pH and Acid Anion Time Trends in Different Elevation Ranges in the Great Smoky Mountains National Park

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Abstract: Quarterly base flow water quality data collected from October, 1993 to November, 2002 at 90 stream sites in the Great Smoky Mountains National Park were used in step-wise multiple linear regression models to analyze pH, acid neutralizing capacity (ANC), and sulfate and nitrate long-term time trends. The potential predictor variables included cumulative Julian day, seasonality, elevation, basin slope, stream order, precipitation, surrogate streamflows, geology, and acid depositional fluxes. Modeling revealed statistically significant decreasing trends in pH and sulfate with time at lower elevations, but generally no long-term time trends in stream nitrate or ANC. The best forecasting models were chosen based on maximizing the r^2 of a holdout data set. If conditions remain the same and past trends continue, the forecasting models suggest that 30.0% of the sampling sites will reach pH values less than 6.0 in less than 10 years, 63.3% in less than 25 years, and 96.7% in less than 50 years. The pH forecasting models explain 65% of the variability in the holdout data.

DOI: 10.1061/(ASCE)0733-9372(2008)134:9(800)

CE Database subject headings: Acid rain; pH; Regression analysis; Time series analysis; Water quality; Monitoring; Elevation; Mountains.

Introduction

The Great Smoky Mountains National Park (GRSM) has more than 3,000 km (1,860 mi) of streams, including five streams designated as Outstanding National Resource Waters. GRSM streams support a great number of aquatic species, and its trout fisheries are considered some of the best in the eastern United States. The GRSM also receives some of the highest amounts of acid deposition amongst all national parks, and the pH of precipitation (Shubzda et al. 1995) is about 4.5 in the GRSM region (USEPA 1999). The acidic deposition raises serious concerns for stream impairment because the GRSM's geology lacks significant buffering capacity [96% of all monitored stream sites have acid neutralizing capacity (ANC) less than 200 $\mu eq/L$ and 59% have less than 50 $\mu eq/L$ and 21% have a base flow pH less than 6.0]. In comparison, Driscoll et al. (2001) stated that aquatic biota living in surface waters having a pH of less than 6, ANC less than 50 $\mu eq/L$, or aluminum concentration greater than 2 $\mu mol/L$ are at risk from surface water acidification. Sulfate and nitrogen are closely associated with acid deposition. Indeed, at least one high elevation watershed in the GRSM is believed to be in Stage 2 nitrogen saturation (Stoddard 1994), with elevated nitrate concentrations in those streams year round (Nodvin et al. 1995, van Miegroet et al. 2001). Importantly, some GRSM streams that once supported native brook trout populations as recently as 20 years ago no longer do, and acid deposition is suspected to have contributed to their extirpation.

Because of the potential impact of acid deposition, long-term base flow stream water quality monitoring began in 1993. Data are available from a core of 90 stream sites with enough historical record to assess long-term water quality trends (Fig. 1). The objectives of this study were to:

1. Determine if pH, ANC, nitrate, and sulfate are improving or degrading with time in select GRSM streams, i.e., to determine how much of the variability in water quality is explained by long term-time trends (hereafter referred to as time trends).
2. Determine if there are differences in time trends for pH, ANC, nitrate, and sulfate within different elevation zones.
3. Determine if statistically significant forecasting models for stream pH, ANC, nitrate, and sulfate can be developed.

Background

The 1970 and 1990 Amendments of the Clean Air Act (CAA) have resulted in declines of power plant emissions and conse-

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Note. Discussion open until February 1, 2009. Separate discussions must be submitted for individual papers. The manuscript for this paper was submitted for review and possible publication on February 6, 2006; approved on February 21, 2008. This paper is part of the ***Journal of Environmental Engineering***, Vol. 134, No. 9, September 1, 2008. ©ASCE, ISSN 0733-9372/2008/9-800–808/$25.00.

