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Decreased Atmospheric Sulfur Deposition across the Southeastern U.S.: When Will Watersheds Release Stored Sulfate?

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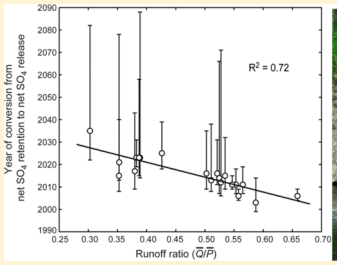
Supporting Information

ABSTRACT: Emissions of sulfur dioxide (SO_2) to the atmosphere lead to atmospheric deposition of sulfate (SO_4^{2-}), which is the dominant strong acid anion causing acidification of surface waters and soils in the eastern United States. Since passage of the Clean Air Act and its Amendments, atmospheric deposition of SO_2 in this region has declined by over 80%, but few corresponding decreases in streamwater SO_4^{2-} concentrations have been observed in unglaciated watersheds. We calculated SO_4^{2-} mass balances for 27 forested, unglaciated watersheds from Pennsylvania to Georgia, by using total atmospheric deposition (wet plus dry) as input. Many of these watersheds still retain SO_4^{2-}, unlike their counterparts in the northeastern U.S. and southern Canada. Our analysis showed that many of these watersheds should convert from retaining to releasing SO_4^{2-} over the next two decades. The specific years when the watersheds crossover from retaining to releasing SO_4^{2-} correspond to a general geographical pattern of later net watershed release from north to south. The single most important variable that explained the crossover year was the runoff ratio, defined as the ratio of annual mean stream discharge to precipitation. Percent clay content and mean soil depth were secondary factors in predicting crossover year. The conversion of watersheds from net SO_4^{2-} retention to release anticipates more widespread reductions in streamwater SO_4^{2-} concentrations in this region.



INTRODUCTION

Sulfur dioxide (SO_2) emissions in the eastern United States (U.S.) have declined by more than 80% since 1970, when the Clean Air Act (CAA) first established limits on emissions from stationary and mobile sources.[1] The decreased SO_2 emissions have translated into widespread declines in atmospheric sulfate (SO_4^{2-}) deposition in the eastern U.S.[2] As a primary component of acidic deposition, SO_4^{2-} can acidify surface waters,[3,4] accelerate base cation depletion in soils,[5] and negatively affect forest health[6,7] and habitat suitability for stream biota.[8] Whereas the connection between declining SO_2 emissions and declining SO_4^{2-} deposition is straightforward, the link between declining SO_4^{2-} deposition and declining streamwater SO_4^{2-} concentrations is, in some watersheds, obfuscated by SO_4^{2-} retention in the soils. This is the case for many forested watersheds in the mid-Atlantic and southeastern parts of the U.S. where streams have exhibited no change or even increases in streamwater SO_4^{2-} concentrations, despite decades of declining SO_4^{2-} deposition.[9−11] Although widespread decreases in streamwater SO_4^{2-} concentrations have remained elusive in this region, we show that such decreases are impending based on SO_4^{2-} mass balance applied to 27 watersheds.

The recognition that unglaciated eastern U.S. watersheds (hereafter, "southeastern") behave differently from their glaciated counterparts (hereafter, "northeastern") is well established. In 1984, the U.S. Environmental Protection Agency (USEPA) initiated the Direct/Delayed Response Project (DDRP), the purpose of which was to assess the risk of eastern U.S. surface waters from acidic deposition.[12,13] The DDRP reports predicted that stream recovery from acidification would vary with the ability of soils to store sulfur (S) by SO_4^{2-} adsorption. Southeastern streamwater response to decreased acidic deposition differs from that in the northeast, because the northeast experienced the most recent continental glaciation, which ended 10 000−15 000 years BP. Northeastern watershed soils are young, thin, rocky, and less able to retain SO_4^{2-}. In contrast, unglaciated soils are older, thicker, more weathered, and have sufficient clay content and associated iron-oxyhydroxide coatings to which SO_4^{2-} in drainage water can adsorb and be stored in the soil. Consequently, there is a spatial

