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The biogeochemistry of sulfur at Hubbard Brook

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Abstract. A synthesis of the biogeochemistry of S was done during 34 yr (1964–1965 to 1997–1998) in reference and human-manipulated forest ecosystems of the Hubbard Brook Experimental Forest (HBEF), NH. There have been significant declines in concentration (−0.44 μmol/liter-yr) and input (−5.44 mol/ha-yr) of SO_4^{2-} in atmospheric bulk wet deposition, and in concentration (−0.64 μmol/liter-yr) an d output (−3.74 mol/ha-yr) of SO_4^{2-} in stream water of the HBEF since 1964. These changes are strongly correlated with concurrent decreases in emissions of SO_2 from the source area for the HBEF. The concentration and input of SO_4^{2-} in bulk deposition ranged from a low of 13.1 μmol/liter (1983–1984) and 211 mol/ha-yr (1997–1998) to a high of 34.7 μmol/liter (1965–1966) and 479 mol/ha-yr (1967–1968), with a long-term mean of 23.9 μmol/liter and 336 mol/ha-yr during 1964–1965 to 1997–1998. Despite recent declines in concentrations, SO_4^{2-} is the dominant anion in both bulk deposition and stream water at HBEF. Dry deposition is difficult to measure, especially in mountainous terrain, but was estimated at 21% of bulk deposition. Thus, average total atmospheric deposition was 491 and 323 mol/ha-yr during 1964–1969 and 1993–1998, respectively. Based on the long-term δ^{34}S pattern associated with anthropogenic emissions, SO_4^{2-} deposition at HBEF is influenced by numerous SO_2 sources, but biogenic sources appear to be small. Annual throughfall plus stemflow in 1993–1994 was estimated at 346 mol SO_4^{2-}/ha. Aboveground litterfall, for the watershed-ecosystem averaged about 180 mol S/ha-yr, with highest inputs (190 mol S/ha-yr) in the lower elevation, more deciduous forest zone. Weathering release was calculated at a maximum of 50 mol S/ha-yr. The concentration and output of SO_4^{2-} in stream water ranged from a low of 42.3 μmol/liter (1996–1997) and 309 mol/ha-yr (1964–1965), to a high of 66.1 μmol/liter (1970–1971) and 849 mol/ha-yr (1973–1974), with a long-term mean of 55.5 μmol/liter and 496 mol/ha-yr during the 34 yrs of study. Gross outputs of SO_4^{2-} in stream water consistently exceeded inputs in bulk deposition and were positively and significantly related to annual precipitation and streamflow. The relation between gross SO_4^{2-} output and annual streamflow changed with time as atmospheric inputs declined. In contrast to the pattern for bulk deposition concentration, there was no seasonal pattern for stream SO_4^{2-} concentration. Nevertheless, stream outputs of SO_4^{2-} were highly seasonal, peaking during spring snowmelt, and producing a monthly cross-over pattern where net hydrologic flux (NHF) is positive during summer and negative during the remainder of the year. No significant elevational pattern in streamwater SO_4^{2-} concentration was observed. Mean annual, volume-weighted soil water SO_4^{2-} concentrations were relatively uniform by soil horizon and across landscape position. Based upon isotopic evidence, much of the SO_4^{2-} entering HBEF in atmospheric deposition cycles through vegetation and microbial biomass before being released to the soil solution and stream water. Gaseous emissions of S from watershed-ecosystems at HBEF are unquantified, but estimated to be very small. Organic S (carbon bonded and ester sulfates) represents some 89% of the total S in soil at HBEF. Some 6% exists as phosphate extractable SO_4^{2-} (PSO_4). About 73% of the total S in the soil profile at HBEF occurs in the Bs2 horizon, and some 9% occurs in the forest floor. The residence time for S in the soil was calculated to be ~9 yr, but only a small portion of the total organic soil pool turns over relatively quickly. The S content of above- and belowground biomass is about 2885 mol/ha, of which some 3–5% is in standing dead trees. Yellow birch, American beech and sugar maple accounted for 89% of the S in trees, with 31% in branches, 27% in roots and 25% in the lightwood of boles. The pool of S in living biomass increased from 1965 to 1982 due to biomass accretion, and remained relatively constant thereafter. Of current inputs to the available nutrient compartment of the forest ecosystem, 50% is from atmospheric bulk deposition, 24% from net soil release, 11% from dry deposition, 11% from root exudates and 4% is from canopy leaching. Comparing ecosystem processes for S from 1964–1969 to 1993–1998, atmospheric bulk deposition decreased by 34%, stream output decreased by 10%, net annual biomass storage decreased by 92%, and net soil release increased by 184% compared to the 1964–1969 values. These changes are correlated with decreased emissions of SO_2 from the source area for the HBEF. Average, annual bulk deposition inputs exceeded streamwater outputs by 160.0 ± 75.3 SD mol S/ha-yr, but average annual net ecosystem fluxes (NEF) were much smaller, mostly negative and highly variable during the 34 yr period (−54.3 ± 72.9 SD mol S/ha-yr; NEF range, +86.8 to −229.5). While several mechanisms may explain this small discrepancy, the most likely are net desorption of S and net mineralization of organic S largely associated with the forest floor. Our best estimates indicate that additional S from dry deposition and weathering release is probably small and that desorption accounts for about 37% of the NEF imbalance and net mineralization probably accounts for the remainder (~60%). Additional inputs from dry deposition would result from unmeasured inputs of gaseous and particulate deposition directly to the forest floor. The source of any unmeasured S input has important implications for the recovery of soils and streams in response to decreases in inputs of acidic deposition. Sulfate is a dominant contributor to acid deposition at HBEF, seriously degrading aquatic and terrestrial ecosystems. Because of the strong relation between SO_2 emissions and concentrations of SO_4^{2-} in both atmospheric deposition and stream water at HBEF, further reductions in SO_2 emissions will be required to allow significant ecosystem recovery from the effects of acidic deposition. The destruction or removal of vegetation on experimental watershed-ecosystems at HBEF resulted in increased rates of organic matter decomposition and nitrification, a lowering of soil and streamwater pH, enhanced SO_4^{2-} adsorption on mineral soil and smaller concentrations and losses of SO_4^{2-} in stream water. With vegetation regrowth, this adsorbed SO_4^{2-} is released from the soil, increasing concentrations and fluxes of SO_4^{2-} in drainage water. Streamwater concentration of SO_4^{2-} and gross annual output of SO_4^{2-}/ha are essentially the same throughout the Hubbard Brook Valley in watersheds varying in size by about 4 orders of magnitude, from 3 to 3000 ha.

Abbreviations: AW – atomic weight, CAAA – Clean Air Act Amendments, dbh – diameter at breast height (1.37 m above ground), EPA – Environmental Protection Agency, HBEF – Hubbard Brook Experimental Forest, HH – high elevation deciduous vegetation zone, HQ – “Headquarters site”; area adjacent to the Robert S. Pierce Ecosystem Laboratory, LH – low elevation deciduous vegetation zone, MSL – mean sea level, nd – no data, NEF – net ecosystem flux (mass balance), NHF – net hydrologic flux (bulk deposition input – streamwater output), NTF – net throughfall flux, PIR – Pre-Industrial Revolution, PSO_4 – phosphate extractable sulfate, RG – rain gauge, SD or sd – standard deviation, se – standard error, S – sulfur, SFWB – spruce, fir, white birch zone, SO_2 – sulfur dioxide, s_{xmean} – standard error of the mean, SF – stemflow, TF – throughfall, W – watershed

Introduction

Biogeochemical properties of sulfur

Sulfur (S, AW = 32.06) is a member of group VIB in the periodic table of elements along with oxygen and selenium. It has four stable isotopes, of which ^{32}S is by far the most common (95.02%) with ^{34}S second (4.21%). The latter has great utility for inferring the importance of individual processes in biogeochemical studies. Sulfur also has six radioactive isotopes among which ^{35}S has the longest half life (87.4d) making it the most practical radioactive tracer for environmental work (Greenwood and Earnshaw 1984). The S atom at ground state has an electronic configuration of $[Ne]3s^23p^4$. This configuration endows S with at least five valence states (−2 to +6) and consequently, very high reactivity. Sulfur participates readily in oxidation-reduction processes within the range of commonly occurring redox states. Many of these reactions are microbially mediated. Except for ionic sulfides formed from highly electropositive elements such as Na, K, Ca and Mg, S bonding in natural environments is covalent (Charlson et al. 1992).

Sulfur is the fifth most abundant (by weight) element in the universe (Stevenson and Cole 1999) and the thirteenth most abundant element in Earth's crust with an average value of 0.0697% in continental crustal rocks (Charlson et al. 1992; Wedepohl 1995), and with about equal abundance in basalts representing oceanic crustal rocks and granites representing continental rocks (Bowen 1979). In igneous and metamorphic rocks, S regularly combines with a limited number of elements ("chalcophiles") mostly among the transitional metals to form the most common S-bearing minerals in rocks. These are primarily sulfides of Mo, Pb, Cu, Zn and especially, Fe. Sulfur is even more concentrated in many sedimentary rocks including sandstones (0.23%), shales (0.24%), but especially gypsum evaporites (hydrated $CaSO_4$) and biogenic sediments like coal (0.1–12%) and petroleum (1.5%) (Bowen 1979). These very high concentrations in biogenic sediments explain why combustion of many coals and petroleum products, especially those of marine origin, can lead to large emissions of sulfur dioxide (SO_2).

In aerobic environments, S weathered from rocks is converted to its most highly oxidized form – sulfate (SO_4^{2-}). Sulfate is a highly soluble anion in well-drained soils, but it can be immobilized by plant and microbial uptake or by anion adsorption. In contrast with humid environments, SO_4^{2-} can accumulate, as gypsum in illuviation zones of semiarid and arid soils. In humid regions, SO_4^{2-} concentrations are usually low in most unpolluted fresh waters (mean concentration = ~ 39 μmol/liter; <5 μmol/liter in pristine areas; Brakke et al. (1989)), but it is the second most abundant anion in sea water with a concentration of $\sim 2.8 \times 10^{-2}$ mol/liter (Holland 1978; Kennish 1989).

As with nitrogen, much ($\sim 90\%$) of the total S found in forest soils is organic in form. Most organic S occurs as ester sulfates (oxygen bonded to organic compounds) or is carbon bonded (including cysteine and methionine). In addition, there are some sulfamates and sulfolipids in soils (Stevenson and Cole 1999). The proportions of ester sulfates and carbon-bonded S in soils is a complex result of litter source phytochemistry, microbial processing, and differential biological mineralization (McGill and Christie 1983).

