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The Potential Acidification of the Mulberry River, Arkansas

Jason Richard Burgess-Conforti
University of Arkansas, Fayetteville

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The Potential Acidification of the Mulberry River, Arkansas

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by

Jason R. Burgess-Conforti
University of Arkansas
Bachelor of Science in Crop, Soil, and Environmental Science, 2014
University of Arkansas
Master of Science in Crop, Soil, and Environmental Science, 2016

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University of Arkansas

This dissertation is approved for recommendation to the Graduate Council.

David M. Miller, Ph.D.
Dissertation Director

Philip A. Moore Jr., Ph.D.
Committee Member

Phillip R. Owens, Ph.D.
Committee Member

Amanda J. Ashworth, Ph.D.
Committee Member

Phillip D. Hays, Ph.D.
Committee Member

Michelle A. Evans White, Ph.D.
Committee Member

Abstract

The Mulberry River is a 110 km long tributary of the Arkansas River in northwest Arkansas and has been designated as a National Wild and Scenic River since 1992. In 2008, the Mulberry River was added to the 303(d) list of impaired water bodies due to the low pH of a 14.6 km segment of the river which has since increased to 68.7 km. To date, there has been little research performed on the Mulberry River and long-term routinely sampled water quality data is unavailable. The objectives of this dissertation were 1) to evaluate changes in water quality of the Mulberry River and its tributaries over a 4-year period and 2) to evaluate the relationship between forest stand type (i.e., deciduous vs coniferous) and both stream and soil chemistry. Water samples were collected monthly from 11 locations on the Mulberry River and 10 of its tributaries from March 2015 until January 2019. Soil samples were collected from 10 locations throughout the watershed with adjacent deciduous and coniferous stands. Several different tests of soil acidity indicated in no significant differences between soil from beneath the deciduous and coniferous stands. Coniferous forest land use was not correlated with stream pH ($P > 0.05$) neither was stream pH predicted ($P > 0.05$; $R^2 < 0.01$) by coniferous forest land use. Trend analyses indicate that there have been significant decreases in specific conductance, total suspended solids, total organic C, total N, SO_4, and flow-adjusted soluble Ca and Mg and a significant increase in Cl and total Al, Fe, and Na. Out of the 21 locations sampled, only three had significant decreases in pH suggesting that the watershed has not been acidified during the duration of this study. The decrease in specific conductance and several constituents as well as the increase in streamflow and precipitation throughout Arkansas implies that the watershed has become more dilute with time. The results of this research indicate that conifer growth is not a significant source of acidity and the watershed has not become more acidic over the last 4 years.

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Introduction

In 1992, the Mulberry River in Arkansas was designated a ‘Wild and Scenic River’ due to the outstanding natural and recreational value it provides to Arkansas and the United States. The Mulberry River is a 110 km long tributary of the Arkansas River and is located within the Ozark National Forest in the Boston Mountain region of northwest Arkansas. In 2008, the Mulberry River was placed on the EPA’s 303(d) list of impaired water bodies by the Arkansas Department of Environmental Quality (ADEQ) due to the low pH of a 14.7 km segment of reach 009 (HUC11110201-009). In 2005, ADEQ monitoring stations ARK0138 and ARK0139 reported a river pH of 5.68 and 5.50, respectively, which is below the Arkansas Pollution Control and Ecology Regulation No.2 ranges of 6.0 to 9.0. The Mulberry River was placed on the EPA 303(d) list of impaired water bodies with the purpose of determining if the low pH levels were the result of non-point source pollution, and/or natural background conditions (Shafii, 2008). Two more segments were added to the 2016 303(d) list increasing the length of impairment from 14.6 km to 68.7 km, indicating further potential acidification of the river. The 2016 303(d) list also included Little Mulberry Creek (a 28 km long tributary of the Mulberry River) and Friley Creek (an 11.6 km long tributary of Little Mulberry Creek) increasing the total length of impairment within the watershed to 108.3 km.

The Mulberry River watershed is approximately 1100 km^2 in area and is comprised of three HUC10 and 13 HUC12 sub-watersheds. The predominant land uses of the watershed are deciduous forest (69.5%), coniferous forest (13.5%) and pasture (8.8%) (Homer et al., 2015) with increasing forest density towards the headwaters. The watershed is located in a rural portion of Arkansas (population < 10,000; average population density ~10 persons/km^2; 2010 US census data) with minimal agriculture (< 0.1%) (Homer et al., 2015) and no approved point source discharge permits (Shafii, 2008). As such, the source of acidity within the watershed is unlikely to be derived from urban sources, agriculture, and/or industry. Instead, the acidity within the watershed may be originating from other non-point sources including (but not limited to) 1) changes in soil chemistry within the Mulberry River watershed due to alteration of forest stand composition, 2) atmospheric acid deposition (both wet and dry), 3) increased soil nitrification from ammonia deposition, 4) change in watershed hydrology, and/or 5) increased rate of pyrite oxidation.

Due to extensive timber harvesting in Arkansas, forest cover decreased from 32 million acres in 1880 to approximately 18 million acres in the mid-1900s (Bragg, 2010). Beginning in the 1980s efforts began to regenerate forest stands in Arkansas resulting in a large increase in forest cover. Although cover of hardwood forests in Arkansas has remained relatively unchanged for the last 60 years, there has been an increase in the area of pine plantations with loblolly pine (*Pinus taeda*) as the predominant species. In 1952, there were approximately 55,000 acres of pine which increased to nearly 3 million acres in 2005 (Rosson and Rose, 2010). Volume of live-tree softwoods increased in the Ozark region of Arkansas (which contains the Mulberry River) from 20 million cubic meters in 1978 to 43 million cubic meters in 2005 (Beltz, 1992; Rosson and Rose, 2005).

Growth of trees on land that is not forested, and/or the conversion of hardwood or mixed hardwood-pine stands to pine monocultures through hardwood group selection are common management practices in the southern United States (Lane, 1975; Berthrong et al., 2009). The potential alteration of native stand composition, especially increasing the area of conifers, could result in acidification of soils, surface water, and groundwater (Lane, 1975). When loblolly pine was planted on an Aquic Hapludult previously cropped with cotton in South Carolina, soil pH in the 0- to 7.5- and 7.5- to 15-cm depth interval decreased by 0.83 and 0.60, respectively, over a 20 yr period (Binkley , 1989). During that same time period, exchangeable Ca decreased by 5.3 and 4.2 $\text{mmol}_c\ \text{kg}^{-1}$ in the 0- to 7.5 and 7.5- to 15-cm depth interval, respectively. Similarly, Brand (1986) reported a decrease of soil pH by 0.86 units over a 40 yr period following conifer afforestation. Needle/leaf organic acid contents, allocation of cations within the tree, and parent material have been identified as three potential processes leading to differences in pH and quantities of exchangeable cations between tree stands by (Finzi et al., 1998). Jenkins et al. (1990) attributed differences in soil acidification of forest soils under deciduous and coniferous stands and subsequent watershed acidification to differences in atmospheric deposition rates, evapotranspiration rates, and base cation uptake. Despite the numerous paired watershed studies that have been conducted in the past, there are still discrepancies in the data regarding the effect of afforestation on stream chemistry. Farley et al. (2008) reported no change in stream pH in watersheds approximately 30 years after afforestation with *Pinus elliotti*, *P. radiata*, and *P. ponderosa* and Clenaghan et al. (1998) reported increasing stream pH along an increasing gradient of pine afforestation.

Ammonia is highly reactive in the atmosphere and tends to form aerosols and solution products quickly (Pearson and Stewart, 1993). Ammonia can enter the soil through wet deposition by reacting with SO_2 and water to form ammonium sulfate, or by reacting with only water to form ammonium (Pearson and Stewart, 1993). Ammonia can also enter the soil through dry deposition. It is estimated similar amounts of ammonia enter the soil profile through wet and dry deposition (Hanson and Lindberg, 1991). Most of the ammonia that enters the atmosphere originates from animal manure (Duyzer, 1994). Poultry production is one of Arkansas's largest industries. In 2013, 1 million broiler chickens were produced resulting in large amounts of ammonia being generated (USDA, 2016). Once in the soil, ammonium is oxidized to nitrate through by nitrifying soil organisms, resulting in the release of H^+ into solution. This was observed in the Netherlands throughout the 1980s and substantial forest die off was attributed to this mechanism (Van Breemen et al., 1982).

Although precipitation is naturally acidic (pH ~5.6) because of the formation of carbonic acid (H_2CO_3), the oxidation of N and S to form nitric and sulfuric acids, respectively, can further decrease precipitation pH and/or increase the total acidity of precipitation. Nitrogen and S oxides can enter the atmosphere from natural or pollutant sources. Once in the atmosphere, these oxides can react with water to form nitric (HNO_3) and sulfuric (H_2SO_4) acids which will then enter the soil and surface water. Once in the soil and surface water, the effects of acid precipitation are similar to those of other acidifying processes. Sudden contribution of acidic precipitation, often called episodic acidification, can be especially damaging to aquatic ecosystems that are unaccustomed to rapid changes in pH. The amount of acid deposition has decreased globally due to environmental regulations but environments that are poorly buffered may still be susceptible to acidification.

The oxidation of sulfide-bearing minerals such as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), galena (PbS), marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$), and pyrite (FeS_2) is a prevalent process resulting in the acidification of natural waters (Rimstidt and Vaughan, 2003). The mechanisms of sulfide oxidation are complex and can result from abiotic or biotic processes, both of which result in the release of protons (H^+) into solution. Acidification of surface waters resulting from sulfide oxidation is typically attributed to acid mine drainage which can produce effluent with pH values <2.0 and with high concentrations of heavy metals and toxic trace elements (Akcil and Koldas, 2006). Tracking the origins of sulfate in aquatic ecosystems can be difficult and global estimates of the amount of sulfuric acid entering surface waters from sulfide oxidation range be between 0.12 x 10^{12} and 0.65 x 10^{12} mol SO_4 yr^{-1} (Francois and Walker, 1992; Calmels et al., 2007; Berner and Berner, 2012). If the rate of sulfide oxidation has for some reason increased within the Mulberry River watershed, this could result in a gradual acidification throughout the watershed.

One of the surest ways to determine whether or not a watershed is undergoing gradual acidification is to quantify changes in water quality over time. The primary objective of this dissertation was to monitor and evaluate changes in water quality of the Mulberry River watershed for a 46-month period to quantify potential degradation and identify potential causes of acidification. The secondary objective of this dissertation was to evaluate the relationship between forest stand type (i.e., deciduous vs coniferous) and both stream and soil chemistry.

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Chapter One: Literature Review

Impairment of the Mulberry River Watershed

The Mulberry River is a 110-km-long tributary of the Arkansas River and is located in the Arkansas River Basin and is within Franklin and Johnson counties. Since 1992, the Mulberry River has been listed as a "National Wild and Scenic River" due to the outstanding natural resource and recreational value it provides to Arkansas and the United States. The watershed draining into the Mulberry River is 18244 hectares and is entirely within the Ozark National Forest (Shafii, 2009). Approximately 95% of the Mulberry River watershed is forested. The Mulberry watershed is located in the Boston Mountains, a heavily dissected section of the Ozark Plateau (USDA-FS, 1996). The Boston Mountains are comprised of Pennsylvanian sandstone and shale and there is no limestone present. The landforms in the Mulberry Watershed range from flat alluvial areas to steep side bluffs.

The Mulberry River was placed on the EPA's 303(d) list of impaired water bodies in 2008 due to the low pH of a 9.1 mile segment (reach 009) reported at the Arkansas Department of Environmental Quality (ADEQ) monitoring station ARK0138. The water quality criterion for pH in Arkansas is between 6.0 and 9.0 as described in Arkansas Pollution Control and Ecology Regulation No. 2 (APCEC, 2007). In 2005, ADEQ monitoring stations ARK0138 and ARK0139 reported a river pH of 5.68 and 5.50, respectively, which lead to the addition of the Mulberry River to the 303(d) list. Over a 6 year period from 1999 to 2005, monitoring station ARK0138 reported 23.1% of samples measured exceeded water quality standards for pH. From 2010 to 2016 the amount of samples exceeding water quality standards increased to 55.6%, indicating further acidification of reach 009 of the Mulberry River. In 2016, reach 007 and 008 of the Mulberry River were added to the EPA 303(d) list for exceeding water quality standards regarding pH increasing the length of impairment from 9.1 to 42.7 miles. There are no NPDES permits approved for discharge into the Mulberry so the low pH may be the result of non-point sources or natural background conditions.

Potential Causes of Acidification

Effect of Land Use/Vegetation Changes on Soil Acidity

Growth of trees on land that has not been forested for more than 50 years has been explored as a land management practice to increase lumber yield and carbon sinks, and to reduce soil erosion (Berthrong et al., 2009). Development of forestry plantations on previously un-forested land, termed afforestation, is a significant perturbation of an ecosystem. The rapid growth of trees substantially increases the uptake of soil nutrients, when compared to native grasses or agricultural crops, and the continuous harvesting of trees can permanently deplete these nutrients from the soil. The permanent removal of base cations such as Ca, Mg, and K can reduce base saturation of a soil, leading to acidification.

Many soils are sensitive to acid deposition because acid deposition can lead to base depletion by cation leaching. McFee (1980) outlined four parameters which affect soil sensitivity to acidification: 1) the cation exchange capacity, which controls buffering capacity; 2) soil base saturation (the ratio of basic to acidic cations); 3) soil management practices; and 4) presence of carbonates from parent material. Soil acidification results in the exchange of adsorbed cations for protons and subsequent leaching of these cations out of the soil profile. This leads to further vulnerability to acidification as well as decreased vegetative growth, mobilization of toxic elements, and surface water acidification.

Ross et al. (2002) examined the effects of afforestation of pasture with Monterey pine (*Pinus radiata*) using paired sites with similar soils and parent material. For the majority of sites examined, soil pH was lower under pine, compared to the control. Following Ross et al. (2002), Parfitt & Ross (2011) examined the changes in soil chemistry in pasture land afforested with *P. radiata* over a 12-yr period (1998 to 2010). From 1998 to 2010, soil pH under the Monterey pine decreased significantly (P = 0.05) by 0.3 to 0.4 units, whereas pH of the pasture soil increased significantly (P < <0.01) by 0.3 units. In a similar experiment, Giddens et al. (1997) conducted a paired study between permanent pasture and *P. radiata* forests across contrasting soil series. Mean pH values of soil under the *P. radiata* were significantly (P = 0.009) lower than the pasture soil. Soil pH under the pasture ranged from 5.3 to 6.5, whereas soil under the *P. radiata* stands ranged from 4.9 to 5.9. Exchangeable Ca was between 70 and 1300 kg ha^{-1} less in the soil under *P. radiata*, compared to the pasture soil. Exchangeable Na and Mg were significantly greater (P =0.021; P=0.019) in soil under *P. radiata*, compared to the pasture soil. The authors attributed the differences in soil Na and Mg to increased dry deposition of sea salt in the forest canopies.

Long-term studies on the effects of afforestation are rare, but Brand et al. (1986) examined the changes in soil characteristics of abandoned farmland in Canada. Forty-six years following afforestation, there was a significant decrease in average pH by an average of 0.86 units. Prior to afforestation, there was no significant difference in soil pH between stands of red pine (*Pinus resinosa*) and white spruce (*Picea glauca*), but after 46 years the white spruce stands were significantly more acidic compared to the red pines. The average decrease in pH for the white spruce and red pine stands was 1.28 and 0.67, respectively.

Changes in soil chemistry following afforestation are affected by the tree species being planted. (Binkley and Valentine, 1991) examined the differences in soil bio-geochemistry of agricultural land 50 years after afforestation with green ash (*Fraxinus pennsylvanica* Marsh), white pine (*Pinus strobus* L.), and Norway spruce (*Picea abies* (L.) Karst). In both water and salt

(0.01*M* $CaCl_2$ and 0.4*M* NaCl) solutions, soil pH was lowest beneath the Norway spruce and highest beneath green ash. Acid neutralizing capacity was also the greatest in soil beneath the green ash (53.5 $kmol_c$ ha^{-1}) and lowest beneath the Norway spruce (15.4 $kmol_c$ ha^{-1}). Exchangeable Ca and Mg in the top 15 cm were 128% and 161%, respectively, greater beneath the green ash compared to the Norway spruce. Cation exchange capacity did not differ between soils, but base saturation differed significantly and was 52% beneath green ash, compared to 29% beneath the Norway spruce.

Berthrong et al. (2009) performed an extensive review of 71 papers published through 2007, examining the effects of afforestation with *Eucalyptus*, *Pinus*, other conifers, and all other vegetation. Afforestation with pines and other conifers resulted in a significant ($P < 0.05$) decrease in soil Ca relative to the control by 31% and 16%, respectively. Afforestation with pines resulted in an 81% increase in soil Na, whereas afforestation with other conifers resulted in a 52% decrease in soil Mg. As a result of the decrease in exchangeable divalent cations, base saturation of soils afforested with pines and other conifers decreased by 21% and 10%, respectively. Exchangeable cations and base saturation are strongly correlated and as a result, afforestation decreased soil pH from 5.7 to 5.4 and 4.6 to 4.4 respectively, for pines and other conifers.

Forest management practices which change stand composition and the dominant species have the potential to alter biological, chemical, and physical processes of the soil. A common management practice in the southern United States is the conversion of hardwood or mixed hardwood-pine stands to pine monocultures through selective cutting of hardwoods (Lane, 1975). Coniferous and deciduous vegetation differ in their ability to cycle nutrients and water, which may result in chemical changes in the soil, alterations in soil biota, and changes in overall ecosystem functions.

Currently, few studies exist on the effects of forest stand conversion on soil chemistry. Lane (1975) examined changes in soil chemistry seven years after conversion of mixed hardwood stands to loblolly pine (*Pinus taeda*). There was no significant change in soil pH after conversion to pine and the soil pH was not significantly different from a control stand that remained in hardwoods. There were also no significant differences in soil P, K, and Ca between the converted stands and the control stands. In a follow up study, Lane (1990) revisited the research area where the mixed hardwood stands were converted to loblolly pine 23 years previously. Similar to the initial report, there were no significant differences in soil pH, Ca, K, or P between the control and converted stands. There were also no changes in soil chemistry within the converted stands over the 23 year period.

Scott and Messina (2009) examined changes in forest floor and soil chemistry 35 years after conversion of mixed pine-oak forests to either mixed oak or loblolly pine forests. The litter thickness on the forest floor within the pine stands was approximately twice as thick (5 to 10 cm) as the litter thickness within the oak stands (0 to 5 cm) and had discernable Oi, Oe, and Oa horizons. Although the litter layer in the mixed oak stands was significantly thinner, the leaf litter had greater concentrations of N and P by 64% and 50%, respectively. Unlike the litter layer there were minimal differences between the two stands, 35 years following the conversion. Soil pH, exchangeable cations, and effective cation exchange capacity did not differ significantly ($P > 0.05$) between the two stands. Similarly, total C and microbial biomass C did not differ between the two stands.

Iwashima et al. (2012) evaluated differences in soil chemical properties between unaltered stands (both deciduous and coniferous) and stands that had been converted (i.e. deciduous to coniferous and coniferous to deciduous) 50 to 60 years earlier. Contrary to the results presented by Lane (1975) and Scott and Messina (2009), the pH of soil beneath the unaltered and converted deciduous stands was significantly greater than the unaltered pine and converted pine stands. Similar to soil pH, exchangeable cations were significantly greater in the deciduous stands compared to the coniferous stands.

Geochemical Oxidation of Sulfides

Abiotic Sulfide Oxidation

The oxidation of sulfide-bearing minerals such as chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), galena (PbS), marcasite (FeS_2), pyrrhotite ($Fe_{1-x}S$), and pyrite (FeS_2) is a prevalent process resulting in the acidification of natural waters (Rimstidt and Vaughan, 2003). Iron-disulfides (FeS_2) are the most common pyrite minerals with pyrite and marcasite being the two major forms (Evangelou, 1995). Pyrite and marcasite have identical chemical composition, but differ crystallographically (isometric and orthorhombic, respectively). Pyrite is commonly found in coal fields, shale deposits, and ore deposits of Au, Ag, Cu, U, and Zn. Pyrite is known to occur in Pennsylvanian-age shale layers in Arkansas and Missouri (Merewether and Haley, 1969; Ainsworth et al., 1982). The distribution of pyrite within geologic strata is not uniformly distributed. Instead, it accumulates in dispersed pockets or clusters (Caruccio & Geidel, 1978; 1980). Massive agglomerations of pyrite are rare and crystals typically vary in size from 400µm to 5µm (Caruccio and Geidel, 1978). Pyrite forms in a reduced environment in the presence of carbon-rich organic matter. The oxidation state of Fe and S in pyrite are +2 and -1, respectively.

Oxidation by O_2

The mechanism and kinetics of pyrite oxidation are complex and can occur through biotic or abiotic processes. The reaction of pyrite upon exposure to water and air are:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \quad (2)$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (3)$$

Oxidation of the pyrite disulfide is shown in equation 1, resulting in the release of ferrous Fe and two protons. The ferrous iron produced in equation 1 is oxidized to ferric iron in equation 2, which immediately hydrolyzes to form ferric hydroxide as shown in equation 3, which subsequently results in the generation of 3 more protons. Following equations 1-3, the oxidation of one mole of pyrite results in the generation of four protons.

Oxidation by Ferric Iron

In addition to oxygen, ferric Fe can also be utilized as an electron acceptor as shown in:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

As shown in equation 4, pyrite oxidation can continue as long as ferric Fe is present or is being generated through equations 1-3 or other processes. The rate of abiotic pyrite oxidation is controlled by pH. Under acidic conditions ($pH < 4.5$) pyrite is oxidized by ferric Fe faster than by O_2 and at a faster rate than ferrous iron is oxidized into ferric iron by O_2 (Nordstrom, 1982). Therefore, equation 2 is recognized as the rate-limiting step of abiotic pyrite oxidation under acidic conditions. Initial research suggested that due to decreasing Fe^{3+} concentrations resulting from the precipitation of Fe-hydroxides, O_2 acted as the primary oxidant of pyrite (Goldhaber, 1983; Hood, 1991). Recent studies have suggested that even at higher pH values, Fe^{3+} is the preferred oxidant and that the role of O_2 is to oxidize Fe^{2+} adsorbed on the pyrite surface, which facilitates the subsequent transfer of electrons from pyrite to Fe^{3+} (Moses and Herman, 1991; Rimstidt and Vaughan, 2003).

Oxidation by Mn(IV) Oxides

The oxidation dynamics of pyrite are further complicated by the ability of certain transition metals to oxidize ferrous Fe. Specifically, it has been observed that ferrous iron can be oxidized in the presence of Mn(IV) oxides (Asghar and Kanehiro, 1981). The reaction is:

$$MnO_2 + 4H^+ + 2Fe^{2+} \rightarrow Mn^{2+} + 2H_2O + 2Fe^{3+} \quad (5)$$

This was demonstrated experimentally when MnO_2 added to anoxic marine sediments significantly increased SO_4 release (Aller and Rude, 1988). Two mechanisms have been proposed for the oxidation of pyrite by Mn oxides; the first is shown in equation 5, the second is direct oxidation of pyrite by MnO_2 as shown by:

$$4MnO_2 + 8H^+ + 0.5FeS_2 \rightarrow 4Mn^{2+} + SO_4^{2-} + 0.5Fe^{2+} + 4H_2O \quad (6)$$

Aller and Rude (1988) reported that oxidation rate was significantly greater with minerals containing Mn^{+4} compared to Mn^{+3} minerals. The reaction was dinitrophenol and azide inhibited indicating biological mediation by bacteria such as *thiobacilli*. Biotic pyrite oxidation has also been experimentally demonstrated using other bacteria.

Oxidation by Nitrate

Under certain conditions, NO_3^- has been observed to act as the terminal electron acceptor during pyrite oxidation, providing another potential mechanism (Van Beek et al., 1988; Postma et al., 1991; Engesgaard and Kipp, 1992; Massmann et al., 2003). The oxidation of pyrite by NO_3^- is thermodynamically favored over oxidation by O_2, but early experimental works demonstrated the inability of nitrate to oxidize pyrite under abiotic conditions. Instead, it was shown that the sulfide within pyrite was oxidized by *Thiobacillus denitrificans,* while *Gallionella ferruginea* oxidized the liberated Fe^{2+} with nitrate (Kölle et al., 1987; Postma et al., 1991). The proposed mechanism of oxidation of pyrite by NO_3^- is:

$$14NO_3^- + 5FeS_2 + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \qquad (7)$$

Biotic Sulfide Oxidation

The two most-studied pyrite oxidizing bacteria are *Thiobacillis ferrooxidans* and *Thiobacillis thiooxidans*, both of which are obligate acidophiles which are able to oxidize S^0 and metal sulfides. Unlike *T. thiooxidans*, *T. ferrooxidans* is also able to oxidize ferrous Fe. It has been suggested that *Thiobacillis ferrooxidans* is a principal catalyst in the oxidation of pyrite because 1) *T. ferrooxidans* is often isolated from acid rock drainage; 2) it has been shown to increase the rate of pyrite oxidation in laboratory experiments; and 3) the observed rate of oxidation of ferrous Fe is five to six times greater than the observed inorganic oxidation rate (Nordstrom, 1982; Evangelou, 1995; Sand et al., 2001; Huynh et al., 2017). The rate of pyrite oxidation is significantly greater in the presence of bacteria than in their absence (Fowler et al., 2001).Two mechanisms of biotic oxidation of pyrite have been observed and are classified into direct metabolic reactions and indirect metabolic reactions. Direct metabolic oxidation requires physical contact between the surface of the pyrite mineral and bacteria, whereas indirect oxidation does not require physical contact: Fe^{2+} is oxidized to Fe^{3+} in solution. A suggested reaction for direct metabolic oxidation of pyrite is:

$$FeS_2 + \frac{7}{2}O_2 + 2H_2O \xrightarrow{\text{Bacteria}} Fe^{2+} + 2SO_4^{2-} + 2H^+ + H_2O \qquad (8)$$

The above equation represents the dissolution of FeS_2 and the immediate oxidation of S_2^- to SO_4^{2-} by surface bound bacteria (Konishi et al., 1990; Evangelou, 1995). Theoretically, the reaction in equation 7 can proceed until all disulfide has been converted to sulfate in contrast to equation 8, where bacteria are only responsible for the oxidation of S_2^-. Palencia et al. (1991) suggested that pyrite is directly oxidized by bacteria and provided the equation:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \qquad (9)$$

Equation 9 is the sum of bacterial-mediated oxidation of S and Fe by O_2. Bennett & Tributsch (1978) also reported the dependency of biotic pyrite oxidation on surface contact and reported that the efficacy of oxidation is dependent on the degree of crystallinity of the pyrite.

Use of Stable Isotopes as Indicators of Pyrite Oxidation

Pyrite oxidation in groundwater or surface waters can be difficult to detect using conventional chemical analyses due to the multitude of potential S and acid sources within a watershed. The oxidation of sulfides results in negligible fractionation when occurring at low pH (pH < 3; [Taylor et al., 1984]). Sulfur isotope enrichment factors (ε_s) of sulfate originating from sulfide oxidation in circumneutral or alkaline conditions range from 0 to 5‰ (Balci et al., 2007). Fractionation of S during controlled pyrite oxidation was also reported to be negligible (Dechow, 1960; Gavelin et al., 1960; Taylor et al., 1984; Massmann et al., 2003).

Minimal $\delta^{34}S$ fractionation during the oxidation of pyrite is useful for isotope studies, due to the large variability in $\delta^{34}S$ of pyrite. Drake et al. (2013) reported a wide range of $\delta^{34}S$ values ranging from -32 to +73‰ in individual pyrite crystals, with minimum and maximum values of -50 and +91‰, respectively. Similarly, Falconer et al. (2006) reported $\delta^{34}S$ values of -45 to

+18‰. The large variability in S isotope composition of pyrite can be attributed to the fact that there are numerous pyrite formation pathways, each of which results in a different S isotope composition in the resulting pyrite. Knowledge of the isotopic composition of the pyrite can be used to identify S sources in groundwater and surface water.

The $\delta^{18}O$ values of sulfate derived from pyrite oxidation are dependent on whether reaction (1) or (4) occurs. Utilization of atmospheric or dissolved oxygen (reaction 1) will yield $\delta^{18}O_{SO4}$ values similar to atmospheric values ($\delta^{18}O = \sim +23.5‰$), whereas utilization of water (reaction 4) will result in $\delta^{18}O_{SO4}$ values representative of typical meteoric water ($\delta^{18}O < 0‰$) (Balci et al., 2007). Measured $\delta^{18}O$ values may vary if multiple reaction pathways are occurring and may be further complicated by differing amounts of abiotic and biotic pyrite oxidation. When pyrite was oxidized in a controlled experiment using a closed system and atmospheric oxygen, the isotopic composition of the residual water became heavier with time, indicating that ^{16}O is preferentially utilized in both biotic and abiotic oxidation of pyrite (Taylor et al., 1984). The enrichment of oxygen isotopes between sulfate and water can range between 0 and +4‰ for acidic abiotic conditions (Balci et al., 2007; Mazumdar et al., 2008; Taylor & Wheeler, 1993; Taylor et al., 1984). Oxygen isotope enrichment between sulfate and oxygen ranges between -9.8 and -4.3‰ for abiotic pyrite oxidation under conditions of varying acidity (Taylor et al., 1984; Balci et al., 2007; Heidel & Tichomirowa, 2011).

Sulfur and O isotopes have previously been used successfully to identify pyrite oxidation as a significant acid or S source. Dogramaci et al. (2017) collected and analyzed 73 surface and groundwater samples throughout the Hamersley Basin in Western Australia to help characterize S cycling in the region. A combination of SO_4^{2-}, Cl^-, and cation concentrations coupled with $\delta^{18}O$, and $\delta^{34}S$ values, were used to identify pyrite oxidation/acid rock drainage as the source of

SO_4^{2-} in the water samples. Water samples collected that had high sulfate values (> 1000 mg/L) also had low $\delta^{34}S_{SO4}$ values that were similar to values obtained from regional pyrite samples. The authors also reported that the presence of carbonate minerals resulted in water samples with high sulfate concentrations, but circumneutral pH. In a similar study, Massmann et al. (2003) collected surface and groundwater samples from 22 locations in a study examining sulfide oxidation and sulfate reduction in the Oderbruch Aquifer in Germany. Two primary sources of SO_4^{2-} were reported in this study: contribution of SO_4^{2-} to the groundwater through infiltration from the river and oxidative weathering of pyrite in the unsaturated zone. Measured $\delta^{34}S$ values of a high SO_4^{2-} concentration pool of water connected to the aquifer were similar to those of regional pyrite values, indicating pyrite oxidation was the primary SO_4^{2-} source. The oxidation of pyrite in the unsaturated zone was attributed to O_2 or NO_3^- acting as the electron acceptor. Tostevin et al. (2016) used S isotopes to identify S contributions to groundwater in contact with the sulfide rich metamorphic rocks of the Otago Schist and to an inland saline lake in New Zealand. Plots of Cl^- against SO_4^{2-} and $\delta^{34}S$ values indicated pyrite oxidation in the groundwater and deposition of marine aerosols as the two primary S sources within the region. Calmels et al. (2007) used $\delta^{34}S$ and $\delta^{18}O$ values of 20 river samples from the Mackenzie River basin in Western Canada to identify S sources in the watershed. Oxidative weathering of pyrite contributed 85% (± 5%) of the sulfate in the surface waters of the Mackenzie River basin. Using the data derived from isotopic analysis, the flux of sulfate originating from oxidative weathering of pyrite was calculated to be 0.13×10^{12} mol/yr.

