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Increased River Alkalinization in the Eastern U.S.

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Supporting Information

ABSTRACT: The interaction between human activities and watershed geology is accelerating long-term changes in the carbon cycle of rivers. We evaluated changes in bicarbonate alkalinity, a product of chemical weathering, and tested for long-term trends at 97 sites in the eastern United States draining over 260 000 km^2. We observed statistically significant increasing trends in alkalinity at 62 of the 97 sites, while remaining sites exhibited no significant decreasing trends. Over 50% of study sites also had statistically significant increasing trends in concentrations of calcium (another product of chemical weathering) where data were available. River alkalinization rates were significantly related to watershed carbonate lithology, acid deposition, and topography. These three variables explained ~40% of variation in river alkalinization rates. The strongest predictor of river alkalinization rates was carbonate lithology. The most rapid rates of river alkalinization occurred at sites with highest inputs of acid deposition and highest elevation. The rise of alkalinity in many rivers throughout the Eastern U.S. suggests human-accelerated chemical weathering, in addition to previously documented impacts of mining and land use. Increased river alkalinization has major environmental implications including impacts on water hardness and salinization of drinking water, alterations of air−water exchange of CO_2, coastal ocean acidification, and the influence of bicarbonate availability on primary production.

INTRODUCTION

Streams and rivers serve as a major conduit for carbon transport from continents to marine systems and therefore act as important links in the global carbon (C) cycle.[1,2] Global riverine inorganic carbon transport is estimated to be between 0.21−0.30 Pg per year.[3] Changes in agricultural liming, urbanization, and mining can contribute to increased inorganic carbon fluxes, in the form of bicarbonate alkalinity in rivers.[4,5] Such impacts carry implications for quantifying the effects of acid rain, transport of acid neutralizing capacity to coastal zones, and consumption of atmospheric CO_2 by regional weathering.[6] Other factors, such as acid rain and weathering of carbonates in bedrock, soils, and cement, can also influence alkalinity and inorganic carbon transport.[6,7] Major questions persist such as the regional extent, rates, and causes of changing alkalinity in rivers, and corresponding mechanistic drivers.[8,9]

Alkalinity is comprised of inorganic and organic acids and bases and typically dominated by bicarbonate and carbonate species in streams at circum-neutral to alkaline pH.[10] It is typically defined as carbonaceous alkalinity or $[\mathrm{Alk}] = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] + [\mathrm{OH^-}] - [\mathrm{H^+}]$ or the equivalent sum of conservative base cations minus conservative anions $[\mathrm{Alk}] = [\mathrm{Na^+}] + [\mathrm{K^+}] + 2[\mathrm{Ca^{2+}}] + 2[\mathrm{Mg^{2+}}] + [\mathrm{NH_4^+}] - [\mathrm{Cl^-}] - 2[\mathrm{SO_4^{2-}}] - [\mathrm{NO_3^-}]$.[10] Many weathering reactions produce alkalinity as a result of acid neutralization by geologic materials and a few examples of these reactions include carbonates such as calcite: $CaCO_{3(s)} + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$ and silicates such as olivine: $FeMgSiO_{4(s)} + 4H^+ \rightarrow Fe^{2+} + Mg^{2+} + H_4SiO_4$. Detailed weathering reactions for a variety of minerals and their influence on alkalinity production are provided in Supporting Information (SI) Table 1.

Alkalinity in running waters reflects a number of terrestrial and in-stream processes. Natural sources of alkalinity include bicarbonate produced from silicate and carbonate weathering and transport of CO_2 from soil respiration occurring in

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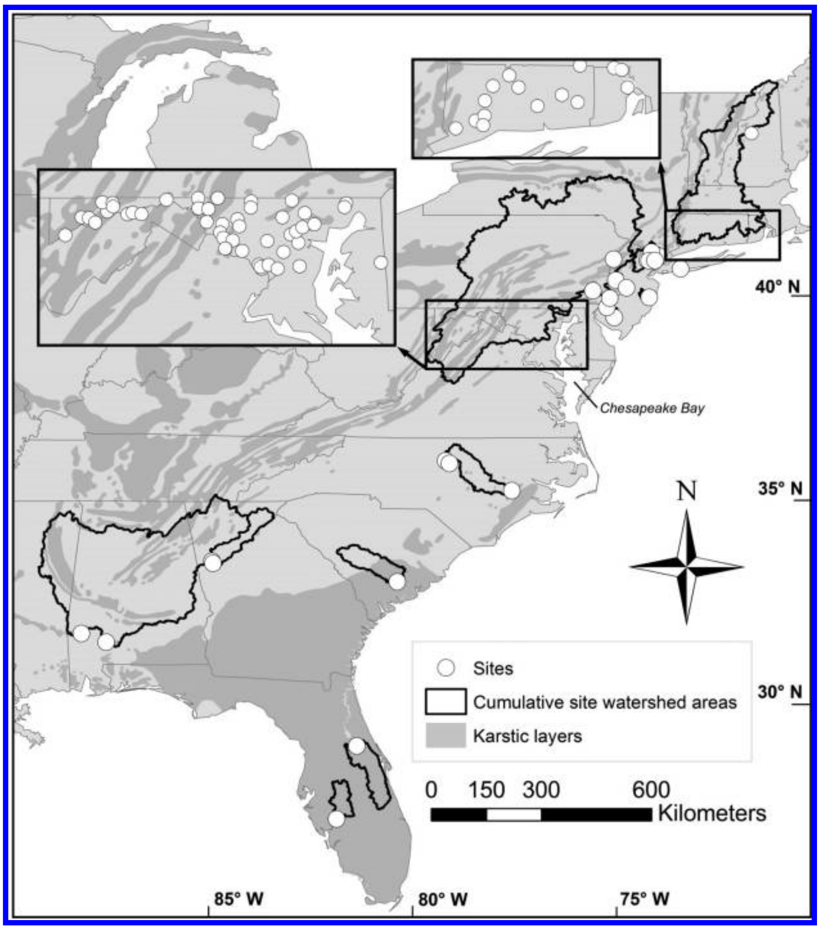

