LC[c]	Limitation	N	-	NP
	Factor 1	F(n)= 12.17; p= 0.010	F(np)= 4.49; p= 0.067	F(np)= 7.32; p= 0.027
	Factor 2	F(p)= 0.22; p= 0.656	F(na)= 0.10; p= 0.759	F(k)= 0.10; p= 0.763
	Interaction	-	-	-
PR[d]	Limitation	N	(*) -	(*) -
	Factor 1	F(n)= 8.63; p= 0.011	F(np)= 2.63; p= 0.125	F(np)= 2.48; p= 0.135
	Factor 2	F(p)= 0.47; p= 0.504	F(na)= 0.01; p= 0.929	F(k)= 4.02; p= 0.062
	Interaction	F= 0.35; p= 0.561	F= 4.21; p= 0.057	F= 0.01; p= 0.905
PO[e]	Limitation	N	NP	NP
	Factor 1	F(n)= 8.86; p= 0.009	F(np)= 7.55; p= 0.014	F(np)= 9.87; p= 0.006
	Factor 2	F(p)= 0.03; p= 0.872	F(na)= 0.26; p= 0.617	F(k)= 0.07; p= 0.792
	Interaction	F= 1.13; p= 0.304	F= 0.01; p= 0.937	F= 0.75; p= 0.398
RO[f]	Limitation	-	-	-
	Factor 1	F(n)= 3.04; p= 0.101	F(np)= 0.43; p= 0.523	F(np)= 0.43; p= 0.522
	Factor 2	F(p)= 0.30; p= 0.590	F(na)= 0.32; p= 0.580	F(k)= 2.10; p= 0.168
	Interaction	F= 2.24; p= 0.154	F= 1.48; p= 0.242	F= 0.51; p= 0.485

a: BF= Black Fork; b: DR= Driver; c: LC= Low Cedar; d: PR= Point Remove; e: PO= Powerline; f: RO= Rock; g: SH= Sis Hollow; h: SS= Sunny Side; (*): indicates the data were log transformed before the analysis was conducted; N: N limitation; -: no limititation; co-limitation: indicates site was limited by both N and P; NP: for cation analyses, indicates treatments with N and P were greater than treatments without.

Table 4 continued: 2-Factor ANOVA results for nutrient (N x P) and cation (NP x Na; NP x K) limitation for the 8 study sites. A loss of half of the sampling racks at Low Cedar resulted in too low of replication for a 2-way ANOVA (n= 3), so only main effects were examined using a 1-way ANOVA.

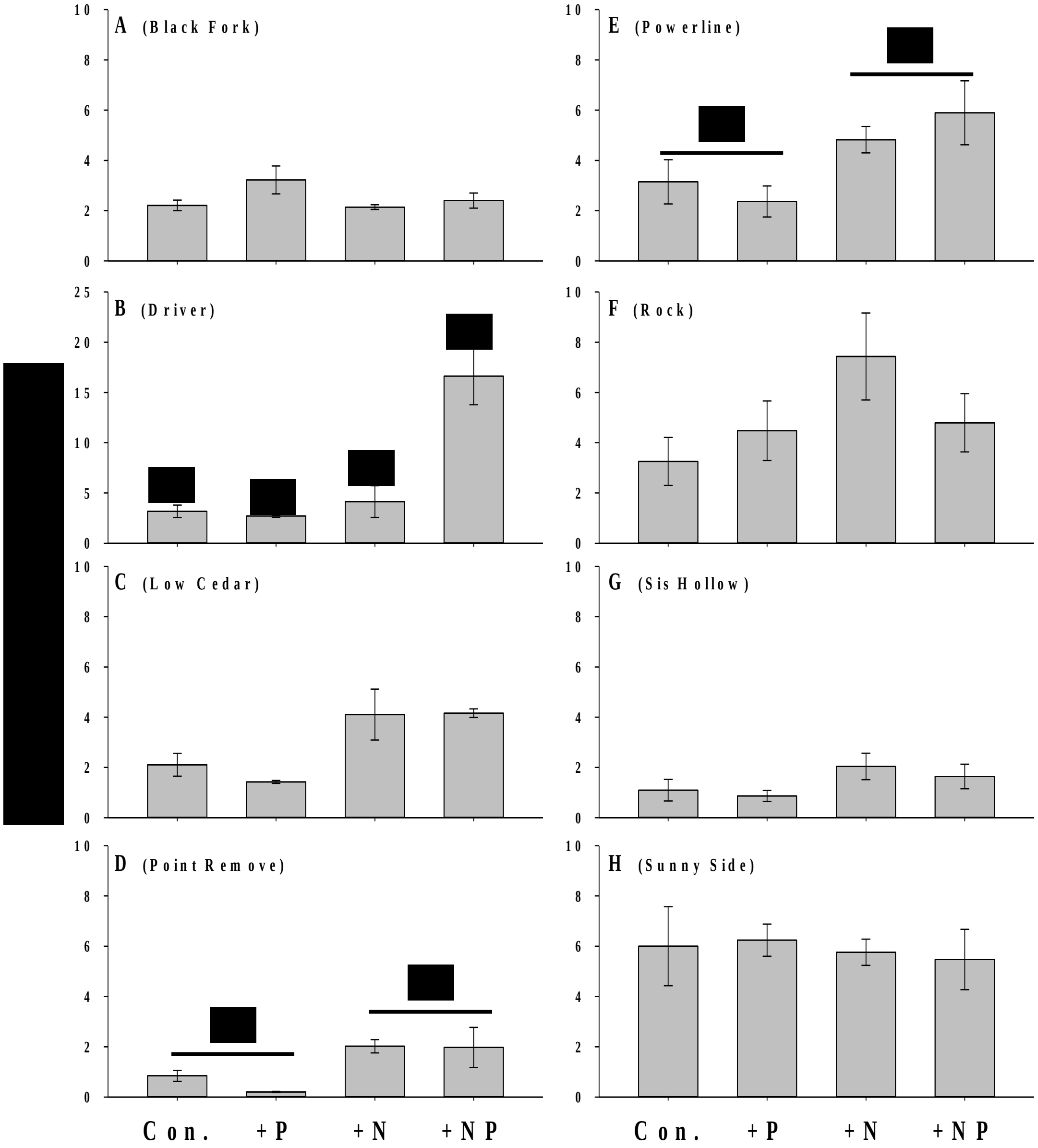
Site		N x P	NP x Na	NP x K
SH[g]	Limitation	(*) -	(*) NP	(*) -
	Factor 1	F(n)= 4.04; p= 0.062	F(np)= 4.95; p= 0.041	F(np)= 1.03; p= 0.325
	Factor 2	F(p)= 0.31; p= 0.588	F(na)= 0.49; p= 0.496	F(k)= 1.32; p= 0.267
	Interaction	F= 0.04; p= 0.854	F< 0.01; p= 0.982	F= 0.24; p= 0.632
SS[h]	Limitation	-	-	-
	Factor 1	F(n)= 0.22; p= 0.644	F(np)= 0.51; p= 0.487	F(np)= 0.36; p= 0.599
	Factor 2	F(p)< 0.01; p= 0.983	F(na)=1.18; p= 0.294	F(k)= 1.70; p= 0.211
	Interaction	F= 0.06; p= 0.809	F= 0.92; p= 0.353	F= 1.05; p= 0.322

a: BF= Black Fork; b: DR= Driver; c: LC= Low Cedar; d: PR= Point Remove; e: PO= Powerline; f: RO= Rock; g: SH= Sis Hollow; h: SS= Sunny Side; (*): indicates the data were log transformed before the analysis was conducted; N: N limitation; -: no limititation; co-limitation: indicates site was limited by both N and P; NP: for cation analyses, indicates treatments with N and P were greater than treatments without.

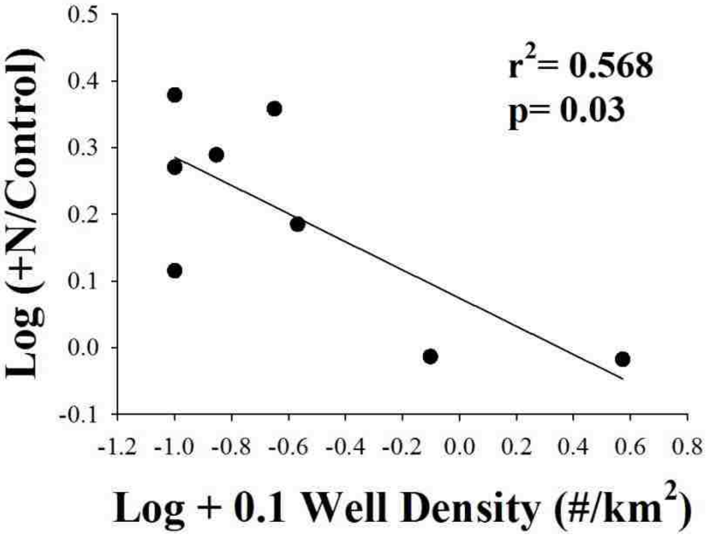

[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
S

[redacted]

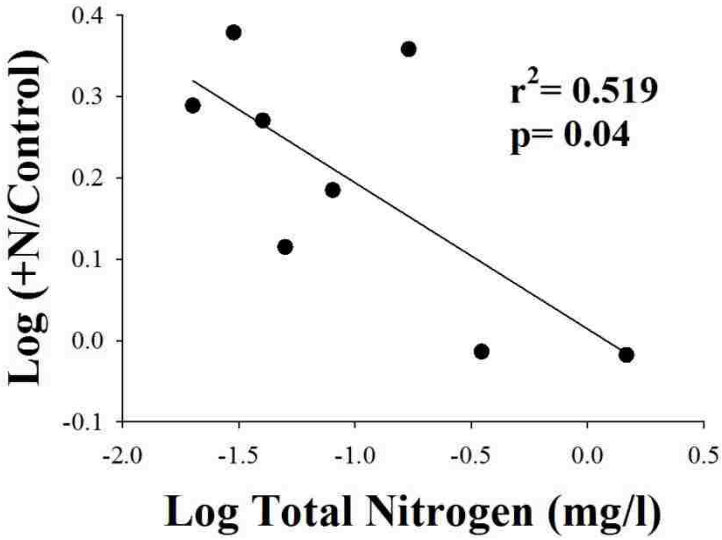
[redacted]


A (Black Fork)
B (Driver)
C (Low Cedar)
D (Point Remove)
E (Powerline)
F (Rock)
G (Sis Hollow)
H (Sunny Side)
0
2
4
6
8
10
5
15
20
25
Con.
+P
+N
+NP
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]
[redacted]

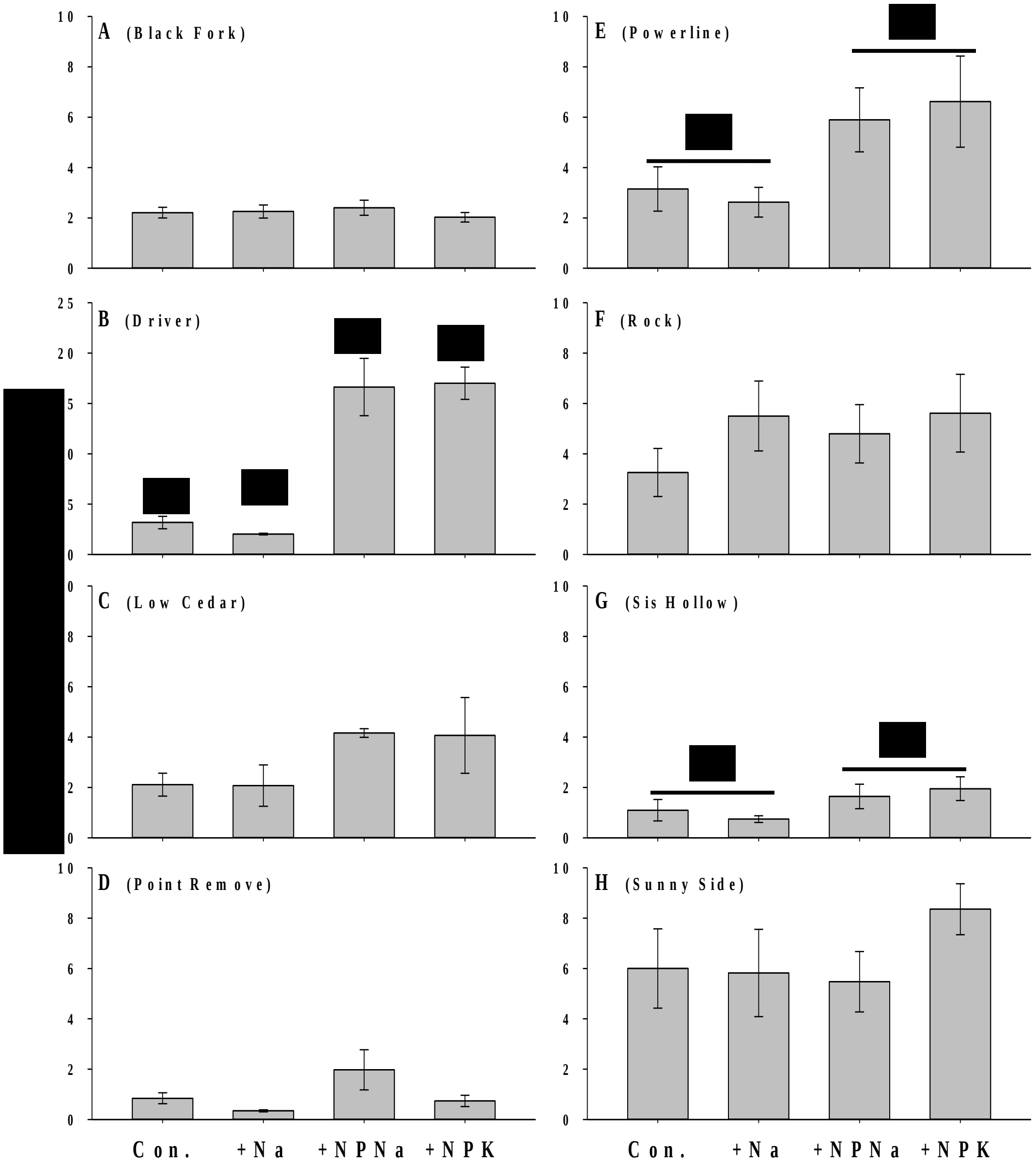
[redacted]


r^2= 0.568
p= 0.03
Log (+N/Control)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
Log + 0.1 Well Density (#/km^2)

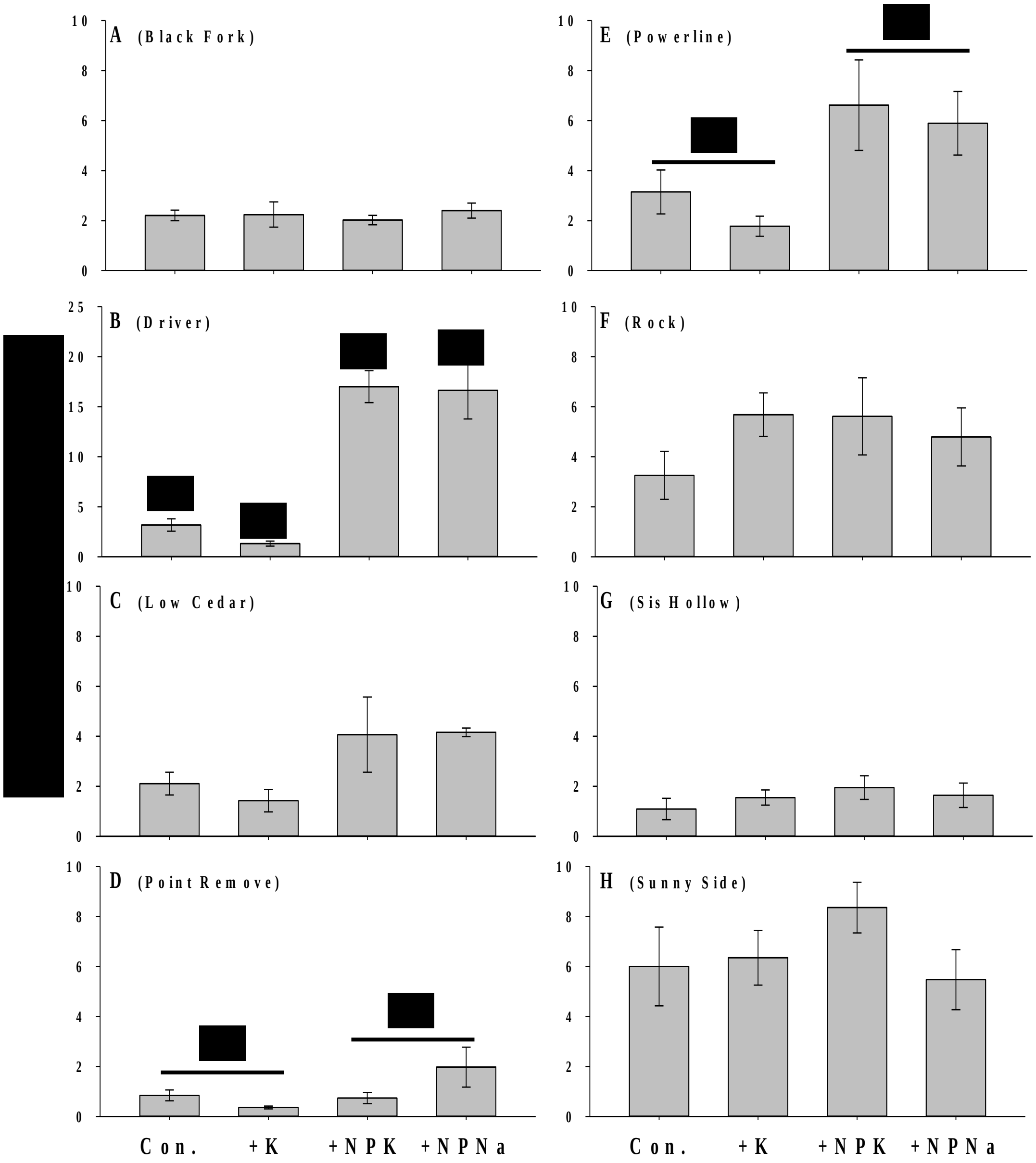
[redacted]


0.4
0.3
0.2
0.1
0.0
-0.1
-2.0
-1.5
-1.0
-0.5
0.0
0.5
Log (+N/Control)
Log Total Nitrogen (mg/l)
r²= 0.519
p= 0.04

[redacted]


A (Black Fork)
0
2
4
6
8
10
E (Powerline)
[redacted]
[redacted]
0
2
4
6
8
10
[redacted]
B (Driver)
[redacted]
[redacted]
[redacted]
[redacted]
0
5
10
15
20
25
F (Rock)
0
2
4
6
8
10
C (Low Cedar)
0
2
4
6
8
10
G (Sis Hollow)
[redacted]
[redacted]
0
2
4
6
8
10
D (Point Remove)
0
2
4
6
8
10
H (Sunny Side)
0
2
4
6
8
10
Con.
+Na
+NPNa
+NPK
Con.
+Na
+NPNa
+NPK

[redacted]


[redacted]
A (Black Fork)
B (Driver)
[redacted]
[redacted]
[redacted]
[redacted]
C (Low Cedar)
D (Point Remove)
[redacted]
[redacted]
E (Powerline)
[redacted]
[redacted]
F (Rock)
G (Sis Hollow)
H (Sunny Side)
0
2
4
6
8
10
5
15
20
25
Con.
+K
+NPK
+NPNa

[redacted]

Chapter III

Effectiveness of Best Management Practices at Reducing Impacts of Natural Gas Development on Stream Function

Bradley J. Austin

Department of Biological Sciences, University of Arkansas,
Fayetteville, AR 72701 USA

ABSTRACT

Production of natural gas (NG) from unconventional sources, such as shale formations, is projected to meet 47-53% of global energy demands by 2050. To accomplish this, many of the world's shale plays must be developed for NG extraction. The development of NG infrastructure in the Fayetteville shale can be a source of sediments and nutrients to streams, which can stimulate benthic autotrophic production. Within the past decade, best management practices (BMPs), such as sediment erosion control, have been implemented to reduce sediment erosion and inputs into freshwaters; however, little has been done to assess their effectiveness. In this study a before-after control-impact (BACI) design was used to examine whether implemented BMPs mitigated NG development impacts in headwater streams and the main stem of the South Fork Little Red River (SFLRR) within the Scott Henderson Gulf Mountain wildlife management area (Gulf WMA) located in the Fayetteville Shale play. In the headwater streams, algal biomass and gross primary production (GPP) were monitored at 6 sites, 3 reference (meant ± 1SE; 0.00 ± 0.00 wells/km^2) and 3 impacted (0.06 ± 0.06 wells/km^2), which were paired by annual stream flow duration, both before and after the construction of NG infrastructure. Within the SFLRR, 4 reaches (1 reference and 3 impacted) were sampled for algal biomass and fine inorganic sediments before and after the development of 3 wells and a pipeline within the Gulf WMA. The level of development was low (0.13 ± 0.01 wells/km^2) compared to that of the surrounding Fayetteville Shale landscape (1.39 ± 0.31 wells/km^2). There were no significant BACI interaction for algal biomass or GPP in the headwater sites or for algal biomass and fine inorganic sediment in the SFLRR. While the BMPs appear to have been effective in the Gulf WMA, the level of NG development was relatively low and further studies should focus on testing BMP effectiveness in the context of a more ambitious build-out scenario.

