The Biogeochemical Response of Eastern U.S. Watersheds to Declines in Acid Deposition

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Abstract

Over recent decades, reductions in acid deposition have led to the recovery of watersheds across the eastern United States. Examining the acid-base status of surface waters is important for understanding the changes in chronic and episodic acidification of surface waters. This thesis investigates the biogeochemical response of forested watersheds to major declines in acidic inputs.

The soils of the southeast U.S. have a high sulfate adsorption capacity compared to the northeast soils, leading to a delay in the recovery of surface waters. To identify regional differences in the recovery of watersheds, a mass balance analysis of sulfur for 16 watersheds (8 in the northeast, 8 in the southeast) was completed. The northeast sites (with the exception of one) have been net exporters since the 1990s to the early 2000s, while the southeast sites have only recently converted from a net retention within the last decade. There is evidence that sulfate adsorption is an irreversible process based on the whole-watershed scale. Additionally, results from the temporal analysis of the flow-normalized concentrations of sulfate reveal that while the majority of the northeast sites have declined to around the same concentration, there is more variation between the southeast sites. This may be due to differences in bedrock, which influences surface water response.

While the watersheds in the southeast have shown a net export of sulfur recently, and thus a trajectory towards recovery from years of excess acid deposition, the main drivers for changes in the stream chemistry during episodic acidification remained unclear, and thus were investigated for three watersheds in Shenandoah National Park. Internal biogeochemical processes were more dominant than deposition in affecting changes in the acid-base chemistry of surface waters. The largest declines in base cation supply were evident at the most base-poor site as the soil buffering capacity at these watersheds is influenced by the underlying bedrock.

This work shows the importance of long-term monitoring of surface waters to evaluate the current acid-base status of watersheds in response to decreases in acid deposition. This study may lead to further research into the effects of levels of acid deposition on soils, as well as a further investigation of the sulfate isotherm.

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Chapter 1: Introduction

1. Sulfur Deposition in the Eastern U.S.

In North America, sulfur dioxide (SO_2) and nitrogen oxide (NO_x) emissions from industrial sources, mainly the combustion of fossil fuels, peaked in the early 1970s, and have posed a major air pollution issue (Burns et al., 2011; Mitchell et al., 2011). These emissions lead to acid deposition, as SO_2 and NO_x are oxidized in the atmosphere, yielding sulfuric acid and nitric acid, which are later deposited on Earth's surface (Stoddard et al., 2003). The emissions can be transported hundreds of miles away from the emitting sources, thus having the potential to negatively impact large areas and populations (Burns et al., 2011). Adverse effects to areas include diminished air quality, impacts to forests or crops, leaching of soil nutrients, and the acidification of lakes and streams (Stoddard et al., 2003; Burns et al., 2011).

In response to the high levels of SO_2 emissions, the U.S. Clean Air Act of 1970 was enacted to control emissions, and was later amended in 1990 (Driscoll et al., 2001; Burns et al., 2011). Title IV of the Acid Deposition Control Program of the Clean Air Act Amendments (CAAA) aimed to further decrease emissions of SO_2 and NO_X from electric utilities in order to reduce the acidity of deposition (Driscoll et al., 2001; Stoddard et al., 2003). There have been significant reductions in emissions attributed to the implementation of the CAAA, which has led to improvements in water chemistry (Kahl et al., 2004; Burns et al., 2011; Mitchell et al., 2011; Rice et al., 2014).

While watershed response to the declines in acid deposition are direct in the northeast (NE) U.S., the direct connection is not evident in the southeast (SE) U.S., as watershed recovery in these regions are predicted to lag behind the recovery of watersheds in the NE by decades, even after significant declines in sulfur (S) deposition (Burns et al., 2011; Rice et al., 2014). The differences of the response between the two regions is due to their soil characteristics, a consequence of the last glaciation, which left the NE soils glaciated, and SE soils unglaciated (Galloway et al., 1983; Rochelle and Church, 1987). As a result, the SE soils exhibit a higher sulfate adsorption capacity (i.e. higher sulfate retention) than the NE soils (Kahl et al., 2004; Rice et al., 2014).

The delayed response of the SE watersheds to reductions in acid deposition poses concerns of recovery from acidification after years of excess S deposition. Modeled data shows evidence that it could take decades to centuries for stream sulfate trends to return to preindustrial stream concentrations (Fakhraei et al., 2016). Rice et al. (2014) predicted that a net export of sulfate within these watersheds should occur within the next couple of decades. Robison et al. (2013) also found there was a net export of sulfate in 2011 at a base-poor watershed located in Shenandoah National Park (SHEN). Extensively monitored watersheds provide an opportunity to compare the recovery of surface waters between the two regions.

2. Chronic vs. Episodic Acidification

The effects of acid deposition on surface waters has been well documented in the U.S. (Kahl et al., 2004; Robison et al., 2013; Rice et al., 2014), however, few studies have focused on episodic acidification due to sampling primarily being taken during baseflow conditions. Baseflow conditions are described as periods between storms, when discharge is low (Lawrence, 2002). Chemical concentrations are stable during baseflow and the sources of water are from deeper soils and groundwater storage (Wigington et al., 1992; Lawrence, 2002). Acid deposition may result in chronic acidification of waters, where surface waters during baseflow conditions have an acid neutralizing capacity (ANC) below zero (Lawrence et al., 2002; Stoddard et al., 2003). During periods of large waterflow events such as rainstorms and snowmelt lasting hours to weeks, the acidification of waters is known as episodic acidification, referring to the short-term decline in pH and ANC (Stoddard et al., 2003; Burns et al., 2011). The flow paths are important in determining episodic characteristics, as there are distinct differences in the water mobilized from the upper soil layer compared to the groundwater source, as stormflow derives from shallow soils (Wigington et al., 1992; Wigington et al., 1996; Riscassi et al., 2019).

Drivers of episodic acidification include anthropogenic sources and natural processes within the soils. Anthropogenic sources stem from emissions of SO_2 and NO_x due to fossil fuel combustion. Base cation depletion, which refers to the accelerated loss of cations from soils, is a possible anthropogenic source, as elevated levels of S and N have caused reductions in base cations (Fernandez et al., 2003; Burns et al., 2011). Natural processes include increases in organic acidity and base cation dilution (Burns et al., 2020). The rate of chemical recovery of lakes and streams is slowed by base cation depletion (Driscoll et al., 2001).

A study examining trends in episodic acidification found that episodic acidification is recovering at rates greater than or equal to chronic acidification in Shenandoah National Park (SHEN) (Riscassi et al., 2019). The research presented here examines trends in baseflow, stormflow, and deposition at three watersheds in SHEN in order to identify if stream chemistry changes during high flow conditions are largely depositional or biogeochemically driven.

3. *Thesis Organization*

This thesis is organized into two self-contained papers examining the effects of acid deposition and the biogeochemical response of watersheds. Chapter 2 investigates watershed response to the reductions in sulfur deposition between the northeast and southeast U.S. There have been previous studies that have focused on the two regions separately, but none have attempted to compare the dynamics across each region. Using the most up-to-date deposition estimates, sulfur mass balances for each of the watersheds were completed. The mass balances reveal sulfate adsorption is the main mechanism behind sulfate retention in the southeast watersheds. The budgets also show the SE watersheds are now exporting sulfate, signifying recovery from years of excess acid deposition.

Chapter 3 focuses on determining the main mechanism causing changes in the acid-base status during episodic conditions in SHEN. Through comparing the temporal trends in concentrations of analytes during baseflow and stormflow events to the temporal changes in deposition, it was determined whether biogeochemical processes or atmospheric deposition play a more dominant role in this shift. The results of this work suggest that soils play a larger role in the changes in stream chemistry during high-flow conditions of these watersheds.

In chapter 4, a summary is provided and implications of this research are discussed. Potential future research based on these findings is also presented. An overall theme of this research is the importance of continuous monitoring of surface waters to better understand recovery of watersheds from years of excess acid deposition in the Eastern U.S.

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Chapter 2: Comparison of Northeastern and Southeastern U.S. Watershed Response to the Declines in Atmospheric Sulfur Deposition

Abstract

Since the implementation of the 1970 Clean Air Act and its 1990 amendments, sulfur dioxide (SO_2) emissions and subsequent sulfur (S) deposition has been declining across the eastern U.S. Although temporal patterns of deposition have been similar in the northeast (NE) and southeast (SE) regions of the U.S., stream and watershed responses have differed. This is primarily due to the spatial extent of the last glaciation, which terminated in northern Pennsylvania, rendering the soils in the SE more clay-rich and deeper than soils in the NE. Through the use of improved estimates of atmospheric deposition and more highly constrained estimates of stream export, we calculated S mass balances from New Hampshire to Georgia for 8 glaciated NE watersheds and 8 unglaciated SE watersheds that have high frequency (i.e. weekly) chemistry data available. Overall, total atmospheric S deposition declined by 70-90% from the early 1990s to the late 2010s across all sites. The resulting S budgets show that the timing of the conversion of the watersheds from net S retention to net S release differ between regions. The SE watersheds converted recently (late 2000s to 2010s), while the majority of NE watersheds have been net exporters of S since the 1990s to early 2000s. This delayed response in the SE is a consequence of the much higher sulfate (SO_4^{2-}) adsorption capacity of the soils in this region. The flow normalized concentrations of SO_4^{2-}, which eliminates variability due to discharge, shows that the majority of NE sites converged to similar concentrations by the mid to late 2010s, whereas the SE sites exhibit much greater spatial variability in concentrations. An evaluation of the storage and release of S within watersheds, using changes in adsorbed S and dissolved S (i.e. flow normalized concentration), suggests irreversibility of the S adsorption processes in NE and SE watersheds.

The conversion of watersheds to a net release of S indicates improvements in watershed recovery due to the declines in acid deposition across the Eastern U.S.

1. Introduction

Since the Industrial Revolution, the sulfur (S) cycle has been significantly altered through anthropogenic activity mostly due to the combustion of coal and oil, the leading anthropogenic sources of sulfur dioxide (SO_2) to the atmosphere (Stoddard et al., 2003; Likens et al., 2002). The implementation of the 1970 Clean Air Act (CAA) and subsequent 1990 amendments has led to significant declines in SO_2 emissions in the United States, resulting in significant decreases in S deposition to ecosystems, especially in the eastern portion of the U.S. (Burns et al., 2011; USEPA, 2017). An intended benefit of the reduced S deposition is improvements in stream water quality, with sulfate (SO_4^{2-}) being a primary acidifying agent. Long-term monitoring of stream water chemistry, together with watershed mass balance, provides insight about the fate of deposited S and the expected trajectory of stream water response to changes in atmospheric deposition (Mitchell et al., 2011; Rice et al., 2014). Here we use improved estimates of atmospheric deposition (Schwede and Lear, 2014) and more highly constrained estimates of stream S export to evaluate the storage and release of S from watersheds across the eastern U.S., which have experienced dramatic changes in atmospheric inputs over recent decades.

Chemical elements are transferred from the atmosphere to the surface through dry and wet deposition, where dry deposition includes aerosols and gases and wet deposition includes rain, snow, sleet, fog, and hail (Driscoll et al., 2001; Likens et al., 2002; Stoddard et al., 2003). Dry deposition is comparatively more difficult to measure, but it accounts for a sizeable portion of total S deposition. In previous studies of watershed S mass balance, it has been common to rely upon dry-to-wet deposition ratios to estimate this component (e.g Robison et al., 2013; Rice et al., 2014;

Aulenbach, 2020), but dry S deposition can be better constrained through products that are now available. In this study, we leverage total deposition (TDep) maps (Schwede and Lear, 2014) that are based on a novel hybrid approach of spatial interpolation and modeling, which allows for estimates of total deposition throughout the U.S.

In forested ecosystems, the main mechanism for the accumulation of SO_4^{2-} in soils is sulfate adsorption (Sokolova and Alekseeva, 2008). Adsorption/desorption processes can lead to a delay in the recovery of a stream from acidification, as desorption of SO_4^{2-} can remain as a persistent source to downstream water bodies (Likens et al., 2002; Mitchell et al., 2011). Retention of SO_4^{2-} can also occur through vegetation uptake, however this component of the overall watershed S budget is considered to be relatively small (Likens et al., 2002). Other internal sources include the mineralization of organic S and mineral weathering, the latter of which may be a significant contributor to SO_4^{2-} mobilization to streams for particular geological settings (Mitchell and Likens 2011; Mitchell et al., 2011).

Although the northeast (NE) and southeast (SE) regions of the U.S. have similar temporal patterns in deposition, watershed response has been different due to the spatial extent of the Late Wisconsinan Glaciation, which ended 10,000-15,000 years ago and covered much of the NE, while leaving the SE unglaciated (Galloway et al., 1983; Rochelle and Church 1987; Stoddard et al., 2003; Fernandez et al., 2010; Rice et al., 2014). The NE soils, characterized as young, thin and rocky, are less able to retain SO_4^{2-}, while the SE soils are older, deeper, and are more clay rich. The iron and aluminum oxides associated with the greater clay content are effective in binding S, which contributes to the higher sulfate adsorption capacity of SE soils (Rice et al., 2014). Since the 1990s, stream water sulfate concentrations in the NE have declined in direct response to the declines in S emission and deposition, whereas the SE has exhibited a delayed response, on account of the contrasting sulfate adsorption properties between regions (Kahl et al., 2004). Predictions of future S dynamics are aided by biogeochemical models such as MAGIC (Cosby et al., 1985a, 1985b) and PnET-BGC (Aber and Driscoll, 1997; Aber et al., 1997; Gbondo-Tugbawa et al., 2001), which assume reversibility of the adsorption processes. However, this assumption may be an oversimplification, as laboratory analyses have indicated that a considerable fraction of the adsorbed S may be irreversibly retained in natural soils (Shanley, 1992). The extent to which such irreversibility affects stream water SO_4^{2-} dynamics can now be evaluated at the whole-watershed scale, using data collected from long-term monitoring programs.

