



Processes affecting the response of sulfate concentrations to clearcutting in a northern hardwood forest, Catskill Mountains, New York, U.S.A.

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Abstract. The effects of disturbance on the biogeochemical processes that affect the sulfur (S) cycle in forested ecosystems are important, but have been studied in only a few locations. In this investigation, the mechanisms that caused large decreases in stream SO_4^{2-} concentrations after clearcutting a small forested catchment in the Catskill Mountains of southeastern New York in 1997 were identified through an examination of pH and SO_4^{2-} concentrations in soil solutions, bulk deposition of SO_4^{2-} in throughfall collectors, adsorbed SO_4^{2-} concentrations in buried soil bags, and spatial variations in SO_4^{2-} concentrations in shallow groundwater. The load of SO_4^{2-} -S in stream water during the first 2 years after clearcutting was about $2 \text{ kg ha}^{-1} \text{ year}^{-1}$ less than the background value of $8\text{--}10 \text{ kg ha}^{-1} \text{ year}^{-1}$. The 10 and 19% decrease in net throughfall flux of SO_4^{2-} -S during the 2nd and 3rd year after the clearcut, respectively, reflects reduced dry deposition of S after removal of the canopy, but this decrease accounts for 0 and 43%, respectively, of the decrease in SO_4^{2-} load in streamflow for these 2 years. The pH of B-horizon soil water decreased from 4.5 to 4.0 within 8 months after the clearcut, and SO_4^{2-} concentrations decreased from $45 \mu\text{mol L}^{-1}$ to less than $20 \mu\text{mol L}^{-1}$ during this time. A strong correlation between SO_4^{2-} concentrations and pH values ($r^2 = 0.71$, $p < 0.01$) in B-horizon soil water during the post-harvest period (1997–1999) reflects increased SO_4^{2-} adsorption in response to soil acidification. Sulfate concentrations in groundwater from 21 spatially distributed wells were inversely related to a topographic index that served as a surrogate for soil wetness; thus, providing additional evidence that SO_4^{2-} adsorption was the dominant cause of the decreased SO_4^{2-} concentrations in the stream after clearcutting. These results are consistent with those from a 1985 whole-tree harvest at the Hubbard Brook Experimental Forest in New Hampshire in which increased SO_4^{2-} adsorption resulting from decreased soil pH was the primary cause of decreased SO_4^{2-} concentrations in stream water.

Introduction

The processes that affect rates of sulfur (S) cycling through forested ecosystems in eastern North America are of interest because S is a major factor in surface-water acidification (Devito 1995; Alewell et al. 1997; Driscoll et al. 1998). Sulfur in the form of SO_4^{2-} is generally the dominant anion in atmospheric deposition in North America and Europe despite decreasing SO_4^{2-} concentrations in these regions during the past two decades (Driscoll et al. 1998; Forsius et al. 1998). Accurate

predictions of the response of surface-water chemistry to reduced S deposition will require an improved understanding of the biogeochemical processes that affect S cycling in catchments such as adsorption/desorption, biological uptake, and precipitation/dissolution of aluminum hydroxy-sulfate minerals (Mitchell et al. 1992; Reynolds et al. 1997). The manner in which these S-cycling processes interact to affect SO_4^{2-} concentrations and loads in surface waters is poorly understood, and many sources of uncertainty remain including (1) the potential for underestimation of dry deposition of S by routine techniques, (2) sources of S derived from mineral weathering of sulfides and S-mineralization that may be unaccounted for in many catchment mass balances, (3) insufficient knowledge of the reversibility of SO_4^{2-} adsorption, and (4) the relation of SO_4^{2-} adsorption to soil chemical properties (Harrison et al. 1989; Driscoll et al. 1998; Manderscheid et al. 2000).

Intensive forest harvesting that includes either clearcutting or whole-tree harvesting generally results in decreased SO_4^{2-} concentrations in streams in the northeastern U.S. and the U.K. (Likens et al. 1970; Martin et al. 1984; Adamson and Hornung, 1990; Reynolds et al. 1995). The mechanisms proposed for reduced SO_4^{2-} leaching following forest harvesting include (1) reduced dry deposition of S resulting from canopy removal (Adamson and Hornung 1990; Neal et al. 1992), (2) dilution from decreased transpiration and the resulting increase in runoff (Likens et al. 1978; Reynolds et al. 1995), (3) changes in decomposition rates that result in greater microbial retention or reduced S-mineralization rates (Likens et al. 1978), and (4) increased adsorption of SO_4^{2-} by soils through the decreased pH of soil and soil water (Nodvin et al. 1986; Fuller et al. 1987).

Enhanced SO_4^{2-} adsorption in soils was observed after a 1985 whole-tree harvest at Hubbard Brook, NH (Nodvin et al. 1986, 1988; Mitchell et al. 1989; Zhang et al. 1999), but has never been documented at other sites. Additionally, the potential roles of enhanced SO_4^{2-} adsorption and decreased dry deposition of S have not been simultaneously studied previously. In this study, we examine the potential roles of increased SO_4^{2-} adsorption and decreased dry deposition of S following clearcutting at a catchment dominated by a northern hardwood forest in the Catskill Mountains of New York. We collected data on SO_4^{2-} concentrations in stream water, soil water and throughfall, adsorbed SO_4^{2-} in buried bags of B-horizon soil, and streamflow at a clearcut and at an adjacent reference catchment in support of the study objective. Finally, we also examine spatial variations of SO_4^{2-} concentrations in shallow groundwater as a function of a surrogate for catchment wetness, the topographic index of Beven and Kirkby (1979).