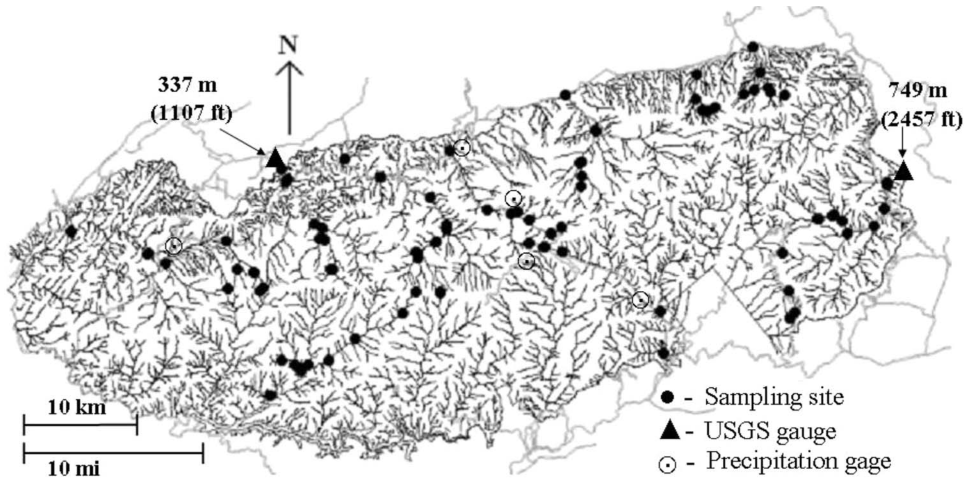

Fig. 1. Stream water quality monitoring sites in the GRSM

quent reductions in acidic deposition in the GRSM. In fact, based on regressions, the GRSM's National Atmospheric Deposition Program (NADP) site near the Elkmont campground has measured reductions in sulfate concentration from about 2.1 mg/L in 1980 to 1.1 mg/L in 2004 and pH has shown a corresponding rise from about 4.4 to 4.7 in wet only precipitation (NADP 2005). Depositional flux has not seen as much of an improvement as have concentrations. Sulfate depositional flux rate decreased from 28 to 20 kg/ha/year from 1980 to 2004. This smaller percentage decline is partly due to a dry period in the 1980s that reduced the total deposition. Interestingly, the proton ($[H^+]$) deposition rate (kg/ha) did not show any trend from 1980 to 1998, and then a drop from about 0.45 to about 0.37 kg/ha the last 6 years. Nitrate concentration has decreased from about 15 to 12 μeq/L from 1980 to 2004, whereas nitrate and total inorganic nitrogen deposition rate has remained about flat. A high elevation deposition monitoring site at Noland Divide in the GRSM has only 12 years of record, but shows similar trends.

Several sites in the United States and Europe have a long enough record of stream water quality in acid deposition impacted and sensitive areas to statistically determine whether water quality has responded to air quality improvements. The Hubbard Brook Experimental Forest site has measured a decline in the depositional flux of sulfate since 1960, and roughly flat nitrate deposition since 1980 (Gbondo-Tugbawa and Driscoll 2002). Stream sulfate concentration has responded to these declines in sulfate deposition by decreasing roughly 30% from 1964 to 1998, and ANC has shown statistically significant increasing trends of 1.2:eq/L/year at the lowest elevation and 2.5:eq/L/year at the highest. However, stream pH data at Hubbard Brook for 1982–2000 indicates either very small or statistically insignificant time trends (Palmer et al. 2004).

Webb et al. (2004) analyzed 1988–2001 data for streams in western Virginia and in Shenandoah National Park (SNP). Sulfate deposition declined roughly 40% from 1985 to 2000, but there was no statistically significant change in median stream concentration of ANC, sulfate, nitrate, and total base cations, except for a 0.17:ed/L/year increase in ANC and a 0.23:ed/L/year decrease in sulfate in SNP streams. Both sets of streams showed a 0.007 :ed/L/year increase in hydrogen ion. Interpretation of the trends was complicated by defoliation by gypsy moth larva.

Burns et al. (2006) evaluated surface water chemistry trends in Catskill streams and Adirondack lakes. Interestingly, they found decreasing trends in sulfate, nitrate, base cations, and H^+ in precipitation during 1984–2001, but few significant trends for 1992–2001. They did find decreasing trends in sulfate at all surface water sites and decreasing nitrate, base cations, and hydrogen ion at most sites. However, ANC increased significantly in only half of the 12 Adirondack lakes and in only one of the five Catskill streams. Flow correction caused several of the trends for nitrate and ANC to become nonsignificant. The authors concluded that local scale processes partly driven by climate are affecting trends in these two regions.

Stoddard et al. (1999) analyzed surface water recovery trends in North America and Europe in response to decreases in acidification. These authors focused on sites with ANC less than 200:eq/L as these sites should benefit most from decreasing acidification. They concluded that there was no regional recovery in ANC in the 1990s, based on data from Maine/Atlantic Canada, south central Ontario, U.S. midwest, Vermont/Quebec, and Adirondacks/Catskills. The authors attributed this lack of recovery, despite decreases in deposition of acid anions, to declines in base cations due to either declines in base cation deposition and/or base cation depletion of watershed soils. They further suggested that there may be a lag time before streams recover. According to Webb et al. (2004), Kahl attributed the lack of response to the delaying effect of sulfur retention in watershed soils. Webb et al. further state that northeastern U.S. watersheds do not retain significant sulfur, whereas southeastern watersheds do.

Not surprisingly, an EPA report (Stoddard et al. 2003) reached similar conclusions. The report concluded that alkalinity increased in the Adirondacks, the Northern Appalachian Plateau, and the Upper Midwest at a rate of 1:ed/L/year and was limited by declines in base cations. In the Adirondacks and the Northern Appalachians, pH increased significantly in the 1990s. However, regional surface water ANC did not change significantly in New England or in the Ridge/Blue Ridge Province of the Appalachians. The report warned that some of the improvements in ANC in the Adirondacks and Northern Appalachian Plateau may have been caused by changes in nitrate, presumably from forest maturation, which would not be expected to continue. The report expected stream ANC and pH to ultimately increase in response to decreasing acidic atmospheric deposition. However, Sullivan et al. (2004) could not confirm the EPA's conclusion. These authors modeled the impact of atmospheric deposition scenarios and concluded that "the percent of potentially acid-sensitive streams