INTRODUCTION

In the past decade, technological advances in horizontal drilling and hydraulic fracturing (fracking) have rocketed natural gas (NG) to the forefront of energy production in the United States (U.S.) (Malakoff 2014). These two processes have made the recovery of NG from unconventional sources, such as shale formations, economically feasible. While NG production from conventional sources, such as coal bed methane, tight gas and oil associated NG, have been prominent in the past, the contribution of these sources to annual NG production is waning and the extraction of NG from unconventional sources is increasing and is projected to meet 47-53% of the global energy demand by 2050 (Rahm and Rhia 2014; Malakoff 2014). This is primarily due to the widespread distribution of shale formations throughout North America and the world (U.S. EIA 2013; Rahm and Rhia 2014). In addition to its ubiquity and abundance, NG also produces one-third less carbon dioxide (CO_2) than oil and half as much as coal per unit energy, making it a potential “bridge fuel” to more environmentally sound energy sources (Shahidehpour et al. 2005; Kintisch 2014). By utilizing this previously untapped resource, the U.S. continues to reduce its demand for imported oil while increasing exports of NG (Malakoff 2014).

Despite the economic and potential atmospheric environmental benefits associated with utilizing unconventional NG resources, the development of NG infrastructure has outpaced environmental regulation and research leading to a paucity of studies exploring environmental impacts. Only within the past 2-3 years have possible issues begun to be addressed in the literature. Some of these studies have focused on methane (CH_4) emissions from NG infrastructure (Alvarez et al. 2012; Allen et al. 2013; Miller et al. 2013; and Kintisch 2014) and consequences for atmospheric chemistry and climate change. Freshwaters may also be impacted due to overuse of surface and groundwater resources for fracking, improper disposal of flowback and produce waters (Entrekin et al. 2011; Olmstead et al. 2013) possible contamination of surface and groundwater from improper disposal (Olmstead et al. 2013), and sediment erosion from construction activities (Williams et al. 2008; Entrekin et al. 2011). With unconventional NG resources so widespread in the U.S. and the world, these potential environmental impacts will expand as more states and countries begin to extract this resource if proper regulation is not in place to mitigate impacts.

The development of NG infrastructure (pipelines, roads and well pads) first requires the removal of trees and vegetation, which exposes soils to erosion in to nearby streams (Williams et al. 2008, Entrekin et al. 2011). In the Fayetteville Shale play, catchment NG activity was positively related to stream algal biomass and gross primary production (GPP) (Austin, Chapter 1). Natural gas activity was also related positively to stream turbidity and total nitrogen (TN) concentrations. Since algal growth in these same study streams can be N-limited (Austin, Chapter 2), NG activity may be increasing primary production by increasing sediment-bound nutrient inputs to streams or by increasing the leaching of these nutrients from below-ground soil pools and into streams by the removal of terrestrial vegetation (Likens et al. 1970). Preventing the movement of soils from the landscape may be an important first step in mitigating impacts of NG activity on nearby streams.

Best management practices (BMPs) are often implemented to prevent or reduce sediment migration from areas disturbed by NG construction activities. BMPs, such as mulching covers exposed soils, slowing overland flow and filteres out sediments before water reaches nearby stream channels (USFWS 2007; 2009). Additional BMPs specify where and how transmission pipelines should cross stream channels, specifically horizontal directional drilling (HDD) should be used to install pipelines under streams (USFWS 2009). Within the logging industry, similar

BMPs have been found to be highly effective at preventing soil erosion into nearby streams (Prud'homme and Greis 2002). While BMPs are becoming more widely used in the NG industry, their implementation has trailed NG infrastructure development in the region by several years and, to date, few efforts have been undertaken to assess their effectiveness.

In the winter of 2009, we set out to examine the effects of NG activities on stream nutrients, algal biomass and primary production within the Scott Henderson Gulf Mountain Wildlife Management Area (Gulf WMA) within the Fayetteville shale region of north central Arkansas (Figure 1). This area was selected due to the anticipated NG infrastructure development starting in the summer of 2010. Additionally, Arkansas Game and Fish Commission (AGFC) officials were present throughout the construction of infrastructure and the implementation of BMPs. Six headwater stream sites and 4 sites along the main stem of the South Fork Little Red River (SFLRR) were selected to examine potential impacts of NG activity within the Gulf WMA and to assess the effectiveness of BMPs implemented within the region. We predicted that effective BMPs would result in no detectable differences between control and impacted sites before and after the disturbance for both headwater streams and SFLRR sites. If BMPs were ineffective, we predicted to consistently observe elevated N, algal biomass and primary production at impacted sites in comparison to control sites. It was not our intent to detect short-term (< 1 month in duration) pulse disturbances.

METHODS

Study Area

This study was conducted in the Scott Henderson Gulf Mountain Wildlife Management Area (Gulf WMA) located in north central Arkansas, roughly 130 km north west of Little Rock, Arkansas (Figure 1). The Gulf WMA covers approximately 60 km^2 of land within the Boston

Mountain Ecoregion adjacent to the eastern extent of the Ozark National Forest (Birdsong 2011). Forest composition consists of 65% oak hardwood (red and white oak *Quercus rubra and Q. alba*) and 35% pine (loblolly and longleaf pine; *Pinus taeda, P. palustris*) (Birdsong 2011) and the landscape is drained by two major catchments, the South Fork Little Red River (SFLRR) drainage in the north and the Point Remove drainage in the south (Figure 1). The geology of this region is Middle Pennsylvanian-Morrowan with the primary rock types consisting of sandstone and shale. The Gulf WMA is managed by the Arkansas Game and Fish Commission (AGFC) for wildlife-oriented recreation, such as hunting and site-seeing. Throughout the extent of the NG development in the Gulf WMA, AGFC officials enforced the implementation of BMPs across impacted areas.

Sampling Locations

Study 1 – Headwater Streams:

For this study, a 200m reach within two 4th order streams from the Point Remove drainage (Powerline and Point Remove) and three reaches from two 3rd-5th order streams from the SFLRR drainage (High and Low Cedar and Dry Hollow) were sampled starting in December of 2009. An additional 200m reach from another 3rd order stream was added from the SFLRR drainage (Sis Hollow) in May of 2010 for a total of six stream reaches. All stream reaches were sampled 1-2 times per year from December of 2009 through April of 2013. During each sample period water samples were collected for the determination of total nitrogen (TN) and phosphorus (TP), and cobbles were collected for periphyton biomass in the form of Chlorophyll *a* (Chl *a*) and ash free dry mass (AFDM). Diel dissolved oxygen (DO) profiles were used to calculate gross primary production (GPP) at each of the six reaches.

Land use land cover (LULC) variables were similar across all six sites for the duration of the study (Table 1), with % forest constituting 80-98% of the land cover across all sites and % pasture ranging from 1-20%. Installation of the three NG well pads within the Gulf WMA began in summer of 2010 and was completed by the spring of 2012. Of these three well pads, only one fell within our sampled catchments, Powerline. However, the installation of NG pipeline and lateral lines to collect the produced gas from each of the well pads was installed during the late spring and summer of 2012 (0.22 – 0.26 km/km^2). The construction of this NG infrastructure occurred within the catchments of Powerline, Point Remove, and Dry Hollow and is outlined in the timeline (Figure 2).

Study 2 – South Fork Little Red River:

The SFLRR was sampled at four locations starting in December of 2010 and continued each spring and winter through December 2013. The most upstream (site 1) and downstream (site 4) reaches sampled coincided with USGS monitoring stations (07075250 and 07075270, respectively). These monitoring stations provided real-time data logged every 15min for stage (ft.), discharge (ft^3/s), precipitation (in.), temperature (ºC), specific conductance (µs/cm), DO (mg/l), turbidity (NTU), and suspended sediments (mg/l). Both upstream and downstream sites occurred just outside of the Gulf WMA. Two additional sites were located within the Gulf WMA and occurred upstream (site 2) and downstream (site 3) of the Cedar Creek catchment (Figure 1). During each sample period at all sites, 5-6 cores were collected for benthic inorganic and organic sediments and 10-12 cobbles were collected for determination of AFDM and Chl *a*. Base flow water samples were collected monthly for determination of nitrate + nitrite (NO_3^-+NO_2^-; here further NO_3^-) and soluble reactive phosphorus (SRP).

Land use and land cover was consistent across all four SFLRR sites with all having approximately 90% forested land cover (Table 2). The catchment area of all sites ranged from 123 – 193 km^2. All sites were impacted to some extent by NG activity occurring outside of the Gulf WMA. However, only disturbances occurring within the Gulf WMA were of concern and all other disturbances upstream of site 1 were viewed to impact all sites equally, allowing site 1 to act as our control site. Within the Gulf WMA sites 2-4 were impacted by the installation of transmission and lateral NG pipelines installed during the spring and summer of 2012, as well as from clear-cut logging practices occurring downstream of site 1 during the same time frame as of the pipeline installation (0.402 km^2).

Water quality

Two 1L whole water samples were collected at each site during each sample period for the headwater stream study from 2009 through 2011 and then monthly unless the streams were dry from 2012 to 2013. Water samples were stored on ice and then transported back to the laboratory for processing. Due to relatively low concentrations of both TN and TP, each water sample was filtered through pre-combusted 1µm glass fiber filters (GFF), then both filter and filtrate were kept at -20ºC until analysis for TN and TP. Filters and filtrate were digested in potassium persulfate following methods described by Ameel et al. (1993; APHA 2005). This digestion process converts all nitrogen sources into NO_3^- and all phosphorus sources into SRP. Digested samples were analyzed for TN by measuring the NO_3^- via the cadmium reduction method on the Lachat QuikChem 8500; the minimum detection limit (MDL) of this method is 1µg/l-N (Method 10-107-4-1-B; Lachat Instruments, Loveland, CO). Digested samples were analyzed for TP by measuring the SRP using the standard colorimetric Ascorbic acid/molybdate method; the MDL of this method is 2 µg/l-P (APHA 2005). Water samples collected for the

SFLRR study were chemically analyzed by the AWRC laboratory for NO_3^- using ion chromatography following EPA Method 300.0 and SRP using methods as described above.

Sediment Samples

Sediment samples were only collected for the SFLRR study at 6 sites distributed evenly across habitat units within a 200-m sampling reach. Percent embeddedness was assessed and benthic sediments were collected at each of six locations within each of the study reaches in the winter of 2010 (December). *In-situ* observation of percent embeddedness from the first sample period was not significantly correlated to benthic sediments, and thus was not taken during subsequent sample periods. At each location, embeddedness was visually assessed as described in Barbour et al. (1999). Following the determination of embeddedness, a 19.5 cm diameter corer was placed into the stream substrate, five depths were taken inside the core to estimate volume and then the top 10cm was disturbed and the suspended sediments were sub-sampled. All samples were stored on ice until returning to the laboratory where they were stored at 4°C until being processed within 48h of collection. In the laboratory, samples were sieved to separate sediments in to 6 size classes (>500µm, 250-500µm, 120-250µm, 64-120µm, 37-64µm, and 1-37µm). Sieved samples were placed into pre-combusted aluminum weigh boats, dried (50°C), weighed to determine dry mass, combusted (500°C), wetted with DI water, dried (50°C), and weighed again to determine ash mass (Steinman and Lamberti 1996). The organic component or AFDM of the samples was determined as the difference between the dry mass and the ash mass.

Algal Biomass

For both studies, cobbles were collected for the determination of algal biomass in the form of Chl *a* and total periphyton biomass measured as AFDM. At the headwater sites, two cobbles were collected at each of three riffles and three pools for a total of twelve cobbles. For the SFLRR study, two cobbles were collected near each of the sediment cores.

All cobbles collected were stored on ice and transported back to the laboratory and frozen (-20ºC) until processing for Chl *a* and AFDM. Each cobble was thoroughly scrubbed with a stiff bristle brush to remove all periphyton from the surface. A subsample of the resulting slurry was filtered onto a pre-combusted pre-weighed filter (Pall GF/F) and then stored at -20ºC until Chl *a* extraction was performed. Chlorophyll *a* was extracted from filters using 10ml of 95% ethanol and incubated at 78.5ºC for 5min as described by Sartory and Grobbelaar (1984), and stored in the dark at 4 ^{o}C for 24 h, after extraction absorbance was measured on a Genesys 10 VIS spectrophotometer (Thermo Fischer Scientific inc., Waltham, MA) as described in APHA (2005).

After the Chl *a* analysis, filters and extract were poured into pre-combusted, pre-weighed tins and placed in a drying oven (50ºC) and then ashed (500ºC, 3h) for determination of AFDM (see detailed methods above). Surface area of each cobble was determined using the aluminum foil method as described by Lamberti et al. (1991) and used to standardize estimates of both Chl *a* and AFDM per unit area.

Gross Primary Production

Within the headwater sites GPP estimates were calculated from diel curves of dissolved oxygen (DO) following the single station method described by Owens (1974) and Bott (1996). DO was measured at 15min intervals for three days with a Hydrolab DS5X multiparameter sonde equipped with an LDO probe (Hach environmental, Loveland, CO), situated in the thalweg of well-mixed area of each stream reach (Mulholland et al. 2005). Winkler titrations were conducted at the beginning and end of each sonde deployment to correct for drift in the DO measurements. Air to water gas exchange (ko_2) was estimated using a night-time regression of the DO fluctuation, whereby the slope of the regression between the changes in DO concentration and the oxygen deficit was equal to the reaeration coefficient (Wiley et al. 1990; Young and Huryn 1996) for headwater streams. Dissolved oxygen, reaeration coefficients, and mean depth were used to calculate an areal rate of change in DO (gO_2 m^{-2} min^{-1}) following calculations described in Bernot et al. (2010). Areal rates of oxygen change were then converted to rates of carbon change (gC m^{-2} min^{-1}) (Bott 1996), daytime rates of C change were then used to calculate GPP.

Data Analysis

For both studies, sampling started prior to the installation of NG infrastructure within the Gulf WMA and continued until after the development was complete. This allowed us to examine the data utilizing a paired reach Before-After Control-Impact (BACI) analysis (Green 1979). For the headwater study, control (no NG activity) and impacted (NG activity) sites were paired based on annual flow duration, with Sis Hollow (control) and Dry Hollow (impacted) having the shortest flow duration (SFD), High Cedar (control) and Point Remove (impacted) having an intermediate flow duration (IFD), and Low Cedar (control) and Powerline (impacted) having the longest flow duration (LFD) (Kelso, master’s thesis). As with the headwater study, the SFLRR sites were analyzed using the paired BACI analysis approach, with the difference being that site 1 was always the control site and was compared with each of the downstream sites individually. An uneven two-way repeated measures analysis of variance (2-way rmANOVA) was utilized to examine the interaction term between the factors “Before-After” and “Control-Impact” (here after BA and CI respectively) for all response variables in both studies; whereby a significant interaction term ($p < 0.05$) indicates impact by the disturbance.

Visual inspection of box plots and scatter plot matrices were used to check that the data for each response variable met the assumptions of independence, homoscedasticity, and normal distribution prior to running the 2-way rmANOVA. Data not fitting the assumptions of the analysis were transformed and re-assessed to verify assumptions were met prior to conducting the statistical test.

RESULTS

Study 1- Headwater streams

Nutrients

Total nitrogen and TP between the headwater reaches ranged from below detectable concentrations to 271.2µg/l and from below detectable concentrations to 53.1µg/l, respectively, across all sample periods. Total nitrogen was not significantly different within each flow duration paring of control and impacted sites prior to the development of NG infrastructure throughout the region (Table 4). Similar to TN, TP was not significantly different between each of the pairings before the disturbance occurred (Table 4). Mean and standard error values of TN and TP across all sites before and after the disturbance are in Table 3. Examination of the 2-way rmANOVA interaction terms between the factors BA and CI found no statistically significant differences for either TN or TP across all flow duration parings (Table 4; Figure 3 and 4 respectively).

Algal biomass

Chlorophyll *a* averaged 0.71µg/cm^2 across all sites and sample periods and ranged from 0.03 to 3.42µg/cm^2. Before the disturbance, Chl *a* at the SFD sites was lower at Dry Hollow (mean ±1SE; 0.21 ± 0.08 µg/cm^2) than at Sis Hollow (1.11 ± 0.37 µg/cm^2). Chl *a* values were similar between the IFD sites [Point Remove and High Cedar (0.51 ± 0.26 µg/cm^2 and 0.69 ±

0.37 respectively)]. They were higher at the LFD site, Powerline, than at Low Cedar (1.84 ± 0.55 and 1.04 ± 0.33 µg/cm^2 respectively). There were no differences between control and impacted sites prior to the disturbance (Table 4). There were no statistically significant 2-way rmANOVA interaction terms between the BA and CI factors for any of the flow duration parings (Table 4; Figure 5).

Gross primary production

Gross primary production values averaged across all sites and sample periods was 0.18gC m^{-2} d^{-1} and ranged from 0.00 to 2.77gC m^{-2} d^{-1}. Prior to the disturbance, GPP at the SFD sites was lower at Dry Hollow than at Sis Hollow (0.05 ± 0.03 and 0.32 ± 0.21gC m^{-2} d^{-1} respectively), GPP was similar between the IFD sites Point Remove and High Cedar (0.04 ± 0.03 and 0.09 ± 0.05gC m^{-2} d^{-1} respectively), and between the LFD sites was lower at Powerline than Low Cedar (0.04 ± 0.03 and 0.24 ± 0.12gC m^{-2} d^{-1} respectively). There were no statistically significant differences in GPP for any of the flow duration pairings prior to the disturbance (Table 4). Additionally, there were no statistically significant interactions between the factors BA and CI for GPP between any of the flow duration pairings (Table 4; Figure 6).

Study 2- SFLRR

Nutrients

Nitrate and SRP on average were similar across SFLRR sites (49.5 ± 8.5 and 30.8 ± 4.9µg/l respectively). Nitrate was lower across all sites prior to the development of NG infrastructure and logging (all sites: $p< 0.01$). Conversely, SRP tended to be higher across sites prior to disturbance than after ($p= 0.03$, $p< 0.01$, and $p= 0.01$ for sites 1v2, 1v3, and 1v4 respectively). There were no significant differences in NO_3^- concentrations between the control site and impacted sites prior to the disturbance (Table 5), nor were there any differences between site pairings for SRP (Table 5). Examination of the interaction between the BA and CI factors found no differences between the control site and each of the impacted sites for either NO_3^- or SRP (Table 5; Figures 7 and 8, respectively).

Fine organic and inorganic sediments

There was a trend of higher fine organic sediments at impacted sites than at the control site, after 3 post-disturbance sampling events, with the control having the lowest (17.87 ± 3.96g/m^2), and site 3 having the highest (33.10 ± 10.05g/m^2). These differences could not be statistically tested due to issues with sample processing, which resulted in a loss all fine organic sediment data during the first two sample periods.

As with the fine organic sediments, fine inorganic sediments tended to be lower at the control site than impacted sites and ranged from 275.63 ± 66.08g/m^2 at the control site to 482.97 ± 111.32g/m^2 at site 2. Again, these differences between the control site and impacted sites were not statistically significant ($P > 0.05$ for all pairings). Fine inorganic sediments did not differ between the control site and the impacted sites prior to disturbance (Table 5). Additionally, there were no significant interactions between the BA and CI factors for any of the pairings between the control site and impacted sites (Table 5; Figure 9).

Algal biomass

Chlorophyll *a* measured across all sample periods was lowest at site 3 (0.49 ± 0.06µg/cm^2) and highest at site 4 (1.17 ± 0.14µg/cm^2). Control and impacted sites did not differ ($p > 0.05$ for all pairings). Further, there were neither statistically significant differences between the control site and impacted sites prior to the NG activity and logging of the SFLRR catchment (Table 5), nor a significant interaction term between the BA and CI factors between any pairing of the control site and impacted sites (Table 5; Figure 10).

DISCUSSION

Study 1: Headwater streams

Previous studies have found positive relationships between NG activity and TN (Chapters 1 and 2). The present study found no consistent effect of NG development in the Gulf Mountain WMA headwater study streams. However, TN and TP exhibited elevated concentrations at impacted sites in comparison to control sites (17 days) post flood disturbance, which is suggestive of a possible pulse disturbance. More frequent water quality sampling directly after and active period of infrastructure development may be a more effective way to verify the existence of these pulse events.