On a regional basis, previous studies (Driscoll et al., 2003; Burns et al., 2006; Robison et al., 2013; Rice et al., 2014; Fuss et al., 2015; McHale et al., 2017) examined long-term trends in S dynamics, focusing on the response of water bodies to declines in S deposition. However, there have been no recent attempts to compare such responses across regions. Using improved estimates of atmospheric deposition and highly constrained estimates of stream S export from long-term sites with high-frequency (i.e. weekly) stream chemistry data, the main objectives of this study are to (1) assess S budgets for watersheds across the eastern U.S., (2) examine changes in flow-normalized concentrations of S, and (3) evaluate the reversibility of sulfate storage and release within watersheds. The results of this study are intended to help evaluate an aspect of surface water recovery in response to the Clean Air Act and Amendments and to improve our predictive framework for watershed S retention and release processes.

2. Methods

2.1 Site Description

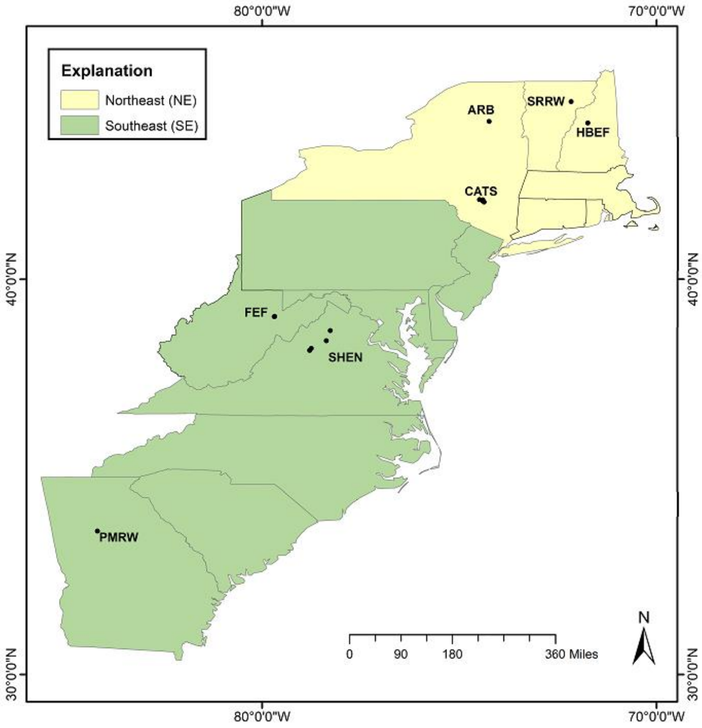

Figure 1. Map showing the locations of the 16 watersheds in the glaciated northeast and unglaciated southeast U.S.

The study sites include 8 glaciated NE and 8 unglaciated SE watersheds spanning the eastern U.S. from New Hampshire to Georgia (Figure 1). Watershed areas range from 13 ha to 2,313 ha, with data collection periods ranging from 1965 through 2016 (Table 1). These watersheds have not been manipulated by experimental treatment such as chemical additions or clearcutting. All sites have long-term, high-frequency (i.e. weekly) stream chemistry data and continuous discharge measurements. The NE sites include Hubbard Brook Experimental Forest (HBEF), Sleepers River (SRRW), the Catskills (CATS), and Arbutus Lake Watershed (ARB). The SE sites include Shenandoah National Park (SHEN), Fernow Experimental Forest (FEF), and Panola Mountain Research Watershed (PMRW). Coweeta Hydrologic Laboratory has data that fits our selection criteria, but were unwilling to share for the present study. Vegetation type cover ranges from hardwood to mixed hardwood (Table S1).

Table 1. Site Name, Site ID, Watershed Area, Period of Record, National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) station, and Clean Air Status and Network Trends (CASTNET) station codes for the 16 watersheds.

Site Name	Site ID	Period of Record	Area (ha)	NADP/ NTN Station	CASTNET Station
Northeast					
New Hampshire					
Hubbard Brook WS 3	HBEF WS3	1972-2016	42	NH02	WST109
Hubbard Brook WS 6	HBEF WS6	1965-2016	13		
Vermont					
Sleepers River	SRRW	1992-2015	41	VT01	LYE145
New York					
Biscuit Brook	CATS BS	1992-2016	963	NY68	CAT175
Winnisook	CATS WN	1992-2016	199		
Tisons	CATS TS	1992-2016	2313		
Rondout	CATS RC	1997-2016	1388		
Arbutus Lake Watershed	ARB	1996-2016	352	NY20	HWF107
Southeast					
Virginia					
Paine Run	SHEN PAIN	1993-2016	1240	VA28	SHN418
Piney River	SHEN PINE	1993-2016	1260		
Staunton River	SHEN STAN	1993-2016	1050		
White Oak Run	SHEN WOR1	1981-2016	513		
West Virginia					
Fernow WS 4	FEF WS4	1984-2015	39	WV18	PAR107
Fernow WS 10	FEF WS10	1986-2015	15		
Fernow WS 13	FEF WS13	1990-2015	14		
Georgia					
Panola Mountain Ck. Trib.	PMRW	1986-2016	41	GA41	GAS153

2.2 S Deposition Estimates

Atmospheric deposition was calculated for individual watersheds on a water-year basis and reported in units of kg S ha^{-1}. The National Atmospheric Deposition Program total deposition (TDep) ESRI ArcGrids deposition maps (TDep v. 2018.1 http:// nadp.slh.wisc.edu/committees/ tdep/) were used to estimate dry S deposition from 2000-2016, initially on a calendar-year basis. To adjust to water years (October – September), we acquired deposition maps through week 40 of each year (G. Lear, pers. comm.) which approximately coincides with the cut-off between water years. Thus, we were able to piece together the dry S deposition on a water-year basis. Further details on TDep dry S deposition estimates are provided in Schwede and Lear (2014).

For years prior to 2000, when TDep maps were not available, weekly dry deposition data available through Clean Air Status and Network Trends (CASTNET; Table 1) was used to estimate TDep-equivalent dry S deposition. The linear relationship between CASNET and the site-specific TDep for overlapping years was determined, and the equation of the line was used to extrapolate estimates of dry S deposition for years prior to 2000. CASTNET data for water year 1996 was missing for half the year at PMRW and the entire year at SRRW. For PMRW, the dry S deposition for the first 25 weeks of 1996 was estimated as being equivalent to the average dry S deposition over the same 25-week timeframe for the three years before and after 1996. For SRRW, dry S deposition in water year 1996 was taken as the average for water years 1995 and 1997.

Study periods of eleven watersheds (HBEF, CATS, SRRW, ARB, SHEN, PMRW, and FEF) extend prior to the availability of CASTNET data. Dry S deposition was calculated using a linear regression between wet and dry deposition from 1989-2000, with the dry deposition estimates based on the TDep equivalent. Relative amounts of dry and wet deposition vary over time; therefore the 1989-2000 time period was assumed to best represent the relationship over the early, pre-CASNET periods. The regressed relationships were applied to the pre-CASTNET wet deposition values to estimate dry S deposition. CASTNET data did not start until water year 2003 for ARB, therefore the 2003-2010 relationship between wet and dry deposition was used. CASTNET data did not start until water year 1990 for HBEF, therefore the 1990-2000 relationship was used. For SRRW and CATS the 1995-2000 relationship was used, as the CASTNET data for these sites did not extend prior to water year 1995.

Wet deposition was estimated using data from the National Atmospheric Deposition Program/ National Trends Network (NADP/NTN) (Table 1). The wet S deposition flux at the NADP/NTN site was multiplied by the ratio of precipitation for the specific watershed to that of the NADP/NTN site. Precipitation for the watersheds was obtained from Oregon State's Parameter-elevation Regression on Independent Slopes Model (PRISM, http://prism.oregonstate.edu). The centroid of each watershed (computed using ArcMap 10.6 and ArcMap 10.7) was used to collect precipitation data from PRISM at 4km resolution using the "interpolation option". HBEF was the only site in which data collection started prior to the NADP data, therefore the wet deposition estimates were calculated using weekly SO_4^{2-} precipitation chemistry data that were available (Likens, 2017). The SO_4^{2-} concentration was multiplied by the site-specific precipitation data from PRISM and then converted to mass of S. All analysis and statistical calculations were performed using MATLAB software [version 9.6.0.1114505, The MathWorks Inc, Natick, MA].

2.3 S Export Estimates

Water year-based S fluxes reported in kg S ha^{-1} were estimated using the Rstudio package, Exploration and Graphics for River Trends (EGRET) which applies the Weighted Regressions on Time Discharge, and Seasons (WRTDS) smoothing method (Hirsch et al., 2010; Hirsch and De Cicco, 2015). Streamflow and water quality data was acquired from online databases for HBEF (Bernhardt et al., 2019; USDA, 2019), CATS (U.S. Geological Survey, 2020), FEF (Edwards and Wood, 2011a, 2011b), and PMRW (Aulenbach, 2019). Data from other sites – SRRW, ARB, and SHEN – were acquired directly from site personnel. Flow-normalized concentrations were computed through WRTDS, which eliminates the variability in concentration due to discharge (Hirsch and De Cicco, 2015), yielding concentrations for an average discharge year.

2.4 S Budgets

Sulfur budgets were calculated for each site to examine long-term trends. The total amount of stored S for each watershed on an annual basis (S_{net}, kg S ha^{-1} yr^{-1}) was calculated as the difference between total S deposition (S_{dep}, kg S ha^{-1} yr^{-1}) and S export (S_{exp}, kg S ha^{-1} yr^{-1}). A net positive flux represents net accumulation of S, while a negative indicates net S release from the watershed. Percent retention of S ($=S_{net}/S_{dep}*100$) was also calculated to observe changes in storage. The cumulative amount of S stored within or released from watersheds (S_{cum}, kg ha^{-1}) was determined by summing up S_{net} over sequential years:

$$S_{cum} = \sum_{t=1}^{N} S_{net,t} \tag{1}$$

where *t* represents time in years and *N* is the total number of years considered. For the current analysis, we consider the cumulative storage over a 25-year period spanning water years 1992-2016, in the aftermath of 1990 CAA amendments. For those watersheds with no stream export data in water year 1992 (SHEN PAIN, SHEN PINE, SHEN STAN), we assumed that S_{net} in 1992 was equivalent to the 1993 value. For watersheds with no stream export computed for 2016 (SRRW, FEF WS4, FEF WS10, FEF WS13) we assumed that S_{net} in 2016 was equivalent to the 2015 value. Cumulative storage was not computed for watersheds missing more than one year from the 1992-2016 timeframe (CATS RC, ARB).

To evaluate the amount of S that is potentially stored/released from solid phase, the non-aqueous cumulative storage/release ($S_{\mathrm{cum\text{-}na}}$, g S kg^{-1} soil) is calculated by:

$$S_{cum-na} = \sum_{t=1}^{N} \left(S_{net,t}\omega - \frac{dC}{dt} DP \right) / BD \tag{2}$$

where *dC*/*dt* is the change in concentration over time (g S m^{-3} yr^{-1}), approximated by finite difference of the flow-normalized concentrations over annual time steps, *D* is the soil depth (m), *P* is the porosity (unitless), *B* is the bulk density of the soil (kg m^{-3}), and ω is used for units conversion (=0.1 g ha kg^{-1} m^{-2}). The parameters *D* and *B* (Table S2) specific to each watershed are taken from the Soil Survey Geographic (SSURGO) database which is maintained by the U.S. Department of Agriculture-Natural Resources Conservation Service (USDA-NRCS). The high-resolution data has detailed geospatial representations of soil properties and is preferable for modeling at the catchment scale (Sheshukov et al., 2011). HBEF was the only watershed where SSURGO data was not available. Campbell et al. (2011) reported a soil depth of approximately 1 m and bulk density was estimated as 1500 kg m^{-3} (K. McGuire, pers. comm). The value of P was not available on the site basis through SSURGO, therefore *P* is assigned as 0.45 for all cases. Porosity may vary from catchment to catchment, but would not contribute significantly to uncertainty in the calculation. The cumulative non-aqueous storage of S is used in the evaluation of the inferred isotherms for each watershed.

3. Results

3.1 Temporal Changes

Atmospheric deposition has declined across all sites for the entirety of the study period and trends were highly significant (p-value < 0.001) (Figure 2a). The annual rate of decline in S deposition was greater at the SE sites as compared to the NE sites (mean slopes of -1.1 and -0.63 kg S ha^{-1} yr^{-2} respectively). Across all sites, there was a 70-90% decline in total deposition from the early 1990s to late 2010s. The greatest declines occurred at FEF WS10 (-1.96 ± 0.26 kg ha^{-1} yr^{-2}) in the SE and CATS WN in the NE (-0.85 ± 0.17 kg ha^{-1} yr^{-2}). Dry deposition in the SE accounted for the majority (56-80%) of total deposition at the start of the 1990s, but decreased to only account for 28-51% by the mid-2010s. This differed in the NE, as the percentage of total deposition coming from dry deposition remained fairly constant (mean = 48%) at CATS, HBEF, and ARB. For SRRW, a minority of the deposition came in dry form (30%) in the early 1990s, then increased to account for 52% of total deposition by the mid-2010s.