Study site

The Catskill Mountains of southeastern New York consist of an uplifted plateau of nearly horizontally bedded sedimentary bedrock that has been dissected by streams and later covered by a variably thick layer of till in the most recent glaciation. The treatment (Dry Creek) and adjacent reference catchments are tributaries of the

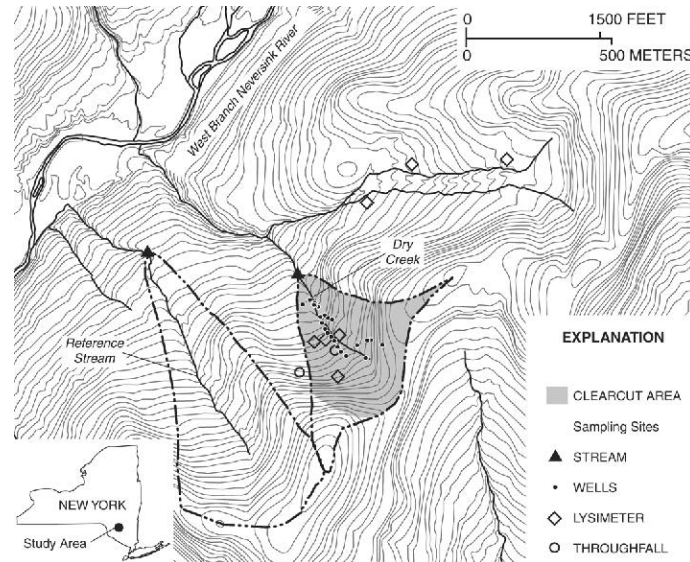


Figure 1. Locations of sampling sites in the Dry Creek catchment, reference catchment, and surrounding reference area.

Neversink River, with drainage areas of 24- and 48 ha, respectively (Figure 1). Catchment elevations range from 650 to 890 m, and the topography has a 'stair-step' appearance controlled by resistant beds within the underlying bedrock. Soils are classified as Inceptisols in the Arnot-Oquaga-Lackawanna association, described as a bouldery silt loam with thin organic horizons (15–80 mm) (Tornes 1979). Soil thickness varies from 0.35 to 1 m, and soils are excessively to moderately drained, predominantly steep, and medium textured. A compacted dense soil layer generally overlies till that is at least 1 m thick. Soil and till are thickest near the stream and toward the catchment outlet. Catchment soils are underlain by Devonian age coarse sandstone interbedded with shale and siltstone (Way, 1972). Vegetation is dominated by American beech (*Fagus grandifolia*), sugar maple (*Acer saccharum*), and yellow birch (*Betula alleghaniensis*) with occasional eastern hemlock (*Tsuga canadensis*) at lower elevations.

The climate is humid continental with cold winters and moderately warm summers. Annual precipitation at Slide Mountain (elevation 808 m), about 5 km northeast of Dry Creek, is among the greatest in the northeastern U.S. with a mean of 1570 mm, of which 20–25% falls as snow. Mean annual air temperature at Slide Mountain is 4.6 °C (NOAA 1990). Precipitation is distributed evenly throughout the year, although 32% of the mean annual runoff of 970 mm in the Neversink River occurs during the snowmelt period (March and April), whereas only 28% occurs from May through September (mean from 1951 to 1994, Firda et al. 1995).

Clearcutting of the Dry Creek catchment began in December 1996 and was completed in March 1997. Slash was left behind, usually in piles 2 m deep or less.

The southeastern corner of the catchment, which encompasses about 20% of the drainage area, remained unharvested because it is located on New York State 'Forever Wild' land. Efforts to minimize erosion and compaction of the soil during the harvest entailed spreading slash along skid trails to protect the soil surface, and harvesting mainly while the catchment was snow covered.

Methods

Stream-water samples at Dry Creek and the reference stream were collected bi-weekly for chemical analysis from January 1997 through September 2001. Stormflow samples were also collected episodically at Dry Creek. Streamflow was determined at an H-flume at Dry Creek and at a natural control in the reference stream according to methods described by Rantz et al. (1982).

Soil water was collected from seven pairs of zero-tension lysimeters at depths of 50–100 mm in the O-horizon and 250–300 mm in the B-horizon. Three of these lysimeter sites were located in a catchment in which about 10% of the biomass was removed during 1995–1996 in a tree-thinning harvest, however, the area within a 10-m radius of each of these lysimeter sites was not disturbed, and the soil-water chemistry did not exhibit any of the changes associated with forest harvesting, such as increased NO_3^- or decreased SO_4^{2-} concentrations; thus, these sites are considered to represent undisturbed conditions. The other four lysimeter sites were in the Dry Creek catchment.

Groundwater was collected from 21 piezometers (190 mm inside-diameter PVC pipe) that were installed throughout the Dry Creek catchment in the autumn of 1997, encompassing a wide range of topographic positions, including mid-bench (flat area), mid-slope, shoulder of slope, base of slope, and hollows or depressions (Figure 1). The screened interval of each piezometer was about 100 mm, and most were 0.75–1.0 m below land surface (depending on soil depth), usually just above the soil–bedrock interface. Groundwater samples were collected with a vacuum pump after each piezometer was purged, and each sample was placed in a 500 ml polyethylene bottle. One sample was collected from each piezometer and from Dry Creek after each of five storms from March through July 1998.

Ten bulk deposition collectors were located at a site in the clearcut catchment and at a site in the adjacent hardwood canopy from May 1997 to October 1999. Each collector consisted of a polyethylene funnel (about 1.5 m above the ground surface) attached to a plastic bag. The bags were collected weekly by combining the contents of each bag, measuring the volume, and thus creating a pooled sample for chemical analysis. Each sample was passed through a 0.4 μm Nuclepore (use of name brands is for identification purposes only and is not meant as an endorsement of a specific product) filter and then stored at 4 °C until analysis of SO_4^{2-} by ion chromatography.

The canopy site represents ambient throughfall, which was compared with data collected in the open at the clearcut during the same period to provide an estimate of dry deposition of S. The difference is known as the net throughfall flux (Lindberg

and Owens 1993; Lovett et al. 1999). Collectors were operated only from May to October of each year when the leaf canopy was present because a previous study at a nearby catchment indicated that dry deposition of S during the dormant season was negligible compared to that during the growing season (Lovett et al. 1999).