Overall, TN and TP across all sites in the headwater study (Table 3) were relatively low in comparison to other NG activity impacted streams within Arkansas, where TN ranged from 0.15 – 2.50mg/l and TP from 0.01 – 0.09mg/l (Austin, Chapter 1) and much lower than reported values from row crop agricultural systems 0.40 – 21.00mg/l for TN and 0.01 – 2.75mg/l for TP (Morgan et al. 2006; Munn et al. 2010). Interestingly, TN and TP values for these sites are comparable to minimally impacted streams throughout the Ozark highlands (0.17 – 0.77mg/l and 0.01 – 0.12mg/l for TN and TP, respectively; Lohman and Jones 1999; Justus et al. 2010). Low nutrient availability across sites likely resulted in low algal biomass and GPP.

Although previous studies have seen a positive relationship between NG activity and algal biomass (Chapter 1), no change in algal biomass was observed in the Gulf WMA headwater sites during the NG infrastructure development. Overall, measured Chl *a* was low across all sample periods for both the control and impacted sites, with all sites falling primarily within the oligotrophic category $<2.0\mu g/cm^2$ (Table 3; Dodds et al. 1998). Chlorophyll *a* measured within the Gulf WMA streams was similar to that measured in the low NG activity impacted sites off of the Gulf WMA, but was lower than the higher impacted sites (0.25 – 9.37μg/cm^2; Austin, Chapter 1). Both the IFD and LFD sites tended to show more variability in Chl *a* between sample periods before the disturbance than after the disturbance, while the SFD sites were fairly consistent across all sample periods (Figure 5). Previous studies indicate that these streams can be N-limited or co-limited by N and P (Chapter 2). Therefore, we might have expected elevated Chl *a* immediately following the disturbance at the impacted sites associated with the elevation in TN and TP. The absence of this effect may have been due to a lag time in an observable effect on algal biomass accrual following increased nutrient availability. It is also possible the timeframe of increased nutrient availability was too short to effectively stimulate algal biomass. A greater frequency of sampling may have been needed to detect short term changes in algal biomass immediately following the installation of pipelines within the impacted catchments.

A previous study found a positive relationship between NG activity and GPP. As with algal biomass GPP was consistently low across all sites throughout the duration of the study suggesting that NG activity with implemented BMPs had little to no effect on GPP. There were few consistencies for GPP across the different flow duration pairings. When compared to other streams proximal to NG activity, GPP was similar to winter measurements (0.03 – 2.03gC m^{-2} d^{-1}), though were much lower than the maximum spring time measurement of 8.2gC m^{-2} d^{-1} (Austin, Chapter 1). With respect to other landscape disturbances the values reported here fall well below agriculturally- and urban-influenced streams sampled in the LINX-II project (0.03 – 4.63 gC m^{-2} d^{-1}, Bernot et al. 2010) and much lower than agriculturally influenced streams in Illinois (0.03 – >15 gC m^{-2} d^{-1}, Wiley et al. 1990). In addition to relatively low rates of GPP across all sites, there were no clear trends in GPP at SFD and IFD impacted sites following the disturbance (Figure 6A & B). Only the LFD impacted site exhibited elevated GPP following the disturbance. However, this was only found for one sample period and similar rates of GPP were measured for this site prior to the disturbance. These data may simply be illustrating natural variability in GPP at this site or could possibly be due to the increased TN and TP that occurred at that site following the disturbance. At this low level of disturbance, it appears that the BMPs are effective at mitigating nutrient enrichment and increased primary production.

Study 2: SFLRR

Logging within privately owned land near site 1 may have resulted in the pulse elevation of NO_3^- occurring across all sites in the fall of 2012, at the end of a 2 year drought, NO_3^- values increased to or near 0.27mg/l across all sites (Figure 7). This increase in NO_3^- at all the sites post disturbance could be an indication that the control site was also impacted by the logging disturbance experienced at sites 2-4 and as such did not serve well as a control. However, this is unlikely due to the relatively low increase in NO_3^-. For reference, the clearing of a watershed at Hubbard Brook in 1965 resulted in an increase from 0.94 to 38.40mg/l N-NO_3^- (Likens et al. 1970). While this reference is an extreme case, I would expect concentrations to increase above those measured in other minimally impacted systems within the region (0.06 – 0.53mg/l) (Austin, unpublished data). Nitrate likely increased in response to increased flow conditions and not to the disturbance.

As seen with NO_3^-, SRP was similar across all sites within each sample period (Figure 8); however, the main increase in SRP occurred before the NG transmission line was installed and catchment was logged. Unlike the pulse of NO_3^-, the pulse in SRP prior to the disturbance had a much greater range (BD – 0.13mg/l) than other NG activity impacted sites (0.003 – 0.004mg/l) (unpublished data). The similarity between control and impacted sites during the pulse in SRP prior to the disturbance adds support that the control site was an appropriate reference site for the disturbed sites and that the implemented BMPs were effective at reducing potential impacts from the disturbance.

Unlike the dissolved nutrients, fine inorganic sediments were fairly consistent across sample periods within each site and were relatively similar across sites (Figure 9). However, site 2 showed a slight increase in fine inorganic sediments in comparison to the control site during the winter sample period following the disturbance. This could be an indication of increased sediment erosion due to the NG transmission line and logging disturbances. There was a slight increase in fine inorganic sediments at sites 3 and 4 but was not as pronounced as at site 2 and levels decreased across all sites in spring of 2013 (Figure 9). Like the nutrients, these trends suggest a pulse event as opposed to a step change in benthic fine inorganic sediments

As with the headwater sites within the Gulf Mtn. WMA, Chl *a* was low across all sites and all sample periods and fell within the oligotrophic status (Figure 10; Dodds et al. 1998). Site 4 was the only impacted site to have increased Chl *a* following the disturbance with respect to the control site. As with NO_3^- and the fine inorganic sediments, this increase in Chl *a* occurred during the fall/winter of 2012, which coincided with the end of a 2yr drought. While both NO_3^- and SRP exhibited pulsed events throughout the extent of the study, with the exception of site 4, these increases in nutrients were not mirrored in the measure of Chl *a* at sites 1-3. However, due to the pulse nature exhibited by the nutrients a similar trend in Chl *a* may have been missed due to less frequent sampling.

BMPs Effectiveness

Two important aspects of the 2-way rmANOVA statistical analyses stand out for all variables analyzed for the headwater study (TN, TP, Chl *a*, and GPP) when compared between the control and impacted sites within each flow duration. First, there were no differences ($p > 0.05$) between the control sites and impacted sites prior to the disturbance. This indicates the control sites were appropriate reference conditions for impacted sites. Secondly, we found no differences in any variable measured between control and impacted sites before and after disturbance. This suggests that BMPs were effective in mitigating, even preventing, impacts of NG infrastructure development at the level observed in the study. Similar to the headwater sites, the SFLRR control site did not differ from the impacted sites, with respect to the measured response variables, prior to the installation of NG infrastructure and logging throughout the area. Additionally, there were no significant interactions between the BA and CI factors for any site pairings or variables (Table 5). This again, suggests that the implemented BMPs were effective at mitigating impacts to the measured response variables for the level of disturbance that occurred in the area.

The degree to which Gulf Mountain WMA watersheds were developed for NG activity was relatively low compared to development outside the WMA within the Fayetteville shale. This low level of NG activity might also explain the lack of detectable impact in either headwater or SFLRR reaches. Previous work within the Fayetteville shale region of north central Arkansas outside of the Gulf WMA found well pad densities ranging from 0.06 – 1.67 #/km^2 and pipeline densities as high as 1.44 km/km^2 (Austin, Chapter 1). The highest well pad density across the headwater sites sampled was similar to the minimally impacted sites in the previous study at 0.17 #/km^2, while pipeline density ranged from 0.22 – 0.26 km/km^2. Well pad density at the SFLRR sites ranged from 0.08 – 0.15 #/km^2 and pipeline density was low in comparison at 0.01 km/km^2 (Table 2); additionally, as noted earlier, sites 2 – 4 of the SFLRR were impacted by logging which covered 0.402 km^2 or a percent catchment area cleared of 0.21 – 0.29%. The effectiveness of particular BMPs would more appropriately be tested in watersheds where NG development and activity match the average pace in the shale play of interest.

Absence of impact may also have been due to a lack of statistical power. A post-hoc power analysis was used to determine if our sample size was large enough to detect an effect to our primary response variable, Chl *a*, for both the headwater and the SFLRR study. On average, for both studies to attain a power of 0.80 based on the effect size and standard deviation within each pairing measured, 6-7 sampling events were needed before and after the disturbance occurred. Had an effect size and standard deviation between control and impacted sites been comparable to what was found across sites outside of the Gulf Mtn. WMA only 3 sample events before and after the disturbance would have been needed. The actual NG development on the Gulf Mountain WMA fell far short of what was originally projected and, thus, a more intense sampling design would have been beneficial to detect smaller changes after impact.

Before-After Control-Impact designs are most effective at detecting disturbances that elicit a press or ramp response in the impacted site. A press change is one where the response variable changes quickly following a disturbance reaching a new constant level, whereas ramp responses changes steadily increasing or decreasing over time, eventually reaching a new constant level (Lake 2000). Though the level of impact in this study was low, both nutrients and GPP elicited a pulse response following the disturbance at 1 or more of the impacted sites. As the 2-Way rmANOVA is examining each point in time as an individual replicate before or after the disturbance pulse events are lost among the mean measurement. Tailoring sampling events to catch elevated values associated with this pulse type disturbance may result in detecting a significant change following the disturbances in future studies.

Unconventional NG development will likely continue to spread throughout out the major plays in the US as NG has become the forefront of energy production in the United States (U.S.) (Malakoff 2014). This study provides results of one of the first reported BACI analyses of the potential effectiveness of BMPs at mitigating NG development impacts. At this current low level of impact, it appears that the BMPs implemented in the Gulf WMA were effective at preventing changes in nutrients, algal biomass, GPP and sediments for both the headwater streams and main stem of the SFLRR. As development continues across plays, more frequent water sampling, particularly during the first storm event after watershed development is recommended. Additionally, sampling events of biological response variables, such as periphyton biomass, should be planned to account for the pulse nature of this disturbance.

ACKNOWLEDGEMENTS

We thank Lindsey Abel, Phillip Bumpers, Chris Fuller, Jessie Green, Jordan Johnson, Julie Kelso, Lindsey Martindale, Chelsea Miller, Adam Musto, Clay Prater, Jason Ramey, Andrew Sanders, Katie Rose, Loren Stearman, and Richard Walker for their assistance in the field. The NSF BIO REU (0755331 and 1063067) funded several undergraduate researchers, Aaron Jackson, Kara Brick, Jordon Patterson, and Zach Eldrige who assisted with the collection and processing of data. We also thank co-authors Sally Entrekin, Michelle A. Evans-White, Ethan Inlander, and Cory Gallipeau as well as project collaborators Ginny Adams, Reid Adams, Brian Haggard, Steve Filipek, and Lindsey Lewis. Additionally, I would like to thank the Evans-White lab, Hal Halvorson, Ayla Smartt, Allyn Fuel, Kayla Sayre, and Brooke Parker along with fellow graduate students Lindsey Bruckerhoff and Matthew Jennings for providing valuable discussion and advice on the writing of the manuscript. This research was funded by State Wildlife Grants Program (Grant#T-31-R) from the US Fish and Wildlife Service through an

agreement with the Arkansas Game and Fish Commission. Additionally, valuable comments and guidance were provided by my dissertation committee that included Michelle Evans-White, Thad Scott, Dan Magoulick, J.D. Willson, and Gary Huxel.

LITERATURE CITED

Allen, D.T., V.M. Torres, J. Thomas, D.W. Sullivan, M. Harrison, A. Hendler, S.C. Herndon, C.E. Kolb, M.P. Fraser, A.D. Hill, B.K. Lamb, J. Miskimins, R.F. Sawyer, and J.H. Seinfeld. 2013. Measurements of methane emissions at natural gas production sites in the United States. Proceedings of the National Academy of Science. 110: 17768-17773.

Alvarez, R.A., S.W. Pacala, J.J. Winebrake, W.L Chameides, and S.P. Hamburg. 2012. Greater focus needed on methane leakage from natural gas infrastructure. Proceedings of the National Academy of Science. 109: 6435-6440.

Ameel, J. R. Axler, and C. Owen. 1993. Persulfate digestion for determination of total nitrogen and phosphorus in low-nutrient waters. American Environmental Laboratory. 10: 1-11.

APHA (American Public Health Association). 2005. *Standard Methods for the Examination of Water and Wastewater*. (21st edn.). American Public Health Association: Washington D.C. 1368 pp.

Barbour, M.T., J. Gerritsen, B.D. Snyder, and J.B. Stribling. 1999. Rapid Bioassessment Protocols for Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinvertebrates and Fish, Second Edition. EPA 841-B-99-002. U.S. Environmental Protection Agency; Office of Water; Washington, D.C

Bernot, M.J., D.J. Sobota, R.O. Hall, JR., P.J. Mulholland, W.K. Dodds, J.R. Webster, J.L. Tank, L.R. Ashkenas, L.W. Cooper, C.N. Dahm, S.V. Gregory, N.B. Grimm, S.K. Hamilton, S.L. Johnson, W.H. McDowell, J.L. Meyer, B. Peterson, G.C. Poole, H.M. Valett, C. Arango, J.L. Beaulieu, A.J. Burgin, C. Crenshaw, A.M. Helton, L. Johnson, J. Merriam, B.R. Niederlehner, J.M. O'Brien, J.D. Potter, R.W. Sheibley, S.M. Thomas, K. Wilson. 2010. Inter-regional comparison of land-use effects on stream metabolism. Freshwater Biology 55:1874-1890.

Birdsong, B. 2011. Wildlife Management Area Details. Acessed February 2nd, 2012. http://www.agfc.com/hunting/Pages/wmaDetails.

Bott, T.L. 1996. Primary productivity and community respiration. Pages 533-556 *in* Methods in Stream Ecology, F. Richard Hauer and G.A. Lamberti (eds), Academic Press, New York, NY, USA.

Brown, S.S., and D.K. King. 1987. Community metabolism in natural and agriculturally disturbed riffle sections of the Chippewa River, Isabella County, Michigan. Journal of Freshwater Ecology 4: 39-51.

Dodds, W.K., J.R. Jones, and E.B. Welch. 1998. Suggested classification of stream trophic state: distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus. Water Resources. 32: 1455-1462.

EIA (Energy Information Administration). 2013. Annual Energy Outlook 2013: with projections to 2040. U.S. Department of Energy; Washington, D.C.

Entrekin, S., M. Evans-White, B. Johnson, and E. Hagenbuch. 2011. Rapid expansion of natural gas development poses a threat to surface waters. Frontiers in Ecology and the Environment. 9:503-511.

Green, R.H. 1979. *Sampling design and statistical methods for environmental biologists.* John Wiley and Sons, Inc. United States. 257pp.

Justus, B.G., J.C. Petersen, S.R. Femmer, J.V. Davis, and J.E. Wallace. 2010. A comparison of algal, macroinvertebrate, and fish assemblage indices for assessing low-level nutrient enrichment in wadeable Ozark streams. Ecological Indices. 10: 627-638.

Kintisch, E. 2014. A bold baby step on emissions. Science. 344: 1070-1071.

Kelso, J. and S. Entrekin. In prep. Differences in macroinvertebrate community structure across a gradient of flow duration. Master's thesis.

Lake PS. 2000. Disturbance, patchiness, and diversity in streams. Journal of the North American Benthological Society 19*:* 573–592.

Lamberti, G.A., S.V. Gregory, L.R. Ashkenas, R.C. Wildman, and K.M.S. Moore. 1991. Stream ecosystem recovery following a catastrophic debris flow. Canadian Journal of Fisheries and Aquatic Sciences. 48:196-208.

Likens, G.E., F.H. Bormann, N.M. Johnson, D.W. Fisher, and R.S. Pierce. 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. Ecological Monographs. 40: 23-47.

Lohman, K., and J.R. Jones. 1999. Nutrient-sestonic chlorophyll relationships in Northern Ozark streams. Canadian Journal of Fisheries and Aquatic Sciences. 56: 124-130.

Malakoff, D. 2014. The Gas Surge. Science. 344: 1464-1467.

Miller, S.M., S.C. Wofsy, A.M. Michalak, E.A. Kort, A.E. Andrews, S.C. Biraud, E.J. Dlugokencky, J. Eluszkiewicz, M.L. Fischer, G. Janssens-Maenhout, B.R. Miller, J.B. Miller, S.A. Montzka, T. Nehrkorn, and C. Sweeney. 2013. Anthropogenic emissions of methane in the United States. Proceedings of the National Academy of Science. 110: 20018-20022.

Morgan A.M., T.V. Royer, M.B. David, and L.E. Gentry. 2006. Relationships among nutrients, chlorophyll-a, and dissolved oxygen in agricultural streams in Illinois.Journal of Environmental Quality 35(4):1110-1117.

Mulholland, P.J., J.N. Houser, and K.O. Maloney. 2005. Stream diurnal dissolved oxygen profiles as indicators of in-stream metabolism and disturbance effects: Fort Benning asa case study. Ecological Indicators 5: 243-252.

Munn, M., J. Frey, and A. Tesoriero. 2010. The influence of nutrients and physical habitat in regulating algal biomass in agricultural streams. Environmental Management. 45: 603-615.

Olmstead, S.M., L.A. Muehlenbachs, J.S. Shih, Z. Chu, and A.J. Krupnick. 2013. Shale gas development impacts on surface water quality in Pennsylvania. Proceedings of the National Academy of Science. 110: 4962-4967.

Owens, M. 1974. Measurements on non-isolated natural communities in running waters. Pages 111-119 *in* R.A. Vollenweider (editor). A manual on methods for measuring primary production in aquatic environments. Blackwell Scientific Publications, Oxford, UK.

Prud'Homme, B.A. and J.G. Greis. 2002. Best management practices in the South. Southern Forest Resource Assessment. 519-535.

Rahm, B.G. and S.J. Riha. 2014. Evolving shale gas management: Water resource risks, impacts, and lessons learned. Environmental Science: Processes Impacts. 16: 1400-1412.

Sartory, D. P. and J.U. Grobbelaar. 1984. Extraction of chlorophyll a from freshwater phytoplankton for spectrophotometric analysis. Hydrobiologia 114: 177-187.

Shahidehpour, M., Y. Fu, and T. Wiedman. 2005. Impact of natural gas infrastructure on electric power systems. Proceedings of the IEEE. 93:1042-1056.

Steinman, A. D. and G.A. Lamberti. 1996. Biomass and pigments of benthic algae. Pages 295-313 *in* Methods in Stream Ecology, F. Richard Hauer and G.A. Lamberti (eds), Academic Press, New York, NY, USA.

U.S. Fish and Wildlife Service. 2007. Best management practices for Fayetteville Shale natural gas activities. U.S. Fish and Wildlife Service. Conway, Arkansas. 30pp.

U. S. Fish and Wildlife Service. 2009. Arkansas best management practices for natural gas pipeline construction and maintenance activities in the Fayetteville Shale area, upper Little Red River watershed. U. S. Fish and Wildlife Service, Arkansas Ecological Services Field Office, Conway, Arkansas. 42 pp. + appendices.

Wiley, M.J., L.L Osbourne, and R.W. Larimore. 1990. Longitudinal structure of an agricultural prairie river system and its relationship to current stream ecosystem theory. Canadian Journal of Fisheries and Aquatic Sciences 47: 373-384.

Williams, H. F. L., D.L. Havens, K.E. Banks, and D.J. Wachal. 2008. Field-based monitoring of sediment runoff from natural gas well sites in Denton County, Texas, USA. Environmental Geology 55: 1463-1471.

Young, R.G., and A.D. Huryn. 1996. Interannual variation in discharge controls ecosystem metabolism along a grassland river continuum. Canadian Journal of Fisheries and Aquatic Sciences 53: 2199-2211.

Table 1: Landscape scale characteristics for each of the sites for study 1, with sites organized by flow duration and control vs. impact.

