

Original Research Article

The impacts of stream acidification on fish assemblages: Assessing three decades of recovery in Shenandoah National Park



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ABSTRACT

Acid deposition, resulting from the atmospheric transport of acidifying compounds emitted during the combustion of fossil fuels, has historically resulted in stream acidification in many headwater streams in the eastern United States, including streams in Shenandoah National Park (SHEN). Though restrictions on these emissions were established by an amendment to the Clean Air Act in 1990, reductions in stream acidification have not been observed in all regions of SHEN due to variations in the geological composition of SHEN watersheds. Before the implementation of these restrictions, fish assemblages were strongly controlled by a stream's acid neutralizing capacity (ANC), which is the ability of a watershed to buffer acid inputs. This study investigated changes in the relationship between fish assemblages and ANC within SHEN 21 years after implementation of more stringent restrictions on the emission of sulfur and nitrogen oxides in 1995. Results indicated that recovery trends in water chemistry were observed in some SHEN watersheds; however, fish species richness and total fish biomass continue to be influenced by the legacy of acid deposition in acid sensitive watersheds. Temporal trend analysis indicated little change in ANC within acid sensitive watersheds and minor decreases in stream sulfate concentrations. These findings indicate a persistent impact from previously deposited sulfur oxides and the continued influence of these compounds on fish assemblages within SHEN. Though no further loss of fish species, and in some cases, increases in species richness, suggest the early stages of recovery, many SHEN streams remain as susceptible to acidification as they were over two decades ago, highlighting the need for continued regulation of acidifying emissions and conservation efforts in headwater streams.

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1. Introduction

Acid deposition, resulting from the atmospheric transport of acidifying compounds emitted during the combustion of fossil fuels, has historically resulted in both chronic and episodic stream acidification in many mountain streams in the

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eastern United States (Kaufmann et al., 1991). Prolonged deposition has depleted watershed reservoirs of base cations associated with acid neutralizing capacity (ANC) (Likens et al., 1996). ANC is the ability to buffer the effects of acid inputs, and is determined by the balance between atmospheric and geological acid anions (SO_4^{2-} , NO_x , Cl^{1-}) and base cation (Ca^{2+} , Mg^{2+} , K^+ , Na^+) concentrations provided by a watershed's underlying bedrock. Stream acidification has been shown to result in fish emigration, decreased biomass, reduced recruitment and decreased fish species diversity (Bulger et al., 1995; Dennis et al., 1995; Baker et al., 1996; Baldigo and Lawrence, 2000). Acidification in headwater streams can be especially detrimental to fish species whose spawning habitat is restricted to the cold, clean water found in these ecosystems. Fish species such as Brook Trout (*Salvelinus fontinalis*) have experienced habitat constraints due to deforestation and agricultural land use. This species has experienced added pressure in the form of a 'habitat squeeze', caused by stream acidification pushing dispersal downstream and rising stream temperatures pushing dispersal upstream (Hudy et al., 2008; McDonnell et al., 2015). The resulting habitat squeeze has the potential to disrupt the function of headwater ecosystems by decreasing or locally extirpating cold-water fish populations. Such disturbances could disrupt linkages between spawning grounds in headwater streams to high productivity riverine habitats required for healthy populations of low-order stream species (Petty et al., 2014).

The Clean Air Act (1970) and an Amendment to the Act (1990) were aimed at reducing sulfur dioxide and nitrogen oxide emissions from power plants and motor vehicles, placing a cap on sulfur dioxide emissions at 8.9 million tons annually, a reduction of 10 million tons when compared to emissions in 1980. Phase 1 of the Amendment was enacted in 1995, placing restrictions on 21 of the largest coal-burning power plants in the eastern and mid-western United States. Phase 2 was implemented in 2000, restricting sulfur dioxide emissions from smaller coal, gas and oil burning plants. Though nitrogen oxide emissions contribute to acid deposition, they do not provide the best representation of the deposition of acidifying compounds due to the ability of natural biological process and the disturbance of these processes from deforestation or defoliation to impact watershed nitrogen levels (Webb et al., 2004). As such, this study focused specifically on the acidification of Shenandoah National Park (SHEN) streams by sulfate (SO_4^{2-}), due to atmospheric sulfur deposition. Between 1990 and 2000 sulfur dioxide emission fell from 15.7 million tons to 11.2 million tons and by 2016 emissions had fallen to 1.5 million tons (EPA, 2001; EPA, 2018), resulting in declines in sulfate deposition across the eastern United States (Lynch et al., 2000; Siemion et al., 2018). Likens et al. (2001) observed that decreases in sulfur dioxide emissions associated with Phase 1 in 1995 were correlated with declines in sulfate deposition in experimental watersheds in New Hampshire. Similar trends were observed within SHEN where Sullivan et al. (2003) identified decreases in sulfate and nitrate deposition trends from 1988 to 2003.

One of the regions most heavily impacted by acid deposition is the eastern United States (Cogbill and Likens, 1974). Decreases in acid deposition have been associated with significant declines in surface water concentrations of SO_4^{2-} in the northeastern United States (Siemion et al., 2018). However, these trends were not observed in SHEN streams where, in some cases, increases in surface water sulfate concentrations have been reported (Jastram et al., 2013; Robison et al., 2013). SHEN streams associated with increases in SO_4^{2-} concentrations were also associated with decreases in ANC. The persistence of stream acidification in SHEN, given reductions in acidifying emissions, can be explained by legacy effects of SO_4^{2-} deposition. As described by Rochelle et al. (1987) and Stanko-Golden et al. (1994), watersheds like those in SHEN that have retained weathered surface material, as a result of exclusion from the Wisconsin continental glaciation (85–11 kya), will have a higher sulfate adsorption capacity. The high adsorption capacity of SHEN soils promotes the accumulation of SO_4^{2-} within these watersheds, which delays the recovery of these systems.

Coinciding with the implementation of Phase 1 of the 1990 Clean Air Act amendment, an investigation of the relationship between fish species richness and minimum ANC levels in thirteen SHEN streams found a significant positive relationship between fish species richness and minimum ANC such that streams with the lowest ANC values supported the lowest fish diversity (Bulger et al., 1995). These findings suggest that ANC, which is influenced by acid deposition and bedrock geology, were acting as a primary control on the spatial distribution of fish species in SHEN. These findings provide a picture of the fish assemblage and ANC relation pre-Clean Air Act (1995).

The purpose of this study was to identify changes in fish assemblages, water chemistry, and the interaction between these two parameter groups given twenty-one years of emissions regulation provided by the Clean Air Act. Differences between fish assemblages and water chemistry between 1995 and 2016, as well as water chemistry trend analyses, were used to identify how environmental regulations have impacted distinct geological regions of SHEN and how land managers might best manage these regions. Specifically, the first objective was to identify the current relationship between fish species richness and ANC, and to compare this relationship to that found in 1995 by revisiting the thirteen SHEN streams investigated in a report by Bulger et al. (1995). In addition to fish species richness, we also investigated the current relationship between fish biomass and ANC. The second objective was to identify trends in stream ANC and sulfate concentrations between 1995 and 2015 in the thirteen streams.