Effect of Increased Atmospheric CO_2 Concentrations

It is theoretically possible that increased concentrations of atmospheric CO_2 could lead to surface water acidification through the formation of carbonic acid (H_2CO_3). Increased loading of CO_2 in the atmosphere has caused ocean acidification by 0.1 units compared to pre-industrial values (Orr et al., 2005). It is estimated that concentrations of atmospheric CO_2 will reach 550 ppmv by 2050 and 788 ppmv by 2100 under the IS92a business-as-usual scenario, which may reduce ocean pH by another 0.3 to 0.4 units (Haugan and Drange, 1996; Brewer, 1997). Carbonic acid is formed when CO_2 dissolves in and subsequently reacts with water:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \tag{26}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{27}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{28}$$

The potential changes in pH of pure water due to increased concentrations of atmospheric CO_2 can be calculated using:

$$K_{CO2} = \frac{(H_2CO_3)}{(H_2O)pCO_2} \tag{29}$$

$$K_1 = \frac{(H^+)(HCO_3^-)}{(H_2CO_3)} \tag{30}$$

Assuming a temperature of 25°C, the equilibrium constants of K_{CO2} and K_1 are $10^{-1.47}$ and $10^{-6.35}$, respectively (Plummer and Busenberg, 1982). These values can be inserted into equation 29 and 30. Assuming an atmospheric CO_2 concentration of 350ppm ($pCO_2 = 10^{-3.5}$), the activity of H_2CO_3 can be solved by:

$$10^{-1.47} = \frac{(H_2CO_3)}{10^{-3.5}} \tag{31}$$

$$(\mathrm{H_2CO_3}) = 10^{-4.97} \tag{32}$$

Using the activity of H_2CO_3 and the charge balance equation, the pH of pure water in equilibrium can be calculated by:

$$(\mathrm{H^+})(\mathrm{HCO_3^-}) = \mathrm{K_1}(\mathrm{H_2CO_3}) \tag{33}$$

$$(\mathrm{H^+})^2 = 10^{-6.35}10^{-4.97} \tag{34}$$

$$(\mathrm{H^+}) = 10^{-5.66} \tag{35}$$

$$\mathrm{pH} = 5.66 \tag{36}$$

Using the estimated CO_2 concentrations from the IS92a business-as-usual scenario, surface water pH will decrease to 5.52 and 5.44 by 2050 and 2100, respectively. The magnitude of decrease in surface water pH from increased CO_2 concentrations would be reduced by the alkalinity of the water. Based on these calculations, it appears that increased concentrations of CO_2 will not have a significant impact on surface freshwater water acidification in the next century. Although the kinetics of carbonic acid formation in natural waters suggests that acidification may not occur, some studies emerging from Europe are suggesting a direct and/or indirect relationship between increased CO_2 and surface freshwater water acidification (Nydahl et al., 2017; Hannan and Rummer, 2018).

Atmospheric Deposition of Acid

Acid or acid-forming compounds can enter an ecosystem in a variety of forms and through numerous pathways. Atmospheric acid deposition can occur as wet deposition (i.e. rain or snow), dry deposition of aerosols, occult deposition (i.e. mist, fog, or cloud droplets), and/or absorption on wet surfaces (Ulrich, 1989; Kennedy, 1992). The effects of acid deposition on a terrestrial or aquatic ecosystem are dependent on the pollutants that react with the ecosystem, rather than what was emitted. Substantial acidification of surface waters has been observed in the United States, Canada, Northern and Eastern Europe, Japan, China, Russia, and South America (Schindler, 1988).

Two strong acids, nitric (HNO_3) and sulfuric (H_2SO_4) are the most common acids within precipitation and can originate from several sources. In addition to nitric and sulfuric acid, precipitation may contain other acids such as hydrochloric (HCl), formic (HCOOH) and acetic (CH_3COOH), depending on the environment. Carbonic acid (H_2CO_3) forms in precipitation through the reaction of water with atmospheric carbon dioxide. Although precipitation is naturally acidic (pH ~ 5.6), the proton concentrations are minimal, at approximately 2.5 µmol (Kennedy, 1992). The amount of acid occurring naturally in precipitation is sufficient to accelerate weathering processes, but is too low to be a major cause of environmental degradation at current atmospheric CO_2 concentrations. Additional cations besides H^+ can be present, including Ca^{2+}, Mg^{2+}, Na^+, K^+, and NH_4^+. The ability of precipitation to acidify an ecosystem is a function of the ratio between acids (strong, weak, and organic) and base cations. Wet deposition of acid is often the most studied and debated form of atmospheric deposition, but dry deposition contributes substantial loads of acid-forming compounds such as sulfur oxides (SO_x), nitrogen oxides (NO_x), and ammonia (NH_3). Anderson et al. (1999) reported that 25% to 50% of total S and N deposition in the high altitudes of the northeastern United States originated from cloud and fog depositions. The combination of wet and dry deposition of acid-forming compounds has had significant effects on ecosystems since the industrial revolution.

Nitrogen Oxides

Nitrogen oxides (NO and NO_2) can enter the atmosphere from natural or anthropogenic sources such as coal-fired power plants, automobile emissions, or soil de-nitrification. Once in the atmosphere, NO_x compounds can react with atmospheric oxygen to form nitrogen pentoxide, followed by reaction with water to form nitric acid:

$$NO + 1/2O_2 \rightarrow NO_2 \qquad (10)$$

$$2NO_2 + 1/2O_2 \rightarrow N_2O_5 \qquad (11)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (12)$$

Nitric acid can also be formed at a slower rate by the direct reaction of NO_x compounds with water:

$$3NO_2 + H_2O \rightarrow 2HNO_3 \qquad (13)$$

The ability of nitric acid to form in either dry or wet conditions increases the amount deposited in watersheds. Regions dominated by either urban development or agricultural production tend to have substantial amounts of nitric acid.

Both ammonia (NH_3) and its reaction by-product ammonium (NH_4^+) are important components of the nitrogen cycle and are important in the generation and deposition of acid. The dominant source of NH_3 emissions is livestock and poultry production, which accounts for more than 90% of total NH_3 emissions in most countries (ApSimon et al., 1995). Ammonia has a short residence time in the atmosphere compared to other compounds and is rapidly converted to ammonium in the presence of water. Within 50 km of the emission source, approximately 6% of NH_3 is wet deposited and 40% is dry deposited (Asman and van Jaarsveld, 1992).

Ammonia readily reacts with SO_3 in the atmosphere to form sulfamic acid (H_3NSO_3), which subsequently reacts with water to form ammonium bisulfate (NH_4HSO_4) (Shen et al., 1990; Larson and Tao, 2001; Bandyopadhyay et al., 2017):

$$SO_3 + NH_3 \rightarrow H_3NSO_3 \tag{14}$$

$$H_3NSO_3 + H_2O \rightarrow NH_4HSO_4 \tag{15}$$

The production of ammonium bisulfate in the atmosphere neutralizes sulfuric acid and increases precipitation pH. The role of NH_3 in acid rain generation is further complicated by the ability of NH_3 to hydrolyze atmospheric SO_2 to sulfurous acid (H_2SO_3) as well as the hydrolysis of SO_3 to H_2SO_4 (Larson and Tao, 2001; Bandyopadhyay et al., 2017). It was estimated by ApSimon et al. (1987) that conversion of H_2SO_4 in the atmosphere can be increased by an order of magnitude in the presence of NH_3.

In addition to generation in the atmosphere, atmospheric NH_3 enters the soil through wet or dry deposition, immediately reacts with soil moisture to form ammonium, and is subsequently nitrified by soil bacteria releasing acid into the soil:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ \tag{16}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{17}$$

Thus, when nitrification occurs, each mole of deposited NH_3 results in the generation of 2 moles of protons in the soil. Ammonium can also undergo assimilation at the root surface, which results in deprotonation and release of 1 mole of H^+ per mole of NH_4^+ assimilated (Rengel, 2003).

$$NH_4^+ + R\text{-}OH \rightarrow R\text{-}NH_2 + H_2O + H^+ \tag{18}$$

Increased concentrations of NH_4^+ and SO_4^{2-} in the Netherlands was reported to decrease soil pH to between 2.8 and 3.5 (Van Breemen *et al*., 1982). The authors attributed the soil acidification to oxidation of both NH_4^+ and SO_4^{2-} into their respected strong acids after entering the soil via throughfall. Ammonium can also volatilize to $NH_{3(g)}$ from soil in alkaline conditions. Ammonium reacts with OH^- ions within soil, resulting in a net decrease in soil pH:

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \tag{19}$$

Ammonia volatilization typically occurs at pH ≥ 7.5 which makes it unlikely to occur in soils which have already been acidified.

Globally, N addition to soils has reduced soil pH on average by 0.26 in terrestrial ecosystems (Tian and Niu, 2015). In a substantial review of the literature regarding soil acidification from N additions, Tian and Niu (2015) reported greater acidification of grasslands from N additions, compared to forested ecosystems. Forested ecosystems, comprised predominantly of deciduous species, were reported to be significantly affected by N additions, whereas forested ecosystems comprised predominantly of conifer species were generally unaffected by N additions. Soil pH began to decrease at a statistically significant rate, once ambient N deposition rates exceeded 0.5 g m^{-2} yr^{-1}.

Sulfur Oxides

Similar to nitric acid, the production of sulfuric acid in the atmosphere can be attributed to anthropogenic sources, primarily the combustion of coal for the generation of energy; it can also enter the atmosphere from the decomposition of organic matter. The predominant S species that is oxidized is H_2S which, reacts with atmospheric oxygen, as shown by:

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O \tag{20}$$

More than half of the S in coal used in coal-fired power plants is present as pyrite, which reacts with oxygen to produce sulfur dioxide, as shown by:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \tag{21}$$

Once in the atmosphere, sulfur dioxide is further oxidized to sulfur trioxide and then sulfuric acid. The reaction is catalyzed by the presence of sunlight and atmospheric humidity at the rate of approximately 0.1% per hour (Bufalini, 1971). The reaction of sulfur dioxide oxidation and sulfuric acid is:

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{22}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{23}$$

The rate of production of sulfuric acid is further increased in the presence of other pollutant species, including NO_x compounds. Nitric acid and NO_x compounds react with SO_2 to form sulfuric acid by:

$$2HNO_3 + H_2O + 2SO_2 \rightarrow 2H_2SO_4 + NO + NO_2 \tag{24}$$

$$SO_2 + H_2O + NO_2 \rightarrow H_2SO_4 + NO \tag{25}$$

Effects of Surface Water Acidification on Biological Communities

Acidification of surface waters occurs throughout the world and can negatively affect aquatic biological communities. Surface waters, especially those adjacent to thin and/or poorly-buffered soils, are particularly susceptible to acidification and subsequent harm to aquatic life. Reduction of pH to ~4.5 can be a direct cause of aquatic life (macroinvertebrate and fish) mortality, depending on species, size, age, and genetic origin (Aston et al., 1989).

In typical freshwater streams and rivers, benthic macroinvertebrates are plentiful, with insects such as *Ephemeroptera, Plecoptera*, *Trichoptera*, and *Diptera* being the most common. Healthy streams with a pH greater than 6 can have between 70 – 90 unique taxa, but as pH decreases below 5.7 and Al becomes mobilized, community composition can change and species richness can be affected (Gensemer and Playle, 1999). Stream acidification affects benthic macroinvertebrate and fish communities by 1) altering the chemical composition of the water, creating intolerable conditions for certain species; 2) changing chemical composition, resulting in alteration of food supply; and 3) reducing fish community diversity, which alters the predator-prey dynamics. These three mechanisms are most likely to interact to determine invertebrate community composition.

H and Al Toxicity

Aluminum, the third most abundant crustal element (Gensemer and Playle, 1999), has little known biological function, and it is generally agreed that biological systems do not require Al to function properly (Eichenberger, 1986; Gensemer & Playle, 1999; Wood, 1985; Wood, 1984). The solubility of Al^{3+} in freshwater systems is driven primarily by pH, with solubility increasing as pH decreases. In solution, Al may exist as the trivalent cation or as hydroxy-aluminum species (i.e. Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, and $Al(OH)_4$). The properties and behavior of these Al-hydroxy species are dependent on pH, ionic strength, and the presence of inorganic ligands such as F^- and SO_4^{2-}. Any of the Al ions can bind with organic material such as fulvic and humic acids and can undergo cation exchange on the surfaces of minerals in soils and sediments. In the absence of Al, low pH (increased activity of H^+) can still be detrimental to aquatic organisms by altering tissue structure or decreasing blood pH, resulting in acidification of tissues and alteration of intracellular enzymes (Thomas, 1989).

Tolerance of Fish to Acidification

Acute toxicity of Al in fish has been attributed to adsorption to the gill surface, interfering with respiratory and iono-regulatory functions (Gensemer and Playle, 1999;

Alexopoulos et al., 2003). Fish excrete a mucus layer rich in NH_3 around their gills, which readily binds Al^{3+} resulting in respiratory impairment, ultimately leading to asphyxiation (Exley et al., 1996). Early research (Schofield & Trojnar, 1980) attributed acute Al toxicity to the precipitation of Al-hyroxides at the gill surface. When examining Al toxicity in rainbow trout, Exley et al. (1996) reported a strong correlation between acute toxicity and the strength of Al association with the gill. Following the binding of Al to the gill mucus, polymerization of Al into larger aggregates can result in interference with O_2 and CO_2 diffusion (Poleo, 1995; Exley et al., 1996). Bertsch and Parker (1996) reported that Al polymerization occurs at the gill due to the alkalinization of the micro-environment surrounding the gill by NH_3 release. The increased pH of the gill environment results in a decrease in Al solubility and subsequent precipitation of Al polymers on the gill surface. Positively charged Al species (e.g., $Al(OH)^{2+}$) can also bind to negative charged groups on the gills, furthering interference with the respiratory system. The presence of Ca^{2+} in acidified water mitigates the iono-regulatory effects of Al, increasing the Al threshold for toxicity. In general, the interaction between concentrations of Al, Ca, and H^+ (pH) dictates the toxicity of acidified waters for fish. Stepwise multiple linear regression performed by Wright & Snekvik (1978) indicated that log [Ca^{2+}] and pH were the most statistically correlated parameters for determination of fish status in Norway.

Exposure of European carp (*Cyprinus carpio*) to acidified water (pH 5.2) and 200 µg Al L^{-1} reduced Ca influx by an average of 33% and a maximum of 55% (Verbost et al., 1992). There was no reduction in Na influx but Ca and Na efflux increased significantly when the fish were exposed to 400 µg Al L^{-1} for more than one hour. In a similar experiment, Poléo et al. (1995) exposed crucian carp (*Carassius carassius*) to 290 µg Al L^{-1} at pH 5.2 for 25 days and reported minimal toxicity despite polymerization of Al on the gill surface demonstrating the potential Al tolerance of anoxia-tolerant fish. The growth of fathead minnows (*Pimephales promelas*) in acidic waters (pH 6.0, 5.5, and 5.2) in the presence of Al (30 to 60 µg Al L^{-1}) resulted in major changes in the histopathology and reduced spawn success at pH 5.5 in the presence of Al and at pH 5.2 in the both the presence and absence of Al (Leino et al., 1990). In a similar experiment, Leino and McCormick (1993) exposed largemouth bass (*Micropterus salmoides*) to acidic conditions (pH 5.0 and 4.5) with and without Al (30 µg Al L^{-1}). When exposed to acidic conditions and Al, gill function was reduced significantly by hyperplasia and blood osmolalities declined to lethal levels, resulting in high mortality rates. Largemouth bass lost osmotic homeostasis when exposed to pH 4.5 and 5 water and 30 µg Al L^{-1} resulting in increased mortality. The mortality rate was amplified when the experiment was conducted in soft water (Ca = 1.5 mg L^{-1}; McCormick & Jensen, 1992). Robust redhorse (*Moxostoma robustum*) were rapidly exposed to acidic waters (pH 4.3 and 4.0), representative of episodic acidification conditions (Walsh et al., 1998). At pH 4.0, the mortality rate was 30% after 6 hr and 100% at 11 hr. At pH 4.3, the mortality rate was 50% after 22.5 hr and 90% at 28 hr but never reached 100%.

Experiments evaluating the toxicity of acidification on fish have primarily focused on trout and salmon species. Rainbow trout (*Salmo gairdneri*) and salmon (*S. salar*) exposed to 200 µg Al L^{-1} at pH 5 for 4 to 7 d had reduced activities (25-40%) of Na-K-ATPase and carbonic anhydrase, enzymes important for ion regulation, within the gills (Staurnes et al., 1984). The decrease in Na-K-ATPase and carbonic anhydrase accompanied an 8% to 39% decrease in plamsa Cl and Na concentrations. Staurnes et al. (1984) identified Al as the sole cause of disruption in the ion regulation system. Results from Witters (1986) agreed with Staurnes et al. (1984) when rainbow trout exposed to 350 µg Al L^{-1} for 3.5 hr at pH 4.1 lost ions through the gills at a rate twice as fast as fish exposed to pH 4.1 in the absence of Al. Brook trout (*Salvelinus fontinalis*) exposed to pH 4.4 to 5.2 and Al concentrations of 110 to 1000 µg Al L^{-1} for 11 d had significant net losses of Cl^- and Na^+ resulting from decreased ion influx and stimulation of ion efflux (Booth et al., 1988). The presence of Al significantly inhibited Na^+ influx and increased Na^+ efflux, when compared to acidic waters without Al. Malte and Weber (1988) demonstrated the respiratory effects of Al on adult rainbow trout by eliminating the iono-regulatry interference through the addition of 150 m*M* NaCl to the water. In pH 5.0 soft water (50 µ*M* Ca) and Al concentrations of 32 µ*M* Al, the rainbow trout suffered severe respiratory stress characterized by low P_{O2}, high P_{CO2}, hyperventilation and high blood lactate concentrations. The addition of NaCl mitigated reductions in plasma Cl^- concentrations but survival times did not differ between treatments (presence and absence of NaCl) indicating impeded gas exchange as the primary cause of death under acidic conditions.

Tolerance of Invertebrates to Acidification

Compared to fish, invertebrates are generally more tolerant to increased concentrations of Al (Gensemer & Playle, 1999; and references within). As with fish, the toxic effects of low pH are attributed to respiratory stress, disruption of ion regulation (primarily Na^+ and Cl^-), and increased membrane permeability (Camargo, 1995; Havas & Advokaat, 1995; Courtney & Clements, 1998). Aluminum interference with respiratory function is uncommon in invertebrates due to the absence of NH_3 in the gill micro-environment. The tolerance of an invertebrate to acidification also differs among life stages and has been attributed to differing membrane permeabilities, ion regulation mechanisms, and habitats (Havas and Advokaat, 1995). Laboratory and field studies have reported greater susceptibility to increased H^+ concentrations, but sudden changes in Al chemistry can result in acute toxicity.

Several experiments have been performed on varying invertebrate species, which have reported varying thresholds for toxicity. At a circumneutral pH (6.6 to 7.2), Truscott et al. (1995) exposed *Lymnaea stagnalis* to 100, 200, 500, and 1000 µg Al L^{-1} and reported decreased invertebrate activity with increasing concentrations. Increasing concentrations of Al had a greater effect on juvenile snails, which was attributed to either a greater surface area to volume ratio and/or greater metabolic rates. When snails were raised in concentrations of 0, 100, and 500 µg Al L^{-1} for one year, there was no difference in snail activity between treatments, indicating acclimation to the increased Al concentrations. In a similar study, *L. stagnalis* was exposed to Al concentrations ranging from 38 (control) to 285 µg Al L^{-1} for a 30-d period (Elangovan et al., 1997). Toxicity was minimal and increased from 5% at the control rate to 13% at the greatest rate. The greatest accumulation of Al was in the kidneys, digestive glands, and stomachs of the snails. Concentrations of Al within the kidneys returned to ambient conditions after 20 d, whereas Al concentrations within the stomach and digestive track continued to increase over the 30 d duration of the experiment. The decrease in Al within the kidneys indicates that the kidneys were an important regulatory site for Al exposure.

Havas (1985) examined the effects of Al and H toxicity on *Daphnia magna* at pH ranging from 4.5 to 6.5 and Al concentrations ranging from 20 to 1020 µg Al L^{-1}. Aluminum was most toxic at pH 6.5 at 320 and 1020 µg L which was attributed to Al oversaturation and subsequent precipitation. At pH 5, toxicity of *D. magna* was attributed to H^+ rather than Al at a concentration of 1020 µg L. When pH was decreased to 4.5, Al temporarily ameliorated H^+ toxicity. In a similar experiment, Havas and Likens (1985) studied the sensitivity of *Daphnia* *catawba*, *Holopedium gibberum*, *Chaoborus punctipennis*, and *Chironomus anthrocinus* to Al concentrations of 20, 320, and 1020 µg Al L^{-1} at pH 3.5 to 6.5. *Daphnia catawaba* demonstrated the greatest sensitivity to pH with rapid death at pH < 5.0. *Holopedium gibberum* was tolerant down to pH 4 whereas *C. punctipennis and C. anthrocinus* were tolerant down to pH 3.5. Minimal toxicity was attributed to Al with the exception of increased mortality rates for *D. catawaba*. The authors concluded that mortality in acidic environments would most probably occur due to decreased food availability or predation, rather than chemical toxicity.

The presence of 200 µg Al L^{-1} at pH 4.5 increased the toxicity of littoral macroinvertebrates *Hyalella Azteca*, *Paratanytarsus* sp., and *Zavrelimyia* sp compared to pH 4.5 alone (Havens, 1993). Similar to Havas (1985), Havens (1993) also reported brief amelioration of H^+ toxicity by Al at pH 4.5 for *Cainis* sp. and *Enallagma* sp. *Arrenurus* sp. demonstrated the greatest tolerance, remaining unaffected by the pH 4.5 treatment with or without the addition of Al. Havens (1993) hypothesized that the presence of gills and/or the greater surface area explained the greater sensitivity of *H. Azteca*, *Enallagma* sp., and *Caenis* sp.

Another way crayfish can be affected by increased concentrations of H^+/Al is through interference with Ca uptake. Calcium is utilized by crayfish to harden the new exoskeleton following molting. Malley & Chang (1985) reported a 30% reduction in Ca uptake by O*rconectes virilism* when water pH was adjusted to pH 5.5 and was reduced to 20% in the presence of Al (200 to 1000 µg Al L^{-1}). The severity of Ca uptake inhibition by the crayfish was not affected by increasing Al concentration, which was attributed to the limited solubility of the Al salts used in the experiment. The reduction in Ca uptake during post-molting exoskeleton hardening by crayfish further reduces the survival of a species that is already acid-sensitive. When three species of common Ontario crayfish (*Orconectes propinquus, Orconectes rusticus,* and *Cambarus robustus*) were exposed to varying levels of pH (4.5 to 5.0) and Al (1 to 2 mg L^{-1}) in soft water (~60 µM) for 15 d, all three species had significant mortality rates, but this mortality was not amplified by the increased Al concentrations. A combined laboratory bioassay and survey of 305 acid-sensitive Canadian lakes with pH ranging from 4.5 to 7 ordered the susceptibility of crustacean zooplankton from the least to the most tolerant as *Daphnia galeata mendotae* < *Daphnia retrocurva* = *Skistodiaptomus oregonensis* < *Diaphanosoma birgei* < *Mesocyclops edax* < *Bosmina longirostris* (Havens et al., 1993). Although thresholds for toxic levels of acid and Al differ by study, acidification of surface waters has detrimental, and often irreversible effects on aquatic biology.

Conclusion

Due to legislative accomplishments throughout the world over the last 50 years, there has been a significant decrease in the acidification of surface waters. Unfortunately, surface waters are still susceptible to acidification and watersheds are still impaired due to acidity. Non-point sources of acid are difficult to identify and even more difficult to mitigate. Excluding point sources, the most common contributors of acid to surface waters are acid rock drainage, atmospheric deposition, and changing vegetative composition.

The number of ecosystems damaged by acidic precipitation, which once damaged ecosystems throughout the world, is consistently decreasing due to reductions in anthropogenic emissions. Although there have been substantial reductions in acidic precipitation, densely-populated regions still receive precipitation that is more acidic compared to rural regions. Acidic precipitation in regions low in acid neutralizing capacity is especially damaging due to the lack of buffering capacity in the watersheds. Episodic acidification resulting from acidic precipitation is especially damaging to ecosystems due to the sudden change in chemical composition.

The oxidation of sulfide-bearing minerals, which can occur through several pathways, produces sulfuric acid which can contaminate surface or groundwater. In extreme cases, acid rock drainage entering surface waters has had $pH < 1.0$ causing immediate, and often irreversible damage. In addition to extreme acidity, acid rock drainage often contains tailings from mining processes, contributing large concentrations of toxic metals and trace elements to aquatic ecosystems. Acid rock drainage can occur on the surface and enter surface waters through overland flow or can occur within the underlying geology, entering surface waters through groundwater. In the presence of acidic precipitation, identification of sulfate sources can be difficult, but the use of stable isotopes can help determine potential sulfide oxidation is a contributing factor.

Altering the species composition of above-ground vegetation through afforestation of prairie and/or agro-ecosystems or conversion of deciduous stands to conifers, changes soil and hydrological characteristics of a watershed. Growth of trees on previously unforested land requires a significant amount of nutrients, which can deplete the soil of base cations resulting in soil acidification. If the trees are continuously harvested, the soil is effectively mined of these elements and has difficulty recovering quickly. Acidification of soil, especially riparian soil, can increase loading of acid and toxic elements such as Al to streams, rivers, and lakes. Conversion of hardwood stands to conifers introduces acidic needle litter, which can acidify the forest floor and surface mineral soil horizons. Conversions of hardwood stands can alter or reduce the quantity of water reaching surface waters, which can change base flow characteristics.

Increased acidity in aquatic ecosystems increases the mortality rate of fish and invertebrates, which will negatively affect species diversity and richness of aquatic ecosystems. Decreasing pH increases the solubility of Al, which interferes with iono-regulatory and respiratory systems. In fish, free Al binds to the gill surface and polymerizes interfering with O_2 and CO_2 diffusion. Macroinvertebrates are more tolerant to increased concentrations of Al, but increased concentrations of H^+ interferes with ion regulation and alters membrane permeability, increasing mortality. Regardless of the source, acidification of surface waters is detrimental and the negative effects can prove difficult to reverse. The non-point sources of acidity reviewed in this paper are anthropogenic in origin and can be prevented through thorough research and planning.

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Chapter Two: Are Soils Beneath Coniferous Tree Stands More Acidic than Soils Beneath Deciduous Tree Stands?

Abstract

In 2008, the Mulberry River, a National Wild and Scenic River, was listed as impaired due to low pH (below pH 6.0). Over the last 50 years, the volume of conifers in the Ozark region has increased 115% since 1978 which may result in the acidification of nearby aquatic ecosystems. The objective of this study was to determine if differences exist in soil and litter chemical properties between deciduous and coniferous tree stands. Aboveground litter (n=200) and soil (n=400) at 0- to 5- and 5- to 15-cm depths were collected at paired deciduous and coniferous stands at 10 locations within the Mulberry River watershed and analyzed for a suite of chemical parameters. There were no differences ($P>0.05$) in several measures of soil acidity between deciduous and coniferous stands. Litter collected from the coniferous stands was more acidic than deciduous litter (4.4 vs 4.7; $P<0.05$). Cation exchange capacity, exchangeable Ca and Mg, and water soluble P and Mg contents differed ($P<0.05$) by stand and depth. Cation exchange capacity and exchangeable Ca and Mg were greatest in the 0- to 5-cm depth interval of the coniferous stands. Water soluble P and Mg contents were greatest within the 0- to 5-cm depth interval which did not differ ($P>0.05$) between stand but were greater than the 5- to 15-cm depth interval. Although limited to the top 15-cm of soil, the similarity in soil acidity between stands suggests that conifer growth may not be a substantial source of acidity to the Mulberry River.

Introduction

In 2008, the Mulberry River, a National Wild and Scenic River within the Ozark National Forest, was placed on the EPA's 303(d) list of impaired water bodies by the Arkansas Department of Environmental Quality (ADEQ) due to the low pH of a 14.7 km segment of the river (Shafii, 2008). Arkansas DEQ defines a waterbody as impaired due to acidity when pH is below 6.0 which was reported for two consecutive samples in 2005. In 2016, two more segments were added to the EPA 303(d) list of impaired bodies because of low pH levels, increasing the length of the river classified as impaired from 14.7 to 68.7 km.

Changes in land use can cause changes in soil properties which, in turn, can lead to degradation of surface waters. Afforestation of grasslands and prairies have been linked to stream acidification in several ecosystems (Nilsson et al., 1982; Hornung et al., 1987; Jenkins et al., 1990a; Farley et al., 2009). Less is known about the effects on soil properties of converting hardwood stands to coniferous stands but because pine needles can be considerably more acidic than the leaves of deciduous trees (Billett et al., 1988), conversion of deciduous forests to pine may lead to soil acidification, which can cause acidification of nearby surface waters. Iwashima et al. (2012) evaluated differences in soil chemistry between unaltered stands (both deciduous and coniferous) and stands that had been converted (i.e. deciduous to coniferous and coniferous to deciduous) 50 to 60 years earlier. The pH of soil beneath the unaltered and converted deciduous stands was greater than the unaltered pine and converted pine stands. Similar to soil pH, exchangeable cations were greater in the deciduous stands compared to the coniferous stands. The results reported by Iwashima et al. (2012) were similar to those reported by Fenwick and Knapp (1982) who reported acidification of a sandy soil following the partial replacement of an oak woodland with pine.

Approximately 95% of the Mulberry watershed is forested and is intensely managed by the United States Forest Service (USFS). Forest management practices in the state have altered, considering pine tree coverage in Arkansas has increased from 23,000 hectares in 1952 to nearly 1.2 million hectares in 2005 (Rosson and Rose, 2010).The volume of live-tree softwoods increased in the Ozark region of Arkansas from 20 million cubic meters in 1978 to 43 million cubic meters in 2005 (Beltz et al., 1992; Rosson and Rose, 2010).

Acidification of forest soils has typically been attributed to growth of conifers, but soil under deciduous tree stands can also have pH values between 4.5 and 5 (Binkley, 1995). Tamm and Hallbacken (1986) reported strong acidification (~1 pH unit) of soil in Sweden after 55 yr of growth of Norway spruce (*Picea abies*) and beech (*Fagus spp.*) trees. Despite the strong acidification, there were no differences in acidity of soils between the Norway spruce and the beech stands. In a similar experiment in Ontario, Canada, Brand et al. (1986) examined the change in pH of afforested agricultural soils under Scots pine (*Pinus sylvestris*), Jack pine (*Pinus banksiana*), red pine (*Pinus resinosa*), and white spruce (*Picea glauca*) over a 46 yr period. Soil pH under the pine stands on average changed from 6.0 to 5.3 whereas the soil under the white spruce stands on average decreased from 6.0 to 4.7. Jenkins et al. (1990) observed a decrease in stream pH following afforestation of arable lands. The decrease in stream pH was attributed to base depletion of the river. During the experiment there was no increase in H^+ concentrations indicating the change in pH was the result of the decrease in alkalinity. The objective of this study was to determine if differences in soil and litter chemical characteristics exist at two depth intervals between soils under mature deciduous and coniferous tree stands in order to assess the possibility that conversion of hardwood stands to pine is responsible for acidification of the Mulberry River.

