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Natural Nutrient Sources in the Cache River Watershed, Arkansas

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Running Title: Natural Sources of Nutrients

Abstract

The growth of the hypoxic 'dead zone' in the Gulf of Mexico in recent years has placed increased focus on potential sources of nutrient pollution, with most of the focus being placed on watersheds where practices, including fertilizer application and land alterations combine to increase non-point source runoff. In this study, nutrient concentrations in surface waters of altered and unaltered areas of the Cache River Watershed, Arkansas, were compared to determine if agricultural land usage was responsible for the majority of nutrient inputs. Results suggest that for dissolved nitrites and orthophosphates, agricultural (altered) sites contribute significantly more than relatively unaltered sites but that for dissolved nitrates, unaltered sites have a large contribution to overall nitrate concentrations, particularly in late summer and fall months.

Introduction

In recent years, the growth of the so-called 'dead zone' in the Gulf of Mexico has placed increased focus on potential causes of this area of hypoxia (Malakoff 1998, Dodds 2006). The primary source of contamination is thought to be nutrient pollution, specifically nitrogen and phosphorus inputs, from the Mississippi River Basin (Rabelais et al. 2002). This watershed drains approximately 41% of the continental United States, including some of the most agriculturally productive regions, in the central and mid-western United States (USEPA 2014).

Agricultural production in the United States accounts for roughly 21% of the overall worldwide production (approximately 1013.37 million metric tons) with major contributions from corn, coarse grains, wheat, soybeans, oilseed and cotton (USDA 2013). Between 1960 and 2011, production of crops more than doubled while fertilizer application nearly tripled (USDA 2013). These fertilizers, along with agricultural land usage practices, are thought to be the primary contributors to the hypoxic zone in the Gulf of Mexico (White et al. 2014)

In the United States, Arkansas is a major contributor to overall crop production, ranking 12th nationwide (USDA ERS 2013), including ranking 1st in rice production, and 5th in cotton production (USDA ERS 2013). The Delta Ecoregion of northeastern Arkansas is the major region of agricultural production in this state, with agricultural land usage ranging between 50 and 80% by watershed (AWIS 2006).

Due to this intense agricultural usage, several watersheds in northeastern Arkansas have been named as focus area watersheds by the Mississippi River Basin Initiative (MRBI) in the attempt to limit the influence on the hypoxic zone in the Gulf of Mexico (USDA NRCS 2012). While the majority of these watersheds have been heavily altered for agricultural production, some relatively unaltered areas remain.

In the Cache River Watershed, the presence of a unique geological feature, Crowley's Ridge, along the eastern side of the watershed, has resulted in a portion of the watershed being left relatively unaltered, due to its unsuitability for traditional row-cropping. Forest cover in these portions of the watershed are as high as 65% of land area compared to less than 10% in agriculturally productive areas of the watershed (AWIS 2006). This watershed, headwatered in southeastern Missouri, accounts for approximately 12.1% of the land area in the Delta ecoregion (Scott et al. 1998). Because of the importance of this watershed as an agriculturally valuable resource as well as a potential source of nutrient contamination leading to the hypoxic zone, it has been identified as a focus area watershed by the MRBI and a watershed of concern by the Arkansas Department of Environmental Quality (ADEQ) (ADEQ 2012).

Here we examine nutrient concentrations in mixed-use sub-watersheds of the Cache River Watershed over two growing seasons (2013-2014). Seven unaltered and three altered sites were examined, ranging across five sub-watersheds of the Cache River. Altered sites were characterized by artificial stream channelization, removal of riparian vegetation and conversion of surrounding land to agricultural usage. Unaltered sites retained natural stream contours, a riparian buffer and overhanging canopy and were primarily surrounded by forested or pasture land.

Based on characteristics of altered sites, namely the lack of stream contours and riparian vegetation, it was predicted that runoff due to precipitation would be greater at these sites than at unaltered sites. Combined with the increased use of artificial fertilizers on land surrounding these sites, this was expected to lead to increased nutrient levels at altered sites when compared to unaltered sites. This difference was predicted to be greatest following heavy precipitation events, when nutrient-containing runoff should be greatest.