Figure 1. (A) Map of monitoring sites and cumulative watershed areas in the Eastern U.S. Five small watersheds are not shown in Connecticut and Florida.

watersheds.[1,2] Weathering of bedrock and overlying soils can be a sink for H^+, and produces alkalinity, base cations, dissolved aluminum, and dissolved silica that can be transported to surface waters.[11,12] Anthropogenic impacts, particularly atmospheric acid deposition, can influence the production and export of alkalinity in headwater streams.[12] Streams draining watersheds with carbonate lithology are buffered against acid deposition, but can develop higher alkalinity due to accelerated weathering and dissolution of carbonates, especially when acid deposition rates are high.[11,13] Thus, chemical weathering and production of alkalinity by weathering of bedrock and overlying soils should be stimulated by elevated H^+ ion concentrations in acid deposition, particularly in areas with carbonate lithology.[13] Although acidification should increase weathering rates and alkalinity generation, quantifying this process in watersheds is complex due to variability in mineral dissolution and differential impacts of mineral versus organic acids.

Land use may also influence stream and river alkalinity by directly increasing weathering rates on land and/or contributing watershed sources of alkalinity, but the regional significance of land use beyond site specific scales warrants evaluation. In addition to acid deposition from combustion of fossil fuels, there may be additional sources of acidification from agricultural sources.[14,15] For example, nitrification following clearcutting and agricultural fertilizer applications (including organic fertilizers) promotes soil acidification, and can consequently accelerate weathering and modify the carbon cycle.[16−18] Agricultural practices can also contribute to stream alkalinity directly, particularly via liming meant to raise the pH of soils for select crops.[19] Finally, urbanization may increase alkalinity via weathering of cement and runoff from impervious surfaces.[20] Although less studied, urban infrastructure containing cement and calcium can also degrade over time and may influence trends in stream chemistry.[21] Overall, the effect of chemical weathering on the carbon cycle across different types of land use will strongly depend on (1) the nature of the rock/geologic substrate weathered and (2) the origin of the acidification process. These factors influence whether there is a correlation between acidification and alkalinity increase (as the role of soil buffering may be somewhat complex).[22]

Here, we present a comprehensive analysis of long-term alkalinity trends ranging from small headwater streams to large rivers on the east coast of the United States, and identify potential drivers behind these trends. Previous studies have analyzed long-term alkalinity trends in only a small number of river sites with important implications.[5,19,23] We document trends and identify predictors of alkalinization at 97 sites cumulatively draining over 260 000 km^2 in the eastern U.S. Alkalinity trends can reflect changes in continental weathering rates and uptake of carbon dioxide by rock weathering. It has been argued that silicate weathering represents a sink for atmospheric CO_2 for millions of years over geologic time scales, whereas carbonate weathering represents a shorter term sink over hundreds to thousands of years due to carbonate precipitation in the ocean.[5,24] An improved understanding of the influence of lithology on river alkalinity is particularly