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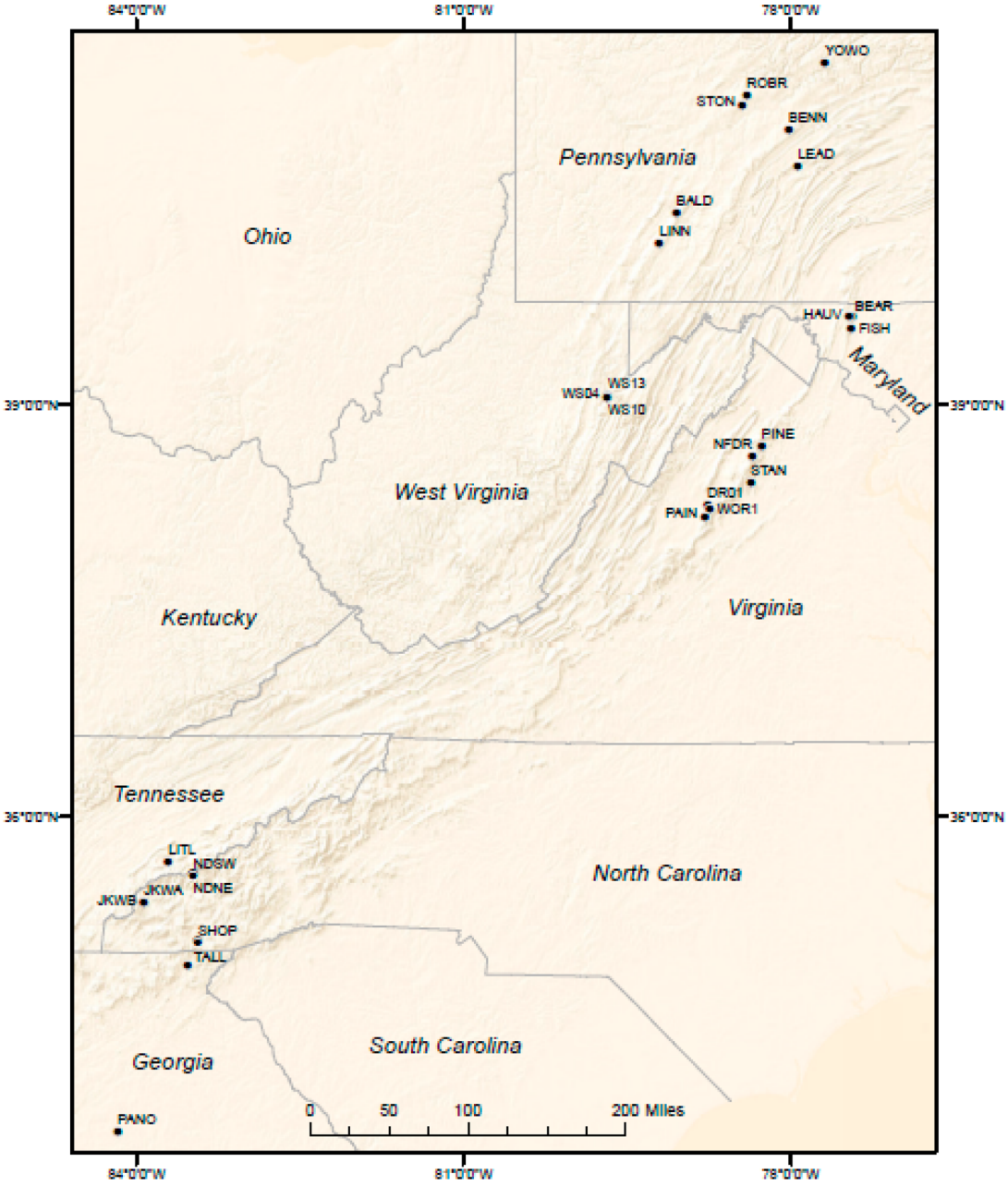

Figure 1. Map showing the 27 study watersheds, spanning a geographical range from northern Pennsylvania to northern Georgia.

difference in SO_4^{2-} retention, with higher retention in unglaciated than in glaciated watersheds.[14−17] As a result, streamwater SO_4^{2-} concentrations in unglaciated watersheds tend to be lower than those in northeastern watersheds, and the timing of the decrease in streamwater concentrations in the two regions differs.

Streamwater monitoring of forested watersheds in the eastern U.S. is conducted for a variety of purposes by a number of groups. By leveraging data from such programs, we provide empirically based quantification of the direct/delayed response of SO_4^{2-} in streamwater from atmospheric deposition. Comparisons of SO_4^{2-} mass balances for up to 20 northeastern watersheds have been made.[18−20] Corresponding analyses for unglaciated watersheds, where soil retention plays a key role in governing the delayed response to SO_4^{2-} deposition, are limited to comparisons of at most five watersheds.[21,22] We compared SO_4^{2-} mass balances from as many unglaciated eastern watershed long-term data sets for which we could obtain data. Our goals were to (1) extract knowledge of SO_4^{2-} behavior from those 27 watersheds; (2) estimate the time-frames for when streamwater SO_4^{2-} concentrations can be expected to decline in response to the significantly decreased deposition; and (3) identify the factors controlling the retention and release of SO_4^{2-} in those watersheds.