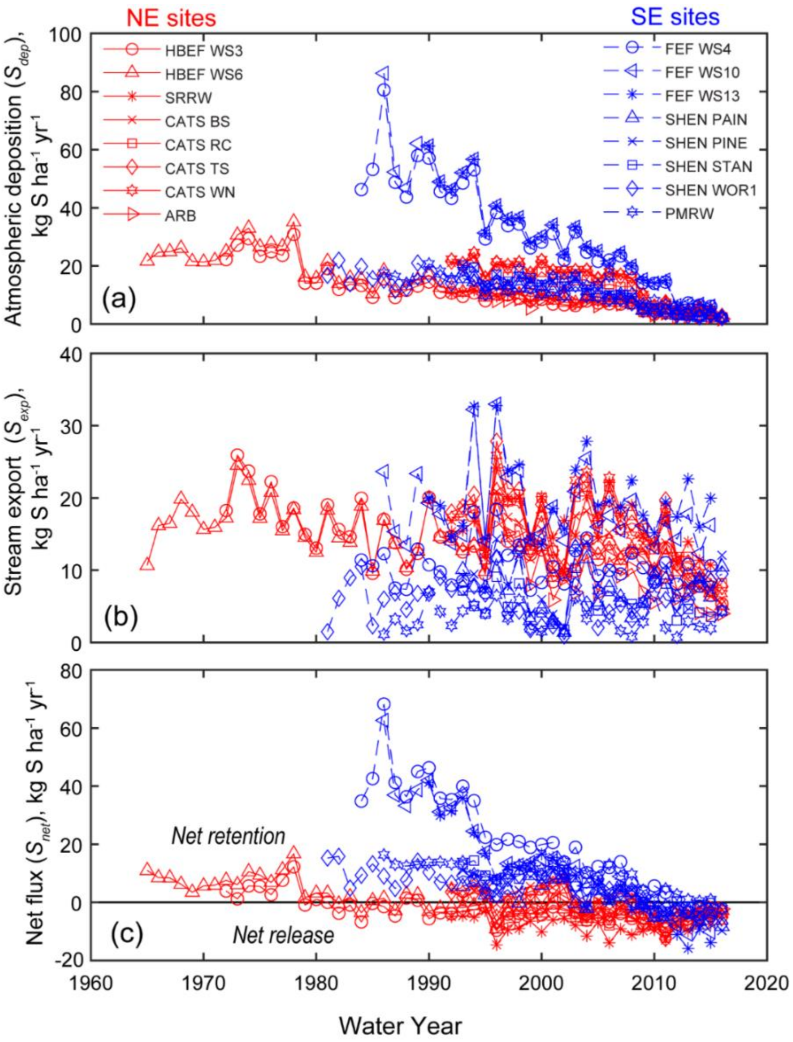

Figure 2. Sulfur mass balance on a water-year basis for 8 northeast watersheds (red) and 8 southeast watersheds (blue), showing (a) total atmospheric deposition (S_{dep}), (b) stream export (S_{exp}), and (c) net flux (S_{net}). Positive values of S_{net} represent net retention of S in the watersheds and negative values of S_{net} represent net release of S from the watersheds.

Over the study periods, there were significant negative trends ($p < 0.05$) in S export for the NE sites, with the exception of SRRW ($p = 0.052$) (Figure 2b). No significant temporal trends in

S export were observed in the SE sites (p > 0.05). The timing of the conversion of the watersheds from the net S retention to net S release differ between regions (Figure 2c), as the SE watersheds have converted relatively recently (from the mid-2000s to mid-2010s) while the NE watersheds (with the exception of CATS BS) have been net exporters of S for a much longer period of time (since the early 1990s to early 2000s). All S_{net} trends in the NE and SE were significant (p < 0.05), except for ARB (p = 0.24) and SRRW (p = 0.08). The SE has a greater percent retention of S than the NE throughout the entire period (Figure 3). The maximum percent retention was observed at PMRW in 1986 (93%), while the maximum retention in the NE occurred at HBEF WS6 in 1965 (51%). Contrast in the timing of the conversion from net storage to net release is also seen from the percentage retention, with the SE watersheds converting to negative values at later dates than the NE watersheds.

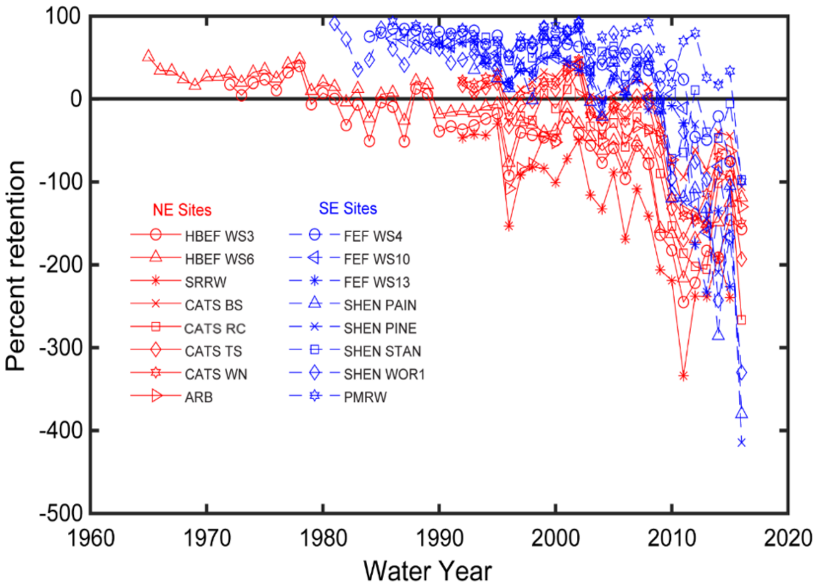

Figure 3. Percent sulfur (S) retention in northeast watersheds (red) and southeast watersheds (blue), calculated as net flux divided by deposition.

3.2 Trends in Flow-Normalized Concentrations

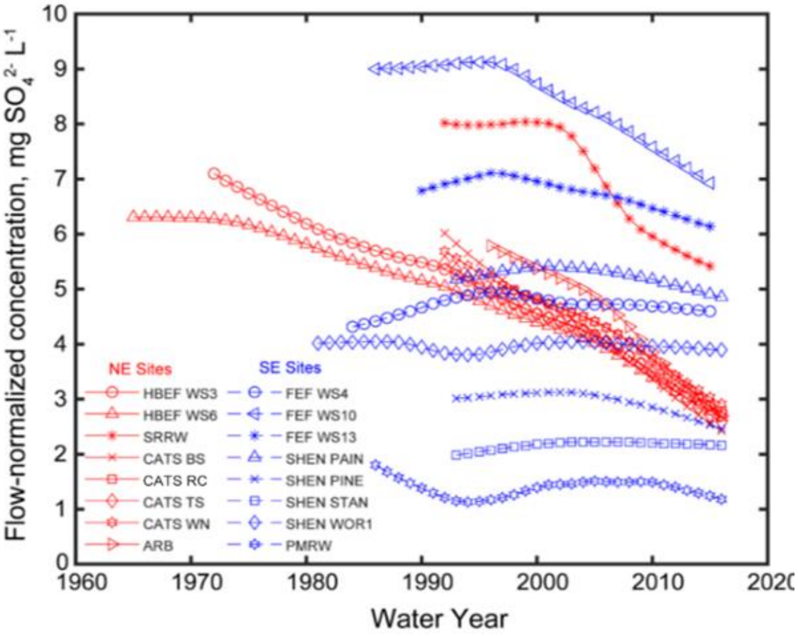

Figure 4. Flow normalized sulfate (SO_4^{2-}) concentrations for northeast sites (red) and southeast sites (blue).

Statistically significant declines in flow-normalized concentrations were observed for all NE watersheds ($p<0.05$), but trends in concentrations for SE watersheds were more mixed (Figure 4). Half of the SE watersheds experienced significant declines in flow-normalized concentrations (FEF WS10, FEF WS13, SHEN PAIN, and SHEN PINE), two showed declines that were not significant (SHEN WOR1, $p = 0.32$; PMRW, $p = 0.53$), and two were positive (FEF WS4, $p = 0.18$; SHEN STAN, $p < 0.05$). A striking feature of the trends in concentration is the degree to which the concentrations clustered between regions. Flow-normalized concentrations in the NE (with the exception of SRRW) converged to similar values by 2016, ranging from 2.40 to 2.91 mg SO_4^{2-} L^{-1}. Meanwhile, much greater variance is observed in the SE, with 2016 values spanning a range from 1.17 to 6.90 mg SO_4^{2-} L^{-1}. Large differences in concentrations were even observed between the multiple watersheds within both FEF and SHEN, despite their geographical proximities.

3.3 Cumulative S storage/release

Cumulative amounts of S stored in or released from watersheds over 25 years, from 1992-2016 (Figure 5), also reveals differences between the NE and SE regions. For all SE sites, there had been an overall net accumulation of S within the watersheds over this period despite the sharp reductions in S deposition. Meanwhile, all of the NE sites (with the exception of CATS BS) exhibited reductions in the amount of S stored within the watersheds over this same period. Even though the amount of S stored in SE watersheds in 2016 exceeded the amount stored in 1992, there is a recent downward trajectory for all of these sites. This implies that the amount of S stored within these SE watersheds will eventually return to pre-1992 levels, although it will likely take years to decades.

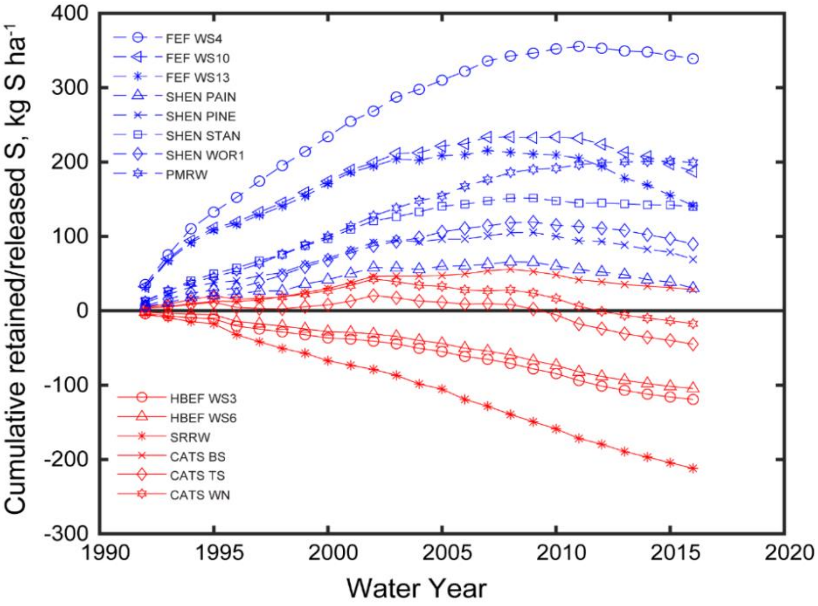

Figure 5. Cumulative S retained or released from northeast (red) and southeast (blue) watersheds for the period 1992-2016.

According to theory, declines in stream SO_4^{2-} concentrations should occur only when S_{net} becomes negative (Cosby et al., 1986), i.e. when there is a reduction in the amount of S stored within watersheds. However, it is clear from the relative timing of S_{net} (Figure 2c) versus the flow-normalized concentrations (Figure 4) that declines in concentrations routinely precede the times when the watersheds convert from net retention to net release of S. Insight about this departure from theory can be gained by reconstructing the isotherms associated with the adsorption processes within the watersheds. To do this, we estimate the changes in adsorbed S by Eq. (2) and relate this to the dissolved S, here taken as the flow-normalized concentrations.

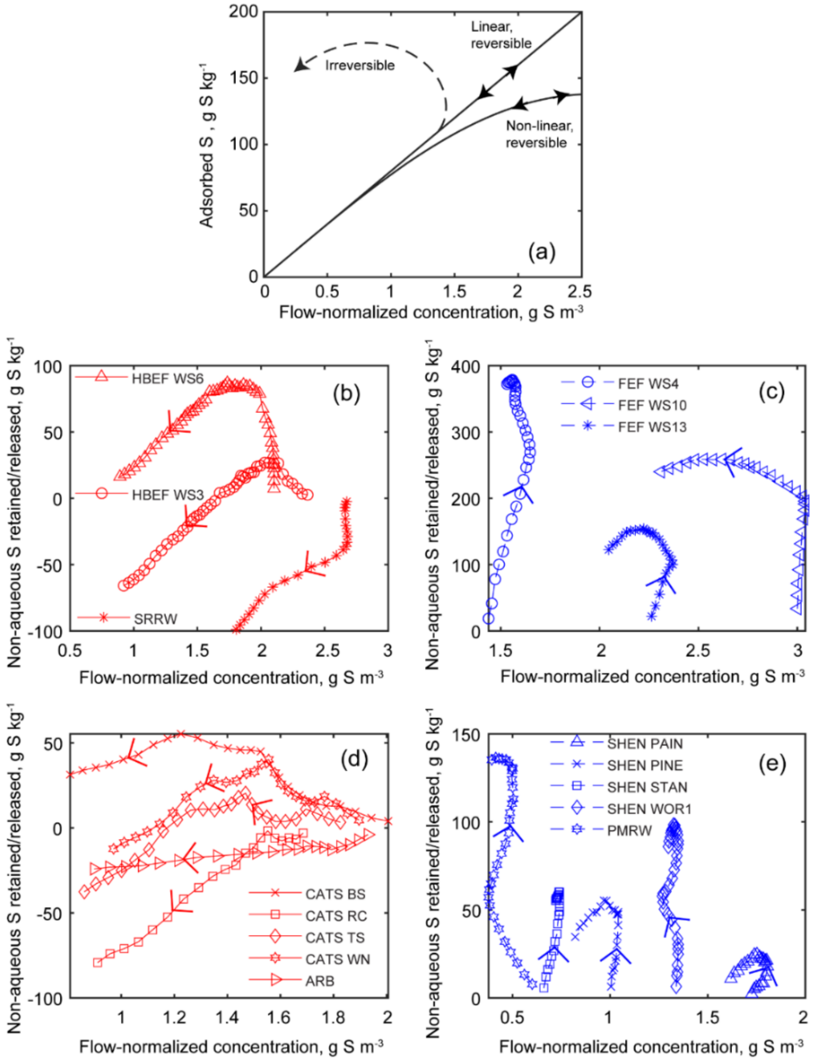

Figure 6. (a) Theoretical isotherms, relating adsorbed S to dissolved S. Linear, non-linear, and irreversible isotherms are shown. Reconstructed isotherms for the (b,d) NE watersheds and (c,d) SE watersheds, based on S mass balance and flow-normalized concentration. The non-aqueous S retained or released is assumed to be equivalent to the changes in adsorbed S.

For a reversible isotherm in the absence of pH dependence, whether it is linear or non-linear, there is a functional relationship between the amount of S adsorbed and the concentration of dissolved S (Figure 6a), i.e. there can only be one value of adsorbed S associated with a particular value of dissolved S. Another feature of a reversible isotherm is that slope in the relationship must be ≥ 0, i.e. increases in dissolved S are associated with increases in adsorbed S. An irreversible isotherm can violate both of these properties, as declines in dissolved S can occur even as the amount of adsorbed S increases. The isotherms for the individual watersheds have been reconstructed to show changes in non-aqueous retained S and dissolved S relative to their initial values (Figure 6b-e). For many of the watersheds, there is counter-clockwise hysteresis in this relationship, consistent with an irreversible isotherm. This includes periods of time during which the slope in the relationship becomes negative, meaning that there are decreases in dissolved S concentration despite coincident increases in the non-aqueous S stored within the watersheds.