Table 1. Descriptive Statistics of Water Quality in the GRSM

Class	Elevation	pH			ANC			Nitrate			Sulfate		
		Mean	Median	π	Mean	Median	π	Mean	Median	π	Mean	Median	π
2	305–457 m (1,000–1,500 ft)	6.66	6.64	0.32	145.8	102.8	140.7	10.51	7.05	9.37	44.18	40.43	12.14
3	457–610 m (1,500–2,000 ft)	6.57	6.47	0.4	201	67.08	370.1	11.5	11.26	7.56	35.63	32.78	12.86
4	610–762 m (2,000–2,500 ft)	6.34	6.39	0.3	59.63	59.71	38.2	12.8	8.99	11.98	32.84	28.66	17.58
5	762–914 m (2,500–3,000 ft)	6.30	6.35	0.3	51.62	45.77	32.3	18.79	16.64	14.6	36.77	28.75	20.19
6	914–1,067 m (3,000–3,500 ft)	6.12	6.17	0.34	30.97	26.69	23.35	23.88	23.77	13.05	42.94	36.79	24.53
7	1,067–1,219 m (3,500–4,000 ft)	6.18	6.17	0.28	41.47	27.27	34.82	35.23	34.85	9.99	71.19	70.67	19.49
8	1,219–1,372 m (4,000–4,500 ft)	5.85	5.85	0.46	22.32	17.63	40.18	34.69	36.94	17.09	74.8	65.83	55.44
9	1,372–1,524 m (4,500–5,000 ft)	5.74	5.95	0.68	31.62	33.99	34.23	34.58	30.52	19.96	72.8	35.69	108.90
10	1,524–1,676 m (5,000–5,500 ft)	5.66	5.8	0.49	18.1	18.05	15.1	49.91	47.34	13.81	37.7	28.63	17.72
11	>1,676 m (>5,500 ft)	5.11	5.05	0.38	2.14	0.34	18.22	64.31	67.41	22.52	38.04	30.57	17.92

having chemistry that is chronically unsuitable for brook trout would increase slightly between 1995 and 2040 under all except the most restrictive emissions control strategy."

Methods

Database

In order to test whether streams in the GRSM are improving as a result of decreased atmospheric deposition, base flow water quality sampling data were analyzed from 90 sites. The samples represent base flow in that they are biased against episodic events and lack the highest 5% of flows. Table 1 summarizes water quality from these sites by several arbitrary elevation classes used historically by the GRSM. Note in Table 1 that there are significant elevational gradients for pH, ANC, and sulfate. The water quality samples were collected approximately quarterly from October 1993 to November 2002 (Robinson et al. 2003) and analyzed for lab pH, ANC, sulfate, and nitrate. Sampling was generally done in late March, late May, late August, and late October, except that sampling was moved to late November in 2000 in order to occur after leaf fall. The pH was measured in the laboratory within 48 h of sampling due to the difficulty of field pH measurements in low conductivity water. ANC was measured by auto-titrator within 48 h. Samples were stored at 4°C and later analyzed for sulfate and nitrate by ion chromatography. Serial independence of the sampling data is required in order to use certain statistical analyses. Based on autocorrelation analysis of a high elevation site sampled biweekly, samples should be independent for all analytes as long as they are collected no more than ten times per year (Odom 2003). As base flow samples were collected no more than six times per year, they should be serially independent.

The water quality database was combined with data on the morphology, geology, and vegetation of each watershed, precipitation, surrogate streamflow, and atmospheric deposition in order to explain as much of the variability in water quality as possible. The rationale for including these variables in evaluating time trends is that environmental data generally show considerable variability. If water quality (i.e., pH, ANC, sulfate, and nitrate) is regressed against only time, then the coefficient of determination, r^2, will be very low because much of the data variability is unexplained. This in turn raises questions about the model's applicability, and moreover, leaves open the possibility that other predictive variables show time trends as well (e.g., precipitation and streamflow). Including watershed and hydrologic factors produces a model that explains more of the variability in the data and has a higher r^2. Table 2 lists all the independent variables in the combined database. The sine and cosine terms listed in Table 2 appear as additive terms in the regression model, i.e., $b_i \sin(Y)+b_j \sin(Y)$, with Y being the fraction of the year times two pi radians. For example, April 1 is one-quarter fraction of the year and thus Y is $\pi/2$. The sum of these two trigonometric functions allows seasonality to be modeled as a sinusoidal function including a phase angle shift (Helsel and Hirsch 1992). In Table 2, the mean daily streamflow at the Little River USGS gauge near the northwestern GRSM boundary and the Cataloochee River USGS gauge at the southeastern GRSM boundary were used as surrogate streamflows. Daily precipitation values were obtained for each sampling site from the closest of five National Weather Service weather stations in the GRSM for the day of sampling to 5 days prior to sampling to account for antecedent conditions. See Fig. 1 for sample site and gauge locations. Only two geology variables were found to be important based on preliminary analyses: the percentage of limestone bedrock and the percentage of Anakeesta bedrock in the watershed as listed in Table 2. Anakeesta has a significant fraction of sulfidic mineralogy.

Statistical Analyses

Stepwise multiple linear regression with SPSS (SPSS 1999) was used to determine whether time was a significant predictor of pH, ANC, sulfate, or nitrate. Regression is a valid method for testing time trends while compensating for the effects of other variables in a single-step process by including them in the model (Helsel and Hirsch 1992). Independent variables entered the regression model if the probability of the partial F statistic was less than or equal to 0.05 and left the model if the partial F statistic probability was greater than or equal to 0.10. Only models with significance levels less than or equal to a p value of 0.05 were considered. All independent variables in the models were significant at a p value of 0.05.