■ MATHEMATICAL FRAMEWORK

For our analysis, we adopted the theoretical framework of Cosby et al.[23] for watershed SO_4^{2-} dynamics. We applied a linear isotherm in the following form:

$$A_s = C^*D_s \tag{1}$$

where A_s is the adsorbed SO_4^{2-} in the soil (μeq kg^{-1}); C is the slope of the linear isotherm (m^3 kg^{-1}), which depends on the adsorption characteristics of the soil; and D_s is the

Table 1. Site Name, Site Identifier, Watershed Area, Period of Record, and Source of Discharge and Sulfate Data for the 27 Study Watersheds[a]

site name	site ID	area, ha	period of record	source of data	
				Q	SO_4^{2-}
Pennsylvania					
Young Womans Ck.	YOWO	1967	1984−2010	01545600s	USGS[b]
Roberts Run	ROBR	1067	1992−2010	01541000s	USEPA[c]
Stone Run	STON	1142	1992−2010	01541000s	USEPA[c]
Benner Run	BENN	1276	1992−2010	01546400s	USEPA[c]
Leading Ridge WS 1	LEAD	123	1983−2007	01558000s	USFS[d]
Baldwin Run	BALD	507	1992−2010	03042000s	USEPA[c]
Linn Run	LINN	839	1992−2010	03042000s	USEPA[c]
Maryland					
Bear Branch	BEAR	98	1991−2003	01640980	USGS[e]
Hauver Branch	HAUV	550	1983−2003	01640965	USGS[e]
Fishing Creek Trib.	FISH	104	1988−1998	01641510	USGS[e]
West Virginia					
Fernow WS 13	WS13	14	1989−2010	USFS[f]	USFS[f]
Fernow WS 10	WS10	15	1985−2009	USFS[f]	USFS[f]
Fernow WS 04	WS04	39	1983−2010	USFS[f]	USFS[f]
Virginia					
Piney River	PINE	1260	1993−2010	UVa.[g]	UVa.[g]
North Fork Dry Run	NFDR	231	1988−2010	UVa.[g]	UVa.[g]
Staunton River	STAN	1050	1993−2010	UVa.[g]	UVa.[g]
Deep Run	DR01	312	1983−2010	UVa.[g]	UVa.[g]
White Oak Run	WOR1	513	1983−2010	UVa.[g]	UVa.[g]
Paine Run	PAIN	1240	1993−2010	UVa.[g]	UVa.[g]
North Carolina/Tennessee					
Little River	LITL	27 454	1986−2009	03497300	USGS[b]
Noland Divide NE	NDNE	9.1	1992−2010	03460000s	NPS[h]
Noland Divide SW	NDSW	8.3	1992−2010	03460000s	NPS[h]
Joyce Kilmer WS A	JKWA	1458	1999−2008	03550000s	USFS/NSF[i]
Joyce Kilmer WS B	JKWB	87	1999−2008	03550000s	USFS/NSF[i]
Shope Branch	SHOP	12	1990−2010	USFS/NSF[j]	USFS/NSF[j]
Georgia					
Tallulah River	TALL	14 633	1983−1989	02178400	USGS[b]
Mountain Ck. Trib.	PANO	41	1986−2010	02203970	USGS[k]

[a]Sites are listed from north to south [ID, identifier; Ck., creek; Trib., tributary; WS, watershed; ha, hectares; Q, stream discharge; SO_4^{2-}, sulfate; USGS, U.S. Geological Survey; USEPA, U.S. Environmental Protection Agency; USFS, U.S. Department of Agriculture Forest Service; UVa., University of Virginia; NPS, National Park Service; NSF, National Science Foundation; PSU, Pennsylvania State University; USGS streamgage station number given in source of Q data column; if followed by "s", it is a surrogate station, see Methods]. [b]http://pubs.usgs.gov/circ/circ1173/Introduction.htm [c]http://www.epa.gov/airmarkt/assessments/TIMELTM.html; courtesy of Jason Lynch, USEPA. [d]http://www.fs.fed.us/ne/global/ltedb/catalogs/cat80.html; courtesy of James Lynch, PSU (retired). [e]courtesy of Karen Rice, USGS. [f]http://www.fs.fed.us/ne/parsons/fefhome.htm; courtesy of Frederica Wood, USFS. [g]http://swas.evsc.virginia.edu/; courtesy of Rick Webb, UVa. (retired). [h]courtesy of Dean Tucker, NPS. [i]http://www.srs.fs.usda.gov/coweeta/ [j]courtesy of Chelcy Miniat, USFS. [k]http://water.usgs.gov/webb/; courtesy of Brent Aulenbach, USGS.