4. Discussion

4.1 Declines in Atmospheric Deposition

The declines in S deposition throughout the study period (Figure 2a), and most notably since the 1990s, reflect the effectiveness of Title IV of the 1990 CAA Amendments. Differences in depositional rates between sites were greatest at the start of the study period, but this variance became progressively smaller as deposition declined. Even FEF, which is in closest proximity to emission sources, had deposition rates that were comparable to other sites by the end of the study period.

Estimates of dry deposition in the current study are generally higher than those reported in previous studies. For example, Driscoll et al. (2016) compared the wet deposition measurements from the NADP and dry deposition estimates from CASTNET in 2003 in the Huntington Forest located in the Adirondacks, and found that dry deposition only accounted for 8% of total deposition. Dry deposition was suggested to typically account for 20-40% of wet deposition for the Catskills (Mitchell et al., 2011; McHale et al., 2017). These estimates differ from our results, in which the relative percentages of dry and wet deposition in these regions were estimated to be about equal. These earlier studies used dry deposition estimates from CASTNET, which may result in lower dry deposition estimates than TDep due to the implementation of higher depositional velocities calculated through the Community Multiscale Air Quality (CMAQ) model (Schwede and Lear, 2014). Our use of TDep-equivalent estimates of dry deposition explains why our historical estimates of total S deposition for HBEF exceed those of other estimates, such as the maximum rate of 17.5 kg ha^{-1} yr^{-1} at HBEF in 1973 cited by Hinckley et al. (in press).

Similarly, our estimates of dry S deposition differ from those of other studies in the SE region. For instance, in a recent study at PMRW, dry deposition was assumed to account for around 55% of total deposition from 1986 to 2014 (Aulenbach, 2020). However, our results based on TDep indicate that the relative percentage of dry deposition declined to only account for 28% by 2016. Estimates of dry deposition are undoubtedly the largest source of uncertainty in watershed S budgets, yet it remains difficult to meaningfully quantify this uncertainty, especially given the diversity of approaches used in its estimation. For the current analysis we used what we considered to be the best available option.

4.2 S budget analysis

The mass balance analysis reveals that the watershed response to the declines in S deposition is notably different between the NE and SE regions. The NE sites have mainly been net exporters over recent decades, while the SE sites have more recently converted from net S retention to net S release (Figure 2c). This is also evident in the lower percent S retention in the NE compared to the SE (Figure 3). A study focusing on watersheds in the NE U.S. and Canada found that a majority of these watersheds were net S exporters (Mitchell et al., 2011). In this recently glaciated region, the similarity between declines in atmospheric deposition and net export are consistent with other studies that found S emissions were strongly related to streamwater SO_4^{2-} concentrations (Fuss et al., 2015; McHale et al., 2017). However, this direct relationship is not seen in the SE, as the timing of the conversion between net retention and net release shows a delayed stream water response, which had been predicted (Rochelle and Church, 1987) and reported in previous studies in the SE (Fernandez et al., 2010; Rice et al., 2014; Aulenbach, 2020).

The higher S retention in the SE indicates that net accumulation due to adsorption is a major factor in the delayed response between atmospheric deposition and stream water response.

The timeframes when watersheds experience a net release of S is largely consistent with the predicted years in Rice et al. (2014), with the exception of PMRW, which appears to be in the process of converting earlier than the predicted year of 2035. This may be due to differences in methodologies for approximating atmospheric S deposition, along with the fact that Rice et al. (2014) analyzed data only through 2010. It is apparent that watersheds in the SE are on a trajectory toward recovery from decades of excess S deposition. However, it is notable that the amount of S stored within SE watersheds remains in excess of the amount stored in the early 1990s when Title IV of the CAA was first enacted (Figure 5).

The runoff ratio is a possible characteristic resulting in a delayed response in the SE. Runoff ratio was shown to explain the greatest variability in the period from when watersheds convert from a net retention to a net release, as watersheds with a higher runoff ratio converted sooner (Rice et al., 2014). Additionally, the residence times of groundwater may contribute to the delay. Groundwater residence times were reported to be 5- 7 years in SHEN, through an analysis using ^{35}S, and assuming approximately 50% of ^{35}S is removed by biomass during recharge (Plummer et al., 2001).

Sulfate adsorption is the main mechanism behind S retention in watersheds, however it is important to consider the other potential sources and sinks. Potential internal sources include mineral weathering from bedrock and mineralization of organic S (Mitchell et al., 2011). Weathering of S-bearing minerals is known to contribute to S export from the SRRW (Shanley et al., 2005) and ARB (Campbell et al., 2006) watersheds, which has the effect of reducing their net S fluxes (Figures 2c and 3) and increasing their stream water SO_4^{2-} concentrations (Figure 4). Mitchell et al. (2011) stated that net mineralization of S derived from years of excess S deposition may contribute ~1 to 6 kg S ha^{-1} $year^{-1}$ from NE watersheds. The effects of such internal cycling would be similar to that of adsorption processes, in that it would result in a delayed export of the S deposited within watersheds. Finally, even though vegetation uptake of S is sometimes considered negligible relative to the other terms in the watershed S budget (e.g. Cosby et al., 1986; Gbondo-Tugbawa et al., 2001), this would have a role in retaining S within watersheds. Estimates of net S uptake by vegetation at HBEF, however, suggest that this is one to two orders of magnitude smaller than stream export (Likens et al., 2002).

4.3 Flow Normalized Concentrations

The declines in flow-normalized SO_4^{2-} concentrations indicate a general recovery from decades of elevated S deposition, as concentrations declined for all NE sites and the majority of SE sites (Figure 4). Similar concentrations among the NE sites (with the exception of SRRW and ARB, which have geological sources) point to the dominance of atmospheric deposition in controlling stream water concentrations, as opposed to watershed-specific S adsorption processes. This is in contrast to the SE sites, where these watershed-specific adsorption processes exert greater influence on these concentrations. For instance, even though they receive roughly the same amount of S deposition, stream water SO_4^{2-} concentrations at the SHEN sites are widely variable, likely due to the influence of the underlying bedrock geology (Table S2) on the sulfate adsorption capacity of the soils (Robison et al., 2013). The felsic bedrock at SHEN STAN is associated with a greater abundance of aluminum and iron oxides that promote S adsorption, relative to the mafic bedrock at SHEN PINE and the siliciclastic bedrock at SHEN PAIN and SHEN WOR1. These differences result in stratification of the stream water SO_4^{2-} concentrations between sites, with SHEN STAN having the lowest concentrations. Such watershed-specific differences in sulfate adsorption capacity are also likely to be the source of the spatially variable SO_4^{2-} concentrations at the FEF watersheds, as it has been noted that underlying bedrock geology plays a role in trajectory of recovery from acid rain at these sites (DeWalle et al., 2006).

4.4 Irreversibility of Sulfate Adsorption

In both regions, there is evidence of the irreversibility of the sulfate isotherm as exhibited by the counter-clockwise hysteresis in the relationship between dissolved S and the cumulative non-aqueous S stored within watersheds (Figure 6b-e). An isotherm consists of the relationship between adsorbed and dissolved SO_4^{2-}. To reconstruct the isotherm, we calculated the cumulative non-aqueous S stored within the watersheds as a proxy for the cumulative amount of adsorbed S. It is important to note that, in actuality, these may differ by the amounts immobilized (Strickland et al., 1985) and the amounts taken up by vegetation. However, rates of mineralization likely exceed those of immobilization, especially during times of declining S deposition (Likens et al., 2002) and vegetation uptake, again, is considered to be minimal. Thus, annual increases in the amount of non-aqueous S stored within watersheds likely underestimates the actual increases in adsorbed S. The phenomenon of decreasing stream water SO_4^{2-} concentrations preceding declines in adsorbed S (Figure 6b-e) therefore cannot be explained by organic matter retention.

The pH dependence of the S isotherm (Nodvin et al., 1986; Gbondo-Tugbawa et al., 2001) is another possible mechanism that could lead to hysteresis in the observed relationship. During the timeframe of the current study, the pH of precipitation has increased, which would theoretically lead to a reduction of the isotherm slope (Figure 6a), consistent with less S retention (Likens et al., 2002). A gradual, pH-imposed change on the S isotherm would result in clockwise hysteresis, which is opposite to the trend observed across sites (Figure 6b-e).

The most likely explanation for the observed counter-clockwise hysteresis is irreversible adsorption of S, which is consistent with findings from batch experiments conducted on soils from

PMRW (Shanley, 1992) and a variety of other sites in the NE and SE regions (Harrison et al., 1989). These short-term experiments were unable to discern the kinetics associated with this irreversibility. However, if the findings from the whole-watershed mass balances from the present study do indeed depict irreversible adsorption, then the strongly held S fraction appears to be irreversible over long timescales. In keeping with this conceptual model, only a portion of the non-aqueous S that accumulates in watershed soils would be readily exchangeable, which could explain why stream SO_4^{2-} concentrations decline prior to watersheds converting from net S retention to net S release.

5. Conclusions

This study presents an evaluation of S budgets for 16 watersheds that span the eastern U.S. In assessing these budgets, it is important to have accurate estimates of total deposition to better understand watershed response to acid deposition. Wet deposition estimates that are relatively accurate are available, but estimates of dry deposition are more uncertain. The TDep product provides improved estimates of dry deposition, which can lead to more accurate total S deposition estimates within these watersheds. The effectiveness of Title IV of the 1990 amendments to the CAA is evident from the dramatic reductions in S deposition seen for all watersheds.

The mass balance analysis highlights regional differences in S dynamics between the NE and SE. The higher sulfate adsorption capacity of SE soils leads to delayed conversion of watersheds from net S retention to net S release and contributes to greater spatial variability of stream water SO_4^{2-} concentrations. While the amount of S stored within NE watersheds largely declined over a 25-year period following the 1990 CAA amendments, SE watersheds saw a net accumulation of S over this same time period. However, all SE watersheds have converted to net annual export of S, which will eventually lead to the S storage within these watersheds returning to 1990 levels within the coming years to decades, provided that the current low levels of S deposition are maintained.

Theoretically stream water SO_4^{2-} concentrations should decline only when watersheds convert from net S retention to net S release (Cosby et al., 1986; Rice et al., 2014), but it is clear that reductions in stream concentrations preceded such conversion in NE and SE watersheds alike. This is likely to be the result of irreversible S adsorption, here expressed at the whole-watershed scale. This study once again highlights the importance of long-term monitoring to better understand watershed response to changes in atmospheric deposition.

Acknowledgments

We thank the personnel and funding agencies associated with each site, whose dedication to collecting long-term datasets has made this analysis possible. In particular, we thank Jamie Shanley (SRRW), Gene Likens (HBEF), Mike McHale (CATS), Pat McHale and Myron Mitchell (ARB), Brent Aulenbach (PMRW), and Frederica Wood and Mary Beth Adams (FEF). Gary Lear of the National Atmospheric Deposition Program provided files that allowed us to calculate S deposition on a water-year basis. This research is a contribution to the Shenandoah Watershed Study and the Virginia Trout Stream Sensitivity Study. Long-term funding and support for these programs has been provided by the National Park Service (NPS) and the U. S. Environmental Protection Agency (EPA).

Supplemental Information

Table S1. Site characteristics including climate type, temperature, precipitation and main vegetation

Site	Climate Type	Mean Annual Temperature (ºC)	Mean Annual Precipitation (cm)	Vegetation	References
HBEF	Warm-summer humid continental	5.6	140	Northern hardwood forest *Fagus grandifolia* Ehrh., *Acer saccharum* Marsh., *Betula alleghaniensis* Britt *Picea rubens* Sarg., *Abies balsamea* (L.) Mill.)	Adams et al., 2008, Campbell et al., 2011
SRRW	Warm-summer humid continental	4.6	132	Northern hardwood forest *Acer saccharum, Betula alleghaniensis, Fraxinus americana, Fagus grandifolia, Picea rubens, Abies balsamea*	Shanley et al., 2004, Peters et al., 2006
CATS	Warm-summer humid continental	4.3	175	Mixed Nothern hardwood forest *Fagus grandifolia, Acer saccharum, Betula alleghaniensis* *Abies balsamea*	Stoddard & Murdoch 1991, Lawrence et al.,2001
ARB	Warm-summer humid continental	4.8	108	Mixed northern hardwood *Fagus grandifolia, Acer saccharum, Acer rubrum, Betula alleghaniensis, Tsuga canadensis, Picea rubens* *Pinue strobus, Abies balsamea*	Park et al., 2003, Piatek et al., 2009
SHEN	Humid subtropical	9.0	132	Hardwood forest *Quercus rubra, Acer* spp., *Liriodendron tulipfera, Tsuga canadensis, Rododendron maximum* *Pinus virginiiana*	Sullivan et al., 2003
FEF	Warm-summer humid continental	8.9	146	Mixed mesophytic hardwood *Liriodendron tulipifera* L., *Acer saccharum* Marsh., *Prunus serotina* Ehrh. , *Betula lenta* L.	Adams et al., 2007, Adams et al. 2008
PMRW	Humid subtropical	15	126	Southern hardwood forest *Carya, Quercus, Liriodendron tulipifera* *Pinus tadeda*	Peters et al., 2003, Peters et al., 2006, Aulenbach, 2020

Table S2. Site characteristics including soil depth, bulk density, and bedrock.