Materials and Methods

Description of Study Area and Sampling

Ten sampling sites were identified in the Ozark National Forest in Arkansas. Their locations are shown in Figure 2-1a. Each of the 10 sites were characterized by adjacent stands of deciduous and coniferous vegetation which had similar topography, parent material, soil series, and were managed using similar practices. The soils of the sampling sites were silt loam typic Udults with clay contents ranging from 2 to 8 % (w/w). The deciduous stands were a mix of oak (*Quercus* spp.), Maple (*Acer* spp.), and Elm (*Ulmus* spp.) and the coniferous stands were a mix of shortleaf (*Pinus echinata*) and loblolly (*Pinus taeda*) pine. At each stand, leaf/needle litter and soil were collected at 10 points along a 50-m transect at 5 m intervals. An example of the sampling scheme is shown in Figure 2-1b. At each sampling point, leaf/needle litter was collected from a 0.5 m^2 area (n=200; 10 sites x 2 stands x 10 replicates). Following collection of leaf/needle litter, approximately 1 kg of soil was collected from the 0- to 5- and 5- to 15-cm depth intervals of the sampling area using a shovel (n=400; 10 sites x 2 stands x 2 depths x 10 replicates). Following collection of litter and soil samples, the method of Page-Dumroese et al. (1999) was used to estimate soil bulk density. This method involves estimating the volume of the extracted soil samples by filling the excavation pits with water to determine pit volume. Rocks that were within the sampling pits were collected and weighed and used in bulk density calculations using an assumed particle density of 2.65 g cm^{-3}. Upon returning to the laboratory, leaf/needle litter and soil samples were dried for 72 hours at 60°C in a forced-air drier prior to analyses and then ground to pass a 2mm sieve.

Soil and Litter Analyses

Mehlich-3 extractable nutrient and metal concentrations of soils were determined by shaking soil samples at an extractant:soil ratio of 10:1 for 5 minutes and then filtered through Whatman #42 filter paper (Zhang et al., 2014). Similarly, water soluble nutrient and metal concentrations were determined by shaking soil samples at a water:soil ratio of 10:1 for 1 hr and then vacuum filtering through a 0.45 µm membrane filter. The filtrates were then analyzed for Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Ti, and Zn by inductively coupled plasma optical emission spectrometry (ICP-OES) on an Agilent 5110 ICP-OES system (Agilent Technologies, Santa Clara, CA). Soil pH in water (pH_{H2O}) and electrical conductivity (EC) were measured following shaking of soil samples at a water:soil ratio of 10:1 in a reciprocating shaker for 1 hour. Soil pH (pH_{KCl}) was also measured on 2*M* KCl:soil slurries following a 1 hour shaking period in a reciprocating shaker. Total extractable acidity (TEA) was measured using the $BaCl_2$-TEA method described by Burt (2014) and Seifferlein et al. (2005). Cation exchange capacity (CEC) was determined by shaking soils in 0.5*M* $BaCl_2$ in an extractant:soil ratio of 10:1 for 1 hour and summing exchangeable Al, Ca, K, Mg, and Na, plus TEA from the $BaCl_2$-TEA method. Base saturation was calculated by dividing the sum of non-acid cations (i.e., Ca, K, Mg, and Na) by the total CEC. Acid neutralizing capacity (ANC) was determined by adding 25 mL of standardized 0.1*M* HCl to 2.0 g of soil and then titrating to pH 7.0 using standardized 0.1*M* NaOH (Ahern et al., 2004).

Total C and N of leaf litter and mineral soil were determined by combustion at 900°C using an EAS VarioMax CN analyzer. Due to the absence of carbonates, total soil C is reported as total organic C (TOC). Soil water soluble and 2*M* KCl extractable NH_4^+ and NO_3^- were determined by shaking samples in water or 2*M* KCl in a reciprocating shaker for 1 hour and then filtering the extract through a Whatman 42 filter. Extracts were analyzed using a SAN++ automated wet chemistry analyzer (Skalar, Buford, GA).

Leaf/needle litter pH was measured following shaking of ground litter samples at a water:litter ratio of 10:1 in a reciprocating shaker for 1 hour. Total concentrations of nutrients and metals were determined by ICP-OES following digestion in concentrated HNO_3 and H_2O_2 at 140°C for 3 hours (Zarcinas et al., 1987). Soil and litter contents (mass/area) were calculated from concentration (mass/mass) data using the soil bulk density or forest floor mass.

Statistical Analyses

Two separate models were analyzed to elucidate the relationship between soil and leaf litter chemical characteristics to tree stands (fixed effect) in efforts to identify potential acidification sources as it relates to land use. In the first model, a two-factor analysis of variance (ANOVA) was used to identify the effects of stand, depth, and their interactions on soil chemistry. Ten replicates of two treatments were established in a split-plot arrangement of a randomized complete block design. The main-plot treatment was the stand (i.e., deciduous vs coniferous) while the split plots were the two depths (i.e., 0- to 5- and 5- to 15-cm depth intervals). Site location was considered a random effect. The first model was used to evaluate the effects of stand, depth, and their interactions on soil pH (water and KCl extractable), TOC, TN, NH_4^+, NO_3^-, TON, C:N ratio, EC, CEC, ANC, TEA, and elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Ti, and Zn). In the second model, a one-factor ANOVA was performed to evaluate the effects of tree stand on leaf/needle litter pH, TC, TN, C:N ratio, and concentrations/contents of 21 elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Ti, and Zn). Elements not reported in the results section were below the detectable limit. For both models, ANOVA assumptions of normally-distributed residuals (Shapiro-Wilk test) and homogeneity of variances (Levene's F-test) were confirmed. When significant differences were found, pairwise post-hoc comparisons of the least square means were conducted using Least Significant Difference (LSD) at $P \leq 0.05$. Mean separations were performed by the SAS macro 'pdmix800' (Saxton, 1998) with Fisher's with a Type-I error rate of 5%. Elements not reported in the results section were below the detectable limit.

Results

Soil Properties

As expected, there were numerous statistical differences between stands and depth intervals. There were no effects ($P>0.05$) of stand, depth, or their interaction on soil pH (H_2O or KCl extractable), ANC, or TEA concentrations (Table 2-1). Cation exchange capacity and base saturation were greater ($P<0.05$) in soils collected under coniferous stands, due to the greater concentrations of exchangeable Ca, Mg, and Na (Table 2-1). Soil CEC, and exchangeable Ca and Mg differed ($P<0.05$) between stand and depth interval (Figure 2-2). The greatest CEC was in the 0- to 5-cm depth interval of the coniferous soil which was 3 $\text{cmol}_c\ \text{kg}^{-1}$ greater than the 0- to 5-cm depth interval of the soil beneath the deciduous stand. There was no difference ($P>0.05$) between the 5- to 15-cm depth intervals of the two stands. Similar to CEC, the greatest exchangeable Ca and Mg were in the 0- to 5-cm depth interval beneath the coniferous stand. Exchangeable Ca and Mg were 80 and 60% greater, respectively, in the 0- to 5-cm depth interval beneath the coniferous stand compared to the deciduous stand. There were no differences in exchangeable Ca or Mg between the 5- to 15-cm depth intervals of the two stands.

With the exception of EC and water soluble Na and Zn, concentrations of all other soil parameters in this study were affected ($P<0.05$) by stand, depth interval, but not the main effect interactions (Table 2-2). Concentrations of soil water soluble Al, Ca, Fe, and Mg were greater ($P<0.05$) in the soil beneath the coniferous stands whereas concentrations of soil water soluble K, Mn, and S were greater beneath the deciduous stands when averaged across depth. Concentrations of Mehlich-3 extractable Ca, Fe, Mg, and Mn were greater in the soil beneath the coniferous stands whereas concentrations of Mehlich-3 extractable Al, K, P, and S were greatest beneath the deciduous stands. Concentrations of soil water soluble Ca, K, Mg, P, and S were greater in the 0- to 5-cm depth interval compared to the 5- to 15-cm depth interval when averaged across stand (Table 2-2). Concentrations of Mehlich-3 extractable Ca, Cu, and K were greatest in the 0- to 5-cm depth interval whereas concentrations of Mehlich-3 extractable Al were greatest in the 5- to 15-cm depth interval.

There were no differences ($P>0.05$) in soil TOC, TN, or KCl extractable NH_4 and NO_3 when averaged across stand (Table 2-3). Water extractable NH_4 and NO_3 were greater in the soil beneath the deciduous stands by 16 and 67%, respectively. The soil beneath the coniferous stands had a C:N ratio of 17.1 which was greater ($P<0.05$) than the C:N ratio of 15.9 for the deciduous soil. Averaged across stand, TOC and TN were greatest in the 5- to 15-cm depth interval whereas KCl extractable NH_4 and NO_3 and water extractable NH_4 were greatest in the 0- to 5-cm depth interval.

Using the measured soil bulk density, soil concentrations were converted to contents to better assess effects of stand on soil storage by soil depth. Compared to the soil concentration data, there were fewer statistical differences between stand and depth main effects. There were no statistical differences in contents of exchangeable Na, water soluble Al, Mg, Na, P, and Zn, TOC, and NO_3 (KCl and water extractable; Tables 2-4 – 2-6). The remaining soil properties measured in this study (list here) were affected ($P<0.05$) by stand, depth interval, or their interactions.

Water soluble P and Mg contents were affected ($P<0.05$) by the interaction of stand and depth (Figure 2-3). Soil water soluble P was greatest in the 0- to 5-cm depth under deciduous stands, but did not differ from the 0- to 5-cm depth under coniferous stands. Water soluble P contents of the 0- to 5-cm depth interval of the coniferous soil was 28% greater than the 5- to 15-cm depth interval. Water soluble Mg contents were greatest in the 0- to 5-cm depth interval of the soil beneath the coniferous stand but did not differ from the 0- to 5-cm depth interval of the deciduous stands (Figure 2-3). There were no differences ($P<0.05$) in water soluble Mg contents between the 5- to 15-cm depth intervals of the two stands which were significantly lower than both 0- to 5-cm depth intervals.

Averaged across depths, CEC and contents of exchangeable Ca and Mg were greatest beneath the coniferous stands whereas exchangeable Al and K contents were greatest beneath the deciduous stands (Table 2-4). Cation exchange capacity and exchangeable Ca, K, and Mg contents were greatest in the 0- to 5-cm depth interval whereas TEA was greatest in the 5- to 15-cm depth when averages across stand. Contents of water soluble Ca and Fe were greatest in coniferous stands, whereas contents of water soluble K, Mn, and S were greatest beneath deciduous stands (Table 2-5). Contents of Mehlich-3 extractable Ca and Mg were greatest beneath coniferous stands, whereas Al, K, P, S, and Zn were greatest under deciduous stands. Total N and NH_4 (water and KCl extractable) were greatest in the soil beneath the deciduous stands (Table 2-6). When averaged across stands, contents of water soluble K and S were greatest in the 0- to 5-cm depth interval. Conversely, contents of all Mehlich-3 extractable nutrients were greatest in the 5- to 15-cm depth (Table 2-5). Water and KCl extractable NH_4 were greatest in the 0- to 5-cm depth compared to the 5- to 15-cm depth interval (Table 2-6).

Litter Properties

Similar to the soil properties examined in this study, stand had a significant effect ($P<0.05$) on several litter characteristics (Tables 2-7 and 2-8). Aboveground needle litter in the coniferous stands was more acidic ($P<0.05$) than the deciduous leaf litter by ~0.2 units. Total C concentrations were greater in the coniferous litter compared to the deciduous litter (451.5 vs 431.3 g kg^{-1}; $P<0.05$), which also resulted in greater C:N ratios (44.3 vs 36.0; Table 2-7). With the exception of Al, Fe, and Zn which did not differ ($P>0.05$) from each other, concentrations of all nutrients within the deciduous litter were greater ($P<0.05$) than the coniferous litter (Table 2-7).

Due to the slow decomposition rate of coniferous needle litter, the mass of forest floor litter per unit area at the coniferous stands was nearly twice as great as the deciduous stands (Table 2-8). Due to the substantial difference in forest floor mass, nutrient concentrations of the litter converted to contents were typically greater in the coniferous litter. With the exception of TC, Ca, Mn, and Na, which did not differ between stands, contents of all nutrients examined were greater ($P<0.05$) in the coniferous litter compared to the deciduous litter.

Discussion

Although differences occurred between deciduous and coniferous soil and litter, the lack of differences in soil pH and TEA indicates conversion of hardwood stands to pine is not causing acidification of soils in the Mulberry River watershed. Although acidity did not differ between the two stands, differences in soil and litter chemical characteristics did exist and were comparable to those previously reported. Finzi et al. (1998a) compared tree species effects on soil chemical properties and reported significantly lower pH in the 0- to 7.5- and 7.5- to 15-cm depths under hemlock compared to sugar maple (*Acer saccharum*), white ash (*Fraxinus americana*), red maple (*Acer rubrum*), and beech (*Fagus grandifolia*) but no difference compared to red oak (*Quercus rubra*). These results reported by Finzi et al. (1998a) differ from those observed in this study and by Alban (1982), who reported higher soil pH under Jack and red pines in the A horizon.

Similar to the approach used in this experiment, Hansson et al. (2011) examined differences in soil properties of adjacent stands of Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*), and silver birch (*Betula pendula*) grown under similar climate, parent material, soil type, and land use. Extractable acidity was greater than reported in this study but also did not differ between stands. Unlike this study, there were no differences in CEC or exchangeable Ca, K, and Al. The results of this experiment agree strongly with results reported by Alban (1982). Examining differences in soil properties between aspen, spruce, and pine stands, Alban (1982) reported significantly greater pH, and exchangeable Ca, and Mg in the A horizon of the coniferous stands compared to the deciduous stand.

Pine needle litter is typically considered nutrient-poor when compared to leaf and needle litter of other tree species (Johansson, 1995). This was also evident in this study where nutrient concentration were significantly greater in the deciduous litter. The significant differences in nutrient contents in the coniferous litter can be attributed to the significantly greater mass of coniferous litter on the forest floor. The accumulation of aboveground needle litter is a result of slower decomposition rates, which is partially a result of the greater C:N ratio of the needle litter.

When examining contents of nutrients in the soil and litter between the deciduous and coniferous stands, differences between stands provides the appearance of stand effects on contents of several nutrients within the mineral soil or aboveground litter. However, the total amount (sum of litter and soil contents) of these nutrients in the respective stand did not differ. What has potentially occurred is the movement of nutrients from the mineral soil to the vegetation and subsequently the return of these nutrients to the forest floor by litterfall. In regards to soil acidity, increased uptake of divalent cations from the surface mineral soil horizons by deciduous vegetation may have resulted in the lower pH of soil beneath deciduous stands than initially expected.

It is generally held that conifers acidify soil and reduce contents of cations resulting in detrimental effects on soils when compared to deciduous trees (Ovington, 1953, 1954, 1958). Certain studies and reviews (Holmsgaard and Holstener-Jorgensen, 1961; Stone, 1975; Alban, 1982; Binkley, 1995; Binkley and Giardina, 1998) examining the effect of tree species on soils have called this theory into question and have proposed that differences in soil characteristics initially attributed to vegetation may have existed prior to vegetative growth. Many studies reporting soil acidification as a result of conifer growth have been conducted by establishing a forested ecosystem on grasslands or agroecosystems which is a dramatic shift in land use (Brand et al., 1986; Giddens et al., 1997; Sparling et al., 2000; Ross et al., 2002). If there is a vegetative species effect on soil, the rate of change of soil characteristics resulting from this effect may be slow to occur and difficult to measure with a single set of samples.

Some studies examining the change in soil chemistry following conversion of hardwood stands over time have reported contrasting impacts on soil chemistry. Lane (1975) examined the changes in soil chemistry seven years after conversion of mixed hardwood stands to loblolly pine

(*Pinus taeda*). There was no significant change in soil pH from pretreatment (pH = 5.1) over the following seven years (pH 5.0 to 5.2) and the soil pH was not significantly different from the control. There was also no significant difference in soil P, K, and Ca between the converted stands and the control stands. In a follow up study, Lane (1990) revisited the research area where the mixed hardwood stands were converted to loblolly pine 23 years following conversion. Similar to the initial report, there were no significant differences in soil pH, Ca, K, or P between the control and converted stands. There were also no changes in soil chemistry within the converted stands over the 23 year period. Scott and Messina (2009) examined the changes in forest floor and soil chemistry 35 years after conversion of mixed pine-oak forests to either mixed oak or loblolly pine forests. The forest floor within the pine stands was approximately twice as thick (5 to 10 cm) as the oak stands (0 to 5 cm) and had discernable Oi, Oe, and Oa horizons. Although the forest floor in the mixed oak stands was significantly thinner, the leaf litter had greater concentrations of N and P by 64% and 50%, respectively. Unlike the forest floor, there were minimal differences in soil chemistry between the two stands, 35 years following the conversion. Soil pH, exchangeable cations, and effective cation exchange capacity did not differ between the two stands. The results of this study and those of Lane (1975;1990) and Scott and Messina (2009) differed from the results reported by Finwick and Knapp (1982) and Iwashima et al. (2012).

This study also only examined differences in soil chemical characteristics only in the top 15 cm of mineral soil. Differences in soil acidity or nutrient concentrations/contents may differ significantly with increasing depth compared to those observed in this experiment. Further research will need to examine soil chemical characteristics deeper in the profile to fully understand soil nutrient and acid cycling within the Mulberry River watershed. Although there were no differences in soil acidity between the two stands, it is possible that heavy rainfalls interacting with the coniferous litter could contribute acidity to the watershed.

Conclusion

Results of this experiment indicate that differences in soils under deciduous and coniferous stands may be more subtle or that changes in soil characteristics resulting from alteration of species composition may occur at slower rates than previously thought. The soil beneath coniferous stands was surprisingly nutrient rich and highlights the amount of research still needed on tree species effects on soil. This experiment was limited to the surface mineral soil horizon which limits interpretations of species effects on the entire soil profile. Based on the results of this experiment, it appears unlikely that growth of conifers are causing soil acidification or adverse environmental conditions within the surface mineral horizon. Due to the only slightly acidic pH and low TEA of the soil beneath both stands, it is unlikely that the soil is acting as a major contributor of acidity. However, it is possible that runoff interacting with the coniferous litter can be acidified as a result of the lower litter pH and consequently contribute greater amounts of acidity than the deciduous litter.

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Tables and Figures

Table 2-1. Differences in soil pH, acid neutralizing capacity (ANC), cation exchange capacity (CEC), base saturation, total extractable acidity (TEA), and exchangeable cations between deciduous (D) and coniferous (C) stands at two depth intervals.

	Stand[a]		Depth[b]	
Parameter	D	C	0 to 5 cm	5 to 15 cm
pH_{H2O}	5.2a[†]	5.3a	5.3a	5.2a
pH_{KCl}	4.6a	4.6a	4.6a	4.6a
ANC (% CCE[c])	2.7a	3.2a	3.5a	2.5a
CEC ($cmol_c\ kg^{-1}$)	5.7b	6.5a	7.9a	3.7b
Base Saturation (%)	47.5b	66.4a	69.8a	40.7b
TEA ($cmol_c\ kg^{-1}$)	2.5a	2.4a	2.3a	2.5a
Exch. Cations ($cmol_c\ kg^{-1}$)				
Al	0.5a	0.4a	0.6a	0.3b
Ca	2.0b	3.4a	4.3a	1.1b
K	0.2a	0.2a	0.3a	0.1b
Mg	0.5b	0.7a	0.9a	0.3b
Na	0.01b	0.02a	0.02a	0.01b

[a] Mean stand values are averaged across depth

[b] Mean depth values are averaged across stand.

[c] Calcium Carbonate ($CaCO_3$) Equivalence

[†] Means with the same letter within a main effect (i.e., stand or depth) are not different from each other $\alpha = 0.05$.

Table 2-2. Differences in soil electrical conductivity (EC) and Mehlich-3 and water extractable nutrient concentrations between deciduous (D) and coniferous (C) stands at two depth intervals.

	Stand[a]		Depth[b]	
Parameter	D	C	0 to 5 cm	5 to 15 cm
EC (µS cm^{-1})	99.5a[†]	100.7a	100.4a	99.8a
Water Soluble (mg kg^{-1})				
Al	12.1b	14.7a	13.3a	13.5a
Ca	33.6b	45.6a	46.2a	32.9b
Fe	5.1b	7.0a	5.9a	6.2a
K	37.6a	30.4b	38.9a	29.1b
Mg	10.5b	11.5a	12.5a	9.5b
Mn	8.4a	6.3b	7.8a	6.9b
Na	11.0a	5.1a	11.1a	4.9a
P	2.6a	2.5a	3.2a	1.9b
S	7.8a	7.2b	8.4a	6.5b
Zn	0.5a	0.5a	0.5a	0.5a
Mehlich-3 (mg kg^{-1})				
Al	698.2a	674.4b	668.1b	704.4a
Ca	365.5b	587.1a	571.1a	381.4b
Cu	0.9a	1.0a	1.0a	0.9b
Fe	91.6b	96.4a	96.3a	91.7a
K	96.7a	83.4b	99.2a	80.8b
Mg	70.4b	90.3a	91.2a	69.4b
Mn	163.8b	186.1a	183.2a	166.7b
Na	84.5a	84.1a	88.6a	80.0b
P	14.1a	10.0b	13.8a	10.2b
Pb	2.2a	2.2a	2.2a	2.1b
S	13.3a	11.7b	13.0a	11.9b
Zn	2.1a	2.0a	2.4a	1.7b

[a] Mean stand values are averaged across depth

[b] Mean depth values are averaged across stand.

[†] Means with the same letter within a main effect (i.e., stand or depth) are not different from each other α = 0.05.

Table 2-3. Differences in concentrations of soil total organic C (TOC), total N (TN), 2*M* KCl and water extractable NH_4 and NO_3, and C:N ratio between deciduous (D) and coniferous (C) stands at two depth intervals.

	Stand[a]		Depth[b]	
Parameter	D	C	0 to 5 cm	5 to 15 cm
TOC (g kg^{-1})	28.9a[†]	30.2a	25.2b	33.9a
TN (g kg^{-1})	1.8a	1.7a	1.6b	2.0a
$NH_{4\text{-KCl}}$ (mg kg^{-1})	42.7a	39.4a	48.8a	33.3b
$NO_{3\text{-KCl}}$ (mg kg^{-1})	11.4a	15.8a	18.1a	9.2b
$NH_{4\text{-H2O}}$ (mg kg^{-1})	17.3a	14.8b	18.6a	13.5b
$NO_{3\text{-H2O}}$ (mg kg^{-1})	13.2a	7.9b	12.4a	8.6a
C:N	15.9b	17.1a	16.5a	16.4a

[a] Mean stand values are averaged across depth

[b] Mean depth values are averaged across stand.

[†] Means with the same letter within a main effect (i.e., stand or depth) are not different from each other α = 0.05.

Table 2-4. Differences in soil contents of cation exchange capacity (CEC), total extractable acidity (TEA), and exchangeable cations between deciduous (D) and coniferous (C) stands at two depth intervals. Mean stand values are averaged across depth and mean depth values are averaged across stand. Means with the same letter within a main effect (i.e., stand or depth) are not different from each other α = 0.05.

	Stand[a]		Depth[b]	
Parameter	D	C	0 to 5 cm	5 to 15 cm
CEC (kmol$_c$ ha^{-1})	26.4b[†]	31.4a	32.1a	26.7b
TEA (kmol$_c$ ha^{-1})	7.3a	7.2a	6.7b	7.9a
Exch. Cations (kmol$_c$ ha^{-1})				
Al	3.4a	2.1b	2.8a	2.8a
Ca	11.6b	17.2a	17.5a	11.2b
K	1.2a	1.0b	1.2a	0.92b
Mg	2.8b	3.8a	3.8a	2.7b
Na	0.09a	0.1a	0.09a	0.10a

[a] Mean stand values are averaged across depth

[b] Mean depth values are averaged across stand.

[†] Means with the same letter within a main effect (i.e., stand or depth) are not different from each other α = 0.05.

Table 2-5. Differences in bulk density and Mehlich-3 and water extractable nutrient contents between deciduous (D) and coniferous (C) stands at two depth intervals.

	Stand[a]		Depth[b]	
Parameter	D	C	0 to 5 cm	5 to 15 cm
Bulk Density (kg m^{-3})	1009.2a[†]	928.8b	892.5b	1045.4a
Water Soluble (kg ha^{-1})				
Al	9.6a	10.9a	11.0a	9.4a
Ca	24.2b	29.9a	27.9a	26.2a
Fe	4.1b	5.3a	5.2a	4.3a
K	27.2a	21.0b	25.3a	22.9b
Mg	7.7a	8.0a	7.9a	7.7a
Mn	6.3a	4.5b	5.1a	5.8a
Na	6.6a	3.7a	3.7a	6.5a
P	1.8a	1.7a	1.6a	1.8a
S	5.7a	4.9b	5.7a	4.9b
Zn	0.4a	0.4a	0.4a	0.4a
Mehlich-3 (kg ha^{-1})				
Al	515.3a	460.2b	313.3b	662.2a
Ca	243.3b	353.9a	258.6b	338.6a
Cu	0.69a	0.66a	0.48b	0.87a
Fe	65.8a	64.3a	44.6b	85.4a
K	67.7a	54.1b	45.9b	75.9a
Mg	49.2b	58.7a	42.5b	65.3a
Mn	117.3a	125.9a	84.5b	158.7a
Na	59.5a	56.6a	41.2b	74.9a
P	9.7a	6.1b	6.4b	9.3a
Pb	1.6a	1.4a	1.0b	2.0a
S	9.6a	7.7b	6.1b	11.2a
Zn	1.5a	1.3b	1.1b	1.6a

[a] Mean stand values are averaged across depth

[b] Mean depth values are averaged across stand.

[†] Means with the same letter within a main effect (i.e., stand or depth) are not different from each other $\alpha = 0.05$.

Table 2-6. Differences in contents of soil total organic C (TOC), total N (TN), 2*M* KCl and water extractable NH_4 and NO_3 between deciduous (D) and coniferous (C) stands at two depth intervals.

	Stand[a]		Depth[b]	
Parameter	D	C	0 to 5 cm	5 to 15 cm
TOC (Mg ha^{-1})	5.7a[†]	5.2a	5.6a	5.3a
TN (Mg ha^{-1})	1.3a	1.2b	1.3a	1.3a
$NH_{4\text{-KCl}}$ (kg ha^{-1})	30.5a	25.6b	34.6a	21.4b
$NO_{3\text{-KCl}}$ (kg ha^{-1})	8.4a	8.1a	9.4a	7.1a
$NH_{4\text{-H2O}}$ (kg ha^{-1})	12.4a	10.0b	14.1a	8.26b
$NO_{3\text{-H2O}}$ (kg ha^{-1})	7.1a	4.8a	6.9a	4.9a

[a] Mean stand values are averaged across depth

[b] Mean depth values are averaged across stand.

[†] Means with the same letter within a main effect (i.e., stand or depth) are not different from each other α = 0.05.

Table 2-7. Differences in litter pH, C:N ratio, and concentrations of total carbon (TC), total nitrogen (TN), and nutrients of deciduous (D) and coniferous (C) litter.

		Stand	
Parameter	Units	D	C
pH	-	4.7a[†]	4.4b
C:N	ratio	36.0b	44.3a
TC	g kg^{-1}	431.3b	451.5a
TN	g kg^{-1}	15.2a	13.0a
Elements			
Al	g kg^{-1}	1.2a	1.4a
Ca	g kg^{-1}	14.5a	7.2b
Cu	mg kg^{-1}	9.7a	7.9b
Fe	g kg^{-1}	0.9a	1.1a
K	g kg^{-1}	1.2a	1.0b
Mg	g kg^{-1}	1.1a	0.9b
Mn	g kg^{-1}	1.4a	0.8b
Na	g kg^{-1}	0.7a	0.3b
P	g kg^{-1}	0.7a	0.6b
S	g kg^{-1}	0.8a	0.7b
Zn	mg kg^{-1}	30.7a	34.3a

[†] Means with the same letter are not different from each other $\alpha = 0.05$.

Table 2-8. Differences in forest floor mass, and contents of total carbon (TC), total nitrogen (TN), and nutrients of deciduous (D) and coniferous (C) litter.

	Stand	
Parameter	D	C
Forest Floor (Mg ha^{-1})	10.7b[†]	21.3a
TC (Mg ha^{-1})	6.4a	5.8a
TN (kg ha^{-1})	163.2b	258.8a
Elements (kg ha^{-1})		
Al	14.7b	29.9a
Ca	158.1a	147.8a
Cu	0.1b	0.2a
Fe	10.0b	22.4a
K	12.3b	20.6a
Mg	12.4b	19.8a
Mn	15.9a	16.7a
Na	7.8a	6.2a
P	6.9b	11.9a
S	8.4b	15.0a
Zn	0.3b	0.7a

[†] Means with the same letter are not different from each other $\alpha = 0.05$.

