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Research Letter

Declining Atmospheric Sulfate Deposition in an Agricultural Watershed in Central Pennsylvania, USA

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Core Ideas

- Sulfate concentrations in an agriculturally dominated watershed respond to atmospheric deposition inputs.
- Rough budget estimates in the watershed suggest a depletion of the sulfur pool.
- Agricultural practices do not seem to mask effects of atmospheric deposition.

Abstract: Sulfur emissions in the northeastern United States are only 20% of levels measured in 1987 due to the enactment of the US federal Clean Air Act. While there are numerous reports of forested ecosystems recovering from acidification as a result of the decline in sulfur deposition, few studies describe such recovery in agricultural watersheds. We used long-term (30+ yr) atmospheric and watershed data from a USDA experimental watershed to investigate whether daily agricultural practices masked the declining sulfur (as sulfate-sulfur) trends seen in mainly forested watersheds. Over the study period, atmospheric wet deposition of sulfate-sulfur decreased 75% while sulfate-sulfur at the watershed decreased by approximately 30%. While the deposition of sulfur is detrimental to stream quality, the reduction of sulfur deposition in recent years has caused many soils in the watershed to develop sulfur deficiencies. Long-term declines in watershed sulfur export reveal emerging concerns about reducing atmospheric sulfur levels.

The 1990 US federal Clean Air Act amendments have successfully improved air and water quality through regulation of power plant air emissions (USEPA, 2015). In particular, sulfur emissions have decreased by 80%, resulting in measured decreases in sulfur deposition (NADP, 2015). Long-term studies have shown improvements in aquatic and terrestrial ecosystem health in forested watersheds due to declining acidic deposition (Beachley et al., 2016; Rice et al., 2014). To date, similar responses of agricultural watersheds to Clean Air Act implementation have not been well documented.

Recently, David et al. (2016) chronicled the decline of sulfur concentrations in streamflow in three agricultural watersheds in the midwestern United States. Such studies are important because they (i) suggest positive responses to national environmental policies, (ii) confirm that agricultural systems respond to changes in diffuse external inputs such as atmospheric deposition, and (iii) inform agricultural producers of emerging issues that may not yet be apparent. The purpose of this study was to show that the effects of declining atmospheric sulfur deposition are not masked by agricultural practices. To that end, we discuss trends in sulfur concentrations in streamflow from a small agricultural watershed in east-central Pennsylvania and call for similar analyses of long-term watershed data in other regions to further document the water quality response to reductions of atmospheric sulfur deposition in agricultural watersheds.

Materials and Methods

The study was performed in the USDA's WE-38 experimental watershed, a 7.3 km^2 subcatchment of Mahantango Creek watershed (420 km^2) in the Ridge and Valley Province of east-central Pennsylvania, USA. Land area is 55% cultivated, 3% pasture, 40% forest, and 2% rural development (Bryant et al., 2011). Geology ranges from well-drained

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sandstone ridges to poorly drained shale and siltstone valleys generating saturation excess runoff (Buda et al., 2009). Soils from 301 of 315 agricultural fields in the watershed were sampled during the 2013 growing season (one composite sample per field, 20-cm depth) and analyzed for agronomic nutrients by Mehlich-3 extraction with ICP determination of the supernatant (Mehlich, 1984).

Discharge at the WE-38 outlet has been recorded from 1968 to present at 5-min intervals via tandem broad-crested and V-notch weirs with 3 mm accuracy (Buda et al., 2011a). Annual discharge averages 500 mm with 82% as baseflow (<0.155 $m^3 s^{-1}$). Sulfur measured as sulfate (SO_4–S) and pH have been collected at the weir by grab sample about thrice weekly since 1984, with analysis methods and detection limits as described by Church et al. (2011). Adjacent to the weir, a 19-m-deep well has been sampled monthly from 2008 to present for water quality, including SO_4–S and pH. Three independent weather stations, within 2 km of the weir, have provided daily precipitation, temperature, wind speed, and evapotranspiration over the same period (Buda et al., 2011b). Wet deposition of sulfur (reported as SO_4–S) from 1979 to present was obtained from a National Atmospheric Deposition Program National Trends Network site located approximately 121 km west-southwest of the watershed (NADP, 2015).

Sulfate-sulfur and pH trends were determined by 3-yr moving averages, and resulting linear trends, of the flow and precipitation normalized annual (water year) means over the 30-yr period of record. Statistical analyses were performed in R (R Core Team, 2016) using the EGRET (Hirsch and De Cicco, 2015) and WRTDS (Hirsch et al., 2010) packages to ascertain long-term trends.