concentration of dissolved SO_4^{2-} in the combined saturated and unsaturated soil solution (μeq m^{-3}), equivalent to the dissolved SO_4^{2-} concentration in the stream. A nonlinear (e.g., Langmuir) isotherm could just as readily be applied but would require at least one additional parameter without meaningfully affecting the main qualitative outcomes described below. The total quantity of SO_4^{2-} per unit area in the watershed (SO_{4tot}, μeq m^{-2}) is the sum of adsorbed and dissolved SO_4^{2-}:

$$SO_{4tot} = Z^*B^*A_s + Z^*P^*D_s \tag{2}$$

where Z is the soil depth (m), B is the soil bulk density (kg m^{-3}), and P is the porosity. The rate of change of SO_{4tot} per unit area is given by the following:

$$\frac{dSO_{4tot}}{dt} = Flux_{in} - Q^*D_s \tag{3}$$

where $Flux_{in}$ is the atmospheric SO_4^{2-} deposition to the watershed, and Q is the flux of water (m yr^{-1}, calculated as volumetric discharge divided by watershed area) through the soil to the stream. This expression of watershed mass balance assumes that atmospheric deposition and hydrological export are dominant relative to rates of mineral weathering and biotic uptake.

Combining the derivatives of eqs 1 and 2 and substituting into eq 3 yields the following:

$$\frac{d(D_s)}{dt} = \frac{Flux_{in} - Q^*D_s}{Z(B^*C + P)} \tag{4}$$

which indicates that for streamwater SO_4^{2-} concentrations to decline ($d(D_s)/dt < 0$), SO_4^{2-} inputs to the watershed ($Flux_{in}$) must be surpassed by SO_4^{2-} exports from the watershed (Q *

D_s) . In other words, there must be a net release of SO_4^{2-} from the watershed soils.

An alternative expression for eq 4 is as follows:

$$\frac{d(D_s)}{dt} = \frac{1}{T_c}[\mathrm{Flux_{in}}/Q - D_s] \quad (5)$$

where T_c is the characteristic time of SO_4^{2-} concentration in the soil and surface waters of the watershed, which takes the form:

$$T_c = \frac{Z(B^*C + P)}{Q} \quad (6)$$

In northeastern watersheds, relatively low Z (soil depth) and low C (SO_4^{2-} adsorption characteristics) allow streamwater SO_4^{2-} concentrations to rapidly respond to reductions in SO_4^{2-} deposition. In contrast, the higher T_c values for unglaciated soils result in a more gradual streamwater response to declining SO_4^{2-} deposition.

An equally important implication of the higher T_c values in unglaciated watersheds is that soil and streamwater D_s increased more gradually during the post-Industrial Revolution period of elevated atmospheric SO_4^{2-} deposition. It can be seen from eq 4 that with lower D_s levels, greater reductions in $\mathrm{Flux_{in}}$ are necessary for the term $\mathrm{Flux_{in}} - Q * D_s$ to become negative, which is needed for reductions in streamwater SO_4^{2-} concentrations. Unglaciated watersheds, therefore, are more likely to continue retaining SO_4^{2-}, and thus experience stable or increasing streamwater SO_4^{2-} concentrations, in contrast to their northeastern counterparts.

METHODS

The study area comprises 27 unglaciated long-term monitoring watersheds along the spine of the Appalachian Mountains, from northern Pennsylvania to northern Georgia (Figure 1). Data collection periods ranged from 1983 through 2010, and watershed areas range from 8 to 27 454 ha (Table 1). Watersheds are more than 90% forested and have mean elevations of 122−1807 m and mean slopes of 8−44% (Supporting Information (SI) Table 1).

Atmospheric input to each watershed was calculated as total (wet plus dry) S deposition, and reported as kg SO_4^{2-} ha^{-1} yr^{-1}. To obtain spatially integrated estimates of wet SO_4^{2-} deposition, we used a high-resolution wet-deposition model for the eastern U.S.[24] Inputs to the model include daily precipitation measurements from 245 National Oceanic and Atmospheric Administration National Weather Service sites; topographic variables (elevation, slope, and aspect) that affect the amount and distribution of precipitation; and wet SO_4^{2-} deposition data from 30 National Atmospheric Deposition Program (NADP) sites in the region.