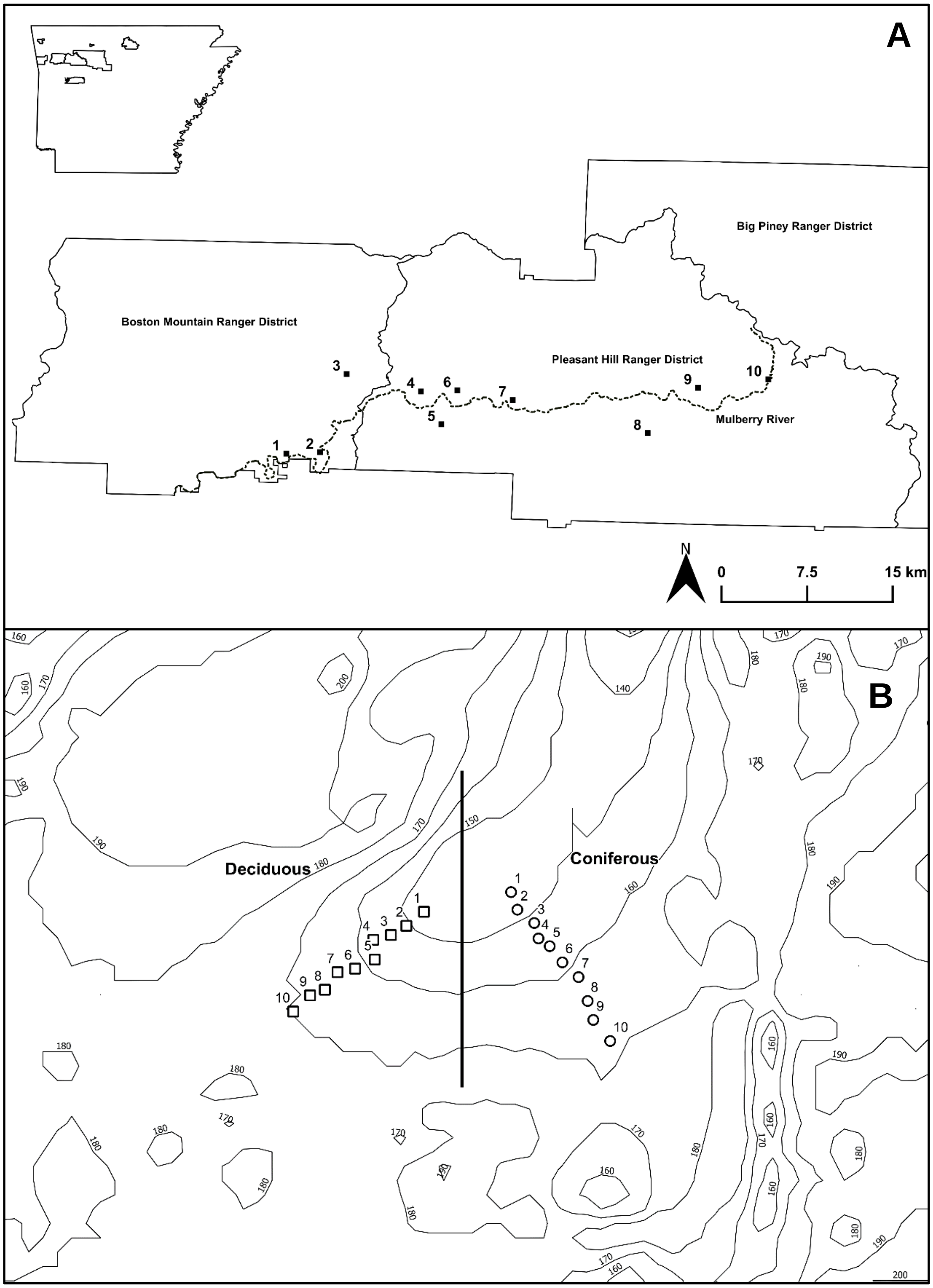

Figure 2-1. (A) Locations of the 10 sampling sites within the Ozark National Forest, Arkansas. (B) Example of sampling organization for adjacent deciduous and coniferous stands.

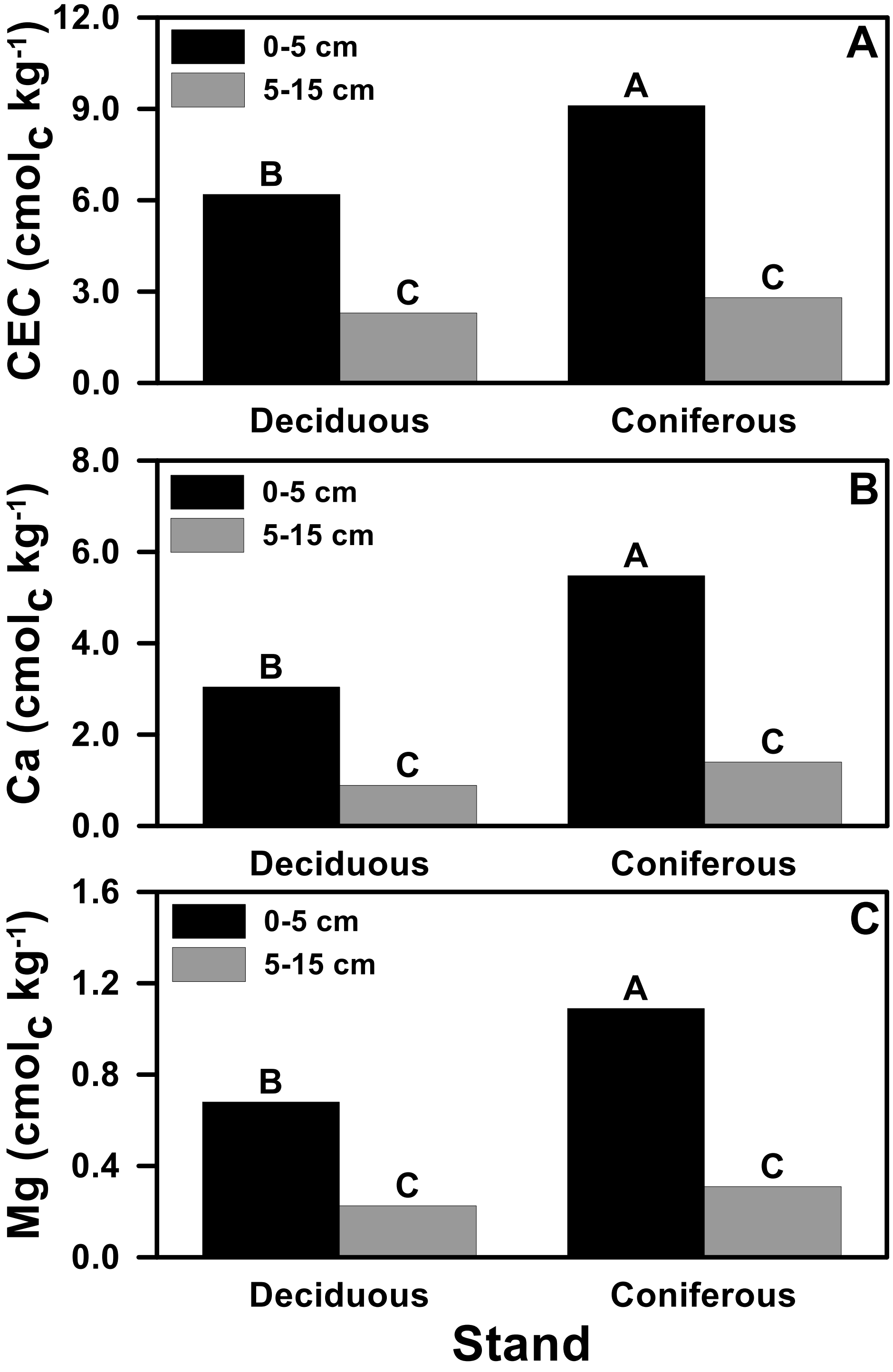

Figure 2-2. Differences in soil cation exchange capacity (CEC;A) and exchangeable Ca (B) and Mg (C) between deciduous and coniferous tree stands at two depth intervals. Bars with the same letter do not differ at $\alpha = 0.05$.

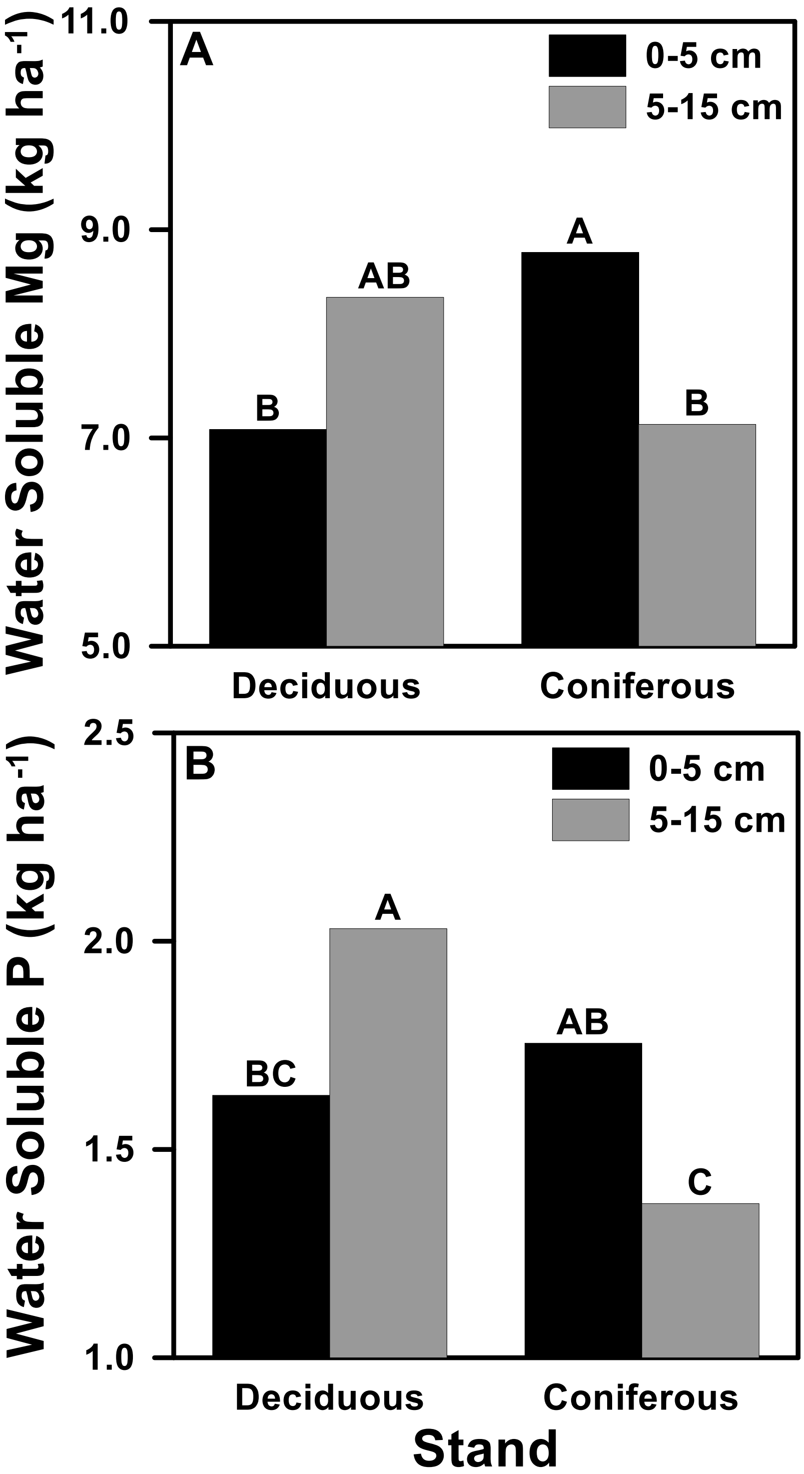

Figure 2-3. Differences in water soluble soil Mg (A) and P (B) between deciduous and coniferous tree stands at two depth intervals. Bars with the same letter do not differ at α = 0.05.

Chapter Three: Effects of Pine Tree Density on Stream Chemistry in the Mulberry River Basin, Arkansas

Abstract

The Mulberry River in Arkansas is one of America's National Wild and Scenic Rivers and has been listed as impaired due to low pH since 2008. Stream chemistry is directly related to land use and changes in land use can result in degradation of surface waters. Growth of conifers, through afforestation or conversion of native hardwood stands, has been attributed to basin acidification in several regions and may be contributing acid to the Mulberry River basin. The objective of this study was to examine the relationship between land use (i.e., coniferous forest, deciduous forest, mixed forest, and pasture) and stream chemistry of 11 tributaries of the Mulberry River over a 2-year period. Mean pH of the 11 tributaries increased with distance from the headwater sub-basin and ranged from 5.6 to 6.5. Coniferous forest land use was not correlated with stream pH ($P > 0.05$) neither was stream pH predicted ($P > 0.05$; $R^2 < 0.01$) by coniferous forest land use. Acid neutralizing capacity (ANC) and stream discharge were negatively correlated ($P < 0.05$) with and partially predicted by coniferous land use ($P < 0.05$). Acid neutralizing capacity was also positively correlated with total organic carbon ($r = 0.68$) which was negatively correlated with coniferous land use ($r = -0.27$) and positively correlated with deciduous land use ($r = 0.20$). Deciduous land use was positively correlated with SO_4 ($r = 0.24$) and negatively correlated with total N ($r = -0.28$) and NO_3 ($r = -0.31$). Spearman's rank correlation and principal component analysis identified significant inverse relationships between stream pH and NO_3 ($r = -0.17$) and between ANC and NO_3 ($r = -0.44$), which may suggest that HNO_3 may be the primary source of acidity within the Mulberry River basin. Although no relationships were observed between coniferous land use and pH, conifer growth may be affecting the stream buffering capacity of the basin which would increase the susceptibility of the river to acidification.

Introduction

The Mulberry River in Arkansas is a 110 km long tributary of the Arkansas River within the Ozark National Forest and has been designated a National Wild and Scenic River since 1992. The Mulberry River was placed on the EPA's 303(d) list of impaired water bodies by the Arkansas Department of Environmental Quality (ADEQ) in 2008 when the pH of a 14.7 km reach decreased below the regulatory limit of pH 6.0 several times in 2005 (Shafii, 2008). Since being listed as impaired, the length of impairment listed on the 303(d) list has increased from 14.7 km to 68.8 km in 2016 due to two more reaches indicating further acidification over time.

According to the total maximum daily load submitted to ADEQ, approximately 90 to 95% of the Mulberry River basin is forested and there are no National Pollutant Discharge Elimination System permits along the impaired segments of the river (Shafii, 2008). This reduces the probability of point or agricultural non-point sources of pollution as being the cause of acidification. A potential cause of catchment acidification is the alteration of species composition within the basin, specifically, afforestation of arable lands or conversion of hardwood stands to pine (Miller, 1985; Neal et al., 1986; Hornung et al., 1987; Farley et al., 2008).

Growth of trees on land that is not forested, and/or the conversion of hardwood or mixed hardwood-pine stands to pine monocultures through hardwood group selection are common management practices in the southern United States (Lane, 1975; Berthrong et al., 2009). Due to forest management practices, the volume of live-tree softwoods in the Ozark region of Arkansas has increased from 20 million cubic meters in 1978 to 51 million cubic meters in 2010 (Beltz et al., 1992; Rosson and Rose, 2015). Afforestation has been attributed to basin acidification in the past (Hornung et al., 1987; Jenkins et al., 1990b; Kreiser et al., 1990; Battarbee et al., 2008) and may be contributing to the acidification of the Mulberry River. The objective of this study was to examine the relationship between land use and stream chemistry (specifically physicochemical parameters related to or affecting stream acidity) in 11 sub-basins of the Mulberry River.

Materials and Methods

Study Area

The Mulberry River basin (35°29' – 35°51'N, 94°4'– 93°24' W) is a 1,100 km^2 catchment located within the Ozark National Forest in northwest Arkansas. The Mulberry River is 110 km long and flows east to west with an annual average discharge of 0.49 km^3 prior to its confluence with the Arkansas River. The basin is comprised of 13 HUC-12 sub-basins ranging in area from 42.4 to 133.1 km^2. The Mulberry River basin lies within a humid subtropical climate zone, and the daily temperature and rainfall vary greatly during the year with the annual average approximately 21.3°C and 1270 mm, respectively.

Water Sampling and Analytical Methods

Water samples were collected monthly over a two-year period from January 2016 to December 2017. Eleven tributaries of the Mulberry River basin were sampled (Figure 3-1), each with differing pine tree densities to determine the relationship between stream chemistry and pine tree density (Table 3-1). The number of water samples taken per tributary (n=11-23) varied due to intermittent flow in the tributaries.

Stream pH, dissolved oxygen (DO), specific conductance (SpC), and temperature were measured *in-situ* using a multi-parameter data sonde (YSI incorporated, Yellow Springs, OH) during the monthly water sampling. Water samples were collected from a single vertical centroid-of-flow using 2-L high-density polyethylene bottles that were rinsed three times with ambient water prior to collection of the sample. Stream discharge was measured using the USGS midsection method (Turnispeed and Sauer, 2010) at the base of the study reach. Water samples were analyzed for soluble concentrations of 21 elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Ti, and Zn) by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an Agilent 5110 ICP-OES system (Agilent Technologies, Santa Clara, CA). Soluble element concentrations were measured in water samples which were vacuum-filtered through a 0.45 µm Pall GN-6 Metricel ® membrane filter (Pall Corporation, Ann Arbor, MI) and then acidified to pH < 2.0 with 37% (w/w) HCl. Chloride and SO_4 concentrations were determined using a Dionex 1600 Ion Chromatography System (Dionex, Sunnyvale, CA). Acid neutralizing capacity (ANC) was determined by potentiometric titration of 100 mL of water with 0.02*N* H_2SO_4 to pH 4.2. Total suspended solids (TSS) were determined by filtering 1L of sample water through a 0.45 µm Pall GN-6 Metricel ® membrane filter and then measuring the change in filter weight. Total organic C (TOC) and total N (TN) were measured on a Shimadzu TOC-L analyzer (Shimadzu Scientific Instruments, Columbia, MD). Soluble reactive P (SRP) and NO_3^- (plus NO_2^-) were measured on a SKALAR SAN++ wet chemistry auto analyzer (SKALAR, Buford, GA). Results are not presented for chemical elements that were below detection limits in ≥ 70% of samples analyzed.

Land Cover Classification

Land-use data were obtained from the National Land Cover Database (NLCD; Homer et al., 2015) which is derived from satellite imagery mapped to a unit of 30 m. Sub-basin boundaries were overlain onto the NLCD and land-use proportions were calculated using the LecoS plugin for QGIS (Jung, 2016). The land use classifications examined in the present study were deciduous forest, coniferous forest, mixed forest, and pasture which comprised more than 98% of each sub-basin.

Statistical Analyses

The Kruskal-Wallis rank test, a non-parametric one-way analysis of variance, was used to analyze the effect of site on the physicochemical water quality parameters measured using the PROC NPAR1WAY procedure in SAS (version 9.4; SAS Institute., Cary, NC). With site 1 being located at the headwaters and site 11 located 32 km west of site 1, the site numbers (i.e., 1-11) are analogous to the east-west spatial variability of the Mulberry River basin. When significant differences were found, the Dwass, Steel, Critchlow-Fligner non-parametric multiple-comparison procedure was used for post-hoc pairwise comparisons at the level of significance set at $\alpha = 0.05$. The Spearman rank correlation coefficient (Spearman's R) was used to examine the relationship between land use and water quality.

Principal component analysis (PCA) was applied to the dataset to help reduce the dimensionality of the data set which contained a large number of variables that are interrelated. Only principal components (PC) with eigenvalues greater than 1 were incorporated into the final analysis. Pearson's correlation coefficients and PCA were performed on log-transformed data. Standardization of the data renders the data dimensionless, which eliminates the influence of different units of measurement (Hirsch et al., 1991; Liu et al., 2003; Singh et al., 2004). Left of center data (i.e., missing or below detectable limit) were estimated using 5 imputations of the Markov chain Monte Carlo (MCM) multiple imputation method (Schafer and Olsen, 1998).

Results and Discussion

Water Quality Characteristics

The nutrient and physicochemical water quality parameters of the Mulberry River at each sampling site are presented in Figures 3-2 and 3-3. Numerous physicochemical properties were affected ($P < 0.05$) by site indicating spatial variability in water quality between sub-basins. Stream pH, specific conductance, ANC, SO_4, and TOC showed an increasing trend from site 1 to site 11. Stream pH increased from a median of 5.6 at site 1 to a median of 6.5 at site 11. Median ANC increased from 4.0 to 16.1 mg $CaCO_3$/L at site 1 and 9, respectively. Specific conductance, Cl, SO_4, and TOC were greatest at site 11. Discharge, TSS, K, Na, and soluble P also differed by site but there were no discernable trends. Although ANC differed among sites, there were no differences in stream Ca and Mg among sites. Total N and NO_3 concentrations were greatest at site 5 and 7 and lowest at site 1 and 11 for TN and NO_3, respectively. Stream temperature, DO, and concentrations of Al, Fe, Mn, total P, SRP, and S did not differ ($P > 0.05$) among sampling sites (Figures 2 and 3).

It is unclear why sub-basins chemical composition differed, whereas basin size, land use, and geology are similar. The trend of increasing pH with distance from the headwater, despite increasing pine tree density, is particularly interesting and may be attributed to the increasing ANC (Figure 3-2). Clenaghan et al. (1998) the spatial variability in stream chemistry of several basins throughout Ireland and reported an increasing pH trend with increasing levels of basin afforestation. Although the geology of the Mulberry River basin is uniformly sandstone and shale, the presence of numerous faults may change groundwater flow paths. Acid neutralizing capacity was typically lower south of the river (Sites 3, 5, 7, and 10) when compared to nearby sampling points north of the river (Sites 2, 4, 6, 8, 9, and 11) further demonstrating the spatial variability within the Mulberry River basin. Similarly, specific conductance increased with distance from the headwaters and was also significantly greater north of the river. The increased concentrations of dissolved constituents would increase ANC and help buffer the tributaries from changes in pH. It is possible that the different sub-basins are receiving water from different groundwater sources which should be studied in the future. Average stream pH ranged by nearly 1 unit from pH 6.5 which is safe for aquatic life to pH 5.5 where Al toxicity becomes a concern. Despite the acidic pH for several sampling periods, Al concentrations were below thresholds deemed toxic for aquatic life (300 to 400 µg L^{-1}; Verbost et al., 1992; Poleo, 1995; Truscott et al., 1995; Gensemer and Playle, 1999; Alexopoulos et al., 2003; Woodburn et al., 2011).

Effect of Land Use on Water Quality

Spearman correlation analysis indicated that there were significant ($P < 0.05$) relationships among land uses and physicochemical water quality parameters (Table 3-2). Across the 11 sites studied, coniferous forests were negatively correlated with tributary discharge, specific conductance, ANC, soluble P, SO_4, and TOC and was positively correlated with TN and NO_3. Deciduous forest cover was positively correlated with TSS, specific conductance, soluble P, SO_4, and TOC and was negatively correlated with TN and NO_3. Similar to coniferous land use, stream discharge, specific conductance, ANC, SO_4, and TOC were negatively correlated with mixed forest land use whereas TN and NO_3 were positively correlated. Unlike the coniferous land use, stream pH and Na were negatively correlated with mixed forest land use. Pasture land use was negatively correlated with TSS, specific conductance, ANC, SO_4, and TOC and was positively correlated with TN and NO_3.

Spearman rank correlations were also determined for stream pH, ANC, and base cation (i.e., Ca, Mg, K, Na) concentrations to help identify potential causes of acidification. Stream pH was positively correlated with discharge which may indicate potential acidification during base flow conditions. Unexpectedly, stream pH, ANC, and Na concentrations were positively correlated with SO_4 and base cation concentrations were positively correlated with S concentrations. Nitrate concentrations were negatively correlated with stream pH and ANC. The positive correlations of pH and ANC with SO_4 and negative correlations with NO_3 indicates that increased NO_3 (as HNO_3) concentrations may be the cause of acidification. Total organic C was positively correlated with both pH and ANC while being positively correlated with deciduous land use and inversely correlated with coniferous land use. This may indicate that increased concentrations of TOC increased the buffering capacity of the streams and suggest that increased deciduous forest land use increases this buffering capacity. The faster decomposition rate of deciduous litter compared to coniferous litter may result in a consistent contribution of organic matter to the watershed via runoff.

Stepwise multiple linear regression analysis of the effects of land use on water quality resulted in several significant models (Table 3-4). Acid neutralizing capacity and TOC were best predicted by the combination of coniferous forest, deciduous forest, mixed forest, and pasture land uses. Stream discharge, K, and NO_3 were best predicted by the combination of mixed forest and pasture land use. Stream pH and SO_4 were best predicted by the combination of deciduous and mixed forest land use. Total suspended solids, specific conductance, SRP, DOP, and TN were only predicted by one land use type. For both 2016 and 2017, there were no significant relationships between increasing coniferous forest density and stream pH (Figure 3-4). Eleven out of 24 water quality parameters were not significantly explained by the four predominant land uses of the Mulberry River basin.

Stepwise multiple linear regression analysis of the effects of land use on water quality resulted in several significant models (Table 3-4). Acid neutralizing capacity ($R^2 = 0.49$) and TOC ($R^2 = 0.37$) were best predicted by the combination of coniferous forest, deciduous forest, mixed forest, and pasture land uses. Stream discharge, K, and NO_3 were best predicted by the combination of mixed forest and pasture land use. Stream pH and SO_4 were best predicted by the combination of deciduous and mixed forest land use. Total suspended solids, specific conductance, and TN were only predicted by one land use type. For both 2016 and 2017, there were no significant relationships between increasing coniferous forest density and stream pH (Figure 3-4). Despite the statistically significant results of the multiple linear regression, the low R^2 of the equations limits their use in predicting stream chemistry from land use data. The largest observed R^2 of 0.49 for ANC suggests that more than 50% of the variability in ANC values can be explained by other factors. The low R^2 values highlight the need for further research to find and better understand the independent variables that are capable of explaining the variability in the water quality parameters.

Previous studies (Neal et al., 1986; Hornung et al., 1987; Jenkins et al., 1990a; Kreiser et al., 1990; Battarbee et al., 2008; Farley et al., 2009) have reported an inverse relationship between growth of conifers and stream pH but that relationship was not found in this study. Threestatistical tests performed in this study (Spearmans rank correlations, multiple linear regression, and simple linear regression) resulted in no statistically significant relationships between coniferous forest land use and stream pH. Instead, stream ANC was negatively correlated with coniferous forest land and was partially predicted by coniferous forest land uses.

Rather than coniferous land uses contributing acidity to surface waters, it is possible that conifer growth may be leading to a decrease in stream flow and base depletion as reported by Swank and Vose (1994). This is supported by the significant negative correlation between stream discharge and coniferous forest land use. Similar to this study, Martinez et al. (2013) reported no differences in stream pH between six sub-basins with pine tree densities ranging from 0.3 to 96.3%. Unlike the results of this study, Martinez et al. (2013) reported no differences in alkalinity between the sub-basins with varying land use compositions.

Principle Component Analysis of Land Use and Stream Chemistry

Understanding the relationships between multiple water quality parameters can be difficult, especially when spatial and temporal variability are introduced. Principal component analysis was used to help reduce dimensionality of the data set and define relationships between the physicochemical parameters measured in this study. For all water quality parameters for the 11 tributaries studied across 2016 and 2017, PC 1 and 2 explained 42.36 and 25.73%, respectively, of the variation in the water quality data, which corresponded to eigenvalues of 6.85 and 3.37, respectively (Table 3-4). The addition of PC3 with an eigenvalue of 2.48 increased the cumulative variance from 68.09 to 87.15%. Principal components 1 and 2 are graphed in a bi-plot in Figure 3-5 to better illustrate factor loadings. Principal component 1 had nine water quality parameters with strong loadings (>0.50) with Ca concentrations possessing the greatest weight at 0.92. Other parameters that had strong loadings for PC1 were specific conductance, pH, ANC, Mg, S, SO_4, TOC and NO_3. Nitrate concentrations were the only parameter in PC1 with a negative loading. Principal component 2 had five parameters with strong loadings. Potassium concentrations had the greatest weight (0.87) followed by Na, temperature, total P, and TSS, all with factor loadings greater than 0.50. For PC3, the greatest coefficient (0.80) was Fe concentrations followed by TSS, Al, and NO_3, all with factor loadings greater than 0.50. Similar to PC1, NO_3 was the only parameter in PC3 with a negative loading greater than 0.50.

When examining PC 1 and 2 loadings and the bi-plot (Figure 3-5), two distinct groups of water quality parameters become apparent. Principal component 1 is primarily comprised of parameters related to base saturation and acid buffering including ANC, Ca, and Mg which are strongly correlated to pH which also had a significant PC1 loading. Total organic C, SO_4, and S concentrations also had significant PC1 loadings which indicates that organic acids or S derived acids may not be related to low pH values. It is also possible that the positive relationship between TOC and pH could indicate increased buffering capacity from organic compounds. Principal component 2 appears to be comprised of parameters related to sedimentation including total suspended solids, and concentrations of Al, Fe, Mn, and total P. Dissolved oxygen has a negative loading in PC2 (-0.48) which may result from increased turbidity and subsequent decrease in photosynthesis. Similar to the Spearman rank correlations, TN and NO_3 concentrations had a strong inverse relationship with stream pH and ANC as well as Ca and Mg concentrations. This inverse relationship might implicate HNO_3 as the driving force behind pH changes in the Mulberry River basin.

Although numerous physicochemical water quality parameters were affected by land use, the data suggests that there is not a strong relationship between stream acidity and coniferous forest land use. In addition to the lack of statistically significant relationships between coniferous forest land use and stream pH, the lowest pH values were observed in the eastern sub-basins which had the lowest pine tree densities. Little Mulberry Creek was recently added to the 303d list due to low pH but has a pine tree density of ~1.8%. Because land management history is unavailable for the Mulberry River sub-basins, it is not known whether the stands within each sub-basin are native or originate from management practices (e.g. conversion of hardwood stands and/or afforestation). If the coniferous stands are native, the tributaries of the Mulberry River may have already reached equilibrium with the ecosystem and other extraneous factors may be introducing acid to the Mulberry River basin.

Beyond the potential land use effects, the results of this study highlights some relationships between water quality parameters which may help direct future research. Understanding the relationship between stream flow and water chemistry can help identify potential sources of constituents. The positive correlation between stream pH and discharge indicate a potential dilution effect as stream flow increases. If acid rain or acidic runoff were causing an episodic decrease in pH, it would be expected that there would be an inverse relationship between discharge and pH. Instead, the lower pH during base flow conditions might implicate groundwater as the source of acidity. It is possible that increased loading of sediment from runoff could buffer the stream but no statistically significant relationships between ANC, TSS, base cation concentrations, and discharge were observed in this study. One of the greatest concerns when studying surface water acidification is the potential for Al toxicity affecting stream biology. Fortunately, soluble Al concentrations were low and below the toxic thresholds typically reported in the literature. It is unknown at this time whether or not Al concentrations are increasing which could negatively affect aquatic life in the future.

Conclusion

This research assessed the relationship between land use and physicochemical water quality parameters within the Mulberry River basin. Based on the results of this study, it is unlikely that coniferous forest land use is contributing to the acidification of the Mulberry River. The inverse relationship between TN and NO_3 and pH and ANC suggests that inorganic N may be the primary proton source with the Mulberry River basin. Due to the limitations of this study, it is unclear whether the NO_3 within the 11 tributaries of the Mulberry River basin is a derivative of extraneous HNO_3 or originates from the natural cycling of N throughout the ecosystem.

The effects of varying land uses on surface water chemistry have been well documented but this is only one factor which may cause changes in stream chemistry. Large scale animal production is prevalent in the areas surrounding the Mulberry River basin and increased loading of atmospheric ammonia and subsequent deposition and nitrification may result in basin acidification. The underlying geology of the Mulberry River basin has a large portion of sulfide bearing minerals and sulfide oxidation may be contributing sulfuric acid to the basin via groundwater flow. A new phenomena being observed throughout Europe is the acidification of surface waters as a result of increased atmospheric concentrations of CO_2. It is possible that increased CO_2 concentrations throughout the United States may soon result in acidification of base-poor rivers.

Regardless of the source of acidity, the low buffering capacity of the Mulberry River basin increases the vulnerability of the basin to acidification from small changes in environmental chemistry. This study began the process of investigating potential causes of acidification, but the short time span limits potential interpretations. Future research should also focus on comparing the Mulberry River basin to similar, non-impaired basins to fully understand why the Mulberry River has begun to show signs of degradation. The Mulberry River was designated as a ‘Wild and Scenic River’ because it provides extraordinary natural, cultural, and recreational value to Arkansas and the United States. It is imperative that Mulberry River be protected from degradation in order to preserve its ecological and recreational function.

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Tables and Figures

Table 3-1. Summary of site information and land use proportions (C, coniferous forest; D, deciduous forest; M, mixed forest; P, pasture) for 11 tributaries of the Mulberry River, Arkansas.

