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DEPARTMENT OF ENERGY AND MINERAL ENGINEERING

RECOVERY FROM ACID RAIN DEPOSITION IN THE MISSISSIPPI RIVER BASIN

DANIEL KOZAR
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Reviewed and approved* by the following:

Mark Klima
Associate Professor of Mineral Processing and Geo-Environmental Engineering
Honors Adviser

Li Li
Associate Professor of Environmental Engineering
Thesis Supervisor

* Signatures are on file in the Schreyer Honors College.

ABSTRACT

Acid rain deposition has been a widespread environmental concern since the mid-twentieth century and has negatively impacted ecosystems across the nation. Although efforts to reduce acid rain deposition itself have been successful, little comprehensive research has investigated recovery in surface waters. This study used United States Geological Survey (USGS) data and modelling program EGRET to investigate the in-stream recovery from acid rain deposition from 1974 to 2017. The Mississippi River, in this case, acts as a proxy for a large portion of the United States as it composes approximately 40% of the United States' land area. Several chemical species and parameters were used in this study to complete this analysis: pH, sulfate (SO_4^{2-}), divalent cations (Ca^{2+} and Mg^{2+}), and nitrate as nitrogen (NO_3-N). The findings of this study suggest recovery throughout the basin on average, as pH increases and sulfate (SO_4^{2-}) concentrations and loads decrease over time. Divalent cation concentration and load increase over time, however, conflicting with recovery. The trend in divalent cation export is suggested to be primarily caused by chemical weathering via nitrogen fertilizers. Previous studies, largely conducted in smaller forested catchments, have found that decreased acid rain deposition rates result in decreased cation export. Comparing the relationship between trends in smaller catchments and large river basins provides a basis for assessing the roles of variables such as land use and catchment size. The findings of this study illustrate both the effectiveness of legislation as well as the environmental effects of agriculture on surface waters.

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Chapter 1: Introduction and Literature Review

Background

One significant environmental effect of industrial activity is the creation of acid rain. While there are many causes of acid rain, the largest two contributing factors are electricity generation and transportation (Perlman, 2018). Acid rain is a broad term that refers to rain with a low pH value, generally below 5.0 (US EPA, OAR, OAP). The relative acidity of acid rain is caused by the release of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). Sulfur dioxide (SO_2) reacts with oxygen and water in the atmosphere to create sulfuric acid (H_2SO_4) (Equation 1):
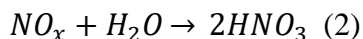
$$SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4 \ (1)$$
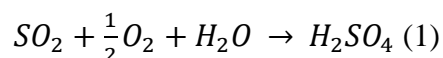
Similarly, nitrogen oxides (NO_x) react with water in the atmosphere to create nitric acid (HNO_3) (Equation 2):

$$NO_x + H_2O \rightarrow 2HNO_3 \ (2)$$

Approximately 25% of acid rain is accounted for by nitric acid (HNO_3) while the rest is largely by sulfuric acid (H_2SO_4). Carbonic acid (H_2CO_3) also contributes to acid rain but to a lesser extent than the two aforementioned compounds (Casiday and Frey, 1998). Acid rain has many negative effects. Lower pH creates survival difficulty for aquatic life and has an especially negative effect on young aquatic species and eggs. Acid rain can deteriorate and kill plant life by leaching essential nutrients from soil (US EPA, OAR, OAP). Dry deposition, which differs from wet deposition in that the acidic compounds come in the form of dust or gas particles rather than precipitation ("Acid Rain," 2019), can deteriorate manmade structures such as statues or buildings, increasing maintenance costs (Baedecker and Reddy, 2009).

In order to reduce the deposition and therefore the effects of acid rain, different legislative actions have been taken. Of the legislation passed, the most considerable in scope is the Clean Air Act (CAA) Amendments of 1990. First passed in 1963, the CAA aims to ensure clean air for the United States populace by reducing emissions. Although the 1963 version of the act had little practical impact, as the legislation mainly pertained to research, the 1970 amendments to the CAA gave much more authority to the federal government, as emission limits from both stationary and mobile sources were established. National Ambient Air Quality Standards (NAAQS) and other regulatory programs were also established by the 1970 amendments. Legislation specifically pertaining to reducing acid rain was introduced in the Amendments of 1990 (US EPA). Title IV of these amendments aimed to cut sulfur dioxide (SO_2) emissions to 10 million tons per year below the emission levels of 1980. Similarly, a goal was set to reduce annual NO_x emission rates by 2 million tons below that of the year 1980. Both goals have been achieved, as SO_2 emissions in 2016 were 2.9 million tons compared to 25.9 million tons emitted in 1980 (US EPA). NO_x emissions in 2016 were 10.8 million tons compared to 27.1 million tons in 1980. Goals for each pollutant have been met, so the sources of acid rain have decreased. In addition to reductions in emissions of pollutants that cause acid rain, evidence shows that the deposition rates of acid rain are also decreasing.

The National Atmospheric Deposition Program (NADP) collects data from rain at 250 locations around the nation. Yearly deposition rates of hydrogen ions (H^+), as well as various other chemical compounds around the nation are publicly accessible through the University of Wisconsin. Following are maps of annual hydrogen ion (H^+) deposition rates in 1985 and 2016 respectively (NADP). Monitoring locations are denoted by black dots (Figures 1a and 1b):

a)

Hydrogen ion wet deposition from measurments made at the Central Analytical Laboratory, 1985
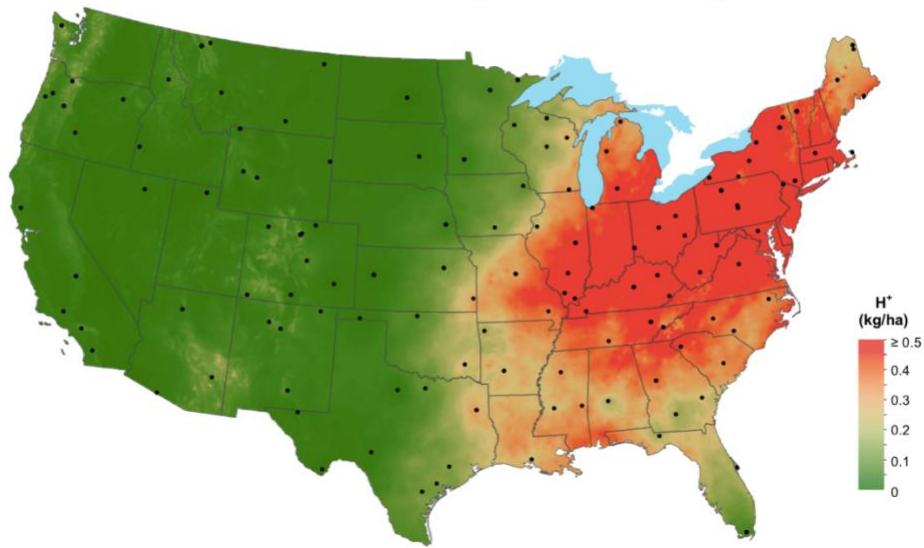
b)

Hydrogen ion wet deposition from measurements made at the Central Analytical Laboratory, 2016
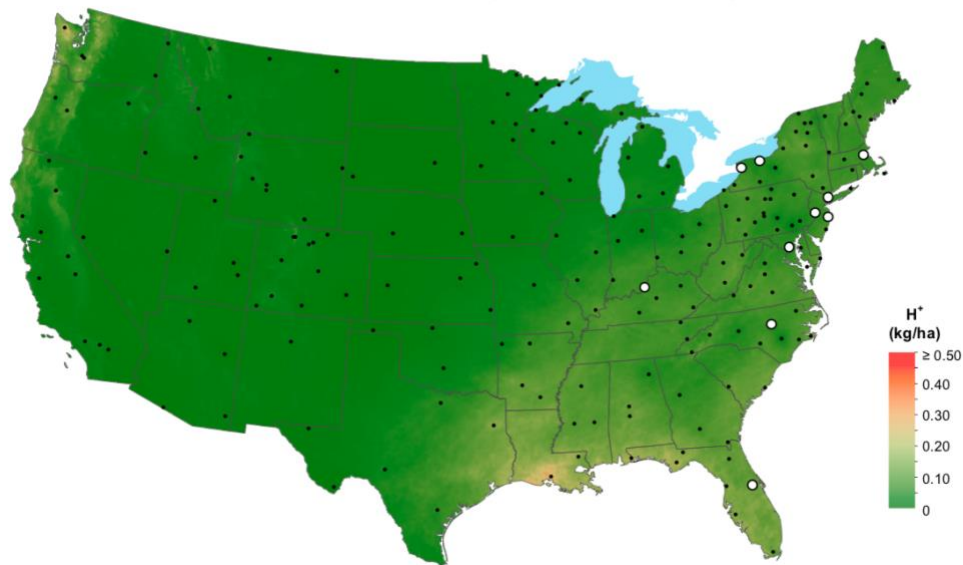

Figure 1. Hydrogen Ion Wet Deposition in a) 1985 and b) 2016

From the above figures it can be observed that the deposition rates of hydrogen ions between 1985 and 2016 decreased drastically. Deposition rates in 1985 were considerably higher in the eastern section of the contiguous United States than in the western section. The annual

deposition rates of H^+ in the east were consistently upwards of 0.5 kg/ha, while deposition rates in the west were negligible, with few regions reaching rates of 0.2 kg/ha (NADP).

Literature Review

Considering legislative action and subsequent success in emissions and hydrogen ion (H^+) deposition, one must ask about the ecological recovery from acid rain. Previous studies have considered soil recovery as well as the recovery of surface waters. Studies analyzing recovery of surface waters, although thorough in scope, have been largely focused on smaller forested catchments ranging between 1.78 km^2 to 820 km^2 (McHale et al., 2017; Likens et al., 2017; Majer et al., 2005; Marx et al., 2017; Clow and Mast, 1999). One larger scale study was conducted in 1999 analyzing recovery from acid rain through 205 sites at various locations in North America and Europe (Stoddard et al., 2007). The results of these studies are generally in agreement that decreased wet sulfate (SO_4^{2-}) and hydrogen ion (H^+) rates correspond with reductions in stream sulfate concentrations (Majer et al., 2005; Clow and Mast, 1999; Stoddard et al., 2007). Studies analyzing lakes found similar results (Jeffries et al., 2003, 2000; Bouchard, 1997; Driscoll et al., 2003; Stoddard et al., 2007). All things considered, the extent to which pH trends correlate with sulfate (SO_4^{2-}) concentrations trends differs. Observed pH increases were not of the same magnitude of sulfate (SO_4^{2-})decreases in the Hubbard Brook Experimental Forest (Likens et al., 2017). Similarly, pH trends were insignificant in relative magnitude in comparison to sulfate (SO_4^{2-}) trends in the Slavkov Forest (Majer et al., 2005). One study of Canadian lakes found that expected pH and sulfate (SO_4^{2-}) trends did not directly correspond in relative magnitude. This behavior was largely attributed to the fact that temporal trends in pH and acid neutralizing capacity (ANC) are more complex than those of sulfate (SO_4^{2-}) (Bouchard, 1997).