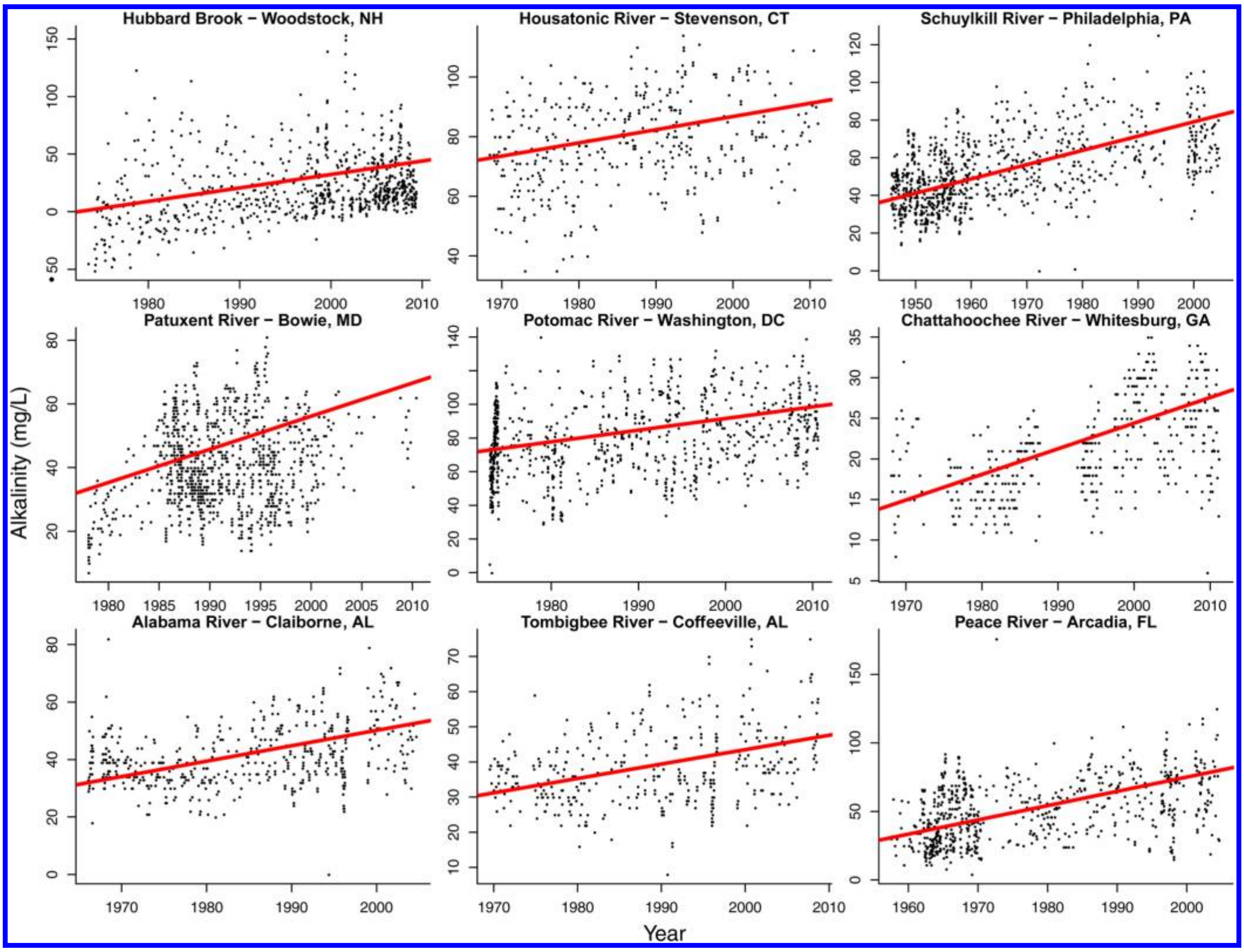

Figure 2. Examples of significant increases in alkalinity in rivers of the eastern U.S ($p < 0.05$). Scatter plots show all time-series data, and Theil-Sen slope estimates were calculated based on seasonal alkalinity averages (shown in red). All time-series data are shown to provide examples of the frequency and duration of the available data. Further details on watershed areas and land use for these sites can be found in the SI.

needed given that an increase in carbonate vs silicate weathering on land could contribute to carbon dioxide release from the coastal ocean due to carbonate precipitation.[5] In addition, changes in riverine alkalinity can influence ecosystem processes and alter the coastal carbonate system.[25,26]

■ MATERIALS AND METHODS

Historical time series of alkalinity measurements were obtained from 97 different stream and river sites located throughout the Eastern U.S. (east of the continental divide, including Florida) (Figure 1 Map and SI Table 2). The Chesapeake Bay watershed provided the largest number of sites with consistent and regular monitoring data. Some sites had multiple locations along the same river or within nested watersheds. Records were compiled from historical water quality measurements made by the U.S. Geological Survey (USGS), Hubbard Brook Experimental Forest, and EPA Chesapeake Bay Program (SI). All the time series included in our analyses were based on at least 25 years of alkalinity data and greater than 156 observations. Although some records had temporal discontinuities, we retained series with less than 6 years of consecutive missing data and a period of monitoring until at least the year 2000. The final time series included in our analysis ranged from 25 to 60 years in length. Further information on methods for alkalinity analyses can be found elsewhere[5,23,27] and in the SI.

Watershed Attributes. Potential watershed attributes that may influence long-term changes in stream and river alkalinity, such as acid deposition, land use, lithologic features including carbonate, elevation, and watershed size, were quantified from a geographic information system. Watershed boundaries were delineated using 30 m resolution elevation data.[28] Low-lying karstic topology or errors in the elevation data set prevented accurate watershed delineation for five sites (the Whippany River, three sites along the Quinnipiac River, and the Pequbuck River), and these were omitted from analyses of predictors at the landscape scale. Land-use data were derived from the National Land Cover Database (NLCD) 2001 coverage.[29] Broad categories of land use were quantified by summing the percentages of related classes (i.e., row crop and hay/pasture were summed to determine percent watershed agricultural cover) that constituted the total land use in each watershed. Impervious surface cover (%) for each watershed was also derived from the 2001 NLCD. The percentage of watershed lithologic attributes comprised of karstic features was calculated by summing the area of carbonate geologic features extracted from a national-scale karst lithology map[30] and dividing by the