Stream	Flow Duration	CI[a]	Catchment Area (km^2)	% For[b]	% Past[c]	% Urb[d]	Pipeline (km/km^2)	Well Pad (#/km^2)
Sis Hollow	SFD	Con	6.67	81	12	0	0.00	0.00
Dry Hollow	SFD	Imp	2.98	99	0	0	0.25	0.00
Low Cedar	LFD	Con	27.17	89	6	1	0.00	0.00
Powerline	LFD	Imp	6.18	92	2	1	0.26	0.17
High Cedar	IFD	Con	18.5	97	0	1	0.00	0.00
Point Remove	IFD	Imp	3.45	99	0	0	0.22	0.00

a: Control or Impact

b: Percent of catchment upstream of study reach forested

c: Percent of catchment upstream of study reach pasture land use

d: Percent of catchment upstream of study reach urban land use

Table 2: Landscape scale characteristics for each of the South Fork Little Red River sites for study 2. Pipeline and well pad densities are based on natural gas activity within the Gulf mountain wildlife management area only.

Site	CI[a]	Catchment Area (km^2)	% For[b]	% Past[c]	% Urb[d]	Pipeline (km/km^2)	Well Pad ($\#/km^2$)
1	Con	122.72	90	8	2	0.000	0.000
2	Imp	140.03	91	8	2	0.005	0.007
3	Imp	168.77	90	7	2	0.005	0.006
4	Imp	192.67	91	7	1	0.008	0.010

[a]CI= Control or Impact; [b]For= forested; [c]Past= Pasture; [d]Urb= Urban

Table 3: Mean (±1 SE) for each response variable measured before disturbance, after disturbance, and overall or throughout all sample periods, for each of the 6 headwater streams in the Gulf Mountains Wild Life Management Area

Site		TN[a] (μg/l)	TP[b] (μg/l)	Chl *a*[c] (μg/cm^2)	GPP[d] gC m^{-2} d^{-1}
Sis Hollow	Before	121.42 (57.98)	4.62 (2.63)	1.11 (0.37)	0.32 (0.21)
	After	19.46 (18.49)	4.16 (4.06)	0.71 (0.37)	0.36 (0.28)
	Overall	87.44 (42.78)	4.47 (1.97)	0.94 (0.26)	0.34 (0.15)
Dry Hollow	Before	56.72 (47.93)	4.45 (2.21)	0.21 (0.08)	0.06 (0.03)
	After	5.84 (0.13)	26.86 (26.25)	0.14 (0.10)	0.07 (0.03)
	Overall	42.18 (34.38)	10.85 (7.23)	0.18 (0.06)	0.06 (0.03)
High Cedar	Before	78.26 (42.50)	6.74 (4.61)	0.69 (0.37)	0.09 (0.05)
	After	6.53 (5.27)	9.82 (9.64)	0.27 (0.12)	1.40 (1.38)
	Overall	57.76 (32.20)	7.62 (3.86)	0.53 (0.24)	0.46 (0.39)
Point Remove	Before	50.41 (45.56)	5.32 (2.47)	0.51 (0.26)	0.04 (0.03)
	After	49.24 (45.86)	15.24 (14.71)	0.16 (0.08)	0.01 (0.01)
	Overall	50.08 (29.85)	8.15 (4.00)	0.38 (0.15)	0.03 (0.02)
Low Cedar	Before	62.82 (52.74)	8.66 (4.33)	1.04 (0.33)	0.24 (0.12)
	After	2.81 (2.45)	6.25 (6.09)	0.56 (0.22)	0.42 (0.19)
	Overall	45.67 (38.04)	7.97 (3.30)	0.83 (0.24)	0.34 (0.10)
Powerline	Before	79.29 (40.45)	6.82 (3.24)	1.84 (0.55)	0.04 (0.03)
	After	19.6 (18.49)	20.50 (20.13)	0.59 (0.21)	0.06 (0.06)
	Overall	88.34 (37.11)	10.73 (5.54)	1.37 (0.41)	0.04 (0.02)

a: Total nitrogen

b: Total phosphorus

c: Chlorophyll *a*

d: Gross primary production

Table 4: two-way repeated measures analysis of variance output for each of the response variables for the pairings of control and impacted sites at the three levels of flow duration among headwater streams within the Gulf Mountain Wildlife Management Area.

		TN[a]		TP[b]		CHL *a*[c]		GPP[d]	
Pairing	Factor	F	P	F	P	F	P	F	P
SFD[e]	BA	0.15	0.71	0.24	0.63	0.57	0.59	0.09	0.81
	CI	0.54	0.48	0.40	0.54	7.09	0.23	3.03	0.33
	BAxCI	0.48	0.50	0.23	0.64	0.01	0.96	0.02	0.92
IFD[f]	BA	0.01	0.93	0.25	0.63	2.49	0.14	0.61	0.46
	CI	0.04	0.84	0.11	0.75	0.48	0.50	0.86	0.38
	BAxCI	1.34	0.27	0.01	0.92	0.09	0.77	0.41	0.54
LFD[g]	BA	0.07	0.79	0.01	0.98	3.48	0.09	0.48	0.51
	CI	2.58	0.14	0.21	0.65	0.77	0.40	7.50	0.03
	BAxCI	0.01	0.99	0.04	0.85	0.48	0.50	0.14	0.72

a: TN= Total nitrogen (µg/l); b: TP= Total phosphorus (µg/l); c: Chl *a*= Chlorophyll *a* (µg/cm^2)

d: GPP= Gross primary production (gC m^{-2} d^{-1})

e: SFD= short flow duration sites, Sis hollow (control) and Dry hollow (impacted)

f: IFD= Intermediate flow duration sites, High cedar (control) and Point remove (impacted)

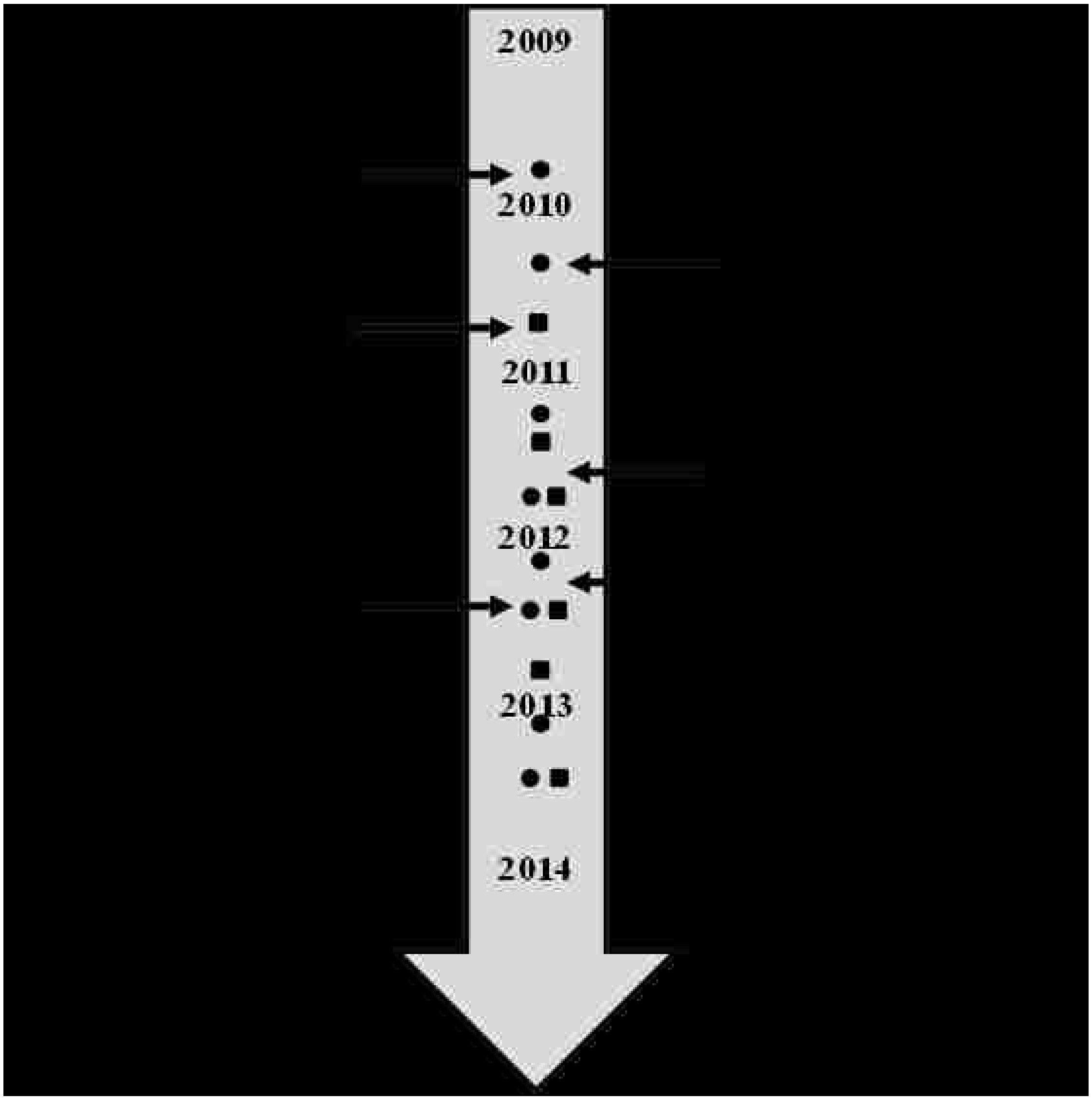
g: LFD= Long flow duration sites, Low cedar (control) and Powerline (impacted)

Table 5: Two-way repeated measures analysis of variance output for each of the response variables for the pairings of control (site 1) and impacted (sites 2-4) sites along the South Fork Little Red River within the Gulf Mountain Wildlife Management Area.

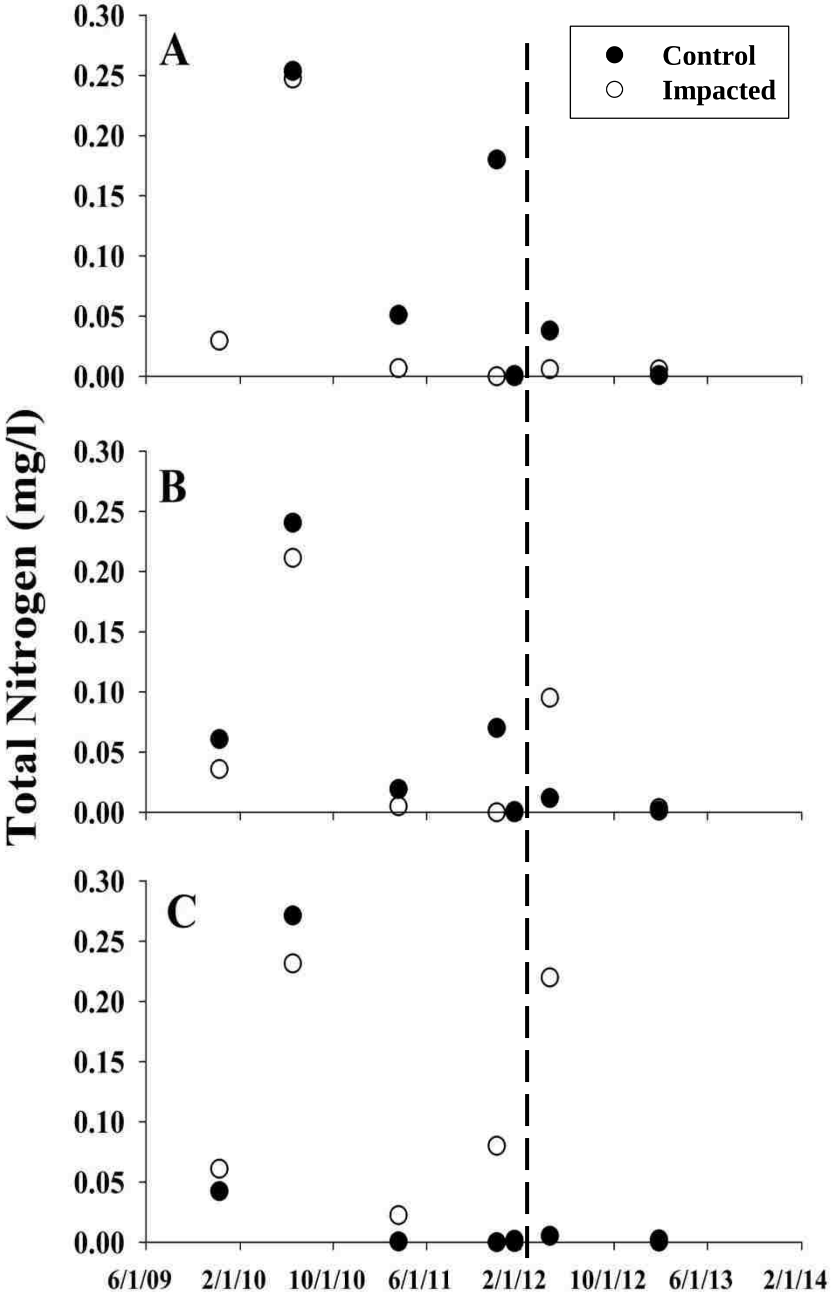
		NO_3^{-a}		SRP[b]		Inorganic Sediments[c]		CHL *a*[d]	
Pairing	Factor	F	p	F	p	F	p	F	p
1V2	BA	41.31	<0.01	5.06	0.03	0.25	0.63	0.20	0.67
	CI	0.01	0.93	0.63	0.43	2.12	0.18	0.33	0.59
	BAxCI	0.01	0.91	0.15	0.70	0.01	0.98	0.05	0.84
1V3	BA	41.61	<0.01	8.17	<0.01	0.70	0.43	0.18	0.68
	CI	0.11	0.75	0.05	0.83	3.08	0.12	1.45	0.27
	BAxCI	0.03	0.87	0.99	0.33	2.38	0.16	0.03	0.87
1V4	BA	35.87	<0.01	6.81	0.01	0.05	0.83	0.07	0.79
	CI	0.06	0.80	0.17	0.69	4.31	0.07	3.99	0.09
	BAxCI	0.06	0.80	0.57	0.46	1.08	0.33	0.22	0.65

a: Nitrate (µg/l); b: Soluble Reactive Phosphorus (µg/l); c: Fine inorganic sediments (g/m^2); d: Chlorophyll *a* ($µg/cm^2$)

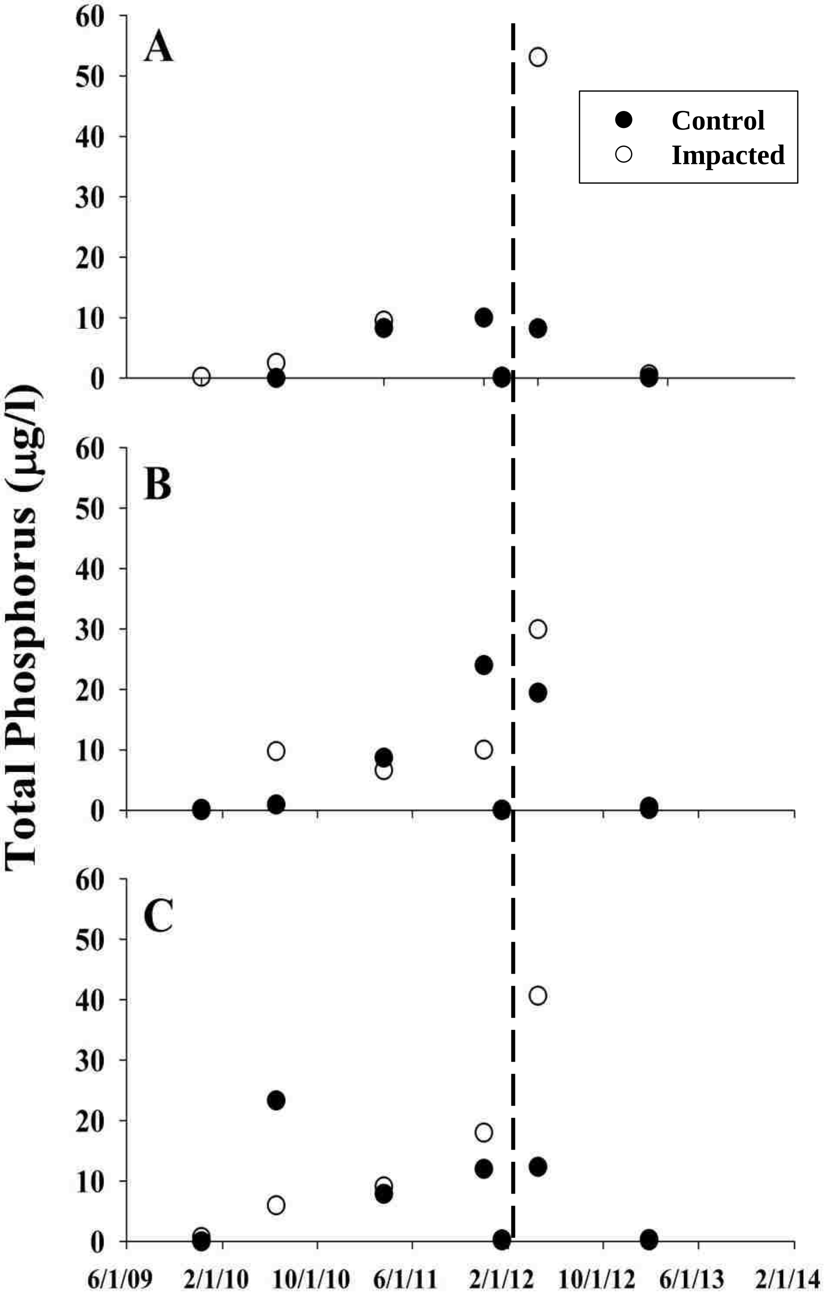
Figure 1: Map of Scott Henderson Gulf Mountain Wildlife Management Area (in gray). Circular symbols represent headwater sites from study 1. Square symbols represent the study sites on the South Fork Little Red River from study 2. Open symbols being the control sites and filled symbols the impacted sites.



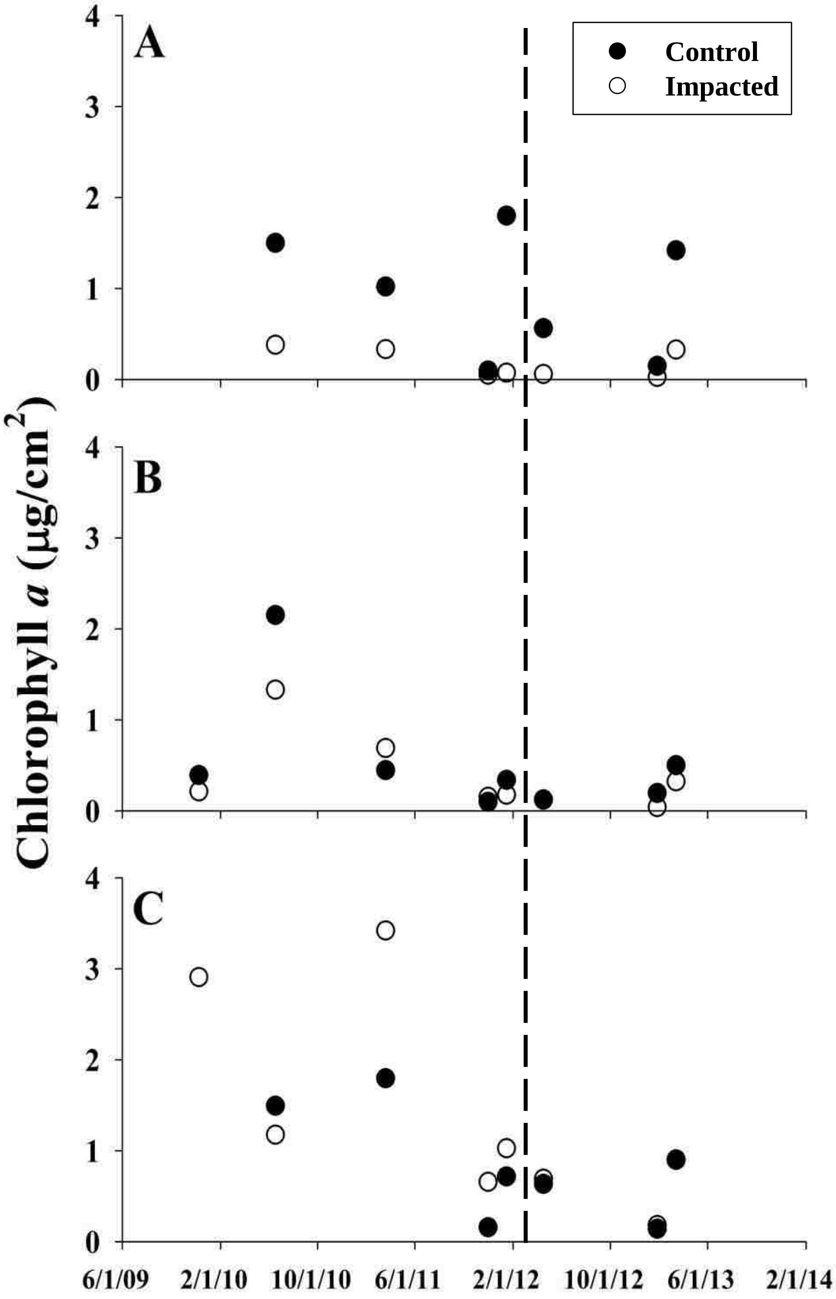
[redacted]