Cation export is believed to be correlated with acid-rain deposition as acid-rain can cause chemical weathering (Likens et al., 2017). Hydrogen ion (H^+) deposition causes increased concentrations of exchangeable aluminum. Aluminum is more readily adsorbed than calcium (Ca^{2+}) and therefore calcium (Ca^{2+}) is displaced (Huntington and Lawrence, 1999). This effect is also observed for magnesium (Mg^{2+})(Walna et al., 1998). Several studies found that decreased acid rain deposition rates leads to decreased cation concentrations in streams and lakes alike (Jeffries et al., 2003; Bouchard, 1997; Waller et al., 2012; Majer et al., 2005). The observed relationship between sulfate (SO_4^{2-}) and cation concentrations differs. In a study of headwaters in the Northeastern United States, relative decrease in sulfate (SO_4^{2-}) led to an equal reduction in cation concentrations (Clow and Mast, 1999). Stoddard et al., 2007 found that decreases in cation concentrations exceeded the relative magnitude of sulfate (SO_4^{2-}) concentration decreases. This suggestion was attributed to the fact that weathering rates exceeded cation loss rates during times of high deposition (Stoddard et al., 2007). One limiting factor when considering cation concentrations is the atmospheric deposition of cations such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). Magnesium (Mg^{2+}) concentrations in rainfall decreased from 1985 to 2016 (NADP, 2017). Calcium (Ca^{2+}) concentrations in rainfall increased throughout the study period, although this increase is negligible in comparison to the concentration trends observed with United States Geological Survey (USGS) water quality data (NADP, 2017). While decreasing cation export is a sign of recovery, this loss ultimately limits the aquatic recovery of ecosystems from acid rain deposition (McHale et al., 2017)

The findings of previous studies suggest that expected trends of recovery will include: increasing pH, decreasing sulfate (SO_4^{2-}) concentration and load, and decreasing concentration

and load of divalent cations (Ca^{2+} and Mg^{2+}). Although the relationship between magnitudes of these trends differs, these are the overall signs of initial recovery from acid deposition. Although the types of land and catchment areas included in these previous studies differ, studying these trends in the Mississippi River Basin (MRB) provides insight into the large-scale ecological condition of the Central United States. Previous studies on this subject have focused on relatively small catchments. The trends in acid rain recovery in large river basins are not clear. This study fills the knowledge gap by providing a holistic perspective on recovery trends throughout the largest river basin in the United States, the MRB. The findings of this study allow for comparison in regards to both catchment size and land use.

Motivation

The motivation of this study is to evaluate the recovery from decreased acid rain deposition rates and indirectly infer the effectiveness of legislation with aims to diminish the negative impacts of acid rain. With varying historical impacts of acid rain in the tributary river catchments within the basin, effectiveness can also be inferred. The recovery from acid rain deposition also has other ramifications.

Chapter 2: Methods

This project uses historical water quality data from the USGS as well as a USGS water quality modelling program to evaluate the temporal trend of acid rain recovery. This study primarily considers data from the outflow of the Mississippi River but also utilizes data from tributary rivers into the Mississippi River to give spatial comparison. By using data from the outflow site, the overall trend throughout the entire basin, and a large portion of the United States, can be inferred. Data from tributary rivers gives insight into the variables affecting the trends seen as these tributary rivers are described by different metrics such as: land use, historical acid rain deposition rates, and size. The conclusions from this study may be simple but have large reach in terms of value for the environmental status of the United States.

Tributary Sites

For supplementary analysis with that of the outflow site, MSSP-OUT, data from several other sites were included in this study (Figure 2). Just as with the outflow site, the tributary sites used in this study are the same as those used in the USGS nitrate export report. These tributary rivers are split into two categories, East and West, for use of comparison with rates of recovery. The purpose for this analysis is outlined in the following section, *Data and Analysis.* The site names, abbreviations, as well as relevant information for site data are given in Table 1:
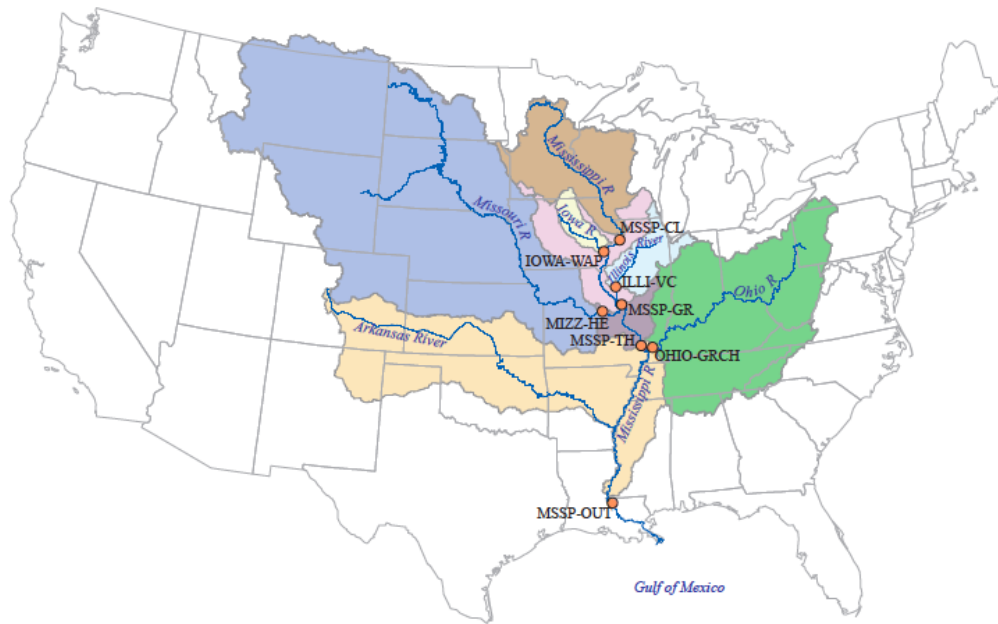
Figure 2. Locations of Tributary Sites in Mississippi River Basin

Table 1. Tributary River Site Information

Site Name	Site Abbreviation	USGS Site Number	Basin Area (km^2)	Data coverage period	Region
Mississippi River at Clinton, IA	MSSP-CL	05420500	221,703	11/12/1974 – 12/1/2016	West
Iowa River at Wapello, IA	IOWA-WAP	05465500	32,375	11/10/1977 – 12/1/2016	West
Illinois River at Valley City, IL	ILLI-VC	05586100	69,264	12/12/1974 – 12/1/2016	East
Missouri River at Hermann, MO	MIZZ-HE	06934500	1,353,269	10/28/1969 – 12/1/2016	West
Ohio River at Dam 53 near Grand Chain, IL[2]	OHIO-GRCH	03612500	526,027	10/11/1972 – 12/1/2016	East

[2] Streamflow for this site was taken at the Ohio River at Metropolis, IL, USGS 03611500

Outflow Site

This study primarily utilized streamflow and water quality data from the USGS as well as from the U.S. Army Corps of Engineers (COE) at the outflow site included in a previous USGS

report on nitrate loading (Murphy et al., 2013). Due to divergence of the river near the outflow into the Gulf of Mexico, this study utilizes water quality data from a site (USGS 07373420) downstream of the divergence of the Mississippi River at the Old River Outflow Channel. There the Mississippi River joins with the Atchafalaya River and the discharge used is the summation of flow rates in the Mississippi River after the divergence (COE 01100) and in the Old River Outflow Channel (COE 02600)(Figure 3). The USGS and COE sites included in the outflow site of this study follow that of a USGS report on nitrate export into the Gulf of Mexico (Murphy et al., 2013). The abbreviation for the outflow site, MSSP-OUT, follows that of the report as well. The use of data from these three sites for the model acts as a proxy for the overall trend throughout the entire MRB. The site names, abbreviations, as well as relevant information for the site data are given in Table 2:
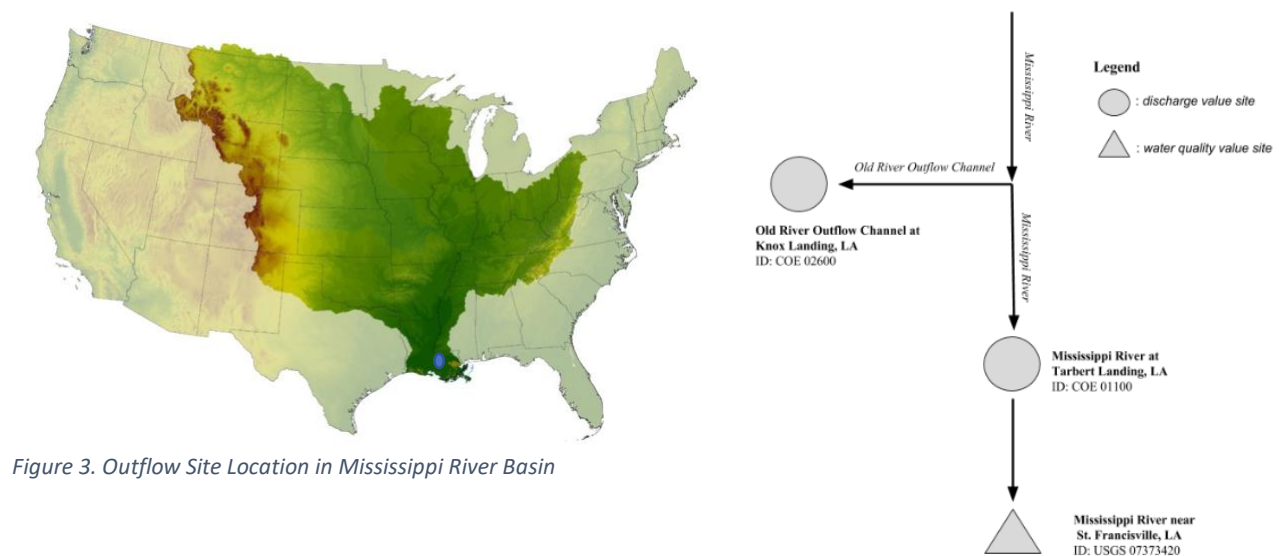