Table 1. Mean Theil-Sen Slope Estimates Describing Rates of Change in River and Stream Water Alkalinity Throughout States of the Eastern U.S.[a]

state	sample size	ranges of observations across sites	significant increasing trends ($p < 0.05$)	significant decreasing trends ($P < 0.05$)	Mean Theil-Sen slope (mg/L/year)	standard error of mean Theil-Sen slope
Alabama	2	1966–2008	2	0	0.340	0.050
Connecticut	18	1952–2011	9	0	0.237	0.045
Florida	4	1957–2011	2	0	0.610	0.130
Georgia	2	1968–2011	1	0	0.220	
Maryland	45	1964–2010	30	0	0.592	0.045
New Hampshire	1	1973–2009	1	0	0.85	
New Jersey	10	1962–2010	9	0	0.272	0.048
New York	2	1966–2001	1	0	0.210	
North Carolina	1	1973–2011	0	0		
Pennsylvania	4	1945–2009	2	0	0.490	0.050
Rhode Island	3	1978–2002	1	0	0.160	
South Carolina	1	1967–2011	0	0		
Washington, DC	2	1973–2010	1	0	0.510	
West Virginia	2	1986–2010	2	0	0.645	0.185
totals	97		62	0		

[a] Theil-Sen Slope estimates, locations, and descriptions for all individual sites can be found in the SI.

watershed area. Mean H^+ concentration in precipitation was determined by first converting 3 × 3 km^2 pixel-scale pH values to H^+ concentrations and then averaging pixel values within each watershed from data provided by the National Atmospheric Deposition Program.[31] Further details on land cover/land use and atmospheric deposition data can be found in SI.

Statistical Analyses. Theil-Sen slopes were estimated to characterize average rates of change in alkalinity per year at each site. Theil-Sen slopes are calculated as the median of all possible slopes and are frequently used with time-series data because they are robust in regards to missing data, non-normal distributions, and occasional outliers.[32] *P*-values <0.05 were considered to be significant for all trends. Due to the large number of sites that had irregular sampling periods, seasonal average values of alkalinity (mg/L) were used to detect long-term trends. Seasonal averages were defined as winter (December, January, February), spring (March, April, May), summer (June, July, August), and fall (September, October, and November). A bootstrap resampling procedure was used to generate confidence intervals and estimate *p*-values.

We evaluated potential effects of landscape-scale watershed attributes on long-term trends in river alkalinity by comparing multiple regression models predicting Theil-Sen slope variation among sites. Thirty candidate models selected a priori were compared for relative goodness of fit using Akaike's information criterion for small sample sizes (AICc),[33] a model selection tool that rewards parsimony and penalizes models based on variable number and/or with redundant variables. Candidate model terms included watershed size, percent impervious surface cover, percent agricultural land, percent of watershed underlain by karstic features (similar to carbonate formations), the pH of precipitation (as observed in 1994), and various interactive effects. Independent variables were not highly correlated with one another (Pearson correlation coefficients among variables were all <0.5). Although multiple linear models were compared, potential nonlinear effects were considered by transforming independent variables data terms in a subset of models. We selected the model with the lowest AIC score as the top candidate model and assessed transformations of candidate variables using multiple linear regression. The appropriateness of a parametric approach was checked using Levene's test on the data and assessing plots of residual versus fitted value plots on the selected model.[34] Further description of statistical analyses can be found in the SI.

■ RESULTS

Significantly increasing alkalinity trends were detected at 62 of 97 stream and river sites of the Eastern U.S. (Figure 2, Table 1, SI Table 2). The remaining watersheds showed no statistically significant trends, and there were no significantly decreasing trends in the entire data set (Table 1). Sites exhibiting the highest Theil-Sen slopes were in the northeastern U.S., where acid precipitation was highest (Table 1, Figure 3). The river with the longest increasing record was the Schuylkill River, where alkalinity increased from approximately 40 to 80 mg/L over 60 years (Figure 2). The river with the most monitoring sites was the Potomac River, the second largest tributary of the Chesapeake Bay. In the Potomac River, alkalinity increased over time consistently from the small headwaters in the Appalachian Mountains to the beginning of its tidal section in Washington, DC (i.e., Potomac River at Washington DC. shown in Figure 2). We also observed increasing alkalinity trends in smaller streams located in urbanized watersheds as, for example, Gwynns Falls of Baltimore, Maryland and the Anacostia River of Washington DC, SI Table 1). In the Southeastern U.S., statistically significant increasing alkalinity trends were detected in the Chattahoochee River, Tombigbee River, Alabama River, and Peace River (Figure 2). Finally, over 50% of study sites had statistically significant increasing trends in calcium concentrations, another product of chemical weathering, for which long-term data were available in a number of cases (Table 2 and SI).