Stream SO_4^{2-} loads were calculated through linear interpolation of SO_4^{2-} concentrations measured biweekly to provide a SO_4^{2-} concentration for each stream for each day in the 4-year record. Dry Creek has less runoff than the reference catchment, probably as a result of groundwater loss through the fracture flow system that is extensive in the sedimentary bedrock of the Catskill Mountains (Burns et al. 1998; Lawrence et al. 2001). This runoff disparity makes direct comparison of output fluxes between catchments difficult. Therefore, changes in loads as a result of the cut were calculated by first obtaining a mean SO_4^{2-} concentration for each stream for each water year (October 1–September 30), then multiplying these mean concentrations by the annual runoff from the clearcut watershed to determine SO_4^{2-} –S loads. The differences in SO_4^{2-} –S loads between the clearcut and reference streams for water years 1993–1996 (pre-clearcut) were then averaged to obtain a background load difference that is attributable to differences in runoff in the two catchments. The reference stream had a mean SO_4^{2-} –S load that was $0.52 \text{ kg ha}^{-1} \text{ year}^{-1}$ greater than Dry Creek. This background difference changes from year to year but is negligible compared to the changes that resulted from clearcutting. Therefore, use of a simple mean difference of pre-cut years to calculate the background load difference between the two catchments is reasonable. We tested the sensitivity of calculated loads using just biweekly samples and all samples including stormflow samples. We find that the difference is negligible and we attribute this to the fact that in these catchments, SO_4^{2-} dilutes significantly with increased flow. Further, our budgets calculated using only baseflow samples are in very close agreement with budgets developed using non-linear regression techniques relating flow to SO_4^{2-} concentration for the same catchment (M. McHale, personal communication). For these reasons, we feel that we are justified in using a single annual average load based on biweekly baseflow samples in these calculations.

Changes in the rate of SO_4^{2-} adsorption through time were assessed with a buried-bag method that was developed in a previous study to overcome the effects of strong heterogeneity in forest-soil chemistry, while allowing assessment of short-term responses to manipulations such as nutrient additions (David et al. 1990). Briefly, B-horizon soil was obtained from a location near the clearcut, passed through a 2-mm sieve, air dried, and homogenized. About 300 g of soil was then placed into $150 \text{ mm} \times 150 \text{ mm} \times 25 \text{ mm}$ nylon mesh ($250 \mu\text{m}$) bags and sewn shut. Ten replicate bags were then buried in 1995 at a depth of 250–300 mm at each of 24 locations in the Dry Creek catchment. The buried bag locations were chosen to represent the range of elevations and aspects in the watershed. Bags were removed over time for analysis – 13 in 1996, 23 in 1997, 22 in 1998, and 20 in 1999.

Catchment topography was mapped with a total station on an approximately 5-m grid. The survey data was placed in real world coordinates using a survey-grade GPS system. The part of the catchment that was not harvested was not surveyed;

the topography in this area was taken from a 10-m digital elevation model (DEM) compiled by the New York State Department of Environmental Conservation. The combination of the DEM and field survey was tessellated to a 10 m DEM. Terrain indices were calculated from the Dry Creek DEM. The topographic index (Beven and Kirkby, 1979) for the location of each well was calculated as

$$TI = \ln\left(\frac{a}{\tan \beta}\right) \quad (1)$$

where a is the upslope contributing area per unit contour length, and $\tan \beta$ is the local slope angle. Calculation of the TI was performed using the method of Quinn et al. (1995). This index incorporates two factors that determine wetness–water movement due to gravity, and the amount of upslope area that contributes lateral flow to a point on the landscape. The result is a theoretical estimation of wetness potential at any point in the catchment (Quinn et al. 1995).

Results

Results are presented in four categories—stream water SO_4^{2-} concentrations and S loads, soil water chemistry, topographic differences in shallow groundwater, and adsorbed SO_4^{2-} in buried bags.

Atmospheric S deposition, stream water SO_4^{2-} concentrations, and S loads

The source of SO_4^{2-} in the two study catchments was assumed to originate from atmospheric deposition in the absence of a mineral S source. This is supported by an S budget for a geologically-similar catchment less than 4 km from Dry Creek in which outputs were equal to inputs derived from only measured wet deposition and estimated dry deposition (Stoddard and Murdoch 1991). Sulfur deposition from May through October 1997 at the clearcut site was similar to that in the undisturbed hardwood canopy site, but was about 10% less than the reference site during 1998 and 19% less during 1999 (Figure 2).

Sulfate concentrations in Dry Creek and the reference stream fluctuated in a similar manner and generally decreased from about $70 \mu\text{mol L}^{-1}$ in 1992 to about $55 \mu\text{mol L}^{-1}$ in 1997 (Figure 3); this general decrease parallels regional decreases in atmospheric S deposition during this period (Lynch et al. 2000). After completion of the harvest, SO_4^{2-} concentrations in Dry Creek decreased rapidly to $25 \mu\text{mol L}^{-1}$ late in 1997, and then slowly increased through early 2000 until values similar to those of the reference catchment were reached ($58 \mu\text{mol L}^{-1}$). Thereafter, values increased through 2001 to $62 \mu\text{mol L}^{-1}$, which exceeded those in the reference catchment.

The annual decrease in SO_4^{2-} loads from Dry Creek during the 4-year study is shown in Figure 4. The background load was subtracted from the difference between the annual loads from each catchment to obtain the decrease in SO_4^{2-} –S

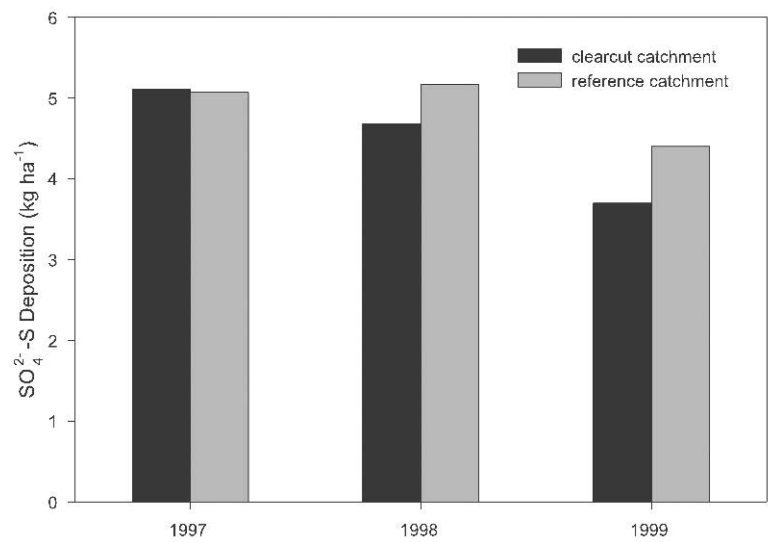


Figure 2. Stream SO_4^{2-} concentration in Dry Creek and the reference stream, 1991–2001.