Figure 3. Outflow Site Location in Mississippi River Basin

Table 2. Outflow Site Information

Site Name	Site Abbreviation	USGS Site Number	Basin Area (km^2)	Data coverage period
Mississippi River near St. Francisville, LA	MSSP-OUT	07373420[1]	2,914,514	10/11/1974 - 8/14/2017

[1] Water quality data is from site 07373420. Discharge is the sum of that taken from Mississippi River at Tarbert Landing, LA (COE site 01100) and Old River Outflow Channel near Knox Landing, LA (COE 02600). This is to estimate a total flux from the river before the Old River Outflow Channel, where the Mississippi River splits and the Old River Outflow Channel joins the Atchafalaya River

Data and Analysis

For this study, annual concentrations and fluxes of several species relevant to acid-rain deposition were estimated by running the USGS software program Exploration and Graphics for RivEr Trends (EGRET). EGRET utilizes the Weighted Regressions on Time, Discharge, and Season (WRTDS) method. WRTDS estimates discharge and concentration values to dates without values by assigning weight to the unknown dates according to their temporal proximity to known values. The annual concentration and flux values were estimated for three different chemical species: sulfate (SO_4^{2-}), magnesium (Mg^{2+}), and calcium (Ca^{2+}). While pH is not measured in units of a concentration or flux, annual pH values were also estimated in order to give insight into in-stream acidity. USGS parameter codes for each chemical species included in this study are presented in Table 3. Values returned from EGRET were plotted over time to gauge temporal recovery from acid rain. The significance of the studied species in the context of acid-rain deposition is included in the introduction of this report.

Table 3. USGS Chemical Species Parameter Codes

Chemical Species	USGS Parameter Code
pH	p00400
Sulfate (SO_4^{2-})	p00945
Calcium (Ca^{2+})	p00915
Magnesium (Mg^{2+})	p00925
Nitrate (NO_3)	p00618

In order to expand on the findings of this study, an additional investigation comparing the rates of recovery for different tributary rivers was included. Figures from the NADP show that river catchments in the eastern section of the MRB have experienced a significant decrease in wet deposition of hydrogen ions (H^+) from 1985 to 2016. These figures also show little to no change in the deposition in western tributaries in the basin. As H^+ is directly related to all chemical acid-rain constituents, comparing the recovery trends of rivers in these two areas of the basin provides an opportunity for investigation. For this, the trends in annual pH, sulfate (SO_4^{2-}), divalent cations, and nitrate as nitrogen (NO_3-N) averages from EGRET were plotted for rivers in the Eastern and Western regions. The studied sites for the Eastern region of the basin include the Illinois River at Valley City, Illinois (ILLI-VC) and the Ohio River at Dam 53 near Grand Chain, Illinois (OHIO-GRCH). The studied sites for the Western region of the basin include: the Mississippi River at Clinton, Iowa (MSSP-CL), the Iowa River at Wapello, Iowa (IOWA-WAP), as well as the Missouri River at Hermann, Missouri (MIZZ-HE)(Table 1).

Chemical Weathering Accelerated by Nitrate

Due to the suggestion of chemical weathering based on increasing cation flux, an analysis of the cause is necessary. Previous studies have found that both acid-rain deposition and fertilizer
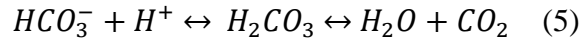
use are causes of cation release into solution. Both of these pathways were considered likely considering the prevalence of acid-rain deposition as well as the largely agricultural use of the MRB. The theoretical ratio of molar concentration of the divalent cations to bicarbonate is 1:2 according to the following equation:

$$Ca_xMg_{(1-x)}CO_3 + H_2O + CO_2 \rightarrow 2HCO_3^- + (1-x)Mg^{2+} + xCa^{2+} \quad (3)$$
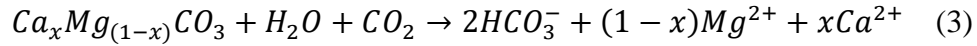
Acid mediated weathering of carbonate rock occurs under the following equation:

$$Ca_xMg_{(1-x)}CO_3 + H^+ \rightarrow xCa^{2+} + (1-x)Mg^{2+} + HCO_3^- \quad (4)$$
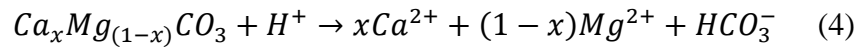
And according to the carbonate buffering system:

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \leftrightarrow H_2O + CO_2 \quad (5)$$

A common fertilizer component ammonium nitrate (NH_4NO_3) dissociates into nitrate (NO_3), water (H_2O) and hydrogen ions (H^+) according to the nitrification process, which can be summarized by the following equation (Song et al., 2017; Perrin et al., 2008):

$$NH_4NO_3 + 2O_2 \rightarrow 2NO_3^- + H_2O + 2H^+ \quad (6)$$
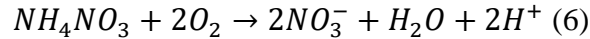
And combining equations 3, 4, and 6 yields the following result:

$$NH_4NO_3 + 2O_2 + 2Ca_xMg_{(1-x)}CO_3 \rightarrow NO_3^- + 2H_2O + xCa^{2+} + (1-x)Mg^{2+} + CO_2 \quad (7)$$
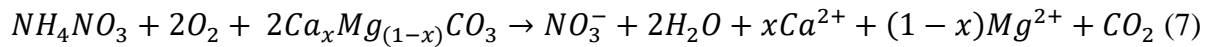
A direct relationship between nitrate (NO_3-N) concentration and the divalent cation concentration (the sum of Calcium (Ca^{2+}) and magnesium (Mg^{2+})) would suggest the source of chemical weathering. In order to investigate the relationship between the aforementioned parameters two analyses were conducted. The first was the direct relationship between NO_3-N and divalent cation concentrations using all data over the study period, both raw USGS daily data and the EGRET yearly estimations. The second was a seasonal analysis of the concentration of

these two parameters for each month over the study period. For the latter analysis, monthly box plots of each parameter were made using the EGRET command "boxConcMonth."

Exploration and GRaphics for RivEr Trends (EGRET)

As mentioned above, EGRET is a R package program for estimating long term changes in water quality developed by the USGS. This program readily accepts data from three sources: USGS water quality data and hydrologic, EPA STORET data, as well as user supplied data. The data supplied to EGRET can be represented with or without the use of the WRTDS model. Weighted Regressions on Time, Discharge, and Season (WRTDS) requires daily discharge records for the entire study period and is designed for larger data sets, such as those used in this study. The WRTDS model was developed out of consideration for changes in water sampling techniques and frequencies. The model uses water quality samples throughout a specific period to fit a statistical model to infer overall trends. Four variables are considered under the WRTDS model as affecting water quality: temporal trend, season, discharge, and "random" causes. Temporal trend is the trend in concentration over many years. Season is considered because the yearly cycle affects geochemical behavior and generally repeats from year to year despite long terms shifts. Discharge is considered because concentration-discharge relationships affect export dynamics. Not only are export dynamics affected by either dilution or runoff processes, but these relationships change over time. Although these three variables are effective at describing water quality trends, there is still random behavior of water quality data. The consideration of this random variation helps make more accurate predictions although more development with this random variation is necessary with the model. Put simply, WRTDS can be summarized as:

$$E[c] = w(Q, T) \quad (8)$$

Where E[c] is the estimation of concentration, and w(Q,T) means that w is a function of discharge, Q, and time, T (manual). The estimations of concentration come from the following equation:

$$ln(c) = \beta_0 + \beta_1 q + \beta_2 T + \beta_3 \sin(2\pi T) + \beta_4 \cos(2\pi T) + \varepsilon \quad (9)$$

In the equation, β values are the regression coefficients, c is concentration in mg/L, q is ln(Q) in m^3/s, T is time in years (decimal), and ε is the error. The model uses this equation with provided data to infer gaps in the water quality record and to create long-term hydrologic trends (Hirsch et al., 2010; Hirsch and De Cicco, 2015). More detail on the mathematical and statistical aspects of the WRTDS model can be found in Hirsch et. al (2010) and Hirsch and De Cicco (2015).

When using EGRET for temporal water quality analysis, it is important that all discharge data points be included within the same time span as the water quality data. If the data for discharge does not coincide with all water quality data or exceed the necessary limits, the model will not efficiently converge or will not converge at all (Hirsch and De Cicco, 2015). With this being said, the daily discharge data should not include points more than a few months before or after the start or end dates of the water quality data included in the study. A short analysis of the effects of variable model coverage period on EGRET estimations was conducted. Sulfate (SO_4^{2-}), nitrate (NO_3), and calcium (Ca^{2+}) concentration trends at the outflow site (MSSP-OUT) for three different periods were plotted using the model (Figures 4a-c). If data points do not seem to appear on the figure, it is because the values of each respective data series are the same for a given year.

a)

SO$_4$ v. Time - Multi-Date - (MSSP-OUT)

b)