Theil-Sen slope estimates were statistically related to multiple landscape-scale watershed attributes. The statistical model with the lowest AICc score among candidate models relating Theil-Sen slopes to landscape-scale attributes included terms for percent watershed karst, H^+ concentration in precipitation, elevation and a watershed karst × elevation interaction term (Table 3, Figure 3, SI Table 4). The full model

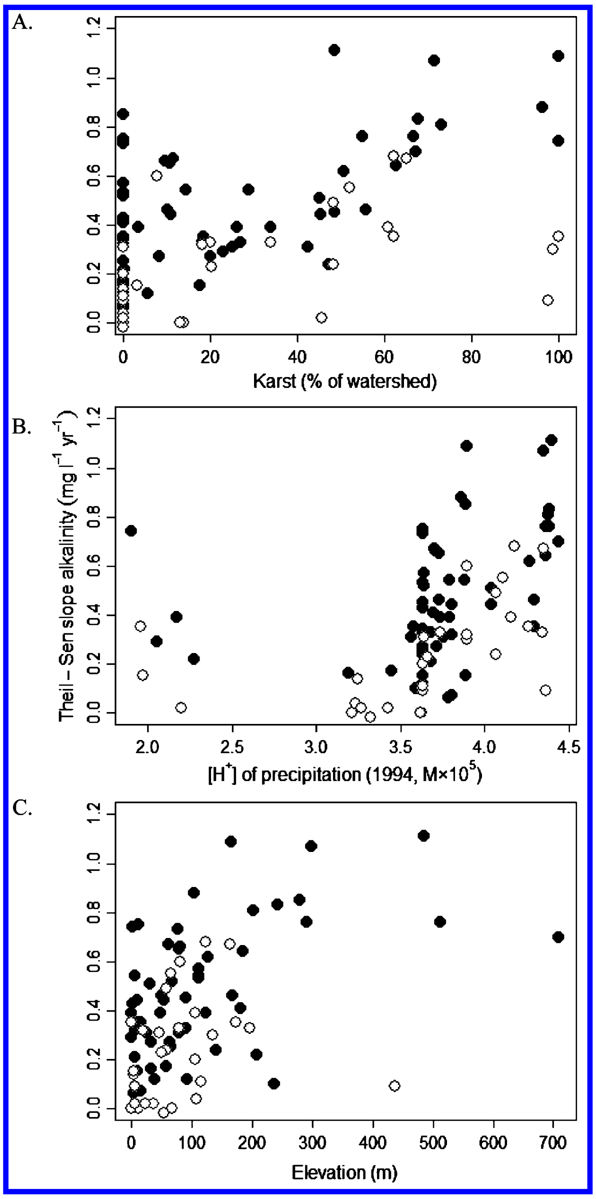

Figure 3. Plots of (a) karst lithology, (b) precipitation pH in 1994, and (c) mean watershed elevation against Theil-Sen slope estimates of alkalinity trends in eastern U.S. rivers. The closed points represent significant Theil-Sen slope estimates (p < 0.05) whereas open points represent all other Theil-Sen slope estimates that were not statistically significant. Because we assessed the relationships between Theil-Sen slopes and independent variables in a multiple linear regression model, lines of fit are not shown for specific variables here. The coefficients for the multivariate model selected using AICc, which included the terms shown in the figure plus a karst × elevation interaction term, are listed in Table 2.

was highly significant ($F_{3,83}$ = 13.2, p < 0.0001) and had an r^2 value of 0.41. All terms in the selected model were statistically significant (Table 3). There were some other models that explain the data well and are likely (SI Table 4) but these models have fairly similar sets of independent variables so that we focus our discussion for brevity on the model with the highest AICc value. The Monte Carlo bootstrapping procedure suggested that the presence of nested watersheds in the full data set did not result in spurious conclusions. Mean p-values of all model terms derived from randomly selected, less-nested sites were consistent with the statistical conclusions of the model run on the full data set (Table 3, SI Table 4).

■ DISCUSSION

Alkalinity is increasing in a majority of running waters throughout the eastern U.S. We observed increasing trends in alkalinity at 64% of 97 sites, from headwater streams to large rivers, particularly those in watersheds draining carbonate lithology. Many of the sites across regions have disparate soil, parent material, vegetation, topographic features, and climatic attributes. Despite this heterogeneity, several patterns emerged that suggest rivers are integrators of heterogeneous geochemical processes in watersheds. Based on our analysis, long-term trends in stream and river alkalinity can be influenced by carbonate lithology, acid deposition, and topography in watersheds. Overall, our results suggest that human-accelerated weathering is influencing stream and river alkalinity across watersheds throughout the Eastern U.S.

Increasing Alkalinity from Streams to Large Rivers. Small streams draining igneous and metamorphic lithology are more susceptible to acidification while larger watersheds are buffered further downstream.[35] Most research has been devoted to understanding alkalinity trends in small watersheds draining acid sensitive areas, and less is known regarding long-term changes in bedrock weathering and acid neutralizing capacity in larger watersheds, especially those with carbonate lithology. We observed consistently increasing patterns of alkalinity from the Hubbard Brook stream at the Hubbard Brook Experimental Forest (<31 km^2) to larger rivers such as the Susquehanna River (71 474 km^2), Alabama River (57 471 km^2), and Tombigbee River (48 108 km^2). Our results suggest that accelerated weathering is influencing alkalinity similarly in both streams and large rivers.