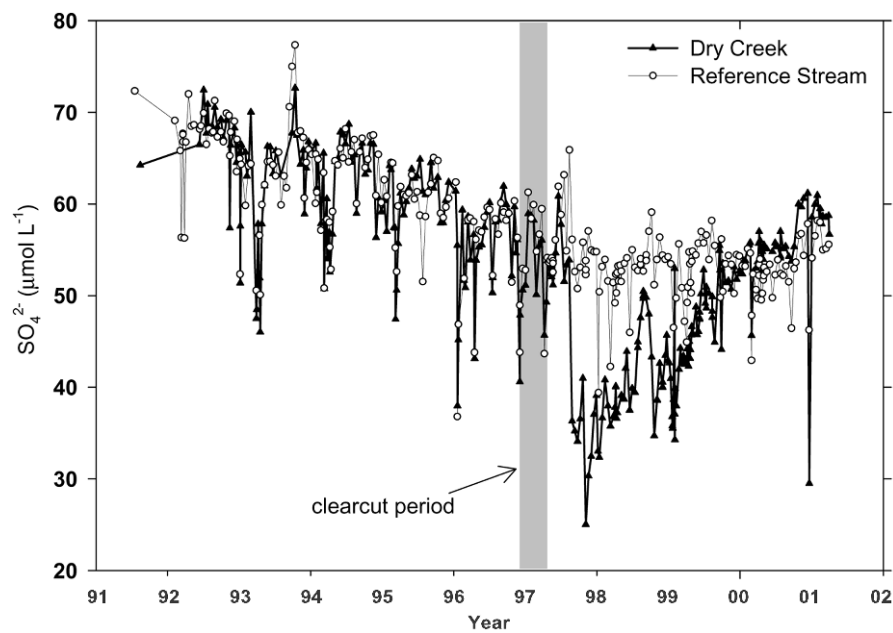


Figure 3. Annual bulk SO_4^{2-} -S deposition in the Dry Creek catchment and in an adjacent forested area, 1997–1999.

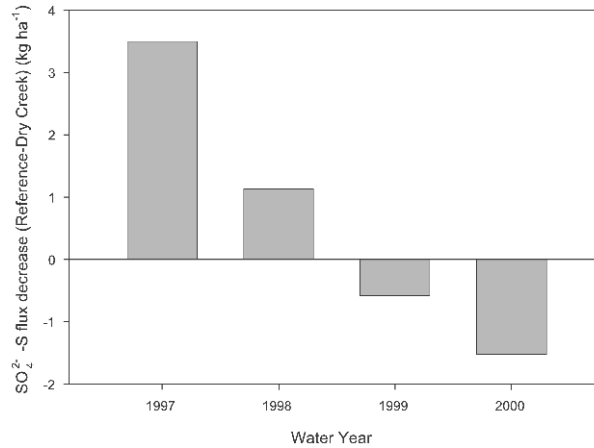


Figure 4. Annual change in SO_4^{2-} -S loads from Dry Creek since the 1997 clearcut, calculated as load from the reference stream minus that from Dry Creek.

load attributable to clearcutting. The Dry Creek loads for 1997 and 1998 indicate a decrease of about 3.5 and 1.3 $\text{kg ha}^{-1} \text{ year}^{-1}$, respectively, followed by increased export of 0.6 and 1.5 $\text{kg ha}^{-1} \text{ year}^{-1}$ above background in 1999 and 2000 respectively (Figure 4).

Soil solution chemistry

Decreased plant uptake of nitrogen after the clearcut allowed excess nitrification and greatly elevated nitrate (NO_3^-) concentrations in stream water and soil water; this resulted in decreased soil-water pH (Figure 5). O-horizon soil water pH decreased from about 4.5 prior to the harvest to between 3.5 and 4.0 within 4 months after the harvest was completed (Figure 5(A)). These values then increased to 4.0–4.5 within 6 months after harvest, and remained within that range throughout the rest of the study, although values were higher during spring and lower during summer. O-horizon soil-water SO_4^{2-} concentrations increased from a range of 20 to 40 $\mu\text{mol L}^{-1}$ soon after the harvest to 70 $\mu\text{mol L}^{-1}$ the following summer, and then sharply decreased to about 30 $\mu\text{mol L}^{-1}$ by January 1998. The concentrations then varied widely through the remainder of the study—from less than 20 $\mu\text{mol L}^{-1}$ to nearly 70 $\mu\text{mol L}^{-1}$. Sulfate concentrations were not significantly related to H^+ concentrations in O-horizon soil water ($r^2 = 0.22$, $p > 0.05$) during the post-harvest period (Figure 6).

B-horizon soil water pH increased briefly from about 4.5 to about 4.8 early in the spring following the clearcut and then sharply decreased to about 4.0 within 4 months after completion of the harvest (Figure 5(b)). These values then followed a cyclical seasonal pattern of highest pH in winter and spring, and lowest pH in