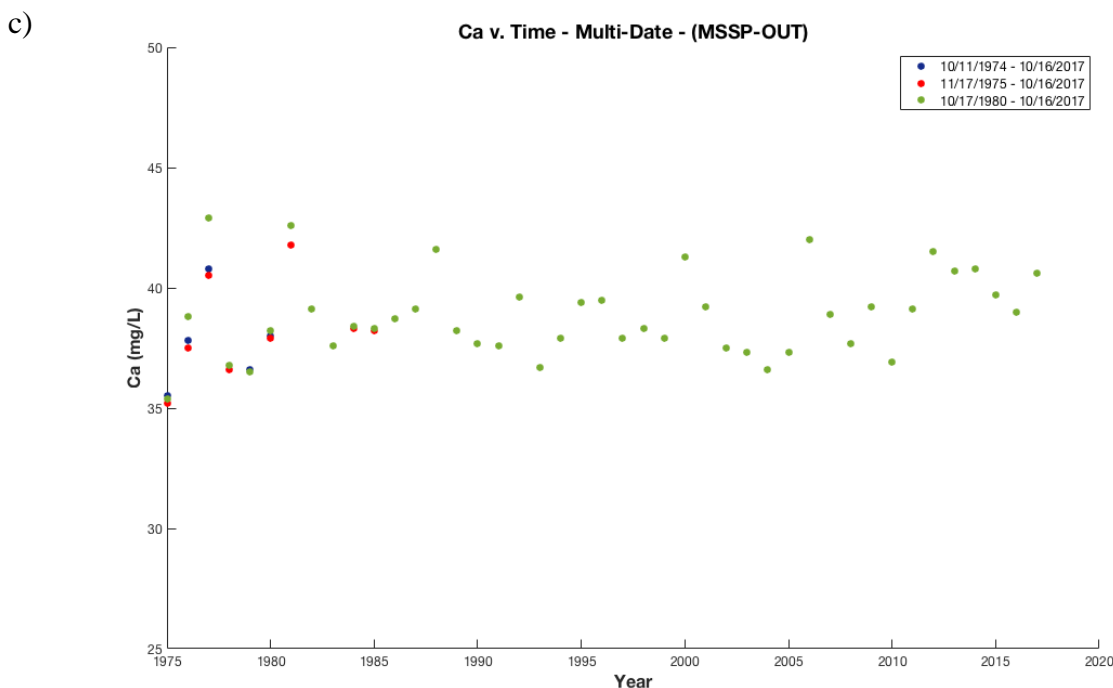**NO$_3$ v. Time - Multi-Date - (MSSP-OUT)**

c)
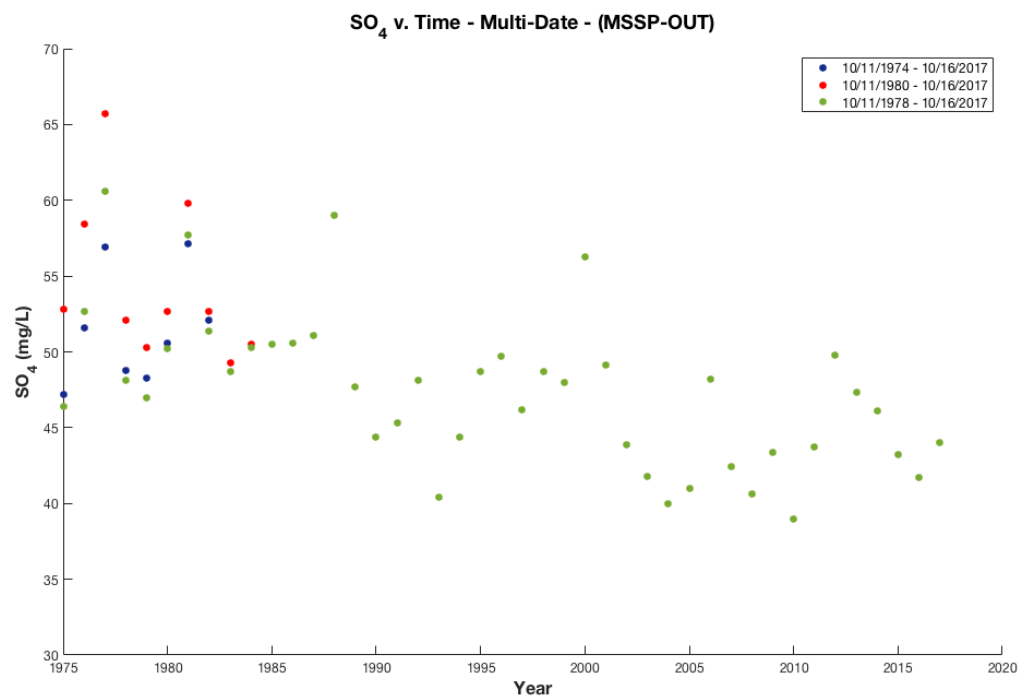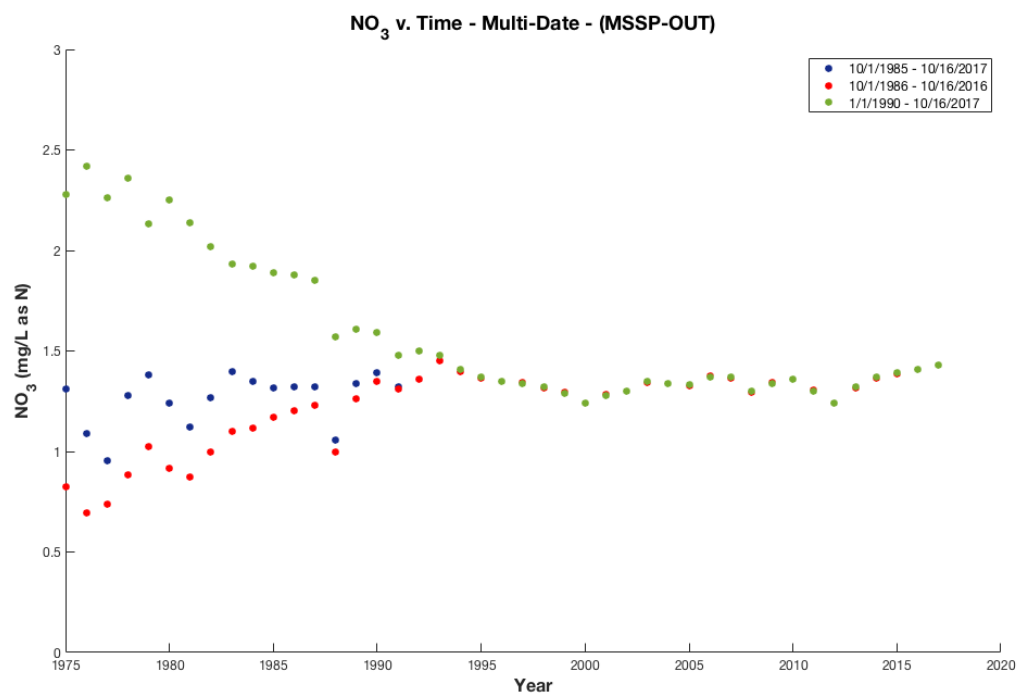
Figure 4. a) Sulfate Concentration b) Nitrate Concentration and c) Calcium Concentration with Variable Data Coverage

Figures 4a-c indicate that variation in calibration span can have a significant effect on the output of the model. Annual estimates for some chemical constituents are more sensitive to variation in calibration period than estimates for others. Sulfate (SO_4^{2-}) and calcium (Ca^{2+}) concentration trends varied little with change in coverage period while nitrate (NO_3) trends before 1993 changed direction entirely with a change in coverage period. Nitrate data for MSSP-OUT begins in 1973 and there is a gap from 1974 to 1985, so the large difference between the start data of discharge data and that of water quality data in the third model run resulted in an extrapolation such that the trend was negative instead of positive for years before 1993 (Figure 4b). Due to the prospect of inaccurate extrapolations, the discharge records used in the program either coincide with water quality data or exceed the limits of water quality data by several months.

Chapter 3: Results

The yearly pH averages from EGRET at MSSP-OUT exhibit increasing behavior (Figure 5a). After a general decline of 0.0286 units per year from 1975 to 1983, the pH increased at an average of 0.0092 units per year. The turning point from decreasing pH to increasing pH is noticeable. There is also a period of decrease in pH at MSSP-OUT from 2006 to 2017. Although the pH fluctuates, there is an overall increasing trend over time. Sulfate load and concentration both decrease over time at MSSP-OUT over the study period (Figure 5b). Unlike the pH trend at the outflow site, sulfate values for both concentration and load decrease from the beginning of the coverage period. There is no turning point in trend anywhere in the study period. Yearly concentration values from EGRET decrease at a rate of 0.2259 mg/L-year while load values from the model estimate an 85.534 million kg/year decrease in sulfate load. The trends of both pH and sulfate (SO_4^{2-}) at the outflow site agree with expected trends of recovery.
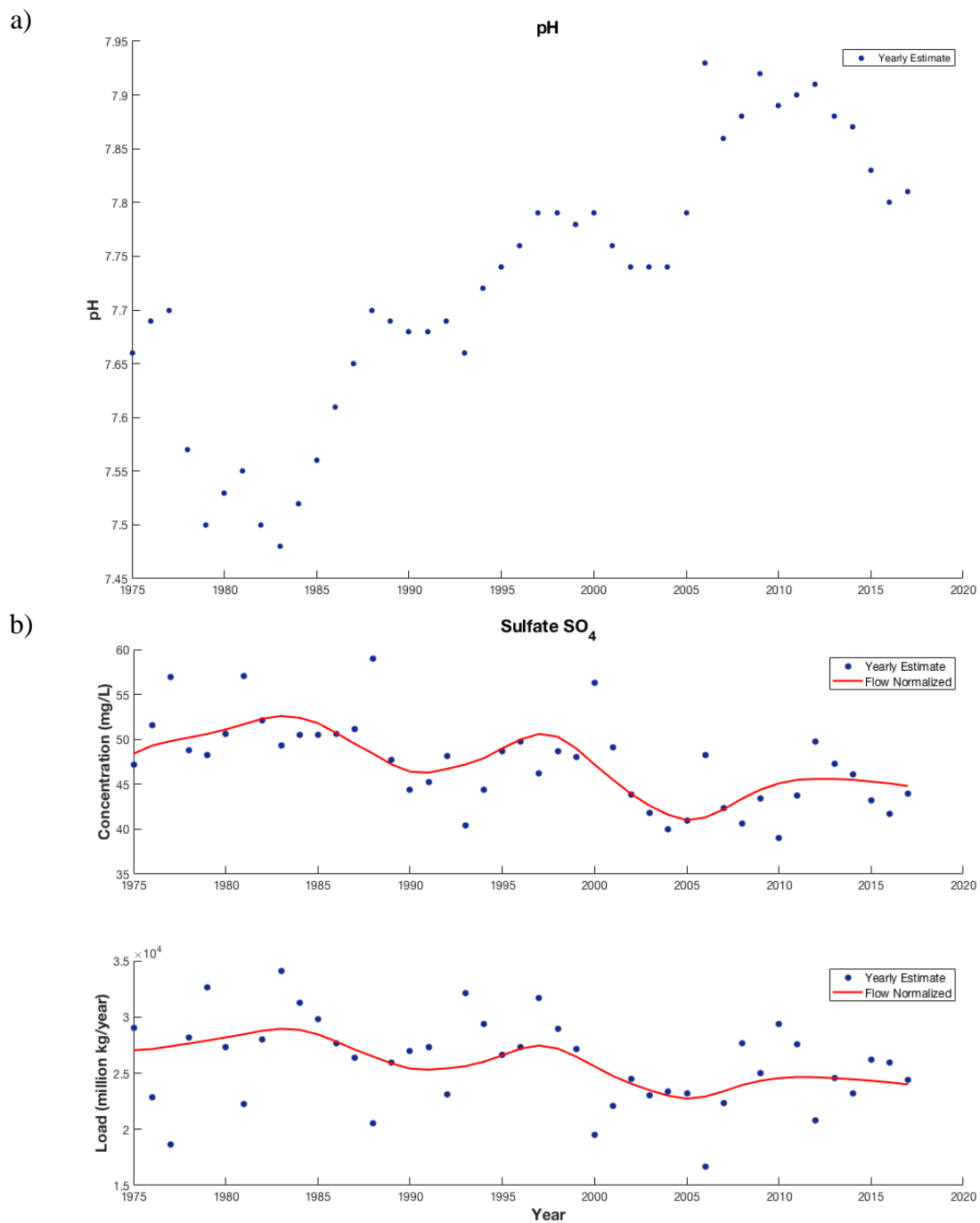
a)

b)