Watersheds (both small and large) are buffered by neutralization of acidic water by geologic materials and production of alkalinity (SI Table 1) as water comes into contact with soils, till, and bedrock.[10] For example, alkalinity production can be substantial throughout drainage networks due to acid neutralization along hydrologic flowpaths.[35,36] River chemistry in large watersheds can reflect an accumulation of weathering products over time, given that watersheds with greater soil development and depth can have longer flow paths and thus greater residence times.[37]

Karst Lithology As a Source of Alkalinity. We found that the sensitivity of a watershed to alkalinization varies substantially in the presence of carbonate lithology. The percentage of karstic features within the watershed was the strongest predictor of rates of increasing alkalinity in our analysis. Dissolution rates are very rapid in watersheds with carbonate lithology relative to those with crystalline lithology.[38] Watersheds draining karst lithology typically exhibit considerably higher weathering rates, even when acid deposition is minimal.[38] In karstic regions impacted by acid rain, neutralization occurs through reactions with carbonate minerals, and this response can prevent sustained watershed acidification in some cases.[13] Even the presence of modest amounts of carbonates as low as ∼1% in watersheds can contribute to a considerable proportion of the alkalinity, generated by chemical weathering, in rivers draining such watersheds.[36] If weathering rates were to equal or exceed rates of H^+ deposition in watersheds,[13] soils would maintain a buffer in base cations and accumulate residual alkalinity explaining our observations of increasing trends in streams and rivers

Table 2. Mean Theil-Sen Slope Estimates Describing Rates of Change in Calcium Concentrations in Stream Water Throughout States of the Eastern U.S.[a]

state	sample size	ranges of observations across sites	significant increasing trends ($p < 0.05$)	significant decreasing trends ($P < 0.05$)	Mean Theil-Sen slope (mg/L/Year)	standard error of the mean Theil-Sen slope
Alabama	2	1966–2001	2	0	0.097	0.006
Connecticut	18	1952–2010	9	3	0.666	0.026
Florida	3	1948–2011	1	0	0.231	
Maryland	1	1978–2010	0	0		
New Jersey	10	1923–2010	8	0	0.159	0.039
North Carolina	1	1955–2001	1	0	0.040	
Pennsylvania	3	1925–2009	0	0		
Rhode Island	1	1953–2010	0	0		
Washington, DC	1	1978–2010	1	0	0.188	
Totals	40		22	3		

[a] Results are for available calcium data at study sites. Theil-Sen slope estimates, locations, and descriptions for all individual sites can be found in the SI.

Table 3. Results from the Multiple Linear Regression Model Relating Site Watershed Attributes to Theil-Sen Slopes of Alkalinity Trends[a]

	full model ($n = 87$)			Monte Carlo mean ($n = 53$)
term	coefficient	F	p-value	p-value
karst (%)	5.1×10^{-3}	4.7	<0.0001	0.0012
$[H^+]$	1.2×10^{4}	2.7	0.0092	0.0341
elevation (m)	1.5×10^{-3}	3.5	0.0008	0.0082
karst × elevation	-2.1×10^{-5}	2.8	0.0064	0.0148

[a] Mean p-values from the 1000 iteration Monte Carlo bootstrapping procedure on the model are also provided.

(particularly in watersheds with karst lithology) (e.g., alkalinity is the equivalent sum of conservative base cations minus conservative anions as discussed previously). As an example, we observed that sites underlain by carbonate rocks had higher river alkalinization rates than Hubbard Brook, New Hampshire underlain by crystalline lithology. This may be due to differences in the availability of base cations and geologic materials to sustain continued acid neutralization and buffering capacity across sites (e.g., Hubbard Brook has shown long-term depletion of base cations in soils over time,[12] whereas the base cation supply may not be exhausted in carbonate watersheds such as those in the Potomac River watershed) (discussed further below).

The extent of karstic geologic attributes at large spatial scales suggests that karst is a key feature in understanding river alkalinization globally. Karst lithology is extensive in the Eastern United States covering 78 729 km^2 or about 30% of our study region. In the contiguous United States, we estimate that karstic features cover approximately 20% of the land area[29] while carbonates represent about 20% of continental rock outcrops globally.[39] Thus, the observation of increasing alkalinity in streams and rivers due to human-accelerated weathering may be important in other regions with karst lithology, particularly areas strongly impacted by acid deposition such as eastern Asia and Europe.[40,41] More work is necessary regarding a comparison of human-accelerated weathering across continents and impacts on alkalinity and the riverine carbon cycle.