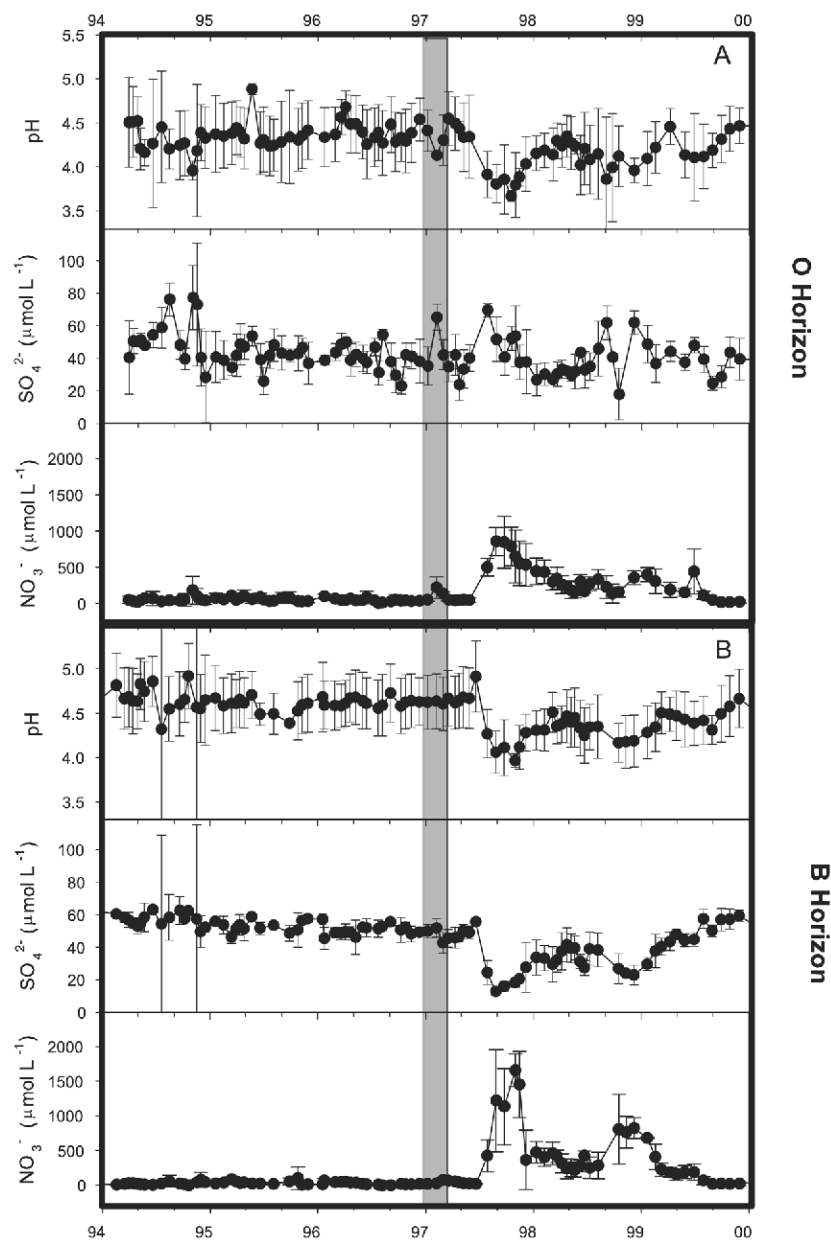


Figure 5. Mean SO_4^{2-} and NO_3^- concentrations and pH in soil water from five zero-tension lysimeters located in the Dry Creek catchment; 1994–2000. (A) O-horizon. (B) B-horizon. Vertical line indicates the timing of the clearcut. Error bars are equal to 1 standard deviation.

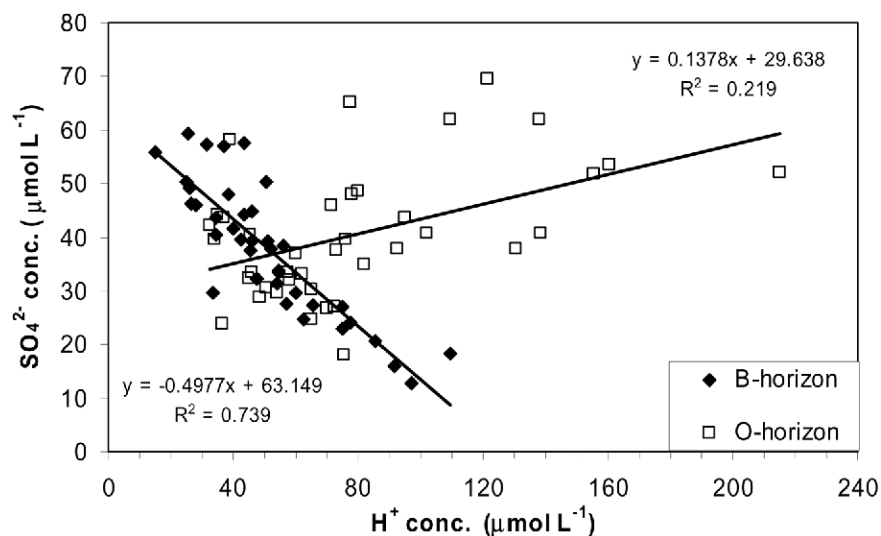


Figure 6. Relationship between proton and sulfate concentrations in O- and B-horizon soil water from Dry Creek.

summer and fall as values progressively increased to about 4.5 by the fall of 1999, 2.5 years after the harvest. B-horizon SO_4^{2-} concentrations paralleled the pH values—rising briefly from about 45 to 55 $\mu\text{mol L}^{-1}$, then decreasing to less than 20 $\mu\text{mol L}^{-1}$ before increasing back to pre-harvest levels by the fall of 1999. Sulfate concentrations were strongly related to H^+ concentrations ($r^2 = 0.74$, $p < 0.01$) in B-horizon soil water during the post-harvest period (Figure 6). The slope of the regression relation is -0.50 , which is consistent with the release of two H^+ ions for each SO_4^{2-} removed from solution during adsorption. A stepwise multivariate regression indicates that both SO_4^{2-} and NO_3^- concentrations are significant predictors of H^+ concentrations, and the r^2 -value of this regression is 0.86. This suggests a complex interrelation between SO_4^{2-} , NO_3^- , and H^+ concentrations (and therefore, pH) in B-horizon soil water after the clearcut. In contrast, when the same multivariate regression approach was applied to O-horizon soil water, NO_3^- but not SO_4^{2-} concentrations were a significant predictor of H^+ concentrations.