Figure 5. a) pH v. Time and b) Sulfate v. Time at MSSP-OUT

Yearly divalent cation (Ca^{2+} and Mg^{2+}) load and concentration values from EGRET increase over time (Figure 6). On average, concentration values increase at a rate of 0.0646 mg/L-year. Load values increase at a rate of 82.801 million kg/year. There is little change in increasing load trend in the study period while the rate of divalent cation concentration increase is highest from 1975 to 1989. Concentration values continue to increase from 1989 to 2017 although the estimations are more sporadic. The increasing trends in divalent cation concentration and load conflict with a claim of recovery, in the case where acid rain is the primary driver of rock weathering. In order to gain a more in-depth analysis of acid rain recovery, the above figures were re-created for the tributary sites into the Mississippi River. As mentioned, categorizing these sites into eastern and western classifications provides a basis for comparison.
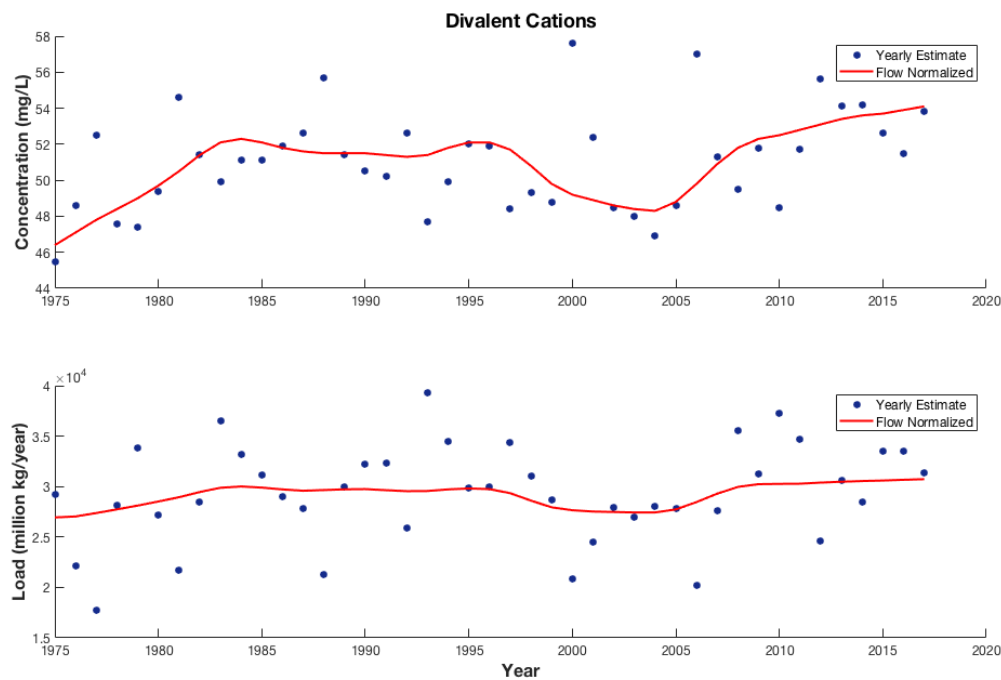

Figure 6. Divalent Cations v. Time at MSSP-OUT

Comparing the tributary values leading into the Mississippi River, the sites that experienced higher rates of acid rain deposition (Eastern tributaries) show stronger signs of recovery than those with less historical deposition (Western tributaries) (Figure 7a-b). The Illinois River measured at Valley City, Illinois (ILLI-VC) and the Ohio River measured near Grand Chain, Illinois (OHIO-GRCH) both experienced pH rise over the test period. The lowest yearly estimated pH values at ILLI-VC were 7.68 in 1982 and 1986. The lowest estimated pH value of 7.26 at OHIO-GRCH was in 1992. The western catchments included in this analysis are: the Mississippi River at Clinton, Iowa (MSSP-CL), the Iowa River near Wapello, Iowa (IOWA-WAP), as well as the Missouri River near Hermann, Missouri (MIZZ-HE). All three of the western sites show decreasing pH over the study period. The highest estimated yearly pH at MSSP-CL of 8.34 was in 1988 with the lowest of 7.87 in 2011. The highest estimated yearly pH at IOWA-WAP of 8.91 was in 1989 with the lowest of 7.88 in 2010. The highest estimated yearly pH at MIZZ-HE of 8.16 was in 1989 with the lowest of 7.64 in 2010.
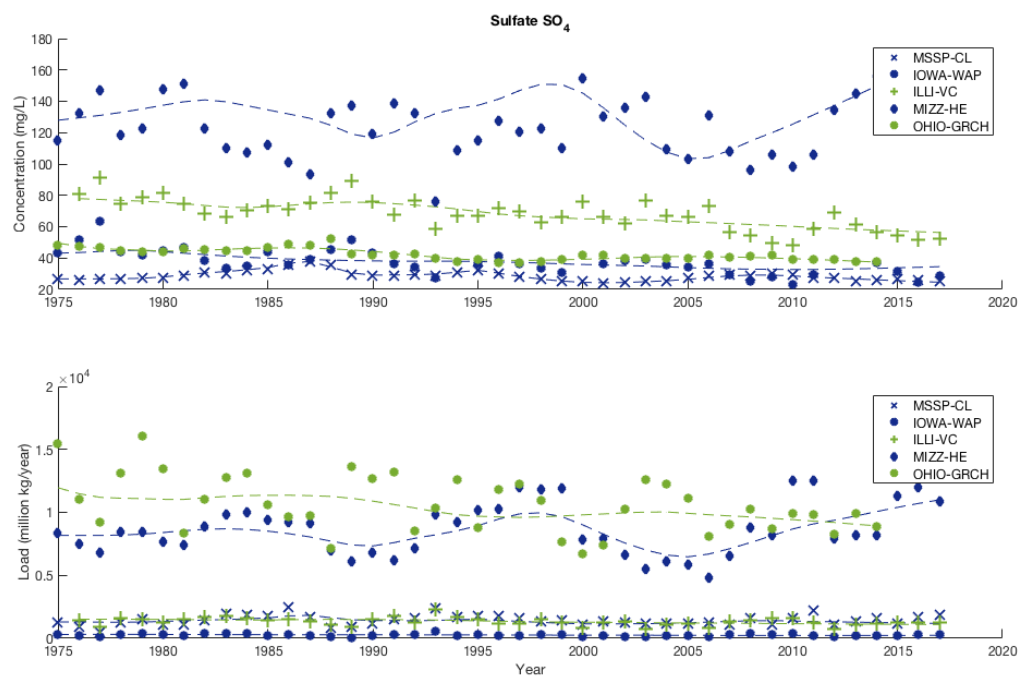
a)
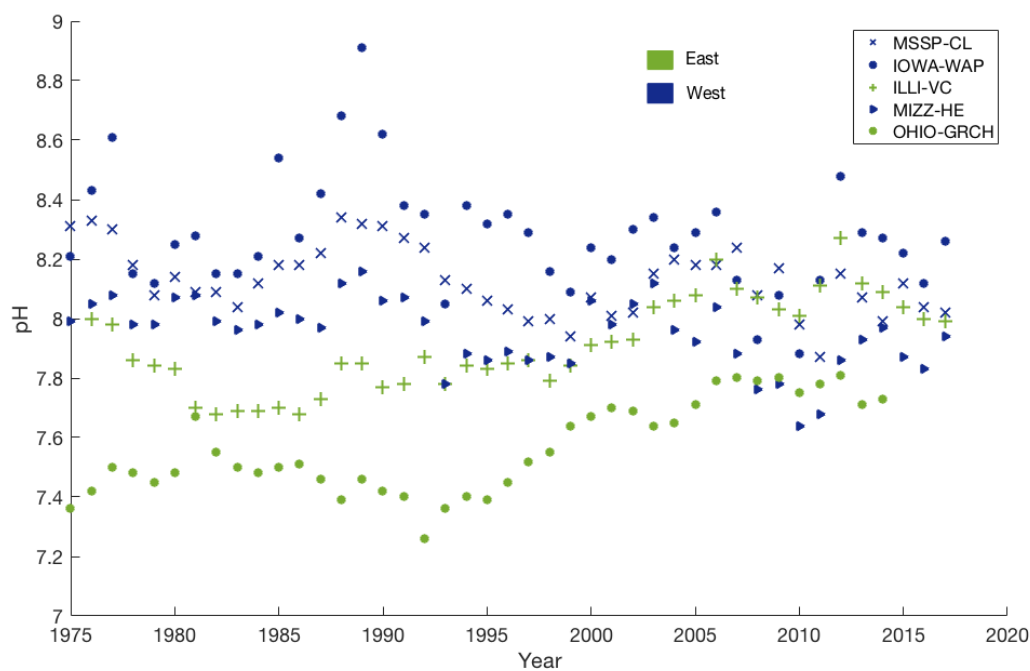
b)

Figure 7. a) pH v. Time and b) Sulfate v. Time for Tributary Rivers

EGRET estimations for sulfate (SO_4^{2-}) concentration and load at each tributary site differ, although the overall trends are decreasing in the Mississippi River (Figure 7b). Estimations of annual concentrations decrease at all tributary sites in the basin except for MIZZ-HE. All annual load trends at the tributary sites also decrease except for at MIZZ-HE. Although western and eastern sites exhibit decreasing trends alike, sites in the eastern section of the basin exhibit greater decreasing trends. As a percent of the initial year concentration estimation, the final annual sulfate (SO_4^{2-}) estimation for the eastern sites are generally lower than those of the western sites. The final annual sulfate (SO_4^{2-}) concentration at ILLI-VC was 64.5% that of the initial year. This same value for OHIO-GRCH was 78.1% that of the initial year. These values for the western sites are: 95.1% for MSSP-CL, 65.7% for IOWA-WAP, and 133% for MIZZ-HE. The significant decrease at IOWA-WAP is likely due to its relative eastern location in the basin. Although IOWA-WAP is binned in the western portion of the basin for the purposes of this study, the river is located in close proximity to those in the eastern bin.