			Sampling Location				Land Use (%)			
#	Reach	n	Lat. (N)	Long. (W)	Basin (km^2)	Order	C	D	M	P
1	Hignite Hollow	23	35° 41' 08"	93° 27' 16"	75.6	3	6.1	84.5	2.1	2.5
2	Panther Creek	16	35° 41' 27"	93° 31' 29"	53.8	3	3.5	90.8	0.6	1.7
3	Bear Branch	13	35° 40' 48"	93° 32' 13"	78.1	1	13.4	77.3	2.4	3.8
4	Estep Creek	13	35° 41' 21"	93° 34' 31"	41.1	2	15.7	70.2	2.2	5.6
5	Washita Creek	15	35° 40' 57"	93° 35' 56"	78.1	3	16.3	71.6	2.4	4.2
6	Little Mulberry	22	35° 40' 24"	93° 39' 54"	66.2	4	1.8	90.3	0.3	3.3
7	Clear Creek	12	35° 40' 24"	93° 42' 11"	56.0	3	11.8	74.4	1.5	7.8
8	Indian Creek	13	35° 41' 03"	93° 42' 41"	45.2	3	3.7	90.5	0.4	1.9
9	Herrods Creek	19	35° 41' 19"	93° 44' 51"	61.8	2	8.6	82.4	1.2	1.1
10	Barron Creek	11	35° 40' 37"	93° 47' 10"	40.1	3	22.5	63.5	1.9	6.8
11	Mountain Creek	11	35° 41' 30"	93° 47' 23"	61.8	1	8.2	79.7	1.5	4.3

n: sample count

Table 3-2. Spearman rank correlations between water quality parameters and land use of 11 tributaries of the Mulberry River, Arkansas from 2016 to 2017.

	Land Use			
Parameter	Coniferous	Deciduous	Mixed	Pasture
Discharge	**-0.17**[a]	0.13	**-0.31**	0.07
Total suspended solids	-0.13	**0.16**	-0.11	**-0.19**
Temperature	-0.03	0.02	-0.11	-0.01
Dissolved oxygen	0.11	-0.11	0.08	0.12
Specific conductance	**-0.23**	**0.16**	**-0.47**	**-0.22**
pH	-0.06	0.02	**-0.33**	-0.01
Acid neutralizing capacity	**-0.19**	0.12	**-0.48**	**-0.21**
Ca	-0.06	0.002	0.04	0.07
Mg	-0.06	-0.02	-0.01	0.12
K	-0.10	0.01	-0.11	0.15
Na	-0.08	-0.02	**-0.17**	0.13
S	-0.04	-0.001	0.01	-0.01
Al	-0.08	0.09	-0.002	-0.06
Fe	-0.001	-0.02	0.03	0.06
Mn	-0.06	0.02	-0.04	0.02
Total P	-0.15	0.15	-0.09	-0.10
Soluble P	**-0.24**	**0.20**	-0.09	-0.12
Soluble reactive P	0.002	0.01	-0.03	-0.06
Cl	-0.08	0.03	0.01	0.003
SO_4	**-0.29**	**0.24**	**-0.59**	**-0.24**
Total organic C	**-0.27**	**0.20**	**-0.52**	**-0.20**
Total N	**0.26**	**-0.28**	**0.16**	**0.39**
NO_3	**0.31**	**-0.32**	**0.33**	**0.37**

[a] Bolded values are significant at α=0.05
n=168

Table 3-3. Spearman rank correlations between water quality parameters and stream pH, acid neutralizing capacity (ANC), and base cation (Ca, Mg, K, and Na) concentrations of the Mulberry River, Arkansas from 2016 to 2017.

Parameter	pH	ANC	Ca	Mg	K	Na
Discharge	**0.31**	-0.05	-0.03	-0.05	0.03	0.04
Total suspended solids	-0.14	0.02	-0.09	-0.09	-0.01	0.01
Temperature	-0.15	**0.31**	-0.03	-0.02	0.10	0.09
Dissolved oxygen	0.02	-0.05	-0.12	-0.12	-0.06	-0.14
Specific conductance	**0.27**	**0.78**	-0.02	0.01	0.10	**0.19**
S	-0.03	0.04	**0.70**	**0.75**	**0.15**	**0.41**
Al	-0.11	-0.13	-0.13	-0.17	**-0.18**	-0.04
Fe	-0.07	**-0.15**	0.02	0.01	-0.03	0.02
Mn	-0.03	0.02	**0.21**	**0.34**	**0.37**	**0.36**
Total P	-0.04	0.08	-0.07	-0.01	0.07	0.05
Soluble P	**-0.21**	-0.11	0.15	0.14	**0.35**	**0.23**
Soluble reactive P	-0.14	0.07	0.00	-0.04	-0.03	0.06
Cl	**-0.19**	0.03	0.06	0.01	-0.04	-0.04
SO_4	**0.48**	**0.57**	-0.02	-0.03	0.00	**0.15**
Total organic C	**0.35**	**0.68**	0.02	0.05	0.08	**0.22**
Total N	0.13	**-0.17**	0.00	0.00	0.11	0.02
NO_3	**-0.17**	**-0.44**	0.01	0.05	0.05	-0.10

[a] Bolded values are significant at $\alpha=0.05$
n=168

Table 3-4. Stepwise multiple linear regression models for water quality parameters and land use types (C, coniferous forest; D, deciduous forest; M, mixed forest; P, pasture) of 11 tributaries of the Mulberry River, Arkansas from 2016 to 2017.

Depend. Variable[a]	Ind. Variable	Regression Equation	R^2	Adj. R^2	*P*-value
Discharge	M, P	0.61 -0.30M+0.09P	0.13	0.12	<0.01
Total suspended solids	P	4.58-0.202P	0.03	0.02	0.03
pH	D, M	9.18-0.03D-0.43M	0.21	0.20	<0.01
Specific Conductance	M	54.5-9.01M	0.07	0.07	<0.01
ANC[b]	C, D, M, P	268.7-2.5C-2.7D-7.6M-3.1P	0.49	0.48	<0.01
K	M, P	0.71-0.01C+0.03M	0.05	0.04	0.01
Soluble P	C, M	10.04-0.47C+2.14M	0.09	0.08	0.03
SO_4	D, M	5.32-0.03D-0.60M	0.07	0.06	0.04
Total organic C	C, D, M, P	40.30-0.39C-0.39D-1.1M-0.4P	0.37	0.36	<.001
Total N	P	34.29+12.50P	0.14	0.13	<.001
NO_3	M, P	5.82+13.04M+8.97P	0.20	0.19	<.001

[a] Parameters not significantly related ($P > 0.05$) with any land use are not shown

[b] Acid neutralizing capacity

n=168

Table 3-5. Principal component factor loadings of water quality parameters for 11 tributaries of the Mulberry River, Arkansas from 2016 to 2017.

	Factor		
Parameter	1	2	3
Discharge	0.04	-0.27	0.44
Total suspended solids	0.05	**0.52**	**0.63**
Temperature	0.13	**0.71**	0.1
Dissolved Oxygen	0.1	-0.48	-0.17
Specific conductance	**0.83**	0.36	-0.09
pH	**0.52**	-0.15	-0.06
Acid neutralizing capacity	**0.79**	0.11	0.01
Ca	**0.92**	0.22	0.08
Mg	**0.85**	0.46	0
K	0.3	**0.87**	0.04
Na	0.43	**0.72**	-0.3
S	**0.89**	-0.12	0.06
Al	-0.05	0.39	**0.53**
Fe	0.01	0.35	**0.8**
Mn	0.3	0.49	0.46
Total P	-0.1	**0.63**	0.31
Soluble P	-0.14	-0.02	0.13
Soluble reactive P	0.04	0.09	0.44
Cl	0.25	0.34	-0.4
SO_4	**0.83**	-0.06	0.07
Total organic C	**0.83**	0.11	0.07
Total N	-0.19	0.15	-0.26
NO_3	**-0.54**	0.21	**-0.56**
Eigenvalue	6.85	3.37	2.48
% of Variance	42.36	25.73	19.06
Cumulative %	42.36	68.09	87.15

Bold values are strong loadings (>0.50)
n=168

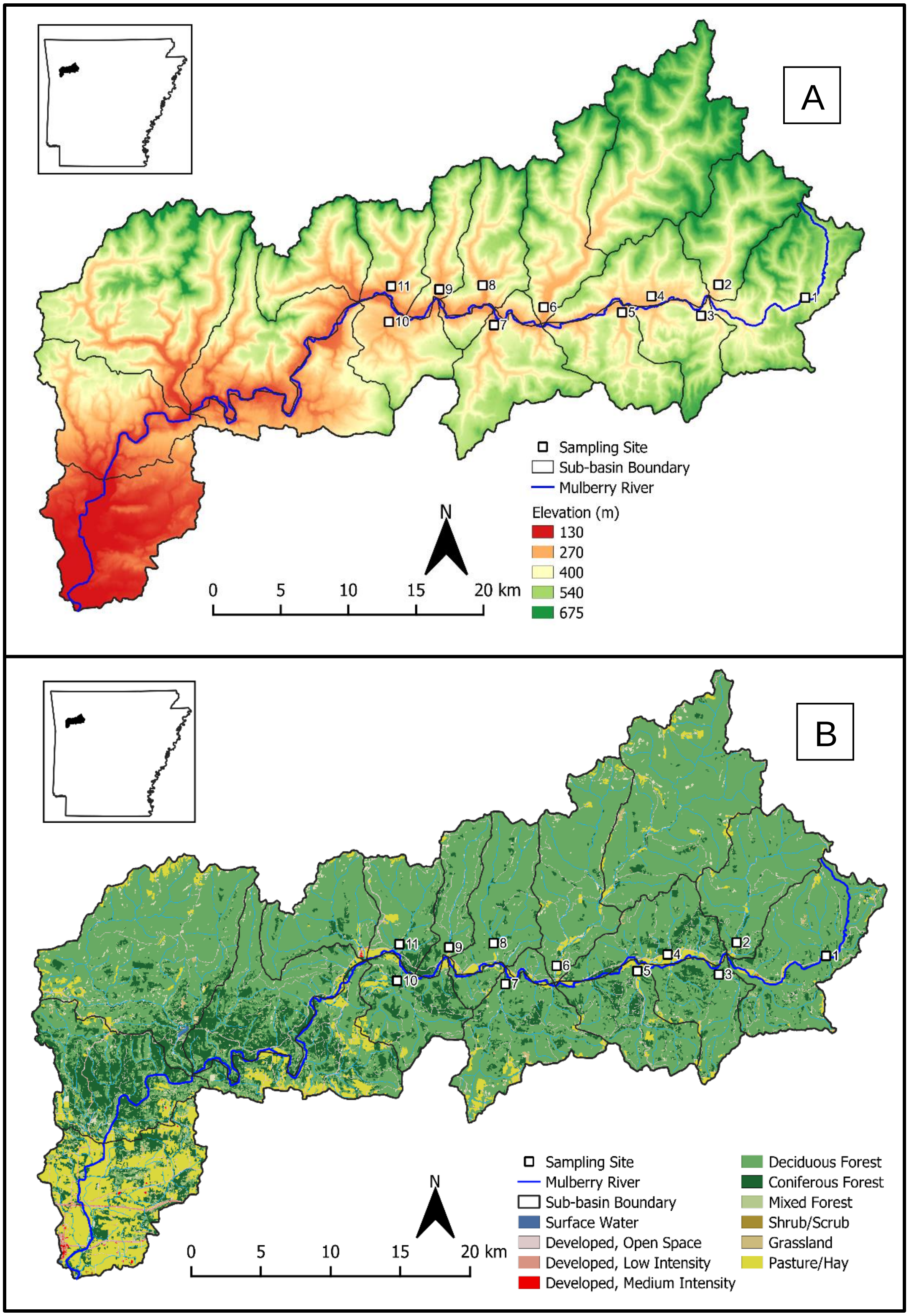

Figure 3-1. The Mulberry River basin showing (A) the water sampling sites, the digital elevation model (DEM), and (B) land use patterns obtained from the National Land Cover Database.

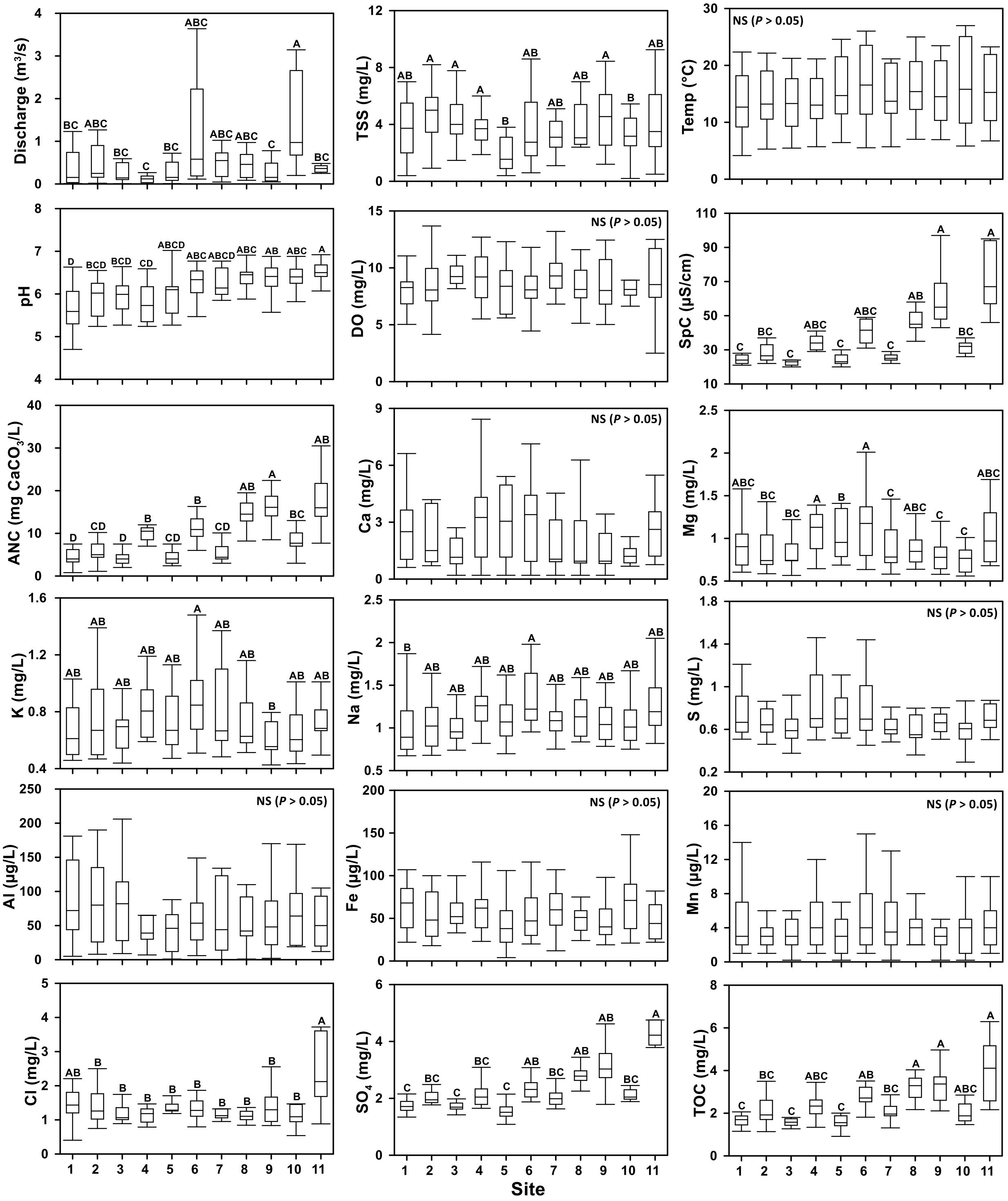

Figure 3-2. Box-and-whisker plots for 18 water quality parameters from 11 tributaries of the Mulberry River, Arkansas measured from 2016 to 2017 (n=168). Boxplots with the same letters are not significantly different at α=0.05 (NS, not significant; TSS, total suspended solids; temp, temperature; DO, dissolved oxygen; SpC, specific conductance; ANC, acid neutralizing capacity; TOC, total organic C).

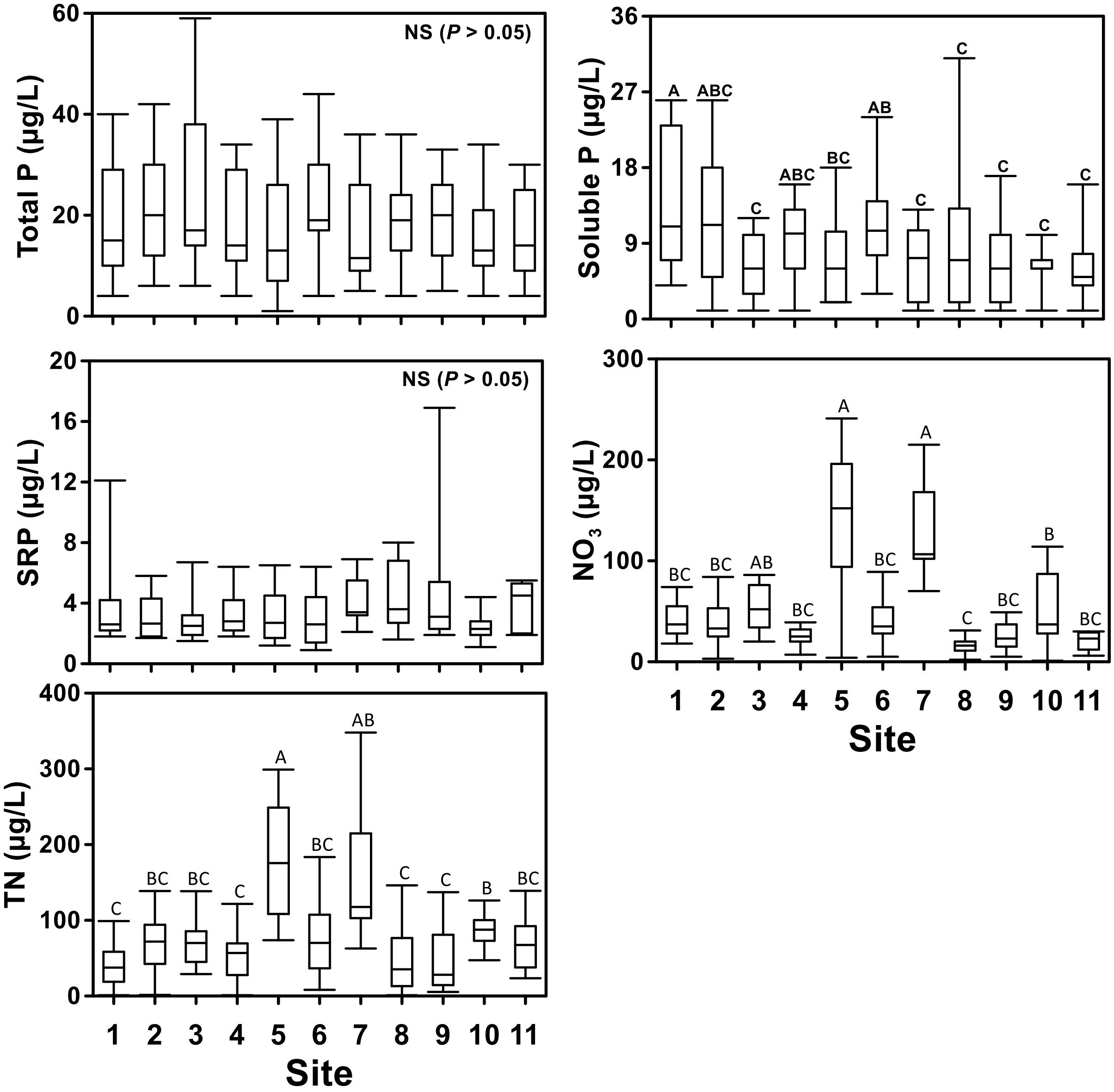

Figure 3-3. Box-and-whisker plots for P and N parameters for 11 tributaries of the Mulberry River, Arkansas measured from 2016 to 2017 (n=168). Boxplots with the same letters are not significantly different at α=0.05 (NS, not significant; SRP, soluble reactive P; TN, total N).

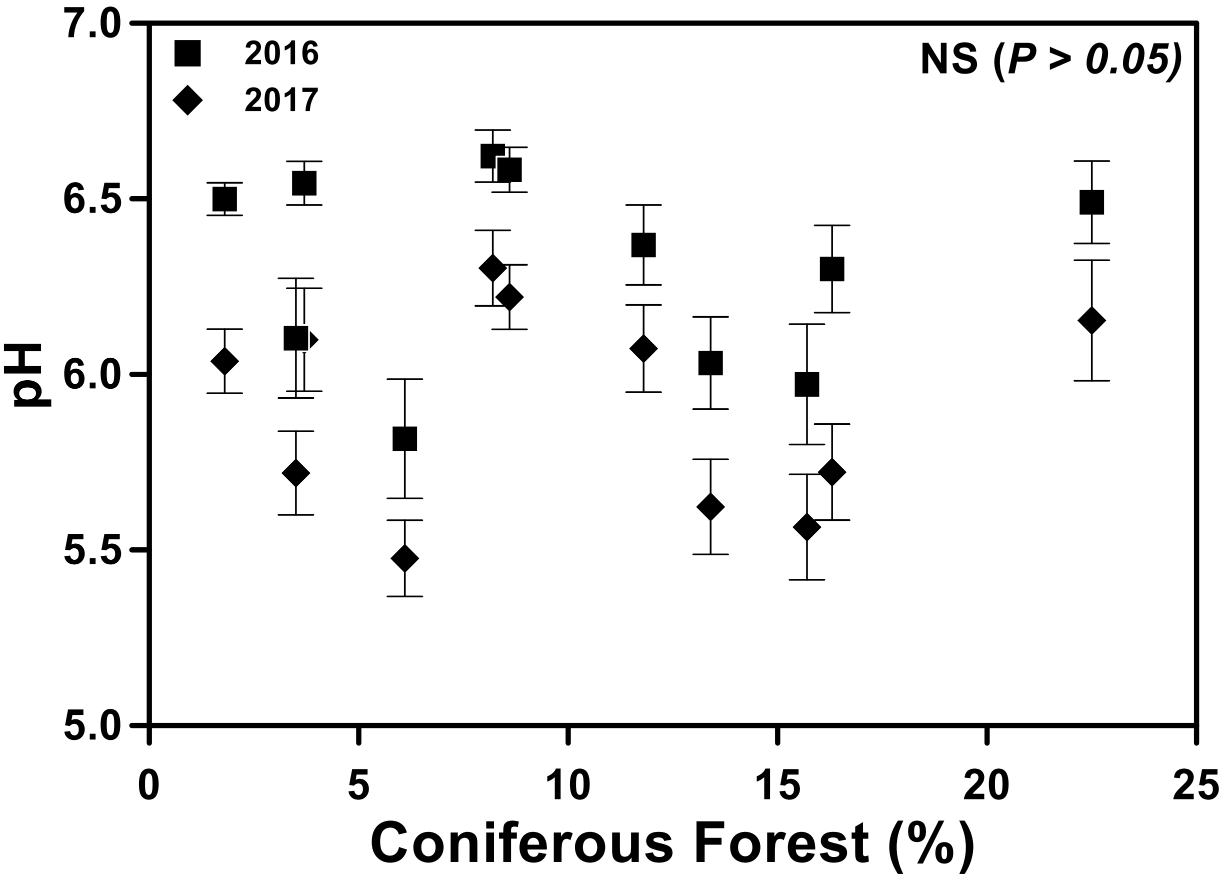

Figure 3-4. Linear regression plots of mean stream pH of 11 tributaries of the Mulberry River, Arkansas for 2016 and 2017 versus the proportion of coniferous forest within the respective sub-basin. Error bars represent standard errors of the mean.

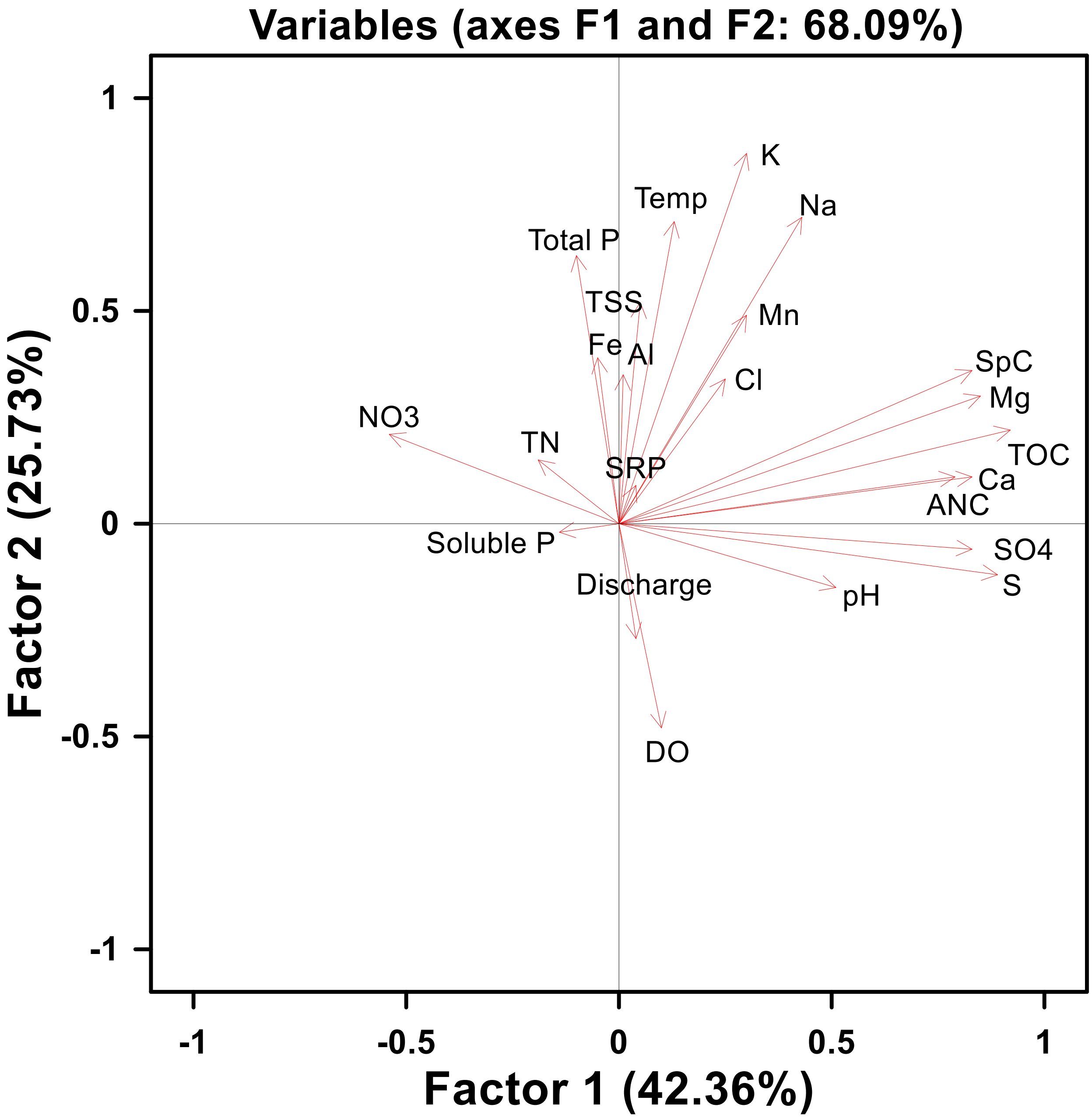

Figure 3-5. Principal component analysis biplots for 24 water quality parameters of the Mulberry River, Arkansas measured from 2016 to 2017 (Temp, temperature; SpC, specific conductance; TOC, total organic C; ANC, acid neutralizing capacity; DO, dissolved oxygen; TSS, total suspended solids; SRP, soluble reactive P; TN, total N).

Chapter Four: Water Quality Trends of the Mulberry River Watershed, Arkansas, 2015-2019

Abstract

The Mulberry River, a National Wild and Scenic River in Arkansas, has been listed as impaired due to low pH since 2008. To date, there have been no long-term monitoring studies on the Mulberry River, the objective of this study was to identify potential changes in chemistry and possible causes of acidification in the Mulberry River watershed. Eleven locations on the Mulberry River and 10 tributaries of the river were sampled monthly from March 2015 to January 2019 (46-mo) and 34 physicochemical parameters were measured. Trend analyses indicated that there were declines ($P<0.05$) in specific conductance, total suspended solids, total organic C, total N, SO_4, and flow-adjusted soluble Ca and Mg and an increase in Cl and total Al, Fe, and Na. Out of the 21 locations sampled, three had decreases in pH suggesting that regions of the watershed may have been acidified during the duration of this study. The decrease in specific conductance and several constituents suggests that the surface waters of the watershed have become more dilute over time. An increase in streamflow and precipitation has been observed throughout Arkansas and an increase in flow within the Mulberry River watershed may be causing this dilution. Not only do the results of this study suggest regions of the watershed have become acidified, the postulated dilution makes the river more susceptible to sudden changes in pH. Further routine sampling will be needed to fully understand these long-term trends on stream chemistry and the aquatic community of this watershed.

Introduction

In 1992, the Mulberry River in Arkansas was designated as a ‘National Wild and Scenic River’ due the outstanding natural and recreational value it provides to Arkansas and the United States. In 2008, the Mulberry River was added to US Environmental Protection Agency (USEPA) 303(d) list of impaired water bodies by the Arkansas Department of Environmental Quality (ADEQ) due to the low pH ($pH < 6.0$) of a 14.6 km segment of the river (Shafii, 2008). The 2016 303(d) list included the addition of two more segments of the river increasing the length of impairment from 14.6 km to 68.7 km, potentially indicating further acidification of the river. The 2016 303d list also included Little Mulberry Creek (a 28 km long tributary of the Mulberry River) and Friley Creek (an 11.6 km long tributary of Little Mulberry Creek) increasing the total length of impairment within the watershed to 108.3 km.

The Mulberry River is a 110 km long tributary of the Arkansas River within an approximately 1100 km^2 watershed located in northwest Arkansas and is comprised of three hydrologic unit code (HUC) 10 and 13 HUC12 sub watersheds. The predominant land uses of the watershed are deciduous forest (69.5%), coniferous forest (13.5%) and pasture (8.8%) (Homer et al., 2015) with increasing forest density towards the headwaters. The watershed is located in a rural portion of Arkansas (population < 10,000; average population density ~10 persons/km^2; 2010 US census data) with minimal agriculture (< 0.1%) (Homer et al., 2015) and no approved point source discharge permits (Shafii, 2008). As such, any source of acidity within the watershed is unlikely to be derived from urban sources, agriculture, and/or industry within the watershed. Instead, acidity within the watershed may be originating from changing atmospheric, soil, land use, and/or groundwater conditions.

To fully assess and understand the potential impairment of the Mulberry River, long-term and routine sampling of the river and tributaries is needed. Unfortunately, to date there is little information in the literature regarding the chemical composition of the river and no comprehensive long-term monitoring studies have been performed. Therefore, the objectives of this study were to 1) measure a suite of physicochemical parameters on the Mulberry River and its tributaries over a 46-month period; 2) perform statistical analyses on this data to identify monotonic trends in physicochemical data; and 3) evaluate the relationship between the physicochemical parameters measured to identify potential sources of acidity. It was hypothesized that the pH of the 21 sampled locations has decreased over the last 46 months.