In addition to organic S, some soils may store considerable quantities of adsorbed SO_4^{2-}. Anion adsorption is an important process in soils with variable-charged clays which, in turn, are associated with hydrous aluminum and iron oxides (Sollins et al. 1988; Harrison et al. 1989; Johnson et al. 1993; Stevenson and Cole 1999). Such soils are not restricted to the tropics but also occur in highly weathered regions of the Temperate Zone (Harrison et al. 1989). Some kinds of organic matter also confer anion exchange capacity to soils, but in general, organic matter interferes with SO_4^{2-} adsorption. The density of net positive surface charge typically increases with decreasing pH. In addition to pH, ionic strength of soil water is important in controlling anion adsorption. Fluxes of sulfuric acid can be buffered by SO_4^{2-} adsorption in soils where anion adsorption is important.

Sulfur is an essential element for all forms of life. Sulfate is the principal source of inorganic S for plants but SO_4^{2-} must undergo energy-requiring assimilatory reduction to the reduced state as most organic S in plants occurs as reduced sulfhydryls and disulfides. Following assimilation, S resides primarily in metabolically active protoplasm rather than in structural materials. Assimilated S occurs primarily as S-amino acids methionine, cysteine, the dipeptide cystine, and their resulting proteins. A smaller amount of sulfhydryls also occurs in coenzyme A and in heterocyclic rings such as thiamine and biotin. In plants, oxidized S also occurs as a sulfolipid of chloroplast membranes, as sulfoxides in the form of mustard oils (Mengel and Kirkby 1979) and as flavonoid sulfates (Clarkson and Hanson 1980). The S content of bacteria is $\sim 0.5\%$, of angiosperm herbs is $\sim 0.06–0.6\%$, and of woody angiosperms is $\sim 0.2–0.87\%$ (Bowen 1979).

At high concentrations, especially in gaseous form (SO_2) S can be a phytotoxicant (Shriner et al. 1990; Zech et al. 1991; Mohren et al. 1992; Skeffington and Sutherland 1995; Burkhardt and Drechsel 1997) or an acidifying agent (Likens et al. 1972; Galloway et al. 1983; Church et al. 1989). Many naturally occurring gaseous forms of S are emitted into the atmosphere. Most of these are primarily of biogenic origin and all biogenic forms are in reduced states. Hydrogen sulfide (H_2S), carbon disulfide (CS_2), carbonyl sulfide (COS), methyl mercaptan (CH_3SH), dimethyl sulfide (CH_3SCH_3) and dimethyl disulfide (CH_3SSCH_3) emanate from soils or marine waters, and to some extent, volcanoes. Sulfur dioxide is the primary source of S from volcanoes and from both natural and anthropogenic combustion. Some of these S gases are deposited back to land or water surfaces still in reduced form, but most reduced S gases are oxidized in the atmosphere to SO_4^{2-} before being returned to land and water surfaces through wet and dry deposition (Charlson et al. 1992).

The biogeochemistry of S is highly complex in ecosystems having anaerobic zones in soils or sediments. Even in well-drained upland forests, however, many processes still must be considered to evaluate S flux and cycling.

Sulfur in northeastern U.S. forest ecosystems

Two major issues with regard to S cycling at the Hubbard Brook Experimental Forest (HBEF) and other northeastern forest ecosystems will be recurrent themes throughout this paper. The first theme is the role of atmospheric deposition in the biogeochemistry of S and its ecosystem effects, and the second is the mass S balance at the watershed-ecosystem scale. Each theme has both complex scientific issues and management relevance.

Acid deposition

The first theme relates to the problem of atmospheric deposition of S (e.g. SO_4^{2-}), emanating from fossil fuel combustion and emissions of SO_2. As the principal component of acid deposition, these sulfur oxides have effects on vegetation, soils and aquatic ecosystems at HBEF.

Since the Industrial Revolution, increasing amounts of S have been emitted to the atmosphere from the combustion of coal and oil, thus altering the biogeochemistry of S at local and regional scales, at numerous locations throughout the world. Volatile sulfurous compounds (e.g. SO_2) can be transported on average about 400–1200 km in the atmosphere before being deposited on Earth's surfaces in wet (mostly as SO_4^{2-}) and dry (SO_2, particulate SO_4) deposition (see e.g. Schwartz (1989)). Sulfate and SO_2 are important components of acidic deposition, popularly referred to as "acid rain", which has occurred widely in eastern North America and in other industrial regions throughout the world since the mid 1950s (e.g. Likens et al. (1972) and Likens and Bormann (1974a), Cogbill and Likens (1974), Weathers et al. (1998).

The northeastern region has among the highest concentrations and atmospheric inputs of SO_4^{2-} for wet deposition in the U.S. (Figure 1). Southeastern Canada and southeastern U.S. also have elevated concentrations of SO_4^{2-} in wet and dry deposition (e.g. Nriagu et al. (1987) and Van Stempvort and Wills (1991), Clair et al. (1995), Environment Canada (1995, 1997), The Acidifying Emissions Task Group (1997), Johnson and Lindberg (1992), Richter and Markewitz (1995). These high levels of S deposition generally reflect the large emission sources of SO_2 and S-containing particles in the midwestern U.S. (e.g. electrical utilities) (e.g. Likens et al. (1979) and Weathers and Likens (1998), Driscoll et al. (2001), which are transported in the atmosphere by prevailing winds, primarily from the west and southwest (Munn et al. 1984; Fay et al. 1985; Mohn and Vong 1993).

The unbalanced mass balance

The second theme concerns the mass balance of S in forest watersheds of the northeastern U.S. Mass balances for watersheds generally have been determined in two ways: (1) as the difference between inputs in bulk deposition and outputs in stream water (we will refer to this balance as NHF = net hydrologic flux), and (2) as the difference between all inputs to the ecosystem including wet and dry deposition and weathering release and all outputs and sinks from the ecosystem, includ-

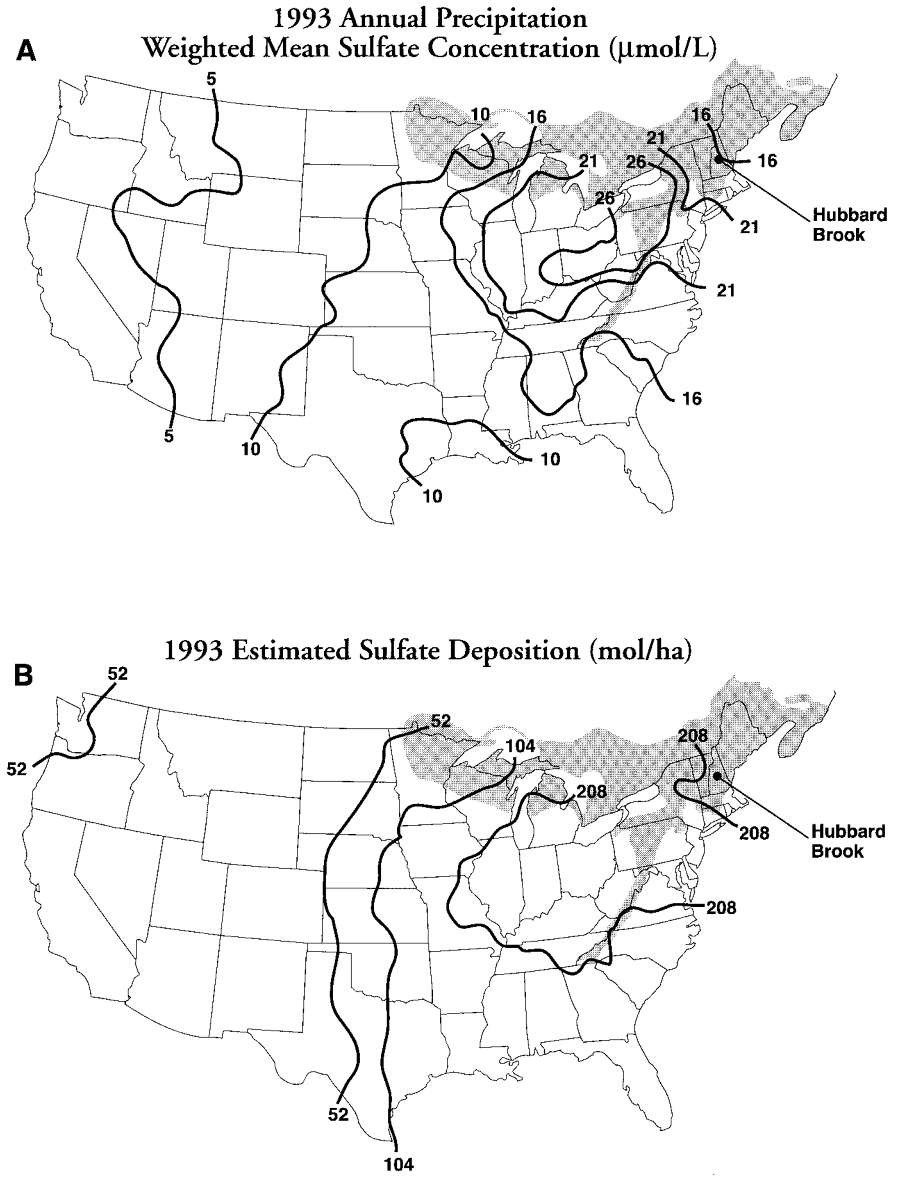

Figure 1. Annual, calendar-year, volume-weighted concentration and estimated wet deposition of sulfate throughout the U.S. during 1993. The shaded area indicates the approximate range of the northern hardwood forest (adapted from precipitation chemistry data from the US National Atmospheric Deposition Program/National Trends Network).

ing streamwater outputs, long-term storage in biomass and net gaseous loss (we will refer to this mass balance as NEF = net ecosystem flux).

Studies during the past 3 decades have indicated that there are large discrepancies in the NHF balance of S for forest watershed-ecosystems in eastern North America (Likens et al. (1977, 1990a); Rustad et al. 1996; Driscoll et al. (1998a, 1998b); Alewell et al. 1999; Mitchell et al. 2001) and Europe (Prietzel 1998; Alewell 2002 (in press)). Throughout most of the 34 years of study at HBEF, the output of SO_4^{2-} in stream water has significantly exceeded the inputs measured in bulk deposition (negative NHF). When estimates for dry deposition, weathering release and biomass storage are included, net flux (NEF) for these watershed-ecosystems during most years is much smaller, but still negative.

This small imbalance implies some additional or undervalued source of S for these watersheds, and the nature of this apparent source has been, and continues to be, an active area of our research. There are four principal hypotheses to explain this apparent net source:

1. Dry deposition. The amount of dry deposition is difficult to estimate accurately for large areas, and especially in mountainous terrain. It is possible that our best estimate of dry deposition (see below) is too low.
2. Sulfate desorption. Sulfate in soil may adsorb onto iron and aluminum oxides, a process that has different rates of reversibility depending on soil type. With declining SO_4^{2-} deposition (see below), the net desorption of soil SO_4^{2-} could be a recent source of S to the ecosystem.
3. Weathering. Weathering release of S from bedrock and glacial till is extremely difficult to measure. It is possible that our estimate of weathering release of S at HBEF is too low.
4. Net mineralization. Sulfate is assimilated by plants and microorganisms resulting in the formation of organic S. When this organic matter decays and is mineralized, organic S is hydrolyzed to SO_4^{2-}. If there were a net loss of soil organic matter in the ecosystem, a concomitant net mineralization of S would be expected. Alternatively, if the C:S ratio of organic matter being formed currently were higher than that of the older organic matter being mineralized, there would be net mineralization of S even if the soil organic matter pool were in steady state. Either scenario would produce an apparent source of S in the watershed-ecosystem.