Annual EGRET concentration and load trends for divalent cations are mostly consistent in the various tributary rivers (Figure 8). Divalent cation concentrations either remain constant or increase. A significant increasing trend in concentration is seen at all of the western sites in the basin. Although load trends may be difficult to discern due to relative magnitudes at each tributary river, all tributaries exhibit increasing load trend. For ease of comparison a linear trendline was fitted for each of the load trends. The area slopes of the eastern sites are 9.78 million kg/year at ILLI-VC and 16.39 million kg/year. The values at the western tributary sites are: 28.54 million kg/year at MSSP-CL, 6.90 million kg/year at IOWA-WAP, and 21.38 million kg/year at MIZZ-HE. While there are wide variations in these area normalized trends, the

western sites, on average, have higher rates of increase than those of the eastern sites. The other message of this figure is that the overall trend throughout the entire study area is one of increase, also contrary to acid deposition recovery.
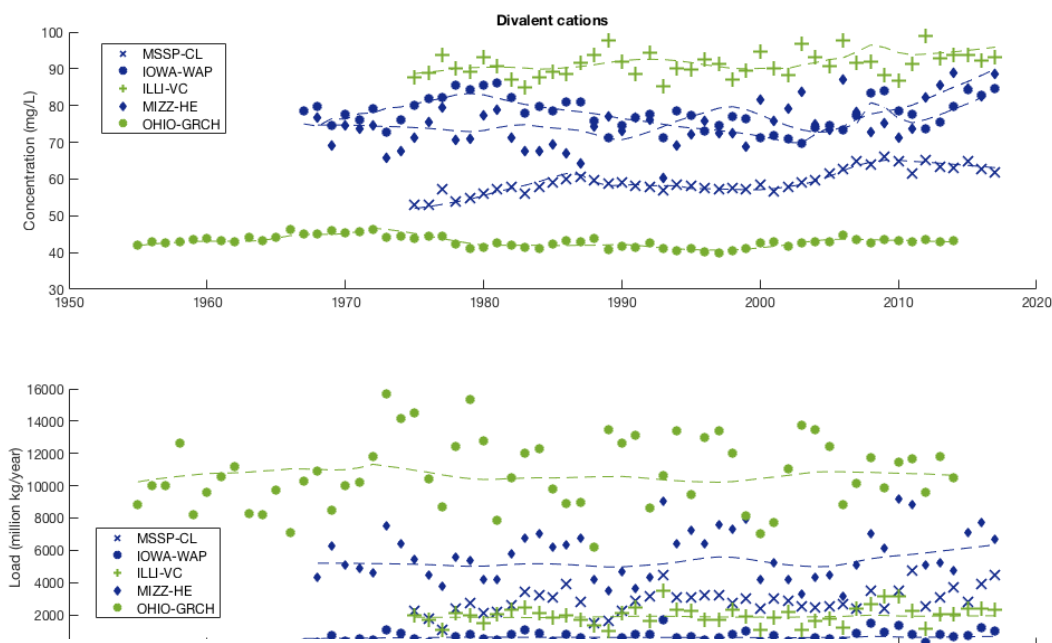
Figure 8. Divalent Cations v. Time for Tributary Rivers

Nitrate as nitrogen (NO$_3$-N) concentrations and load values both increase over time at all tributary sites (Figure 9). Although the relative concentrations and loads for each site vary in magnitude, all sites exhibit an increasing trend. The greatest contributor of nitrogen, in terms of load, in the basin is the Ohio River (OHIO-GRCH). As mentioned previously, the possibility of fertilizer driven weathering is largely dependent on the export of nitrate. If divalent cation trends do not correspond with the trends of nitrate, the suggestion of this weathering pathway would be unlikely. This figure merely acts as an initial metric for analyzing the cause of the divalent cation export observed.
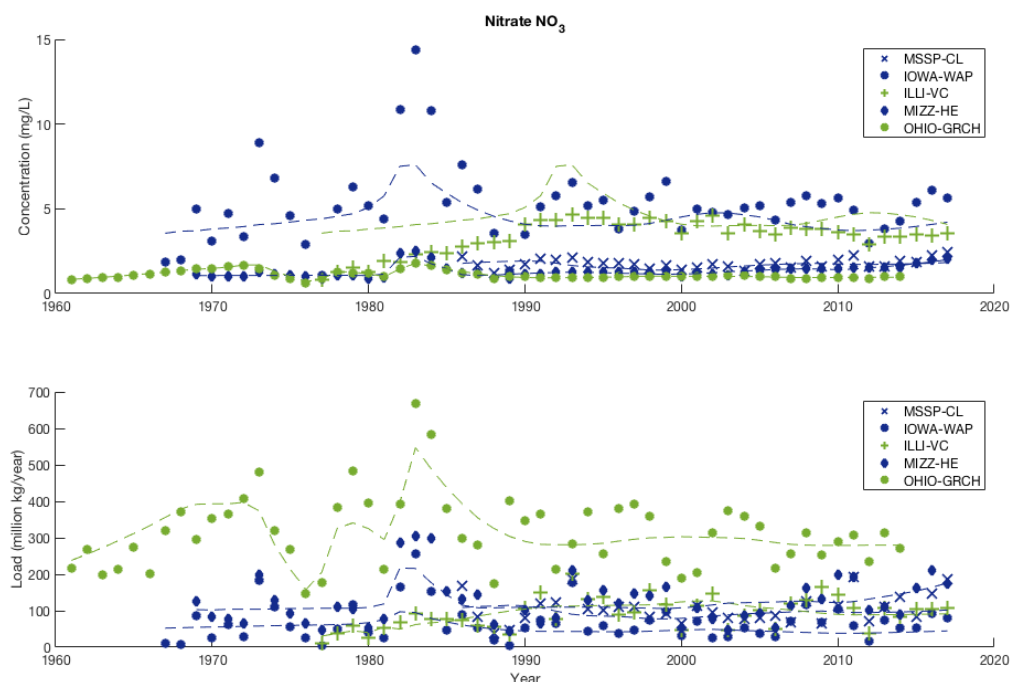
Figure 9. Nitrate as N v. Time for Tributary Rivers

In order to pinpoint the source of cations in the MRB, an analysis of the possibility of chemical weathering at MSSP-OUT was conducted (Figure 10). When looking at the relationship between nitrate concentration and divalent cation concentration, there is a difference between the yearly EGRET estimations and the raw USGS data. The raw USGS data exhibit an overall direct relationship between nitrate and divalent cation concentrations while the yearly concentration averages from EGRET do not exhibit much of a relationship. The linear trendline of the raw data at the outflow site exhibits a slope of 4.78 mg DIV/mg NO_3. The relationship between the yearly estimation values and the raw USGS data points supports the acceptance of the model for this use, as the yearly estimations fall in the average range of the individual USGS data points.
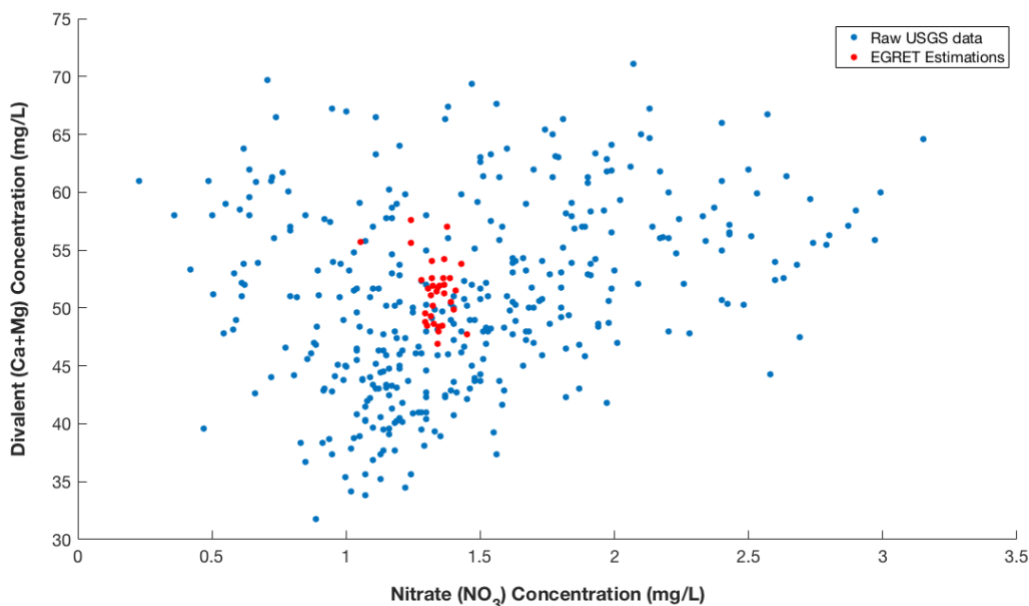
Figure 10. Divalent Cations v. Nitrate at MSSP-OUT

To further investigate the relationship between nitrate as nitrogen (NO_3-N) and divalent cations, the same relationship was plotted for all sites as was conducted (Figure 11). Both raw data and yearly concentration estimations for divalent cations were plotted against those of NO_3-N for all tributary sites: MSSP-CL, IOWA-WAP, ILLI-VC, MIZZ-HE, and OHIO-GRCH. The trend at MSSP-OUT is included in Figure 11 for reference. As in previous figures, eastern sites are plotted in green while western sites are plotted in blue. The yearly estimation values for all sites are in red. Raw data for MSSP-OUT is plotted in black. Similar to the trend of MSSP-OUT, there is a direct relationship between NO_3-N and divalent cations at all sites. The relationships, though, between these two constituents differ. The slopes of the raw data linear trendlines differ from site to site and there is little relationship between eastern and western sites. The strongest relationship between the two constituents is at OHIO-GRCH where the slope of the linear fit is 6.74 mg DIV/mg NO_3-N. The weakest trend is at ILLI-VC where the linear slope is 0.60 mg