2. Methods

2.1. Study area

SHEN encompasses 777 km² of the Blue Ridge Mountains in northern and central Virginia and contains 90 headwater streams that drain into the James, Rappahannock and Potomac rivers. Headwater streams within SHEN provide habitat for 38 species of fish (Jastram et al., 2015). Streams within SHEN vary in response to acid inputs due to variations in its underlying

bedrock (Deviney et al., 2006). SHEN contains three major bedrock classes: a region of siliciclastic bedrock on the western slope, a region of basaltic rock along the ridge, and a region of granitic rock along the eastern slope. Watersheds associated with these bedrock classes vary in ANC such that siliciclastic regions that are composed of sand and siltstone provide the lowest ANC, granitic regions composed of granitoid gneiss provide relatively moderate ANC levels, and basaltic regions composed of meta-basalt and pockets of calcite provide the highest ANC (Fig. 1).

This study re-surveyed the same thirteen streams surveyed from 1992 to 1995 by Bulger et al. (1995), which were dispersed throughout three bedrock types within SHEN (Fig. 2). Study streams included five streams from siliciclastic watersheds: Madison Run, Meadow Run, Paine Run, Twomile Run and White Oak Run; four granitic streams: Brokenback Run, Hazel River, North Fork Dry Run and Staunton River; and four basaltic streams: Jeremy's Run, North Fork Thornton River, Piney River and Rose River (Table 1).

2.2. Water chemistry

Water chemistry was collected via grab sampling on a quarterly basis by the Shenandoah Watershed Study (SWAS) from the University of Virginia. SWAS is an ongoing study which has been monitoring and researching mountain streams in western Virginia since 1979. Changes in instrumentation and methods occurred in October 2005 for acid anion measurements and in October 2006 for pH and ANC measurements. Before October 2006, pH and ANC were measured with a standard pH meter and electrode (APHA, 1985; APHA, 1998). Beginning in October 2006, an automated titration system was used to measure pH and ANC (EPA, 1987; Gran, 1952). Sulfate and nitrate were measured using ion chromatography methods based on EPA Method 300.1 (EPA, 1997). Water chemistry in the SWAS database (available at waterqualitydata.us/portal) has been adjusted to correspond to the new methods and instrumentation (documented in Table 1 within Robison et al., 2013).

2.3. Fish sampling

Fish sampling methods and time periods in the study by Bulger et al. (1995) varied, with 100-m single pass electrofishing from 1992 to 1994 at Jeremy's Run, Madison Run, Meadow Run, North Fork Dry Run, Paine Run, Rose River and Twomile Run, 100-m three pass electroshocking in 1995 in Brokenback Run, Hazel River, North Fork Thornton, Piney River and Staunton River (Haskell, 1984; Atkinson, 2002). In 1994 a basin-wide visual estimation (snorkel survey) was used in White Oak Run, Brokenback Run, Twomile Run and Meadow Run (Dolloff and Underwood, 1995). This visual estimation consisted of counting

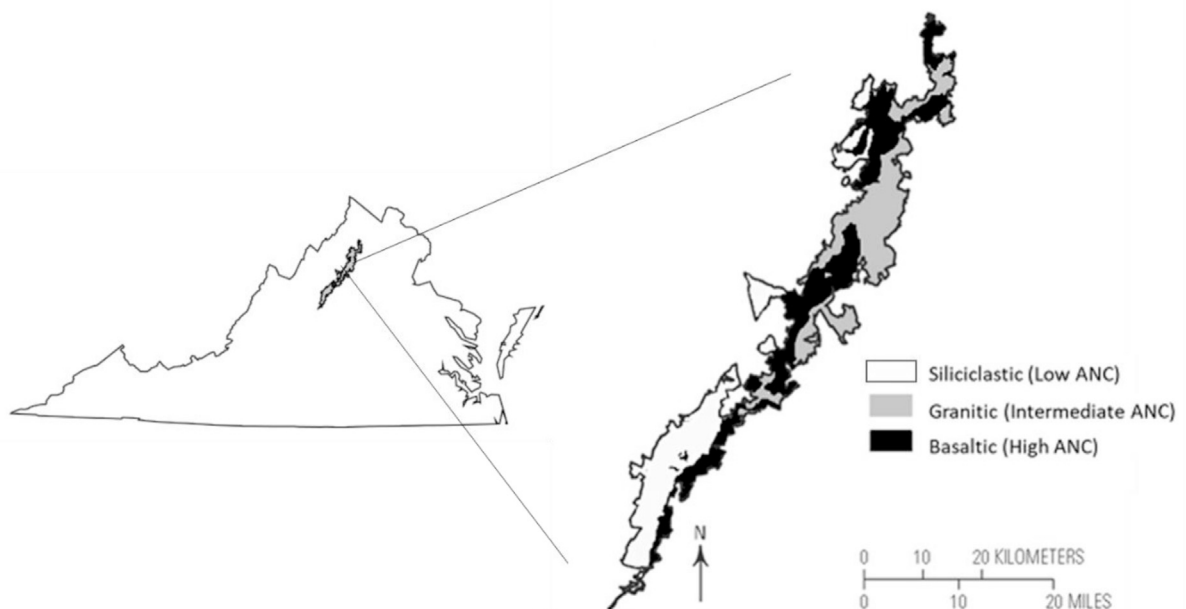


Fig. 1. Shenandoah National Park encompasses 777 km² of the Blue Ridge Mountains in the Commonwealth of Virginia. Headwater streams within the Park are part of three major watersheds in Virginia: the Potomac River, the Rappahannock River and the James River. Shenandoah National Park is composed of three major bedrock classes: siliciclastic, granitic and basaltic. Acid neutralizing capacities range from low in siliciclastic regions to intermediate in granitic regions to high in basaltic regions.

