Watershed Sulfur Biogeochemistry: Shift from Atmospheric Deposition Dominance to Climatic Regulation

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ABSTRACT: North American atmospheric S emissions peaked in the early 1970s followed by a dramatic decrease that resulted in marked declines in sulfate (SO$_4^{2-}$) concentrations in precipitation and many surface waters. These changes in S biogeochemistry have important implications with respect to the mobilization of toxic (Al$^{3+}$, H$^+$) and nutrient (Ca$^{2+}$, Mg$^{2+}$, K$^+$) cations and the acidification of watersheds. We used the continuous long-term record for watersheds 1, 3, 5, and 6 (37–44 years from 1965 through 2008) of SO$_4^{2-}$ concentrations and fluxes at Hubbard Brook Experimental Forest in New Hampshire (U.S.) for evaluating S budgets. Analysis revealed that the annual discrepancies in the watershed S budgets (SO$_4^{2-}$ flux in drainage waters minus total atmospheric S deposition) have become significantly ($p < 0.001$) more negative, indicating the increasing importance of the release of S from internal sources with time. Watershed wetness, as a function of log$_{10}$ annual water flux, was highly significant ($p < 0.001$) and explained 57% ($n = 157$) of the annual variation for the combined results from watersheds 1, 3, 5, and 6. The biogeochemical control of annual SO$_4^{2-}$ export in streamwater of forested watersheds has shifted from atmospheric S deposition to climatic factors by affecting soil moisture.

INTRODUCTION

Atmospheric deposition of sulfur (S), resulting from S emissions, has been the dominant factor in causing widespread, deleterious impacts of acidic deposition on aquatic and terrestrial ecosystems. North American atmospheric S emissions peaked in the early 1970s followed by a dramatic decrease (Figure 1a) that resulted in marked declines in sulfate (SO$_4^{2-}$) concentrations in precipitation and many surface waters including those at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of NH (U.S.) (Figure 1b). Much of the decline of anthropogenic emissions of sulfur dioxide (SO$_2$) in North America was driven by the enactment of the U.S. Clean Air Act (CAA) in 1970 and subsequent Title IV Amendments of the CAA in 1990, as well as other regulatory controls on SO$_2$ emissions. Similarly, implementation of the Eastern Canada Acid Rain Program reduced Canadian emissions such that total Canadian–U.S. emissions of SO$_2$ were 14 million tonnes in 2006: a 50% reduction relative to 1980 levels. These historical emission trends are matched by changes in precipitation concentration and S deposition. The decreases in atmospheric deposition have also resulted in decreases in SO$_4^{2-}$ concentrations in surface waters with notable decreases across southeastern Canada and northeastern U.S. Elevated atmospheric S deposition has been closely linked with the acidification of surface waters and soils. This acidification has resulted in the mobilization of toxic cations (e.g., Al$^{3+}$, H$^+$) and the depletion of soil nutrient cations (e.g., Ca$^{2+}$, Mg$^{2+}$, K$^+$) that have resulted in deleterious impacts to both aquatic and terrestrial ecosystems. Temporal changes in SO$_4^{2-}$ concentrations of surface waters have also been related to changes in microbial dissimilatory SO$_4^{2-}$ reduction, an increase in methane (CH$_4$) production, and the methylation of mercury (Hg). Increased concentrations of atmospheric CH$_4$ are a concern due to the high heat-trapping capacity of this greenhouse gas. Methyl Hg is bioaccumulated along food chains, and this chemical form of Hg is highly toxic to biota, including humans.

Mitchell et al. evaluated the S budgets of 15 well-studied watersheds in southeastern Canada and northeastern U.S. and found that, especially for those watersheds subjected to elevated levels of atmospheric S deposition, S outputs in drainage waters significantly exceeded atmospheric inputs from 1985 to 2002 by ~1–6 kg S ha$^{-1}$ yr$^{-1}$. Large amounts of S have likely accumulated in the soil from past, large inputs of atmospheric deposition. Now, with declining inputs of atmospheric S, the higher outputs of SO$_4^{2-}$ in drainage waters relative to precipitation inputs are driven by the S stored in the soil. Some studies have suggested the potential importance of the role of drying and wetting in affecting SO$_4^{2-}$ mobilization of this stored S.

The objectives of the current study were to use the long-term record at the Hubbard Brook Experimental Forest in New

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Hampshire of climate, hydrology, and atmospheric deposition of S and discharge losses of SO$_4^{2-}$. These data were used to evaluate the role of climate change as a function of discharge in affecting discrepancies in the S mass balances of watersheds. Our analyses focused on the role of changing water availability in affecting the amount of S mobilized from internal watershed sources and resultant changes in the S budget discrepancies over time.

**METHODS**

Our current study provides a comprehensive analysis of the relationships between atmospheric deposition and hydrology in affecting SO$_4^{2-}$ losses in drainage waters at the HBEF in the White Mountains of New Hampshire (U.S.) which has the longest and most complete historical record of S watershed biogeochemistry. We used the long-term historical record from the HBEF for which information on precipitation amount, bulk precipitation chemistry, streamflow, and streamwater chemistry was available. We focused our analyses on the biogeochemical reference watershed (watershed 6), which had the longest record from 1965 through 2008 (44 years), but also utilized results from adjacent watersheds 1 and 3 (1971 through 2008; 38 years) and watershed 5 (1972–2008; 37 years) to support our findings. Our more detailed and extensive analysis of the influences due to atmospheric deposition and hydrology differed from a more limited study where data from only 18 years (1985–2002) were available and only watershed 6 at the HBEF was evaluated.