The unbalanced, S mass balance is a critical issue for assessments of current pollution abatement legislation in the U.S. Title IV of the 1990 Amendments to the US Clean Air Act (CAAA) focused on the ecosystem effects of acidic deposition by mandating decreases in atmospheric emissions of SO_2, and to a lesser extent, NO_x. Section 404 of Title IV of this Act states that the US Environmental Protection Agency (EPA) is required to report to the US Congress on the feasibility and effectiveness of an acidic deposition standard to protect sensitive and critically sensitive aquatic and terrestrial resources. As a result, the EPA released the Acid Deposition Standard Feasibility Study report to the US Congress suggesting that there will be clear improvements in the water quality of surface waters resulting from decreases in emissions of SO_2 mandated from the CAAA (Anonymous 1995).

However, these calculations do not consider any additional, unmeasured source of S to forest ecosystems. The extent and nature of this S source has important implications for the recovery of terrestrial and aquatic systems from acidic deposition.

If the unaccounted for input of S to forest ecosystems were unmeasured dry deposition, then greater recovery of stream SO_4^{2-} following future decreases in SO_2 emissions would be expected relatively quickly (Driscoll et al. 1998a). However, if the additional input of S were associated with mineral weathering, then the recovery of stream SO_4^{2-} concentrations would be less than expected in response to decreased SO_2 emissions and would vary with the bedrock and mineralogical types within a region. Finally, if the source of the additional watershed release of S were from mineralization of previously formed soil organic S, then a decrease in stream SO_4^{2-} would be expected to occur, but over a longer time. Each type of S supply or release has a very different implication with respect to the recovery of surface waters following mandated decreases in SO_2 emissions (Driscoll et al. 1998a).

Throughout this paper, we will evaluate long-term data from the HBEF and other evidence relating to these two themes. As a result, we will consider how sensitive ecosystems might respond to mandated and proposed changes in atmospheric emissions of SO_2. We provide an analysis based on 34 years of intensive study (1964 to 1998) of S biogeochemistry in forest and experimentally-manipulated, deforested watershed-ecosystems at HBEF. We will summarize the long-term changes that have occurred, consider spatial patterns and changes, particularly in response to long-term changes in atmospheric inputs and forest disturbance, and present the details of ecosystem mass balances for S, particularly during two 5-yr periods: 1964–1965 to 1968–1969, early in the Hubbard Brook Ecosystem Study, and the most recent period, 1993–1994 to 1997–1998. We refer to S in aqueous samples as SO_4^{2-} because that was the form measured and in solids as S. All calculations are done in units of moles of S.

The Hubbard Brook Experimental Forest

General conditions

The HBEF (43°56′ N, 71°45′ W) comprises most of the Hubbard Brook Valley in the White Mountain National Forest of central New Hampshire. Details about the forest ecosystem (Figure 2), and general procedures and analytical methods used in our studies are summarized in Likens et al. (1994, 1998) and Likens and Bormann (1995), Buso et al. (2000).

Mean annual precipitation at the HBEF is 1417 mm (SD = 191), with 25–33% of the total occurring as snow (see Federer et al. (1990)). Mean annual precipitation has varied from 975 mm in 1964–1965 to 1888 mm in 1973–1974 (1995–1996 was the second wettest year on record with 1806 mm). Mean annual streamflow is 893 mm (SD = 194), and has varied from 496 mm in 1964–1965 to 1401 mm in 1973–1974 (1395 mm in 1995–1996). Some 50% of annual streamflow occurs during March, April and May of each year due to snowmelt (see Federer et al. (1990) and Likens and Bormann (1995)).

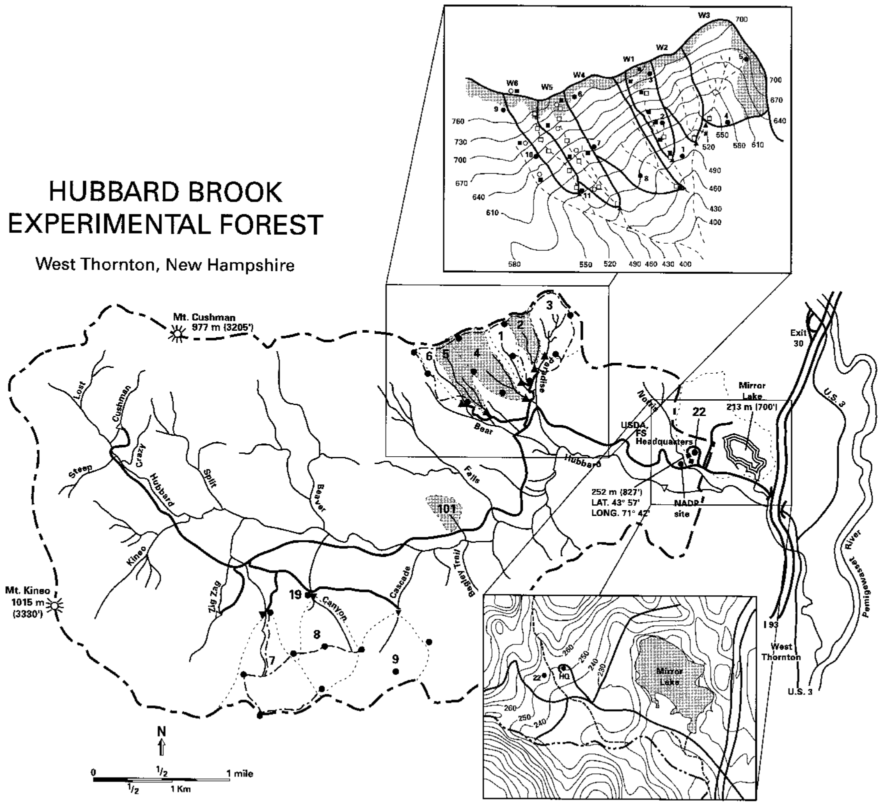

Figure 2. Map of the HBEF. Watershed 2 was deforested in 1965–1966, W101 was commercially harvested in 1970, W4 was progressively clear cut and harvested in 1970–1974, and W5 was whole-tree harvested in 1983–1984. Enlarged Sections: Weather stations/rain gauges (RG) (●), stream-gauging stations (▲), lysimeter plots (■), stream sampling sites (□), throughfall plots (○), hillslope hydrology plots (#), contour lines in m (–), stream channels (- - - and –), watershed boundaries (– and --- -- ---) and roads (—). The stippled area in the upper enlargement is the spruce-fir-white birch zone.

Procedures of study

Only the procedures unique to this paper are given. Unless specified otherwise, data presented here are for water-years from 1 June through 31 May and for south-facing watersheds of the HBEF, primarily Watershed 6 (W6), the long-term, biogeochemical reference watershed. These first- and second-order tributary watersheds with mature forest vegetation are generally representative of such ecosystems in northern New England (Likens and Bormann 1995).

Vegetation

A total stem inventory (all living trees on the watershed ⩾ 9.6-cm dbh) has been done every 5 yr since 1977 on W6. Allometric equations (Whittaker et al. (1979); revised in Siccama et al. 1994) are used with height estimating functions (derived on site for each species) to estimate the living biomass by species, plant part and elevation zone. Diameters of all dead trees (separated as to dead standing and snags) were also measured. Dead biomass was estimated as above, after modifying the dead trees and snags for lost parts and for decomposition (personal observation and data and the application of a decomposition factor; Onega and Eickmeier (1991)). These data were used with S concentration data by plant part and species to estimate the S in living and dead biomass for the watershed.

Because of new technology and more reliable methodology, vegetation samples collected in 1965 were reanalyzed for total S. Samples were analyzed using both a total S analyzer (LECO; David et al. (1989)) and wet-chemistry techniques [oxidation followed by Johnson and Nishita (1952) analyses; Landers et al. (1983)]. These reanalyses included extensive replication and comparisons with standard reference materials and have resulted in some modification of the original estimates (Likens and Bormann 1970) of S concentrations in specific tissue types. In addition, as part of the W5 whole-tree harvest experiment at HBEF, chipped material was analyzed for total S, providing an alternate estimate of the total S content of the aboveground woody vegetation (see section *Living and dead biomass pools and accretion*).

Soils

Soils were sampled quantitatively at each sampling site (see Zhang et al. (1999) by excavating a square 0.5-m^2 soil pit using the method of Hamburg (1984). Soil samples were collected from the faces of the excavation pits. Coarse fragment contents were obtained from direct measurements from the quantitative pits and subtracted from the horizon mass estimates.

Dry mass of soils was determined by drying at 65 °C for 2 days to avoid loss of volatile organic S constituents (Mitchell et al. 1989). Subsamples were oven-dried at 105 °C to correct for moisture. Total S was analyzed using a LECO-135® S analyzer. Hydriodic acid-reducible S (HI-S) was determined using a modified version of the Johnson and Nishita (1952) apparatus as described by Landers et al. (1983). Phosphate-extractable SO_4^{2-} (PSO_4) was determined by shaking the samples in 15 mmol/liter Na_2HPO_4 for an hour, then centrifuging the sample for 30 minutes. After centrifugation, about 10 ml of the supernatant solution was passed through a Gelman® 0.45-μm pore filter and analyzed for SO_4^{2-} by ion chromatography. Three replicates were analyzed for each sample. Ester SO_4^{2-} was determined by subtracting PSO_4 from HI-S. Carbon-bonded S was estimated by subtracting HI-S from total S. For soil solutions, SO_4^{2-} and total-S concentrations were determined by ion chromatography and by sodium hypobromite oxidation followed by HI-reduction, respectively (Landers et al. 1983). Organic S was calculated as the difference between total-S and PSO_4. Phosphate is commonly used as an extractant for adsorbed and water-soluble components, and here we report results that include both. It is assumed that phosphate recovers all inorganic SO_4^{2-} and that no SO_4^{2-} is occluded within iron and aluminum oxides. The HI-reducible fraction recovers both occluded inorganic SO_4^{2-} and organic sulfates.