Materials and Methods

Sampling occurred on a monthly basis over a 46-month period from March 2015 to January 2019. Eleven locations on the Mulberry River and 10 tributaries of the Mulberry River were sampled which represented eight out of 13 HUC-12 sub-watersheds (Figure 4-1; Table 4-1). Water samples were collected from a single vertical centroid-of-flow using 2-L high-density polyethylene bottles that were rinsed three times with ambient water prior to collection of the sample. Stream temperature, pH, dissolved oxygen (DO), and specific conductance (SpC) were measured *in-situ* using a YSI multi-parameter data sonde.

Stream discharge was measured using the USGS midsection method (Turnispeed and Sauer, 2010) at the base of the study reach. Discharge samples were measured several times between December 2017 and August 2018 during flow stages when it was safe to sample (Table 4-1). Due to the accessibility and danger of sampling several locations on the Mulberry River, only a select number of locations (R1, R2, R4, R10, and R11) were ever sampled. Streamflow of all 10 tributaries were measured a varying number of times (Table 4-1). A strong relationship ($R^2 > 0.95$) was derived from the measured streamflow and discharge data from USGS gauge 07252000. This relationship was used to calculate the discharge for days when streamflow was not measured. A strong relationship ($R^2 > 0.95$) was also derived for the evolution of the streamflow along the Mulberry River from R1 to R11 which was used to calculate discharge for sites that were unable to be sampled.

Water samples were analyzed for total and soluble concentrations of 20 elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Ti, and Zn) by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an Agilent 5110 ICP-OES. Total elemental concentrations were measured in water samples which were digested at 140° C in 70% (w/w) HNO_3. Soluble concentrations of elements were measured in water samples that were first vacuum-filtered through a 0.45 µm membrane and then acidified to $pH < 2.0$ with one drop of 37% (w/w) HCl per 10 mL of sample. Sulfate and Cl concentrations were determined using a Dionex 1600 Ion Chromatography system on unacidified samples. Total organic C (TOC) and total N (TN) were measured on a Shimadzu TOC-L analyzer. Soluble reactive P (SRP) and NO_3^- (plus NO_2^-) were measured on a SKALAR SAN++ wet chemistry auto analyzer. Acid neutralizing capacity (ANC) was determined by potentiometric titration of 100 mL of water with $0.02N$ H_2SO_4 to pH 4.2 on a Metrohm Titrino Plus auto-titrator. Total suspended solids (TSS) were measured by passing 1 L of water through a 1-µm glass-fiber filter and measuring the difference in filter mass. Inorganic suspended solids (ISS) were determined by combusting the filter at 550° C and measuring the filter mass. Organic suspended solids (OSS) were calculated as the difference between TSS and ISS measurements. Chlorophyll-a was determined fluorometrically following the filtration of 750 mL of water through a 1-µm glass-fiber filter in accordance with EPA method 445.0. Results are not presented for As, Cd, Co, Cu, Mo, Ni, Pb, Se, and Ti concentrations which were consistently below detection limit.

To evaluate the effect of sampling location on physicochemical properties, the Kruskal-Wallis rank test was used in SAS (version 9.4; SAS Institute., Cary, NC) using the PROC NPAR1WAY procedure. Spearman's non-parametric rank correlation coefficient was used to examine the relationship between water quality parameters directly related to acidity (pH, ANC, SpC, and concentrations of nonacid cations [Ca, K, Mg, and Na]) and the remaining physicochemical parameters measured. Two trend analyses were used to identify monotonic trends in water quality. First, the Mann-Kendall test, which is a nonparametric form of monotonic trend regression analysis, was used to identify statistically significant trends. The second trend analysis used was analyzing trends in flow-adjusted parameters over the duration of this study. The parameters were flow-adjusted by plotting residuals from locally estimated scatterplot smoothing (LOESS) regression of log-transformed parameters versus log-transformed discharge. Further details of this statistical analysis method is provided in (White et al., 2004).

Results

Spatial Variability

Thirty-four physicochemical parameters were analyzed for differences along the length of the Mulberry River. Of the 34 parameters analyzed over 46 months, 17 parameters were affected by sampling location. River discharge was lowest at the headwaters (R1) and increased from an average of 0.4 to 7.5 m^3/s for river sampling site 1 (R1) and R11, respectively (Figure 4-2). Similarly, pH, SpC, ANC, and TOC increased from R1 to R11 (Figure 4-2). Similar to the relationship between site and both pH and ANC, averaged across the 4 years of the study both pH and ANC were strongly predicted (R^2=0.91) by distance from the headwater. Specific conductance and TOC increased ($P < 0.05$) from R5 to R6 (before and after the confluence of T5). Concentrations of NO_3 showed a parabolic trend with the greatest concentrations occuring at R4 and the lowest concentrations at R1 (Figure 4-3). Sulfate concentrations were greatest at R8 (2.4 mg/L) but did not differ from R6, R7, R9, R10, and R11, and were lowest at R1 (1.8 mg/L; Figure 4-4). Concentrations of soluble S and total S were greatest at R6 but did not differ from R7 to R11. Soluble S was lowest at R1 whereas total S was lowest at R4 and R5.

An inverse trend in concentrations of Ca and Al along the length of the river was observed (Figure 4-5). Concentrations of soluble Ca (0.95 mg/L) and total Ca (0.96 mg/L) were lowest at R1 and greatest at R6. There were minimal differences in concentrations of total and soluble Ca suggesting that Ca^{2+} was the primary species of Ca present. Soluble Al concentrations were greatest at R1 (94 µg/L) and lowest at R10 and R11 (55 µg/L). Concentrations of soluble and total Mg showed a similar trend to Ca. Concentrations were lowest at R1 to R5 and greatest at R6. Similar to Ca, differences between soluble and total Mg were very small suggesting Mg^{2+} was the primary Mg species. Soluble Mn and Na concentrations were lowest at R2 and greatest at R11.

There were greater differences in physicochemical properties among tributary sampling locations compared to river sampling locations. Of the 34 parameters measured, 22 parameters differed by tributary. Stream discharge was greatest at T5 and T9 and did not statistically differ among the other seven tributaries (Figure 4-6). Stream pH showed a general increasing trend with site number with lowest pH being observed at T2 (pH = 5.9) and greatest pH observed at T10 (pH = 6.6). Tributary SpC and ANC had a similar trend of alternating high and low values with the low values being observed at T2, T4, T6, and T9 and comparatively higher values observed at T3, T5, T7, T8, and T10. Total suspended solids were primarily comprised of ISS. Thus, similar trends in ISS and TSS were observed with lowest values at T4 and greatest values at T8. Total organic C showed a general trend of increasing from T1 to T10 with the lowest concentrations observed at T4 (1.6 mg/L) and greatest at T10 (3.2 mg/L; Figure 4-7). There was no discernable pattern in TN concentrations and the lowest concentrations were observed at T8 (0.1 mg/L) and greatest concentrations at T2 (0.5 mg/L) and T6 (0.6 mg/L), which did not differ from each other. Nitrate concentrations were greatest at T4 (0.19 mg/L) and T6 (0.15 mg/L) which did not differ from each other, and lowest at T8 (0.35 mg/L). A similar trend in sulfate, soluble S, and total S concentrations was observed among tributary sites (Figure 4-8). A general increasing trend was observed from T1 to T10 with the lowest S concentrations at T4 and the greatest locations at T10.

Soluble Al and Fe concentrations showed a similar pattern among tributary sampling sites but exhibited no discernable pattern (Figure 4-9). Concentrations of soluble Al and Fe were lowest at T4 and greatest at T3. The large variability in concentrations resulted in few differences among tributaries. Soluble Ca and Mg concentrations demonstrated a similar trend among tributaries with the lowest mean values observed at T4 and the greatest at T10. Soluble Na concentrations did not differ among eight out of 10 sampling locations and the greatest values were observed at T10. The greatest soluble K concentrations were observed at T8 (0.9 mg/L) and the lowest at T4 (0.66 mg/L) and T2 (0.66 mg/L).

A similar trend of increasing concentrations of total Ca, Mg, and Na with increasing site number was observed (Figure 4-10). Total Ca and Mg concentrations were lowest at T4 (0.95 mg Ca/L and 0.71 mg Mg/L) and greatest at T10 (6.5 mg Ca/L; 1.6 mg Mg/L). Total Na concentrations were lowest at T2 (1.1 mg/L) and greatest at T10 (2.1 mg/L). Concentrations of total Al and Fe were greatest at T8 (1.1 mg Al/L; 0.7 mg Fe/L) and lowest at T4 (0.3 mg Al/L; 0.3 mg Fe/L). Total K concentrations were greatest at T8 (1.0 mg/L) and lowest at T2 (0.69 mg/L) and T4 (0.7 mg/L), which did not differ (*P*>0.05) from each other. There was no discernable trend in total Mn concentrations and the greatest values were observed at T1 and T9 and the lowest observed at T4.

Water-Quality Parameter Correlations

Spearman's rank correlation analysis was performed to evaluate the relationship between parameters directly related to acidity (i.e., pH, SpC, ANC, and concentrations of Ca, K, Mg, and Na) and the remaining physicochemical parameters measured to provide insight on the factors influencing stream acidity. As expected, numerous ($P < 0.05$) correlations were observed between the water quality parameters measured along the Mulberry River (Table 4-2). Stream pH and concentrations of K, Mg, and Na were inversely correlated with discharge. Specific conductance, chlorophyll-a, TOC, and SO_4 were positively correlated with stream pH, ANC, and base cation (i.e. Ca, K, Mg, and Na) concentrations. Stream pH was inversely correlated with Cl, total Al, total Cu, and total Fe and positively correlated with SpC, ANC, OSS, soluble Ca, soluble Fe, soluble Mg, total base cation (i.e., Ca, K, Mg, and Na) concentrations, total Mn, total P, and total S. Specific conductance was positively correlated with ANC, chlorophyll-a, TOC, TN, SO_4, total Mn, total P, total S, total Zn and both total and soluble base cation (i.e., Ca, K, Mg, and Na) concentrations. Specific conductance, Ca, K, Mg, and Na were all inversely correlated with ISS, soluble and total Al, and total Fe. Nitrate was inversely correlated with SpC and Ca but positively correlated to ANC and K.

Similar to the sampled locations along the Mulberry River, numerous statistically correlations were observed among the tributary locations between pH, SpC, ANC, and base cations (i.e., Ca, K, Mg, and Na) and the other water quality parameters (Table 4-3). Stream discharge was inversely correlated with SpC and concentrations of Ca, K, Mg, and Na. Specific conductance, TOC, soluble Ca and Mg, and total Ca, K, Mg, Mn, and Na were all positively correlated with the pH, SpC, ANC, and soluble base cation concentrations. Stream pH was only inversely correlated to total Al. Specific conductance was only inversely correlated with NO_3 and soluble Al. Sulfate and total S were positively correlated with pH, SpC, ANC, and all base cations except K. In addition to SpC, NO_3 was inversely correlated with ANC, Ca, and Mg and TN was inversely correlated with ANC, Ca, and Mg. Total, inorganic, and organic suspended solids were correlated with SpC, ANC, Ca, Mg, and Na.

Trend Analyses

Kendall's Tau

The Mann-Kendall analysis for monotonic trends in the water quality parameters along the Mulberry River resulted in numerous ($P<0.05$) trends over the 46-month period of study (Table 4-4). Across the 11 locations sampled along the Mulberry River, 15 parameters had a decreasing trend whereas nine parameters had an increasing trend. Specific conductance (8 out of 11 locations), TSS (9 out of 11 locations), OSS (8 out of 11 locations), TOC (6 out of 11 locations), TN (11 out of 11 locations), and SO_4 (6 out of 11 locations) had the greatest occurrence of decreasing trends. Chloride (11 out of 11 locations), total Al (8 out of 11 locations), and total Na (7 out of 9 locations) had the greatest occurrence of increasing trends.

Similar to the sites sampled along the Mulberry River, numerous statistically significant monotonic trends were observed at the sites sampled along 10 tributaries contributing water to the Mulberry River (Table 4-5). Across the 10 sampling locations on tributaries, 14 parameters had decreasing trends whereas nine parameters had increasing trends. Specific conductance (6 out of 10 locations), TN (9 out of 10 locations), and total P (5 out of 10 locations) had the greatest occurrence of decreasing trends. Chloride (8 out of 10 locations), total Al (6 out of 10 locations), and total Fe (5 out of 10 locations) had the greatest occurrence of increasing trends.

Trends in Flow-adjusted Parameters

To remove the influence of changing flow conditions on water chemistry, the physicochemical parameters measured in this study were flow-adjusted to help further assess changes in stream chemistry over time. Similar to the Mann-Kendall trend analysis, numerous flow-adjusted physicochemical parameters. Across the 11 sampling locations on the river, 10 parameters increased whereas 14 parameters decreased (Table 4-6). Specific conductance (11 out of 11 locations), TSS (8 out of 11 locations), TOC, (7 out of 11 locations), soluble Ca (7 out of 11 locations), and soluble Mg (9 out of 11 locations) were the parameters that had the greatest occurrence of decreasing trends. Chlorophyll-a (6 out of 11 locations), Cl (10 out of 11 locations) soluble S (6 out of 11 locations), total Al (11 out of 11 locations), total Fe (9 out of 11 locations), and total Na (6 out of 11 locations) were the parameters that had the greatest occurrence of increasing trends.

Across the 10 sampling locations on tributaries, 10 parameters decreased whereas 9 parameters increased (Table 4-7). Specific conductance (8 out of 10 locations), TSS (5 out of 10 locations), TOC (5 out of 10 locations), TN (9 out of 10 locations), soluble Ca (5 out of 10 locations), and soluble mg (6 out of 10 locations) had the greatest occurrence of decreasing trends. Cl (6 out of 10 locations), total Al (5 out of 10 locations), total Fe (5 out of 10 locations), and total Na (5 out of 10 locations) had the greatest occurrence of increasing trends.

Discussion

The results of this study highlight the spatial complexity and heterogeneity of watershed chemistry and indicate that the chemistry of the Mulberry River and its respective tributaries has changed over the approximately 4-yr sampling period. Spatially, there was a very distinct pattern in the evolution of chemistry from the headwaters of the Mulberry River (site R1) to the final downstream sampling point. For almost all parameters that differed by site (except soluble Al and NO_3), there was a general trend of concentrations increasing from the headwaters towards downriver. This trend was expected due to the increased contribution of constituents from tributaries as the length of the Mulberry River increases. The increase in TOC, Ca, Mg, and Na concentrations would increase the buffering capacity which is evident in the increased SpC and ANC and the subsequent increase in pH along the river. As a result of the increased buffering capacity, the average pH of the Mulberry River increased 0.7 units from 5.87 to 6.57 for R1 and R11, respectively. Averaged across 46 months, there were significant linear relationships ($P<0.01$) between the distance of each sampling point from the headwaters and both pH and ANC (Figure 4-11). This relationship highlights the east-to-west spatial variability in acidity throughout the watershed. Concentrations of soluble Al were greatest at R1 due to the lower pH and a further decrease in pH could result in increased mobilization of Al which can further amplify the detrimental effects of acidification. Another trend observed in the spatial variability among the sampled river sites is the sudden, and often significant, increase in concentrations at site R6. Between R5 and R6 is the confluence of Little Mulberry Creek (LMC; T5) with the Mulberry River. Little Mulberry Creek is a fourth order stream and a significant contributor of water to the Mulberry River. Stream pH, SpC, ANC, and concentrations of TOC, SO_4, soluble and total S, soluble and total Ca, soluble and total Mg, soluble Na, and total Mn all increased at R6 following the confluence of LMC and the Mulberry River.

Unlike the sampled river sites which had a general trend of concentrations increasing from the headwaters downstream, there was a tendency for tributaries north of the Mulberry River (T1, T3, T5, T7, T8, and T10) to have greater concentrations than the sampled tributaries south of the river (T2, T4, T6, and T9). This trend is especially evident when examining SpC, ANC, and concentrations of ISS, TOC, soluble and total Al, soluble and total Ca, soluble and total Mg, soluble and total K, total Fe, and total Mn. The inverse pattern was observed for TN concentrations which were greatest at sites T2, T4, T6, and T9. It is currently not known why this pattern exists, and what could be causing such a difference in stream chemistry between the northern and southern tributaries. It is possible that there are different relative amounts of groundwater compared to precipitation contributing to the tributaries on the north and south side of the watershed. Although the geology of the Mulberry River watershed is predominantly sandstone and shale, the greater concentrations in base cations in tributaries north of the Mulberry River may suggest communication with pockets of limestone which can be found in the region (Merewether and Haley, 1969). Despite the differences in chemistry between the tributaries north and south of the river, there was still a general trend of increasing pH from east (T1) to west (T10).

The relationships between parameters, especially stream flow and stream chemistry can be used to infer the relative contributions of precipitation, surface runoff, and groundwater to the flow in the Mulberry River watershed. A positive relationship of concentrations with streamflow can highlight precipitation or surface runoff as the primary H^+ source whereas an inverse relationship can indicate either groundwater as a source and/or a dilution effect from an increase in the volume of water. At both the river sites and tributary sites there were no relationships between discharge and stream pH but there were significant inverse relationships between discharge and both SpC and base cation concentrations. This inverse relationship suggests a dilution of the Mulberry River and its tributaries during high flow events rather than a contribution of base cations from surface runoff.

Two different statistical approaches to trend analysis (Mann-Kendall's tau rank coefficient, and trends in flow adjusted concentrations) were used to evaluate the changes in chemistry of the Mulberry River and its tributaries. The two statistical tests yielded different results but positive and negative trends were consistent across the river and tributaries (Table 4-8). Parameters such as SpC, TSS, TOC, TN, SO_4, soluble Ca, and soluble Mg had consistently negative trends; whereas, Cl, total Al, total Fe, and total Na had positive trends (Tables 4-48). Of the 21 sites studied in the Mulberry River watershed, only three locations showed a negative trend in pH over the duration of the study.

The lack of statistically significant trends in pH during the duration of this study can be attributed to the increase in pH at all locations starting in May 2018 (Figure 4-12). From March 2015 until May 2018 there were statistically significant decreasing trends in pH at 18 of the 21 locations. Since May 2018, there has been an increase in pH by approximately 1 unit at all sites except T4 which has not been sampled since May 2018. This upswing in pH may be the product of an abnormally wet year throughout the region which may have diluted the proton concentrations in the river and tributaries. It is possible that the pH of the watershed will decrease during a dryer year, but this study does not have enough data to adequately predict future trends.

The decrease in TOC, TN, SO_4, Ca, and Mg throughout the watershed may correspond to the decrease in SpC observed at nearly all sampled locations. A decrease in SpC throughout the watershed could indicate that there has been an increase in streamflow which would decrease constituent concentrations (Moore et al., 2008). An increase in stream flow has been observed throughout the United States (McCabe and Wolock, 2002) and Arkansas (Wagner et al., 2014) and could be diluting the Mulberry River watershed. Since 1960, data from USGS monitoring station 07252000 indicates mean annual discharge, minimum annual base flow, and maximum annual base flow have increased (Figure 4-13). This increased base flow could result in an increased rate of groundwater flow throughout the watershed.

Along the Mulberry River and at the tributaries sampled there were decreases in SO_4 and flow-adjusted soluble Ca and Mg which may be the result of an increased rate of groundwater flow and decreased residence time in the parent material. This would limit the interaction of water with sandstone, shale (including pyrite [FeS_2] and other sulfides), and limestone parent material. Pyrite oxidation is a common occurrence in regions with shale and a significant contributor of SO_4 to surface waters (Calmels et al., 2007). A key geochemical indicator of pyrite oxidation are SO_4/Cl ratios greater than 3 (Dogramaci et al., 2017) and the significant decreases in SO_4 observed throughout the watershed brings the SO_4/Cl ratio closer to 1 which may indicate a reduced rate of pyrite oxidation. Residence time of water is an important factor in determining the rate of pyrite oxidation (Moses and Herman, 1991; Rimstidt and Vaughan, 2003; Balci et al., 2007) and this may be further evidence of increased groundwater flow.

An increase in the proportion of water entering the watershed from the underlying geology would also decrease the amount of water interacting with soil and soil organic matter which could explain the decreases in TOC and TN observed at a majority of the sampled sites. The decrease in TOC and TN could also be due to decreased residence time in the soil. Increased groundwater flow may also be evident in the decreases in total, inorganic, and organic suspended solids which could occur from an increase in the amount of surface water but no change in runoff. Despite the t decrease in suspended solids, there were increases in total Al and Fe throughout the watershed but not soluble Al and Fe. A possible explanation is an increase in the amount of suspended fine colloids which would pass the 1 µm pore size filter used for TSS but not the 0.45 µm filter used for soluble metals. Clay minerals including Al and Fe oxides such as gibbsite [$Al(OH)_3$] and goethite (FeOOH), smectites, vermiculites, chlorites, and mica can have diameters between 0.1 and 1 µm.

It is unclear why there has been a increase in Cl throughout the watershed but the increase coincides with increases in Cl concentrations observed by ADEQ at monitoring station 0042 since 2015 despite a general decrease in concentrations since 1991 (data not shown). The state of Arkansas has made a shift towards increasing the amount of road salt applied as a weather management practice in the last approximately 5 years (Kellog, 2018) which may have resulted in increased Cl and Na concentrations in runoff.

Conclusion

This study evaluated the changes in the chemistry of the Mulberry River and 10 of its tributaries over a 46-month period. Of the 21 locations studied, three locations showed reduction in pH indicating that portions of the watershed may have become more acidic. Although there have been minimal changes in pH over the duration of this study, numerous trends in water quality were observed. The decreases in SpC, TSS, TOC, TN, SO_4, and flow-adjusted soluble Ca and Mg suggest that the watershed may be undergoing dilution. An increase in stream flow and precipitation has been observed throughout Arkansas and the dilution of base-poor watersheds may be a consequence of this shift. Four years of study is not enough to fully understand the changing dynamics of the Mulberry River watershed and continuing long-term monitoring is needed to fully understand the changes occurring. Future research should also focus on studying adjacent watersheds to identify potential differences between The Mulberry River and non-impaired watersheds. The Mulberry River was designated a ‘Wild and Scenic River’ due to the outstanding recreational and ecological value it provides to Arkansas and the United States. It will continue to be important to monitor changes in watershed characteristics in order to protect the watershed from potential degradation.

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Tables and Figures

Table 4-1. Site ID, corresponding site name, sample count, and count of streamflow samples for the 21 locations within the Mulberry River watershed.

Site ID	Site Name	Sample Count	Streamflow Count
River Locations			
R1	Mulberry River at Hignite Hollow	49	9
R2	Mulberry River before Bear Branch	48	8
R3	Mulberry River in Oark, AR	39	-
R4	Mulberry River after Washita Creek	47	6
R5	Mulberry River at Wolf Pen Campground	47	-
R6	Mulberry River after Little Mulberry Creek	44	-
R7	Mulberry River before Indian Creek	47	-
R8	Mulberry River at Byrds Campground	45	-
R9	Mulberry River at Low Bridge	47	-
R10	Mulberry River at Redding Campground	47	3
R11	Mulberry River at Turner Bend Outfitters	46	3
Tributary Locations			
T1	Panther Creek	41	8
T2	Bear Branch	25	2
T3	Estep Creek	34	6
T4	Washita Creek	36	6
T5	Little Mulberry Creek	47	8
T6	Clear Creek	22	2
T7	Indian Creek	33	6
T8	Herrods Creek	43	9
T9	Baron Branch	25	3
T10	Mountain Creek	27	4

Table 4-2. Spearman correlation matrix between select physicochemical water quality parameters and stream pH, specific conductance (SpC), acid neutralizing capacity (ANC), and soluble base cation concentrations from 11 locations on the Mulberry River from 2015 to 2019 (n=506).

Parameter	pH	SpC	ANC	Soluble Ca	Soluble K	Soluble Mg	Soluble Na
Discharge	0.04	**-0.31**[a]	0.04	0.02	**-0.50**	**-0.39**	**-0.47**
pH	**1**	**0.24**	**0.32**	**0.45**	0.03	**0.41**	0.05
SpC	**0.24**	**1**	**0.28**	**0.56**	**0.54**	**0.74**	**0.58**
ANC	**0.32**	**0.28**	**1**	**0.46**	**0.27**	**0.45**	**0.11**
CHL-a[b]	**0.18**	**0.17**	**0.20**	**0.28**	**0.30**	**0.27**	**0.24**
TSS	-0.06	0.08	-0.02	-0.05	**-0.12**	**-0.10**	**-0.22**
ISS	-0.06	**-0.11**	-0.04	**-0.10**	**-0.27**	**-0.23**	**-0.33**
OSS	**0.13**	**0.18**	0.03	0.06	0.03	**0.14**	0.02
TOC	**0.17**	**0.54**	**0.23**	**0.47**	**0.30**	**0.53**	**0.40**
TN	0.06	**0.28**	-0.06	**0.14**	-0.02	**0.19**	**0.15**
NO_3	-0.05	**-0.10**	**0.18**	**-0.11**	**0.10**	-0.03	0.05
SO_4	**0.17**	**0.33**	**0.09**	**0.34**	**-0.10**	**0.24**	**0.11**
Cl	**-0.14**	**-0.31**	0.07	-0.03	**0.13**	-0.07	**0.18**
Soluble Al	-0.06	**-0.49**	**-0.14**	**-0.29**	**-0.43**	**-0.46**	**-0.40**
Soluble Ca	**0.45**	**0.56**	**0.46**	**1**	**0.31**	**0.77**	**0.42**
Soluble Fe	**0.12**	-0.06	0.05	0.02	**-0.16**	-0.07	**-0.14**
Soluble K	0.03	**0.54**	**0.27**	**0.31**	**1**	**0.63**	**0.66**
Soluble Mg	**0.41**	**0.74**	**0.45**	**0.77**	**0.63**	**1**	**0.64**
Soluble Na	0.05	**0.58**	**0.11**	**0.42**	**0.66**	**0.64**	**1**
Soluble S	0.02	**0.13**	**0.13**	**0.40**	**-0.14**	0.09	**0.12**
Total Al	**-0.22**	**-0.35**	**-0.09**	**-0.27**	**-0.16**	**-0.44**	**-0.21**
Total Ca	**0.42**	**0.58**	**0.55**	**0.82**	**0.37**	**0.74**	**0.45**
Total Fe	**-0.16**	**-0.26**	-0.08	**-0.19**	**-0.23**	**-0.36**	**-0.22**
Total K	**0.17**	**0.41**	**0.30**	**0.25**	**0.75**	**0.56**	**0.53**
Total Mg	**0.33**	**0.59**	**0.43**	**0.61**	**0.61**	**0.80**	**0.66**
Total Na	**0.17**	**0.32**	**0.21**	**0.22**	**0.53**	**0.42**	**0.58**
Total Mn	**0.18**	**0.31**	**0.33**	**0.34**	**0.42**	**0.41**	**0.38**
SRP	-0.09	-0.06	**-0.12**	**-0.17**	**-0.16**	**-0.25**	**-0.15**
Total P	**0.11**	**0.16**	**0.10**	0.06	**0.24**	**0.21**	**0.19**
Total S	**0.23**	**0.15**	**0.24**	**0.40**	**-0.29**	**0.13**	-0.03
Total Zn	-0.08	**0.23**	**0.18**	0.03	**0.36**	**0.20**	**0.18**

[a] Values in bold are significantly different from 0 at α=0.05

[b] Abbreviations: CHL-a, chlorophyll-a; TSS, total suspended solids; ISS, inorganic suspended solids; OSS, organic suspended solids; TOC, total organic C; TN, total N; SRP, soluble reactive P

Table 4-3. Spearman correlation matrix between select physicochemical water quality parameters and stream pH, specific conductance (SpC), acid neutralizing capacity (ANC), and soluble base cation concentrations from 10 tributaries of the Mulberry River from 2015 to 2019 (n=333).

Parameter	pH	SpC	ANC	Soluble Ca	Soluble K	Soluble Mg	Soluble Na
Discharge	-0.06	**-0.40**[a]	-0.08	**-0.24**	**-0.48**	**-0.39**	**-0.36**
pH	**1**	**0.30**	**0.25**	**0.31**	-0.10	**0.33**	0.08
SpC	**0.30**	**1**	**0.51**	**0.77**	**0.55**	**0.86**	**0.61**
ANC	**0.25**	**0.51**	**1**	**0.60**	**0.25**	**0.60**	**0.29**
CHL-a[b]	-0.10	0.01	-0.06	-0.04	**0.24**	0.05	**0.17**
TSS	-0.08	**0.28**	**0.15**	**0.23**	**0.17**	**0.25**	**0.15**
ISS	-0.01	**0.20**	**0.14**	**0.24**	0.04	**0.21**	**0.12**
OSS	0.03	**0.20**	**0.14**	**0.14**	**0.17**	**0.23**	**0.17**
TOC	**0.17**	**0.58**	**0.46**	**0.54**	**0.34**	**0.60**	**0.40**
TN	0.02	-0.04	**-0.27**	**-0.22**	**-0.11**	**-0.16**	-0.05
NO_3	-0.05	**-0.27**	**-0.18**	**-0.35**	0.02	**-0.24**	-0.01
SO_4	**0.29**	**0.55**	**0.26**	**0.46**	0.05	**0.43**	**0.23**
Cl	0.07	-0.04	**0.18**	**0.18**	**0.20**	**0.17**	**0.33**
Soluble Al	0.10	**-0.15**	**0.17**	0.06	**-0.24**	-0.07	-0.09
Soluble Ca	**0.31**	**0.77**	**0.60**	**1**	**0.38**	**0.88**	**0.56**
Soluble Fe	0.10	0.03	**0.19**	**0.12**	**-0.11**	0.06	-0.04
Soluble K	-0.10	**0.55**	**0.25**	**0.38**	**1**	**0.59**	**0.64**
Soluble Mg	**0.33**	**0.86**	**0.60**	**0.88**	**0.59**	**1**	**0.68**
Soluble Na	0.08	**0.61**	**0.29**	**0.56**	**0.64**	**0.68**	**1**
Soluble S	**0.25**	**0.51**	**0.50**	**0.74**	0.09	**0.58**	**0.37**
Total Al	**-0.12**	-0.06	**0.18**	0.10	0.00	-0.01	0.01
Total Ca	**0.32**	**0.76**	**0.65**	**0.91**	**0.42**	**0.88**	**0.57**
Total Fe	-0.09	-0.02	**0.23**	**0.13**	-0.04	0.04	0.00
Total K	**0.12**	**0.50**	**0.34**	**0.43**	**0.73**	**0.61**	**0.59**
Total Mg	**0.30**	**0.76**	**0.57**	**0.79**	**0.58**	**0.89**	**0.69**
Total Mn	**0.14**	**0.30**	**0.30**	**0.31**	**0.39**	**0.44**	**0.32**
Total Na	**0.22**	**0.43**	**0.26**	**0.39**	**0.51**	**0.51**	**0.70**
SRP	0.06	0.03	-0.05	-0.01	**-0.18**	-0.07	0.05
Total P	**0.17**	**0.22**	0.05	0.11	**0.23**	**0.22**	**0.31**
Total S	**0.36**	**0.56**	**0.56**	**0.74**	0.01	**0.61**	**0.32**
Total Zn	-0.18	0.11	0.07	-0.01	**0.28**	**0.12**	**0.11**

[a] Values in bold are significantly different from 0 at α=0.05

[b] Abbreviations: CHL-a, chlorophyll-a; TSS, total suspended solids; ISS, inorganic suspended solids; OSS, organic suspended solids; TOC, total organic C; TN, total N; SRP, soluble reactive P

Table 4-4. Summary of Mann-Kendal rank correlations between physicochemical parameters and time at 11 locations on the Mulberry River from March 2015 to January 2019.