Acid Deposition Increases Regional Weathering. Early research on the effects of acid deposition predicted increased weathering,[10,42] and previous work in Europe and Asia has suggested that acidification has increased weathering rates.[40,41,43−45] However, considerable work in the Northeastern U.S. has suggested more complex results regarding the impacts of acid deposition on weathering products in small watersheds.[45−47] Weathering reactions generally increase with acidity:[10] a 10-fold increase in hydrogen ions can result in a 2–3 fold increase in dissolution rates.[42] While these results indicate the importance of both acid deposition and weathering, our analysis did not detect a statistically significant interaction between karst and acid deposition, an interaction term which was included in several candidate regression models between landscape-scale variables and Theil-Sen slopes. Previous work on weathering kinetics has shown a fractional order dependence of mineral dissolution on hydrogen ion activity suggesting the importance of acidity.[10] Silicates and other minerals may be less impacted by weathering processes, and increased weathering may not be evident due to variability in mineralogy and weathering agents. Our analysis at 97 sites throughout the eastern U.S. suggest that acid deposition has increased alkalinity by stimulating weathering through neutralization reactions, particularly in watersheds with substantial carbonate lithology. More acid deposition has led to increased outputs of alkalinity from watersheds and contributed to long-term, increasing trends in rivers.

Acid deposition should increase weathering of carbonates, but most research has focused on understanding acid deposition effects in sensitive small watersheds with minimal buffering capacity. Our database can be used in order to identify more clearly the role of the various mineralogies through comparison of watersheds with contrasting lithology. As an example, the Potomac River watershed showed long, sustained, and continuous increases in alkalinity concentrations at multiple sites underlain by carbonate lithology. In contrast, changes in the chemistry of atmospheric deposition can result in relatively rapid and shifting responses in alkalinity in watersheds draining crystalline lithology. Because of the Clean Air Act Amendments of 1990,[12] acid deposition has recently declined in eastern North America and such trends likely influence alkalinity in watersheds with crystalline lithology.[12,48] For example, at Hubbard Brook Experimental Forest in the White Mountains of New Hampshire, there has been a long-term hysteresis response following acidification (decreasing alkalinity in streams) from 1963 to 1970 and then recovery in response to more recent air pollution regulations (increasing alkalinity in streams).[12,48] Such patterns in stream alkalinity are driven by the changing (increasing and decreasing) atmospheric input of acid anions (SO_4^{2-} and NO_3^-).[12] In comparison, impacts of acid deposition on carbonate watersheds may show less hysteresis due to ample capacity for acid neutralization, but these processes are less studied.

The increasing alkalinity trends in rivers that we observed are a response to historical acidification. Regional responses to acid rain vary and there are direct responses in alkalinity in some cases and lag times in other watersheds. Previous studies in the Northeastern and Southeastern U.S. have shown a change in alkalinity over time but the response time varies. For example, there is a relationship between cumulative acid deposition and cumulative export of alkalinity in the Hubbard Brook watershed of the northeastern U.S.,[12] but there are lag times in the alkalinity response of watersheds in the Shenandoah mountains.[49] These lag times can be related to differences in the weathering of geologic materials and available base cation supply suggesting that some systems can be transport limited (e.g., weathering processes are efficient at generating chemical weathering products but transport processes can be inefficient at removing them from the watershed).

In the Northeastern U.S., acid deposition due to anthropogenic factors has persisted for over five decades.[12] When acid precipitation is deposited onto soils, elevated H^+ concentrations deplete soil alkalinity but also increase alkalinity in receiving waters, resulting in river alkalization.[37] Over time, there can be drainage basin retention of weathering byproducts, and these can be observed in the longest records of river alkalinity measurements. The most rapid rates of increasing river alkalinity are in areas with higher acid deposition in the Northeastern U.S., patterns that are likely due to the greater rates of historical chemical weathering in acidic environments.[12,37] Acid deposition is often neutralized to geologically normal pH levels by the time it reaches larger rivers. This neutralization occurs via weathering reactions that take place as water travels through watersheds (generating alkalinity),[37] and this process has been demonstrated by experimental acidification in watersheds draining crystalline lithology that are more resistant to weathering.[50]

Elevation as a Predictor of Alkalinization. Our results suggest that watershed elevation plays a role in alkalinization rates, a pattern that may also be related to acid deposition. There may be greater acid deposition at higher elevations in mountainous areas, and higher elevations tend to be more sensitive to the effects of acid deposition due to thinner soils and lack of buffering capacity.[51] Rates of physical weathering can be considerable on steep slopes and physical weathering can be an order of magnitude greater than chemical weathering.[38] Physical weathering can further enhance chemical weathering by providing fresh surface areas for chemical weathering, and contribute to greater river alkalinization rates with increasing elevation in watersheds.[52] Our study region included the Appalachian Mountains of the Eastern U.S., which may be particularly vulnerable to accelerated weathering based on both higher acid deposition rates and large areas of higher elevation in this region.[51,53,54]

Contributions of Mining, Agriculture, and Urbanization. The effects of land use were not evident in our regional analysis, but have been previously shown to influence alkalinity concentrations at specific sites,[5,19] including some in the present study. Sites downstream of mining activities, agriculture, and urbanization can be influenced by acid mine drainage, soil liming, and runoff from impervious surfaces, respectively. At the site scale, riverine alkalinity concentrations in crop-lands that received agricultural lime applications were 5−6 times greater than alkalinity concentrations draining forested lands in the Mississippi watershed.[19] Mining can also further contribute to alkalinization.[5] However, we did not consider mining activities in our analysis due to a lack of comprehensive geographic data and large variability in subsurface and surface mining practices among our study watersheds.