Multicollinearity was addressed using the variance inflation factor (VIF) and informal multicollinearity diagnostics such as Kendall's tau and Pearson bivariate correlations. A VIF value over 10 is frequently taken as an indication that multicollinearity may be unduly influencing the least-squares estimates (Helsel and Hirsch 1992; Neter et al. 1996). Independent variables with VIF >10 were removed from the models in reverse order of their explanatory ability in order to produce the best adjusted r^2 values with minimal multicollinearity. Individual observations that had

Table 2. Description of Regression Variable

Variable	Description	Value range
Cumulative Julian date	Julian date counted from Jan. 1 1900	34,678–37,213 days
sin(θ), cosine(θ)	θ=2π* (fraction of a year), sine and cosine functions used to model seasonal fluctuations in water quality	−1 to 1
Elevation (m)	Elevation of sampling site in meters above mean sea level (MSL)	335–1,689 m
Precipitation code	0—no precipitation in the 48 h preceding sample collection, 1—some precipitation	0, 1
Little River flow (cfs), Cataloochee flow (cfs)	Mean daily flow from USGS gauge for sampling date	18–1,160 cfs
Number of days since last measurable precipitation (days)	The number of days preceding sample collection since a measurable precipitation occurred at the closest of the five National Weather Service weather stations within the GRSM	0–32 days
Stream order	Stream order for sampling site using Hortons method	1–5
Average basin slope (%)	Average land slope of the contributing area	25–72%
% limestone, % Anakeesta (%)	Percentage of contributing area (geology type); note: Geology information unavailable for sites in southwestern GRSM	0–21% (limestone) 0–100% (anakeesta)
Closest precipitation (0)	The precipitation at the closest NWS weather station to the sampling site in inches for the same day as sample collection, 1 day prior, 2 days prior, 3 days prior, 4 days prior, and 5 days prior	0–3 in.
Closest precipitation (1)		
Closest precipitation (2)		
Closest precipitation (3)		
Closest precipitation (4)		
Closest precipitation (5)		
Monthly TF precipitation [cm (in.)]	Data obtained from an intensive monitoring site at the Noland Divide watershed within the GRSM: TF=through fall, i.e., precipitation collected under forest canopy, and OS=open site precipitation collected out in the open; all fluxes in kg/ha/year	2.5–51 TF cm (1–20 in.)
Monthly TF flux NO_3^-		7–181 TF NO_3^-
Monthly TF flux SO_4^{2-}		61–320 TF SO_4^{2-}
Monthly TF flux H^+		27–254 TF H^+
Monthly OS precipitation [cm (in.)]		5.1–53 OS cm (2–21 in.)
Monthly OS flux NO_3^-		0–56 OS NO_3^-
Monthly OS flux SO_4^{2-}		11–259 OS SO_4^{2-}
Monthly OS flux H^+ (kg/ha/year)		8–112 OS H^+ kg/ha/year

high leverage on the regression models and were large outliers were evaluated by Cook's D statistic and by inspecting partial regression plots, which can also reveal nonlinearity (Fox 1997). If removal of that observation could be well justified, and its removal improved the amount of variability explained by the model, then it was removed.

Curvature, randomness, and heteroscedasticity of the residuals were checked by plotting each of the independent variables. Normality of the residuals was checked using the Shapiro–Wilk test and observation of the normal probability plot. Partial regression or leverage plots were also observed to ensure a linear relationship exists between the independent variable and the dependent variable when the other independent variables have been accounted for.

The reasonableness of predicted constituent values was also checked (e.g., the model should not predict negative values for pH). The principle of parsimony was also used in the model selection process. This principle is used for choosing among models and means that, everything else being equal, a simpler model is better (DeLurgio 1998). Therefore, the simplest model that explains a comparable amount of the variability was chosen as the best model.

The best pH forecasting models were developed using the same procedures as mentioned earlier, but the 2002 data were used as a holdout data set. Stepwise regression was run again on the 1993—2001 data, but this time an r^2 was calculated at each step for the holdout, i.e., 2002, data set. The stepwise regression model with the highest r^2 for the holdout data set was used as the best temporal forecasting model. Using a holdout data set is good practice in forecasting because it helps to prevent overfitting the model, i.e., developing a model that fits the data set very well, but does not predict new data very well (John et al. 2001).

Results and Discussion

Table 3 presents the best model obtained for each water quality constituent, as well as the adjusted r^2 and overall model p value for data from all sampling sites within the GRSM. Adjusted r^2's for pH and ANC were 0.706 and 0.856, respectively. If individual sites are analyzed by bivariate linear regressions of pH, ANC, nitrate, or sulfate versus time, then 62% of the individual sites saw decreasing pH with time, 49% decreasing ANC, 73% decreasing nitrate, and 79% decreasing sulfate. The 95% confidence intervals for these are 52–72%, 40–58%, 65–81%, and 71–87%, respectively. These results are generally consistent with Table 4. However, the results can be misinterpreted. For example, the decline in nitrate is probably due to an overall decline in streamflow and precipitation over the time period. Also, most of these individual site bivariate regressions were not statistically significant because the variability of, e.g., pH, is much greater than the trend level for the number of data points available at each site. Both problems can be overcome by combining the data from all sites or from sites in particular classes and then performing multiple linear regression, as was done in this work.