A
B
C
Control
Impacted
Total Nitrogen (mg/l)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
6/1/09
2/1/10
10/1/10
6/1/11
2/1/12
10/1/12
6/1/13
2/1/14

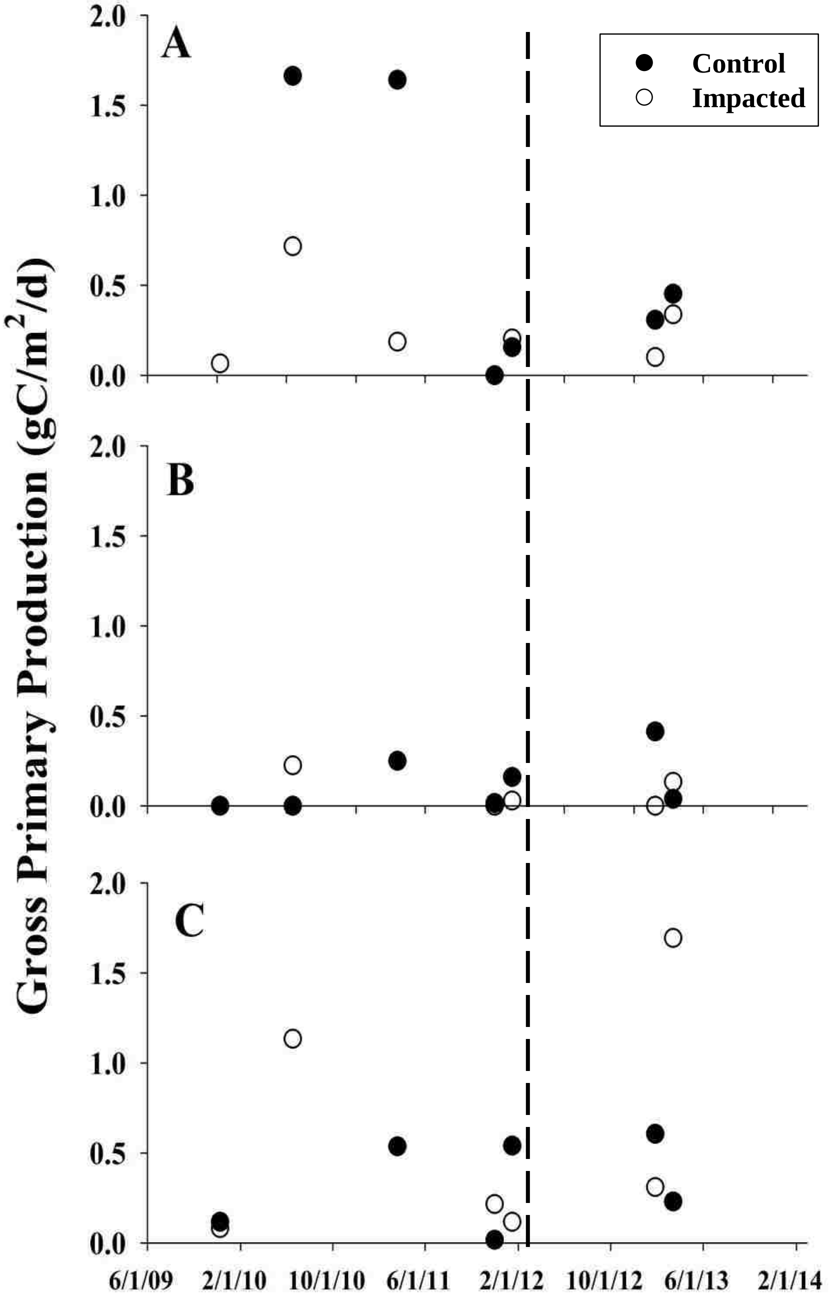
[redacted]


Total Phosphorus (µg/l)
A
B
C
Control
Impacted
0
10
20
30
40
50
60
6/1/09
2/1/10
10/1/10
6/1/11
2/1/12
10/1/12
6/1/13
2/1/14

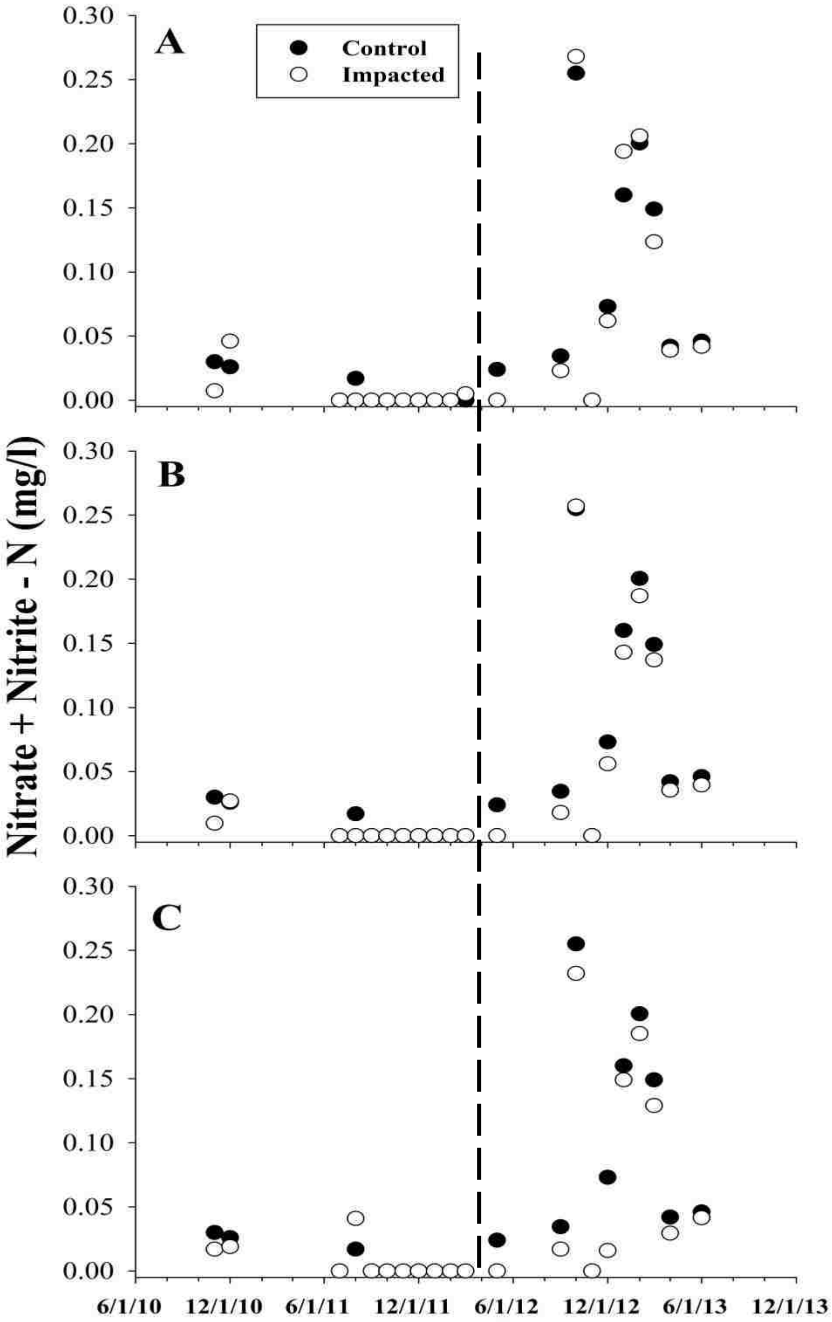
[redacted]


A
B
C
Control
Impacted
Chlorophyll *a* (µg/cm^2)
0
1
2
3
4
6/1/09
2/1/10
10/1/10
6/1/11
2/1/12
10/1/12
6/1/13
2/1/14

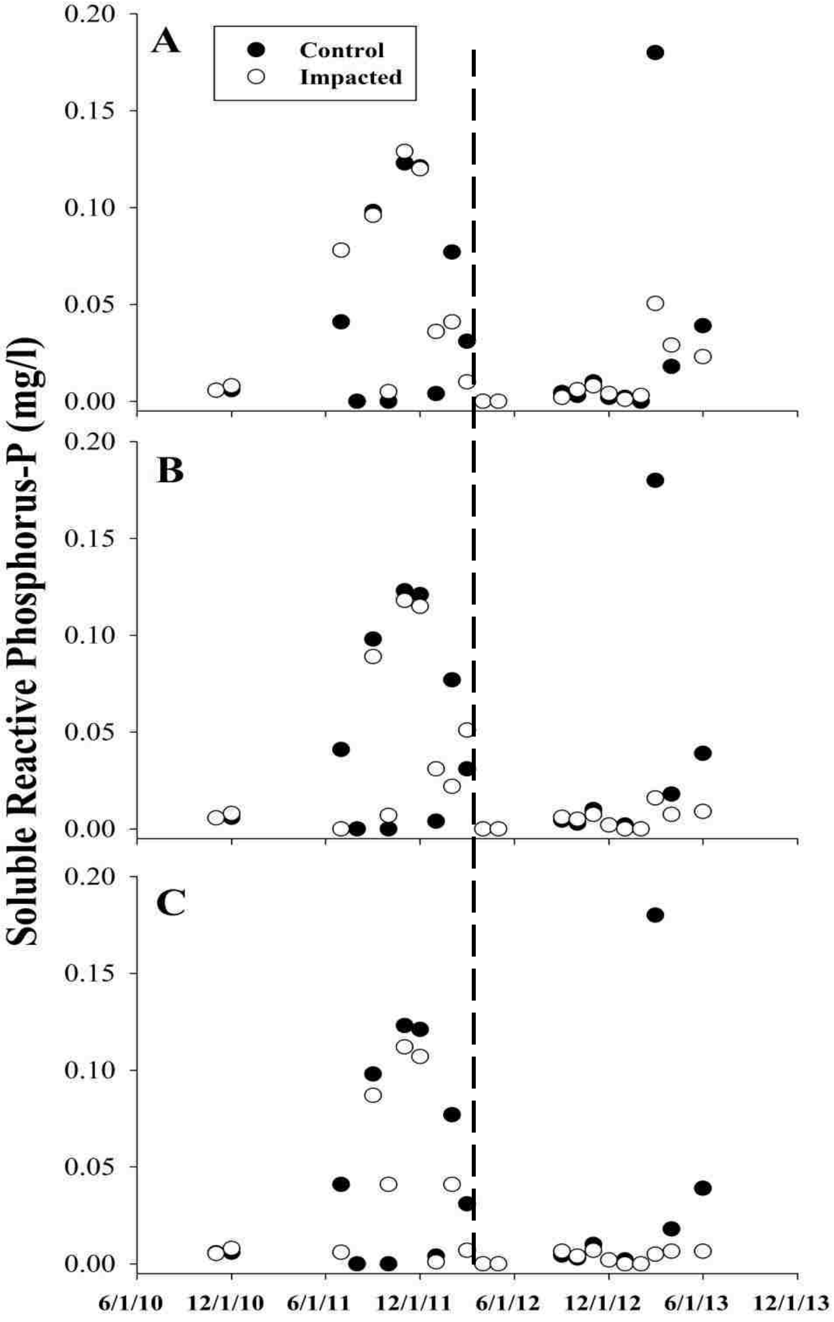
[redacted]


A
B
C
Control
Impacted
Gross Primary Production (gC/m²/d)
0.0
0.5
1.0
1.5
2.0
6/1/09
2/1/10
10/1/10
6/1/11
2/1/12
10/1/12
6/1/13
2/1/14

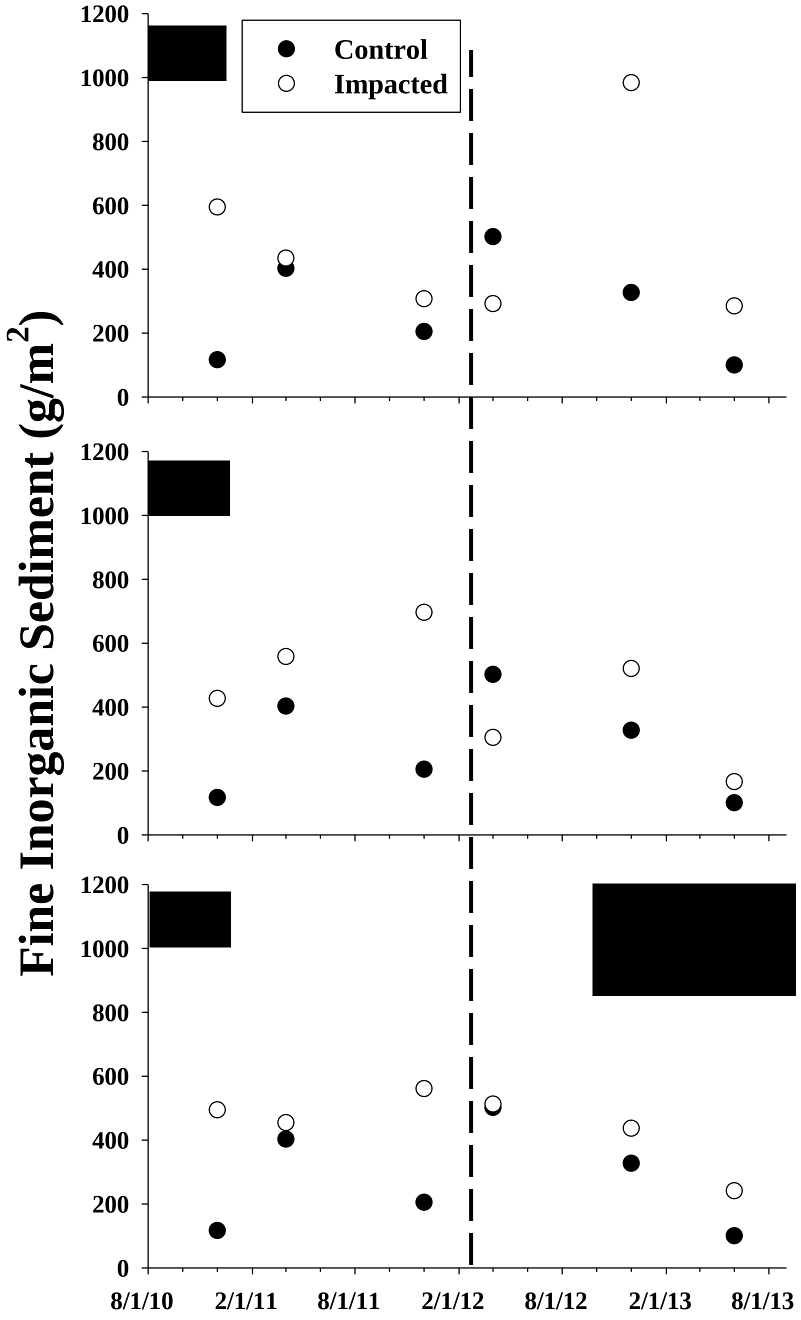
[redacted]


A
B
C
Control
Impacted
Nitrate + Nitrite - N (mg/l)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
6/1/10
12/1/10
6/1/11
12/1/11
6/1/12
12/1/12
6/1/13
12/1/13

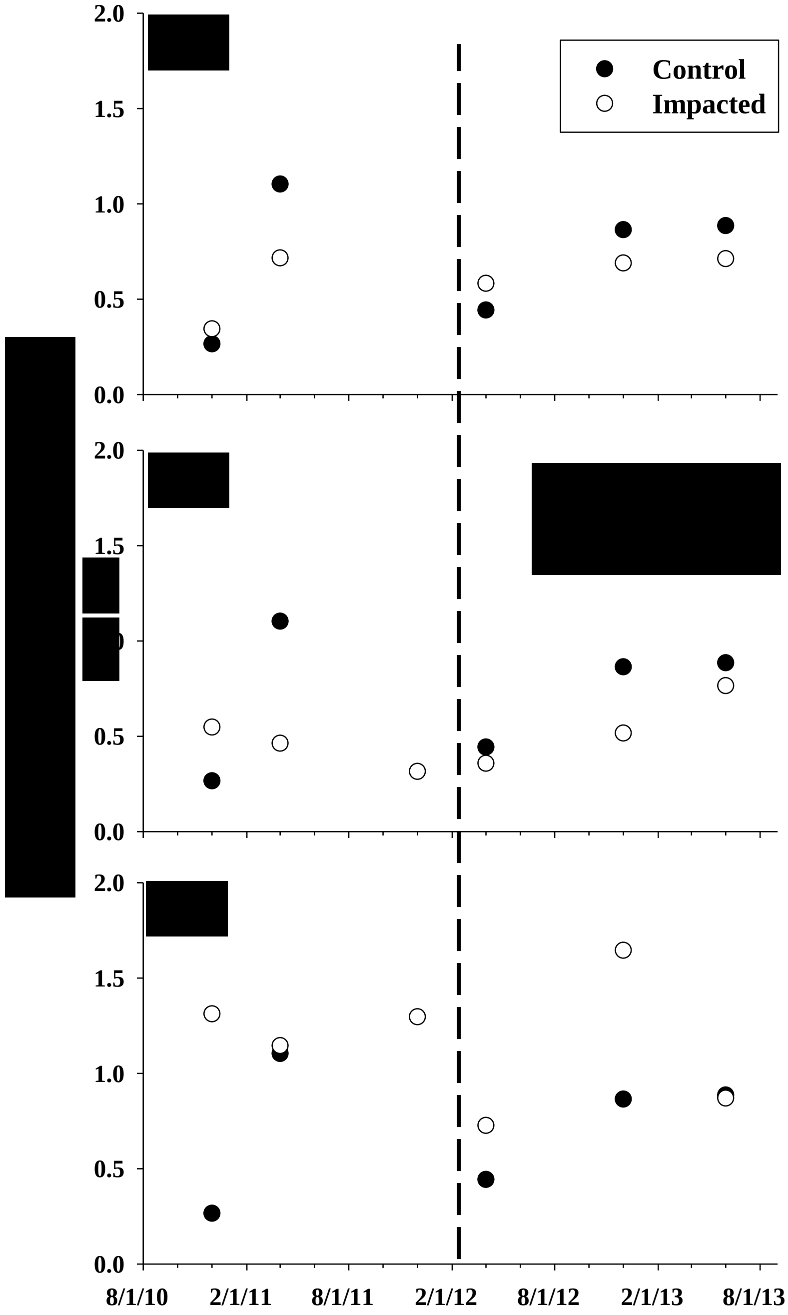
[redacted]


Soluble Reactive Phosphorus-P (mg/l)
A
B
C
Control
Impacted
0.20
0.15
0.10
0.05
0.00
6/1/10
12/1/10
6/1/11
12/1/11
6/1/12
12/1/12
6/1/13
12/1/13

[redacted]


[redacted]
[redacted]
[redacted]
[redacted]
Control
Impacted
Fine Inorganic Sediment (g/m^2)
1200
1000
800
600
400
200
0
8/1/10
2/1/11
8/1/11
2/1/12
8/1/12
2/1/13
8/1/13

[redacted]


[redacted]
2.0
1.5
1.0
0.5
0.0
Control
Impacted
[redacted]
[redacted]
2.0
1.5
[redacted]
0.5
0.0
[redacted]
[redacted]
2.0
1.5
1.0
0.5
0.0
8/1/10
2/1/11
8/1/11
2/1/12
8/1/12
2/1/13
8/1/13

[redacted]

Chapter IV:

Land-Use Effects on Recovery of Algal Biomass and Stream Metabolism Following Flood Disturbances in Ozark Streams.

Bradley J. Austin

Department of Biological Sciences, University of Arkansas
Fayetteville, AR 72701 USA

ABSTRACT

Watershed land use can regulate the delivery of water, nutrients, and organic matter (OM) to stream ecosystems and may alter the recovery of stream ecosystem processes after hydrologic disturbance events. To examine controls of land use on ecosystem processes, we measured water chemistry, benthic algae (chlorophyll *a*) and metabolism in agricultural (n=3), urban (n=4), and forested (n=4) Ozark streams prior to and after two flood events in autumn 2009 and spring 2010. Soluble reactive phosphorus [SRP (µg/L)] and nitrate-nitrogen [NO_3-N (mg/L)] concentrations were greater in agricultural (mean±1SE; SRP=38±20; NO_3-N=2.3±0.2) and urban (SRP=18+8; NO_3-N=0.7±0.1) than in forested streams (SRP=8±5; NO_3-N=0.3±0.04). Periphyton biomass was lower (F=18.4 $p<0.001$) and took longer to recover in forested (mean±1SE=25±11) compared to agricultural and urban streams (mean±1SE=12±3; F=4.7 p=0.026; Figure 1). In addition, periphyton biomass in the spring was greater (F=7.6 p=0.014) and took longer to recover than periphyton in autumn (F=10.8 p=0.005). Further, gross primary production (F=4.1 p=0.038), ecosystem respiration (F=4.6 p=0.030), and net ecosystem metabolism (F=4.25 p=0.036) took almost twice as long to recover in agricultural and urban compared to forested streams. These results indicate that human land use change alters the recovery of community structure and ecosystem function to disturbance. Given that climate change is expected to alter the magnitude and frequency of flood events in lotic ecosystems, our study suggests that stream community and ecosystem responses to those hydrological changes will likely depend upon watershed land use within biomes.