Site ID	Soil Depth (m)[a]	Bulk Density (kg m^{-3})[a]	Bedrock	Resources
Northeast				
HBEF WS3	1.00	1500	Metasedimentary	Likens et al., 2002
HBEF WS6	1.00	1500	Metasedimentary	
SRRW	1.80	1108	Phyllite, calcareous schist	Shanley et al., 2004
CATS BS	1.02	1055	Sandstone, shale, conglomerate	Murdoch, 1991; Rich, 1934; Ver Straeten, 2013
CATS RN	1.02	1070	Sandstone, shale, conglomerate	
CATS TS	1.02	1055	Sandstone, shale, conglomerate	
CATS WN	1.02	1070	Sandstone, shale, conglomerate	
ARB	2.01	1100	Anorthosite massif with calcium rich feldspar	Piatek et al., 2009
Southeast				
SHEN PAIN	1.98	1234	Siliclastic	Webb et al., 2004
SHEN PINE	1.27	1350	Basaltic	
SHEN STAN	1.68	1367	Granitic	
SHEN WOR	1.78	1318	Siliclastic	
FEF WS4	1.30	1433	Shale, sandstone	Williard, et al., 2005; Adams et al., 2008
FEF WS10	1.30	1433	Shale, sandstone	
FEF WS13	1.30	1433	Shale, sandstone	
PMRW	1.52	1373	Granodiorite, amphibolite	Peters et al., 2006

[a] Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture. Soil Survey Geographic (SSURGO) Database. Available online at https://sdmdataaccess.sc.egov.usda.gov. Accessed [5/24/2020].

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Chapter 3: Controls on Changes in Stream Chemical Concentrations during Chronic and Episodic Acidification

Abstract

Declines in acid deposition have led to changes in the acid-base chemistry of watersheds in the Eastern U.S. Stream chemical concentrations of three watersheds located in the southeastern U.S. were examined to determine whether changes in precipitation chemistry or internal watershed biogeochemical processes were driving the changes in acid-base chemistry during stormflow conditions. To evaluate the main drivers, trends in deposition and stream chemistry concentrations during baseflow and stormflow conditions were analyzed. If trends in deposition were consistent with trends during stormflow, changes in deposition were likely causing changes in the stream chemistry concentrations. However, the changes in acid anions and base cations during baseflow and stormflow conditions did not reflect the changes in deposition. The inconsistent trends reveal that the main mechanisms behind the changes during episodic conditions is likely biogeochemical. Additionally, base cation depletion occurred at the most acid sensitive site. A mass balance analysis of the anions and cations was completed to help determine primary drivers. The mass balance of sulfur shows a conversion to net release in the early 2010s, while there is a net retention of nitrogen throughout the study period. As sulfate is the main acidifying agent in these watersheds, it is important to examine trends in nitrate, as nitrate becomes a more important acidifying agent as reductions in sulfate occur. Additionally, the increasing trends in the net export of base cations reveals that mineral weathering is a primary source of base cations in these watersheds. Overall, the soils play a large role in controlling the acid-base chemistry within these watersheds.

1. Introduction

Emissions of sulfur dioxide and nitrogen oxides (NO_x) have resulted in adverse effects in aquatic ecosystems in North America (Driscoll et al., 2001; Burns et al., 2011). Declines in acid deposition due to the implementation of the Clean Air Act have led to changes in the acid-base chemistry in watersheds (Stoddard et al., 2003). Surface waters in the Eastern US have experienced the greatest levels of historical deposition since they are downwind from emission sources (Burns et al., 2011). These waters are now recovering from the high levels of deposition (Mitchell et al., 2011; Rice et al., 2014).

Surface water response to acid deposition is mediated by processes occurring in the soil such as mineral weathering, cation exchange, and biological uptake (Driscoll et al., 2001; Stoddard et al., 2003; Likens, 2013). In regions exposed to acid deposition, soil cation loss occurs, hindering the capacity of surface waters to recover (Driscoll et al., 2003). Water quality changes also include a decline in pH, reduced acid-neutralizing capacity, and increases in aluminum concentrations (Galloway et al., 1983; Driscoll et al., 2001). The harmful effects of acidification on the biological health of the ecosystem is a major concern, as a low pH stemming from acidification can lead to toxic concentrations of inorganic monomeric aluminum (Al_{im}) to biota (Stoddard et al., 2003).

Acidification of surface waters during lower flow periods between runoff events, which is the status of streams the majority of the time, is known as chronic acidification, whereas acidification during higher flow periods is known as episodic acidification (Lawrence, 2002). Episodic acidification refers to the short-term decline in pH and acid neutralizing capacity (ANC) during hydrological events such as rainstorms and snowmelt (Wigington et al., 1992). Episodic acidification most frequently occurs during seasons of high precipitation and is least common in summer in the eastern U.S., when evapotranspiration reduces soil moisture (Lawrence, 2002).

Baseflow conditions have been the main focus of assessments of acid recovery because routine monitoring programs collect a majority of their samples during these conditions. Although less focus is placed on episodic conditions, episodic acidification is an important part of studying not only stream chemical response to declines in deposition, but also understanding the impacts on the biological recovery of biota. The main drivers of the severity of episodic acidification vary by region, but include base cation dilution, organic acidity, and trends in acid deposition (Kline et al., 2007; Burns et al., 2020). In order to understand the impacts on aquatic ecosystems with the changing environment, it is important to examine chronic and episodic stream acidification (Dewalle and Swistock, 1994).

In headwater streams located in Shenandoah National Park (SHEN), episodic acidification is recovering at rates greater than or equal to those of chronic acidification at the most acid sensitive site (Riscassi et al., 2019). Improvements in pH have only occurred during higher flow events at the most acid sensitive site. This reveals that even in the absence of change in chronic conditions, the acid-base status during high-flow episodes may show improvement. Riscassi et al. (2019) examined the differences between episodic and chronic acidification in SHEN, however the study did not investigate the main mechanisms for these changes. These changes may be due to changes in rainfall chemistry and/or improvement in the soil buffering capacity.

Previous studies (Dewalle and Swistock, 1994; Wigington et al., 1996; Lawrence, 2002; Kline et al., 2007) have analyzed episodic conditions based on only a few years of record. The need for a longer, continuous record of high flow data is necessary to obtain a better evaluation of the sources of the shifts between baseflow and stormflow data. A 25-year record of stormflow data in three watersheds in SHEN provides a unique opportunity to analyze such changes. The goals for this study were to: (1) assess changes in stream chemistry during baseflow versus stormflow conditions, (2) examine watershed mass balances for multiple analytes, and (3) determine the main mechanisms for changes in stream chemistry during both low- and high-flow conditions.

2. Methods

2.1 Site Description

The three study watersheds of similar size (10.5-12.6 km^2), Piney River (PINE), Staunton River (STAN), and Paine Run (PAIN), are located within the north, central, and southern parts of Shenandoah National Park, respectively, in the Blue Ridge Mountains of western Virginia (Figure 1; Table 1). Water quality parameters such as alkalinity and base cation concentrations in SHEN are strongly influenced by underlying bedrock (Lynch and Dise, 1985). The three main bedrock types in SHEN are basaltic, granitic, and siliciclastic, which are the dominant bedrock for Piney River, Staunton River, and Paine Run respectively (Webb, 2004). The three watersheds represent a gradient of response to acid deposition as the sensitivity to acid deposition varies across the bedrock, with siliciclastic being the most sensitive and basaltic the least sensitive (Sullivan et al., 2003; Robison et al., 2013).

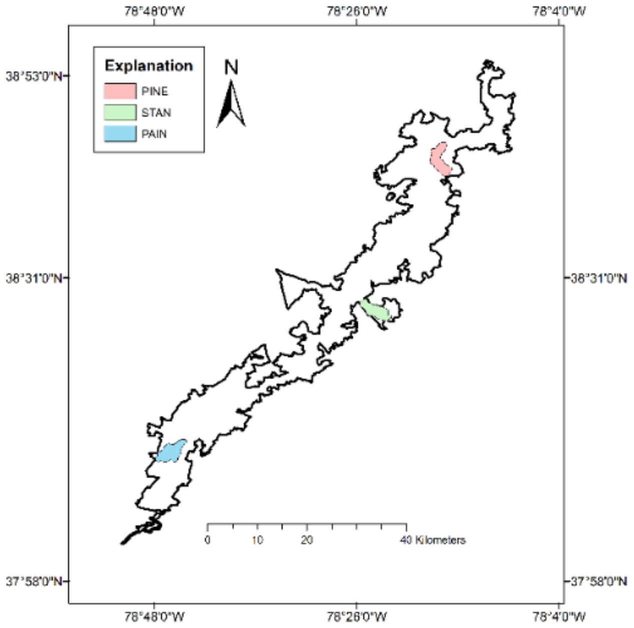

Figure 2. Map showing the locations of the three watersheds located in Shenandoah National Park.

Table 1. Site characteristics including area, dominant bedrock, and dominant vegetation of three watersheds located in Shenandoah National Park.

Site	Area (km^2)	Dominant Bedrock	Vegetation
Paine Run	12.4	Siliciclastic	*Quercus prinus, Quercus rubra, Betula lenta*
Piney River	12.6	Basaltic	*Quercus rubra, Quercus alba, Fraxinus americana, Acer rubrum, Quercus prinus, Carya ovalis*
Staunton River	10.5	Granitic	*Quercus prinus, Quercus rubra, Liriodendron tulipifera, Fraxinus americana, Aesculus flava, Cercis canadensis*

Daily stream flow and weekly chemistry data were collected as part of the Shenandoah Watershed Study and the Virginia Trout Stream Sensitivity Study (VTSSS, https://swas.evsc.virginia.edu/). Weekly grab sampling is augmented by bi-hourly automated sampling (Teledyne ISCO) during storm events. The automated samplers are triggered when flows are greater than or equal to the 5% exceedance for each season (winter/spring season is November 14- May 14 and summer/fall is May 15- November 13). All automated event samples on the rising limb of the hydrograph are analyzed for chemistry, while 20% are analyzed from the falling limb of the hydrograph. The weekly grab samples and the subset of automated samples are analyzed for the following water quality parameters: ANC, acid anions (SO_4^{2-}, NO_3^-, Cl^-), base cations (K^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+), and pH. Further details of water sample collection and analysis methods are described in Riscassi et al. (2019).

2.2 Mass Balance

To examine whether stream chemistry trends are due to biogeochemical processes or trends in precipitation chemistry, mass balances from water year 1993 to 2018 for all analytes were completed in units of kg ha^{-1} yr^{-1}. Ammonium data was not collected until water year 1997, therefore the nitrogen mass balance was completed for water years 1997-2018. The mass balances will aid in revealing the main mechanism for the changes in stream chemistry by identifying changes in deposition and examining if there is a net storage or release of the analytes. Site specific total deposition included dry and wet deposition, except for pH, where wet deposition at Big Meadows was used.

Wet deposition was calculated using the water year-based analyte data available through the NADP/NTN at Big Meadows (VA28). Site-specific precipitation was obtained from the Parameter-elevation Regressions on Independent Slopes Model (PRISM) using the centroid (computed using ArcMap 10.7) of each watershed with the interpolation option selected. The wet deposition flux for each analyte was multiplied by the ratio of the total precipitation of the watershed to that of total precipitation at VA28.

Dry deposition was calculated on a water-year basis using dry deposition estimates from the recently released total deposition (TDep) product (Schwede and Lear, 2014). Calendar year dry deposition maps and maps (TDep v. 2018.02 http://nadp.slh.wisc.edu/committees/tdep/) of the cumulative dry deposition during the calendar year up to week 40 (*pers. comm* Greg Beachley) served as the basis for these water-year estimates. Week 40 of each year represents the time around the start of the water year. Using these two available maps, we were able to calculate dry deposition based on water year. These maps were only available for 2001 – 2018, therefore CASTNET data at Big Meadows (SHN418) was utilized to calculate dry deposition from 1993-2000, prior to the availability of the TDep product. A linear, site-specific TDep to CASTNET relationship for the 2001-2018 period was used and then extrapolated to calculate dry deposition for water years 1993 – 2000 for sulfur to generate TDep-equivalent estimates of dry deposition from the CASTNET data. Dry nitrogen deposition is comprised of NO_3^-, HNO_3, NH_4^+, and NH_3, which were available via the TDep product. TDep week 40 grids were not available, therefore, an inflation factor was used to estimate dry deposition of NH_3. For water years 1993 – 2000, NO_3^-, HNO_3, NH_4^+ were estimated using the linear relationship between TDep and CASNET and NH_3 was estimated using the trend line of NH_3 from TDep for the 2001-2018 period. For the base cations, CASTNET data did not extend prior to 2000, therefore the 2001 – 2010 linear relationship between wet deposition and TDep dry deposition was used to calculate years prior. CASTNET data for Cl^- was not available prior to 2003, therefore the 2004- 2010 wet to dry deposition linear relationship was used to calculate Cl^-.

TDep maps were available for wet deposition estimates, however these maps do not extend prior to 2000. In order to maintain a consistent method in estimating wet deposition, the calculation based on PRISM and data from the NADP was utilized.

Net export and flow-normalized concentrations (mg L^{-1}) for all analytes were calculated using the Weighted Regressions on Time, Discharge, and Season (WRTDS) model (Hirsch and De Cicco, 2015). Weekly grab samples and bi-hourly high flow data when available were used to calculate a daily concentration for each analyte. There were a number of samples that were below detection limit for NO_3^- and NH_4^+, therefore, these were changed to the corresponding method detection limit (MDL) for the specific year. In order to calculate the net export of nitrogen, the net export of NO_3^- and NH_4^+ was converted to units of kg N ha^{-1} then summed together for each water year. To examine the storage and release of the analytes, the net flux was calculated as the difference between the total deposition and net export.

2.3 Concentration – Discharge Analysis

To characterize the differences between baseflow and stormflow chemistry, we chose two percentiles to represent the two flow regimes. The 40th percentile of daily flows represents baseflow, and the 95th percentile of daily flows represents stormflow. A three-year moving average for water years 1993-2018 (sample number range 209-545) was used for all analytes, except NH_4^+, where water years 1997-2018 were used (sample number range 99-493). The three-year moving average included enough samples for a robust statistical relationship. There is a close relationship between pH and ANC across all three sites (Scanlon et al., 2020), therefore ANC was not included in this study. Sites underlain by siliciclastic bedrock have the lowest pH and ANC, while mafic sites have the highest pH and ANC (Scanlon et al., 2020).

To identify the concentrations associated with the two flow regimes, concentration-discharge (C-Q) relationships of the base cations, acid anions, and pH were analyzed. To do this, linear regression was applied to the log concentration (C) log-specific discharge (Q) data, taking the form:

$$\log(c) = a + b\ \log(Q) \qquad (1)$$

where a and b were calculated by a linear regression. For pH, C was not log transformed. By taking the inverse log of (1), the concentrations during baseflow (c_{40}) and stormflow (c_{95}) were found for each three- year period for all analytes (except pH which was not log transformed):

$$\mathrm{c} = 10^{a+b\ \log(Q)} \qquad (2)$$

The difference between c_{95} and c_{40} yields Δc, the difference in concentration between stormflow to baseflow conditions.