Materials and Methods

Site selection and sampling frequency

Seven unaltered and three altered sites were selected within five sub-watersheds of the Cache River. Channel widths and depths were relatively constant for all sites sampled, with widths less than 10 m and depths ranging from 0.2 m to 1.5 m, depending on precipitation. Samples were collected bi-monthly over the length of the agricultural season (May-October) for two years, 2013 and 2014.

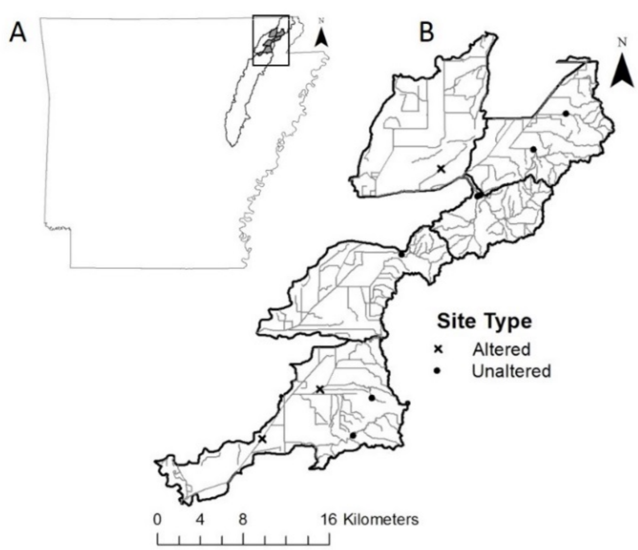

Figure 1. A) Location of Cache River watershed in Arkansas and sampled sub-watersheds within Cache River watershed (in box). B) Location of sites sampled within five sub-watersheds of the Cache River.

Sample analysis

Water samples were collected from vertical centroid of the water column and immediately analyzed for temperature, dissolved oxygen (DO), conductivity and pH using an Orion Star A329 multiprobe field meter (Thermo Scientific). Collected water was placed in an acid-washed Nalgene container and stored at 4°C until analyzed. For each sampling year, one 10 mL sample was filtered using a 0.45 µm filter (Environmental Express) for analysis of dissolved nutrients (nitrate (NO_3^-), nitrite (NO_2^-), orthophosphate(PO_4^{-3})) using either a discrete nutrient analyzer (DA 3500, OI Analytical) or a flow-through analyzer (Skalar San++). For year two, an additional 40 mL of unfiltered water was collected and transported to the Arkansas State University Ecotoxicology Research Facility (ASU ERF) for digestion (APHA method 4500-NO_3F and 4500-P (APHA 2005)) and analysis of total nitrogen and total phosphorus (Skalar San++). At this time, nutrient criteria for this region have not been set by the state of Arkansas. Therefore, 25 percentile values for total nitrogen and total phosphorus were compared to recommended nutrient criteria for the ecoregion as proposed by the United States Environmental Protection Agency (USEPA 2001).

Statistical analysis was performed using R and R Studio (R Core Team 2015). All data sets were tested for normality using a Shapiro-Wilks test and transformations were applied when data were not normally distributed. If transformations failed to achieve normality, non-parametric statistical tests were employed.

Results

Dissolved nutrient data was not normally distributed and transformations failed to achieve normality. Thus, non-parametric statistical tests were used for comparisons. Dissolved NO_2^- and PO_4^{-3} values were significantly lower at unaltered sites than at altered sites (Mann-Whitney U-test, $p<0.001$ (NO_2^-), $p<0.001$ (PO_4^-)). No significant difference was detected between site types for dissolved NO_3^- (Mann-Whitney U-test, $p=0.17$), though levels were greater at unaltered sites than altered sites.

NO_3^- concentrations at altered sites were correlated with precipitation (Spearman's rank correlation, $p=0.03$) with spikes in NO_3^- typically occurring 24-48 hours after heavy rainfall. No correlation was found between NO_2^- or PO_4^{-3} at altered sites or between any dissolved nutrients and precipitation at unaltered sites.