Key words: periphyton, primary production, respiration, urban, agriculture

INTRODUCTION

Disturbance is a major determining factor structuring communities and ecosystems (Connell 1978; Huston 1979). Disturbances alter the ecology of ecosystems (White and Pickett 1985) and are further defined by their abiotic properties, such as their intensity relative to background conditions, their temporal duration, and their spatial extent (Lake 2000). Floods are one of the main physical disturbances structuring stream ecosystems and their effects on stream populations and communities have been studied extensively (Lake 2000; Stanley et al. 2010). However, few studies have examined the effect of floods on ecosystem processes such as stream metabolism, nutrient spiraling and decomposition (Stanley et al. 2010). Human-driven climate change and anthropogenic modifications of watersheds and water channels can alter the timing, duration, and frequencies of flood events and studies examining ecosystem responses to flood events are needed to provide the data necessary for forecasting the consequences of human-driven ecosystem change.

Stream metabolism, which represents the balance between ecosystem respiration (ER) and gross primary production (GPP), is a key ecosystem function linked to many other important ecosystem processes such as nutrient uptake and spiraling (Meyer et al. 2005). Recent technological advances in dissolved oxygen (DO) sensors have made possible long-term measurements of DO dynamics in streams, allowing for examination of flood disturbance effects on metabolism (Uehlinger 2000; Roberts et al. 2007). Most studies have found that floods cause a greater decline in GPP than in ER, resulting in a decrease in P:R (Uehlinger 2000; Uehlinger et al. 2003, Roberts et al. 2007). Recovery patterns of GPP and ER depend upon seasonal changes in environmental conditions that affect photosynthesis and metabolic rates, such as light availability and temperature (Uehlinger 2000, Roberts et al. 2007). For example, Roberts et al.

(2007) found that GPP responded negatively to a spring flood event, but positively to an autumn flood event. The positive response of GPP to an autumn flood may have been due to autumn-shed leaf litter covering the stream and blocking light availability prior to the event. Studies exploring stream metabolism responses to floods must therefore consider seasonal variation in environmental conditions and resources required for photosynthesis and respiration.

Characteristics of watersheds and riparian zones may also affect environmental conditions and resources available for photosynthesis and respiration (Bernot et al. 2010), thereby altering the response of stream metabolism to flood disturbances. Agricultural streams usually have shorter riparian vegetation than forested streams, allowing more solar radiation to reach the stream (Wiley et al. 1990). In addition, agricultural and urban streams usually receive higher nutrient inputs compared to streams draining less human-impacted watersheds, resulting in greater GPP (Wiley et al. 1990; Herlihy et al. 1998; Paul & Meyer 2001; Bernot et al. 2010). Higher light and nutrient conditions of agricultural and urban streams might also influence recovery of metabolic processes following flood events. Recovery of autotrophic processes from disturbance is the time required to return to a pre-disturbance state (Peterson 1996; Uehlinger 2000; Mulholland et al. 2001) or the time to reach a new stable state (Figure 2).

The main objective of this study was to investigate the effects of land use on the recovery of benthic algal biomass and whole stream metabolism following flood disturbances in the spring and autumn. We hypothesized that greater nutrient concentrations in agricultural and urban streams would shorten recovery times of benthic algal biomass and stream metabolism in our study system. We also expected that urban streams will take longer than agricultural streams to recover to pre-flood biomass levels because they would have higher flood intensity due to the increased amount of impervious surfaces in the watershed (Hollis 1975).

METHODS

We measured algal biomass and stream metabolism in 1st to 3rd order forested (N=4), agricultural (N=3), and urban streams (N=4) in the Ozark region of Northwest Arkansas (Figure. 1). Streams were sampled prior to and after at least one flood event in autumn 2009 and in spring 2010. Land-use composition was estimated for HUC 12 watersheds using 2006 land use land cover data (Table 1). Recovery in each variable was defined as the return interval to pre-flood conditions (Uehlinger 2000) or as the point where each response variable stabilized after a flood event. A repeated-measures analysis of variance (rmANOVA) was used to test for individual and interactive effects of season and land use on recovery times.

Water level and discharge were monitored using gaging station data for 6 of the 11 streams. Mounted water level loggers (HOBO®; Onset, Bourne, MA, USA) were used to monitor water level in the remaining study streams. In addition, washable finger paint underneath a downstream bridge was used to keep track of maximum water level in between sampling events in case of technical difficulties or loss of pressure transducers during flood events. Discharge measured with a Marsh-McBirney flow meter (Hach Company, Loveland CO) was measured along with stream depth near the water level logger and at the bridge at least every other week until a relationship between discharge and depth could be obtained.

Cobble benthic algal samples were collected before and weekly after flood events from three riffle and pool complexes within each stream reach that were at least 20 m apart. Cobbles were placed in an iced cooler for transport and then frozen (-4°C) until analysis. Chlorophyll *a* (chl *a*) pigment was extracted by submerging cobbles in ethanol (78°C, 5 min) followed by 24 h in a dark refrigerator (4°C, 24 h) before spectrophotometric measurement (Sartory and

Grobellaar 1984). Absorbances were measured on a Gensys spectrophotometer using standard chl *a* methods (APHA 2005).

Gross primary production and ecosystem respiration were estimated using an open-system, single-station diel approach (Odum 1956; Bott 2006). Luminescent dissolved oxygen (DO), temperature, turbidity (nephalometric turbidity units; NTU) and conductivity were continuously recorded at 15 minute intervals using Hydrolab multi-parameter sondes (DSX5; Hach, Loveland,CO, USA). Sonde measurements over time were corrected for drift in DO measurements based on Winkler DO titrations for 5 water samples during deployment and pick up. Winkler chemistry (APHA 2005) was completed in the field using a digital burette to ensure that calibration samples varied less than ± 0.05 mg/L. Daily gross primary production (GPP) and ecosystem respiration (ER) were calculated using the difference between consecutive DO concentration readings (every 15 minutes) using the following equation,

$$\Delta DO = GPP - ER + E$$

where ΔDO is the change in dissolved oxygen concentration (g O_2 m^{-3}), ER is volumetric ecosystem respiration (g O_2 m^{-3}), and E is the reaeration coefficient or the net exchange of O_2 with the atmosphere (g O_2 m^{-3}) between consecutive measurements. Daytime ER was estimated by interpolating average night-time ER. Interval GPP was the difference between the net metabolism flux and the interpolated ER. Reaeration was estimated using night-time regression (Wiley et al. 1990).

Stream water samples were collected and filtered through a glass fiber filter (Pall 1µm) 4-5 times during the study period and at least 2 of the samples were taken during separate storm events. Nitrate and nitrite nitrogen (NO_3+NO_2-N) were measured using the cadmium reduction method on a Lachat Rapid Flow Autoanalyzer (Lachat Instruments, Hach Company, Loveland, Colorado). Soluble reactive P (SRP) was measured using the ascorbic acid method and ammonium was measured using the phenol-hypochlorate method (APHA 2005).

RESULTS

Water quality differed with land use (Figure 3). Forested streams had lower NO_3+NO_2-N, NH_4^+, and SRP than agricultural and urban streams, which did not differ. Flood events occurred in September and October of 2009 and May 2010. Unfortunately, a subset of water level loggers (2 out of 5 sites) was lost due to a flood event as well as human interference. In addition, many of our USGS gaged sites did not log data for the storm occurring in October. Therefore, we are reporting the average proportion of algal chl *a* removed as a measure of storm intensity. The mean proportion of algal chl *a* removed ranged from 0.48 to 0.99 (mean $\pm$ 1SE = 0.73 $\pm$ 0.04) across all sites and did not differ based on land use ($p = 0.273$) or with land use by time ($p = 0.198$). However, the mean ($\pm$ 1SE) proportion of algal chl *a* removed was higher ($p = 0.041$) in the spring (0.78 $\pm$ 0.04) than in the autumn (0.67 $\pm$ 0.05).

Land use and season did not interact to affect benthic algal chl *a* levels in streams ($p=0.84$). However, chl *a* levels were higher in the spring than in autumn ($F=7.58$; $p=0.014$; Figure 4A). In addition, forested streams had lower chl *a* levels than did agricultural and urban streams ($p<0.001$; Figure 4B), which did not differ ($p > 0.05$). Benthic algal chl *a* recovery times were dependent on season ($F = 10.84$; $p = 0.005$) and land use ($F = 4.71$; $p = 0.026$), but did not depend upon the interaction of these two factors ($p = 0.97$). Recovery times were longer in the spring than in the autumn and were shorter in urban streams than in forested streams (Figure 4C and D). However, recovery times in agricultural streams did not differ statistically from forested or urban streams.

Gross primary production was primarily explained by land use (F=4.13, p=0.037) with agricultural sites having greater rates than forested sites (p < 0.05) (Figure 5A). Urban stream GPP estimates did not differ from rates measured in the other land uses (p > 0.05). Season (p = 0.475) and the interaction between season and land use (p = 0.700) did not explain a significant amount of variation in GPP. Season and land use did not interact to explain variation in GPP recovery time (p = 0.425). It took less time for GPP to recover after a flood in the autumn (mean ± 1SE = 12 ± 2 days) relative to the spring (mean ± 1SE = 16 ± 1 days; F=5.76, p = 0.032). In addition, GPP recovery time depended on land use type (F = 4.13, p = 0.038) with GPP taking approximately 6 days longer to recover in forested streams than in agricultural streams (Figure 6A). Urban sites tended to take less time to recover than forested streams, but recovery times did not differ statistically (p > 0.05).

Ecosystem respiration did not differ across land use (p = 0.375) or between seasons (p = 0.118) and these two factors did not interact (p = 0.418) to explain variation (Figure 5B). Recovery times for ER were dependent upon land use type (F=4.56, p = 0.030) with forested streams taking approximately 12 days longer to recover after flood events than did agricultural streams (Figure 6B). Urban stream recovery times did not differ from forested or agricultural recovery times (p > 0.05).

Net ecosystem production was negative in each stream type and did not differ across land use (p = 0.344), between seasons (p = 0.124), or across season and land-use (p = 0.697; Figure 5C). Recovery times did differ based on land use (F=4.25, p = 0.036), but season (p=0.873) and the interaction between season and land use (p = 0.340) were not statistically significant. Similar to patterns observed in GPP and CR, agricultural streams recovered more quickly, approximately 12 days faster, than did forested streams and urban stream recovery times did not differ from the other land use types ($p > 0.05$).

DISCUSSION

Pre-flood disturbance estimates of algal biomass were variable between seasons with higher values measured in the spring. These higher values in the spring were likely due to higher light availability from the pre-leaf out conditions of the riparian (Sumner and Fisher 1979; Lohman et al. 1992; and Rosemond et al. 2000). In addition to seasonal variability, algal biomass varied across land use types. While light likely played a significant role in seasonal differences of algal biomass, variability in algal biomass across land-use types was likely drive by increased light and nutrients in the urban and agricultural influenced streams (Allan 2004).

Seasonal effects of light on algal biomass did not result in greater GPP in the spring compared to autumn, but land use effects on GPP mirrored patterns in chl *a*. Many studies have found greater GPP in agricultural versus reference streams in the same region (Wiley et al. 1990; McTammany et al. 2007; Bernot et al. 2010) and this same pattern occurred in the present study. I was expecting to find greater GPP in the urban compared to the forested sites; though GPP was elevated across the urban streams in comparison to the forested, this relationship was not statistically significant. However, similar rates of GPP in urban versus reference sites is not uncommon (Izagirra et al. 2008). Within Basque streams in Spain, GPP was slightly elevated in reference streams compared to streams polluted by urban and industrial waste water, likely due to increased turbidity from organic wastes which reduced light availability (Izagirra et al. 2008). While light availability to the stream surface was likely greater in our urban streams, higher levels of turbidity, from increased suspended sediments (Allan et al. 1997), may have reduced the effect of light availability on GPP.

Ecosystem respiration and NEP were similar across land use types as seen in McTammany et al. (2007). Measured ER and NEP in this study across reference forested streams (0.61 – 2.38 $gC/m^2/d$ ER and -2.01 – -0.54 $gC/m^2/d$ NEP) were similar to reference streams near Atlanta, GA (1.57 – 2.28 $gC/m^2/d$ ER and -2.15 – -1.21 $gC/m^2/d$ NEP; Meyer et al. 2005) and fell within the lower end of the ranges measured by Bernot et al. (0.12 – 6.93 $gC/m^2/d$ ER and -5.88 – 0.00 $gC/m^2/d$ NEP; 2010). Ecosystem respiration and NEP across the urban streams (0.04 – 1.93 $gC/m^2/d$ ER and -1.03 – -0.01 $gC/m^2/d$ NEP) were again most similar to values measured from urban streams in Atlanta, GA (0.39 – 2.62 $gC/m^2/d$ ER and -2.39 – -0.12 $gC/m^2/d$ NEP; Meyer et al. 2005), but were much lower than polluted Basque streams in Spain (6.41 $gC/m^2/d$ ER and -4.84 $gC/m^2/d$ NEP; Izagirre et al. 2008). Across the agricultural streams ER and NEP (0.65 – 2.00 $gC/m^2/d$ ER and -1.48 – -0.05 $gC/m^2/d$ NEP) were within the lower range of values measured in agricultural streams across a larger regional scale (0.27 – 4.71 $gC/m^2/d$ ER and -3.78 – 1.44 $gC/m^2/d$ NEP; Bernot et al. 2010). Comparable ER rates across land-use types may be an indication of similar organic matter (OM) availability between sites, though variability in the form of OM (e.g., allochthonous- vs. autochthonous-derived detritus) could play an important role in how the streams respond to flood disturbance.

I expected to find that the pasture agricultural streams in the present study may have lower GPP compared to those measured in row-crop streams due to lower nutrient concentrations in my study streams. While NO_3^- and SRP were elevated at our pasture agricultural land sites (mean ± SE; 2.374 ± 0.22 and 0.019 ± 0.01 mg/l respectively); these nutrient levels tended to be less than what might be found in row crop systems (8.40 ± 0.542 mg/l NO_3^- and 0.056 ± 0.024

mg/l SRP; Figueroa-Nieves et al. 2007). Interestingly, our agricultural streams contained similar algal biomass (9.12 ± 3.724, range 7.51 – 11.34 μg/cm^2) to row crop agricultural streams in the Ozarks (11.01 ± 1.49; 4.68 – 21.67 μg/cm^2; Lohman et al. 1992) as well as row crop agricultural sites in central Illinois (>5 – 13.0 μg/cm^2; Figueroa-Nieves et al. 2007). However, GPP measured across pasture sites in this study (0.80 ± 0.19; 0.49 – 1.18 gC/m^2/d) was lower than that measured for row crop agricultural sites in central Illinois (3.61 ± 0.67; 0.03 - >15gC/m^2/d; Wiley et al. 1990), as well as agricultural sites measured as a part of the Lotic Intersite Nitrogen eXperiment II (LINX II) project (0.03 – 4.63 gC/m^2/d; Bernot et al. 2010). While algal biomass has been found to be positively associated with GPP across multiple biomes (Bernot et al. 2010), biomass does not have to equal production as was the case when comparing pasture and row crop agriculture. Both forms of agricultural land use supported similar levels of benthic algal biomass; however, row crop systems supported higher GPP, likely due to increased nutrients. In addition to elevated GPP in row crop systems, ER has been reported as high as 53.10 gC/m^2/d within row-crop agricultural influenced streams in central Illinois (Wiley et al. 1990), indicating an increased biological oxygen demand along with the increased nutrient availability.

Physical attributes of disturbance, such as maximum stage or bank-full discharge, allows for the impact of the disturbance on the biota of one stream to be compared to another and separates the response of the biota from the disturbance (Poff 1992; Lake 2000). While measuring maximum stream stage was the intended method for determining flood intensity across land use types and seasons, loss of equipment resulted in a need for a secondary metric. Instead, flood intensity was determined based off of percent removal of algal biomass, because of this algal biomass resistance, or percent remaining, was only viewed as a metric of intensity and not a response to the disturbance. Flooding intensity as determined by percent removal of algal biomass was similar across land-use types within each season sampled, but was greater in spring than autumn. This could be due to variability in the flooding intensity or a product of the periphyton community composition. Lower-biomass communities comprised of low profile adnate taxa are less susceptible to scour (Wellnitz and Rader 2003); whereas thicker communities have poor basal structural integrity due to decreased resources reaching basal cells (Biggs and Close 1989; Uehlinger 1991; Biggs and Thomsen 1995), increasing the susceptibility to scour. Higher biomass estimates prior to the flood disturbance in the spring time suggest that the greater percent removal might have been due to a higher susceptibility to scour. This higher level of biomass removal during the spring flood event likely drove faster recovery in autumn than spring.

Variable recovery of algal biomass between seasons was likely driven by light availability and initial biomass. Algal biomass recovered almost 2 times faster in autumn than in spring (10.7d vs. 17.7d respectively), indicating strong seasonal control over recovery of algal communities to flood disturbance. In Arizona at Sycamore creek, post-flood recovery of algal biomass was also variable across seasons, with recovery in summer and fall taking 21d and 20d respectively, and up to 78d in the winter (Grimm and Fisher 1989). As noted earlier, greater light availability to streams prior to leaf out in the spring promoted greater pre-disturbance algal biomass across all streams. Additionally, systems with lower initial biomass should take less time to recover than systems with higher initial biomass (Lohman et al. 1992). Greater removal of algal biomass in the spring coupled with decreased light availability due to leaf out, slowed the recovery process for algal biomass in the spring. Slower recovery of benthic algal communities in the spring can result in reduced nutrient retention efficiency of streams and if flooding becomes more frequent due to GCC streams will remain in this reduced nutrient retention state for longer periods.

Unlike seasonal recovery, light and nutrient availability likely played a greater role in algal biomass recovery between forested reference sites and agricultural and urban impacted sites; however, differences in initial algal biomass likely drove variability between agricultural and urban recovery time. Comparing across land-uses algal biomass at forested sites required the most time to recover regardless of season (~17d), despite having lower pre-flood biomass, whereas, urban streams recovered the quickest (~10d). These rates of recovery are similar to recovery rates previously documented of a few weeks (Peterson and Stevenson 1992; Fuller et al. 2008) to longer than a month (Lohman et al. 1992). Cross-biome comparisons have found that agricultural and urban streams tend to have greater GPP (Bernot et al.2010) and areal N uptake rates (Mulholland et al. 2008), but reduced efficiency of nutrient uptake compared to reference streams in similar regions (Mulholland et al. 2008). The eutrophic state of Ozark agricultural and urban study streams promoted faster recovery times; however this faster rate of recovery may not equate to greater efficiency of nutrient removal and, thus, these streams likely allow movement of considerable nutrient loads to downstream ecosystems. Gross primary production has been found to be closely associated with stream algal biomass in studies of recovery to flooding (Uehlinger and Naegeli 1998; Roberts et al. 2007). Unlike algal biomass, there were no seasonal effects on the recovery of GPP, ER, or NEP. However, again as hypothesized, forested streams required the most time for recovery for all three processes. In addition to algal biomass recovery, light (Biggs et al. 1999, Uehlinger 2000) and nutrient availability (Biggs et al. 1999) can also strongly influence the rate at which GPP recovers from floods. Further, pre-disturbance processing rates can influence recovery time for GPP. For example, pre-disturbance GPP can be positively related to recovery time in forested Tennessee streams (Roberts et al. 2007). In streams with minimal allochthonous inputs, such as desert, prairie, and agricultural streams, ER is often reliant on OM derived from primary producers (Jones et al. 1995). Ecosystem respiration and GPP recovery rates may be coupled in these systems, making ER recovery dependent on the same variables as GPP. Alternatively, in forested watersheds ER has been found to recover quickly due to the influx of allochthonous matter during floods (Roberts et al. 2007); however, this was likely not the case due to the slower recovery in our forested streams compared to urban and agricultural streams. Faster recovery rates for ER than GPP in the agricultural and urban streams might suggest increased substrate oxygen availability due to flows that disturb bed material (Gerull et al. 2012), or may be due to an influx of OM from watershed (Meyer et al. 2005). In general metabolic processes are positively related to nutrient uptake and cycling (Izagirra et al. 2008; Bernot et al. 2010); however, reductions in fine benthic organic matter often associated more intense flows in impacted systems can reduce uptake and retention of nutrients (Meyer et al. 2005). So, while our impacted streams recovered more quickly from both flood disturbances their capacity to remove nutrients from the stream was likely reduced.