Results and Discussions

Atmospheric and Water Quality Trends

Atmospheric wet deposition of SO_4–S decreased by 75% during the 30-yr study period from 10 kg $ha^{-1} yr^{-1}$ to approximately 2.7 kg $ha^{-1} yr^{-1}$. During the same period, flow-normalized SO_4–S concentrations at the watershed outlet decreased 30%, from 15 mg L^{-1} to approximately 10.5 mg L^{-1}. Annual mean SO_4–S concentrations declined similarly between precipitation-normalized deposition of SO_4–S and flow-normalized SO_4–S (Fig. 1).

In both precipitation and streamwater, pH demonstrated similar but inverse trends as those of SO_4–S. From 1984 to 2015, precipitation pH increased from 4.15 to 5.0, with the majority of the change coming in the later quarter of the 30-yr period. However, streamwater pH decreased from pH 6.8 in 1984 to pH 6.0 in 2008 and then increased sharply back to about 6.8, paralleling trends observed in precipitation pH (Fig. 2).

The observed discrepancy between the reduction in atmospheric wet deposition of SO_4–S and the decrease in the observed streamwater concentration over the study period indicated that deposition may not be the only contributing source of sulfur. Deep well samples taken in 2013 had a SO_4–S concentration of 28.6 mg L^{-1} (SD = 2.5), suggesting that subsurface geology contributes to the overall sulfur pool in the watershed (Gburek et al., 2006; Needelman et al., 2004). Indeed, under baseflow conditions, groundwater sampling studies confirmed substantial sulfur contributions into the streams through lateral flow in the subsurface aquifer (Gburek and Urban,1990). According to the detailed management record for the watershed, concentrations in the stream were not dependent on fertilizer inputs, which are primarily via manure or nitrogen-based chemical starters (Veith et al., 2015).

In 1990, the net deposition of atmospheric sulfur was about 39% of the total sulfur export, whereas in 2013 it was only 22%. This suggests that reduced atmospheric

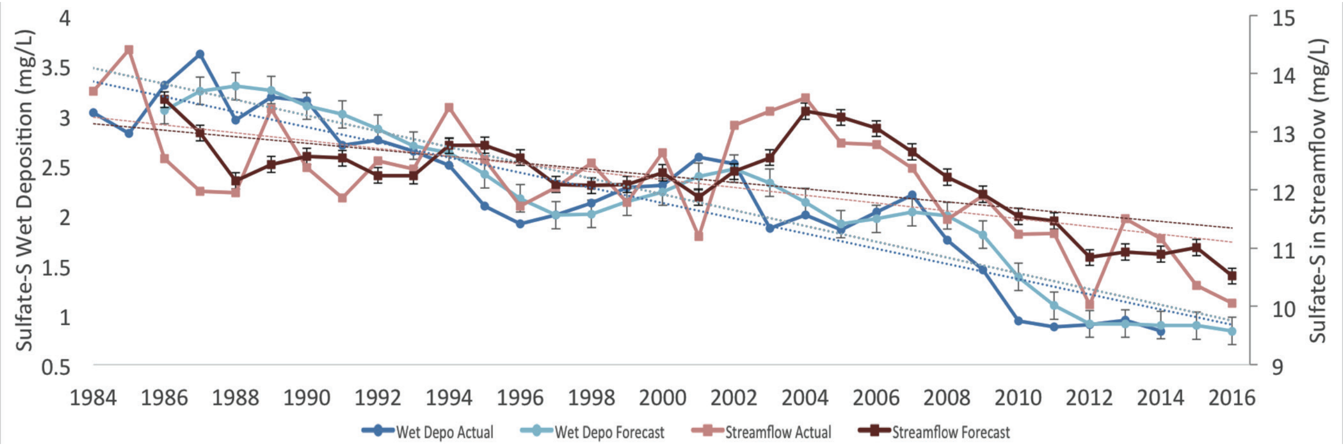

Fig. 1. Comparison of sulfate trends in atmospheric wet deposition and streamflow. Data points indicate actual annual mean values. Lines indicate the normalized concentration for streamflow (squares) and precipitation (circles). The forecasted regressions show a 3-yr moving average, with error bars showing the standard error. Dashed lines show the linear trends of the moving averages: streamflow SO_4–S concentration ($y = -0.076x + 3.413$, $R^2 = 0.82$) and wet deposition SO_4–S concentration ($y = -0.076x + 13.32$, $R^2 = 0.40$).