Stable isotopes

Archived, weekly bulk deposition and stream water samples from 1969 through 1994 for Rain Gauge (RG) 11 at W6 and from 1983 to 1994 for RG 22 at Headquarters Site (HQ) (Figure 2) were subsampled and composited to form half-year samples divided into "summer" (1 June through 30 November) and "winter" (1 December through 31 May) periods. The composited water samples were analyzed for SO_4^{2-} by ion chromatography. We found no evidence of changes in SO_4^{2-} concentrations in the stored samples that would suggest changes in the $\delta^{34}S$ composition in these samples (Alewell et al. 1999). Sulfate was precipitated as $BaSO_4$ by adding $BaCl_2$ and the S isotopic composition of the $BaSO_4$ was measured on-line with an elemental analyzer coupled to an isotope ratio mass spectrometer at the stable isotope laboratory at the University of Calgary. The international standard used was troilite (FeS) from the Canon Diablo meteorite for which the $^{34}S/^{32}S$ ratio is 1/22.22. Precision of the $\delta^{34}S$ measurement was $\leqslant$ 0.8‰.

Dry deposition

Concentrations of SO_2 and particulate SO_4 have been measured since 1989 at the HQ site at 250 m MSL (Lovett et al. (1992, 1997)), as part of the US EPA's Clean Air Status and Trends Network (CASTNet). This site is about 3 km from W6 (Figure 2). Atmospheric concentrations were measured weekly on a filter pack described by US EPA (1998). Estimates of dry deposition were made from the measured concentrations using a model parameterized with local canopy conditions and micrometeorological variables measured on site (Clarke et al. 1997).

SO_2 source area

Annual emissions of SO_2 were based on 15-hr air-mass, back-trajectory analysis (see Butler et al. (2001) for details). As a result, emissions from CT, DE, MA, MD, NH, NJ, NY, OH, PA, VA, VT and WV constituted the SO_2 source area for the HBEF.

Other pertinent long-term efforts

Monthly streamwater samples have been collected from six elevations since 1982. Soil water samples have been collected monthly since 1984, using zero-tension lysimeters from three horizons within three elevations zones (LH, HH, SFWB), immediately west of W6 (Driscoll et al. 1988). Soil solutions were collected using triplicate lysimeters positioned at each horizon in the two lowest elevation zones (LH, HH) and using duplicate lysimeters at the highest elevation zone (SFWB). Episodic samples of throughfall were collected in 1969 (Eaton et al. 1973) and from 1989 to present (Lovett et al. 1996).

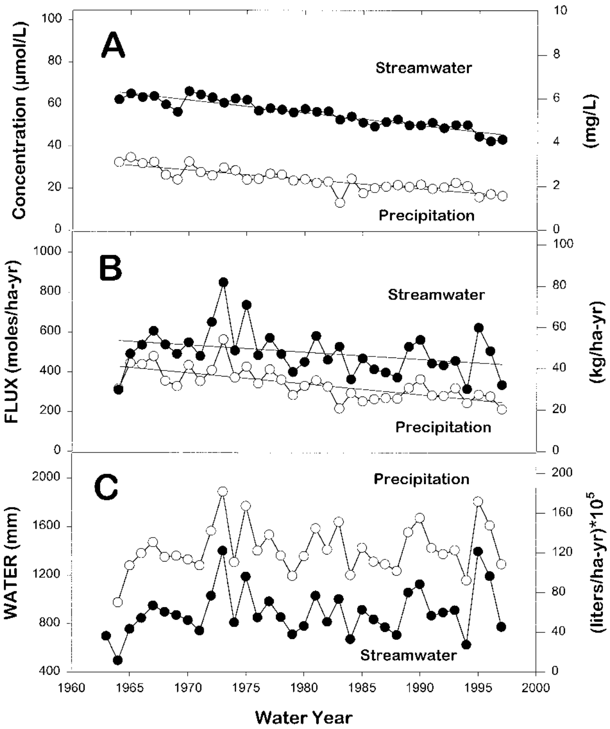

Figure 3. **A.** Annual, volume-weighted concentrations of SO_4^{2-} in bulk deposition (-○-) and streamwater (-●-) for W6 of the HBEF during 1964–1997. The probability for a larger F-ratio for both regression lines is $p < 0.001$; the r^2 for bulk precipitation is 0.72, and for streamwater is 0.87. **B.** Annual inputs of SO_4^{2-} in bulk deposition (-○-) and outputs in stream water (-●-) for W6 during 1964–1997. The probability of a larger F-ratio for the regression line for stream water is $p = 0.067$, $r^2 = 0.10$; and for bulk deposition is $p < 0.001$, $r^2 = 0.48$. **C.** Annual amount of precipitation (-ˆ-) and streamflow (-●-) for W6 of HBEF during 1964–1998.

Flux and cycling of sulfur in a forest ecosystem

Sources of sulfur for watershed-ecosystems of the HBEF

Atmospheric inputs in bulk deposition – concentrations, fluxes and trends

Rain and snow are major sources of S for forests and associated aquatic ecosystems of HBEF (e.g. Likens et al. (1985) and Bormann and Likens (1979), Likens and Bormann (1995)). The long-term (1964–1998), volume-weighted mean concentration of SO_4^{2-} was 23.9 μmol/liter (2.3 mg SO_4^{2-}/liter) in bulk deposition. Annual, volume-weighted mean concentrations ranged from a low of 13.1 μmol/liter in 1983–1984, to a high of 34.7 μmol/liter in 1965–1966 (Figure 3, Table 1).

Following the Clean Air Act of 1970, emissions of SO_2 to the atmosphere in the U.S. decreased markedly (Figure 4). Concurrent with these changes in emissions, concentrations of SO_4^{2-} in bulk deposition (and SO_4^{2-} in stream water, see Figure 3)

Table 1. Annual volume-weighted average concentrations of sulfate in bulk precipitation at HBEF for south-facing watersheds

Water – Year	W1	W2	W3	W4	W5	W6	Mean[a]	±sd
1964–1965	32.4	32.6	32.2	32.6	32.5	32.4	32.5	0.1
1965–1966	34.9	34.9	35.0	34.8	34.7	34.7	34.9	0.1
1966–1967	31.9	32.0	32.1	31.8	31.8	31.8	31.9	0.1
1967–1968	32.6	32.7	32.5	32.5	32.5	32.5	32.6	0.1
1968–1969	26.5	26.4	26.4	26.6	26.3	26.3	26.4	0.1
1969–1970	24.3	24.3	24.2	24.2	24.2	24.1	24.2	0.1
1970–1971	32.9	33.2	33.0	32.6	32.8	32.6	32.8	0.2
1971–1972	27.5	27.5	27.4	27.5	27.5	27.6	27.5	0.0
1972–1973	26.1	26.1	26.3	26.5	26.4	26.0	26.2	0.2
1973–1974	29.9	29.8	29.9	30.0	29.9	29.7	29.9	0.1
1974–1975	30.2	30.3	30.1	30.4	30.5	28.4	30.0	0.7
1975–1976	24.1	24.1	23.9	24.1	24.1	24.0	24.1	0.1
1976–1977	24.5	24.5	24.4	24.6	24.5	24.4	24.5	0.1
1977–1978	27.1	27.1	27.3	27.0	26.9	26.8	27.0	0.1
1978–1979	26.7	26.7	26.5	26.4	26.4	26.4	26.5	0.1
1979–1980	23.7	23.6	23.5	23.8	23.7	23.6	23.7	0.1
1980–1981	24.7	24.8	24.8	24.5	24.4	24.2	24.6	0.2
1981–1982	23.1	23.1	23.1	22.9	22.8	22.5	22.9	0.2
1982–1983	23.2	23.2	23.2	23.0	23.1	23.0	23.1	0.1
1983–1984	13.1	13.1	13.2	13.3	13.3	13.1	13.2	0.1
1984–1985	24.9	25.0	24.9	24.7	24.6	24.4	24.7	0.2
1985–1986	17.9	17.9	17.9	17.7	17.7	17.6	17.8	0.1
1986–1987	20.5	20.5	20.4	20.4	20.3	20.0	20.3	0.2
1987–1988	20.8	20.9	21.0	20.7	20.8	20.7	20.8	0.1
1988–1989	21.5	21.6	21.6	21.5	21.5	21.4	21.5	0.1
1989–1990	20.7	20.7	20.6	20.6	20.6	20.5	20.6	0.1
1990–1991	22.0	22.0	22.0	21.9	21.8	21.6	21.9	0.1
1991–1992	19.8	19.8	19.8	19.9	19.8	19.7	19.8	0.0
1992–1993	20.6	20.6	20.8	20.4	20.4	20.3	20.5	0.2
1993–1994	22.8	22.9	22.7	22.6	22.6	22.5	22.7	0.1
1994–1995	21.5	21.5	21.6	21.2	21.1	21.0	21.3	0.2
1995–1996	16.0	16.1	16.0	15.8	15.8	15.7	15.9	0.1
1996–1997	17.4	17.4	17.4	17.3	17.3	17.1	17.3	0.1
1997–1998	16.4	16.4	16.5	16.4	16.4	16.3	16.4	0.1
Individual ANNUAL MEAN (μmol/L)	24.2	24.2	24.2	24.1	24.1	23.9	24.1	
±sd	5.2	5.2	5.2	5.2	5.2	5.2	5.2	

[a] Mean and ±sd applied to all watersheds

at HBEF have also decreased. Overall, annual, volume-weighted concentrations of SO_4^{2-} decreased by 49.5% from 1964–1965 to 1997–1998 (Figure 3, Table 1). Indeed, the relation between emissions of SO_2 from the source area for HBEF (based

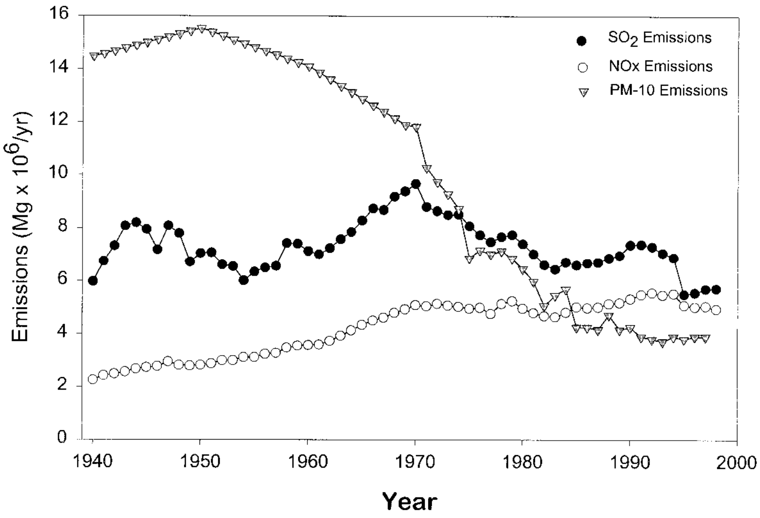

Figure 4. Long-term trends in emissions of SO_2 (●), and NO_x (○) for the HBEF source area and particulate matter 10 μm in size (PM-10; ▼), excluding fugitive dust sources for the U.S. (US EPA 2000). The pattern of PM-10 emissions for the smaller HBEF source region would follow the same general trends as for the US source area assuming that sources and air-mass trajectories were similar to the relationships found for SO_2 and NO_x emissions on a regional and national level.

on 15-hr air-mass, back trajectories; Butler et al. (2001) and Likens et al. (2001)) and concentration of SO_4^{2-} in bulk precipitation at HBEF was linearly and statistically correlated ($r^2 = 0.65$; $p < 0.001$) from 1964 through 1998 (Figure 5A). Likewise, bulk deposition input of SO_4^{2-} was significantly correlated ($p < 0.001$) with emissions of SO_2 from the source area ($r^2 = 0.51$) from 1964 through 1998 (Figure 5B).