	Site										
Parameter	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11
pH	-	-	-0.30[a]	-	-	-0.28	-	-	-	-	-
SpC	-0.35	-0.34	-	-0.23	-0.29	-	-	-0.19	-0.26	-0.24	-0.24
ANC	-	-	-	-	0.21	-	0.22	-	-	-	-
CHL-a	0.23	0.31	-	-	-	0.29	-	-	-	-	0.24
TSS	-	-0.24	-0.23	-0.42	-0.27	-0.27	-0.27	-	-0.32	-0.32	-0.30
ISS	-	-	-	-0.29	-	-0.25	-0.23	-	-	-	-
OSS	-0.29	-	-0.27	-0.29	-0.21	-0.25	-	-0.21	-0.28	-0.21	-
TOC	-0.49	-0.44	-0.43	-0.36	-0.30	-	-	-	-0.22	-	-
TN	-0.70	-0.53	-0.42	-0.36	-0.29	-0.28	-0.57	-0.50	-0.60	-0.44	-0.41
NO_3	-	-	-	0.26	0.35	-	0.23	0.23	-	0.34	-
SO_4	-	-	-0.40	-	-	-0.22	-0.28	-0.26	-0.24	-0.28	-
Cl	0.34	0.53	0.50	0.45	0.53	0.52	0.42	0.31	0.51	0.47	0.53
Soluble Ca	-0.20	-0.18	-0.20	-	-	-	-	-	-	-	-
Soluble Fe	-	-	-0.25	-0.29	-	-	-	-0.23	-	-	-0.25
Soluble Mg	-0.27	-0.23	-0.22	-0.17	-0.19	-	-	-	-	-	-0.17
Soluble Na	-0.22	-	-	-	-	-	-	-	-	-	-
Soluble S	-	-	-	-	-	-	0.30	0.20	0.23	-	-
Total Al	0.34	0.22	-	0.28	0.27	-	0.25	-	0.25	0.27	0.24
Total Fe	-	-	-	0.24	0.21	-	0.22	-	0.20	0.22	-
Total Mn	-	-	-	-	-	0.22	-	-	-	0.23	-
Total Na	-	0.20	0.23	0.21	0.21	0.21	0.21	-	0.26	-	-
SRP	-	-	-	-	-	-0.24	-	-	-	-	-
Total P	-	-	-	-0.20	-0.21	-0.24	-0.22	-	-	-	-
Total S	-	-	-	-0.22	-0.19	-	-	-	-	-	-

[a] Tau values presented represent significant trends at α=0.05

Table 4-5. Summary of Mann-Kendal rank correlations between physicochemical parameters and time at 10 tributaries within the Mulberry River watershed from March 2015 to January 2019.

	Site									
Parameter	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
pH	-	-0.32[a]	-	-	-	-	-	-	-	-
SpC	-0.31	-	-0.29	-0.39	-0.28	-	-0.38	-0.32	-	-
ANC	-	-	-	-	-	-	-	-	-	0.38
CHL-a	0.22	0.41	-	-	-	0.34	-	-	0.29	-
TSS	-	-	-0.31	-	-0.23	-	-0.30	-0.29	-	-
ISS	-	-	-	-	-	-	-	-0.26	-	-
OSS	-0.37	-	-0.29	-	-	-	-	-	-0.35	-
TOC	-	-0.32	-	-0.48	-	-0.37	-	-	-	0.37
TN	-0.38	-0.64	-0.59	-0.37	-0.46	-0.44	-0.39	-0.54	-	-0.48
NO_3	-	-	-	-	0.33	-	-	0.31	-	-
SO_4	-0.28	-	-	-	-0.39	-	-	-0.38	-	-
Cl	0.41	0.30	0.47	-	0.48	-	0.58	0.56	0.48	0.31
Soluble Ca	-	-	-	-0.34	-	-	-	-	-	-
Soluble Fe	-	-0.29	-	-0.25	-	-	-	-	-	-
Soluble K	-	0.29	-	-	-	-	-	-	-	-
Soluble Mg	-	-	-	-0.33	-	-	-	-	-	-
Soluble S	-	-	-	0.25	-	-	-	-	-	-
Total Al	0.31	0.30	0.35	0.30	-	-	0.36	0.22	-	-
Total Fe	-	0.28	0.30	0.27	-	-	0.28	-	-	0.32
Total Na	0.31	-	-	-	0.23	-	0.27	-	-	-
SRP	-	-	-	-	-	-	-	-0.21	-0.30	-0.29
Total P	-	-0.52	-	-	-0.37	-0.45	-0.25	-	-	-0.33
Total Zn	-	-	-	-	-	-	-	-	-	-0.29

[a] Tau values presented represent significant trends at α=0.05

Table 4-6. Summary relationship between flow-adjusted physicochemical parameters and time at 10 tributaries within the Mulberry River watershed from March 2015 to January 2019.

	Site											
Parameter	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	#[a]
pH			-			-						2
Specific conductance	-	-	-	-	-	-	-	-	-	-	-	11
Acid neutralizing capacity	+						+					2
Chlorophyll-a		+			+	+			+	+	+	6
Total suspended solids	-	-		-	-		-		-	-	-	8
Inorganic suspended solids							-					1
Organic suspended solids	-							-	-		-	4
Total organic C	-	-	-	-	-		-		-			7
Total N	-	-	-	-	-	-	-	-	-	-	-	11
NO_3				+	+				+	+		4
SO_4			-			-			-	-		4
Cl	+	+	+	+	+	+	+		+	+	+	10
Soluble Ca	-	-	-	-	-				-	-		7
Soluble Fe			-	-				-				3
Soluble Mg	-	-	-	-	-	-		-	-	-		9
Soluble Na	-											1
Soluble S			+	+		+	+	+	+			6
Total Al	+	+	+	+	+	+	+	+	+	+	+	11
Total Ca							+					1
Total Fe	+		+	+	+	+	+	+	+	+		9
Total Mn									+	+		2
Total Na		+		+	+	+	+	+		+		6
Total P					+		+					2
Total S	-			-	-							3

[a] Number sites with statistically significant trends

+ Indicates a positive trend

- Indicates a negative trend

Table 4-7. Summary relationship between flow-adjusted physicochemical parameters and time at 11 locations on the Mulberry River from March 2015 to January 2019.

	Site										
Parameter	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	#[a]
pH	-										1
Specific conductance	-		-	-	-		-	-	-	-	8
Acid neutralizing capacity										+	1
Chlorophyll-a					+						1
Total suspended solids	-		-	-			-	-			5
Inorganic suspended solids								-			1
Organic suspended solids	-		-	-				-			4
Total organic C	-	-	-	-		-					5
Total N	-	-	-	-	-		-	-	-	-	9
NO_3				+	+			+		+	4
SO_4	-	-			-		-	-	-		6
Cl	+		+		+		+	+		+	6
Soluble Ca	-			-	-		-	-			5
Soluble K		+									1
Soluble Mg	-		-	-	-		-	-			6
Soluble S										+	1
Total Al	+		+	+			+	+			5
Total Fe	+		+	+			+	+			5
Total K							+				1
Total Na	+				+		+	+		+	5
Total P					-						1

[a] Number sites with statistically significant trends
+ Indicates a positive trend
- Indicates a negative trend

Table 6. Summary of results from the two statistical analyses of monotonic trends of 21 locations throughout the Mulberry River watershed, Arkansas, from March 2015 to January 2019.

	Statistical Test	
Parameter	Mann-Kendall	Flow-Adjusted
Temperature	0 (0)[a]	0 (0)
pH	3(14.3)	3(14.3)
Specific conductance	14 (66.7)	19 (90.5)
Dissolved oxygen	0 (0)	0 (0)
Acid neutralizing capacity	3 (14.3)	2 (9.5)
Chlorophyll-a	8 (38.1)	7 (33.3)
Total suspended solids	13 (61.9)	13 (61.9)
Inorganic suspended solids	4 (19.0)	2 (9.5)
Organic suspended solids	11 (52.4)	8 (38.1)
Total organic C	10 (47.6)	2 (57.1)
Total N	20 (95.2)	20 (95.2)
NO_3	7 (33.3)	8 (38.1)
SO_4	9 (42.9)	10 (47.6)
Cl	19 (90.5)	16 (76.2)
Soluble Al	0 (0)	0 (0)
Soluble Ca	4 (19.0)	13 (61.9)
Soluble Fe	6 (28.6)	3 (14.3)
Soluble K	1 (4.8)	0 (0)
Soluble Mg	7 (33.3)	15 (71.4)
Soluble Na	0 (0)	1 (4.8)
Soluble S	4 (19.0)	7 (33.3)
Total Al	14 (66.7)	16 (76.2)
Total Ca	0 (0)	1 (4.8)
Total Fe	10 (47.6)	14 (66.7)
Total K	0 (0)	1 (4.8)
Total Mg	0 (0)	0 (0)
Total Mn	2 (9.5)	2 (9.5)
Total Na	10 (47.6)	12 (57.1)
Soluble Reactive P	4 (19.0)	0 (0)
Total P	9 (42.9)	3 (14.3)
Total S	2 (9.5)	3 (14.3)
Total Zn	1 (4.8)	0 (0)

[a] Number of sites out of 21 that had statistically significant trends at α=0.05.

[b] Flow-adjusted

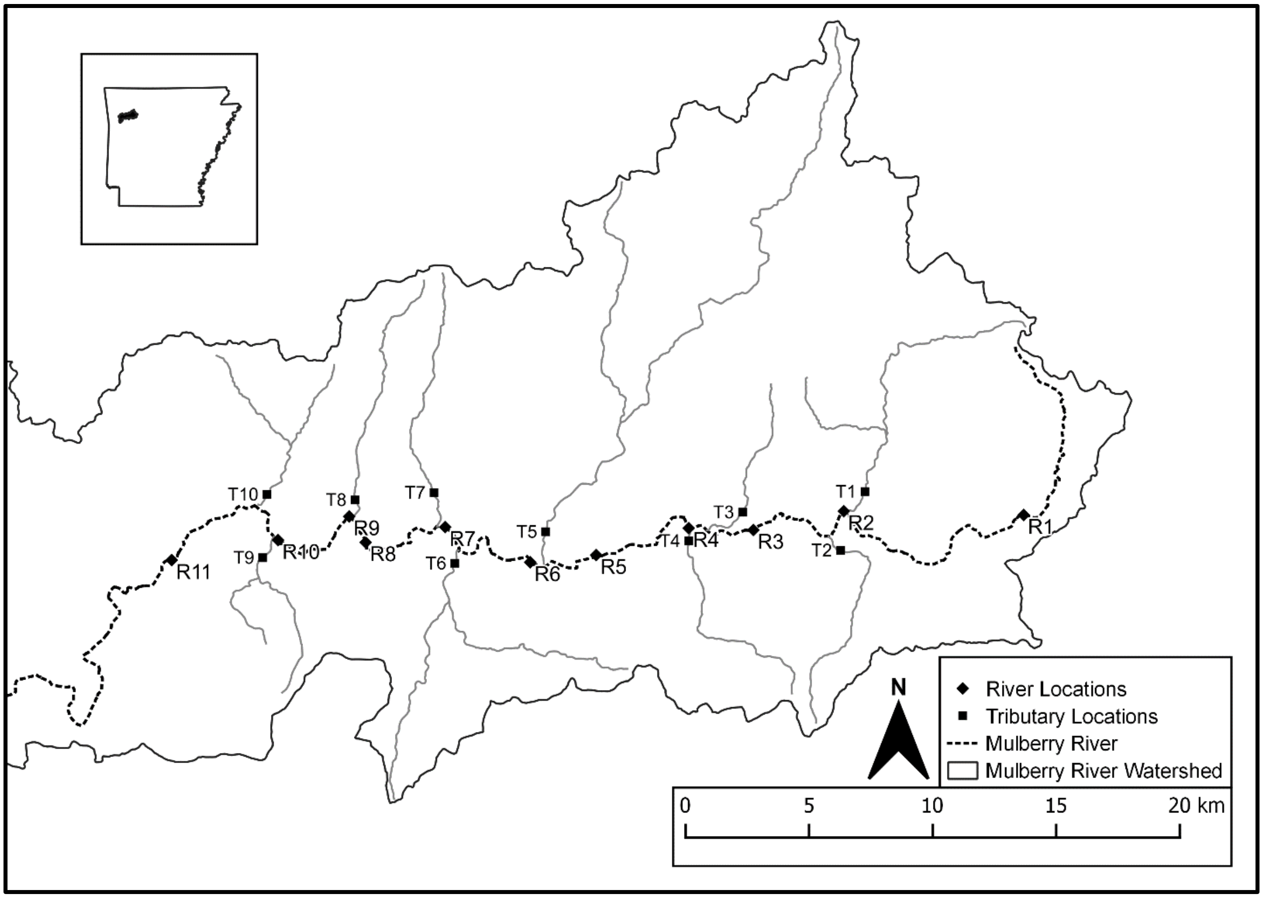

Figure 4-1. Locations of the 21 sampling sites within the Mulberry River watershed, Arkansas.

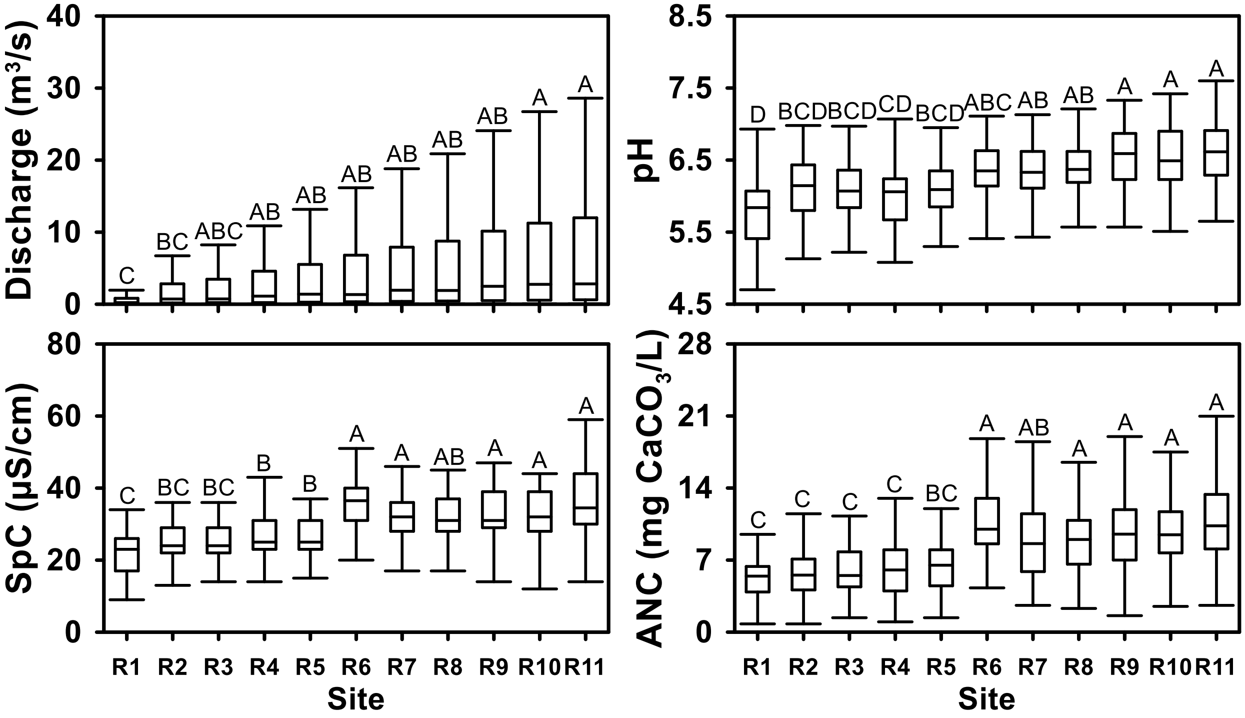

Figure 4-2. Discharge, pH, specific conductance (SpC), and acid neutralizing capacity (ANC) at 11 sampling sites on the Mulberry River, Arkansas averaged over a 46-month period from March 2015 to January 2019. Site R1 is furthest upstream and R11 is furthest downstream. Bars labelled with the same letter were not significantly different at $\alpha = 0.05$.

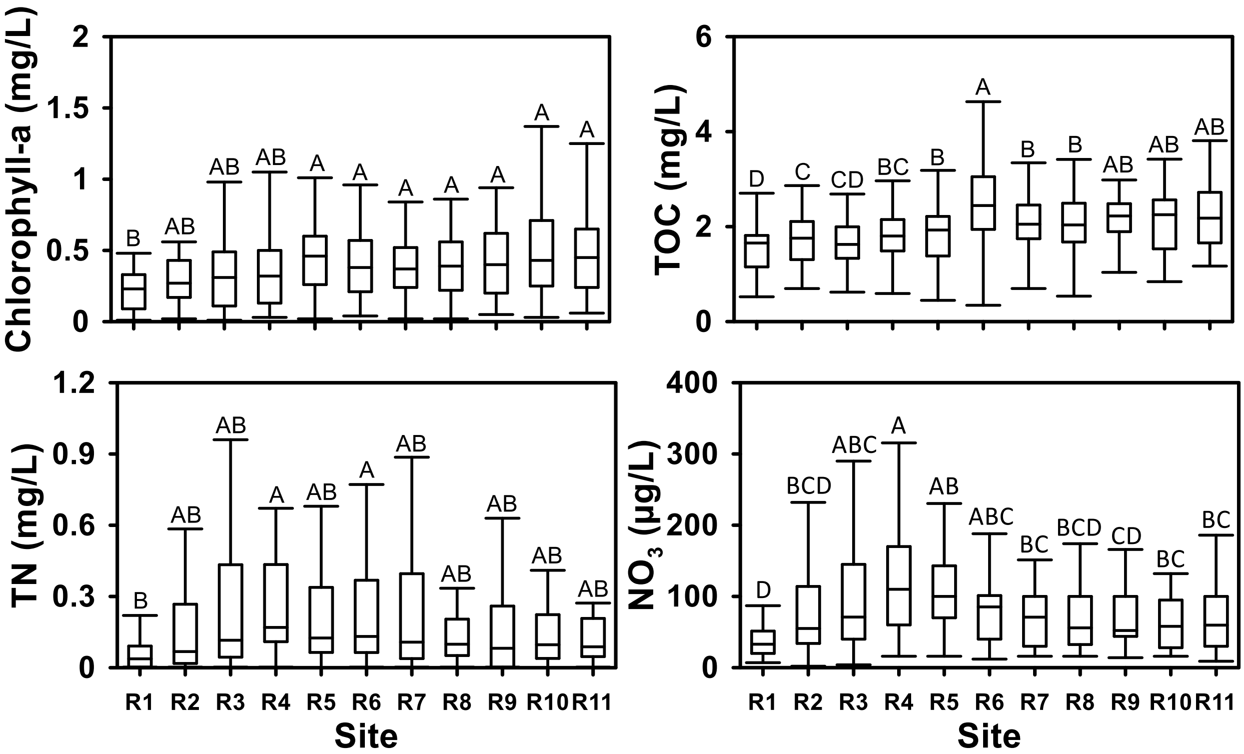

Figure 4-3. Chlorophyll-a, total organic C (TOC), total N (TN), and NO_3 at 11 sampling sites on the Mulberry River, Arkansas averaged over a 46-month period from March 2015 to January 2019. Site R1 is furthest upstream and R11 is furthest downstream. Bars labelled with the same letter were not significantly different at $\alpha = 0.05$.

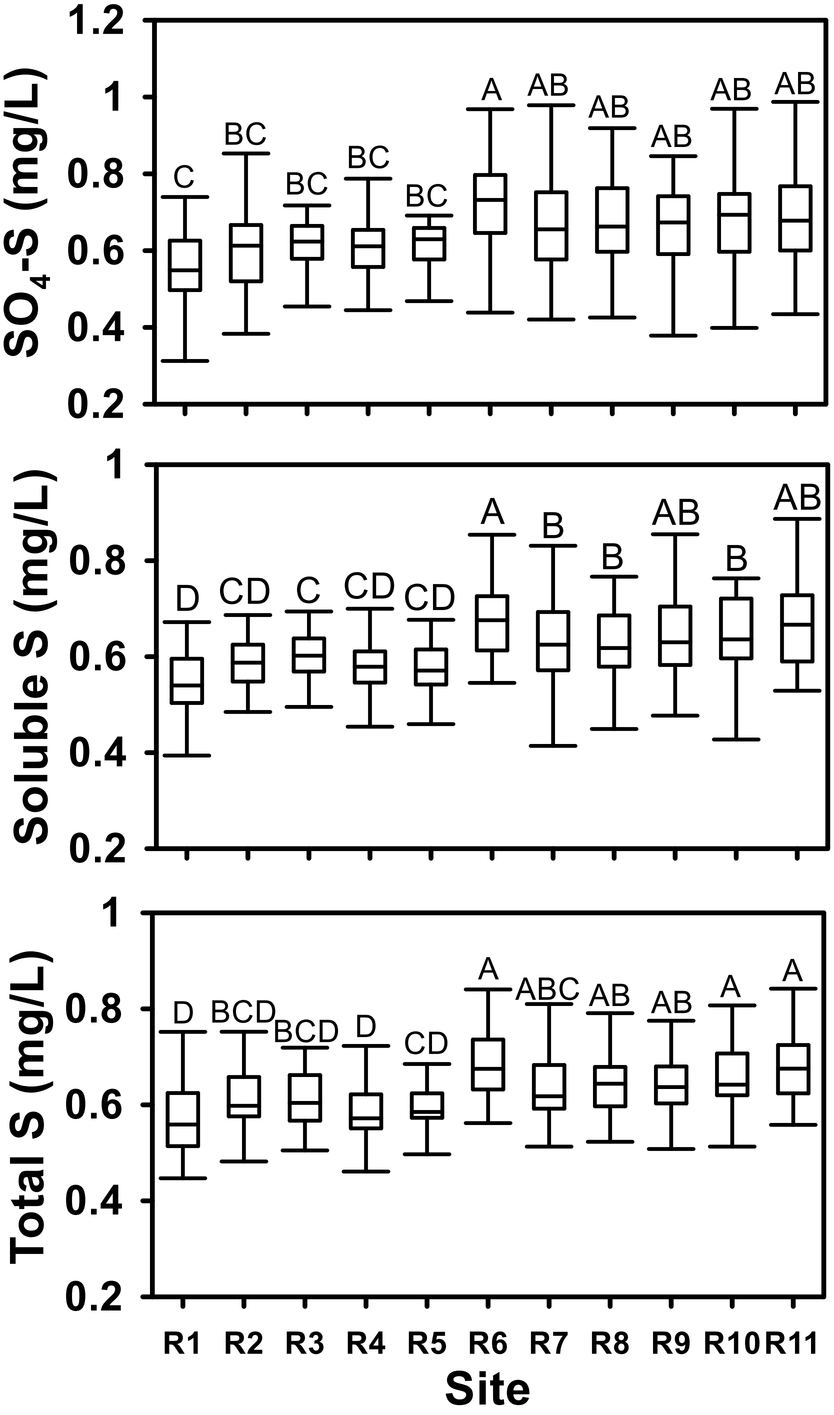

Figure 4-4. Sulfate, soluble S, and total S at 11 sampling sites on the Mulberry River, Arkansas averaged over a 46-month period from March 2015 to January 2019. Site R1 is furthest upstream and R11 is furthest downstream. Bars labelled with the same letter were not significantly different at $\alpha = 0.05$.

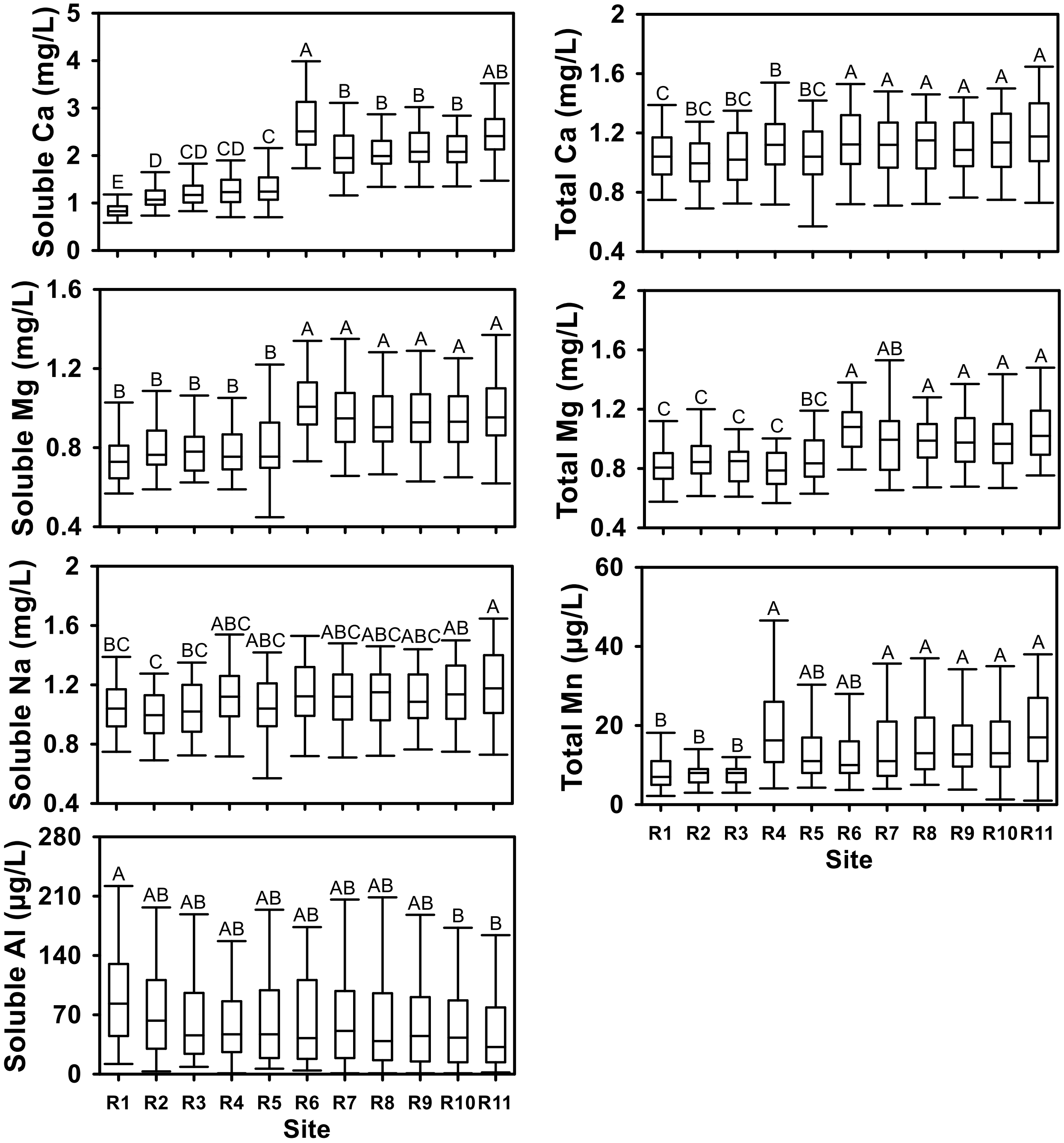

Figure 4-5. Soluble Al, Ca, Mg, and Na, and total Ca, Mg, and Mn at 11 sampling sites on the Mulberry River, Arkansas averaged over a 46-month period from March 2015 to January 2019. Site R1 is furthest upstream and R11 is furthest downstream. Bars labelled with the same letter were not significantly different at α = 0.05.

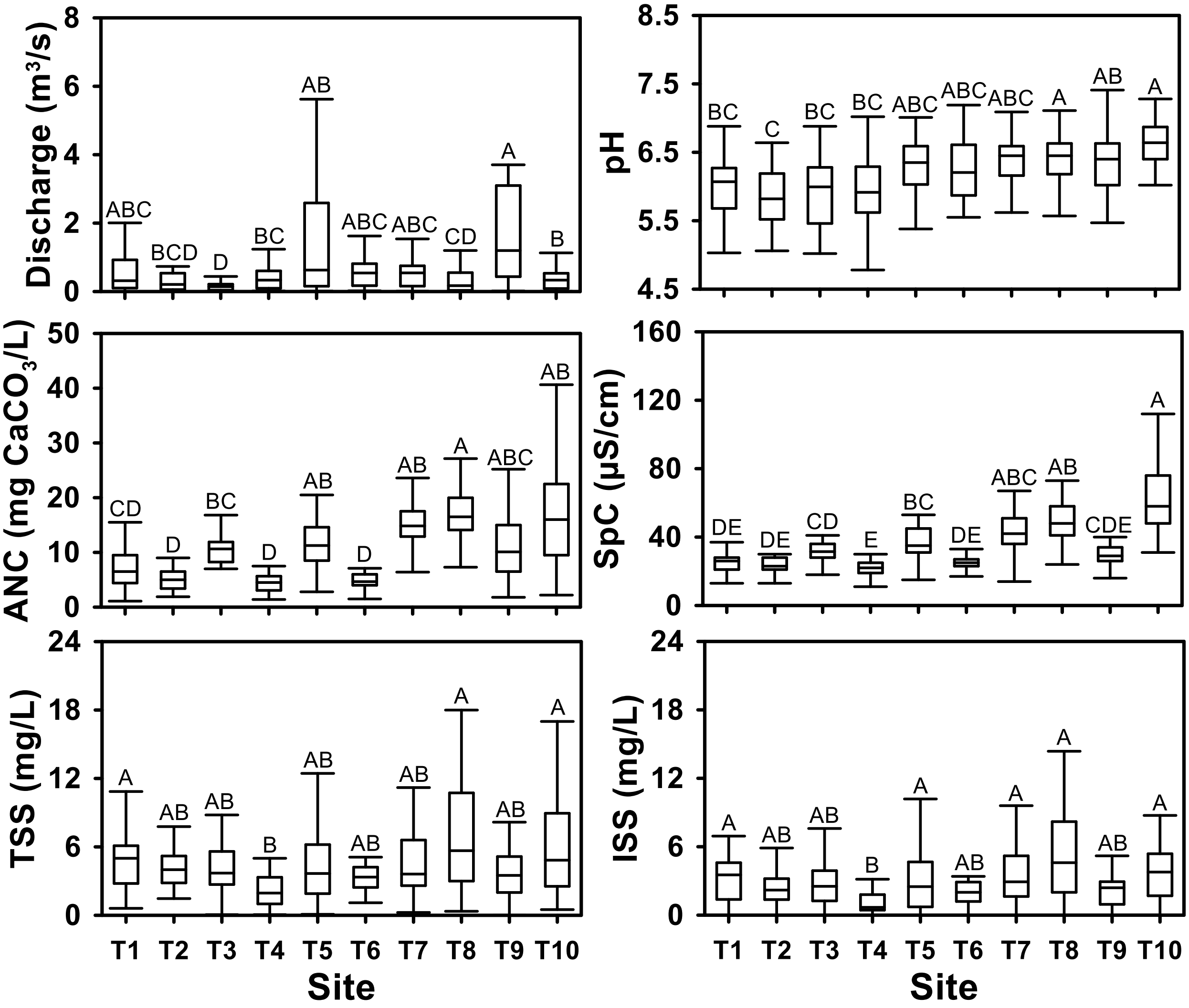

Figure 4-6. Discharge, pH, total suspended solids (TSS), specific conductance (SpC), inorganic suspended solids (ISS), and acid neutralizing capacity (ANC) at 10 tributaries within the Mulberry River watershed, Arkansas averaged over a 46-month period from March 2015 to January 2019. Bars labelled with the same letter were not significantly different at α = 0.05.