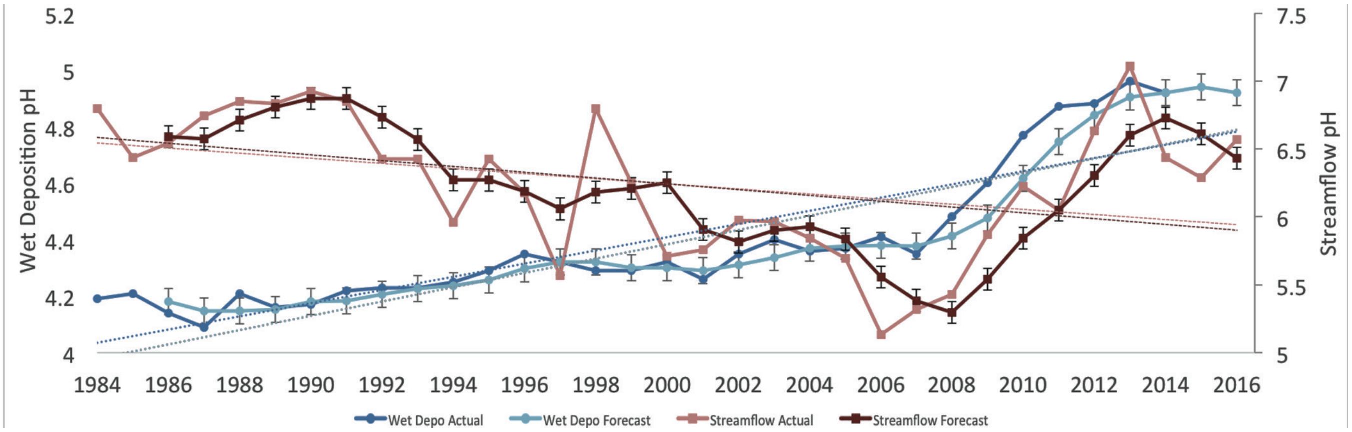

Fig. 2. Comparison of pH trends in atmospheric wet deposition and streamflow. Data points indicate actual annual mean values. Lines indicate the normalized pH for streamflow (squares) and precipitation (circles). The forecasted regressions show a 3-yr moving average, with error bars showing the standard error. Dashed lines show the linear trends of the moving averages: streamflow pH ($y = -0.018x + 6.54$, $R^2 = 0.13$) and wet deposition pH ($y = 0.023x + 4.01$, $R^2 = 0.75$).

deposition is the primary driver of declining sulfur concentration in the watershed.

Emerging Sulfur Deficits for Agriculture

Soil data from the 2013 sampling period is consistent with the water quality trends, with average soil pH of 6.05 (SD = 0.6) and average soil test sulfur concentration of 13.7 mg kg^{-1} (SD = 3.4) (Pennsylvania State University, 2016). Of the fields sampled, 26% tested below the agronomic optimum value of 10 mg kg^{-1} SO_4–S (Beegle et al., 2014). It is well established that more SO_4–S is typically removed than applied in agricultural watersheds, primarily through exportation of harvested crops and in the case of WE-38, which has a groundwater boundary similar to the surface water boundary, manure (Dick et al., 2008; Gburek and Urban,1990). In the WE-38 crop rotation of corn (*Zea mays* L.), soybean [*Glycine max* (Merr.) L.], and small grain (*Triticum aestivum* L.), 80 to 85% of which is exported, total dry matter sulfur concentrations are 0.10 to 0.25% (Blanchar, 1986; Miller, 1993). In WE-38, only 2 of the 315 fields received $(NH_4)_2SO_4$ and less than 10% received manure, with estimated sulfur contents of 0.25 and 0.50% for dairy and poultry manures, respectively (Banwart and Bremner, 1975). The remaining animal manure produced within watershed was exported to fields outside the WE-38 hydrologic boundary.

Conclusion

Long-term monitoring of watersheds like WE-38 and those studied by David et al. (2016) provides evidence of the Clean Air Act's effect on sulfur deposition as well as the kinetics and responses of the watersheds themselves. Such data are critical in providing insight about the main drivers that affect sulfur flux through soil and subsurface paths. In the future, monitoring of sulfur as a nutrient rather than a pollutant will become increasingly important in crop production. With continued net export of sulfur, soils will require amendments of sulfur-enriched fertilizers to meet the agronomic needs of crops.

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