CONCLUSIONS

Our findings suggest that studies that examine flood disturbance effects on ecosystem processes within human-modified ecosystems would contribute to our basic knowledge on disturbance ecology and would provide important information on how to better manage riverine ecosystems to maintain benthic communities' structure and function. The benthic community comprised of algae and microbes constitutes the primary food source to food webs and their metabolic processes are responsible for carbon (C) cycling and nutrient uptake, which are important ecosystem services. These services are pivotal to the removal of OM waste and nutrients, reducing the cost of cleaning water for human consumption. Alterations in hydrology and light and nutrient availability, associated with altered land-use, may reduce the capacity for these communities to naturally clean our water. Continued expansion of agriculture and urbanization to meet global demands will intensify the impacts of altered landscapes on benthic communities and ecosystem functions.

To my knowledge, this was one of the first studies examining the effects of flooding on algal biomass and whole stream metabolism across multiple land uses. Higher nutrient agricultural and urban systems resulted in faster recovery rates for algal biomass and metabolic processes. Further studies are needed to elucidate the relationship between flood disturbance and algal and microbial communities, specifically within the context of altering hydrological disturbances across variable land-uses. Within a single forested system, inter-annual variability in flood timing, frequency and intensity drove variability in both GPP and ER. Higher flood frequency resulted in greater annual ER, whereas flooding occurring pre-leaf out in the spring reduced annual GPP (Roberts et al. 2007). Greater flood frequency and intensity due to increased watershed impervious surface and decreased stream channel sinuosity as found in agricultural and urban systems (Allan 2004) may result in similar increases annual ER. Effects of land-use changes on stream flow conditions may be exacerbated due to GCC; increasing the frequency and intensity of flooding (IPCC 2007), which may further increase annual ER or possibly result in decreases if OM pools becomes depleted from local stream systems (Meyer et al. 2005). It may be difficult to detect these changes in algal biomass and metabolic processes without implementing a more extensive sampling regime. To date only a few studies have examined daily metabolism (Uhelinger 2006, Roberts et al. 2007, Marcarelli et al. 2010) and even fewer have examined annual metabolism at multiple sites varying in anthropogenic disturbance

(Izagirre et al. 2008); however, this level of sampling will be necessary in the future to better assess the combined effects of land-use disturbances and GCC.

ACKNOWLEDGEMENTS

This research was funded through the Arkansas Water Resource Center's USGS104b program and in part through the National Science Foundation (REU 0755331) for funding undergraduate researchers. I would like to thank the numerous REU undergraduate researchers, Aaron Jackson, Zach Eldridge, and Jordan Patterson as well as honors undergraduate researchers, McKinley Case, Autumn Allison, Joseph Kanopsic, Stephanie Grise, Phillip Bumpers, and Eric Norman who assisted in the collection and processing of baseline and post disturbance data. I would also like to thank the members of the Evans-White lab, Hal Halvorson, Ayla Smartt, Allyn Fuell, Kayla Sayre and Brooke Parker as well as fellow graduate students Lindsey Bruckerhoff and Matthew Jennings for providing valuable comments and suggestions in the editing of this manuscript. Additionally, valuable comments and guidance were provided by my dissertation committee that included Michelle Evans-White, Thad Scott, Dan Magoulick, J.D. Willson, and Gary Huxel.

LITERATURE CITED

Allan, J.D. 2004 Landscapes and riverscapes: the influence of land use on stream ecosystems. Annual review of Ecology and Evolution 35:257-284.

Allan, J.D., D.L. Erickson, and J. Fay. 1997. The influence of catchment land use on stream integrity across multiple spatial scales. Freshwater Biology. 37: 149-161.

American Public Health Association (APHA). 2005. Standard methods for the examination of water and wastewater. A.D. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg (eds), American Public Health Association, Washington, D.C.

Bernot, M.J., D.J. Sobota, R.O. Hall, JR., P.J. Mulholland, W.K. Dodds, J.R. Webster, J.L. Tank, L.R. Ashkenas, L.W. Cooper, C.N. Dahm, S.V. Gregory, N.B. Grimm, S.K. Hamilton, S.L. Johnson, W.H. McDowell, J.L. Meyer, B. Peterson, G.C. Poole, H.M. Valett, C. Arango, J.L. Beaulieu, A.J. Burgin, C. Crenshaw, A.M. Helton, L. Johnson, J. Merriam, B.R. Niederlehner, J.M. O'Brien, J.D. Potter, R.W. Sheibley, S.M. Thomas, K. Wilson. 2010. Inter-regional comparison of land-use effects on stream metabolism. Freshwater Biology 55:1874-1890.

Biggs, B.J.F. and M.E. Close. 1989. Periphyton biomass dynamics in gravel bed rivers: the relative effects of flows and nutrients. Freshwater Biology. 22: 209-231.

Biggs, B.J.F., R.A. Smith, and M.J. Duncan. 1999. Velocity and sediment disturbance of periphyton in headwater streams: biomass and metabolism. Journal of the North American Benthological Society 18: 222-241.

Biggs, B.J.F. and H.A. Thomsen. 1995. Disturbance of stream periphyton by perturbations in shear stress: time to structural failure and differences in community resistance. Journal of Phycology. 31: 233-241.

Bott, T.L. 2006. Primary productivity and community respiration. Pages 663-690 in Hauer, F.R. and G.A. Lamberti (eds) Methods in Stream Ecology. Second edition. Academic Press, Burlington, MA.

Connell, J.H. 1978. Diversity in tropical rain forests and coral reefs. Science. 199: 1302-1310.

Figueroa-Nieves, D., T.V. Royer, and M.B. David. 2007. Controls on chlorophyll-*a* in nutrient-rich agricultural streams in Illinois, USA. Hydrobiologia. 568: 287-298.

Fuller, R.L., C. LaFave, M. Anastasi, J. Molina, H. Salcedo, and S. Ward. 2008. The role of canopy cover on the recovery of periphyton and macroinvertebrate communities after a month-long flood. Hydrobiologia. 598: 47-57.

Gerull, L., A. Frossard, M.O. Gessner, and M. Mutz. 2012. Effects of shallow and deep sediment disturbance on whole-stream metabolism in experimental sand-bed flumes. Hydrobiologia. 683: 297-310.

Grimm, N.B., and S.G. Fisher. 1986. Nitrogen limitation in a Sonoran desert stream. Journal of the North American Benthological Society. 5: 2-15.

Huston, M. 1979. A general hypothesis of species diversity. The American Naturalist. 113: 81-101.

Herlihy, A.T., J.T. Stoddard, and C.B. Johnson. 1998. The relationship between stream chemistry and watershed land cover data in the mid-Atlantic Region, USA. Water, Air, and Soil Pollution 105:377-386.

Hollis, G.E. 1975. The effects of urbanization on floods of different recurrence interval. Water Resources Research 8:431-435.

IPCC, 2007: Climate Change 2007: Impacts, Adaptation, and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Parry, Martin L., Canziani, Osvaldo F., Palutikof, Jean P., van der Linden, Paul J., and Hanson, Clair E. (eds.)]. Cambridge University Press, Cambridge, United Kingdom, 1000 pp.

Izagirre, O., U. Agirre, M. Bermejo, J. Pozo, and A. Elosegi. 2008. Environmental controls of whole-stream metabolism identified from continuous monitoring of Basque streams. Journal of the North American Benthological Society. 27: 252-268.

Jones Jr., J.B., S.G. Fisher, and N.B. Grimm. 1995. Vertical hydrologic exchange and ecosystem metabolism in a Sonoran desert stream. Ecology. 76: 942-952.

Lake P.S. 2000. Disturbance, patchiness, and diversity in streams. Journal of the North American Benthological Society 19*:* 573–592.

Lohman, K., J.R. Jones and B.D. Perkins. 1992. Effects of nutrient enrichment and flood frequency on periphyton biomass in Northern Ozark streams. Canadian Journal of Fisheries and Aquatic Sciences. 49: 1198-1205.

Marcarelli, A.M., R.W. Van Kirk, and C.V. Baxter. 2010. Predicting effects of hydrologic alteration and climate change on ecosystem metabolism in a western U.S. river. Ecological Applications. 20: 2081-2088.

McTammany, M.E., E.F. Benfield, and J.R. Webster. 2007. Recovery of stream ecosystem metabolism from historical agriculture. Journal of the North American Benthological Society 26: 532-545.

Meyer, J.L., M.J. Paul, and W.K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society 24:602-612.

Mulholland, P.J., C.S. Fellows, J.L. Tank, N.B. Grimm, J.R. Webster, S.K. Hamilton, E. Martí, L. Ashkenas, W.B. Bowden, W.K. Dodds, W.H. McDowell, M.J. Paul, and B.J. Peterson. 2001. Inter-biome comparison of factors controlling stream metabolism. Freshwater Biology. 46: 1503-1517.

Mulholland, P.J., A.M. Helton, G.C. Poole, R.O. Hall Jr., S.K. Hamilton, B.J. Peterson, J.L. Tank, L.R. Ashkenas, L.W. Cooper, C.N. Dahm, W.K. Dodds, S.E.G. Findlay, S.V. Gregory, N.B. Grimm, S.L. Johnson, W.H. McDowell, J.L. Meyer, H.M. Valett, J.R. Webster, C.P. Arango, J.J. Beaulieu, M.J. Bernot, A.J. Burgin, C.C. Crenshaw, L.T. Johnson, B.R. Niederlehner, J.M. O'Brien, J.D. Potter, R.W. Sheibley, D.J. Sobota, and S.M. Thomas. 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature. 454: 202-206.

Odum, H.T. 1956. Primary production in flowing waters. Limnology and Oceanography 2:102-117.

Paul, M.J. and J.L. Meyer. 2001. Streams in the urban landscape. Annual Review of Ecology and Systematics 32:333-365.

Peterson, C.G. 1996. Response of benthic algal communities to natural physical disturbances. Pages 375-402 *in* Algal Ecology: Freshwater Benthic Ecosystems, R.J. Stevenson, M.L. Bothwell, and R.L. Lowe (eds), Academic Press, San Diego, CA, USA.

Peterson, C.G. and R.J. Stevenson. 1992. Resistance and Resilience of lotic algal communities: Importance of disturbance timing and current. Ecology. 73: 1445-1461.

Poff, N.L. 1992. Why disturbance can be predictable, a perspective on the definition of disturbance in streams. Journal of the North American Benthological Society. 11: 86-92.

Roberts, B.J., P.J. Mulholland, and W.R. Hill. 2007. Multiple scales of temporal variability in ecosystem metabolism rates: results from 2 years of continuous monitoring in a forested headwater stream. Ecosystems 10:588-606.

Rosemond, A.D., P.J. Mulholland, and S.H. Brawley. 2000. Seasonally shifting limitation of stream periphyton: response of algal populations and assemblage biomass and productivity to variation in light, nutrients, and herbivores. Canadian Journal of Fisheries and Aquatic Science. 57: 66-75.

Sartory, D.P. and J.U. Grobbelaar. 1984. Extraction of chlorophyll a from fresh-water phytoplankton for spectrophotometric analysis. Hydrobiologia 114: 177-187.

Stanley, E.H., S.M. Powers, and N.R. Lottig. 2010. The evolving legacy of disturbance in stream ecology: concepts, contributions, and coming challenges. Journal of the North American Benthological Society. 29: 67-83.

Sumner, W.T., and S.G. Fisher. 1979. Periphyton production in Fort River, Massachusetts. Freshwater Biology. 9: 205-212.

Uehlinger, U. 1991. Spatial and temporal variability of the periphyton biomass in a prealpine river (Necker, Switzerland). Hydrobiologia. 123: 219-237.

Uehlinger, U. 2000. Resistance and Resilience of ecosystem metabolism in a flood-prone river system. Freshwater Biology. 45: 319-332.

Uehlinger, U., B. Kawecka, C.T. Robinson. 2003. Effects of experimental floods on periphyton and stream metabolism below a high dam in the Swiss Alps (River Spöl). Aquatic Sciences. 65: 199-209.

Uehlinger, U. and M.W. Naegeli. 1998. Ecosystem metabolism, disturbance and stability in a prealpine gravel bed river. Journal of the North American Benthological Society. 17: 165-178.

Wellnitz, T. and R.B. Rader. 2003. Mechanisms influencing community composition and succession in mountain stream periphyton: interactions between scouring history, grazing, and irradiance. Journal of the North American Benthological Society. 22: 528-541.

White, P.S., and S.T.A. Pickett. 1985. Natural disturbance and patch dynamics: an introduction. pp. 3-13 in The Ecology of Natural Disturbance and Patch Dynamics. Pickett, S.T.A. and P.S. White (eds.). Academic Press. New York. NY. USA.

Wiley, M.J., L.L. Osborne, and R.W. Larimore. 1990. Longitudinal structure of an agricultural prairie river system and its relationship to current stream ecosystem theory. Canadian Journal of Fisheries and Aquatic Sciences 47:373-384.

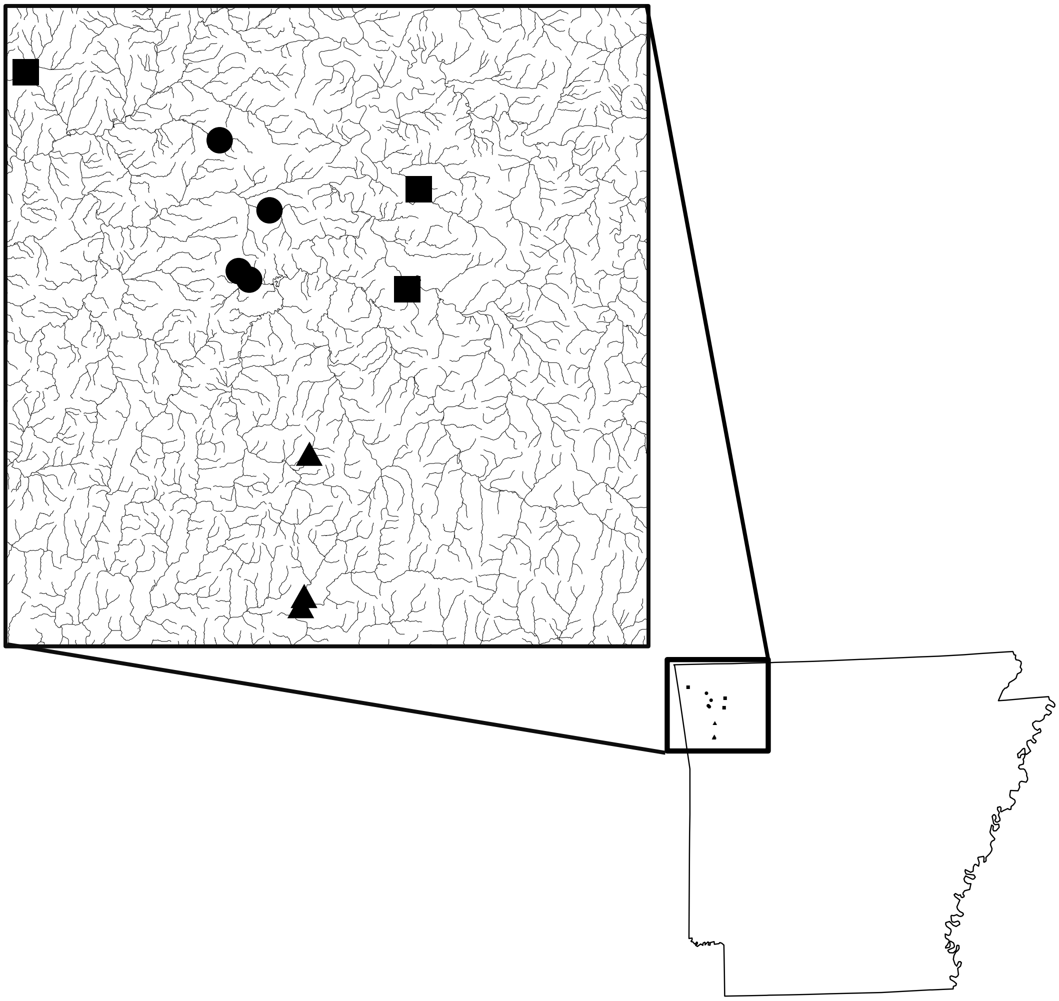
Table 1. Mean percent land use land cover (±1SE) across sites within each stream type sampled.

	% Forest	% Pasture	% Urban
Forested Streams	85.3 (3.2)	8.7 (1.4)	2.5 (1.1)
Agricultural Streams	38.3 (6.8)	48.6 (7.1)	6.2 (0.7)
Urban Streams	33.3 (8.8)	24.3 (9.0)	36.3 (7.7)

Table 2. Repeated measures analysis of variance results for flood intensity, pre-disturbance biomass and rates, and post-disturbance recovery for the factors “Season”, “Land-use” and the interaction between both factors.

	Season	Land-Use	Season x Land-Use
Flood Intensity	F= 5.25; p= 0.041	F= 1.45; p= 0.273	F= 1.86; p= 0.198
Pre-disturbance biomass and rates			
Algal Biomass	F= 7.58; p= 0.014	F= 18.37; p< 0.001	F= 0.18; p= 0.836
GPP[b]	F= 0.54; p= 0.475	F= 4.13; p= 0.037	F= 0.36; p= 0.700
ER[c]*	F= 2.75; p= 0.118	F= 1.05; p= 0.375	F= 0.92; p= 0.418
NEP[d]*	F= 2.64; p= 0.124	F= 1.15; p= 0.344	F= 0.37; p= 0.69
Post-disturbance recovery			
Algal Biomass	F= 10.84; p= 0.005	F= 4.71; p= 0.026	F= 0.03; p= 0.975
GPP[b]*	F= 5.76; p= 0.031	F= 4.13; p= 0.039	F= 0.91; p= 0.426
ER[c]*	F= 0.08; p= 0.779	F= 4.56; p= 0.030	F= 0.70; p= 0.515
NEP[d]*	F= 0.03; p= 0.873	F= 4.25; p= 0.036	F= 1.16; p= 0.340

(*) indicates data was logarithmically transformed before the analysis was conducted.
a: Flood intensity measured as percent algal biomass removed.
b: GPP: Gross Primary Production (gC/m^2/d)
c: ER: Ecosystem Respiration (gC/m^2/d)
d: NEP: Net Ecosystem Production (gC/m^2/d)



[redacted]