DIV/mg NO₃-N. A table of the linear fit equations for the raw data relationships is given in

Appendix A. Unlike that of MSSP-OUT, the trendlines for EGRET annual concentration

estimations at the tributary sites also show a direct relationship (Figure 11). From visual

inspection it can be noted that the tributary relationships of the yearly estimations follow closely

to those of the raw data. This may be caused by lack of variation from year to year within each

tributary river shed in comparison to the large heterogeneous MRB which is comprised of

several river systems.
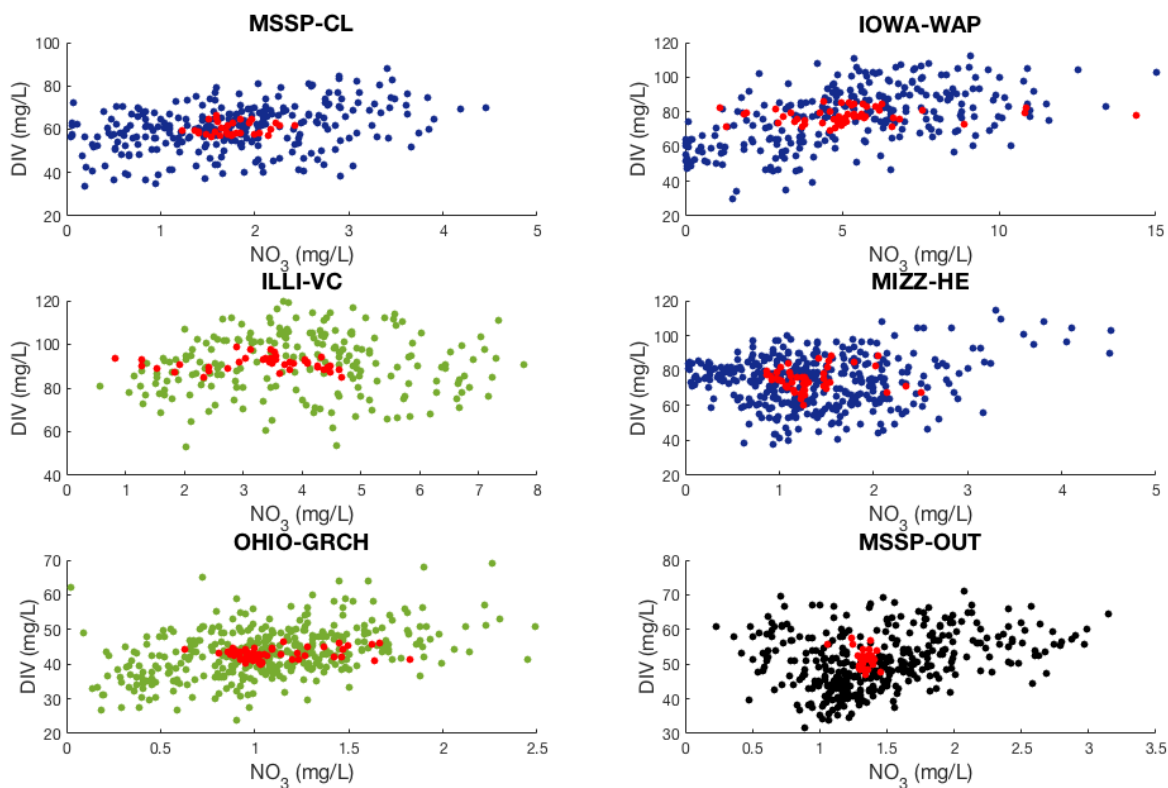
Figure 11. Divalent Cations v. Nitrate for Tributary Rivers

Seasonal trends in nitrate and divalent cation concentrations at MSSP-OUT are suggested

to be related (Figure 12). Nitrate concentrations spike from spring through mid-summer (May to

July). The lowest average nitrate and nitrogen (NO₃-N) concentration of 0.8 mg/L is experienced

in September. The highest average nitrate as nitrogen (NO$_3$-N) concentration of 1.9 mg/L is experienced in July. Divalent cation concentration trends follow a similar pattern as that of nitrate as nitrogen (NO$_3$-N) although on a slightly different timescale. An increase in divalent cation concentration is experienced later in the summer months than that of NO$_3$-N and with a more dampened trend in relation to the average. Divalent cation concentrations rise between June and November with the highest average concentration of 59 mg/L observed in September. The lowest average monthly divalent cation concentration observed in the study period is in February and March, both with a value of 45 mg/L.

Figure 12. Seasonal Trends - Divalent Cations and Nitrate at MSSP-OUT

Chapter 4: Discussion

It is known that acid-rain decreases the pH of surface waters, although soils have the capability of buffering the effects of acidity (US EPA, OAR, OAP). As seen in Figure 5a, pH is increasing on average in the MRB, suggesting recovery f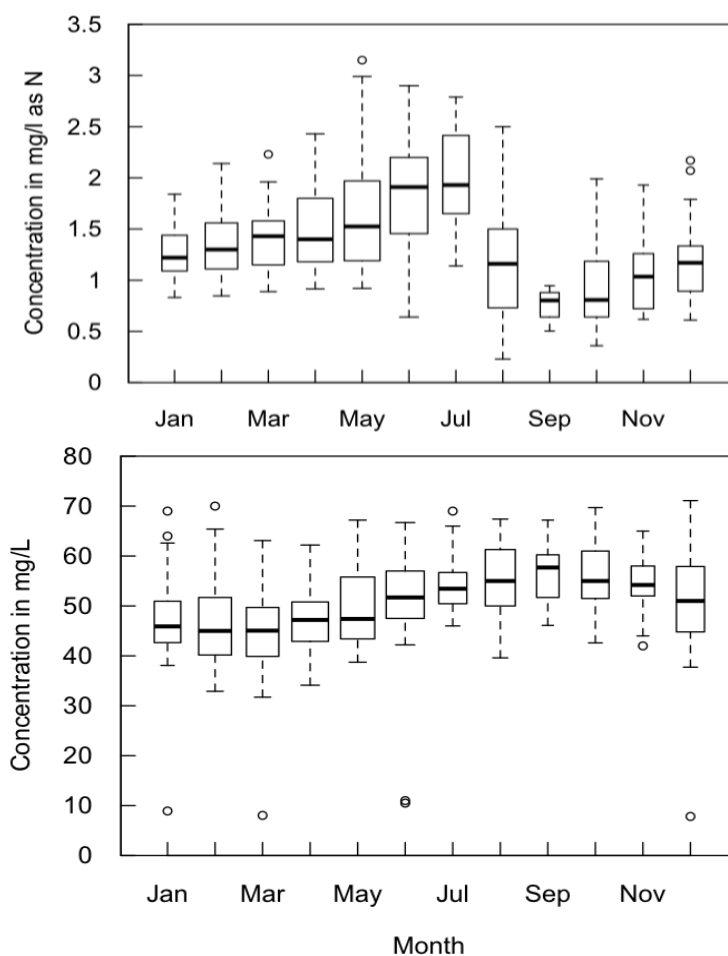rom acid-rain deposition. Although there is a decrease in pH during the first few years of the study period, the overall trend increases over time. Trends in sulfate (SO_4^{2-}) concentration and flux lead to similar conclusions. Both concentration and flux of sulfate (SO_4^{2-}) decrease over time. Unlike the temporal trend in pH, trends in sulfate metrics decrease over the entire study period. The general trend of pH over the first eight years of the study period is a decrease while the trend increases after 1983. If the temporal effects of decreasing acid rain deposition were the same for both pH and sulfate (SO_4^{2-}), it would be expected that trends would act in unison. Instead, sulfate (SO_4^{2-}) metrics suggested recovery before pH trends did. Therefore, it is suggested that pH changes over a longer time scale than sulfate (SO_4^{2-}).

Trends comparing tributary rivers from eastern and western areas provide further supporting evidence that the MRB is recovering from acid rain. The wet deposition, or atmospheric deposition from rain, of H^+ decreased significantly between 1985 and 2016 in the eastern region of the basin (NADP, 2017). Deposition rates in the western region of the basin have been historically minimal and averages between this time period changed little. Tributary rivers with catchments in the eastern region of the basin show increasing pH over the study period while tributary rivers with catchments in the western region of the basin exhibit decreasing pH (Figure 7a). Regions with decreasing acid-rain deposition experienced signs of recovery while regions with little change in deposition rates did not. Although sulfate (SO_4^{2-}) concentration and load decreases overall in the Mississippi River, both concentration and load in

the Missouri River (MIZZ-HE) increase over the study period. This may be caused by anthropogenic sources such as municipal discharges, increased atmospheric deposition, or erosion of minerals such as gypsum (KY NREPC). All other tributary rivers in this study exhibited a decrease in sulfate (SO_4^{2-}) export to agree with the notion of recovery. Both pH and sulfate (SO_4^{2-}) trends suggest that efforts to reduce the effects of acid rain were largely successful in relation to surface waters.

Acidity in soil is known to release cations into surface waters - it would be anticipated that a trend in recovery would result in decreasing cation load. This was not the case. The divalent cation trends at MSSP-OUT show that the cation load is increasing throughout the basin. Divalent cation export trends for tributary rivers also increased. It cannot be concluded that sites are fully recovering from acid-rain deposition if this is the case. Under the consideration of chemical weathering, since there can be many sources of cations into surface waters other than acid-rain deposition, results indicate a high likelihood of chemical weathering of carbonate rock. From tributary river trends, it is suggested that the driver of cation export is also present in all areas of the MRB.