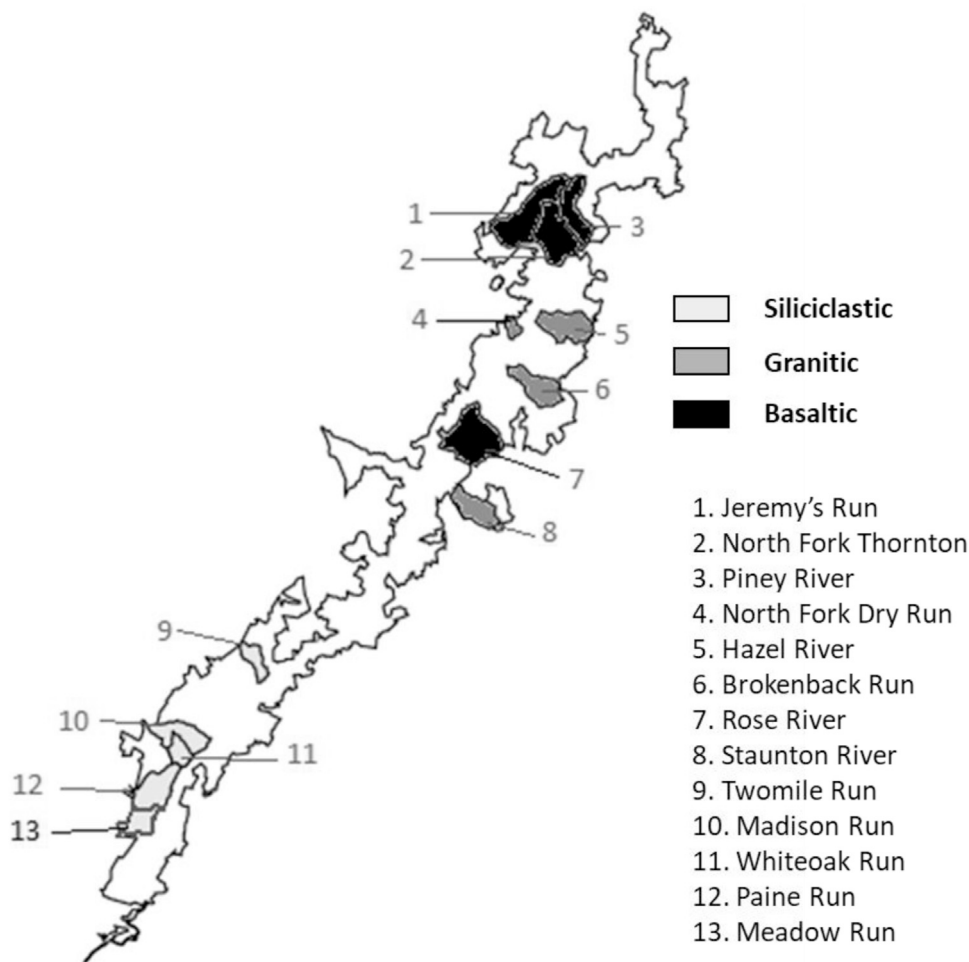


Fig. 2. The study surveyed the same thirteen streams investigated in 1995 by Bulger et al. (1995). Study streams included five siliciclastic streams: Madison Run, Meadow Run, Paine Run, Two Mile Run and White Oak Run, four granitic streams: Brokenback Run, Hazel River, North Fork Dry Run and Staunton River, and four basaltic streams: Jeremy's Run, North Fork Thornton River, Rose River and Piney River.

Table 1

Watershed and water chemistry characteristics (N = 28) for the 13 study streams in Shenandoah National Park (2009–2015). Standard deviation in (–).

Stream Name	Bedrock Class	Slope (m/m)	Area (km ²)	Minimum ANC (μeq/L)	Median ANC (μeq/L)	Maximum SO ₄ (μeq/L)	Maximum NO ₃ (μeq/L)	Stream Power (m ² *(m/m))
Madison Run	Siliciclastic	0.02	16.0	38.34	112.60 (51.75)	84.45 (7.42)	0.53 (0.16)	292,837
Meadow Run	Siliciclastic	0.03	8.9	–4.32	2.92 (3.12)	104.51 (10.25)	4.17 (1.09)	242,624
Paine Run	Siliciclastic	0.02	12.7	0.42	8.49 (5.50)	121.3 (5.55)	36.36 (0.79)	313,463
Twomile Run	Siliciclastic	0.02	5.6	3.26	22.0 (10.19)	107.21 (12.48)	5.05 (1.47)	135,600
White Oak Run	Siliciclastic	0.02	5.1	15.02	26.56 (22.33)	87.76 (4.73)	56.02 (2.63)	87,644
Brokenback Run	Granitic	0.04	11.6	41.58	91.09 (31.49)	55.39 (7.07)	0.56 (0.18)	446,297
Hazel River	Granitic	0.05	13.2	50.15	106.18 (29.19)	50.39 (7.24)	6.12 (1.30)	703,922
NF Dry Run	Granitic	0.04	2.3	37.77	59.35 (26.02)	109.2 (6.60)	41.53 (9.19)	85,020
Staunton River	Granitic	0.06	10.6	42.68	83.34 (16.68)	72.12 (4.67)	72.12 (0.15)	689,828
Jeremy's Run	Basaltic	0.01	22.0	108.86	214.82 (99.52)	124.36 (17.15)	5.46 (1.31)	220,181
NF Thornton River	Basaltic	0.01	18.7	162.98	297.26 (90.50)	106.06 (16.72)	19.76 (5.52)	187,193
Piney River	Basaltic	0.03	12.5	106.5	207.31 (74.01)	93.68 (10.19)	39.03 (3.66)	356,843
Rose River	Basaltic	0.06	23.7	93.44	166.54 (46.92)	66.67 (9.90)	15.75 (4.63)	1,466,393

fish by species in 27 percent of pools and 15 percent of riffles throughout the habitat suitable for supporting fish within a drainage. The visual estimation was enhanced by using multiple pass electrofishing in approximately 10 percent of the units to check the accuracy of the species observed. All three sampling methods were conducted during the summer season.

For the current study, a single fish sampling used three-pass electroshocking for each stream. Sampling occurred between May and August 2016. Fish sampling locations were located within 400 m of SWAS water sampling locations nearest the SHEN boundary and co-located with fish sampling sites used by SNP park staff in 1995 (Table S1). Sample reaches (the length of stream sampled) were 100 m long and collections were made with a backpack electrofishing unit (Smith Root LR-24). During sampling, the 100-m sample reach was cordoned off using block nets. All fish were identified to species.

An additional 200 m above the 100-meter sample reach were surveyed for total fish biomass. This analysis was not limited by the 100-meter sampling reaches assessed by Bulger et al. (1995) thus biomass was sampled in a representative manner using contemporary methods (Reynolds et al. (2003)). In addition, ANCOVA analysis, using an interaction term for data type (ANC $\times$ sample length) indicated no significant difference between slopes and y-intercepts between the two sampling methods ($p = 0.81$, $p = 0.77$ respectively). This suggests that sampling efficiency was not impacted by increased sample reaches. In this 300-meter reach, total wet mass was determined for each species. Average wetted width and channel slope were measured at each of the thirteen sample streams. Channel slope was measured using a hand-held clinometer at reach scale. The surface area of each fish sampling reach was determined by multiplying the average wetted width by the sample reach length. Total fish biomass within each 300-meter sample reach was determined by dividing the total wet mass for each species in a sample reach by the surface area of the corresponding sample reach.