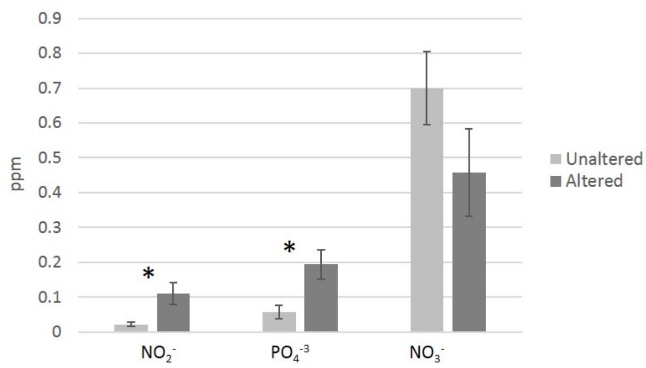

Figure 2. Comparison of dissolved nutrient (mean ± S.E.) concentrations at altered (n=3) and unaltered sites (n=7). Asterisk denotes a significant difference between mean concentrations at site types (α=0.05).

Comparing total nutrient concentrations between site types showed a similar statistical pattern. Total phosphorus was significantly greater at altered sites than at unaltered sites (t-test for unequal variance, t= -2.434, p=0.03) while no significant difference was detected between total nitrogen based on site type (t-test for unequal variance, t=-1.911, p=0.076).

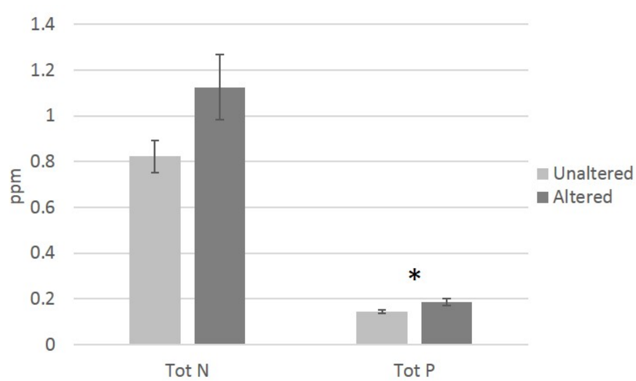

Figure 3. Comparison of total nitrogen and total phosphorus (mean ± S.E.) concentrations at altered (n=3) and unaltered sites (n=7). Asterisk denotes a significant difference between mean concentrations at site types (α=0.05).

Discussion

In highly managed agroecosystems, fertilizer application, combined with altered landscape features, may often result in increased loss of nutrients to receiving waterways (Carpenter et al. 1998, Sims et al. 1998), especially when compared to relatively unaltered areas (Wang et al. 2014). In the Cache River Watershed, we measured this pattern to hold true for our sampling period, with significantly higher concentrations of dissolved PO_4^{-3} and NO_2^- in waterways surrounded by altered, agriculturally productive land than in those with less altered, forested watersheds. However, we found decreased concentrations of NO_3^- at altered sites, compared to unaltered sites.

Nutrient criteria are typically described in terms of qualitative data rather than quantitative. As such, no numeric criteria have been set by the state of Arkansas at this time for this ecoregion. However, the USEPA has proposed nutrient criteria for total nitrogen and total phosphorus based on a larger ecoregion (Ecoregion X) composed of the Texas/Louisiana coastal plains and Mississippi Alluvial plains. This criteria is based on the 25th percentile. Accordingly 25th percentile values were calculated for total nitrogen and total phosphorus for both altered and unaltered sites. In all cases 25th percentile values fell below or just slightly above proposed criteria limits, indicating that the levels detected are probably not of immediate environmental concern. During the course of this study, site observations did not indicate any qualitative indicators of enrichment, such as algal blooms.