Dry deposition cannot be measured directly, making accurate estimates of total S deposition difficult. A combination of monitoring data for air concentrations from the Clean Air Status & Trends Network (CASTNET) and deposition velocities from the Community Multiscale Air Quality (CMAQ) model were used to derive dry S deposition for each watershed. Air concentrations of bisulfate (HSO_4^-), SO_4^{2-}, and SO_2 are measured at 10 CASTNET monitoring sites (http://epa.gov/castnet) in the eastern U.S., which were used to estimate ambient air concentration for 1990−2010 for each watershed. CASTNET air concentrations were combined with deposition velocities from CMAQ (v. 5.0)[25] with a reference year of 2002 to provide annual estimates of dry deposition for each watershed. Dry deposition values for HSO_4^-, SO_4^{2-}, and SO_2 were calculated weekly and summed on a calendar year. CASTNET monitoring data are not available prior to 1990, therefore watershed-specific dry:wet ratios were applied to annual wet deposition values to estimate total deposition (SI Table 1). The annual dry:wet ratios prior to 1990 were derived by extrapolating trends in the 1990−2010 ratios of CASTNET-based dry deposition to NADP wet deposition values. The dry deposition values are estimates to the receiving surface, whether it is vegetation or soil. No interactions between dry deposition and the leaf canopy were considered using these estimates.

Daily streamwater SO_4^{2-} flux values were calculated by using daily discharge values and daily streamwater SO_4^{2-} concentrations, which were derived from the measured concentrations by linearly interpolating between samples. Although episodic data were available for a subset of the watersheds, these data were not used in the flux calculations in order to maintain a standardized methodology for all sites. Because SO_4^{2-} concentrations typically increase with discharge, the exclusive reliance on routine grab samples for the streamwater SO_4^{2-} fluxes could result in conservative estimates. Daily fluxes and daily runoff were summed on a calendar year to yield annual SO_4^{2-} output flux and annual runoff. Annual average volume-weighted SO_4^{2-} concentrations were calculated by dividing the annual output flux by the annual runoff at each site. For the 11 ungaged streams (Table 1), discharge data from the geographically closest unregulated USGS-gaged stream were used as a surrogate.[26] Change in SO_4^{2-} storage within watersheds was calculated as total atmospheric inputs minus streamwater outputs, so that a positive value indicates net retention of SO_4^{2-} in the watershed and a negative value indicates net release. The potential for geologic sources of SO_4^{2-} in each watershed was assessed and in each case was considered negligible.

Linear regression applied to the mass balance was used to identify "crossover" years of dSO_{4tot}/dt, when watersheds convert from being net sinks ($dSO_{4tot}/dt > 0$, retention) to net sources ($dSO_{4tot}/dt < 0$, release) of SO_4^{2-}. Linear regression is the simplest model, but there is no reason to justify a more complex, nonlinear form of analysis. Uncertainty bounds in crossover years were established at the 95% confidence interval by considering uncertainties associated with the slopes and intercepts of the ordinary least-squares model fits by use of Matlab. The distribution of crossover years for the 27 watersheds was explored via linear regression analysis with respect to relevant watershed characteristics (e.g., latitude, annual precipitation, annual discharge, soil depth, clay content; see SI Table 1). Average watershed soil depth and clay content were obtained from the STATSGO database.[27] Although uncertainty was considered for the projections of the crossover years, as influenced by the mean temporal trends and the year-to-year variability in net SO_4^{2-} storage, uncertainty was not applied to the calculations of the annual SO_4^{2-} storage values themselves. Errors and uncertainty are inherent in the estimates of wet and dry SO_4^{2-} deposition, stream discharge, precipitation, and streamwater SO_4^{2-} fluxes; however, quantifying these cumulative uncertainties for each year at each watershed would be difficult to accomplish in a meaningful manner.

RESULTS AND DISCUSSION

The key to when streamwater SO_4^{2-}concentrations start to decrease, according to eqs 3 and 4, is when dSO_{4tot}/dt converts from being positive to negative, i.e., the crossover when watersheds transition from net SO_4^{2-} retention to net SO_4^{2-} release. On the basis of linear regression applied to the dSO_{4tot}/dt time series computed for each watershed, best estimates for the crossover timing range from 2003 to 2035 (Table 2). In seven cases, due to a limited period of record and/or high interannual variability of net SO_4^{2-} storage (dSO_{4tot}/dt), statistically significant trends were not found ($p > 0.05$), therefore crossover years were not determined. In each such instance, the watershed was either retaining or was approximately in steady state with respect to SO_4^{2-} storage (i.e., $dSO_{4tot}/dt \approx 0$). The overall finding that many southeastern watersheds are still retaining SO_4^{2-} is in contrast to what has been observed in the northeastern U.S. and southeastern Canada, where watersheds now act predominantly as net SO_4^{2-} sources to streams.[19] Watersheds in the Hubbard Brook Experimental Forest, New Hampshire, have served as net SO_4^{2-} sources, dating as far back as the 1970s, as atmospheric deposition began to decline.[20]