2.4. Statistical analysis

Simple linear regression was used to identify the relationship between fish species richness and the seven-year minimum ANC for the two time periods as well as to allow comparison between the previous study (Bulger et al., 1995) and the current study. The minimum ANC value was used as it has been shown to be an indicator of episodic acidification conditions (Bulger et al., 1995). The first time period represents conditions prior to implementation of the Clean Air Act Amendment in 1995 and used seven years of water chemistry (1989–1995) to determine the correlation between minimum ANC and fish species richness (Bulger et al., 1995). Consistent with this approach, seven years of water chemistry data (2009–2015) was used for the second time period to assess potential recovery of fish and water chemistry post-implementation of the Amendments. Regression slopes and y-intercepts of the relationship between fish species richness and minimum ANC were compared between the two time periods using ANCOVA with the addition of an interaction term representing the year of each study (ANC $\times$ year). To account for changes in ANC analysis methods in October 2005, the relationship between fish species richness and minimum ANC observed by Bulger et al. (1995) was recreated using data adjusted to new instrumentation (documented in Table 1 within Robison et al., 2013). Linear regression indicated that there was no significant difference between y-intercepts and slopes of the recreation of the 1995 dataset and the original dataset published by Bulger et al., (1995) ($p = 0.78$, $p = 0.78$; respectively). This result indicates that changes in water chemistry values due to change in instrumentation do not impact the statistical relationship between fish species richness and ANC identified by Bulger et al. (1995).

A statistical model for total fish biomass observed in 2016 was constructed using forward and backward step-wise regression with maximum SO_4^{2-} , maximum NO_3^- , median ANC from 2009 to 2015, an index of stream power (watershed area (m^2) $\times$ channel slope (m/m)), as well as the six possible pairs of interactions between the four variables (Table 1). Median ANC was selected for these models over minimum ANC to represent more chronically acidified conditions in the study streams. Maximum SO_4^{2-} and NO_3^- were used to represent the maximum potential for acid input into the watersheds. Differences in total fish biomass between the three bedrock classes were investigated using ANOVA and Tukey's HSD Test.

Temporal trends in ANC and SO_4^{2-} from 1996 to 2016 were determined using a Seasonal Kendall test with Sen's slopes to account for seasonal variation in water chemistry between summer, fall, winter and spring in each stream. The Seasonal Kendall test is non parametric test which has been shown to be robust given missing data points, non-normality and seasonality (Hirsch and Slack, 1984). For trend analyses, weekly and episodic data were removed from the dataset so that only trends in the consistently collected quarterly data were analyzed. Differences in ANC and SO_4^{2-} trends (1996–2015) among bedrock classes were analyzed using ANOVA and Tukey's HSD Test. All statistical analyses were conducted in R (v.3.2.5) except for all ANCOVA analyses, which were conducted in SPSS (v.24).

3. Results

There was a significant and positive relationship between fish species richness and minimum ANC during both time periods (Fig. 3A). The first time period represents conditions prior to implementation of the Clean Air Act Amendments and the second time period represents conditions post-implementation of the Amendments. In comparing fish species richness observed during the two time periods, ANCOVA indicated a significant difference between slopes ($p = 0.01$) but not y-intercepts ($p = 0.19$). Divergence between the two regressions as minimum ANC increases illustrates an increase in percent change in fish species richness from -6.6% (a decrease in fish species richness) at an ANC of $25 \mu\text{eq/L}$, to 38.3% at an ANC of $160 \mu\text{eq/L}$. The observed divergence in the relationship between fish species richness and minimum ANC between 1995 and 2016 is based upon increases in fish species richness, which occurred primarily in basaltic streams. Decreases in fish species richness occurred in two siliciclastic streams (Madison Run and White Oak Run). All other siliciclastic and granitic streams showed no change in fish species richness.

Fifteen species of fish were identified during the 1995 survey, with fish species richness ranging from one to nine species in the 13 streams investigated (Table S2). Brook Trout and Blacknose Dace (*Rhinichthys atratulus*) were the primary fish species

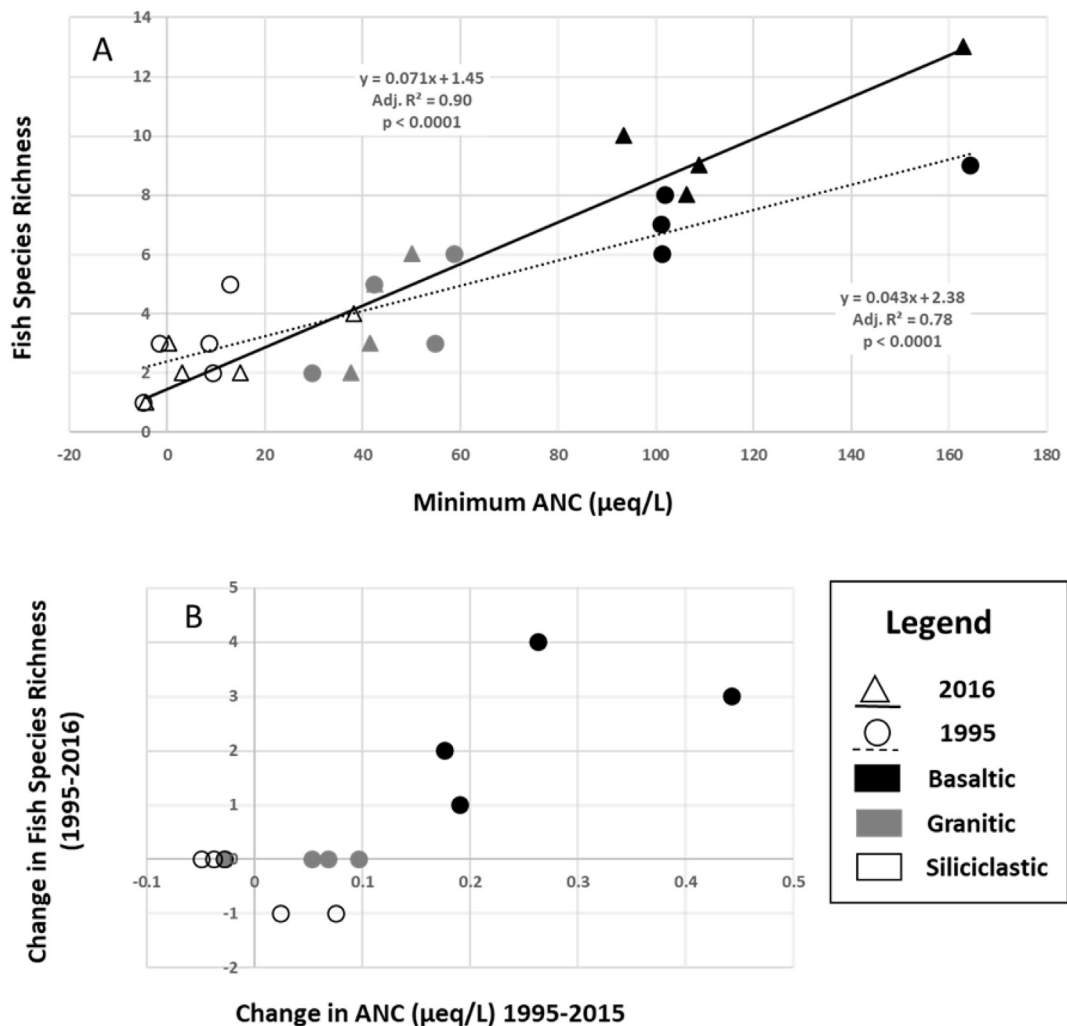


Fig. 3. A: Simple linear regression indicated a significant relationship between minimum ANC and fish species richness in 1995 and 2016. A divergence in trend lines between 1995 and the current study illustrates the increase in fish species richness in basaltic watersheds. B: Increases in fish species richness primarily occurred in watersheds where increases in ANC were above 0.1 $\mu\text{eq/L}$.