Changes in stream concentrations over the period of record are attributed to either trends in precipitation chemistry or changes in soil processes that influence runoff chemistry. Using the Mann Kendall test (Mann, 1945; Kendall, 1975), the temporal trends in analyte concentrations and total deposition were determined. All statistical analysis was completed using MATLAB (version 9.6.0.1335978 The MathWorks Inc, Natick, MA).

To compare trends in analyte concentration to total deposition, deposition was converted to units of µeq L^{-1} yr^{-1} by dividing deposition by total rainfall. For a direct comparison of deposition to stream chemistry, total S deposition was converted to units of SO_4^{2-} µeq L^{-1} yr^{-1} and the analyte specific deposition for NO_3^- and NH_4^+ was converted to µeq L^{-1} yr^{-1}. The difference between deposition and the temporal trends of analyte concentrations at each percentile were calculated. The difference helps to infer what primary mechanisms are causing changes in streamflow concentrations over time during the two flow conditions. If stream trends are not consistent with deposition trends, biogeochemical processes are likely influencing the stream concentrations. The main changes in the biogeochemical processes may include increases or decreases in desorption, mineral weathering, mineralization, adsorption, immobilization, and uptake. Differences in depositional versus stream concentration trends can provide some information about potential changes in internal biogeochemical processes within the watersheds (Table 2).

Table 2. The main biogeochemical changes resulting from the trends in deposition and the difference between deposition and streamflow trends.

	Increasing Deposition	**Decreasing Deposition**
Stream trends exceed magnitude of deposition trends	Rates of desorption, mineral weathering, and/or mineralization increasing	Rates of adsorption, immobilization, and/ or uptake increasing
Magnitude of deposition trends exceed stream trends	Rates of adsorption, immobilization, and/or uptake increasing	Rates of adsorption, immobilization, and/or uptake increasing

3. Results

3.1 Trends in Mass Balances

Sulfur had the largest amount of total deposition compared to the other analytes at PAIN, PINE, and STAN (Figures 2a and 3a). The declining trends in S deposition were statistically significant ($p < 0.05$) for all three sites (Table 3). The declines in total deposition of nitrogen were also statistically significant across all sites. Similar declines in nitrogen occurred at PINE and STAN (slope = -0.41, -0.40 kg ha^{-1} yr^{-2} respectively) which were greater than the west-facing site, PAIN (slope = -0.24 kg ha^{-1} yr^{-2}). Total atmospheric deposition of base cations was low compared to S and N deposition (Figures 2a and 3a). Total deposition of Ca^{2+} was similar at PINE and STAN, but was on average about 1 kg ha^{-1} greater than total deposition at PAIN. For Ca^{2+}, a significant decline in deposition occurred at PAIN, but there were no significant declines at PINE and STAN ($p = 0.27, 0.12$). There were no significant trends in deposition for Cl^-, K^+, Mg^{2+} or Na^+ at any of the sites.

No significant trends in export were observed for any of the analytes except for nitrogen at STAN, where an increasing trend occurred (Figures 2b and 3b). Regarding net flux, at all the sites, there were significant negative slopes for S and N (Table 3). A key difference between the net fluxes of S and N is that a conversion to net release of S occurred at all sites in the late 2000s, while a net retention of N was observed for all sites (with the exception of STAN in 2010, due to elevated N export) (Figures 2c and 2c). The net flux decline of N at STAN was more than double that at PAIN (Table 2). There were no significant trends in the net flux for Cl^-, Ca^{2+}, K^+ or Mg^{2+} across all sites (Figures 2c and 3c). Sodium was the only base cation where a small significant negative trend in the net flux occurred at PAIN, but no significant temporal trend was observed at PINE or STAN ($p = 0.22, 0.89$).

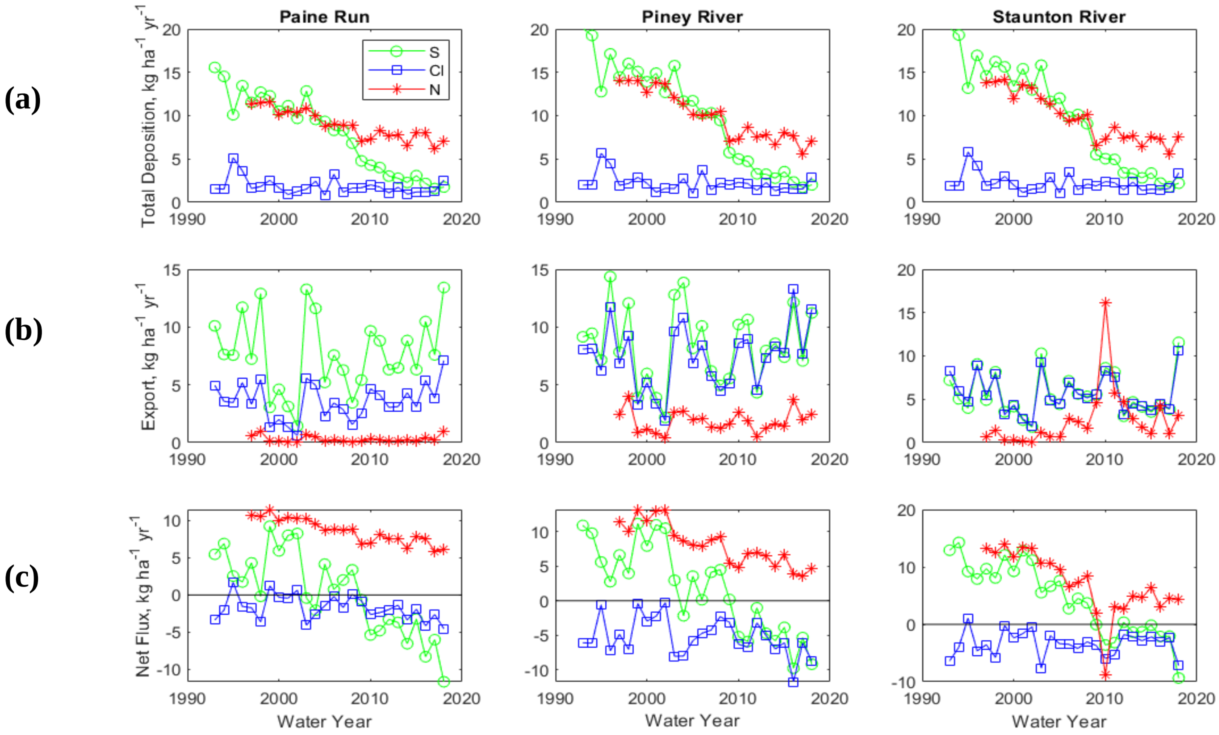

Figure 2. Mass balance of sulfur and chloride for three watersheds located in Shenandoah National Park for water years 1993 – 2018, and nitrogen (water years 1997 – 2018). (a) total deposition (kg ha^{-1} yr^{-1}), (b) export (kg ha^{-1} yr^{-1}), (c) net flux (kg ha^{-1} yr^{-1}) calculated as total deposition minus export. The y-axis limits may differ for each site.

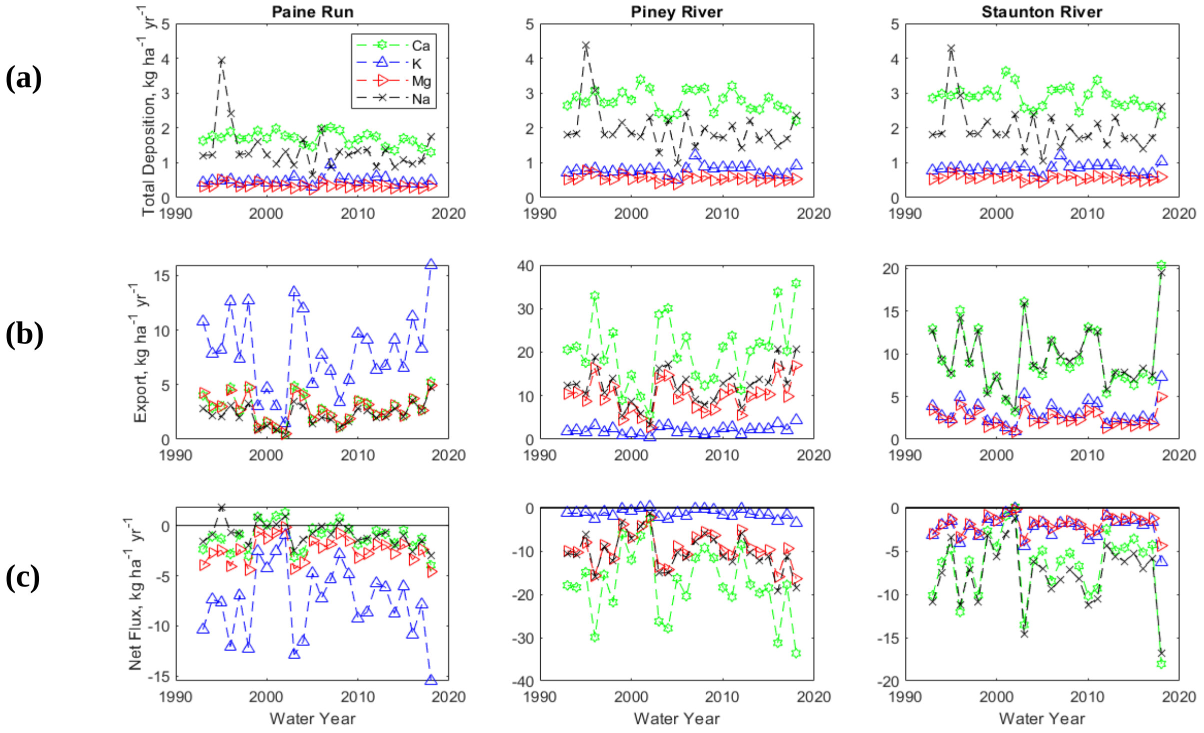

Figure 3. Mass balance of base cations (calcium, potassium, magnesium, and sodium) for three watersheds located in Shenandoah National Park for water years 1993 – 2018. (a) total deposition (kg ha^{-1} yr^{-1}), (b) export (kg ha^{-1} yr^{-1}), (c), net flux (kg ha^{-1} yr^{-1}) calculated as total deposition minus export. The y-axis limits may differ for each site.

Table 3. Trends in deposition, export, and net flux (kg ha^{-1} yr^{-2}) of acid anions and base cations at three watersheds located in Shenandoah National Park. Bold indicates statistically significant trends ($p < 0.05$).

Analyte	Paine Run	Piney River	Staunton River
Deposition			
S	**-0.57**	**-0.75**	**-0.76**
Cl$^-$	-0.02	-0.02	-0.02
N	**-0.24**	**-0.41**	**-0.40**
Ca^{2+}	**-0.01**	-0.01	-0.01
K$^+$	4.9 x 10^{-4}	4.5 x 10^{-3}	3.6 x 10^{-3}
Mg^{2+}	-1.4 x 10^{-3}	-2.6 x 10^{-3}	-2.6 x 10^{-3}
Na$^+$	-0.01	-0.01	-0.01
Export			
S	0.04	0.01	-0.02
Cl$^-$	0.04	0.06	-0.05
N	5.9 x 10^{-3}	0.02	**0.13**
Ca^{2+}	0.01	0.18	-0.06
K$^+$	0.06	0.03	-0.01
Mg^{2+}	4.5 x 10^{-3}	0.07	-0.02
Na$^+$	0.04	0.12	-0.03
Net Flux			
S	**-0.60**	**-0.75**	**-0.74**
Cl$^-$	-0.10	-0.13	-0.01
N	**-0.24**	**-0.40**	**-0.53**
Ca^{2+}	-0.02	-0.18	0.05
K$^+$	-0.07	-0.03	0.01
Mg^{2+}	-0.01	-0.07	0.02
Na$^+$	**-0.07**	-0.17	0.01

3.2 Trends in Flow- Normalized Concentrations

Trends in flow-normalized concentration varied across sites, and the differences in the acid-base chemistry of the watersheds is revealed through the differences in the dominant analytes (Figure 4). Sulfate was the dominant analyte at all sites and the second most dominant analyte was a base cation that differed at each site. The dominant base cations at PAIN, PINE, and STAN were K$^+$, Ca^{2+}, and Na$^+$ respectively.

The significance of the trends in flow-normalized concentrations varied between acid anions. The flow-normalized concentration of SO$_4^{2-}$ declined significantly at PAIN and PINE, but not STAN (p = 0.32). There were no significant temporal trends in Cl^- at PAIN and PINE, while a slight decline was observed at STAN which was significant (Table 4). Nitrate significantly declined at PAIN and PINE, but not at STAN (p = 0.16). The majority of the trends for base cations across all sites were significant except for NH_4^+ at PAIN and Ca^{2+} at PINE. At all the sites, Na^+ increased slightly over time, and Mg^{2+} decreased slightly. Calcium declined at both PAIN and STAN significantly. Flow-normalized concentrations of K^+ increased significantly at PINE and STAN, and slightly declined at PAIN.