Topographic differences in shallow groundwater

During the five storms sampled in the spring and summer of 1998, SO_4^{2-} concentrations were significantly inversely correlated with the topographic index (mean r^2 and p -value across five storms: 0.38 and 0.005, respectively) (Figure 7). This inverse correlation indicates that SO_4^{2-} concentrations in shallow groundwater decrease as the topographic index increases (soil becomes wetter). The slope of the linear regression line for the earlier storms sampled (e.g. -7.6 on March 20) is

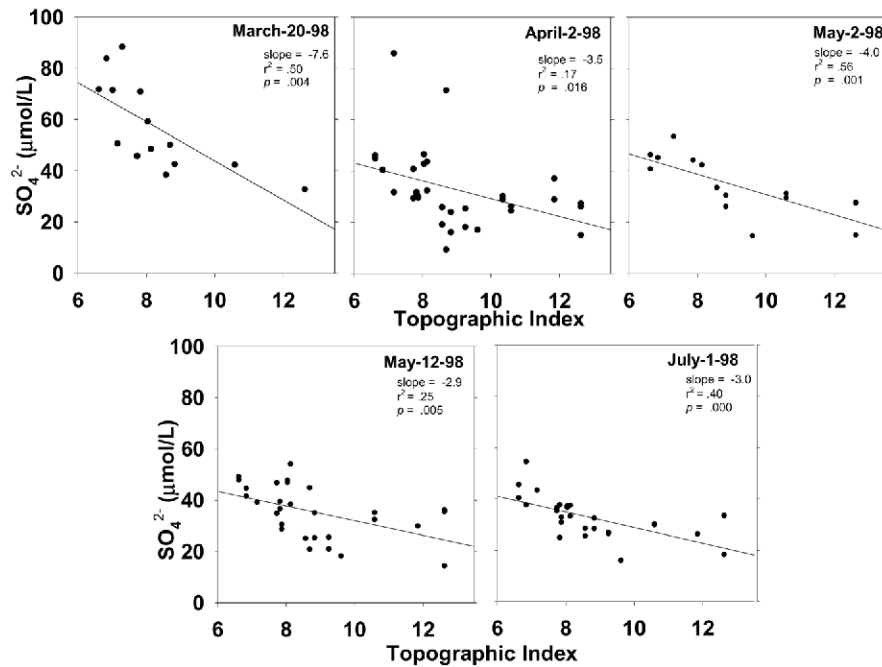


Figure 7. Sulfate concentrations in shallow groundwater at 21 piezometers in the Dry Creek catchment as a function of the topographic index during five storms in 1998.

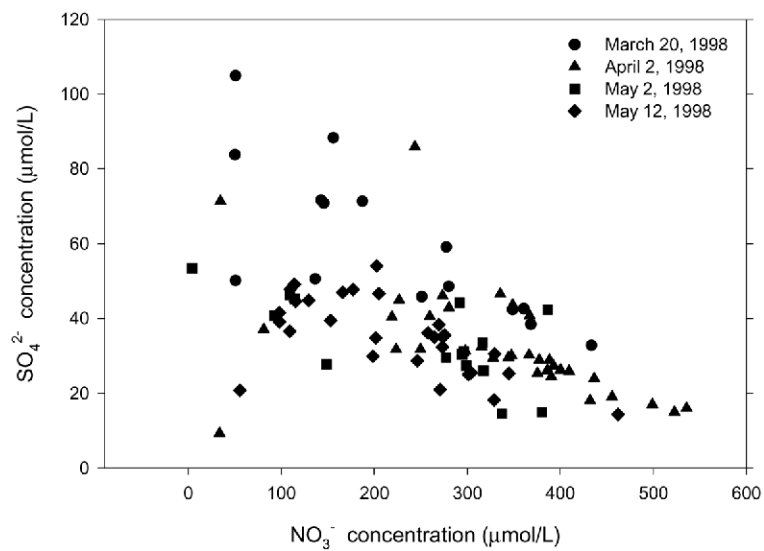


Figure 8. Sulfate concentrations in shallow groundwater at 21 piezometers in the Dry Creek catchment as a function of NO_3^- concentrations during five storms in 1998.

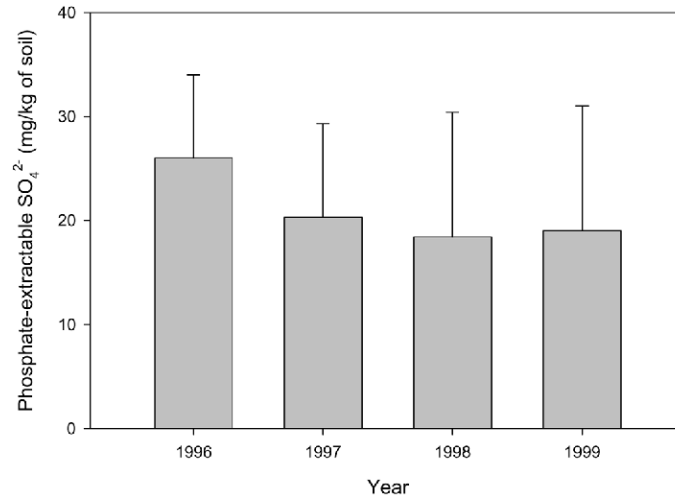


Figure 9. Phosphate-extractable SO_4^{2-} concentrations in extractions of mineral soil from buried bags retrieved from the Dry Creek catchment.

generally steeper than for later storms (e.g. -3.0 on July 1). The topographic-index differences among the sites sampled represent a continuum from dry to seasonally wet soil conditions. The topographic index is not an actual measurement of soil moisture, rather it represents the potential for a site to become saturated at the surface; and thus, can be viewed as a relative indicator of soil wetness. Plotting SO_4^{2-} concentrations in shallow groundwater against NO_3^- concentrations from the same piezometers reveals a distinct inverse correlation, which suggests concomitant adsorption of SO_4^{2-} with increasing nitrification and resulting acidification of soil and soil water ($r^2 = 0.33$, $p < 0.01$) (Figure 8).

Buried soil bags

The mean PO_4^{3-} -extractable SO_4^{2-} concentration of soil from buried bags collected in the Dry Creek catchment decreased from $>25 \text{ mg kg}^{-1}$ soil in 1996 to about 20 mg kg^{-1} soil in 1997 (Figure 9). These concentrations then decreased slightly in 1998, and increased slightly in 2000, but remained close to 20 mg kg^{-1} soil. The highest mean concentration obtained was in 1996—after 1 year of burial, but prior to the forest harvest.