found in the 13 study streams during that time period. Brook Trout were found in all streams whereas Blacknose Dace were found in all streams except Meadow Run, 1995 being the first year that no Blacknose Dace were found in the stream (Bulger et al., 1995). Fish species found only in basaltic watersheds include Bluehead Chub (*Nocomis leptocephalus*), River Chub (*Nocomis micropogon*), Tessellated Darter (*Etheostoma olmstedi*), White Sucker (*Catostomus commersoni*) and Brown Trout (*Salmo trutta*), a non-native species. Fish species found only in granitic watersheds included Torrent Sucker (*Thoburnia rathoeceae*) and Fallfish (*Semotilus corporalis*). There were no species of fish found uniquely in siliciclastic watersheds. The number of fish species across bedrock classes during the time period of the original study increased along the ANC gradient of the watersheds such that siliciclastic watersheds supported the lowest number of species (1–5), granitic watersheds supported the next highest number of fish species (2–6), and basaltic watersheds supported the highest number of fish species (6–9).

Eighteen species of fish were identified in the 2016 survey (Table S2). Brook Trout and Blacknose Dace were found in all 13 of the study streams whereas Blacknose Dace were, again, found in all study streams except Meadow Run. It is notable that low densities of Blacknose Dace have been observed in the stream since 1995 (Shenandoah National Park, unpublished data). Ten fish species were only found in basaltic watersheds and include White Sucker, Tessellated Darter, Cutlips Minnows (*Exoglossum maxillingua*), Mountain Redbelly Dace (*Chrosomus oreas*), Central Stoneroller (*Camptostoma anomalum*), non-native Brown Trout, Mottled Sculpin (*Cottus bairdii*), River Chub, and American Brook Lamprey (*Letenteron appendix*). Four species detected in 2016 were not observed in the 1995 survey, including Cutlip Minnow, Mountain Redbelly Dace, Central Stoneroller, and American Brook Lamprey. Fallfish were absent from the 2016 survey but were present in the 1995 survey;

however, these fish are migratory and may not have been detected due to slight seasonal differences in sampling. Consistent with the original study, no fish species were uniquely found in siliciclastic watersheds.

Increases in fish species richness primarily occurred in basaltic watersheds, where the greatest increase in ANC were observed (Fig. 3B). The average change in ANC, calculated using Sen's slopes, among bedrock types ranged from $-0.0126 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in siliciclastic streams, $0.050 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in granitic streams and $0.27 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in basaltic streams; however, none of the trends were significant (Fig. 4A). Furthermore, ANC decreased from 1996 to 2015 in three siliciclastic streams (Paine Run, Meadow Run and Twomile Run) and in one granitic stream (Staunton River). Using ANOVA, a significant difference in ANC trends from 1996 to 2015 was observed between the three watershed classifications ($F(2) = 13.7$, $p = 0.001$). Tukey's HSD test indicated that ANC trends in basaltic watersheds were significantly higher than in both siliciclastic and granitic watersheds ($p = 0.0014$ and $p = 0.008$; respectively).

There were negative trends in SO_4^{2-} in all of the study streams, with the exception of Staunton River. There were significant declines in SO_4^{2-} in two siliciclastic streams: Paine Run ($p < 0.001$) and Madison Run ($p = 0.05$). One granitic stream, North Fork Dry Run, and one basaltic stream, Jeremy's Run, indicated significant decreases in SO_4^{2-} ($p = 0.01$ and $p < 0.001$, respectively). Average changes in SO_4^{2-} concentrations ranged from $-0.027 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the four granitic streams, $-0.068 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the five siliciclastic streams, to $-0.14 \mu\text{eq L}^{-1} \text{yr}^{-1}$ in the four basaltic streams. Using ANOVA, there were no significant difference in SO_4^{2-} trends from 1996 to 2015 between the three watershed classifications.

Total fish biomass ranged between 0.98 and 8.89 g/m² across the three bedrock classes (Table 2). Consistent with fish species richness, total fish biomass similarly differed among bedrock classes, with the lowest biomass (and fish species richness) in siliciclastic watersheds and the greatest biomass (and fish species richness) in basaltic watersheds (Fig. 5). Using ANOVA, a significant difference in total fish biomass was observed between the three watershed classifications ($F(2) = 18.03$, $p < 0.001$). Tukey's HSD Test indicated that there was no significant difference in total fish biomass between siliciclastic and granitic watersheds. There was a significant difference between siliciclastic and basaltic watersheds ($p < 0.001$) as well as between granitic and basaltic watersheds ($p = 0.005$). Total fish biomass ranged from 0.98 to 3.17 g/m² in siliciclastic streams, 2.30–6.09 g/m² in granitic streams, and 5.58–8.89 g/m² in basaltic streams. Stepwise regression produced a significant statistical model predicting total fish biomass based upon median ANC, maximum SO_4^{2-} , maximum NO_3^- , the stream power index, and an interaction term between median ANC and maximum NO_3^- as predictor variables (Adj. $R^2 = 0.90$, $p < 0.001$) (Table 3). The total fish biomass model is as follows:

Total fish biomass (g/m²) = $-4.1 + 0.012(\text{Median ANC}) + 0.045(\text{Maximum SO}_4) + 0.0048(\text{Maximum NO}_3) + 4.6e^{-6}(\text{Stream Power}) + 4.0e^{-4}(\text{Median ANC} \times \text{Maximum NO}_3)$.

Median ANC, maximum sulfate and maximum nitrate were measured in $\mu\text{eq/L}$. The stream power index was measured in meters³/meters.

4. Discussion

Recovery, in the form of increased fish species richness, was primarily observed in streams underlain with basaltic bedrock, which has the greatest buffering capacity of any bedrock class in SHEN. Increases in fish species richness in basaltic streams represents a recovery of fish species richness in acid impacted streams without the use of active restoration methods such as stocking or watershed liming. Streams in basaltic watersheds are also more productive for fish growth, relative to the other two bedrock types, as evident by the significantly higher biomass. Given the greater capacity for acid neutralization in basaltic streams and thus the best potential for recovery from past acidification, larger increases in fish species richness would be expected in these streams. The comparison between the 1995 relationship and the 2016 relationship supports this outcome. Significant difference between slopes of the two regressions are driven by increases in fish species richness in basaltic streams and a lack of increased richness in granitic and siliciclastic streams. These results indicate that fish species richness has remained the same or decreased in acid-sensitive streams underlain by granitic and siliciclastic bedrock since the implementation of more stringent emission restrictions in 1995.