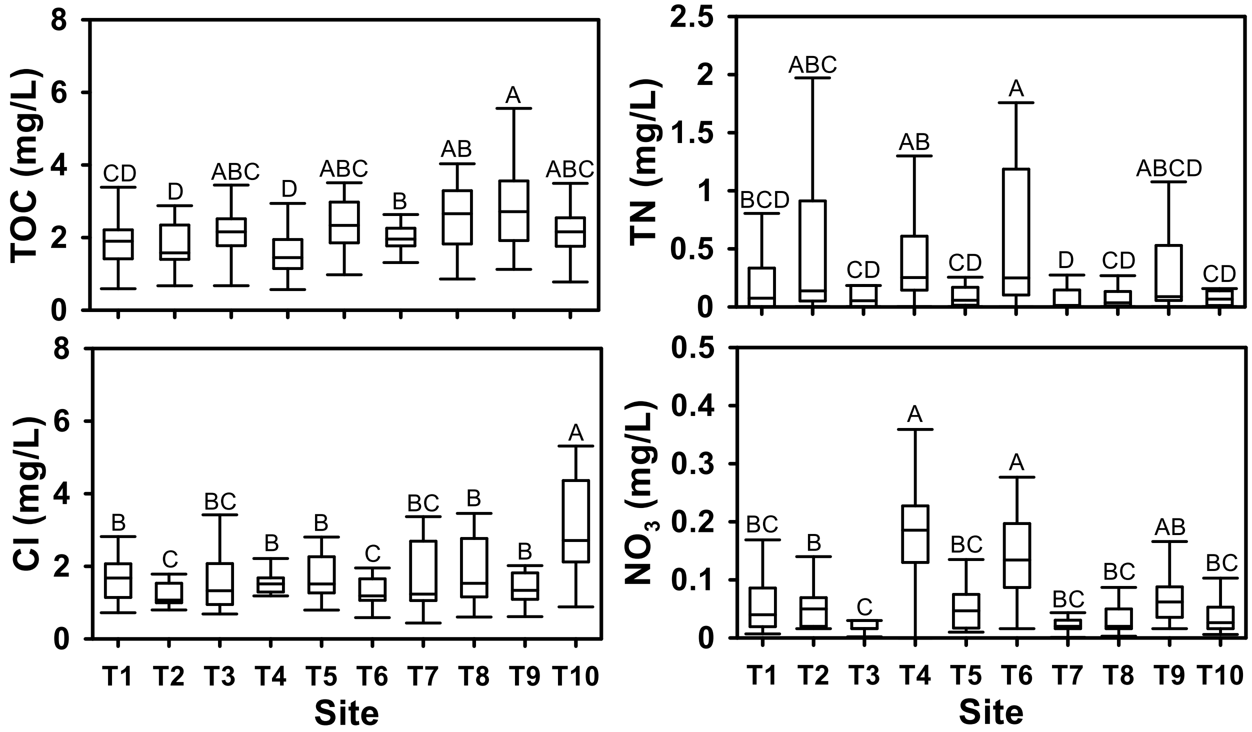

Figure 4-7. Total organic C (TOC), total N (TN), Cl, and NO_3 at 10 tributaries within the Mulberry River watershed, Arkansas averaged over a 46-month period from March 2015 to January 2019. Bars labelled with the same letter were not significantly different at $\alpha = 0.05$.

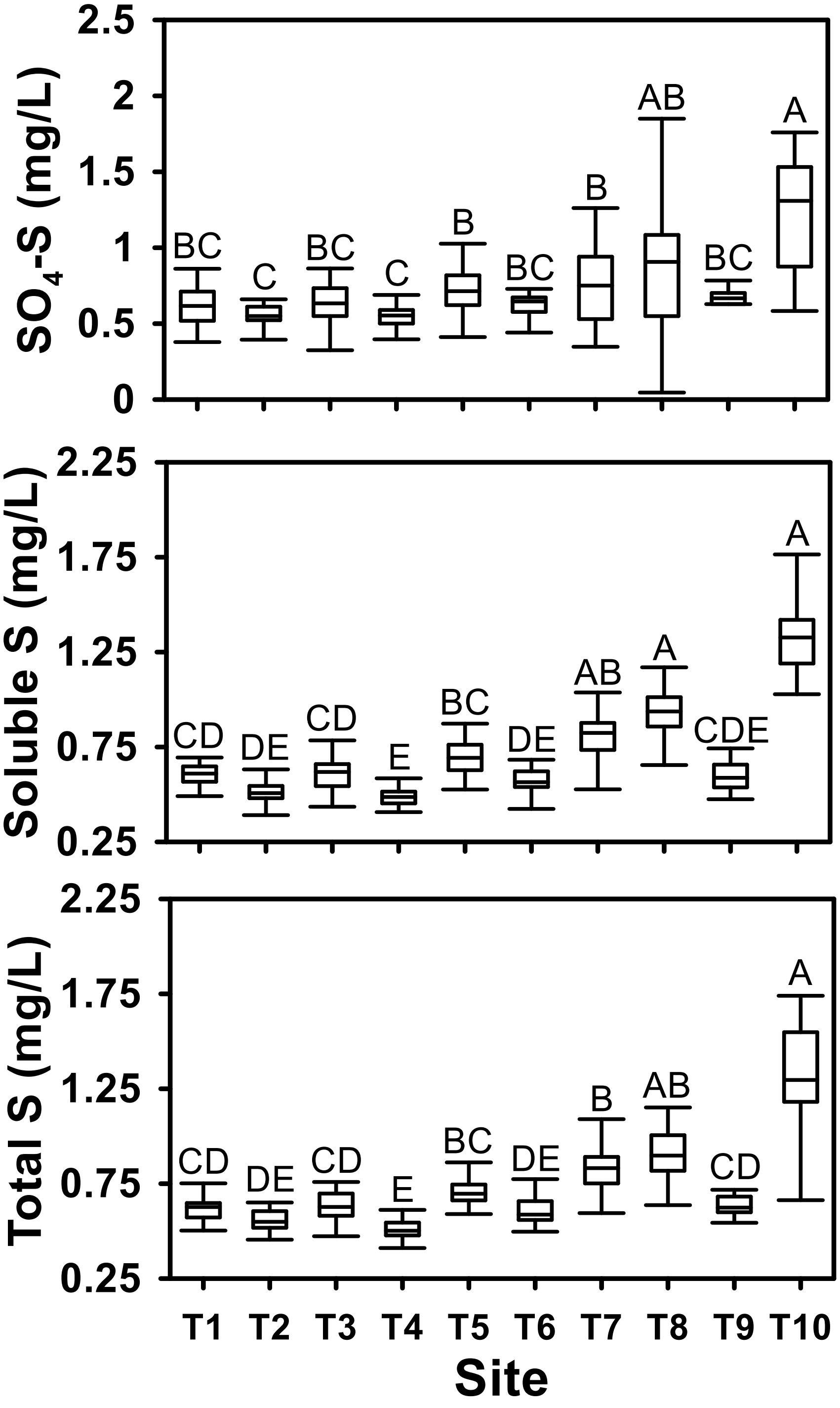

Figure 4-8. Sulfate, soluble S, and total S at 10 tributaries within the Mulberry River watershed, Arkansas averaged over a 46-month period from March 2015 to January 2019. Bars labelled with the same letter were not significantly different at α = 0.05.

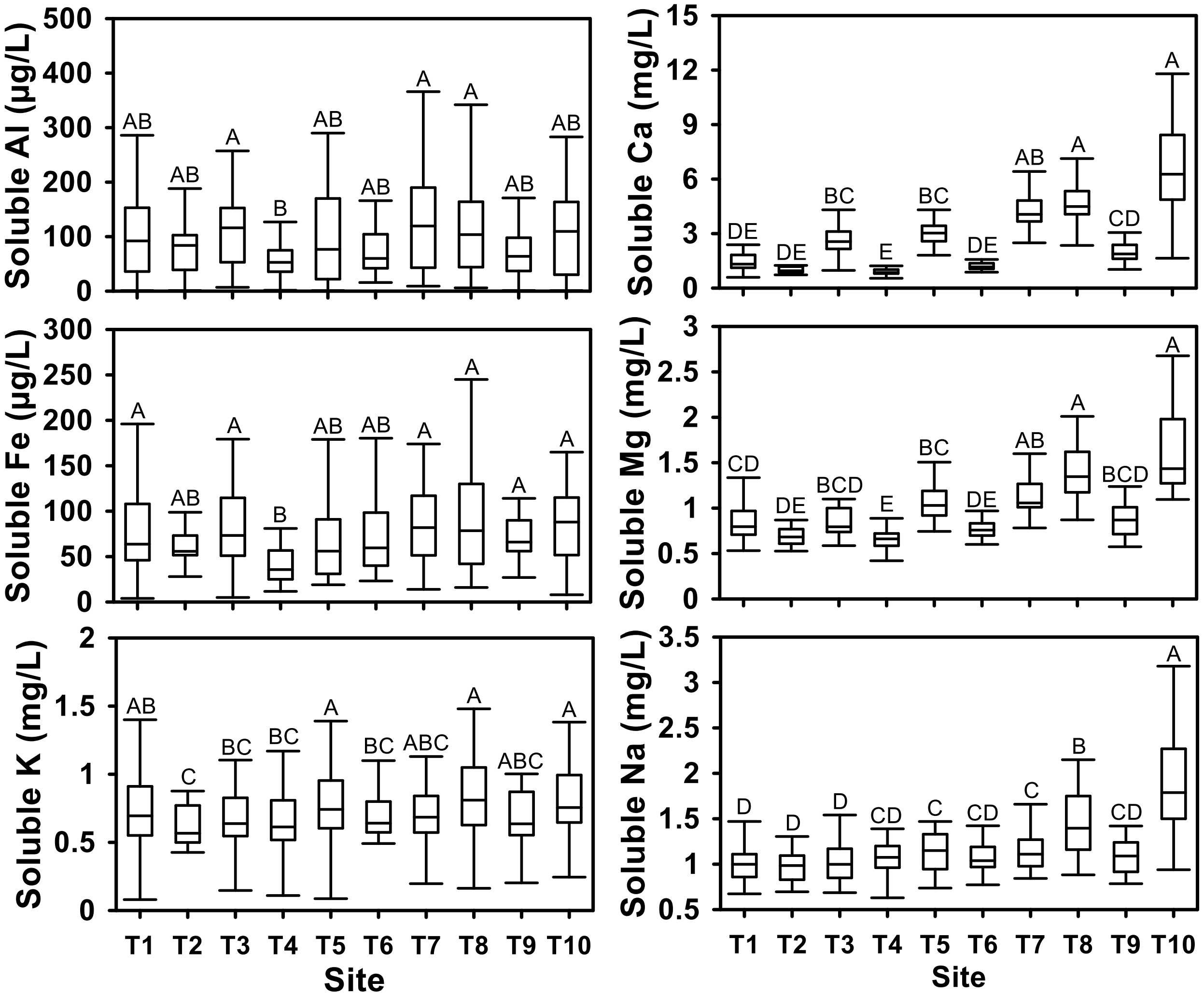

Figure 4-9. Soluble Al, Ca, Fe, Mg, K, and Na at 10 tributaries within the Mulberry River watershed, Arkansas averaged over a 46-month period from March 2015 to January 2019. Bars labelled with the same letter were not significantly different at α = 0.05.

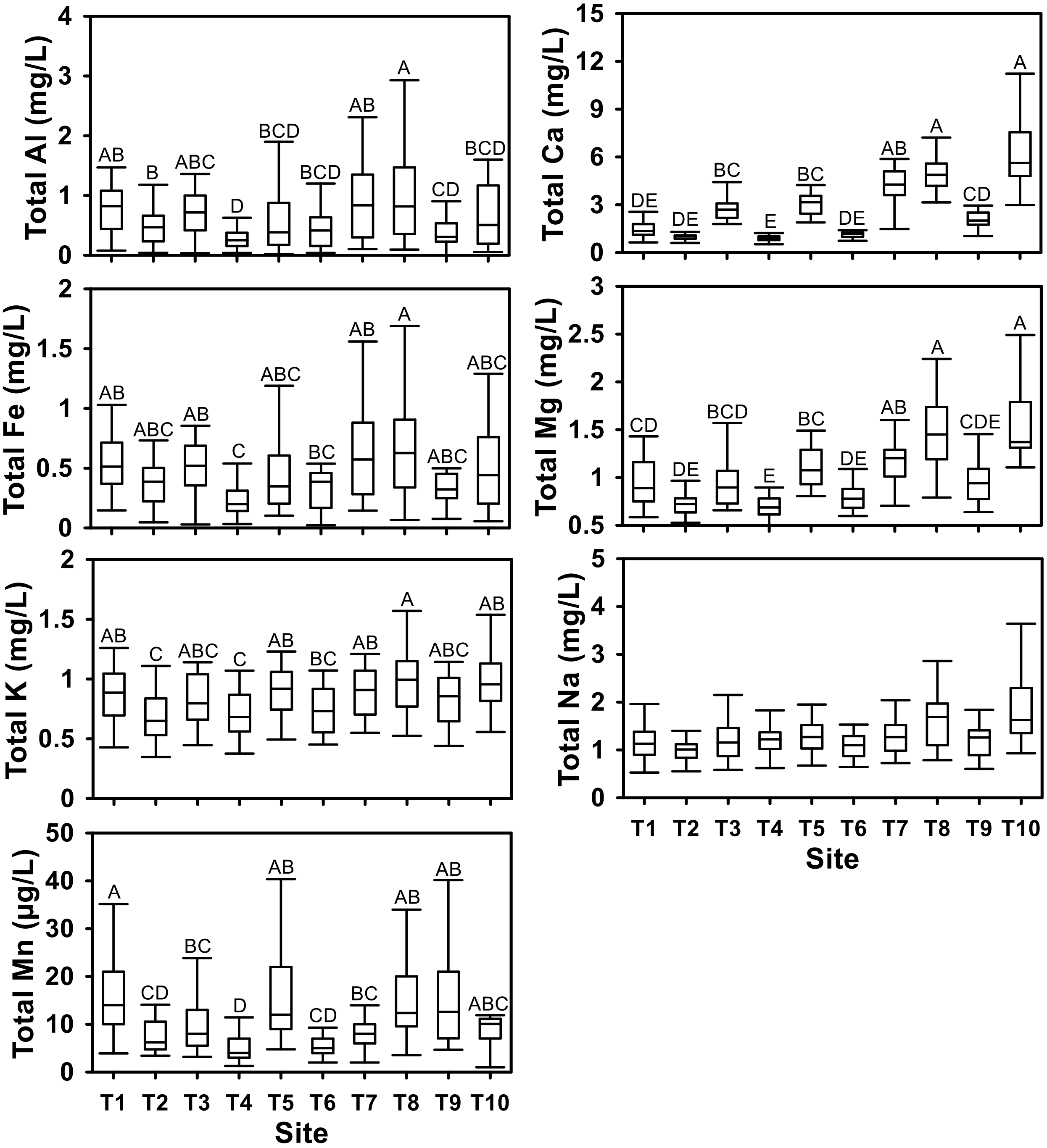

Figure 4-10. Total Al, Ca, Fe, Mg, K, Na, and Mn at 10 tributaries within the Mulberry River watershed, Arkansas averaged over a 46-month period from March 2015 to January 2019. Bars labelled with the same letter were not significantly different at α = 0.05.

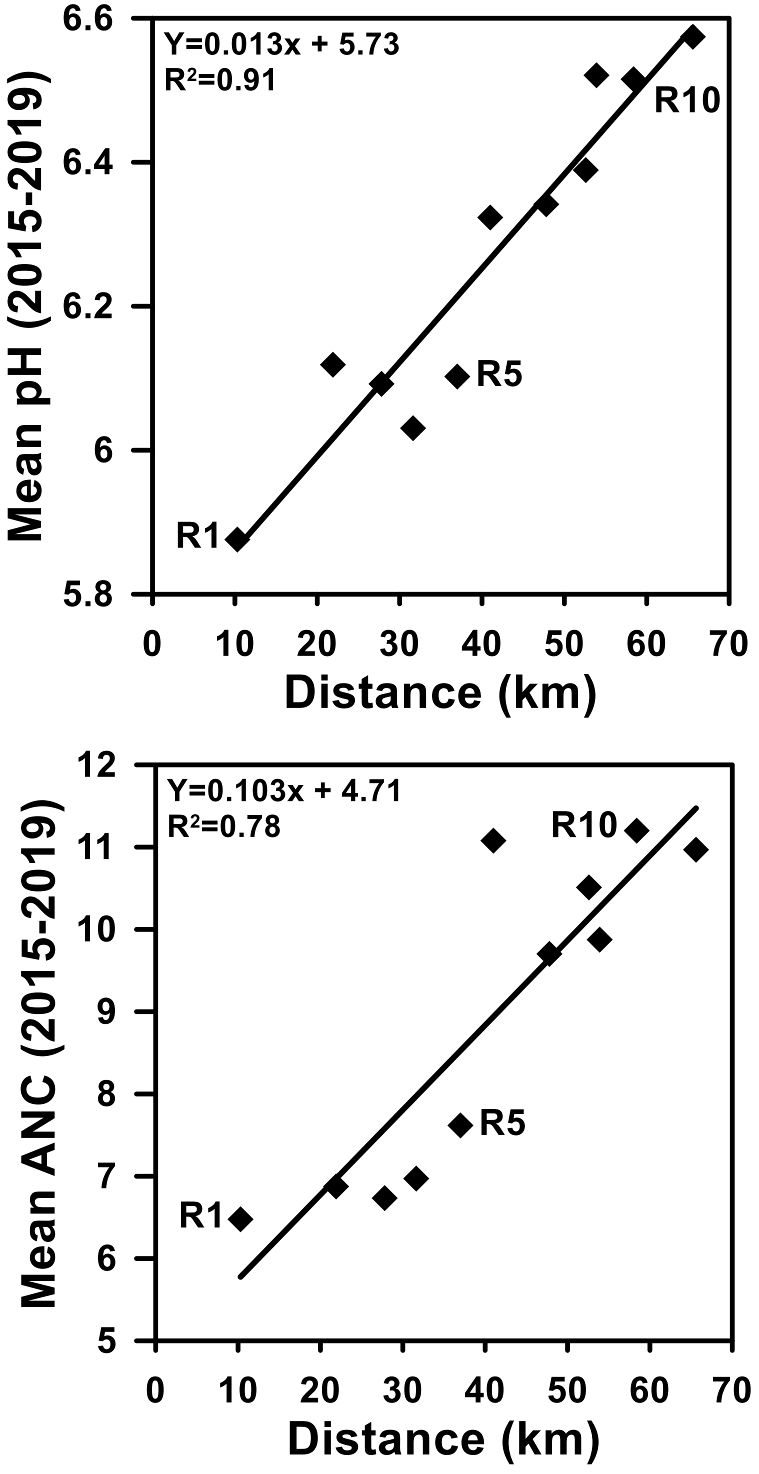

Figure 4-11. Average pH and acid neutralizing capacity of 11 locations on the Mulberry River averaged over a 46-month period as a function of distance from the headwaters.

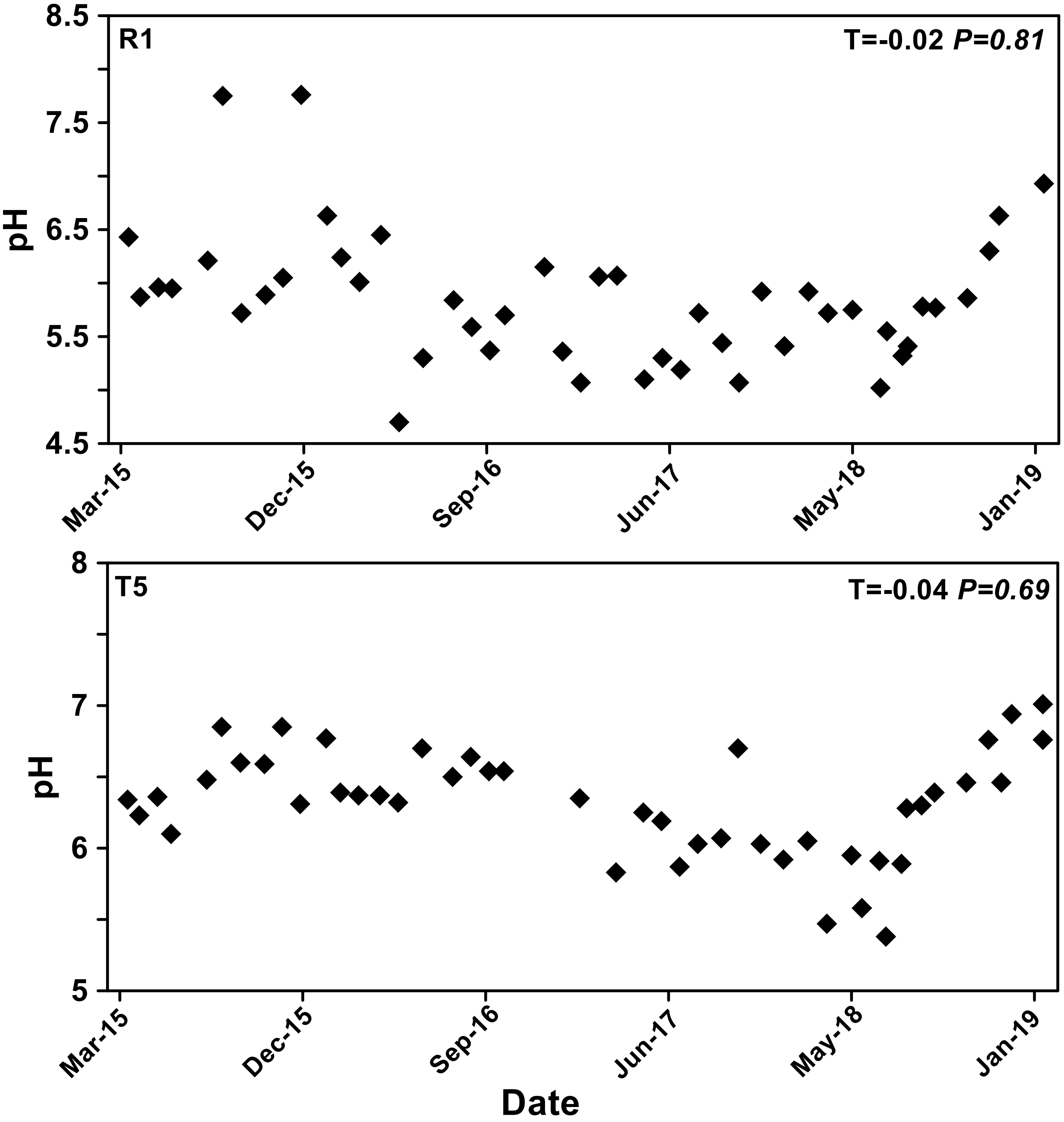

Figure 4-12. pH of site R1 and T5 within the Mulberry River watershed from March 2015 to January 2019. Mann-Kendall analysis of trend results in a non-significant trend (*P* > 0.05).

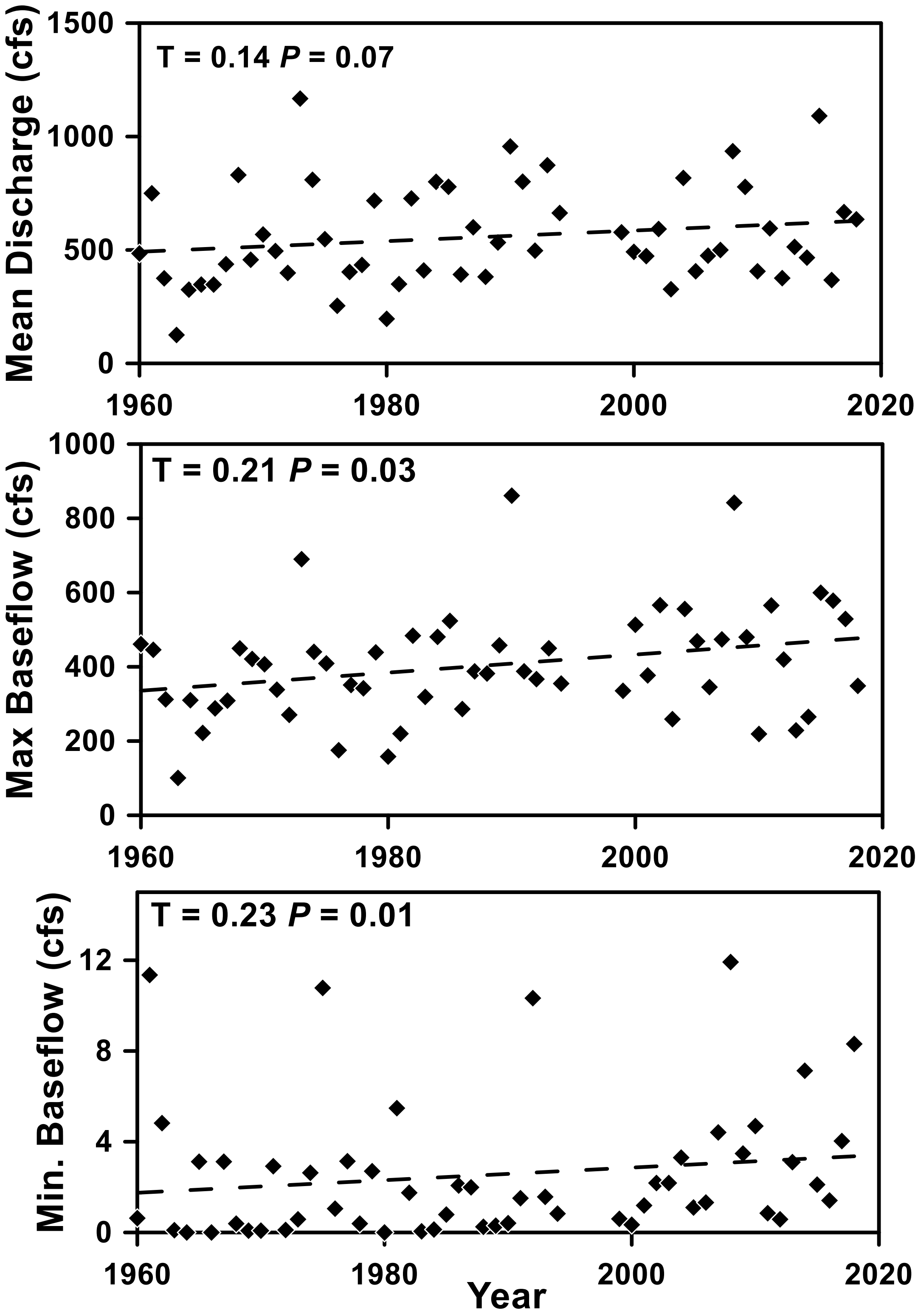

Figure 4-13. Trends in annual mean discharge, maximum base flow, and minimum base flow from USGS monitoring station 0725200 on the Mulberry River from 1960 to 2018. Mann-Kendall trend analysis indicates a significant increasing trend at α = 0.10.

Summary and Overall Conclusions

Studying and understanding of watershed dynamics is complicated due to spatial and temporal variability of precipitation, surface water, and groundwater chemistry and this research reaffirms those difficulties. The Mulberry River was listed as impaired due to low pH in 2008 and long-term monitoring data from ADEQ indicates a decrease in pH over the last 20 years. Despite this apparent decrease in pH, the results of this research suggest that the pH of the Mulberry River watershed has not changed from March 2015 to January 2019. However, changes in chemistry being observed throughout the watershed may be the result of a changing climate rather than changes in land use. Throughout the state of Arkansas and portions of the conterminous United States, there has been a statistically significant increase in the amount of precipitation and subsequently the amount of streamflow. This increase in water movement throughout a watershed has the potential to decrease residence time in soil and parent material and cause a dilution of surface water.

Over the duration of this study numerous physicochemical parameters changed significantly, and these changes could be attributed to a changing hydrology. Over the approximately 4 years of this study there were significant decreases in TOC, TN, TSS, SO_4, soluble Ca and Mg and a subsequent decrease in SpC. This decrease in numerous constituent concentrations resulted in the dilution of surface water that was already relatively. The average SpC of the Mulberry River decreased from 35.1 to 18.4 $\mu S\ cm^{-1}$ from 2015 to 2019 and increases the vulnerability of the watershed to greater shifts in pH.

This research also tested the hypothesis that growth of conifers, either through afforestation or conversion of native hardwood stands, was a source of acidification. Soil samples were collected from 10 paired deciduous and coniferous stands throughout the Mulberry

River watershed and five measures of soil acidity (pH in H_2O, pH in KCl, TEA, base saturation, and ANC) indicated no significant differences between stands. Average soil pH_{H2O} of both deciduous (pH = 5.2) and coniferous (pH = 5.3) stands was less acidic than other forest soils reported in the literature. Concentrations and contents of water-extractable, Mehlich-3 extractable, and exchangeable Ca and Mg were also significantly greater in soil beneath the coniferous soil compared to the deciduous soil.

Similar to the watershed soils, there were no significant differences in the pH of streams draining sub-watersheds containing primarily conifers or deciduous. Coniferous forest land use was not correlated with stream pH neither was stream pH predicted by coniferous forest land use. Instead, ANC and stream discharge were negatively correlated. This decrease in buffering capacity and stream flow may negatively affect stream chemistry but this was not observed in this study. Nitrate was inversely related to both stream pH and ANC which may indicate that HNO_3 is the primary acid cycling throughout the watershed. Land use data for the Mulberry River watershed not available from 2012 to the present, but there was a decrease in the amount of coniferous forest land use from 1991 to 2011. This decrease in the area of pine tree density reduces the likelihood that conifer growth has been detrimental to the watershed.

While the changes observed over the duration of this study indicate the watershed has become more dilute, the changes in chemistry observed do not currently warrant remedial efforts. Four years is not enough time to fully understand watershed dynamics and future efforts should instead focus on continued monitoring of the Mulberry River and should also include monitoring of a neighboring, non-impaired watershed. It is still unknown why only segments of the Mulberry River have shown change in pH over the last 20 years. The Mulberry River was designated a National Wild and Scenic River due to the outstanding natural, cultural, and recreational value it provides and continued monitoring will be necessary in order to ensure this value remains.