Table 3. Regression Model Results for All Sampling Sites

Constituent (n)	Model	Adjusted r^2	Model p
pH (1,439)	9.10+(4.08E−02*%limestone)+(−1.47E−02*average basin slope in%) +(−3.64E−04*Little River flow in cfs)+(−7.23E−04*elevation in meters) +(**−4.38E−05*cumulative Julian date**)+(−8.90E−02*cosine theta) +(−6.03E−02* closest precipitation (5) in inches)	0.706	<0.001
ANC (μeq/L) (1,441)	110.70+(5.48E+01*%limestone)+(−7.57E−02*Little River flow in cfs) +(−2.82E+01*sine theta)+(−5.63E+01*closest precipitation (0) in inches) +(1.73E+01*stream order)+(−2.09E+00*average basin slope in%)	0.856	<0.001
Nitrate (μeq/L) (1,370)	−18.23+(1.50E−02*Little River flow in cfs)+(5.49E−01*average basin slope in%) +(3.62E−02*total monthly OS flux of H)	0.272	<0.001
Sulfate (μeq/L) (1,429)	29.17+(−5.30E−02*elevation in meters)+(6.32E−01*average basin slope in%) +(2.28E−02*Little River flow in cfs)+(−4.98E+00*sine theta) +(4.11E+00*closest precipitation (5) in inches) +(4.79E+00*closest precipitation (3) in inches)	0.238	<0.001

Note: Bold indicates time trend predictor.

pH and ANC

Fig. 2 shows the measured pH versus the pH predicted by the regression model in Table 3. The pH regression model shows a time trend of base flow stream average pH decreasing at 0.016 units/year, whereas the ANC was not found with significant time trend. Although the objectives of this paper are only to discern time trends, a short discussion of the other predictive variables in the regression models is warranted in order to lend credence to the model.

The regression model indicates a lower pH with increasing basin slope, which is consistent with the observations of Clow and Sueker (2000), who hypothesized that steeper slopes had shallower soils and more runoff, and thus less chance of attenuation of acidic deposition by soil. Annual precipitation and run-off patterns can influence hydrological flow paths from shallow and short periods of soil contact to deep and relatively long soil–groundwater contact, which also influences the potential for attenuation of acidic deposition (Potter et al. 1988; Mulholland 2004). This interpretation is further supported by the fact that the regression model showed a lower pH with higher Little River flow and higher recent precipitation. Therefore, consistent with effects from acidic deposition, stream acidification was found during periods with greater precipitation and higher streamflows. This is discussed further in the following with ANC.

The model also shows a strong elevation trend of −0.72 pH unit/1,000 m increase in elevation. Given that there is a 1,300 m (4,270 ft) difference in elevation within the GRSM, this means that pH should be about one unit lower at higher elevations

Table 4. Time Trend Results for Specific Elevation Classes

Elevation class	Elevation range m (ft)	Number of sites (data points)	Julian date coefficient, μeq/L/year or pH units/year (model adjusted r^2) ANC	Nitrate	Sulfate	pH
1	<305 m (<1,000 ft)	0	NA	NA	NA	NA
2	305–457 m (1,000–1,500 ft)	7 (175)	−5.91 (0.734)	None (0.687)	−0.836 (0.551)	−0.0127 (0.670)
3	457–610 m (1,500–2,000 ft)	13 (234)	None (0.881)	None (0.362)	−1.31 (0.115)	−0.0186 (0.715)
4	610–762 m (2,000–2,500 ft)	16 (289)	None (0.609)	None (0.484)	−1.15 (0.649)	−0.0260 (0.775)
5	762–914 m (2,500–3,000 ft)	18 (305)	−2.08 (0.616)	None (0.489)	−0.898 (0.834)	−0.0194 (0.610)
6	914–1,067 m (3,000–3,500 ft)	13 (307)	None (0.314)	−0.566 (0.257)	−0.832 (0.781)	−0.0175 (0.414)
7	1,067–1,219 m (3,500–4,000 ft)	4 (71)	None (0.610)	None (0.333)	None (0.593)	None (0.697)
8	1,219–1,372 m (4,000–4,500 ft)	6 (90)	None (0.445)	None (0.441)	None (0.447)	None (0.616)
9	1,372–1,524 m (4,500–5,000 ft)	7 (109)	−5.08 (0.308)	None (0.562)	None (0.279)	−0.0905 (0.506)
10	1,524–1,676 m (5,000–5,500 ft)	3 (38)	None (0.237)	None (0.177)	None (0.185)	None (0.299)
11	>1,676 m (>5,500 ft)	3 (28)	None (NA)	None (NA)	None (NA)	None (NA)