In addition to fish species richness, stepwise regression indicated that acidification has an effect on total fish biomass. Lower mean ANC levels tended to be associated with lower total fish biomass. Total fish biomass in basaltic watersheds was almost four times higher than in siliciclastic streams and roughly two times higher than in granitic watersheds (Table 2). Previous research has indicated that fluctuations in fish biomass result in alterations to trophic structure and ecosystem function (Carpenter et al., 1985; Post et al., 1997). The predicted influence of stream acidification on total fish biomass in SHEN indicate that continued stream acidification has had, and may continue to have, a top-down effect on stream trophic structures. Though SO_4^{2-} and NO_3^- were included in the model due the negative impact on stream pH associated with these compounds, the model indicated that increases in either compound are associated with increased total fish biomass. In the absence of disturbance, such as defoliation by gypsy moth invasion, NO_3^- is controlled by natural biological function, in which case increases in NO_3^- can be associated with increases in primary production. The positive coefficient associated with NO_3^- in the model could possibly be explained by a bottom-up effect from primary producers to fish communities in SHEN if streams are nitrogen limited. At the moment, this study cannot explain the positive influence of SO_4^{2-} on total fish biomass found in the model.

A twenty-year trend analysis from 1996 to 2015 of stream SO_4^{2-} concentrations and ANC indicated that, though there have been significant declines in stream SO_4^{2-} concentrations in some cases, the decrease has not translated to a recovery of ANC in most of the study streams. Previous research has indicated that the sulfate adsorption capacity of SHEN watersheds has

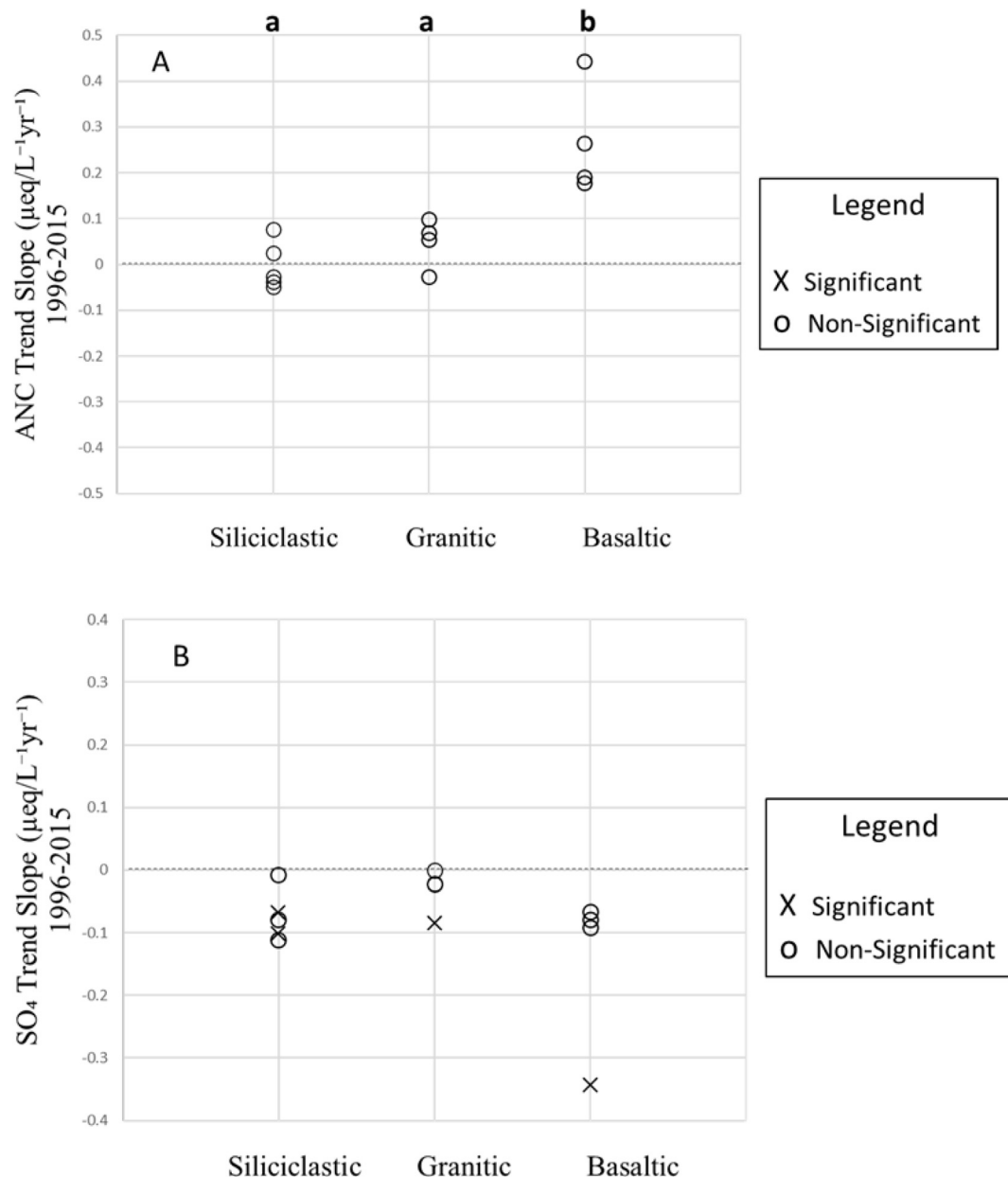


Fig. 4. A: Seasonal Kendall tests indicated no significant trends in ANC among streams found in the three bedrock classes (1996–2015). Positive trends were observed for all four basaltic watersheds while both positive and negative trends were observed in siliciclastic and granitic streams. Trend slopes in basaltic watersheds were significantly higher than trends in both siliciclastic and granitic watersheds. B: Negative trends in stream SO_4 concentrations were observed in all study streams. Significant declines were observed in two siliciclastic streams, one granitic stream and one basaltic stream.

resulted in a legacy effect in which previously deposited SO_4^{2-} remains in watersheds despite decreases in atmospheric deposition (Garmo et al., 2014). The continued leaching of SO_4^{2-} from watershed soils, combined with the depletion of available base cations, has resulted in the continuation of stream acidification in acid sensitive siliciclastic and granitic streams, which continues to impact fish species richness and biomass.

Given a lack of significant change in ANC over the past twenty years, it can be assumed that current fish assemblages in sensitive SHEN streams are under similar acidification pressures as those pre-1995 emission restrictions. The absence of increases in fish species richness in siliciclastic and granitic streams, in light of increases in basaltic streams, suggest that stream response to acidification continues to be the limiting factor for fish assemblages in these sensitive streams. Negative impacts associated with stream acidification include decreased total fish biomass, species emigration, and low recruitment (Bulger et al., 1995; Dennis et al., 1995; Baker et al., 1996; Baldigo and Lawrence, 2000).