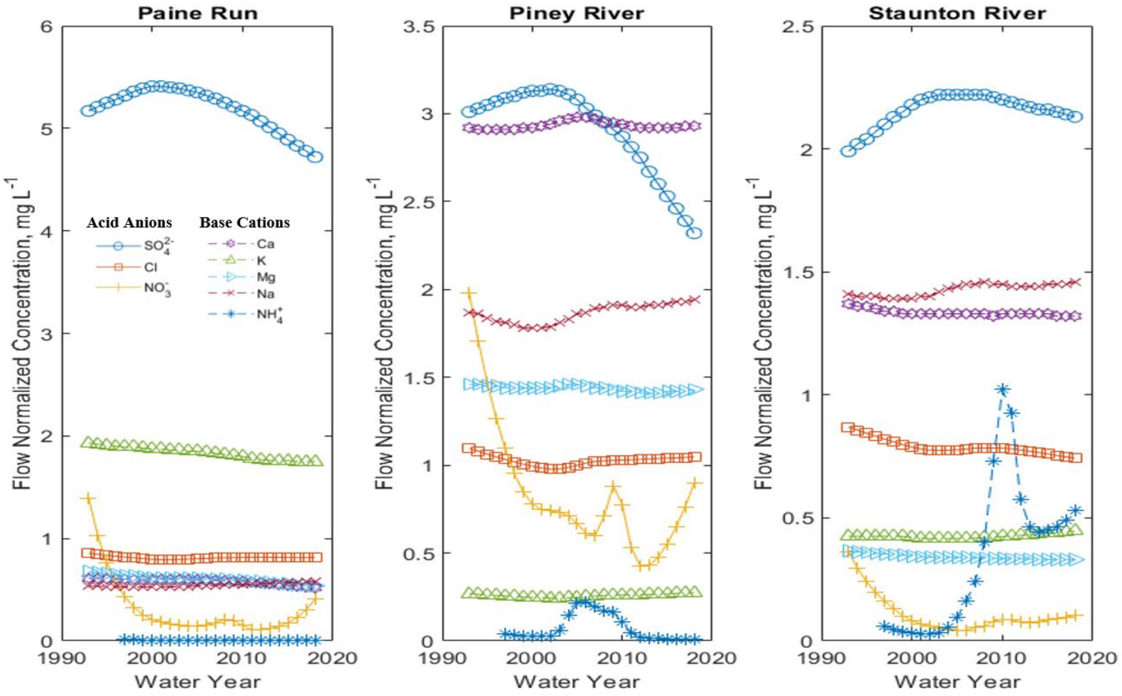
(a) (b) (c)

Figure 4. Flow-normalized concentration (mg L^{-1}) of sulfate, chloride, nitrate, calcium, potassium, magnesium, sodium for water years 1993 - 2018, and ammonium (water years 1997 -2018) for three watersheds in Shenandoah National Park. (a) Paine Run, (b) Piney River, and (c) Staunton River. The y-axis scale differs between the panels.

Table 4. Temporal trends of flow-normalized concentration (mg L^{-1} yr^{-1}) for acid anions and base cations at three watersheds located in Shenandoah National Park. Bold indicates statistically significant trends ($p < 0.05$).

Analyte	Paine Run	Piney River	Staunton River
SO_4^{2-}	**-0.02**	**-0.03**	2.0×10^{-3}
Cl^-	0	2.0×10^{-3}	-3.6×10^{-3}
NO_3^-	**-9.8×10^{-3}**	**-0.03**	-2.9×10^{-3}
Ca^{2+}	**-2.9×10^{-3}**	5.3×10^{-4}	**-7.7×10^{-4}**
K^+	**-7.5×10^{-3}**	**1.0×10^{-3}**	**6.1×10^{-4}**
Mg^{2+}	**-4.8×10^{-3}**	**-1.5×10^{-3}**	**-1.0×10^{-3}**
Na^+	**2.6×10^{-3}**	**5.8×10^{-3}**	**2.5×10^{-3}**
NH_4^+	-3.9×10^{-5}	**-1.4×10^{-3}**	**0.03**

3.3 Differences between Deposition and Stream Chemistry Concentrations

For many of the analytes, deposition trends differed from stream chemistry trends (Figures 5 and 6). Sulfate deposition significantly declined at a faster rate than stream concentrations during both flow regimes. At all sites, no significant declines in Cl^- deposition occurred and no significant changes in Cl^- concentrations occurred during either flow regime. The rate of nitrate deposition exceeded the rate of decline in stream concentrations at PAIN and STAN. At PINE, NO_3^- deposition declined at a slower rate than the stream concentrations. Increases in rainfall pH at Big Meadows and streamflow pH was observed, however rainfall pH increased at a faster rate than the observed increases during both flow regimes at all sites (Figure 5e).

Despite the lack of significant changes in Ca^{2+} deposition concentrations at all three sites, significant decreases in stream Ca^{2+} concentrations were found at PAIN. A similar pattern was observed for K^+ at PAIN and STAN. No significant changes were observed in Mg^{2+} deposition chemistry at any of the sites, yet significant declines in stream Mg^{2+} concentrations were found at all sites. Changes in Na^+ deposition was not significant over time, although stream chemistry trends increased significantly at PAIN and PINE. No significant changes were observed in NH_4^+ deposition and stream concentration.

To identify if trends are statistically different from each other, the overlap of confidence intervals was examined. For the majority of analytes, trends between deposition and the two flow regimes are not statistically different, as the confidence intervals overlap one another (Figures 5 and 6). At PAIN, depositional trends are statistically different from baseflow and stormflow trends for Ca^{2+} and K^+. At PINE, depositional trends are statistically different from stormflow trends for NO_3^- and K^+. At STAN, depositional trends are different from both flow regimes for K^+. Across all sites, depositional trends are different from both flow regimes for Mg^{2+} and Na^+. No trends between baseflow and stormflow are statistically different from one another for any analyte except K^+ at PAIN and STAN and Mg^{2+} at PAIN and PINE.

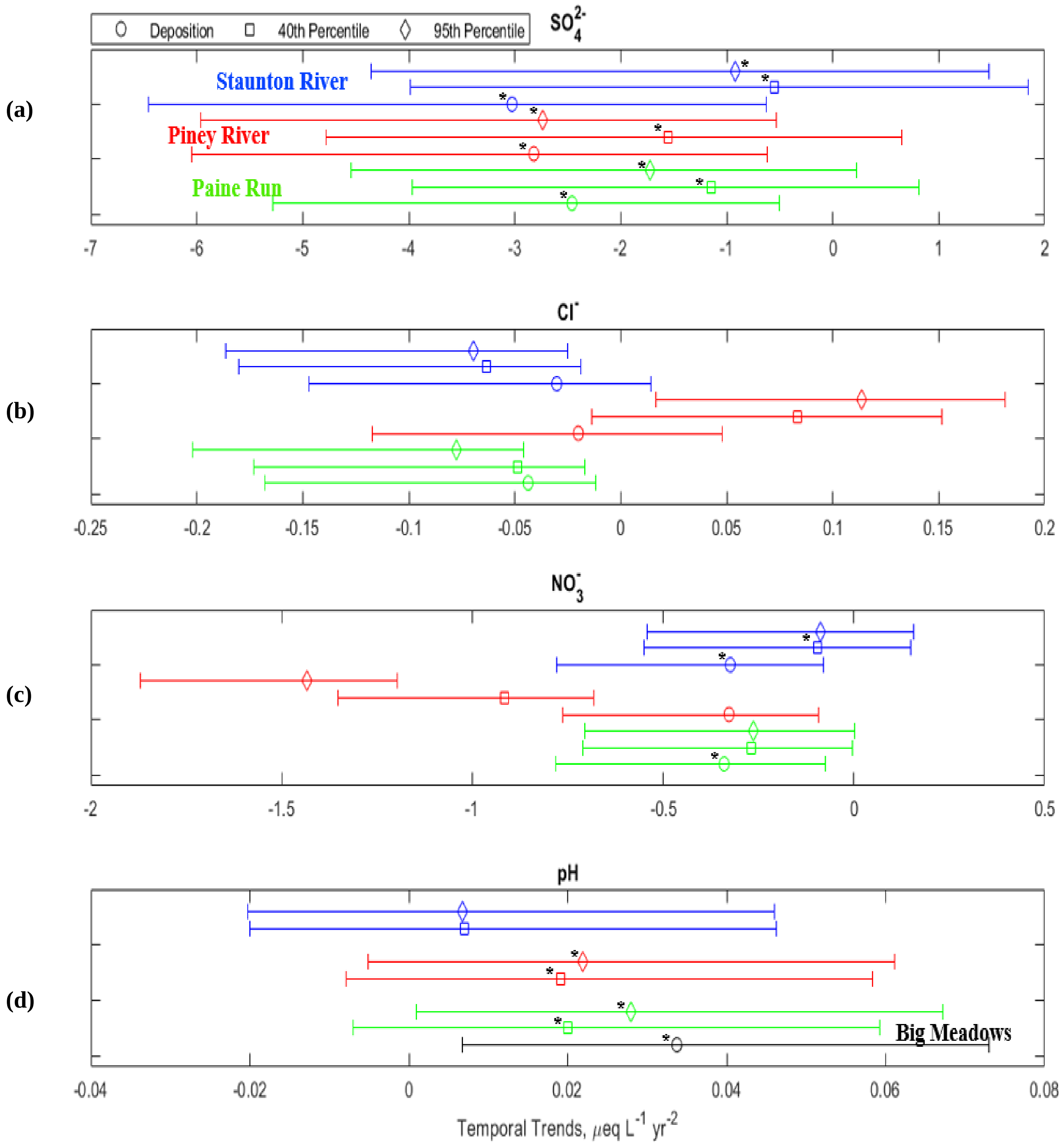

Figure 5. Temporal trends (μeq L^{-1} yr^{-2}) for (a) sulfate, (b) chloride, (c) nitrate concentrations, and (d) pH for a 3-year moving average for the deposition, 40th percentile (baseflow), and 95th percentile (stormflow) at three watersheds located in Shenandoah National Park for water years 1993 – 2018. Asterisk indicates a statistically significant trend ($p< 0.05$). Error bars indicate 95% confidence intervals.

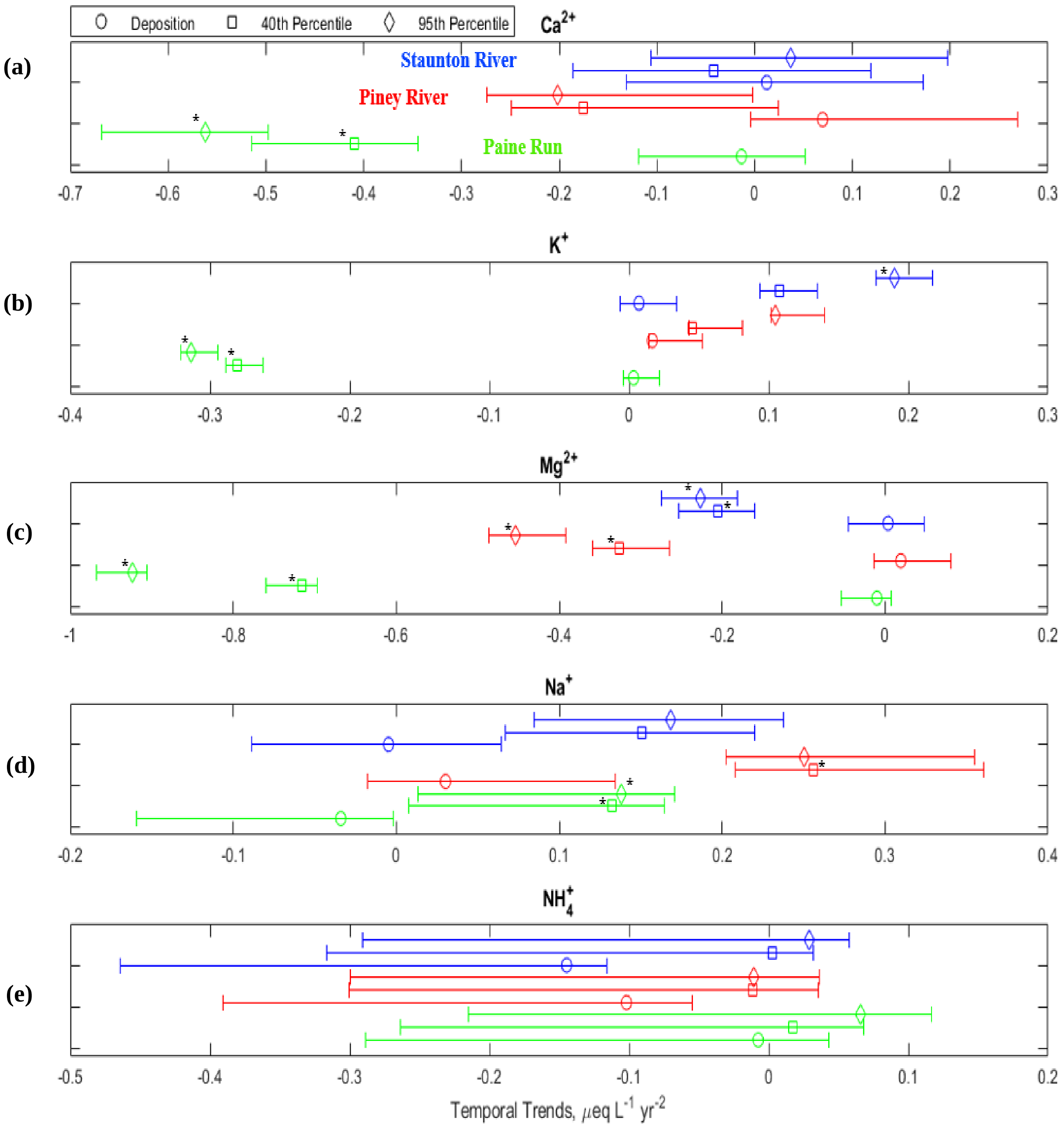

Figure 6. Temporal trends (μeq L^{-1} yr^{-2}) of (a) calcium, (b) potassium, (c) magnesium, and (d) sodium concentrations for a 3-year moving average for the deposition, 40th percentile (baseflow), and 95th percentile (stormflow) at three watersheds located in Shenandoah National Park for water years 1993 – 2018. (e) ammonium trends are from water years 1997 – 2018. Asterisk indicates a statistically significant trend ($p < 0.05$). Error bars indicate 95% confidence intervals.

3.4 Temporal Trends in Analytes for Two Flow Regimes

Trends in stormflow are hypothesized to closely follow trends in deposition, as stormflow is comprised of more recent precipitation into the watersheds. Sulfate was the only acid anion that decreased in streamflow concentrations across all sites and this decrease was statistically significant for both flow regimes ($p < 0.05$). Declines in sulfate concentrations during stormflow were greater than the declines in baseflow concentrations, but the relative magnitude of these trends were not consistent with depositional trends, with the exception of stormflow at PINE. Chloride deposition remained stable throughout the study period, and no significant increases in Cl^- concentrations occurred at PINE, and no significant decreases occurred at either PAIN or STAN, Significant declines in NO_3^- were observed for depositional chemistry across all sites, but the declines in streamflow concentrations were not found to be statistically significant during stormflow conditions. There was no consistency between the relative magnitudes of the baseflow versus stormflow NO_3^- trends across sites. Similar significant increases in pH during both flow regimes occurred at PINE, while at PAIN, increases in stormflow pH were greater than increases in baseflow pH. The rate of increase in pH at PAIN was less than the rate of increase in rainfall pH at Big Meadows. At PINE, the rate of increase in pH during stormflow was consistent with the increase at Big Meadows.

