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Long-term response of surface water acid neutralizing capacity in a central Appalachian (USA) river basin to declining acid deposition

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HIGHLIGHTS

- Data from multiple synoptic spring baseflow surveys were used to characterize the acid-base status of USRW streams.
- Decreasing trends in surface water SO_4^{2-} and NO_3^- were explained by declining S and N emissions and deposition onto USRW.
- We observed significant ANC recovery in 10–20% of the USRW stream network, despite not detecting a regional ANC trend.
- Surface water ANC recovery was significantly moderated by decreasing trends in K^+, Mg^{2+}, and Ca^{2+} concentrations.
- RKT appears to be a robust method for identifying basin-wide trends for some key chemical constituents.

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ABSTRACT

Long-term changes in acid-base chemistry resulting from declining regional acid deposition were examined using data from repeating synoptic surveys conducted within the 275 km^2 Upper Savage River Watershed (USRW) in western Maryland (USA); a randomly-selected set of 40 stream reaches was sampled 36 times between 1999 and 2014 to: (1) repeatedly characterize the acid-base status of the entire river basin; (2) determine whether an extensive network of streams of varying order has shown signs of recovery in acid neutralizing capacity (ANC); and (3) understand the key factors controlling the rate of ANC recovery across the river network. Several non-parametric analyses of trends (i.e., Mann Kendall Trend: MKT tests; and Regional Kendall Trend: RKT) in streamwater acid-base chemistry suggest that USRW has significantly responded to declining acid deposition during the study period; the two most robust, statistically significant trends were decreasing surface water SO_4^{2-} (~1.5 μeq L^{-1} yr^{-1}) and NO_3^- (~1 μeq L^{-1} yr^{-1}) concentrations—consistent with observed downward trends in regional wet S and N deposition. Basin-wide decreasing trends in K^+, Mg^{2+}, and Ca^{2+} were also observed, while Na^+ concentrations increased. Significant ANC recovery was observed in 10–20% of USRW stream reaches (depending on the p level used), but the magnitude of the trend relative to natural variability was apparently insufficient to allow detection of a basin-wide ANC trend using the RKT test. Watershed factors, such as forest disturbances and increased application of road deicing salts, appeared to contribute to substantial variability in concentrations of NO_3^- and Na^+ in streams across the basin, but these factors did not affect our overall interpretation of the results as a systematic recovery of USRW from regional acidification. Methodologically, RKT appears to be a robust method for identifying basin-wide trends using synoptic data, but MKT results for individual systems should be examined closely (e.g., to identify trends for specific subpopulations).

Abbreviations: CAAA, U.S. Clean Air Act Amendments of 1990; SO_2, sulfur dioxide; NO_x, nitrogen oxide; μeq, microequivalents; ANC, acid neutralizing capacity, μeq L^{-1}; DOA, dissolved organic acids, μeq L^{-1}; DOC, dissolved organic carbon, mg L^{-1}; SBC, sum of base cations, ($Na^+ + K^+ + Mg^{2+} + Ca^{2+}$), μeq L^{-1}; MKT, Mann-Kendall Trend Test; RKT, Regional Kendall Trend Test; USRW, Upper Savage River Watershed; NADP, National Atmospheric Deposition Program; DI, Disturbance Index.

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1. Introduction

Atmospheric deposition of acidifying pollutants originating primarily from fossil fuel combustion contributed to acidification of surface waters in many regions of Europe and North America during the 20th century (Sullivan et al., 1988; Kaufmann et al., 1991; Herlihy et al., 1991). Title IV of the Clean Air Act Amendments (CAAA) of 1990 reduced emissions of SO_2 and NO_x from stationary electricity-generation sources in the United States (U.S.), resulting in reductions in wet deposition of acidifying pollutants, as well as in the acidity of precipitation, throughout much of the country (Lynch et al., 2000). By the late 1990s, these emission controls had led to ~40% reductions in sulfate deposition in the eastern U.S. with the greatest improvements observed in the mid-Appalachian mountain region (Burns et al., 2011). Furthermore, other regulatory programs implemented in the late 1990s and early 2000s (e.g., Ozone Transport Commission NO_x Budget Trading Program, the NO_x State Implementation Plan Call, the Clean Air Interstate Rule, the Cross-State Air Pollution Rule, as well as improved vehicle emission standards) effectively controlled NOx emissions from both stationary and mobile sources, contributing to reductions in NO_3^- deposition (Butler et al., 2011). By 2009, reductions of approximately 27% in inorganic N deposition had been observed in the eastern U.S. (Burns et al., 2011); more recently, even greater (32–47%) reductions in inorganic N deposition were reported for some high elevation subwatersheds and major tributaries, as well as the main stem, of the Potomac River (Eshleman and Sabo this issue).