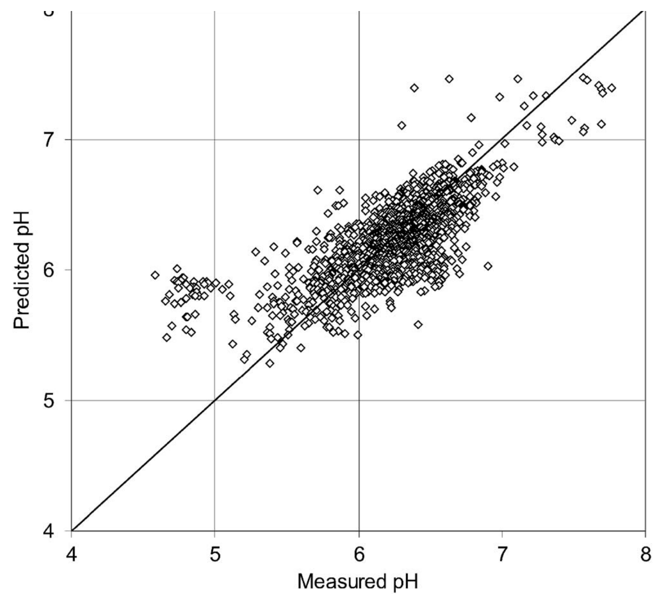

Fig. 2. Plot of actual versus predicted pH values for all elevation classes

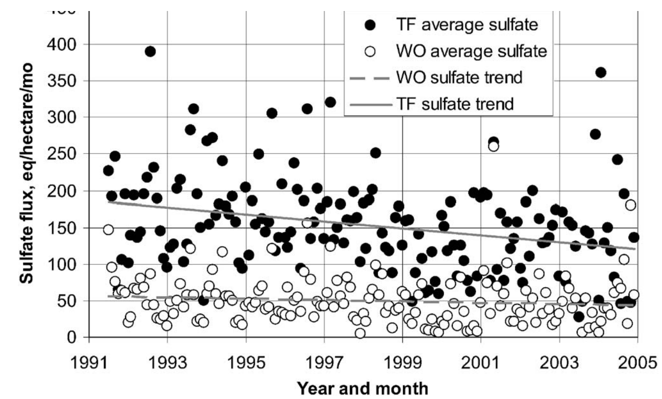

Fig. 3. Throughfall (TF) and open site sulfate trends at Noland Divide

(1,725 m or 5,660 ft) compared to lower (425 m or 1,390 ft). This is consistent with observations in the GRSM, and that found by others (Cook et al. 1994; Fitzhugh et al. 1999; Sullivan et al. 2007). Seasonality is indicated in the model by the "$8.90 \times 10^{-2} \cos(Y)$" term. As Y=fraction of the year times 2π, $\cos(Y)$ has a value of 1 on Jan. 1 ($Y=0$) and a value of -1 on July 1 ($Y=\pi$). Hence, the pH will be lowest on January 1 and highest on July 1, all else being equal. The regression model could have included a $\sin(Y)$ term to reflect a different phase angle, but did not.

Regressions were also performed on the proton concentration, $[H^+]$, but the r^2 values were worse, near 0.5, with nonnormally distributed residuals. Therefore, a log transformation of $[H^+]$ (i.e., pH) greatly improves the regression results.

Except for time as a predictive variable, ANC and pH models were similar and both strongly influenced by percentage of limestone bedrock, average basin slope, Little River flow, and precipitation. Also, the ANC model indicated lower ANC with lower stream order, Seasonality is also found in the ANC model by the $-28.2 \sin(Y)$ term. Deviney et al. (2006) also found geology, watershed elevation, and streamflows as the dominant variables to predict ANC. Webb et al. (2004) and Burns et al. (2006) observed moderately increasing base flow ANC over the past decade although precipitation sulfate concentrations have declined. This study found a slight decline in ANC or no trend for various elevation classes (Table 4).

Watershed biogeochemical processes appear to influence base flow ANC, although one would expect declining ANC over time as a response to declines in atmospheric deposition of sulfate (Copper et al. 2004; Wright et al. 2006; Sullivan et al. 2007). Largely unknown is the influence of sulfate retention in the soil (Lawrence 2002), and the influence of other ion concentration trends in soil chemistry such as base cation depletion and nitrogen assimilation by vegetation (Fernandez et al. 2003; Chen et al. 2004; Palmer et al. 2004). Sulfate retention in soils and nitrate assimilation over time would tend to increase stream ANC, whereas reduced base cation inputs to the stream from soil cation depletion would decrease ANC. In-stream nitrate is strongly influenced by periphyton uptake, whereby the uptake rate is dependent on season and can be rapid during spring and autumn months (Roberts and Mulholland 2007). Another watershed process that appears to be important to stream acidification is input rates of organic acids, also seasonally influenced with highest input rates occurring during summer (Inamdar et al. 2004; Wellington and Driscoll 2004). How these biogeochemical processes influence stream pH and ANC is watershed dependent (Sullivan et al. 2007). For the GRSM streams showing concurrent decline of pH and ANC over time, the regression models suggest a possibility that base cation depletion and increases in organic acid concentrations may be occurring, particularly with the models also showing sulfate declines (discussed in the following). However, these suggested causes of GRSM acidification must be viewed as highly speculative without analysis that includes base cations and dissolved organic carbon.

Nitrate and Sulfate

Neither nitrate nor sulfate stream concentrations show any time trends in the regression model based on the entire data set. Nitrate and sulfate concentrations were strongly influenced by basin slope and Little River flow, and sulfate was additionally influenced by elevation, precipitation, and seasonality (Table 3). The influence of precipitation and streamflow on nitrate and sulfate stream concentrations is evident, and is consistent with pH and ANC results discussed earlier. It should also be noted that a simple bivariate regression of Julian date versus stream sulfate concentration for all sites shows sulfate concentration is decreasing at a rate of 2.5% per year ($p<0.001$). This compares to a decline in sulfate depositional flux of 4.1% per year ($p<0.001$), which is driven by a precipitation volume decrease of 4.3% per year (0.007) as there is no statistical change in sulfate concentration in the throughfall ($p=0.98$). Similarly, the lack of a time trend in stream nitrate concentration is against a background of no significant time trend in throughfall total inorganic nitrogen flux for this time period, although precipitation is declining as noted earlier, nitrate throughfall concentration shows no time trend ($p=0.66$) but throughfall ammonia is increasing 10.9% per year ($p=0.007$).