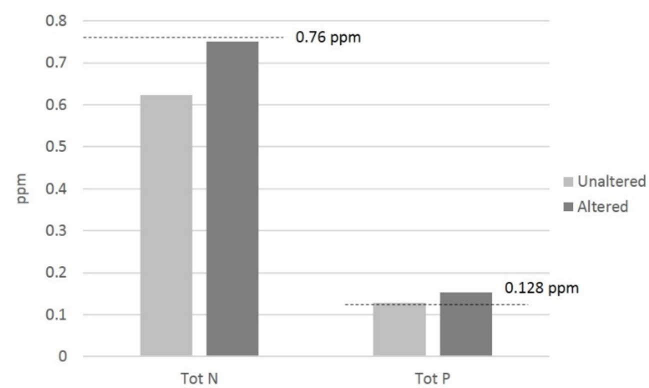

Figure 4. Comparison of total nitrogen and total phosphorus (25th percentile) concentrations at altered (n=3) and unaltered sites (n=7) to USEPA proposed criteria for Ecoregion X (dashed lines).

The decrease in NO_3^- at altered sites occurs in late summer/early fall and matches the time when maximum nutrient uptake by crops would be expected to occur (University of Arkansas, Cooperative Extension Service 2015). Earlier in the growing season, losses to waterways were greater, most likely due to lower uptake by crops and greater precipitation. A significant correlation did exist for precipitation in the 48-hr period before sampling and NO_3^- concentrations in waterways surrounded by altered landscapes

More puzzling is the increased concentrations of NO_3^- in waterways surrounded by unaltered landscapes in summer/fall months. Typically, NO_3^- concentrations follow a seasonal pattern with a summer minima and a late fall/winter maxima (Jayasinghe et al. 2012). However, we saw NO_3^- levels begin to increase in summer (August 2014, July 2013). While in the beginning of the growing season, NO_3^- concentrations were greater at altered sites than unaltered sites, this relationship reversed for the latter half of the season. This increase was largely attributable to values from three of the seven natural sites but was not correlated with precipitation in the 72-hr period preceding sampling, indicating it was most likely not a result of surface runoff.

The increase in NO_3^- at unaltered sites is most interesting as these sites typically display better water quality (lower concentrations of potential pollutants) than altered sites. An examination of NO_3^- concentrations in agricultural watersheds using the SWAT model indicates that NO_3^- concentrations are generally positively correlated with acres of land used for row cropping (summarized in Jayasinghe et al. 2012).

Several possible explanations exist to explain the increase in NO_3^- at unaltered sites. Firstly, it is possible that an unrecognized artificial source of nutrients exists in these watersheds. While crop-based agriculture is not prevalent, some animal-based agriculture does exist, primarily pastured cattle. Nutrient outputs from animal agriculture have been recognized as a source of nutrient impairments in other Midwestern watersheds (Keeney and DeLuca 1993). Nitrogen leaching from grazed pastures has been found to be similar in amount to nitrogen leached from row-cropped areas, largely due to the urination of animals (Di and Cameron 2002). Because increased NO_3^- concentrations were only noted in three of the seven unaltered creeks, a further examination of these sites is in order.

Secondly, the increase could represent a combination of increased soil nitrogen and decreased plant uptake. Unaltered sites have much more forest cover and thus more vegetative litter. As this litter falls to the ground, its decomposition by nitrifying organisms leads to increases in soil reservoirs of NO_3^-. These reservoirs would typically be depleted by plant growth. However, later in the growing season, plant uptake of nutrients would decrease, leaving more to wash into surface waters either as runoff or via subsurface flows. Bechtold et al. (2003) found that subsurface inputs of water were enriched in NO_3^- and took longer to reach surface channels than surface runoff.

An examination of precipitation data indicates no significant correlation between in-stream NO_3^- levels at unaltered sites and precipitation totals for the 72 hrs prior to sampling. This indicates that surface runoff of NO_3^- is not the primary contributor to stream NO_3^- levels. Extending this analysis to precipitation totals for one week and two weeks prior to sampling also reveal no significant correlation, indicating that subsurface flow is also unlikely to be the primary contributor to elevated surface water concentrations. It is important to note that because this is a highly agricultural area, irrigation during dry seasons is common. Thus, precipitation totals alone might not account for all water inputs to a stream. The influx of irrigation water at altered sites could potentially dilute surface water concentrations of dissolved NO_3^-. Because unaltered sites would not receive similar amounts of irrigation water, such dilution would not occur at these sites, making them appear to have elevated NO_3^- concentrations when compared to altered sites.