This study provides the opportunity to discuss two drivers of carbonate weathering and their effect on such a large area of the United States. It is believed that acid-rain deposition causes carbonate weathering (Likens et al., 2017). It is also believed that the use of nitrogen-based fertilizers causes carbonate weathering (Perrin et al., 2008; Gaillardet et al., 2004). Stoddard et al. (2007) found evidence that cation export decreased with sulfate (SO_4^{2-}) concentrations in excess. In contrast, this study on a large river network found cation concentration increased as sulfate concentrations decreased. The relationship between nitrate as nitrogen (NO_3-N) and divalent cation concentrations are suggested to be related from the data in

this study. There is an overall positive relationship between nitrate as nitrogen (NO_3-N) and divalent cations at all sites in this study. There is certainly more of a positive relationship between the two chemical constituents at some sites than at others. Granted that both the strongest and weakest correlation of the two are exhibited at the eastern tributary sites, there is little evidence to suggest that there is any spatial trend between eastern and western areas of the basin. The relationship between NO_3-N and divalent cations is not clear using the yearly values obtained from EGRET. Yearly estimations for tributary sites follow raw data trends more in comparison to that of the outflow site. If the relationship changes depending on the time period of a data point, then the relationship between these two constituents is likely highly dependent on season. When considering monthly trends at the outflow site (MSSP-OUT), a relationship between these two constituents can be observed. Nitrate concentrations spike throughout spring and early summer. The concentration of divalent cations increases concurrently with NO_3-N but continues later through the year and is muted in degree. The combination of trends in both raw USGS data and monthly averages support the conclusion that, in the MRB, divalent cation export is significantly driven by fertilizer use.

The findings of this study expand on the findings of previous studies and close the knowledge gap in several ways. While there have been investigations on the effects of decreased acid-rain deposition, almost all of these studies have been conducted on smaller forested catchments. In addition to the limitation of studies in terms of land use, these catchments have mostly been relatively small in terms of area. Finally, it is known that both acid-rain deposition and fertilizer use can cause carbonate weathering and here a comparison is possible between the two.

A study in a forested New Hampshire catchment suggested that acid-rain deposition causes carbonate weathering and large losses of calcium and magnesium (Likens et al., 2017). A study on small watersheds in the Catskill Mountains saw that decreased acid-rain deposition resulted in decreased cation concentrations and decreased soil weathering rates (McHale et al., 2017). These findings were shown in an analysis of decreased deposition rates in the Slavkov Forest in the Czech Republic, as divalent cations decreased approximately 10% in the ten-year study (Majer et al., 2005). Similar decreased cation export is also suggested in other studies (Clow and Mast, 1999; Jeffries et al., 2003, 2000; Driscoll et al., 2003). Although the findings in the aforementioned studies conflict with the conclusions of this study, the previously studied regions experience limited agricultural land use and are heavily forested, while those included in this study have been subjected to more agricultural land use. The findings here are supported by the studies on small forested catchments, as there is little reason for agriculturally mediated carbonate weathering.

This study expands the type of catchments studied for acid-rain recovery. Almost all previous studies analyzing decreases in acid-rain deposition have been conducted on small scale catchments (McHale et al., 2017; Majer et al., 2005; Marx et al., 2017; Likens et al., 2017; Clow and Mast, 1999). With this being said, a large-scale study investigated in stream recovery of acid rain deposition at 205 stream and lake sites throughout the northeastern United States as well as Europe (Stoddard et al., 2007). This study, utilizing data from 1980 to 1995, found evidence that efforts to reduce acid-rain were successful. The study by Stoddard et al. (2007) was conducted on a relatively short timescale due to the relative proximity in time to the efforts to reduce acid rain. The current study, while using fewer sites, expanded the time perspective of the Stoddard et al. (2007) study. Stoddard et al. (2007) also looked at sites strewn across various areas:

North/Central Europe, Nordic Countries, Maine/Atlantic Canada, Vermont/Quebec, South/Central Ontario, Adirondack/Catskill mountains, as well as Midwestern North America. While their study offered a wide spread of comparison for analysis, this study takes a holistic approach for comparison of one large river system, making for easy comparison between catchments subject to different stressors.

Chapter 5: Conclusion

Through analysis of USGS data at the outflow site (MSSP-OUT) as well as five tributary river sites leading into the Mississippi River, it is suggested that the MRB is recovering from historic acid rain deposition. pH increases and sulfate (SO_4^{2-}) export decreases on average at the outflow site throughout the study period. pH and sulfate (SO_4^{2-}) trends at the tributary sites act in accordance with those at the outflow site as eastern catchments exhibit stronger trends of recovery than western catchments. Trends in divalent cation export (Ca^{2+} and Mg^{2+}) conflict with pH and SO_4 trends and increase over the study period. Studies in the past have found that decreases in acid-rain deposition result in decreased cation export. These previous studies have largely been conducted in small forested catchments with limited agricultural activity. Analyses of the relationship between NO_3-N and divalent cation export both in terms of concentration and season have suggested that the increase in divalent cation export is largely caused by the use of nitrogen-based fertilizers in the MRB as the basin is largely agricultural and nitrate export has increased over the study period as well. Therefore, it is suggested that the MRB is recovering from acid rain deposition and that legislation has been effective in terms of in-stream effects. It is also suggested that the use of fertilizers in the basin is causing widespread losses of cations from terrestrial sources.

Appendix A

Table 4. Available USGS data for studied constituents

		USGS Data Dates		
Site Name	USGS Site ID	Discharge (m³/s)	pH	Sulfate (SO₄²⁻) (mg/L)
MSSP-CL	05420500	11/12/1974 – 12/1/2016	11/12/1974 – 8/14/2017	2/11/1974 – 7/27/2017
IOWA-WAP	05465500	11/10/1977 – 12/1/2016	12/12/1966 – 7/26/2017	12/12/1966 – 7/26/2017
ILLI-VC	05586100	12/12/1974 – 12/1/2016	12/12/1974 – 8/17/2017	12/12/1974 – 8/17/2017
MIZZ-HE	06934500	10/28/1969 – 12/1/2016	7/31/1969 – 8/16/2017	7/31/1969 – 8/16/2017
OHIO-GRCH	03612500	10/11/1972 – 12/1/2016	10/1/1954 – 10/29/2014	10/1/1954 – 1/14/2015
MSSP-OUT	07373420	10/11/1974 – 8/14/2017	8/22/1954 – 10/16/2017	8/22/1954 – 10/16/2017

		USGS Data Dates	
Site Name	USGS Site ID	Nitrate as Nitrogen (NO₃-N) (mg/L)	Divalent Cations (Ca+Mg) (mg/L)
MSSP-CL	05420500	11/19/1985 – 8/14/2017	2/11/1974 – 7/27/2017
IOWA-WAP	05465500	12/12/1966 – 10/4/2017	12/12/1966 – 10/4/2017
ILLI-VC	05586100	2/27/1986 – 10/3/2017	12/12/1974 – 10/3/2017
MIZZ-HE	06934500	7/13/1969 – 10/26/2017	6/22/1971 – 10/26/2017
OHIO-GRCH	03612500	10/1/1959 – 1/14/2015	10/1/1954 – 1/4/2015
MSSP-OUT	07373420	1/9/1973- 10/16/2017	11/7/1973 – 10/16/2017

Table 5. Dates Used in EGRET

		USGS Data Dates		
Site Name	**USGS Site ID**	**Discharge (m^3/s)**	**pH**	**Sulfate (SO$_4^{2-}$) (mg/L)**
MSSP-CL	05420500	11/12/1974 – 12/1/2016	11/12/1974 – 12/1/2016	11/12/1974 – 12/1/2016
IOWA-WAP	05465500	11/10/1977 – 12/1/2016	11/10/1977 – 12/1/2016	11/10/1977 – 12/1/2016
ILLI-VC	05586100	12/12/1974 – 12/1/2016	12/12/1974 – 12/1/2016	12/12/1974 – 12/1/2016
MIZZ-HE	06934500	10/28/1969 – 12/1/2016	10/28/1969 – 12/1/2016	10/28/1969 – 12/1/2016
OHIO-GRCH	03612500	10/11/1972 – 12/1/2016	10/11/1972 – 12/1/2016	10/11/1972 – 12/1/2016
MSSP-OUT	07373420	10/11/1974 – 8/14/2017	10/11/1974 – 8/14/2017	10/11/1974 – 8/14/2017

		USGS Data Dates	
Site Name	**USGS Site ID**	**Nitrate as Nitrogen (NO$_3$-N) (mg/L)**	**Divalent Cations (Ca+Mg) (mg/L)**
MSSP-CL	05420500	11/19/1985 – 12/1/2016	11/12/1974 – 12/1/2016
IOWA-WAP	05465500	11/10/1977 – 12/1/2016	11/10/1977 – 12/1/2016
ILLI-VC	05586100	2/27/1986 – 12/1/2016	12/12/1974 – 12/1/2016
MIZZ-HE	06934500	10/28/1969 – 12/1/2016	6/22/1971 – 12/1/2016
OHIO-GRCH	03612500	10/11/1972 – 1/14/2015	10/11/1972 – 1/4/2015
MSSP-OUT	07373420	10/11/1974 – 12/1/2016	10/11/1974 – 12/1/2016

Appendix B

Table 6. Slopes of NO3-N v. DIV

Site Name	USGS Site ID	NO$_3$-N v. DIV Slope
MSSP-CL	05420500	3.90
IOWA-WAP	05465500	3.04
ILLI-VC	05586100	0.60
MIZZ-HE	06934500	2.37
OHIO-GRCH	03612500	6.74
MSSP-OUT	07373420	4.78

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Academic Vita

Daniel Kozar

Education

Pennsylvania State University, University Park, PA (Graduation: May 2019)
College of Earth and Mineral Sciences
Schreyer Honors College
Major: Environmental Systems Engineering
Minor: Arabic

Penns Valley Area High School, Spring Mills, PA (Class of 2015)

Employment and Research

Pennsylvania State University Department of Civil and Environmental Engineering (2017-)

Researcher, Li Reactive Transport Group
Conduct research of recovery from acid rain deposition in the Mississippi River Basin using USGS data and software for my senior thesis

Fraunhofer Institute for Molecular Biology and Applied Ecology (2018)

Research Intern, DAAD RISE Germany
Assisted PhD student Prasit Shrestha in Schmallenberg on his project studying degradation of hydrophobic organic chemicals in aqueous solution

Pennsylvania State University Department of Energy and Mineral Engineering (2016-)

ENVSE 406 Grader/TA (Spring 2019)
Grade statistics homework, attend class, and hold office hours for Dr. Randy Vander Wal

EME 301 Grader (Spring 2017)
Graded thermodynamics homework assignments for Dr. Jeffrey Brownson

Skills

MATLAB, Microsoft Office Suite, WRTDS-EGRET, Adobe Illustrator, R

Language Proficiency

English - Native Language
Arabic - Proficient
German - Proficient