Table 2. Estimated Crossover Year, When the Watershed Converts from Net Retaining to Net Releasing SO_4^{2-}, Based on Linear Regression of Watershed Mass Balances[a]

site ID	lower bound	predicted	upper bound	p-value[b]
		Pennsylvania		
YOWO	2007	2011	2018	<0.01
ROBR	2007	2014	2066	0.02
STON	2008	2013	2038	<0.01
BENN	2019	2023	2031	<0.01
LEAD	1999	2003	2014	<0.01
BALD	2007	2011	2019	<0.01
LINN	2009	2015	2032	<0.01
		Maryland		
BEAR	not significant—retaining			
HAUV	not significant—retaining			
FISH	2009	2016	2035	<0.01
		West Virginia		
WS13	2004	2006	2009	<0.01
WS10	2004	2006	2009	<0.01
WS04	2009	2011	2015	<0.01
		Virginia		
PINE	2006	2012	2071	0.02
NFDR	not significant—no bias toward retaining or releasing			
STAN	2011	2016	2031	<0.01
DR01	2009	2017	2043	<0.01
WOR1	2013	2021	2040	<0.01
PAIN	2008	2015	2078	0.02
		North Carolina/Tennessee		
LITL	not significant—retaining			
NDNE	not significant—no bias toward retaining or releasing			
NDSW	not significant—retaining			
JKWA	2014	2023	2088	0.02
JKWB	2015	2023	2058	0.01
SHOP	2018	2025	2039	<0.01
		Georgia		
TALL	not significant—retaining			
PANO	2022	2035	2082	<0.01

[a]Lower and upper bounds represent the lower and upper 95th percentiles, respectively. Sites are listed from north to south. [b]Describes the significance of slope in net SO_4^{2-} storage through time

The delayed response of the unglaciated watersheds is seen in the time series of streamwater SO_4^{2-} concentrations and net SO_4^{2-} fluxes for the 27 sites (Figure 2). The observed streamwater SO_4^{2-} concentrations naturally segregate into three distinct groups, with highest concentrations in the more northerly sites (i.e., Pennsylvania, Maryland, and West Virginia) and lowest concentrations in the more southerly sites (i.e., North Carolina, Tennessee, and Georgia) (Figure 2a). The tendency for watersheds to retain SO_4^{2-} throughout the majority of the study period is apparent, as is the tendency toward an eventual net release of SO_4^{2-} (Figure 2b−d).