Interestingly, open site monthly H^+ flux (precipitation volume times mean hydrogen ion concentration at the acid deposition monitoring site) was a predictor of nitrate stream concentration, but was not a predictor of stream pH, ANC or sulfate. The open site monthly hydrogen ion flux did not have a statistically

Table 3. Model Results for Elevation Classes 2–6 with and without Using a Holdout Data Set to Maximize r^2

Constituent (n)	Model	Adjusted r^2	Model p	Adjusted r^2 (2002 data)
pH Full model (1,184)	8.99+(−2.29E−02*average basin slope in %)+(6.55E−02*stream order)+(3.37E−02*% limestone) +(**−4.58E−05*cumulative Julian date**)+(−9.73E−02*closest precipitation (1) in inches) +(−2.02E−04*elevation in meters)+(−9.72E−02*closest precipitation (2) in inches) +(−5.50E−02*sine theta)+(−4.99E−02*cosine theta)+(−1.03E−01*closest precipitation (0) in inches) +(−3.51E−02*closest precipitation (5) in inches)	0.678	<0.001	0.323
pH model maximizing r^2 holdout (1,184)	8.90+(−2.45E−02*average basin slope in %)+(9.46E−02*stream order) +(−3.80E−04*Little River flow in cfs)+(3.35E−02*% limestone) +(**−4.70E−05*cumulative Julian date**)	0.650	<0.001	0.322

Note: Bold indicates time trend predictors.

significant Kendall's tau (τ) correlation with either pH (p=0.349, τ=0.016) or sulfate (p=0.195, τ=−0.022), but did have a statistically significant correlation with ANC (p=0.002, τ=−0.053) and nitrate (p<0.001, τ=0.097). It is possible that open site H^+ flux is a surrogate for precipitation and seasonality. Cronan and Schofield (1990) did find elevated leaching of nitrate in acid sensitive soils with anion additions. Time trends for sulfate were found to highly dependent on elevation (discussed in the following), but is consistent with Burns et al. (2006). Burns et al. (2006) suggest that sulfate declines are a result of depletion from loadings retained in the soils when atmospheric inputs were greater.

Streamflow as a Predictor of pH, ANC, Nitrate, and Sulfate

Although the focus of this paper is on time trends, adjustment for streamflow is very important and its association with water quality warrants discussion. Analyses show that pH, ANC, nitrate, and sulfate are statistically significantly correlated (p <0.05) with the streamflow with Kendall's tau values of −0.14, −0.22, 0.11, and 0.03, respectively, for the Little River and −0.12, −0.20, 0.09, and 0.01 for the Cataloochee, although the last value, 0.01, was not significant at p <0.05. There are also statistically significant correlations of pH with ANC, nitrate, and sulfate (0.67, −0.41, and −0.23, respectively). Hence, lower pH and ANC are associated with higher sulfate and nitrate, and also, lower pH and ANC and higher sulfate and nitrate are associated with higher streamflow. An understanding of the relationship between streamflow and water quality is aided by the following points. One year of storm event sampling near the lower end of a 124 km^2 (48 mi^2) watershed ranging in elevation from 418 to 2020 m (1,370 to 6,621 ft) showed that the mean nitrate and sulfate in the wet only precipitation were 30.4 μeq NO_3^-/L and 51.2 μeq SO_4^{2-}/L, which were nearly the same as the average nitrate and sulfate in storm event stream samples, 31.0 μeq NO_3^-/L and 48.6 μeq SO_4^{2-}/L. Also, 15 min pH data from a limited number of sites show consistent pH depressions of 0.5–2.0 units during storm events (Robinson and Roby 2006). Additionally, the GRSM has very little carbonate geology and thus limited capacity to neutralize acid deposition (King et al. 1968).

The regression models do show that watersheds with steeper slopes produce lower stream pH. This is presumably because steeper slopes have shallower soils and thus less ability to interact with and neutralize acid precipitation, These points together lead the writers to believe that greater amounts of precipitation, which is acidic in the GRSM region, causes greater amounts of acidity, sulfate, and nitrate and less ANC to enter streams, causing an association of these analytes with streamflow.

Results by Elevation Class

GRSM watersheds show distinct differences in geology and morphology with elevation (e.g., steeper slopes at higher elevations). Also, different fish species are more predominant in different elevation ranges. In order to evaluate differences in time trends with elevation, the sites were grouped into arbitrary 1,000 ft elevation classes (Table 4). Regression analyses were performed separately on each elevation class. Table 4 summarizes the results for the time trend coefficient in the models. All regression models for Elevation Classes 2–9 were significant at a p value <0.001 except for Class 10, which were significant at a p value <0.05. The adjusted r^2 values given in Table 4 correspond to the multivariate regression model in each case. Based on these regression derived time trends in Table 4, pH is decreasing at a rate of −0.0127 to −0.0260 pH units/year for Elevation Classes 2–6 (305–1,070 m or 1,000–3,500 ft) but there is very little time trend at higher elevations (>3,500 ft). The regressions also show time trends of declining sulfate at lower elevations but generally no time trends for nitrate, which is consistent with results the above-mentioned ANC results were somewhat mixed, but the few significant ANC time trends were declining rather than improving, which is consistent with pH. The time trend of decreasing sulfate at lower elevations is consistent with declining sulfate deposition as shown in Fig. 3 for Noland Divide deposition data, but it is unknown why there is no trend at higher elevations. Differences in time trends for pH, ANC, nitrate, and sulfate among elevation classes suggest complex biogeochemical processes influence individual watersheds, such as soil properties, vegetation, precipitation volumes, and varying sulfate and nitrate atmospheric inputs. In general, the regression models generally had a similar structure to those in Table 3, with the most significant variables being basin slope, Little River flow rate, limestone, and precipitation. The decline in pH and sulfate with no significant change in ANC is seemingly contradictory. Chemically, other cations must be decreasing and/or other anions increasing. The magnesium and calcium data are insufficient over the years of record to determine their ability to account for the discrepancy and neither sodium nor potassium show a significant time dependence. However, chloride does show a significant increase with time of the same order as hydrogen but not enough to compensate for the decline in sulfate.