Average monthly concentrations of SO_4^{2-} in bulk deposition were highest during summer months and lowest during the winter months (Figure 6). Average volume-weighted concentrations were the most variable during the summer (Figure 6). Monthly deposition of SO_4^{2-} was highest during the summer (Figure 6A), and monthly inputs were larger than streamwater outputs during June, July, August and September (Figure 6B and C).

Volume-weighted average annual SO_4^{2-} concentrations were not related to the amount of annual precipitation (Figure 7), but annual bulk deposition of SO_4^{2-} was (Figure 7; $p = 0.038$; $r^2 = 0.13$). The annual bulk deposition input of SO_4^{2-} ranged from 210 mol/ha-yr (20.1 kg SO_4^{2-}/ha-yr) in 1997–1998 to 562 mol/ha-yr (53.9 kg SO_4^{2-}/ha-yr) in 1973–1974, and averaged 336 mol/ha-yr (32.4 kg SO_4^{2-}/ha-yr) (SD = 78) during the study (Table 3). Statistically significant decreases in inputs of SO_4^{2-} in bulk deposition occurred during the period (Figure 3; $p < 0.001$; $r^2 = 0.72$).

Concentrations and inputs of SO_4^{2-} in bulk deposition varied little among south-facing watersheds within HBEF, although W6 had the largest average annual input from bulk deposition during the 34-yr period (Tables 1 and 3). Concentration of SO_4^{2-} in bulk deposition measured at W6 (549 m MSL) for calendar-year, 1979 to

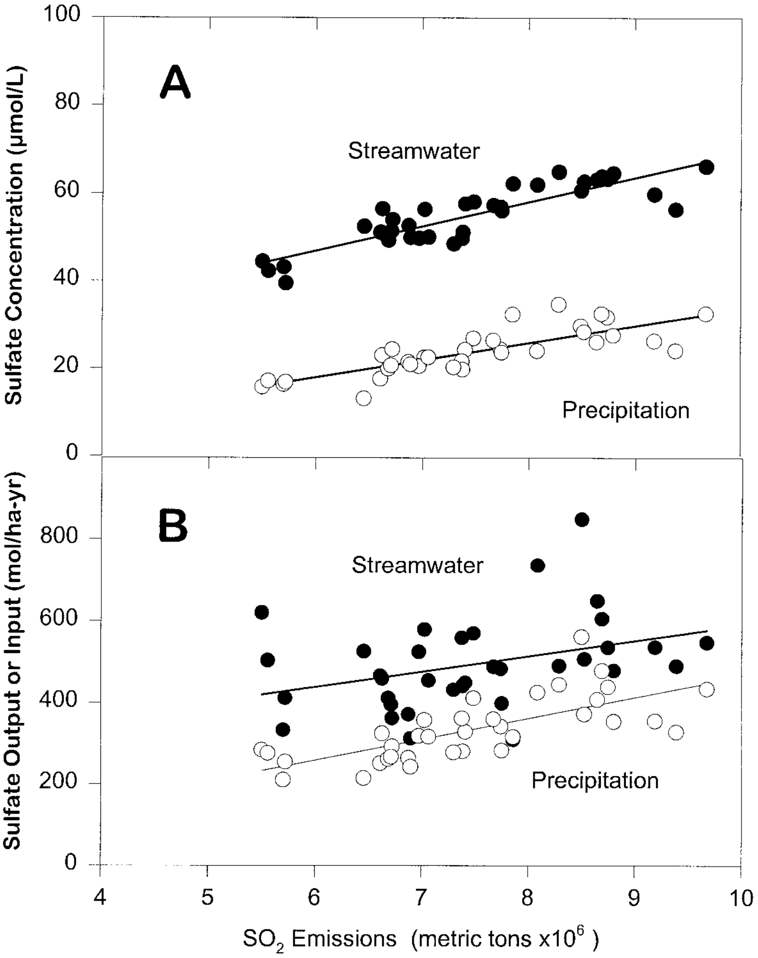

Figure 5. Relation between: **A.** sulfate concentrations in bulk deposition (-○-) or stream water (-●-) for the HBEF and SO_2 emissions for source region based on 15-hr air-mass, back trajectories (Butler et al. 2001; Likens et al. 2001) during 1970–1997. (r^2 for bulk deposition is 0.65, and for stream water is 0.75). **B.** sulfate inputs in bulk deposition or outputs in stream water and SO_2 emissions for the HBEF source region during 1970–1997 (r^2 for inputs is 0.51, and for outputs is 0.13).

1989 averaged 21.0 μmol/liter, and was not significantly different from bulk deposition at the lower-elevation (250 m MSL) HQ site for the same period (Martin et al. 2000a). However, because the precipitation amount was 17.0% higher at the W6 site (1979–1989), calculated bulk deposition was 5.3% higher at W6 than at the HQ site.

Changes in anion composition of bulk deposition

Large changes in anion composition of bulk deposition (Figure 8A) have occurred since 1964. For example, during 1964–1965 some 71%, 13% and 16% of the total

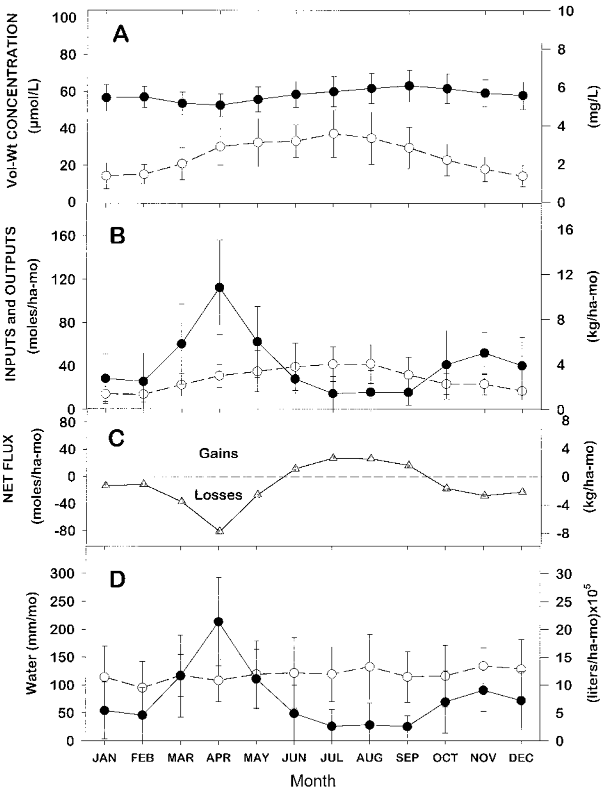

Figure 6. **A.** Average monthly volume-weighted concentrations of SO_4^{2-} in bulk deposition (-○-) and stream water (-●-) for W6 at HBEF during 1964–1998. The vertical bars are ± one standard deviation for the mean value. **B.** Average monthly inputs of SO_4^{2-} in bulk deposition (-○-) and outputs of SO_4^{2-} in stream water (-●-) for W6 during 1964–1998. The vertical bars are ± one standard deviation for the mean value. **C.** Average monthly net flux of SO_4^{2-} (average bulk deposition input minus average stream-water output from B above) for W6 during 1964–1998. **D.** Average monthly amounts of precipitation (-○-) and stream water (-●-) for W6 during 1964–1998. The vertical bars represent ± one standard deviation for the mean value.

anion charge in bulk deposition was provided by SO_4^{2-}, NO_3^- and Cl^-, respectively, whereas in 1997–1998, SO_4^{2-} had declined to provide only about 53%, NO_3^- had increased to provide some 40%, and Cl^- contributed 7%. If these trends (Figure 8A) were to continue, NO_3^- would become the dominant anion in bulk deposition at HBEF early in the second decade of the 21st Century.

Atmospheric inputs in dry deposition

Atmospheric concentrations of SO_2 and particulate SO_4 averaged 19.8 and 27.1 nmol/m^3, respectively, at the HQ site, during 1989–1995. Both constituents showed a seasonal cycle, with high SO_2 concentrations in the cold season and low in the warm season, and particulate SO_4 showing the opposite pattern (Figure 9). The dry deposition velocities for SO_2 are considerably higher than for particulate SO_4, be-

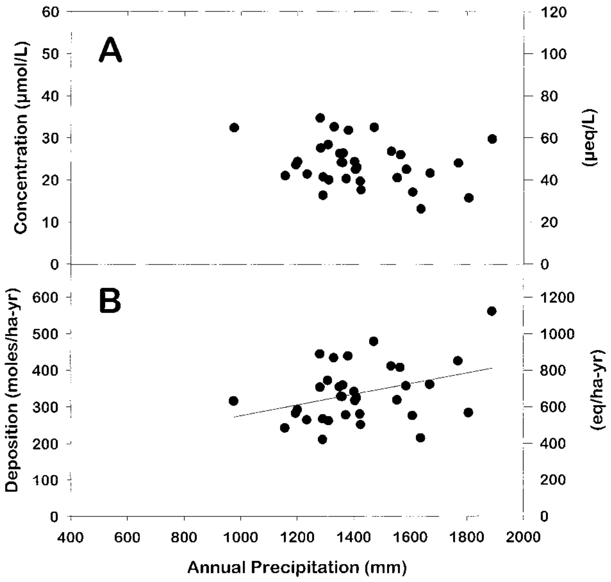

Figure 7. Relationship between the: **A.** Annual volume-weighted concentration of SO_4^{2-} in bulk deposition and amount of annual precipitation. **B.** Annual input of SO_4^{2-} in bulk deposition and amount of annual precipitation for W6 at HBEF during 1964–1998. The probability for a larger F-ratio for the regression line for 1964–1997 is $p = 0.038$; $r^2 = 0.13$.

Table 2. Sulfur content of soil in W5 of HBEF prior to 1983. Values in mol/ha (modified from Zhang et al. (1999))

Horizon	Total sulfur	HI-S	PSO_4	Ester sulfate	C-bonded sulfur
O_{ie}	1370	271	na	na	1098
Oa	3326	861	na	na	2464
E	1466	424	15.6	384	1033
B_h	3566	1033	78.0	858	2430
Bs1	4608	1697	250	1316	2783
Bs2	38699	18106	2876	14771	19894
Total	53033	22393	3219	17329	29702

cause particulate SO_4 occurs primarily as fine particles that do not deposit efficiently to canopy surfaces (Lovett 1994). Consequently, the model-calculated dry deposition fluxes were dominated by the SO_2 component, which averaged 21.5 mol S/ha-yr, compared to 8.2 mol/ha-yr for particulate SO_4, during the water-years, 1988–1989 to 1994–1995.