Discussion

Increased leaching of NO_3^- after harvesting has been shown in previous studies to acidify the soil resulting in decreased soil-water pH (Likens et al. 1969). The

correlation between soil-water H^+ and SO_4^{2-} concentrations is especially striking among B-horizon soil-water samples during the 1997–1999 post-harvest period (Figure 6). The slope of -0.50 of this regression relation is consistent with H^+ – SO_4^{2-} exchange associated with the hypothesized SO_4^{2-} adsorption reaction. The lack of a similar significant correlation among post-harvest O-horizon soil-water samples suggests that pH-driven SO_4^{2-} adsorption probably occurs in the mineral soil somewhere below the depth of the O-horizon lysimeters. These soil-water data are consistent with the reported increase in adsorbed SO_4^{2-} in the E and Bh mineral soil horizons of a Spodosol at the Hubbard Brook Experimental Forest after a whole-tree harvest (Mitchell et al. 1989), and are generally consistent with the hypothesis that SO_4^{2-} adsorption in mineral soil was enhanced by the decrease in pH that followed the whole-tree harvest at this site (Fuller et al. 1987; Nodvin et al. 1988). The soil-water pH at this Catskill catchment is generally lower than that at Hubbard Brook and, thus, indicates that SO_4^{2-} adsorption due to clearcutting can increase to a soil-water pH as low as 4.0, which was reached during the first year after the harvest. The maximum SO_4^{2-} adsorption based on laboratory experiments with Spodosols from Hubbard Brook occurred at a pH of about 4.0. Minimum soil pH after whole-tree harvesting at Hubbard Brook was 4.3, whereas minimum soil pH at Dry Creek after clearcutting was 4.0, consistent with the laboratory results of Nodvin et al. (1986).

The relative net throughfall flux of SO_4^{2-} during the growing season was about 5% less (total for 1997–1999) after the clearcut than before. The maximum decrease in annual stream SO_4^{2-} –S load that resulted from the clearcut was about 25% in 1997 – about five times the measured decrease in dry deposition. Therefore, the decrease in dry deposition of SO_4^{2-} after clearcutting was only a minor contributor to the decreased stream SO_4^{2-} concentrations and loads measured in Dry Creek. These data cannot be compared with those of Hubbard Brook because dry deposition of SO_4^{2-} –S was not measured during either the original clearcut study or the whole-tree harvest study. The Catskill Mountains generally receive more dry deposition of S than Hubbard Brook (Ollinger et al. 1993); therefore, the effects of decreased dry deposition of S after harvesting were probably greater in the Catskills than at Hubbard Brook.

Of the annual decrease in output load of SO_4^{2-} –S in Dry Creek during 1997–1999 after clearcutting, 0, 43, and 100%, respectively could have originated from sources other than specific adsorption, including decreased dry deposition of SO_4^{2-} based on the decreases in net throughfall flux that were calculated for those years, and release of adsorbed soil SO_4^{2-} in the 1988 and 1999. The majority of the decrease in stream load during 1997 and 1998 probably originated from increased adsorption resulting from post-harvest changes in soil chemistry (100 and 57%, respectively). The decreased output load from baseline during 1999 was $-0.58 \text{ kg ha}^{-1} \text{ year}^{-1}$ indicating greater export from Dry Creek than from the control stream, and sharply less than the previous year ($1.1 \text{ kg ha}^{-1} \text{ year}^{-1}$). Adsorbed SO_4^{2-} probably began to be released in 1999, which resulted in increased stream loads in Dry Creek which were actually greater in Dry Creek than in the reference stream. This is consistent with results from Hubbard Brook which show that soil solution from the Bh and Bs2 horizons had

decreased SO_4^{2-} concentrations for less than 1 year following the harvest, and then showed slightly higher concentrations than the same soil horizon in the reference watershed for several years following harvest (Mitchell et al. 1989; Zhang et al. 1999). Therefore, reduced dry deposition of SO_4^{2-} to the incipient canopy relative to the reference forested site in 1999 played a relatively greater role in the reduced stream SO_4^{2-} flux than during the two previous years.

The processes responsible for changes in stream SO_4^{2-} loads in Dry Creek contrast sharply with those inferred from studies of the effects of clearcutting in the UK, where reduced dry deposition played a dominant role in decreased stream SO_4^{2-} concentrations after harvest of Sitka Spruce (*Picea sitchensis*) (Adamson and Hornung 1990; Neal et al. 1992). These results probably reflect higher rates of dry deposition capture by coniferous trees in the U.K. compared to that of hardwoods in the Catskills.

Data collected in another study and by a Clean Air Status and Trends Network site located less than 10 km from Dry Creek indicate that dry deposition of S varies from 2.5 to 3 kg S ha⁻¹ year⁻¹ (Lovett et al. 1999; www.epa.gov/castnet), whereas the net throughfall flux measured in the current study averaged only 0.4 kg S ha⁻¹ for the 6-month collection period each year. This difference in estimates of dry deposition rates between studies can be partly attributed to different collection methods. The method used at Dry Creek does not consider stemflow, which may contribute an additional 5% to dry deposition estimates (Lindberg and Lovett 1992) or direct deposition of SO_4^{2-} to the forest floor (Meyers and Baldochi 1993). Additionally, because throughfall samples were filtered prior to analysis, contributions of particulate sources of S that may be included in other measurement methods were not considered here. Another factor could be complex 'edge effects' known to occur in atmospheric deposition at sharp transitions between different canopy types (Weathers et al. 1995). The reference throughfall collectors in the current study were located only about 50 m from the clearcut area, and thus, may have been affected by "edge effects".

Despite the possibility that reductions in dry deposition of SO_4^{2-} resulting from clearcutting may have been underestimated in the current study by a factor of 2–3, the significant correlation with a slope of 0.5 between H^+ and SO_4^{2-} concentrations in B-horizon soil solutions strongly suggests that enhanced SO_4^{2-} adsorption is the principal process that caused the reduced SO_4^{2-} concentrations observed in stream water after the harvest.