Annual deposition of S was estimated from the measured total in bulk deposition (weekly measurements) combined with annual dry deposition estimates using established formulations. Annual streamwater SO$_4^{2-}$ fluxes were based upon the summation of weekly sampling of chemistry and continuous monitoring of stage height converted into daily flow values (Figure 2a). Chemical measurement techniques were identical for the precipitation and streamwater determinations.

**RESULTS AND DISCUSSION**

There was a significant decrease in the annual precipitation and streamwater SO$_4^{2-}$ fluxes during the study as shown for watershed 6 (Figure 2a,b). Also, for almost all years there was a net negative discrepancy in the difference between atmospheric
deposition and stream export (Figure 2c) as has been found previously at HBEF6 and many other watersheds in eastern North America,15 as well as Europe.21 For a few watersheds such as Sleepers River in Vermont22 and Arbutus Watershed in New York,24,25 the weathering of S minerals is also an important source of SO4^2- in drainage waters. Our current study shows for watershed 6 at the HBEF that these discrepancies have become significantly more negative at an average rate of −0.094 kg S ha^{-1} yr^{-1} (Figure 2c), indicating the increasing importance of the release of S from watershed internal sources with time.

Internal S sources in watersheds may include the weathering of S minerals, mineralization of organic S, and desorption of adsorbed SO4^2-. We evaluated this discrepancy further by converting kg S ha^{-1} yr^{-1} to annual SO4^2- concentration to normalize these data with respect to annual water discharge15 (Figure 3). An evaluation of the relative proportion of this discrepancy versus time revealed that the increase in this discrepancy was highly significant (p < 0.001) showing that the relative importance of internal S sources is increasing over time. There was considerable annual variation in this discrepancy, and hence, we evaluated a range of factors that could be affecting this internal source. We found that watershed wetness, as a function of log,10 annual water flux, was highly significant (p < 0.001) and explained 58% (n = 45) and 57% (n = 157) of the annual variation for watershed 6 and combined results for watersheds 1, 3, 5, and 6, respectively (Figure 3). A multiple linear regression using two independent variables, the log10 of annual water discharge flux and normalized annual concentration of SO4^2- (assuming that all S deposition was converted to SO4^2- in precipitation), was highly significant (p < 0.0001) and explained 72% (n = 44) and 67% (n = 157) of the annual variation in the annual budget SO4^2- concentration discrepancy for watershed 6 alone and the combined results from watersheds 1, 3, 5, and 6, respectively.

Within the northeastern U.S. as well as other regions of the world there is considerable evidence that the climate is changing with respect to temperature and precipitation with resultant effects on the amount of surface water discharge.24,25 Results at the HBEF showed that discharge has significantly (p = 0.08) increased (+3.5 mm yr^{-1}) from water years 1964 to 2008 for watershed 6 suggesting increasing soil wetness for a total increase of ∼154 mm of discharge for this period. These analyses demonstrate that this hydrologic, climatic component is becoming the predominant controlling factor for S outputs at HBEF. These patterns observed at the HBEF, however, may vary in other locations that differ in the temporal precipitation patterns and hydrological responses. Hence, further analyses across a broader range of sites are warranted. Regardless, the changes in the sulfur budget at the HBEF are markedly different compared to earlier years during which atmospheric deposition of S was the major determinant of the export of SO4^2- in drainage waters.6,15

The importance of hydrologic regulation of SO4^2- loss from internal sources of S can be attributed to the close linkage between soil—water increases and the mobilization of SO4^2- by SO4^2- desorption, weathering of S bearing minerals, and organic S mineralization, all of which can contribute to SO4^2- mobilization to drainage waters as shown in the conceptual model provided in the abstract. Greater amounts of soil water, associated with high drainage water losses, will result in SO4^2- desorption,27 but other studies have suggested that within the northeastern United States the desorption of SO4^2- cannot account for discrepancies in sulfur budgets.28 The importance of SO4^2- adsorption and desorption in affecting S budgets at HBEF was clearly shown in forest harvesting experiments that resulted in enhanced nitrification, acidification, and SO4^2- desorption.29 Although the presence of S bearing minerals has been established at the HBEF,30 these S minerals are believed to be a minor internal source of S.6 However, it would still be expected that greater amounts of soil water would enhance the weathering of these S minerals.31 Soil organic S is the largest (generally >90% of total ecosystem S content) S pool at the HBEF and forested watersheds throughout the world.16 The major importance of mineralization of organic S in the S budget has been suggested from mass balance and stable isotopic analyses.6 The mineralization of this organic S is regulated by soil microbial activity, and the importance of soil water in affecting microbial activity has been clearly documented32 with specific evidence on how increasing available soil moisture enhances microbial activity at the HBEF.33 There is some possibility at very high soil moisture conditions coupled with reduced oxygen availability that there could be decreased microbial activity,34 but there is no evidence that these conditions are important at the HBEF with its well drained soils.19

### IMPLICATIONS

We predict that the role of climate in affecting the long-term as well as short-term temporal patterns of SO4^2- drainage water losses across watersheds in eastern North America and Europe will continue to increase, especially for those watersheds, which are recovering from previous inputs of high levels of atmospheric S inputs and resultant increase in soil S pools. These biogeochemical responses at the HBEF and likely other watersheds with stored S from past anthropogenic sources will be amplified with further climate change including greater annual stream discharge and watershed wetness.24,25,35

This climatic change will potentially increase SO4^2- mobilization and hence may slow the resultant recovery from acidification of both aquatic and terrestrial ecosystems. This mobilization of internal S sources not only has important implications in understanding long-term changes in watershed mass balances, but also has ramifications on the
recovery of surface waters from acidification and efficacy of policy considerations associated with regulation of atmospheric emissions of sulfur.

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