These estimates of S dry deposition should be interpreted with caution because of the uncertainties of modeling dry deposition in mountainous terrain (Lovett et al. (1997, 1999)). We compared several methods of estimating S dry deposition at HBEF, and the methods do not agree. For example, one way to calculate dry depo-

Table 3. Annual bulk deposition input of sulfate to HBEF south-facing watersheds

Water - Year	W1	W2	W3	W4	W5	W6	Mean[a]	±sd
1964–1965	305	306	302	312	313	316	309	5
1965–1966	428	425	427	435	439	444	433	7
1966–1967	416	416	410	425	429	438	422	10
1967–1968	454	454	453	461	470	479	462	10
1968–1969	329	327	335	341	345	355	339	9
1969–1970	309	308	313	315	319	328	315	7
1970–1971	404	404	405	413	422	434	414	11
1971–1972	334	334	335	335	340	354	339	7
1972–1973	396	396	395	392	397	407	397	5
1973–1974	554	551	547	557	556	562	554	5
1974–1975	369	367	374	370	375	371	371	3
1975–1976	398	396	397	398	401	425	402	10
1976–1977	325	325	323	328	329	342	329	6
1977–1978	391	389	390	391	394	411	395	8
1978–1979	339	337	341	345	346	360	345	7
1979–1980	269	268	268	275	274	282	273	5
1980–1981	310	309	313	318	319	329	316	7
1981–1982	346	344	353	359	356	357	353	5
1982–1983	306	304	308	318	319	324	313	8
1983–1984	201	200	201	211	212	215	206	6
1984–1985	269	267	271	283	286	292	278	10
1985–1986	236	235	235	247	247	251	242	7
1986–1987	247	247	247	258	259	262	253	6
1987–1988	246	245	250	257	260	267	254	8
1988–1989	248	248	249	256	258	264	254	6
1989–1990	304	302	303	315	315	318	309	7
1990–1991	349	349	350	359	360	361	355	6
1991–1992	268	267	268	279	279	281	274	6
1992–1993	272	272	277	279	280	278	276	3
1993–1994	300	300	299	309	313	317	306	7
1994–1995	233	233	235	241	242	242	238	4
1995–1996	268	266	268	280	281	284	274	7
1996–1997	264	262	264	279	278	276	270	7
1997–1998	201	200	202	207	209	211	205	4
TOTAL (mol/ha)	10889	10852	10908	11148	11225	11435	11076	
ANNUAL MEAN (mol/ha-yr)	320	319	321	328	330	336	326	
±sd	76	76	75	75	75	78	76	

[a] Mean and ±sd applies to all watersheds

sition is to assume that the entire imbalance in NEF of S is attributable to dry deposition (Likens et al. 1990a). Such a calculation yields higher estimates of dry

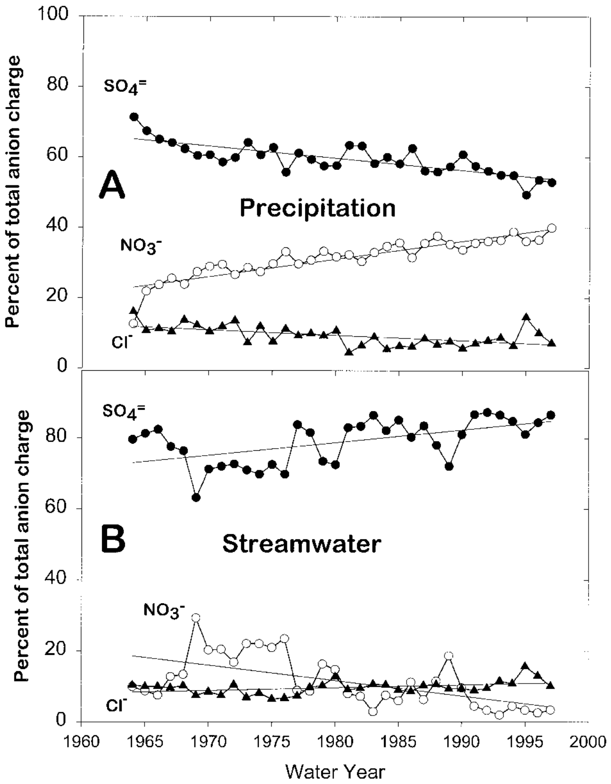

Figure 8. Percent of total anion charge for SO_4^{2-}, NO_3^- and Cl^- in: **A.** bulk deposition, and **B.** stream water for W6 of the HBEF from 1964–1998.

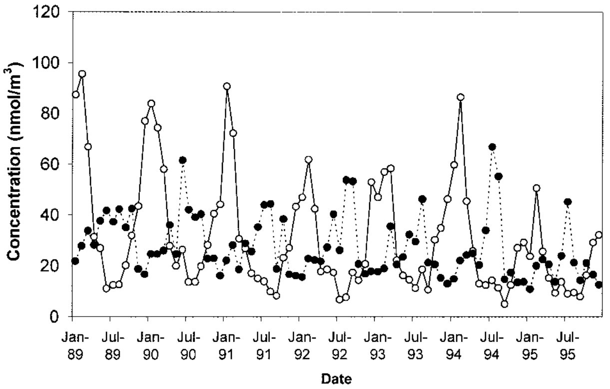

Figure 9. Monthly atmospheric concentrations (nmol/m^3 of SO_2 (-○-) and particulate SO_4^{2-} (-●-) at HBEF from 1989–1995.

deposition than either the "inferential" modeling approach discussed above or the mass balance of S in throughfall (Lovett et al. 1996). Direct comparison of the three methods for 1989 indicates a difference of almost a factor of 4, ranging from 63 mol S/ha for the inferential method, to 103 for the throughfall plus stemflow method, and 244 for the watershed mass balance (Lovett et al. 1992). These dry deposition values represent 21, 34, and 81%, respectively, of the bulk deposition of S for the year. The high value for the watershed mass balance suggests that one of the other sources of S hypothesized above: desorption of previously adsorbed SO_4^{2-}, weathering-release or release of organically bound S – contributes to the NEF of S. All methods of estimating dry deposition have substantial uncertainty, so dry deposition remains an elusive component of our S budgets.

A decline has occurred in both gaseous SO_2 and particulate SO_4 concentrations after 1989 (Figure 9), and was statistically significant over the longer period analyzed by Holland et al. (1999). The decline parallels the decline in SO_4^{2-} concentrations in bulk deposition (Figure 3), and is largely a result of reductions in SO_2 emissions (Figures 4 and 5).

Our dry deposition estimates from the inferential method do not include large-particle SO_4, which has been shown to be an important S source at some forest sites in the eastern U.S. (Lindberg and Lovett 1992). We do not believe that large-particle SO_4 contributes significantly to S deposition at HBEF, however, because if it did, large-particle deposition into the open funnel of the bulk deposition collectors would result in higher SO_4^{2-} concentrations than in wet-only precipitation. In fact, co-located wet-only and bulk deposition collectors (collected weekly for 11 years, 1979–1989) at the HQ site had mean SO_4^{2-} concentrations of 20.4 and 21.7 μmol/liter, respectively, which are not significantly different (Martin et al. 2000a).

Based on one year of comparison (1993), atmospheric concentrations of SO_2 near RG 10 (W6 site; $\sim$690 m elevation; Figure 2) were about 50% higher than those at the HQ site (250 m elevation; Figure 2), while concentrations of particulate SO_4 were similar at the two sites (Lovett et al. 1997). Model-calculated dry deposition velocities also increased with elevation. As a result, total dry deposition of S was approximately twice as high at RG 10 as at the HQ site.

Our best estimate for current dry deposition at W6 is 57 mol/ha-yr, which is derived from measured air and meteorological data from W6 (Lovett et al. 1997). The W6 estimate is based on data from one year (1993) only, but 1993 was a fairly typical year in terms of air concentrations compared to the entire 1989 through 1996 period for which we have data at the HQ site (Figure 9). The estimated flux of 57 mol/ha-yr represents 21% of the estimated S bulk deposition for the 1993–1998 pentad (266 mol/ha-yr).

We estimate the uncertainty range of dry deposition to be roughly 30–120 moles/ha-yr (60 plus or minus a factor of 2). Major sources of uncertainty are: (1) the relationship between air concentrations at the well-measured HQ site and the sporadically measured W6 site, and (2) the model estimates of deposition velocity in complex terrain. We have no perfect way to test this dry deposition estimate. Our estimate of 57 mol/ha-yr is somewhat less than the net throughfall plus stemflow flux, and is much less than the difference between bulk deposition inputs and streamwater outputs (see section *Throughfall and stemflow*).

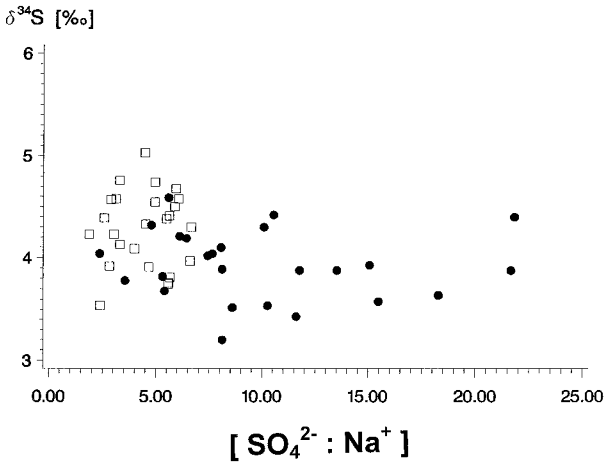

Figure 10. $\delta^{34}S$ values (‰) related to the [SO_4^{2-}: Na^+] ratio in bulk deposition at W6 of the HBEF. □ = winter; ● = summer (modified from Alewell et al. (2000)).

Origin of atmospherically-deposited sulfate

To assess the origin of SO_4^{2-} in bulk deposition at HBEF, a 26-yr record of S stable-isotope values in archived samples of bulk deposition and stream water were compared to anthropogenic SO_2 emissions, the relative contribution of sea salt aerosols and the effects of air temperature and solar radiation (Alewell et al. 2000). The long-term pattern of $\delta^{34}S$ in bulk deposition was significantly correlated with SO_4^{2-} concentrations and fluxes ($r = -0.31$, $p = 0.026$ and $r = -0.39$, $p = 0.005$), i.e. the $\delta^{34}S$ values became heavier with decreasing SO_4^{2-} concentrations (Alewell et al. 2000). This $\delta^{34}S$ pattern was affected by the relative contribution of marine SO_4^{2-} (Figure 10) and possibly by variation of solar radiation, but not by atmospheric temperature changes (Alewell et al. 2000). Moreover, annual differences in SO_2 emissions did not provide any clear explanation of the temporal trends in the $\delta^{34}S$ values (Figure 10). The high variability of $\delta^{34}S$ in various fossil fuels makes it difficult to use stable S isotopes for identifying whether changing fossil fuel utilization is affecting the $\delta^{34}S$ values in bulk deposition. So, if any conclusion can be drawn from the long-term $\delta^{34}S$ pattern regarding anthropogenic emissions, it would be that SO_4^{2-} deposition at HBEF is influenced by numerous SO_2 sources within the source area (Alewell et al. 2000).