The data from buried mineral soil bags in the Dry Creek catchment do not indicate increased adsorption of SO_4^{2-} at 250–300 mm deep in the B-horizon after harvesting. Rather, these data seem to support just the opposite contention; the mean concentration of adsorbed SO_4^{2-} in August 1997 was less than the mean concentration in August 1996, and the mean concentration in August 1998, after more than a year with decreased stream SO_4^{2-} concentrations, was still less than in August 1997. The soil water lysimeters are in the B-horizon (250–300 mm deep), and represent an integration of the interactions of water with soil between the surface and that depth. Soil-water SO_4^{2-} concentrations from the O-horizon (Figure 5(A)) suggest that increased adsorption did not occur in the forest floor. In the

absence of any soil-chemistry data that could identify the exact depth of enhanced SO_4^{2-} adsorption in these soils, the buried soil-bag and lysimeter data suggest that increased SO_4^{2-} adsorption resulting from the clearcut occurred between about 50 and 250 mm deep in the soil profile.

The shallow groundwater data as a function of topographic index provide further evidence of enhanced SO_4^{2-} adsorption by forest soils after the clearcut. The piezometers with high topographic-index values indicative of wetter sites had lower SO_4^{2-} concentrations than those with low topographic-index values (Figure 7). Previous work by Welsch et al. (2001) in the Dry Creek catchment showed that piezometers with high topographic-index values had high groundwater NO_3^- concentrations, indicating enhanced nitrification and associated NO_3^- leaching presumably resulting from higher soil moisture. The enhanced nitrification rates at locations with high topographic-index values lower the soil solution pH, thus, increasing SO_4^{2-} adsorption; this results in an inverse correlation between NO_3^- and SO_4^{2-} concentrations in shallow groundwater (Figure 8). Sulfate reduction can be excluded as a process responsible for the observed topographic index results because these Catskill soils are generally well drained and aerobic except in small wetland areas that represent less than 2% of the catchment. Additionally, dry deposition should be reduced relatively uniformly over the entire Dry Creek catchment, except for a possible edge effect near the border with tree canopy. Therefore, if reduced dry deposition of S was primarily responsible for the decrease in stream SO_4^{2-} concentrations, a predictable topographic variation of shallow groundwater SO_4^{2-} concentrations would not be observed. Thus, landscape variation in SO_4^{2-} adsorption as a function of pH and soil wetness remains the most likely explanation for these results.

It is possible that lower SO_4^{2-} concentrations with increasing catchment wetness could be caused at least partially by dilution of high solute soil water with low solute groundwater. However, we feel that this is unlikely in this system. Soils in this catchment are relatively shallow and as such are disconnected from deeper groundwater stores. Further, if dilution was occurring, we would expect to see a depression of other ions with increasing wetness. Nitrate increases with wetness and Cl^- shows no discernable trend, indicating that if dilution is occurring, it is negligible compared to other processes.

These findings contrast with the results of Zhang et al. (1999) who showed that phosphate-extractable SO_4^{2-} increased with increasing elevation in all mineral soil horizons at Hubbard Brook following clearcutting, and attributed these changes to increased nitrification at the high elevations because vegetation recovered more slowly there than at low elevations near the catchment outlet. The data from the current study indicate an inverse correlation between SO_4^{2-} and NO_3^- concentrations in B-horizon soil water that presumably reflects an inverse correlation between SO_4^{2-} concentrations and nitrification rates. Additionally, the topographic index used to represent landscape soil wetness potential in the current study is only indirectly related to elevation; piezometers at high elevation have small contributing areas, resulting in lower TI values. At Dry Creek, vegetation recovery did not appear to be dependent on elevation, and elevation and SO_4^{2-} concentrations in groundwater were not correlated.

Conclusions

Stream SO_4^{2-} concentrations decreased after a clearcut in the Dry Creek catchment as a result of enhanced pH-dependent specific adsorption of SO_4^{2-} to soil surfaces as evidenced by three observations: (1) H^+ and SO_4^{2-} concentrations of B-horizon soil solutions changed in parallel soon after the harvest and were strongly inversely correlated, (2) decreased dry deposition of SO_4^{2-} -S could only account for a small proportion of the decrease in stream SO_4^{2-} load, and (3) shallow groundwater SO_4^{2-} concentrations and a surrogate for soil wetness were inversely related, consistent with increased nitrification and resultant soil acidification in moist soils after clearcutting. Data from mineral-soil bags buried 250–300 mm deep in the soil did not show increased adsorption of SO_4^{2-} during the post-harvesting period, nor did O-horizon soil water show the strong inverse correlation between H^+ and SO_4^{2-} concentrations that was observed in the B-horizon. Together these observations indicate that increased SO_4^{2-} adsorption occurred between depths of 50 and 300 mm in the soil. The results of this study are consistent with those from a whole-tree harvest at the Hubbard Brook Experimental Forest and indicate that increased SO_4^{2-} adsorption, driven by decreased soil pH, extends to pH values as low as 4.0, about 0.3 pH units lower than observed at Hubbard Brook. The decrease in dry deposition of SO_4^{2-} had only a minor effect on stream SO_4^{2-} concentrations, in contrast to conclusions from studies in the UK where dry deposition was found to play a dominant role in the decrease of stream SO_4^{2-} concentrations after harvesting of Norway pine (Adamson and Hornung 1990; Neal et al. 1992).

The results of this study indicate that the close correlation between SO_4^{2-} concentrations and pH in soil water should be considered in models of the expected response of stream SO_4^{2-} concentrations and pH to future changes in loads of SO_4^{2-} in atmospheric deposition. The increased concentrations and stream loads of SO_4^{2-} in the third year after harvest indicate that SO_4^{2-} adsorption is at least partially reversible. This is consistent with the parallel decrease in precipitation and stream SO_4^{2-} concentrations that have been observed in streams in eastern North America and Europe during the past two decades, and suggests that soil adsorbed SO_4^{2-} values will recover toward pre-disturbance levels as pH increases following forest harvest or decreased loads of acid deposition.

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