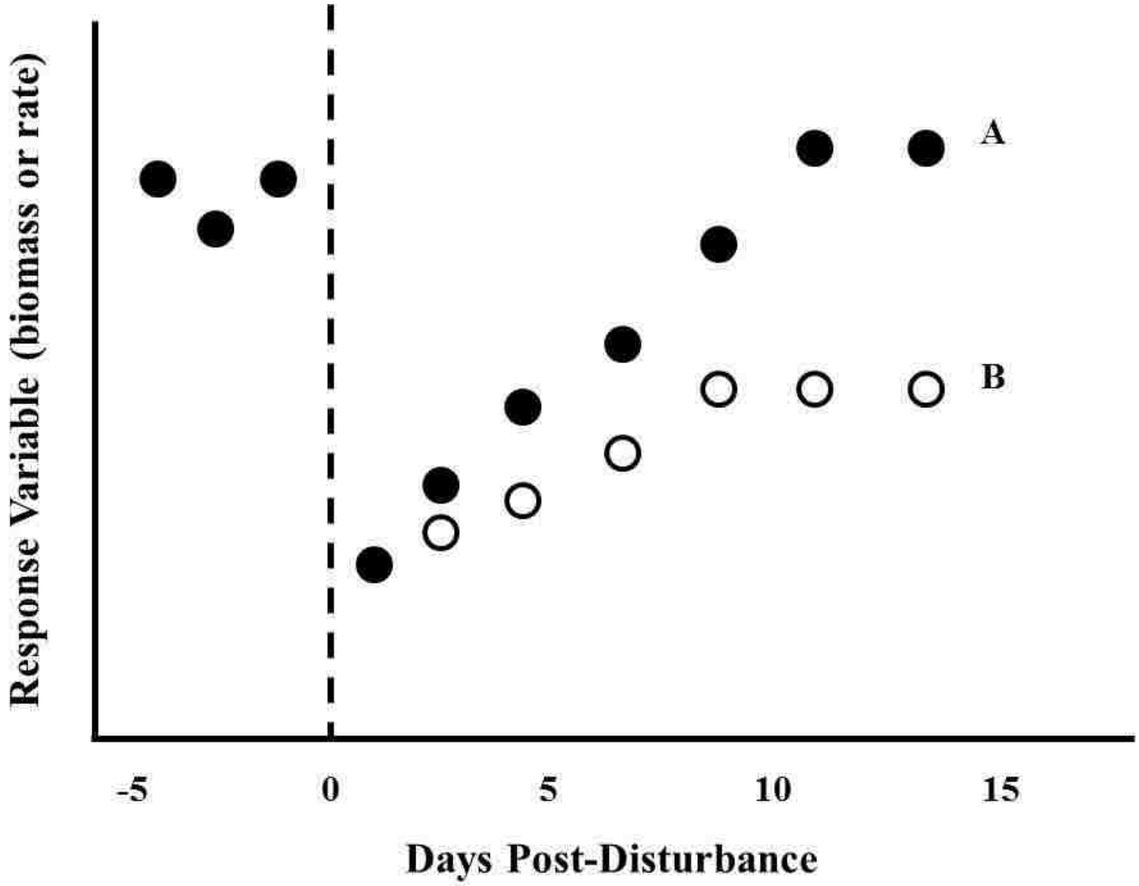
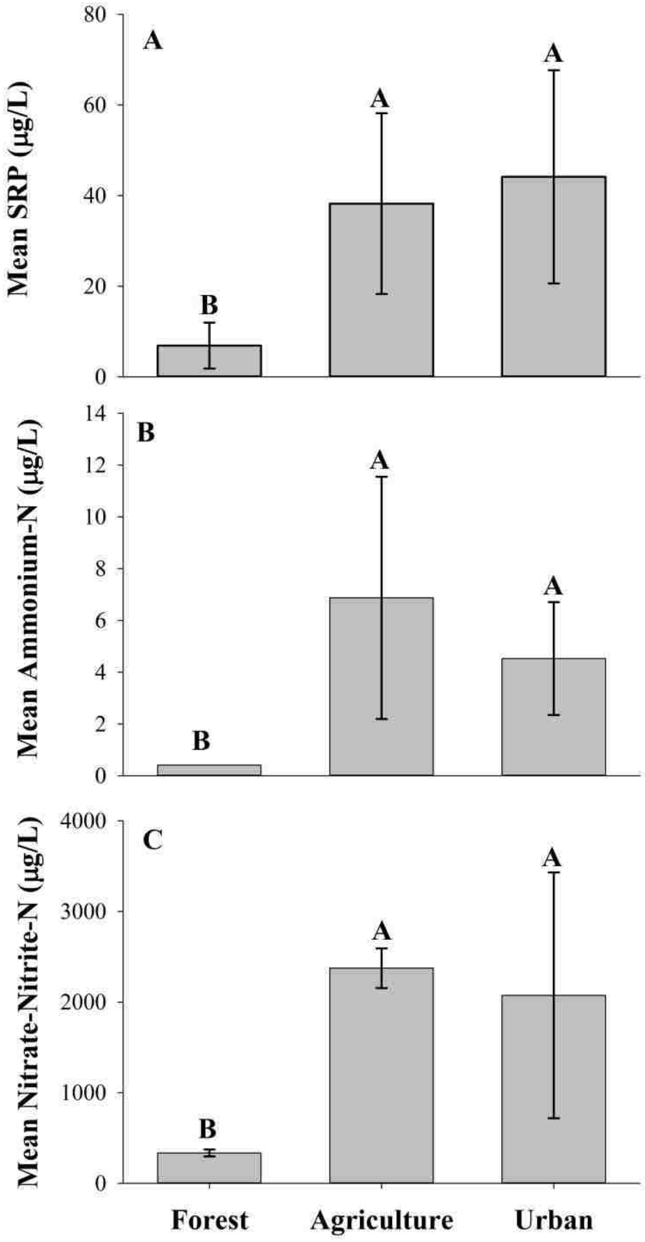
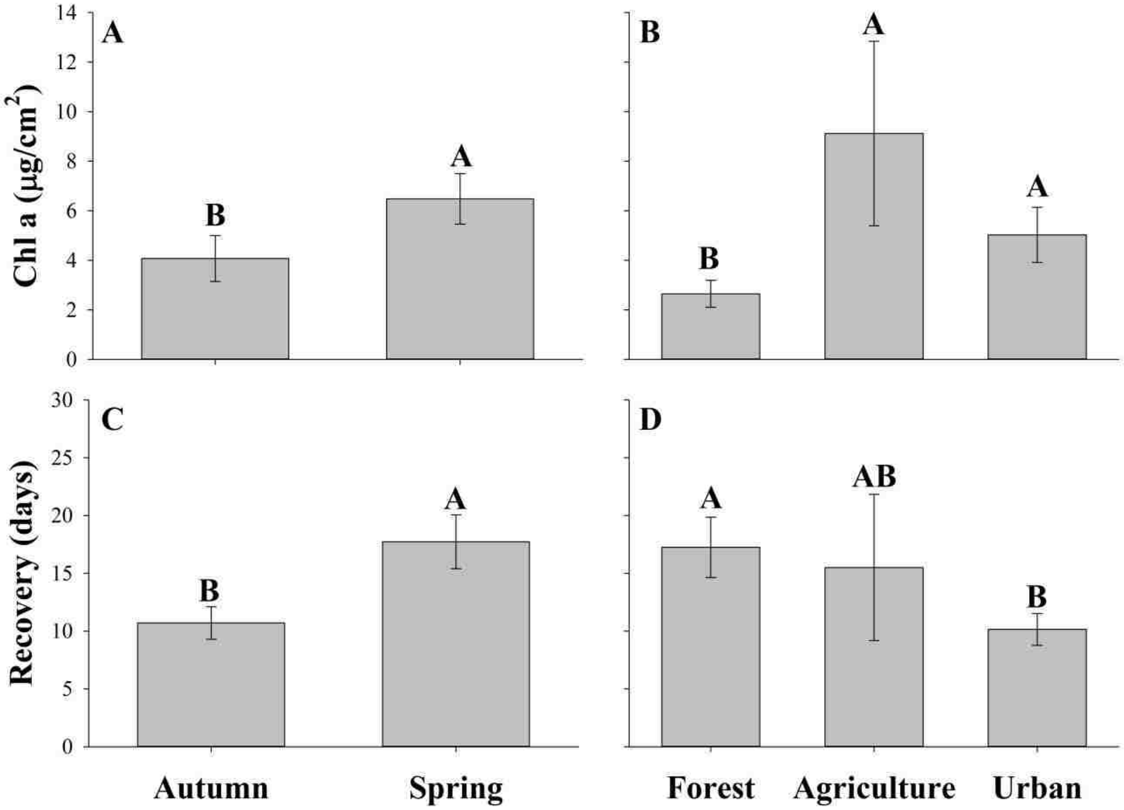


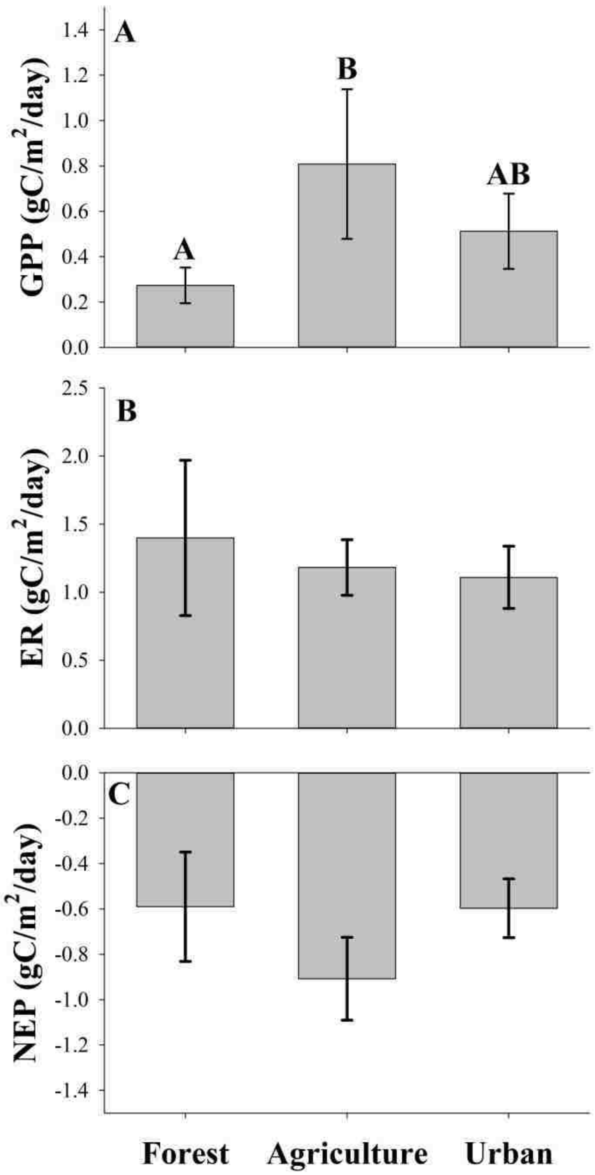
Figure 2: Hypothetical depiction of recovery for algal biomass and metabolic processes, where recovery is equivalent to either **(A)** time to reach or exceed pre-disturbance biomass or rate, or **(B)** time to reach a new stable biomass or rate.


A
Mean SRP (µg/L)
0
20
40
60
80
B
A
A
B
Mean Ammonium-N (µg/L)
0
2
4
6
8
10
12
14
B
A
A
C
Mean Nitrate-Nitrite-N (µg/L)
0
1000
2000
3000
4000
B
A
A
Forest
Agriculture
Urban

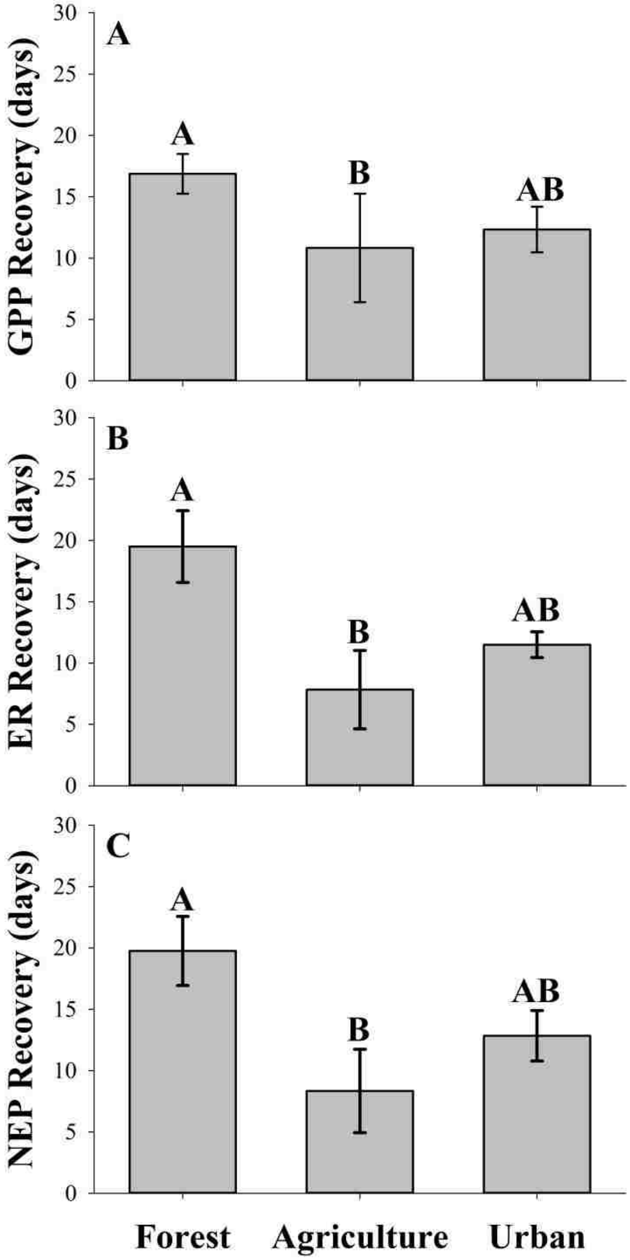
[redacted]


A
B
C
D
Chl a (µg/cm^2)
Recovery (days)
14
12
10
8
6
4
2
0
30
25
20
15
10
5
0
B
A
B
A
A
A
AB
B
A
B
Autumn
Spring
Forest
Agriculture
Urban

[redacted]


A
GPP (gC/m^2/day)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
A
B
AB
B
ER (gC/m^2/day)
2.5
2.0
1.5
1.0
0.5
0.0
C
NEP (gC/m^2/day)
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Forest
Agriculture
Urban

[redacted]


A
GPP Recovery (days)
A
B
AB
B
ER Recovery (days)
A
B
AB
C
NEP Recovery (days)
A
B
AB
0
5
10
15
20
25
30
Forest
Agriculture
Urban

[redacted]

CONCLUSION

Landscape scale disturbance can influence light, nutrient and sediment availability to streams (Allan 2004). The impacts of agricultural and urban land-use along with natural gas (NG) infrastructure development on algal biomass and whole stream metabolism are examined in this dissertation. To assess impacts of NG activity on streams 10 sites along a gradient of NG disturbance within north central Arkansas were sampled in the winter and spring of 2010 and 2011. Natural gas activity was found to relate positively to both algal biomass and gross primary production (GPP). This relationship was likely driven by the positive association between NG activity and total nitrogen (TN) measured across sites, though within this study there neither algal biomass nor GPP were directly related to TN. In addition, flow conditions leading up to the sampling event were found to be important in controlling the response variables. Stable flow conditions allowed for landscape disturbances to be detected, while sampling during less stable flow conditions resulted in no detectable landscape effects on algal biomass and GPP.

Hydraulic fracturing is a necessary process to stimulate NG production in unconventional wells. This process creates waste water that flows back up the well with the NG produced. If this “produced water” is improperly stored and or disposed of can result in contamination of nearby streams (Entrekin et al. 2011; Olmstead et al. 2013). High concentrations of cations, such as sodium (Na^+) and potassium (K^+), can be major components of produced water that may influence benthic algal biomass. In March of 2011, measures of conductivity, K^+, and Na^+ were all positively related with well density across the 10 sites from chapter 1 (Austin, unpublished data). The increase in K^+ corresponded with an increase in algal biomass, and both were also related to increased N availability. Therefore, it was not clear whether K^+ or N was stimulating algal production.

To separate out the effects of nutrients [N and phosphorus (P)] and cations (Na^+ and K^+), nutrient diffusing substrates were placed into 8 streams with varying NG activity. The primary finding of this study confirmed minimally impacted sites were N-limited as was previously determined for Ozark streams (Lohman et al. 1991); additionally, N-limitation across sites was negatively related to NG activity (R^2= 0.57; p= 0.03). With the exception of one site, which was co-limited by N and P, none of our sites were limited by P, Na^+, or K^+. While we recognize these findings only represent a snapshot in time and might vary seasonally (Francoeur et al. 1999), these results add to the body of evidence supporting the assertion that NG activity promotes algal growth via increased N availability in Fayetteville Shale streams (Austin, Chapter 1). Additionally, the lack of response to Na^+ and K^+ indicates the positive relationship between K^+ and algal biomass in March of 2011 was spurious and likely only an autocorrelation driven by K^+ association with N. Similar to other land use changes, increased NG activity may have the potential to increase stream nutrient concentrations, decreasing nutrient limitation of algal growth in nearby streams and resulting in greater primary production. Increasing nutrients in Fayetteville shale streams may transform these systems from nutrient sinks into sources as nutrient demand by stream communities is maxed out and as nutrient uptake lengths increase (Mulholland et al. 2008). Future studies examining effects of NG activity on nutrient-limitation should also look at aspects of nutrient transport in systems.

To reduce impacts of NG development on sediment erosion to streams best management practices (BMPs) have been within the Fayetteville shale region of north central Arkansas. In my third chapter I examined the effectiveness of BMPs at reducing the impacts of NG activities on stream algal biomass and GPP. This study was conducted in the Scott Henderson Gulf Mountain wildlife management area (Gulf WMA), which is an area managed by the state primarily for hunting and recreation. During the development of NG infrastructure throughout the area, Arkansas Game and Fish officials enforced the implementation of BMPs by the NG responsible for the development. I used a paired catchment before-after control-impact analysis where by reference or control streams were paired with impacted streams. All stream reaches were sampled both prior to and after the installation of NG infrastructure. From this design the "no change" in the impacted site in comparison to the reference site following the disturbance gave support to BMP effectiveness.

The primary finding from this chapter was that, at low levels of impact, BMPs are effective at mitigating the effects of NG activity on streams. However, it should be noted that the level of NG activity within the Gulf WMA is well below the average level of NG activity across the region. Further tests of effectiveness of these BMPs should focus on stream systems with greater levels of impact. As development continues in the Fayetteville shale region, more frequent water sampling is recommended. Additionally, sampling events should be planned to account for the pulse nature of this disturbance. Overall, within this system at this low level of impact any potential disturbance occurring that is not stopped by implemented BMPs does not appear to have long lasting effects.

The final chapter examines the response of algal biomass and whole stream metabolism to flooding within altered landscapes and between seasons. Eleven streams, 3 agriculture, 4 urban, and 4 forested streams were sampled leading up to and following flooding events in the autumn of 2009 and spring of 2010. Algal biomass and whole stream metabolism parameters, GPP, ecosystem respiration (ER), and net ecosystem production (NEP) were sampled within each stream. Both agricultural and urban streams had increased algal biomass, GPP, ER, and NEP prior to flood disturbances due to greater nutrient availability.

Higher nutrient agricultural and urban systems resulted in faster recovery rates for algal biomass and metabolic processes. Further studies are needed to elucidate the relationship between flood disturbance and algal and microbial communities, specifically within the context of altering hydrological disturbances across variable land-uses. Within a single forested system, inter-annual variability in flood timing, frequency and intensity drove variability in both GPP and ER (Roberts et al. 2007). Effects of land-use changes on stream flow conditions may be exacerbated due to GCC; increasing the frequency and intensity of flooding (IPCC 2007), which may further increase annual ER or possibly result in decreases if OM pools becomes depleted from local stream systems (Meyer et al. 2005). It may be difficult to detect these changes in algal biomass and metabolic processes without implementing a more extensive sampling regime. These findings highlight the defining role of nutrient availability as the driver of effects of human land-use change on autotrophic processes in stream ecosystems.

LITERATURE CITED

Allan, J.D. 2004 Landscapes and riverscapes: the influence of land use on stream ecosystems. Annual review of Ecology and Evolution 35:257-284.

Entrekin, S., M. Evans-White, B. Johnson, and E. Hagenbuch. 2011. Rapid expansion of natural gas development poses a threat to surface waters. Frontiers in Ecology and the Environment. 9:503-511.

Francoeur, S.N., B.J.F. Biggs, R.A. Smith, and R.L. Lowe. 1999. Nutrient limitation of algal biomass accrual in stream: seasonal patterns and a comparison of methods. Journal of the North America Benthological Society. 18: 242-260.

IPCC, 2007: Climate Change 2007: Impacts, Adaptation, and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Parry, Martin L., Canziani, Osvaldo F., Palutikof, Jean P., van der Linden, Paul J., and Hanson, Clair E. (eds.)]. Cambridge University Press, Cambridge, United Kingdom, 1000 pp.

Lohman, K., J.R. Jones, and C. Baysinger-Daniel. 1991. Experimental evidence for nitrogen limitation in a Northern Ozark stream. 1991. Journal of the North American Benthological Society. 10: 14-23.

Meyer, J.L., M.J. Paul, and W.K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society 24:602-612.

Mulholland, P.J., A.M. Helton, G.C. Poole, R.O. Hall Jr., S.K. Hamilton, B.J. Peterson, J.L. Tank, L.R. Ashkenas, L.W. Cooper, C.N. Dahm, W.K. Dodds, S.E.G. Findlay, S.V. Gregory, N.B. Grimm, S.L. Johnson, W.H. McDowell, J.L. Meyer, H.M. Valett, J.R. Webster, C.P. Arango, J.J. Beaulieu, M.J. Bernot, A.J. Burgin, C.C. Crenshaw, L.T. Johnson, B.R. Niederlehner, J.M. O’Brien, J.D. Potter, R.W. Sheibley, D.J. Sobota, and S.M. Thomas. 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature. 454: 202-206.

Olmstead, S.M., L.A. Muehlenbachs, J.S. Shih, Z. Chu, and A.J. Krupnick. 2013. Shale gas development impacts on surface water quality in Pennsylvania. Proceedings of the National Academy of Science. 110: 4962-4967.

Roberts, B.J., P.J. Mulholland, and W.R. Hill. 2007. Multiple scales of temporal variability in ecosystem metabolism rates: results from 2 years of continuous monitoring in a forested headwater stream. Ecosystems 10:588-606.