The $\delta^{34}S$ values in bulk deposition at HBEF are significantly higher in the winter than in the summer (Alewell et al. 2000). Caron et al. (1986) has suggested that a seasonal decrease in air temperature would cause an increase in $\delta^{34}S$ during the oxidation of SO_2 to SO_4^{2-} in the atmosphere. The difference in mean air temperature between summer and winter seasons at the HBEF is about 13 °C. This seasonal temperature difference could cause an increase of $\delta^{34}S$ in the winter of as much as 1.04 to 1.89‰. Since summer to winter differences in $\delta^{34}S$ at HBEF are generally less than 1.2‰ (Alewell et al. 2000), the temperature dependence of the isotopic shift during SO_4^{2-} formation in the atmosphere could explain the seasonal pattern at HBEF. A greater relative contribution of marine SO_4^{2-} during the winter also may have contributed to the higher $\delta^{34}S$ values in winter. As a result, previous investigations in North America (e.g. Nriagu et al. (1987) and Nriagu and Krouse (1992)) may have overestimated the role of biogenic emissions in affecting the $\delta^{34}S$ pattern (Alewell et al. 2000).

Supply of S from weathering release and sulfate desorption

Bedrock and glacial till deposits within the HBEF contain S (Johnson et al. 1981), which may be released through weathering of rock minerals, thereby adding to the available SO_4^{2-} within watershed-ecosystems of the area. Weathering can be an important source of solutes for terrestrial ecosystems, but rates are difficult to quantify because of heterogeneous distribution of substrates, incongruent processes and difficulty in separating weathering release from measurements of other soil processes. Since weathering occurs within ecosystem boundaries, it is referred to as "release" in mass balance calculations (Likens and Bormann 1995).

Despite the relatively high concentrations of S in HBEF bedrock as compared to other rocks in the White Mountains region of NH as well as to the crustal average, watershed mass balance (Likens and Bormann 1995) and isotopic analysis (Alewell et al. 1999) do not provide clear evidence of S weathering release or a reliable indication of its magnitude. Likens et al. (1990a) calculated an average S weathering flux of 20 mol/ha-yr based on the difference in a watershed mass balance calculation. In an attempt to constrain estimates of S weathering release for HBEF based on available geochemical data and field observations, the following analysis of potential bedrock and soil weathering is presented.

Published New Hampshire bedrock S concentrations range from <0.01% to 0.66% S (Billings and Wilson 1964), with the highest values reported for the Rangeley Formation, the bedrock unit which underlies the eastern portion of HBEF, including W1-6 (Figure 2). Two analyses of HBEF Rangeley Formation schist samples gave 0.2% and 0.9% S (Bailey et al. 2002a). Kinsman granodiorite, the bedrock in the western portion of the HBEF and dominant contributor to glacial till (Bailey et al. 2002b), contains moderate S concentrations at 0.10% to 0.19% (Billings and Wilson 1964). Sulfur concentrations in the Rangeley and Kinsman bedrock units are high compared to the average concentration for Earth's continental crust (0.0697%; Wedepohl (1995)).

At HBEF, bedrock surfaces under >1 m of soil retain their glacial polish, suggesting that they have not undergone significant weathering since glaciation (Johnson et al. 1968). Such is not the case for bedrock under shallower soils, bedrock outcrops, and rock fragments in the glacial till. Weathering of pyrrhotite (iron sulfide) in surface exposures of Rangeley Formation has left a thick, rusty weathering rind characteristic of this bedrock unit (Moench et al. 1995). Inspection of coarse fragments in the soil reveals that interior pits and weathered fractures are common (Bailey and Hornbeck 1992), indicating weathering. This finding is consistent with the recent work of Ugolini et al. (1996) in Europe that has shown that coarse fragments in forest soils are much more permeable and reactive than previously thought.

Assuming an average bedrock S concentration of 0.5% and bulk density of 2.7 g/cm^3, there would be a bedrock S pool of 42 kmol/ha per cm of bedrock thickness. If we assume an average weathering rind thickness of 20 cm for bedrock <1 m from the soil surface (estimated from Moench et al. (1995)), and a constant weathering rate since deglaciation, we could roughly estimate a weathering flux of 40 mol S/ha-yr from bedrock. Similarly, assuming a solum thickness of 1 m, 20% by volume rock, rock bulk density of 2.7 g/cm^3 and 0.1% S would give a rock fragment S pool of 169 kmol/ha. Perhaps additional small amounts of S are released from weathering of coarse rock fragments in the soil. No quantitative data are available on the distribution of weathering rinds in coarse fragments of various sizes to further evaluate this hypothesis.

Although sulfide minerals are common in HBEF rocks, none have ever been identified in the fine earth fraction (<2 mm) of the soil, suggesting that weathering in the 14,000 years since deglaciation (Likens and Davis 1975) has depleted this S pool. This conclusion is in agreement with the only known total S determination of 10 mg/kg for a relatively unweathered deep till sample collected near the base of W6 at a depth of 1.65 m (Bailey et al. 2002a). Thus, unless the sulfide content of the soil has been greatly underestimated, it does not appear that weathering release of S occurs in the fine earth fraction of the soil.

Based on the crude estimates above, an S weathering flux from rock fragments and shallow bedrock exposures as high as 50 mol/ha-yr might be possible, contributing some, but not all, of the discrepancy in the NEF (see section *Budgetary considerations – watershed mass balances*).

Net soil release has been used to capture the total mobilization of an element in the soil via weathering, exchange, changes in secondary mineral pools, and mineralization (Likens et al. (1994, 1998)), and can be estimated by the algebraic sum of streamwater losses, net biomass storage and atmospheric inputs. The net soil release term will be evaluated in following sections.

Intrasystem cycling

Living and dead biomass pools and accretion

Total biomass of the mature northern hardwood forest on W6 of the HBEF was measured in 1965, 1977 and at 5-yr intervals thereafter (Table 4)(Likens et al. (1994, 1998)). Significant rates of aboveground plus belowground living biomass accumulation were evident during 1965 to 1977 (4.85 Mg/ha-yr; Bormann and Likens (1979) and Whittaker et al. (19724), Likens and Bormann (1995)). However, since 1982, annual total biomass accumulation has been negligible (Likens et al. (1994, 1998)). Except for the experimentally manipulated watersheds, W6 is representative of south-facing watershed-ecosystems of the HBEF (Figure 2).

The S content in this above- and belowground living biomass was about 2885 mol/ha in 1997 (Table 4). As with living biomass, S accumulated in biomass from 1965 to 1982 on an areal basis ($\sim$ 59 mol/ha-yr), but ceased thereafter (Table 4). The pool of S in standing dead trees is small compared to that in living trees, representing some 3–5% of the total pool of S in biomass (Table 4). The biomass of

Table 4. Total above- and belowground biomass and sulfur content of live and dead standing trees on W6 of the HBEF

Size class	Year					
	1965	1977	1982	1987	1992	1997
Biomass (Mg/ha)						
Live						
⩾9.6	149	218	235	234	237	235
1.6–9.5 cm dbh	11	–	8	10	12	15
Dead						
⩾9.6	–	10	11	14	15	13
1.6–9.5 cm dbh	–	–	0.52	0.62	0.45	0.15
Sulfur (moles/ha)						
Live						
⩾9.6	1736	2547	2746	2722	2749	2720
1.6–9.5 cm dbh	144	–	92	114	131	165
Dead						
⩾9.6	–	83	96	111	150	132
1.6–9.5 cm dbh	–	–	5	5	3.9	1.4

standing dead trees has been increasing since these components were first inventoried in 1977. Between 1982 and 1997, while the living biomass pool of S was nearly constant, the pool in larger, dead standing trees (⩾9.6 cm dbh) increased by 38% (Table 4).

Chemical analysis of all aboveground chipped biomass from quantitative plots was done during an experimental whole-tree harvest on W5 in 1983. The results were 1092 mol S/ha as compared to 1485 mol S/ha estimated by allometric analysis of vegetation on these plots and separate chemical analysis of component plant tissues. We do not consider these values to be significantly different given the different methods used, and have used the allometric approach for results presented in this paper.

Somewhat smaller aboveground living biomass (>1.6 cm dbh) pools of S (~1465 mol/ha) were found at the highest elevation, spruce-fir-white birch (SFWB) zone as compared to ~1825 mol/ha in the lower-elevation, more deciduous zone (LH) of W6. There were no obvious temporal trends in these data (Figure 11).

The three dominant tree species (yellow birch, American beech and sugar maple) accounted for 89% of the S in trees of W6 at HBEF in 1997 (Table 5). Within the trees, the largest S pools were found in branches (31%), roots (27%), and light-

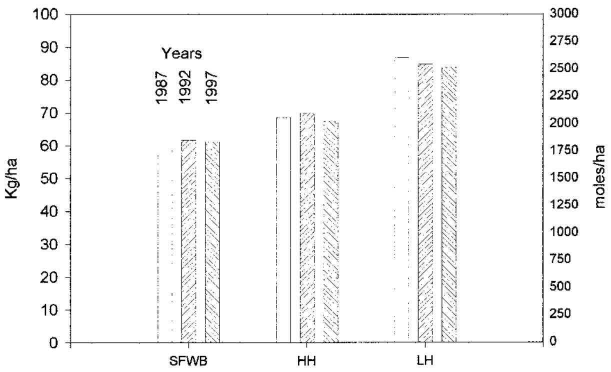

Figure 11. Sulfur content of aboveground live tree biomass on W6 in 1982, 1987 and 1992. SFWB = the upper elevation (ca. 760 m MSL) stand dominated by spruce, fir and white birch; HH = the higher elevation deciduous stand (ca. 700 m MSL) dominated by beech, sugar maple and yellow birch on very shallow soil and somewhat exposed topographically; LH = the lower elevation (ca. 600 m MSL) mixed deciduous stand on deeper soils dominated by sugar maple, beech and yellow birch.

wood (25%). Lightwood contained appreciably more S than darkwood, and bolewood (lightwood and darkwood) contained some 26% of the S, slightly less than roots. Limited data on the concentration of S in leaves of American beech, sugar maple and yellow birch showed somewhat higher concentrations for sugar maple (~ 2.2% dry wt), but no clear trends with elevation for any species or with time (1993–1997).