Table 2

Fish species richness and total fish biomass for the 13 study streams in Shenandoah National Park.

Stream Name	Bedrock Class	Species Richness (1995)	Species Richness (2016)	Total Fish Biomass (g/m ²) (2016)
Madison Run	Siliciclastic	5	4	0.98
Meadow Run	Siliciclastic	1	1	1.72
Paine Run	Siliciclastic	3	3	3.17
Twomile Run	Siliciclastic	2	2	2.41
White Oak Run	Siliciclastic	3	2	1.78
Brokenback Run	Granitic	3	3	2.56
Hazel River	Granitic	6	6	2.30
NF Dry Run	Granitic	2	2	2.37
Staunton River	Granitic	5	5	6.09
Jeremy's Run	Basaltic	6	9	5.58
NF Thornton River	Basaltic	9	13	7.82
Piney River	Basaltic	7	8	7.23
Rose River	Basaltic	8	10	8.89

It is important to acknowledge that, though decreases in acid deposition over the past two decades signify a positive step in the control of anthropogenic air pollution, the continued legacy effects observed in SHEN streams indicate that these streams are still in the early stages of recovery from acid deposition. These findings agree with estimates for the eventual net shedding of previously deposited SO_4^{2-} as late as 2021 in SHEN watersheds (Rice et al., 2014). As described by Sullivan et al. (2007), sulfate retention associated with SHEN streams attenuates stream acidification, to an extent, by keeping SO_4^{2-} contained in watershed soils. This being said, the leaching of retained SO_4^{2-} in SHEN watersheds, as described by Driscoll et al. (1998), provides a continued source of acid anions to SHEN streams. Recovery of ANC in these streams is dependent on decreases in SO_4^{2-} input that exceed decreases in base cations. Decreases in SO_4^{2-} input into streams require decreases in the reservoir of SO_4^{2-} available in soils (Robison et al., 2013; Rice et al., 2014). Robison et al. (2013) observed that the export of SO_4^{2-} from the White Oak Run watershed in SHEN exceed atmospheric SO_4^{2-} deposition in 2009 and 2010. This observation represents the net depletion of stored SO_4^{2-} , which is an important precursor to increases in ANC.

Continued reductions in sulfur emissions, thus continued reductions in atmospheric SO_4^{2-} deposition, will expedite the shedding of SO_4^{2-} retained in SHEN soils and thus recovery in SHEN streams. Between 2005 and 2016, sulfate emission rates have declined by 81% in the United States (EPA, 2018). Despite these reductions in acidifying emissions, siliciclastic streams in SHEN continue to be impacted by acidification. Mitigation measures such as liming acidic streams should be considered to maintain existing fish populations and to promote increases in fish species richness in siliciclastic streams in SHEN.

Differences in watershed area exist between the thirteen study streams. As observed by Baldigo and Lawrence (2000) and Jastram et al. (2013), increased watershed size can correspond to increased fish species richness. Though average watershed area is comparable between siliciclastic and granitic watersheds in this study (9.66 km² and 9.42 km², respectively), average watershed area for the basaltic streams were twice as large (19.22 km²) (Table 1). In the absence of stream acidification, species-area relations indicate that one could expect to find higher fish species richness in the basaltic streams surveyed in this study when compared to the siliciclastic and granitic streams. By comparing three basins of comparable size (10.6–12.7 km²), fish species richness conformed to the overall relationship (Fig. 3) imposed by differences in bedrock classes. Paine Run, Staunton River, and Piney River, with species richness of 3, 5 and 10, demonstrate the gradient of species richness across bedrock classes with similar watershed area.

Unequal sampling methods between the 1995 study and the current study also represent potential confounding factors. The relationship between fish species richness and minimum ANC identified in 1995 used three fish sampling methods: 100-meter one-pass electroshocking, 100-meter three-pass electroshocking, and basin wide visual surveys. In 2016, fish sampling consistently used 100-meter three pass electroshocking. Though a direct comparison between the 1995 methods and the current methods could not be assessed, if sampling efficiency had increased in 2016, then species richness would be expected to increase in all streams; however, this study predominantly documented richness increases in streams where acidification had decreased.

Stream network connectivity, specifically the connectivity of the study streams to reservoirs of potential immigrant fish species, could influence the rate at which species richness numbers increase and could influence the precision of assessment metrics in the Park (Hitt and Angermeier, 2008). The presence of culverts, falls or the seasonal drying of stream sections in Madison Run, Meadow Run, Paine Run and Two-Mile Run could inhibit or slow recolonization in SHEN streams. Future research into the role of stream network connectivity in determining fish movements within SHEN could help to better understand variations in fish species richness between the study streams.

The immigration of non-native fish species into SHEN streams could influence fish assemblages and effect the precision of fish assessment metrics. Bulger et al. (1995) and the current study identified the presence of Brown Trout in Rose River. It is unlikely that the presence of Brown Trout influenced the conclusions of the study since this species was present during the 1995 and 2016 surveys. During sampling for the biomass analysis, a single Rainbow Trout was identified, most likely due to stocking outside of SHEN. This fish was not included in the fish species richness analysis because it was found outside of the

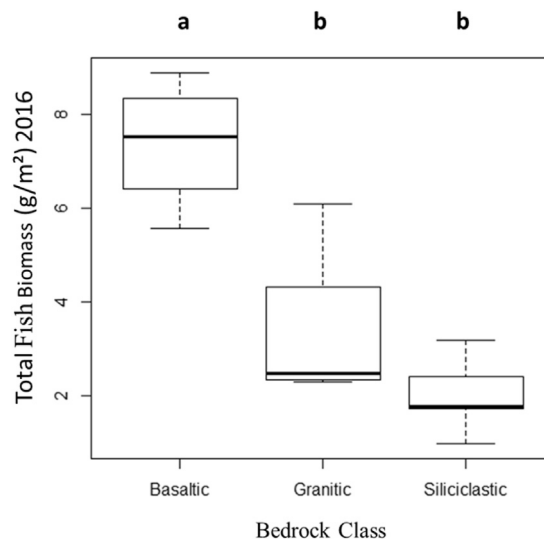


Fig. 5. Using ANOVA, significant differences in total fish biomass were observed between the three bedrock classes ($F(2) = 18.03, p < 0.001$). The statistical relationship between bedrock classes is denoted by letters.

Table 3

Akaike information criterion (AIC) produced by stepwise regression for the total fish biomass model.