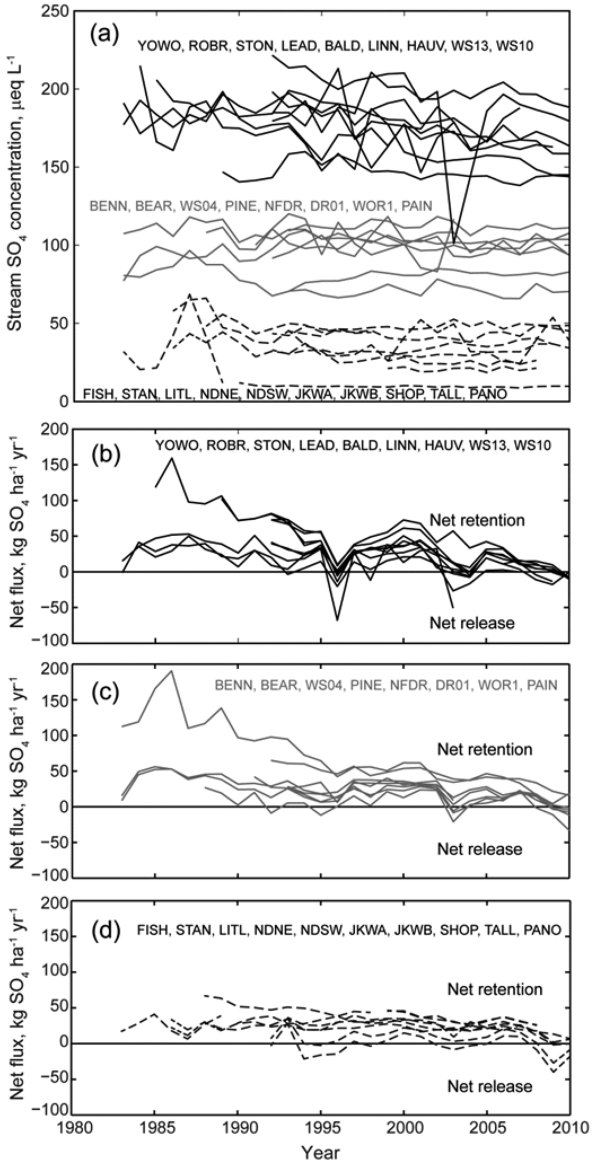

Figure 2. (a) Streamwater SO_4^{2-} concentrations and (b−d) net SO_4^{2-} fluxes for the 27 watersheds. Stream-water SO_4^{2-} concentrations naturally segregate into three main groups, with highest concentrations associated with the northerly sites and lowest concentrations associated with the southerly sites. The net fluxes associated with these groups are plotted separately in (b), (c), and (d).

On the basis of the mathematical framework presented in eqs 1−6, declines in streamwater SO_4^{2-} concentrations should

occur only when watersheds exhibit a net release of SO_4^{2-}. Deviations from this theoretical expectation, however, can be seen in the more northerly sites, where stream SO_4^{2-} concentrations have generally declined (Figure 2a) despite the fact that the majority of the watersheds still retain SO_4^{2-} (Figure 2b). A possible explanation is that a portion of streamflow bypasses the soil adsorption−desorption processes represented in the simple, well-mixed model. In watersheds where such shallow flowpaths contribute a significant amount to the total discharge, streamwater SO_4^{2-} concentrations would be more heavily influenced by concomitant declines in atmospheric deposition. Additional factors not considered in the mathematical framework include the potential for irreversibility of SO_4^{2-} adsorption and the potential for pH and soil organic carbon to affect the isotherms.[28,29] Although the conversion from net SO_4^{2-} retention to net SO_4^{2-} release in these watersheds does not appear to be a strict prerequisite for declines in streamwater SO_4^{2-} concentrations, the eventual crossover to net SO_4^{2-} release is significant because declining streamwater SO_4^{2-} concentrations likely are ensured once this condition occurs.

The calculated crossover years exhibit a high degree of variability (Table 2), but there is a geographical pattern of later conversion to watershed SO_4^{2-} net release from north to south. Correlations between latitude and crossover year, and correspondingly, annual mean air temperature, and crossover year, are statistically significant ($p < 0.01$) (Table 3). Despite this, there are geographical clusters of watersheds where crossover years exhibit a notable range. For instance, the three watersheds in West Virginia have crossover years that range from 2006 to 2011, and crossover years for five of the watersheds in Virginia range from 2012 to 2021 (Table 2). Therefore, other site-specific factors that could affect the timing of watershed conversion from net SO_4^{2-} retention to net SO_4^{2-} release were investigated (Table 3). Such factors include clay content and soil depth (Z), which are known to influence soil SO_4^{2-} adsorption.[16] No significant correlations between clay content or Z with crossover year, however, were found (Table 3).

Table 3. Correlations among Crossover Year, Describing Year of Conversion from Net SO_4^{2-} Retention to Net SO_4^{2-} Release, and Select Variables for the 20 Watersheds with Statistically Significant Crossover Years

variable	Pearson correlation coefficient (P)	*P*-value	R^2 value
latitude	−0.72	$P < 0.01$	0.52
watershed area	0.04	0.88	0.001
% wetlands	0.10	0.68	0.01
annual mean air temperature	0.70	$P < 0.01$	0.49
annual mean precipitation ($\bar{P}$)	0.47	$P = 0.04$	0.22
mean watershed elevation	−0.20	$P = 0.39$	0.04
mean slope	0.21	$P = 0.38$	0.04
mean soil % clay content	0.37	$P = 0.11$	0.14
mean soil depth (Z)	0.09	$P = 0.70$	0.01
% clay content * soil depth	0.37	$P = 0.11$	0.14
annual mean discharge ($\bar{Q}$)	−0.34	$P = 0.15$	0.12
annual mean evapotranspiration ($\bar{P} - \bar{Q}$)	0.79	$P < 0.01$	0.62
runoff ratio ($R_R = \bar{Q}/\bar{P}$)	−0.85	$P < 0.01$	0.72
$-69.3*R_R + 0.092*(\%clay * Z) + 2039$[a]	0.88	$P < 0.01$	0.77

[a]Results from multiple linear regression.