There were no significant changes in the deposition of base cations at any of the sites, however, significant changes during both flow regimes were observed for a few of the base cations (Figure 6). Across all sites, Mg^{2+} concentrations during stormflow conditions declined at a greater rate than declines during baseflow conditions. There were significant decreases in Ca^{2+} and K^+ concentrations at PAIN, but stormflow concentrations declined at a greater magnitude than declines in baseflow. Significant increases in K^+ concentrations occurred during both flow regimes, however, there was no consistency between the relative magnitudes of the baseflow versus stormflow K^+ trends at STAN. Sodium was the only base cation where trends in streamflow concentrations increased at all sites, but significant changes only occurred at PAIN (both flow regimes) and PINE (baseflow). Trends were not consistent between baseflow and stormflow stream concentrations of Na^+ at either site.

To analyze changes in the difference between stormflow and baseflow concentrations (Δc), temporal trend tests were completed. The temporal changes in Δc were not statistically significant for the majority of analytes. There was an increasing significant trend in the temporal changes in pH at PAIN and PINE (slope = 0.008, 0.002 μeq L^{-1} yr^{-2} respectively), meaning that the difference between stormflow and baseflow pH increased over time), but no significant trends were found at STAN ($p = 0.56$). There were significant declines in the temporal changes in Δc of SO_4^{2-} at all sites, thus the differences in sulfate between stormflow and baseflow are declining over time.

4. Discussion

4.1 Mass Balance Analysis

Major declines in sulfur deposition show the effectiveness of the 1990 Clean Air Act Amendment (Figure 2a). The net release of sulfur indicates recovery of watersheds from years of acid deposition. Sulfur was the only analyte to experience a distinct crossover period from a net retention to a net release in these watersheds. The net export of sulfate indicates recovery of surface waters, as the soil pool of available sulfur is now being depleted. This observation reveals that sulfate adsorption plays a major role in delaying the watershed response to acid deposition, as the net export has only occurred within the last decade (Robison et al., 2013; Rice et al., 2014).

When analyzing the mass balance of nitrogen, the influence of the gypsy moth defoliation in these watersheds should be considered, as this event caused elevated NO_3^- levels during the beginning of the study. As the defoliation occurred during the late 1980s and early 1990s, the major impacts diminished throughout the study period. Riscassi et al. (2019) compared stream chemistry trends during the post-impact period (2001-2015) and full study period (1993-2015) and found that the influence of the defoliation did not significantly impact the long-term chemical trends.

There is a net retention of nitrogen across all the sites throughout the study period (Figure 2c). The net retention of nitrogen within these watersheds may be due to the net uptake into forest biomass (Goodale et al., 2002). The soil storage is the largest sink of nitrogen within these watersheds and denitrification also contributes to the net retention, although there is a large uncertainty in the estimation of denitrification (Coughlin, 2019).

Nitrogen export is a combination of NO_3^- and NH_4^+ and the high levels at STAN (Figure 2c) are due to large fluxes in NH_4^+ export. This spike is plausible, but may be due to how the WRTDS model computes the export. There were a number of samples below detection limit, but the model may be accounting for the higher values, therefore resulting in a higher estimation.

The mass balance of base cations reveals how the supply of base cations is shifting with declines in acid deposition. Across all sites, there was a net release of base cations, indicated by the negative net flux (Figure 3c). The greater net export compared to the deposition of base cations is due to the weathering of bedrock, as the primary source of base cations in most watersheds is mineral weathering (Driscoll et al., 2001).

It is important to note that, while fairly accurate wet deposition estimates can be made, there is a large uncertainty in dry deposition. The dry deposition estimates from TDep are greater than dry deposition from CASTNET. This is due to differences in the modeling approaches, specifically the Community Multiscale Air Quality (CMAQ) model calculates higher depositional velocities compared to the multi-layer model (MLM) used for CASTNET (Schwede and Lear, 2014). The estimates of deposition for all these analytes are the best estimates to our knowledge.

4.2 Flow- Normalized Concentrations

The dominant base cation varied between the sites, while the dominant anion was sulfate at all sites (Figure 4). These differences in analyte concentrations reflect the dominant bedrock mineralogy for the sites. Although SO_4^{2-} is the dominant anion at all three sites, the concentrations of SO_4^{2-} and the changes in concentrations over time differ. This is a result of the differences in sulfate adsorption capacity of the bedrock (Robison et al., 2013). The two sites with slight declines in concentrations, PAIN (siliciclastic) and PINE (basaltic), have lower sulfate adsorption capacities than STAN (granitic) due to the differences in the mineralogy of the bedrock.

In these watersheds, there are slight, but significant changes in base cation supply at PAIN, PINE, and STAN (Figure 4). The greatest declines in Ca^{2+}, Mg^{2+} and K^+ occurred at the most acid-sensitive site, PAIN, whereas increases in base cations occurred at PINE. These differences are likely the result of the larger base cation supply in soils due to the underlying mafic bedrock at PINE, which is more base-rich and has a greater buffering capacity (Robison et al., 2013). Therefore, PINE is less affected by acidic inputs compared to the base-poor site, PAIN.

4.3 Differences Between Deposition Trends and Water Chemistry Trends

At all sites, sulfate deposition is declining at a faster rate than stream concentrations, with the exception of stormflow at PINE, where the trend in stormflow approximately parallels the trend in deposition (Figure 5a). Deposition declining at a faster rate than the stream concentrations, suggests that some of the adsorbed sulfate is being desorbed, which is subsidizing some of the streamflow. A source of sulfur in watersheds is mineral weathering, however there are no major sources of sulfur in the bedrock of these watersheds, thus mineral weathering rates of S are relatively low in this area. An increase in the importance of the mobilization of internal S sources (i.e. weathering, mineralization, desorption) in watersheds is expected with declines in atmospheric S deposition (Mitchell and Likens, 2011). When comparing differences between baseflow and stormflow sulfate concentrations, baseflow trends are likely reflecting characteristics of deeper soils that have a greater retention of S, compared to shallow soils, where stormflow reflects these characteristics (Riscassi et al., 2019). A study of soils in an unglaciated watershed showed that deeper soils had a higher retention of sulfate compared to shallow soils (Shanley, 1992).

A discrepancy between changes in flow-normalized concentrations and changes in sulfate concentrations occurs at STAN. Although significant declines in deposition and SO_4^{2-} concentrations during the two flow regimes are the greatest at STAN, the flow-normalized concentration of SO_4^{2-} is increasing. This contradiction could be due to heavier rainfall in more recent years, resulting in more dilution in stream sulfate concentrations, which would not be present when taking into account an average discharge year (i.e. flow-normalized concentrations).

Significant changes in base cations at PAIN are likely not from changes in deposition of cations, as there were no significant trends in deposition (Figure 6). These changes are likely linked to changes in acid deposition, as elevated levels of N and S resulted in a decline of exchangeable cations within the soils in a Northeast U.S. watershed, thus leading to a limited base cation supply to surface waters (Fernandez et al., 2003). Base cation depletion is seen at the most base-poor watershed. Long-term trends in soils showed declines in exchangeable calcium and magnesium in unglaciated soils (Bailey et al., 2005). Additionally, model simulations (PnET-BGC) of southeast watersheds have shown that base cation leaching continues to occur even with the declines in sulfate and nitrate deposition (Fakhraei et al., 2016). The declines in base cations at PAIN are in contrast to observed increases in calcium in surface soils in the northeastern U.S. and Canada (Lawrence et al., 2015). These differences are likely due to soil characteristics, as deeper unglaciated soils in the southeastern U.S. are more highly weathered (Bailey et al., 2005; Rice et al., 2014). Therefore, rates of weathering inputs of base cations are likely not surpassing rates of base cation leaching.

The temporal trends in Δc for pH indicates that the contrast between stormflow and baseflow has increased over time. This is likely due to pH improving at a faster rate during episodic conditions than during chronic conditions at PAIN. As for SO_4^{2-}, the difference between stormflow and baseflow is declining. This can likely be attributed to the differences in flow paths during baseflow and stormflow, where water passes through the soils quickly during high flow periods, and sulfate pools in the shallow subsurface are flushed. This would result in minimal adsorption/desorption occurring, as the precipitated water flows through the upper soil layer.

Although declines in deposition were significant for NO_3^-, there were no significant changes in the concentrations at either flow regime, except at STAN during baseflow (Figure 5c). Comparing the deposition trends and temporal trends of the concentrations, it can be inferred that rates of uptake by vegetation and/or immobilization are increasing. Losses of nitrate in watersheds have been attributed to terrestrial factors (Scanlon et al., 2010; Lovett and Goodale, 2011). In terms of stream acidification, SO_4^{2-} is found in much larger concentrations (μeq L^{-1}) than NO_3^- within these watersheds. In SHEN, SO_4^{2-} is the main acid anion associated with acidic streams (Sullivan et al., 2003). However, since the declines in S deposition, NO_3^- is becoming a more important acidifying agent.

The importance of NO_3^- has been observed in the Catskills, as NO_3^- has increased to account for a larger percentage of the anion concentrations, as a result of the decline in SO_4^{2-}, rather than an increase in NO_3^- (McHale et al., 2017). Additionally, modeled data in the Great Smoky Mountains showed the declines in SO_4^{2-} and NO_3^- deposition resulted in the greatest recovery of ANC, due to a combination of the desorption of SO_4^{2-} and the delay of watershed progression toward N saturation (Zhou et al., 2015). Zhou et al. (2015) indicated that decreases in nitrate deposition were more effective in facilitating increases in ANC compared to decreases in sulfate, however both are important to achieve the greatest recovery in stream water.

5. Conclusion

Through examining changes in the acid-base chemistry during baseflow and stormflow conditions, it was determined that internal watershed biogeochemical processes are the main drivers in the changes in stream chemistry concentrations during stormflow conditions. Soil processes include adsorption/desorption, and enhanced rates of immobilization, uptake, and/or mineral weathering. Differences in bedrock play a major role in the soil buffering capacity of the watersheds, with the largest decline in base cation concentrations occurring at the site underlain by siliciclastic bedrock (most base-poor).

The mass balance analysis reveals that while there are dramatic reductions in sulfur and nitrogen deposition over recent decades, there are very few significant changes in base cation deposition. The sites exhibit a net release of base cation supply, and a major contributor to the net export of base cations is mineral weathering. As declines in deposition continue, monitoring of these watersheds is important to better understand the biogeochemistry of these watersheds. Long term datasets are important to evaluate changes during both episodic acidification and chronic acidification.

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Chapter 4: Summary and Prospects for Future Research

1.1 Watershed Recovery from Years of Acid Deposition

Sulfur budgets were created for 16 watersheds with weekly chemistry data available to examine recovery from years of excess acid deposition. These watersheds span the Eastern U.S from New Hampshire to Georgia. The northeast watersheds have a direct response to the declines in S deposition, as the majority of watersheds have been net exporters of S since the early 1990s to mid-2000s. In contrast, the southeast watersheds have a delayed response, as there has been a recent conversion from a net retention to a net release of sulfate (late 2000s to 2010s). These differences are due to differences in soil characteristics. The main process delaying the recovery of these watersheds is due to sulfate adsorption, as sulfate adsorption capacity is larger in the unglaciated soils of the southeast compared to the glaciated soils in the northeast. Examining the behavior of the sulfate isotherm at the whole-watershed scale, this study suggests sulfate adsorption is an irreversible process. This study demonstrates the importance of long-term monitoring of watersheds and shows the effectiveness of the 1990 Clean Air Act Amendment.

1.2 Main Mechanisms Behind Episodic Acidification Recovery

The main mechanisms driving changes in the acid-base status of watersheds in Shenandoah National Park (SHEN) were investigated. Mass balances of acid anions (SO_4^{2-}, Cl^-, NO_3^-) and base cations (Ca^{2+}, K^+, Mg^{2+}, Na^+, NH_4^+) were created for water years 1993-2018. To identify changes during baseflow and stormflow regimes, the concentration-discharge relationships (*C*-*Q*) for the analytes and pH were used to calculate concentrations for water years 1993-2018. The *C*-*Q* analysis shows that concentrations of the majority of analytes over time are declining during the two flow regimes. Through comparing trends in streamflow chemistry and deposition, this study suggests that the main mechanisms behind changes during stormflow are primarily biogeochemical, as many of the trends during stormflow are not consistent with trends in deposition. At the most base-poor site, there is evidence of base cation depletion. This study demonstrates that the soils within SHEN play a major role in affecting the acid-base chemistry of the watersheds.

2. Future Research Opportunities

This research shows the regional differences between the northeast and southeast U.S. and the beginnings of recovery in the southeast. Since watersheds in the SE have only recently converted from a net retention to a net exporter of S, continued monitoring is necessary to compare watershed dynamics to major reductions in acid deposition. This study expressed the sulfate adsorption isotherm at the whole watershed-scale, but evaluating the isotherm at different soil horizons and considering pH dependence would provide a further investigation into the behavior of the isotherm.

To identify changes in baseflow and stormflow concentrations of the analytes, the concentration-discharge relationship was assumed to be linear, but while examining each of the *C*-*Q* relationships for three-year periods, it was clear that some relationships were not linear. To better depict the *C*-*Q* relationship, a LOWESS (locally weighted scatterplot smoothing) relationship may be used, which does not require linearity (Helsel and Hirsch, 2002). This would provide a more accurate representation of the *C*-*Q* relationships, and therefore, a more accurate examination into the concentrations during baseflow and stormflow events. Additionally, to better understand what is occurring in the soils, an updated soil survey from the one previously conducted in 2000 in SHEN should be completed. This would provide an assessment into examining how the base saturation of soils has changed with major declines in acid deposition.

Reference: Chapter 4

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