Implementation of emission controls produced almost immediate declines in surface water sulfate concentrations, especially in the northeastern U.S., Canada, and Europe, as well as decreases in surface water nitrate concentrations in some studies (Clow and Mast, 1999; Stoddard et al., 1999; Driscoll et al., 2003; Kahl et al., 2004; Eshleman et al., 2013; Eshleman and Sabo, this issue). In some cases, reductions in acid anion concentrations in surface waters contributed to modest recovery in acid neutralizing capacity (ANC), such as in an intensively-monitored first order stream in Savage River watershed on the Appalachian Plateau of western Maryland (Eshleman et al., 2008). Previous analyses have suggested a recovery rate of ANC for this region of about 1.5 $\mu eq\ L^{-1}\ yr^{-1}$ (Skjelkvale et al., 2005; Stoddard et al., 2003; Eshleman et al., 2008). In contrast, ANC recovery in streams has not been observed at other locations, particularly in the glaciated northeastern U.S. and the southeastern U.S., where it has been hypothesized that concomitant decreases in base cation deposition (Likens et al., 1996; Clow and Mast, 1999; Stoddard et al., 1999); increases in surface water dissolved organic carbon (DOC) (Evans et al., 2006; Erlandsson et al., 2011); decreasing surface water base cation concentrations from depleted soil base saturation (Lawrence et al., 1999; Driscoll et al., 2001); or soil sulfate sorption (Cosby et al., 1986, 2001) have limited or delayed recovery.

Prior ANC recovery studies conducted in the late 1990s and early 2000s focused primarily on either a few individual stations (Likens et al., 1996; Eshleman et al., 2008) or multiple stations throughout relatively large regions (Clow and Mast, 1999; Stoddard et al., 1999; Kahl et al., 2004; Skjelkvale et al., 2005; Garmo et al., 2014; Strock et al., 2014). Our objectives in this study were to: (1) repeatedly characterize the acid-base status of an entire river basin over a 15-year period; (2) determine whether an extensive network of streams of varying order within a single river basin has shown signs of ANC recovery from earlier acidification during a period of dramatic declines in sulfuric and nitric acid deposition; and (3) understand the key factors controlling the rate of ANC recovery from acidification across a stream network.

2. Materials and methods

We examined recovery trends for a random sample of stream reaches of varying order (1st through 4th) in the Upper Savage River Watershed (USRW) located on the rugged Appalachian Plateau in western Maryland, USA (Fig. 1). Geographically, Savage River is a major tributary of the North Branch of the Potomac River. The USRW covers an area of 275 km^2 in the headwaters of Savage River upstream of Savage River Dam and Reservoir; the basin is bordered by Meadow Mountain to the west and by Big Savage Mountain to the east, and is situated on a fluvially-dissected anticline consisting of gently-folded sedimentary rocks of Permian, Pennsylvanian, and Mississippian age (Brezinski and Conkwright, 2013). The basin is minimally populated and mostly undeveloped; 80% is forested, 15% is in agriculture, and there are only a few small developed areas (<5%) within USRW. Savage River State Forest covers 46% of the basin.

Thirty-six repeating, synoptic stream surveys were conducted between 1999 and 2014 at 40 randomly-selected stream reaches within the USRW (Hypio, 2000). The survey design was based on 1:24,000-scale digital river reach data included in the National Hydrography Dataset for the USA (www.nhd.usgs.gov) with the 40 reaches selected randomly from the entire digital stream network for the USRW (grouped by major subwatershed to ensure broad geographic representation) with the probability of selecting a particular reach proportional to the individual reach length (Hypio, 2000). With the exception of a few surveys intentionally conducted under stormflow conditions, all of the field sampling was performed under seasonal baseflow conditions (using on-line discharge data from a USGS station within the watershed to ensure that baseflow conditions prevailed during sampling). Each survey was normally completed in either one day or on two consecutive days to minimize the effects of hydrologic variations on water chemistry; for consistency, all water samples were collected at fixed locations at, or near (in the few cases where logistics prohibited it), the downstream end of each stream reach.

"Grab" water samples were collected in triple-rinsed, 1L polyethylene cubitainers and kept on ice in a cooler until returned to the laboratory where they were filtered (0.45 μm membrane) for analysis of acid anions (chloride, Cl^-; nitrate, NO_3^-; sulfate, SO_4^{2-} by ion chromatography), base cations (sodium, Na^+; potassium, K^+; magnesium, Mg^{2+}; calcium, Ca^{2+} by flame atomic absorption spectrometry), and dissolved organic acids (DOA) estimated from dissolved organic carbon (DOC by UV-assisted persulfate digestion) using the model of Oliver et al. (1983); specific conductance (conductivity meter; μS/cm) and acid neutralizing capacity (ANC by automated, acidimetric Gran titration) were measured on unfiltered aliquots. Blanks and independent check samples were used in each batch to ensure that our analyses met rigorous quality control standards. Conductivity and ion balance calculations were used as internal quality control checks.

Since the various surveys were conducted on an irregular basis, we relied on long-term water chemistry data from two intensively-monitored, gaged subwatersheds nested within the USRW (Upper Big Run: BIGR; area = 162 ha and Black Lick: BLAC; area = 558 ha) to determine which synoptic surveys were likely to provide data that were most representative of annual average conditions. BIGR was selected for long-term study because of its extreme acid sensitivity (ANC < 50 $\mu eq\ L^{-1}$), while BLAC was determined to exhibit less acid sensitivity (100 $\mu eq\ L^{-1}$ < ANC < 200 $\mu eq\ L^{-1}$). While both watersheds are predominantly forested, neither is pristine; BIGR is bisected by a county-maintained road and a power line corridor, while BLAC has considerable agricultural land in its headwaters. Monthly and annual discharge-weighted mean concentrations for major chemical constituents were estimated using

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