We also observed increased alkalinization in urbanizing areas near Baltimore, Maryland, Washington, DC, and Atlanta, Georgia, which have been heavily impacted by increasing impervious surface cover and cement use.[21,55−57] Urbanization may result in alkalinization due to a number of processes, including the removal of organic soils and the dissolution of cement, which is rich in base cations.[57] In addition, urban wastewater and enhanced organic matter loadings and river metabolism can contribute to increased alkalinity concentrations in streams.[58−60] In the present study, we observed increasing alkalinity concentrations in urban watersheds that have been experiencing aging infrastructure, degradation of cement, and potential changes in organic matter metabolism.[21,60] The effects of urban land use on alkalinity concentrations in streams and rivers warrant further study (SI).

The effects of mining and land use may be more evident in subsets of catchments with more homogeneous parameters in our data set. For example, we did observe a long-term increase in river alkalinity concentrations in the Susquehanna River similar to previous work,[5] which attributed this response to decreased acid mine drainage and intense mineral weathering of carbonates since the 1940s by pryrite oxidation. In our regional analysis, the locations with the highest alkalinization rates were influenced by percentage karst lithology, acid deposition rates, and elevation, and these may have included some mountainous watersheds with mining activity. While mining and land use can contribute to river alkalinization at the individual site scale, lithology and weathering processes are the most important explanatory variables across broader regional scales. More research is necessary to investigate the interaction between watershed geology and human activities and alteration of river alkalinization patterns across local, regional, and global scales.

Implications for Regional Carbon Cycles and the Environment. Increased chemical weathering has elevated bicarbonate concentrations in streams and rivers throughout the Eastern U.S. Chemical weathering consumes 50 Mt of atmospheric CO_2−C per year in North America, and almost 50% of this weathering originates from only 10% of the area of North America.[6] Weathering by sulfuric and nitric acids from acid rain decreases the capacity for permanent uptake of atmospheric carbon dioxide during continental weathering.[41,45] It has also been suggested that accelerated weathering on land may cause total alkalinity in coastal marine zones to increase by almost 3% by the year 2100 above its historical concentration in the year 1850.[26] Thus, human-accelerated land weathering may alter the coastal carbon cycle with implications for coastal ocean acidification and air−water exchange of CO_2.[25,26]

Changes in buffering capacity are critical to biological processes, as large swings in H^+ concentration can be detrimental to organisms. For example when pH drops below 5.9, there can be potentially adverse effects on Atlantic salmon.[61] In contrast, elevated values of pH in the range of 7.6 - 8.2 may contribute to ammonia toxicity in some lowland streams.[62] Alkalinity may influence efficiency of carbon fixation and primary productivity of aquatic ecosystems.[63] Primary production can be an important sink for bicarbonate, particularly in nutrient-rich streams.[64] Running waters with higher alkalinity tend to exhibit elevated rates of primary productivity[65] and support greater abundances of secondary and tertiary consumers.[66] Long-term increasing alkalinity will likely induce changes at multiple levels of lotic food webs.

Finally, river alkalinization can also impact water quality and increase water hardness and concentrations of calcium and magnesium, which impact scaling of pipes and water treatment processes. Alkalinization and accelerated weathering contribute to increased total dissolved solids in rivers, and this change may exacerbate salinization of fresh water,[21,55] particularly in watersheds with carbonate lithology. Freshwater salinity is already increasing in the Northeastern U.S., and if current trends continue, some drinking water supplies in the region may not be potable for human consumption within the next century.[55]

Overall, our analysis suggests that the interaction between watershed geology and human activities are accelerating weathering throughout large regions of the U.S., particularly in watersheds with extensive carbonate. Further work is necessary to elucidate ecosystem scale cycling, generation of alkalinity by stream and river processes, and calcite precipitation.[64,67] Increasing temperatures may further enhance future weathering rates[25,26] and water temperatures in some major rivers in the U.S. have increased over time.[68] Our results have implications for geological studies of weathering of the continental crust, given that stream and river chemistry is used to infer processes, rates and intensity. Given that human activities are affecting weathering and river chemistry at such large regional scales, river alkalinization also raises implications regarding quantifying and tracing sources of increasing chemical fluxes from human-accelerated land weathering to coastal zones.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information includes examples of dissolution reactions ranked in approximate order from most easily weathered to most resistant to weathering; descriptions of alkalinity measurements and quality assurance/quality control; Further descriptions of watershed attributes and statistical analyses; significant rates of increase in river alkalinity for sites determined by Theil-Sen slope analyses; Trends in calcium concentrations determined by Theil-Sen slope analyses; mulitple linear regression model comparisons of landscape-scale watershed attribute effects on Theil-Sen slope values using Aikiake's Information Criterion for small sample sizes (AICc); watershed characteristics for sites in Figure 2 of the manuscript; examples of long-term trends in calcium concentrations for selected sites; further discussion of land use and carbonate sources in watersheds; distribution of the pH of precipitation in the U.S. from the National Atmospheric Deposition Program; examples of long-term alkalinity concentrations in other U.S. regions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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