The single watershed characteristic that explained the greatest variability in crossover year ($R^2 = 0.72$) was runoff ratio (R_R), computed as the ratio of annual mean discharge ($\bar{Q}$) to annual mean precipitation ($\bar{P}$). Watersheds with higher R_R tend to convert sooner from net retention to net release of SO_4^{2-} (Figure 3). As indicated by eq 3, watersheds release SO_4^{2-} when $D_s > 1/R_R{*}c_{in}$, where c_{in} is the concentration of total atmospheric S deposition expressed as SO_4^{2-}. For similar levels of atmospheric deposition, D_s exceeds this threshold ratio more readily for watersheds with higher R_R. This also can be understood with respect to the characteristic time scale (T_c) of eq 6, where higher R_R promotes a shorter time scale of watershed response, leading to more rapid conversion toward net SO_4^{2-} release. A multiple linear regression including R_R, % clay content, and Z is justified according to the Akaike Information Criterion,[30] indicating that the better model fit, as exemplified by the increase in correlation with crossover year (Table 3), is worth the "cost" of this additional term. Neither "% clay content" nor "% clay content * Z" were significantly correlated with R_R, which was mainly driven by climate factors over the extensive geographical region. The positive sign associated with the "% clay content * Z" term in the multiple linear regression indicates that a greater abundance of clay in watershed soils leads to a more delayed crossover from retention to release of SO_4^{2-}. This conforms with the general paradigm used to explain the delayed response of unglaciated watersheds relative to their glaciated counterparts, and is supported by the mathematical framework in terms of the influence that C and Z have on T_c in eq 6. Our results suggest that for the watersheds examined, and perhaps other unglaciated watersheds in the eastern U.S., R_R is the dominant factor related to the crossover year, with soil characteristics playing a secondary role.

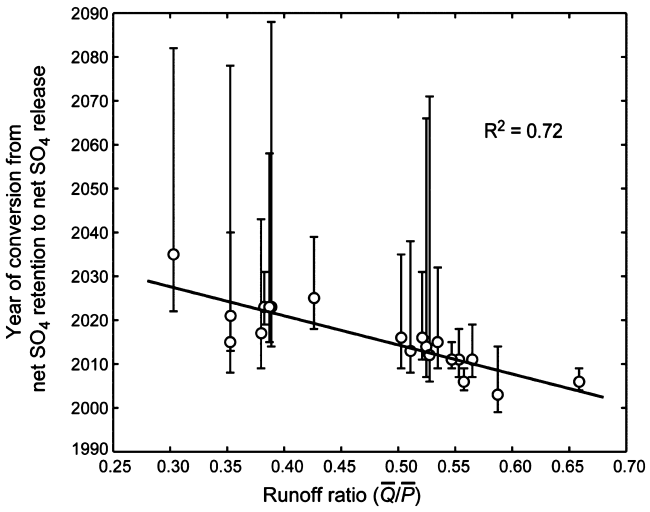

Figure 3. Predicted crossover years for watersheds transitioning from net retention to net release of SO_4^{2-} based on linear regression of the net SO_4^{2-} storage time series (with 95% confidence intervals) versus watershed runoff ratios.

Our analysis does not distinguish between watershed responses based on depositional histories at the sites, including deposition prior to the time frame of the study. The results do

suggest, however, that the timing of the crossover year is more sensitive to the storage/release dynamics of the watersheds (as characterized by T_c) than to the timing and magnitude of atmospheric deposition. For instance, the more southerly sites experienced the lowest deposition (primarily because the dry deposition was lower), and consequently retain less SO_4^{2-} (Figure 2d) compared with the other watersheds. But the long time until their conversion from net retention to net release is driven mainly by their low R_R and secondarily by their high clay contents.

It should be noted that the unglaciated watersheds considered here are all characterized by relatively old soils with high SO_4^{2-} adsorption potentials, which contrasts with the young soils in glaciated watersheds. The finding that R_R best predicts the timing of crossover to net SO_4^{2-} release by watersheds should only be interpreted in the context of unglaciated eastern U.S. watersheds. If glaciated watersheds were to be included in an expanded analysis, then the significance of soil adsorption characteristics would certainly play a more prominent role in a predictive model.

In 2003, southeastern watersheds were deemed a "red flag for regulators,"[31] because of their lack of response to the CAA and its Amendments. Our analysis showed that we might expect a decline in SO_4^{2-} concentrations within the next two decades, finally fulfilling one of the anticipated outcomes of the CAA and its Amendments.[31] Long-term monitoring of these watersheds provides empirical evidence about the actual timing of the delayed response, previously theorized by Church et al.[12,13] In addition, the long-term monitoring data provide some insight about the main controls influencing the timing of the SO_4^{2-} release from these watersheds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table of study watershed characteristics. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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