Model	AIC
Median ANC + Maximum SO ₄ + Maximum NO ₃ + Stream Power + (Median ANC × Maximum SO ₄) + (Median ANC × Maximum NO ₃) + (Maximum SO ₄ × Maximum NO ₃)	1.27
Median ANC + Maximum SO ₄ + Maximum NO ₃ + Stream Power + (Median ANC × Maximum SO ₄) + (Median ANC × Maximum NO ₃)	0
Median ANC + Maximum SO ₄ + Maximum NO ₃ + Stream Power + (Median ANC × Maximum NO ₃)	−0.64

100-meter fish sampling reach. Though it is unlikely that non-native fish species impacted this study, the potential future impacts of non-native fish species on SHEN fish assemblages should be closely monitored.

Findings of this study indicate that water quality impacts can have persistent effects on fish species richness and biomass. Despite slow recovery in SHEN streams due to sulfate retention capacity of SHEN soils, minor reductions in sulfate and increases in ANC have resulted in substantial increases in fish species richness in well-buffered streams. These increases in fish species richness could represent the recovery of fish assemblages from stream acidification without the aid of active restoration methods, i.e. fish stocking or watershed liming. Previous research has modeled critical load targets focusing on relatively low ANC streams ($ANC < 100 \mu\text{eq/L}$) (Sullivan et al., 2008). The four basaltic streams investigated in this study suggest that acid deposition mitigation measures are also having a large impact on well-buffered streams ($ANC > 100 \mu\text{eq/L}$). Future assessments could interpret critical loads of acidifiers in terms of these well-buffered streams. In contrast to well buffered streams (basaltic), in poorly buffered streams (granitic/siliciclastic) in which decreases or small increases ($< 0.1 \mu\text{eq/L/yr}$) in ANC have been observed fish species richness has remained unchanged. These results underline the importance of existing restrictions on emissions of acidifying compounds and the need for continued monitoring and research into acid sensitive headwater streams in the eastern United States.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.gecco.2020.e01386>.

Supplemental Tables

Table S1

Location of SWAS water collection sites nearest the Shenandoah National Park boundary and fish sampling sites used during Bulger et al. (1995) and the current study.

Stream	SWAS Site Location	Fish Sampling Location	Sample Date
Madison Run	N 38°15'5.436"	N 38°15'30.276"	June 8, 2016
	W 78°44'49.56"	W 78°46'43.32"	
Meadow Run	N 38°9'31.32"	N 38°9'32.148"	June 6, 2016
	W 78°48'21.24"	W 78°48'42.48"	
Paine Run	N 38°11'54.9"	N 38°11'55.392"	June 14, 2016
	W 78°47'36.24"	W 78°47'36.24"	
Two-Mile Run	N 38°20'1.968"	N 38°20'3.192"	June 15, 2016
	W 78°40'16.284"	W 78°40'17.76"	
White Oak Run	N 38°15'2.664"	N 38°15'4.896"	June 21, 2016
	W 78°44'55.0681"	W 78°44'56.04"	
Brokenback Run	N 38°34'13.8"	N 38°34'12.72"	July 20, 2016
	W 78°18'15.84"	W 78°18'15.48"	
Hazel River	N 38°36'58.32"	N 38°36'55.404"	July 7, 2016
	W 78°15'49.878"	W 78°15'41.76"	
North Fork Dry Run	N 38°38'1.3921"	N 38°37'58.584"	June 1, 2016
	W 78°21'27.828"	W 78°21'28.8"	
Staunton River	N 38°26'40.596"	N 38°26'40.596"	June 29, 2016
	W 78°22'14.88"	W 78°22'18.12"	
Jeremy's Run	N 38°42'56.7721"	N 38°42'56.268"	July 27, 2016
	W 78°22'53.652"	W 78°22'53.04"	
Piney River	N 38°42'6.3359"	N 38°42'10.872"	June 27, 2016
	W 78°16'3.96"	W 78°16'7.32"	
North Fork Thornton River	N 38°41'34.6921"	N 38°41'42.252"	July 26, 2016
	W 78°16'26.616"	W 78°16'45.84"	
Rose River	N 38°30'55.692"	N 38°30'55.512"	July 18, 2016
	W 78°22'0.372"	W 78°21'59.04"	

Table S2

Fish species found in 13 study streams in Shenandoah National Park for Bulger et al., (1995) and the current study. (*) indicates a species added to the species list since the 1995 survey, (–) indicates a species present in the 1995 survey but not observed in the 2016 survey.

Stream	1995 (Bulger et al., 1995)	2016
Madison Run	Blacknose dace, Brook Trout, Creek chub, Fantail darter, Roseyside dace	Blacknose dace, Brook Trout, Fantail darter, Rosyside dace
Meadow Run	Brook Trout	Brook Trout
Paine Run	Blacknose dace, Brook Trout, Fantail darter	Blacknose dace, Brook Trout, Fantail darter
Two-Mile Run	Blacknose dace, Brook Trout	Blacknose dace, Brook Trout
White Oak Run	Blacknose dace, Brook Trout, Fantail darter (–)	Blacknose dace, Brook Trout
Brokenback Run	American eel, Blacknose dace, Brook Trout	American eel, Blacknose dace, Brook Trout
Hazel River	American eel, Blacknose dace, Brook Trout, Fallfish (–), Longnose dace, Rosyside dace(–)	American eel, Bluehead chub(*), Blacknose dace, Brook Trout, Longnose dace, Torrent sucker (*)
North Fork Dry Run	Blacknose dace, Brook Trout	Blacknose dace, Brook Trout
Staunton River	American eel, Blacknose dace, Brook Trout, Longnose dace(–), Torrent sucker	American eel, Bluehead chub(*), Blacknose dace, Brook Trout, Torrent sucker
Jeremy's Run	Blacknose dace, Brook Trout, Fantail darter, Longnose Dace, Mottled sculpin, Rosyside dace	

(continued on next page)

Table S2 (continued)

Stream	1995 (Bulger et al., 1995)	2016
North Fork Thornton River	American eel, Blacknose dace, Brook Trout, Longnose dace, Mottled sculpin, River chub(–), Rosyside dace, Tessellated darter, White sucker	Blacknose dace, Brook Trout, Central stoneroller(*), Creek chub(*), Fantail darter, Longnose dace, Mottled sculpin, Rosyside dace, White sucker(*) American brook lamprey(*), American eel, Bluehead chub(*), Blacknose dace, Brook Trout, Cutlip minnow(*), Longnose dace, Mountain redbelly dace(*), Mottled sculpin, Rosyside dace, Tessellated darter, Torrent sucker, White sucker
Piney River	American eel, Bluehead chub, Blacknose dace, Brook Trout, Creek chub(–), Longnose dace, Mottled sculpin	American eel, Bluehead chub, Blacknose dace, Brook Trout, Longnose dace, Mottled sculpin, Rosyside dace(*), Torrent sucker(*)
Rose River	American eel, Blacknose dace, Brook Trout, Brown trout, Longnose dace, Mottled sculpin, River chub, Torrent sucker	American eel, Bluehead chub(*), Blacknose dace, Brook Trout, Brown Trout, Longnose dace, Mottled sculpin, River chub, Rosyside dace(*), Torrent sucker

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