A final possibility for increased surface water concentrations at unaltered sites is due to nitrifying organisms in the stream, which would convert substrate or particulate bound nitrogen into NO_3^-. While altered stream sites could have similar nitrification rates, these streams are less likely to retain nitrogen, due to a decrease in habitat heterogeneity as a result of channelization and removal of riparian vegetation (Kemp and Dodds 2002). This is supported by our observation of similar amounts of total nitrogen in altered and unaltered streams, but dissimilar amounts of dissolved NO_3^-.

This hypothesis is also supported by a negative (though only marginally significant ($p=0.11$)) relationship between precipitation and NO_3^- concentrations at unaltered sites. When precipitation is greater, NO_3^- concentrations are lower (indicating dilution) and vice-versa. The same dilution could occur during times of low precipitation at altered sites when irrigation would add water to the system, thus explaining the low NO_3^- concentrations at times of low precipitation at altered sites. A similar inverse relationship between flow and NO_3^- concentrations was described in headwater streams in the Northeastern United States, though the streams in question had a seasonal snowpack, thought to contribute to overall NO_3^- (Goodale et al 2009). These authors also noted a seasonal pattern similar to what we observed, with peaks in NO_3^- in summer months, during the peak of the growing season.

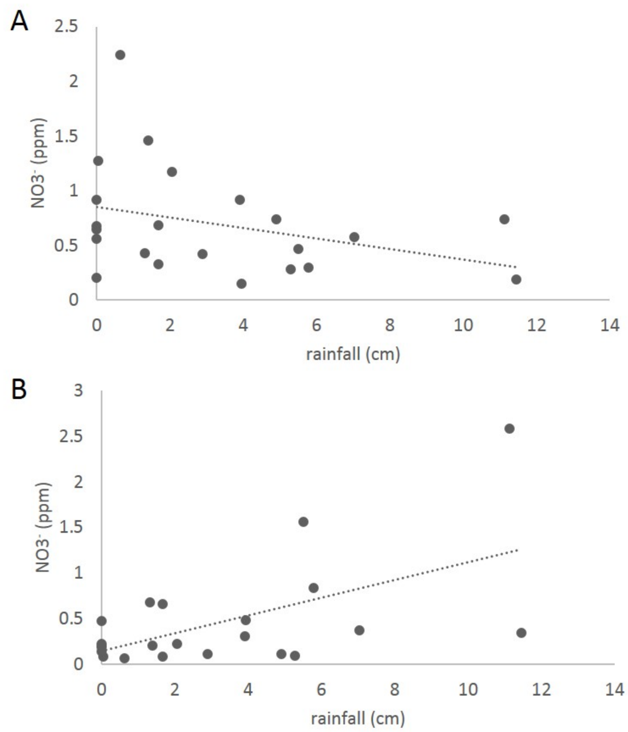

Figure 5. A) Relationship between NO_3^- concentrations and total precipitation for one week prior to sampling for unaltered sites B) Relationship between NO_3^- concentrations and total precipitation for one week prior to sampling for altered sites.

Conclusions

Differences in dissolved NO_2^- and PO_4^{-3} between site types were as expected. However, the increase in dissolved NO_3^- observed at unaltered sites indicates that an unidentified, and possibly natural, source of nutrients exists. Future testing should include an examination of other potential sources of nitrogen, including potential contributions from vegetation, subsurface flows, in-stream nitrification or unidentified anthropogenic sources. Also, extending sampling throughout the year, rather than just during the growing season, would provide greater insight into typical annual fluctuations in nutrients at these sites. Concentrations of total nitrogen and phosphorus were below or very similar to proposed nutrient criteria for the ecoregion, indicating that levels measured are most likely not of immediate environmental concern.

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