Table 6. Time to Significant pH Values for Elevation Classes 2–6 Based on Regression Models in Table 5

Elevation class	Elevation in meters (ft)	Median pH	pH prediction model		
			Decrease in median pH per year	Time to median pH 6.0 (years)	Time to median pH 5.0 (years)
2	305–457 (1,000–1,500)	6.58	−0.017042	34.0	92.7
3	457–610 (1,500–2,000)	6.40	−0.017042	23.5	82.1
4	610–762 (2,000–2,500)	6.28	−0.017042	16.4	75.1
5	762–914 (2,500–3,000)	6.31	−0.017042	18.2	76.9
6	914–1,067 (3,000–3,500)	6.16	−0.017042	9.4	68.1

pH Forecasting

GRSM management is very concerned about the potential impact of continued acid deposition and what the future stream pH will be if current trends continue. Specifically, it was desired to forecast the time to reach target pH levels of 6.0 and 5.0 in GRSM streams. Based on a literature review (Neff 2007), a pH of 6 was chosen as an approximate threshold pH for biological effects on fish, and a pH of 5 as an approximate threshold for mortality. It is not possible to identify precisely the threshold levels for toxic pH effects on trout because of many complexities such as species, age, egg versus fry versus adult, background water quality, exposure duration, etc. The base flow pH levels of 5.0 and 6.0 were chosen in Table 6 as round numbers. A pH above 6.0 should not cause much toxic concern, whereas pH levels from 5 to 6 can be toxic in the presence of aluminum above 0.2 mg/L and can be harmful to eggs and fry in very soft waters in the lower end of the range, and pH levels below 5 create increasingly serious toxicity. Based on the pH time trends in Table 4, Elevation Classes 2–6 (1,000−3,500 ft) showed similar decreasing trends and similar models, so these classes were combined to have greater statistical power. These elevations also contain the majority of stream miles in the GRSM. As discussed earlier, the forecasting model was determined by maximizing the adjusted r^2 of the holdout data set, which produced an r^2 only slightly less than without maximizing holdout r^2. This model also had fewer variables than one produced without using a holdout data set, thus supporting the principle of parsimony (as discussed earlier) in time series modeling. Table 5 shows results for models with and without maximizing the holdout r^2 and shows little difference in time trend between models. Table 6 shows forecasted times to reach pH 6.0 and 5.0 if present trends continue and shows that, on average, streams in elevation ranges from 305 to 1067 m (1,000 to 3,500 ft) could reach pH 6.0 within 10−34 years and reach pH 5.0 in 69−93 years. There are many caveats about forecasting pH, but regardless, the trend is not in the right direction and could ultimately impact GRSM fisheries.

Conclusions

1. Time trends for pH, ANC, nitrate, and sulfate in streams of the GRSM were assessed with regression models using hydrologic data, watershed characteristics, and time as predictor variables. The regression models for all sites explained 71, 86, 27, and 24% of the variability in pH, ANC, nitrate, and sulfate, respectively. Outcomes from this study suggest that soil retention of sulfate and vegetation assimilation of nitrate were potentially dominant biogeochemical processes in GRSM streams. A pH forecasting model for lower elevation sites was developed with an r^2 of 0.65 for 2002 data used as a holdout data set.
2. Based on the regression results, base flow stream pH has not yet shown an upward trend despite improvements in acidic deposition. The time trend is a decreasing pH at lower elevations and stable pH at higher elevations. The pH forecasting model for elevations 305−1,070 m (1,000−3,500 ft) (1067 m) predicts that median pH values will reach 6.0 in less than 34 years if current statistical trends continue. Over half of the sampling sites in this same elevation range are predicted to reach pH 6.0 in less than 25 years. In elevation ranges where there was a statistically significant pH decline, the rate was from −0.013 to −0.091 pH units/year. This compares with a rate of pH decline of about −0.01 pH units/years in Shenandoah National Park (Webb et al., 2004), based on a proton increase of 0.007 μeq/year at a median pH of 6.5.
3. Regression results for ANC generally did not show time trends. The few trends seen for specific elevation ranges were declines on the order of −1 μeq/L/year. The results of this study for pH and ANC are consistent with others (Gbondo-Tugbuwa and Driscoll 2002; Palmer et al., 2004; Stoddard et al., 1999; USEPA 2003). Chen et al. (2004) suggest this phenomenon may be due to base cation depletion in soils.
4. Sulfate is decreasing at a rate of −0.83 to −1.3 μeq/L/year at elevations less than 3,500 ft consistent with decreasing atmospheric sulfate deposition. These rates compare with the −1.2 μeq/L/year (low elevation) to −2.5 μeq/L/year (high elevation) rates seen at Hubbard Brook (Gbondo-Tugbawa and Driscoll, 2002). Basin slope, elevation, and precipitation appear to strongly influence stream sulfate over the time variable. Although this regression outcome did not recognize sulfate as a dominant variable the observed decreasing rates may suggest that soil desorption processes may influence stream water chemistry.
5. Nitrate stream concentration generally did not show any statistical time trends.

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