Throughfall and stemflow

As precipitation passes through a forest canopy, several processes can affect the chemistry of the resulting throughfall: evaporation of water, dissolution of soluble material on canopy surfaces, including previously dry-deposited material, and exchange of solutes between the surface water and the plant. At HBEF, the concentration of SO_4^{2-} in growing season (June–September) throughfall averaged 10–50% higher than the concentration in bulk deposition for the same period (Lovett et al. 1996), but this concentration increase resulted partly from evaporation of water in the canopy. Growing-season throughfall fluxes of SO_4^{2-} ranged from 4% less than bulk deposition fluxes in some young (<10 yr) aggrading stands to 23% greater in mature northern hardwood stands (Lovett et al. 1996).

Canopy exchange (foliar leaching and uptake) of SO_4^{2-} often is considered to be relatively small compared to dry deposition fluxes; if true, then the net throughfall flux (throughfall – bulk deposition) would be a good estimate of S dry deposition (Lindberg and Garten 1988; Lindberg and Lovett 1992). If we assume the net throughfall flux (NTF) of S were equal to dry deposition, then dry deposition to the hardwood canopies in the growing seasons of 1989–1992 would average 7 mol S/ha-month, about 19% of the bulk deposition flux for the same period. There were no significant differences in concentration, flux, or NTF SO_4^{2-} at different elevations ranging from 530–705 m MSL in W6 (Lovett et al. 1996). However, the

Table 5. Sulfur content in living trees ($\geqslant$ 1.6 cm dbh) of W6 at the HBEF in 1997 (in mol/ha)

Species	Lightwood	Darkwood	Bark	Branches[a]	Leaves	Roots	Total above-ground	Total above + below-ground
Sugar Maple	283	7	114	281	80	305	765	1070
American Beech	275	11	67	334	74	210	761	971
Yellow Birch	93	22	33	181	26	172	356	528
Balsam Fir	8	0	3	5	7	13	23	36
Red Spruce	8	0	4	6	7	14	25	39
White Birch	30	4	11	51	12	52	108	160
Other[b]	19	1	5	32	4	19	61	80
Total	716	45	237	890	211	785	2099	2884
As % of grand total	24.8	1.6	8.2	31.6	6.7	27.0	73.0	100.0

[a] Includes twigs and dead branches

[b] Includes white ash, striped maple, choke cherry, pin cherry, mountain ash, hemlock, red maple and mountain maple

NTF for aggrading hardwood stands (dominated by pin cherry) and a SFWB stand were substantially less, perhaps indicating some uptake of deposited S by these canopies. The NTF may underestimate dry deposition if some dry deposition were to pass directly to the forest floor, and thus this S would not be measured in throughfall (Meyers and Baldocchi 1993). Likewise, NTF would overestimate dry deposition of S if there were leaching of SO_4^{2-} from the canopy (Lovett and Hubbell 1991).

Eaton et al. (1973) measured throughfall SO_4^{2-} during the growing season in 1969 at HBEF, and reported a total throughfall S flux for the June–September period of 685 mol/ha and a total bulk deposition flux of 148 mol/ha. These fluxes are much higher than the June–September 1989–1992 means of 172 and 144 mol/ha reported by Lovett et al. (1996). The mechanism responsible for these differences in throughfall flux is unclear, but we suspect it may be partly due to different analytical methods. Eaton et al. (1973) used an automated wet chemical procedure that is now known to suffer from interferences from color in water samples. Throughfall samples frequently are colored by elevated concentrations of dissolved organic carbon (Eaton et al. 1973; Lovett et al. 1996). Lovett et al. (1996) used an ion chromatograph to measure SO_4^{2-} concentrations.

We estimated the annual fluxes of throughfall and stemflow in HBEF as follows. For 1993–1994, the total annual flux is the sum of annual bulk deposition (266 mol/ha) plus growing season net throughfall plus stemflow flux (80 mol/ha) for a total of 346 mol/ha. This value assumes no leaching from or dry deposition to the leafless canopy in winter. Of the 80 mol/ha of net throughfall plus stemflow flux, our independent estimate indicates that 57 mol/ha are from dry deposition (Lovett et al. 1997), and we assume the remainder (23 mol/ha) is from canopy leaching. For 1969 we use the measured bulk deposition of 406 mol/ha and assume that dry deposition was 21% of bulk deposition, as it was in 1993–1994 ($0.21 \times 406 = 85$ mol/ha). Lacking other information, we assume the canopy leaching is the same as was calculated for 1993–1994 (23 mol/ha), yielding an estimated total throughfall plus stemflow flux of 514 mol/ha.

A small amount of organic S occurs in throughfall, ranging from 2 to 18 μmol/liter in various forest sites (Homann et al. 1990). At the Huntington Forest in the Adirondack Mountains of NY, which has similar vegetation to that at HBEF (David et al. 1987), organic S in throughfall was 3 μmol/liter, or 8% of total S in solution (Homann et al. 1990).

Litterfall

Based on a study of litterfall in 1968–1969, Gosz et al. (1972) found that the flux of S to the forest floor in aboveground litterfall averaged 180 mol/ha-yr (Table 6), with higher inputs for the deciduous forest zone (190 mol/ha-yr) than for the upper-elevation, SFWB zone (172 mol/ha-yr) of W6. This same pattern was observed for K and Ca (Likens et al. (1994, 1998)). The proportion of litterfall S flux in perennial tissues (19%) was intermediate relative to Ca (31.5%) and K (11.5%). Flux of S by deciduous tissues dominated (76%) in aboveground litterfall (Table 6). Most input of S from overstory litter occurred during leaf fall in October (Table 7). Currently (based on data from 1993 and 1997), there is no difference among species or with elevation in S concentration of leaf litter. It averages about 1% of dry weight.

The amount of litterfall at HBEF has not changed significantly from the earlier measurements (1968–1969) to the present time (Likens et al. 1998). As a result of increased mortality of trees at HBEF (Likens et al. 1998), however, it is expected that increased branch and stem inputs will increase litterfall flux of S to the forest floor. Currently, about 63% of the gross uptake of S in biomass is returned to the forest floor each year in litterfall. The estimated flux of S by canopy leaching (23 mol/ha-yr) is about 13% of the litterfall return (181 mol/ha-yr) to the forest floor. Thus, like Ca at HBEF (Likens et al. 1998) cycling between plants and soil is dominated to a greater extent by aboveground plant uptake from the soil and loss in leaching and litter, than occurs for N and P, because vegetation at HBEF retranslocates Ca and SO_4^{2-} to only a limited degree (Ryan and Bormann 1982; Likens and Bormann 1995).

Table 6. Aboveground litterfall (kg/ha) and sulfur content (mol/ha) on W6 during 1968-69 (after Gosz et al. (1972))

	Litter [weighted watershed average] (kg/ha)	% of total litter	Sulfur (mol/ha)	% of total sulfur
Perennial tissue	2169	38	34.3	19
Deciduous tissue	3419	60	137	76
Shrub layer	66	1	3.1	2
Herbaceous layer	48	1	6.2	3
Total	5702	100	181	100

Table 7. Sulfur content in overstory litter in selected months for W6 during 1968–1969 (after Gosz et al. (1972))

	mol/ha-mo
June	6.55
August	15.3
October	88.3
February	4.06

Patterns in soil water chemistry

Mean annual, volume-weighted soil water concentrations of SO_4^{2-} were relatively uniform by soil horizon and across landscape position adjacent to W6 (Figure 12). In all three elevation zones, mean annual, volume-weighted concentrations of SO_4^{2-} increased slightly (not statistically significant) from waters draining the Oa horizon to Bh horizon to the lower mineral soil (Bs horizon). This subtle pattern of an increase in SO_4^{2-} may be due to concentration of solutes associated with transpiration. Another subtle (and not statistically significant) pattern was a decrease in mean annual volume-weighted concentrations of soil water SO_4^{2-} with decreasing elevation. Concentrations of SO_4^{2-} in soil water draining the high elevation SFWB zone were slightly higher (mean annual volume-weighted Oa = 45.9 ± 10.5 μmol/liter, Bh = 54.8 ± 10.7 μmol/liter and Bs = 57.7 ± 8.5 μmol/liter) than the high-elevation hardwood zone (mean annual volume-weighted Oa = 37.8 ± 7.3 μmol/liter, Bh = 42.6 ± 6.9 μmol/liter and Bs = 47.3 ± 8.1 μmol/liter). These values were, in turn, higher than soil waters in the low-elevation hardwood zone (mean annual volume-weighted Oa = 35.1 ± 9.5 μmol/liter, Bh = 36.1 ± 9.7 μmol/liter and Bs = 44.5 ± 8.0 μmol/liter).

Average, annual fluxes of SO_4^{2-} were computed for each soil horizon and are presented below (see e.g. Figure 29).

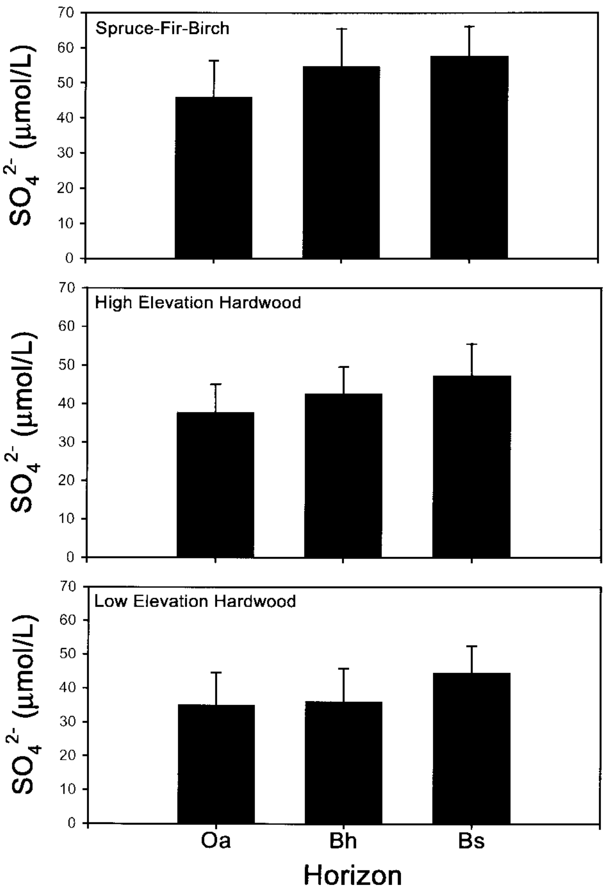

Figure 12. Mean annual volume-weighted concentrations and standard deviation of SO_4^{2-} in soil water draining horizons within different elevation zones adjacent to W6 at the HBEF.

Forest floor and mineral soil pools and dynamics

The forest vegetation cycles S through the ecosystem by taking up inorganic SO_4^{2-} through the roots and converting it into organic S, which then is returned to the forest floor in above- and belowground litter. Direct foliar uptake of atmospherically deposited SO_2 has been observed (Garland and Branson 1977), but in general is considered to be small (<20% of S in throughfall; Lindberg and Garten (1988)).

As in most forest ecosystems, most of the S at HBEF is carbon-bonded with a small but variable proportion in foliage and especially in roots, occurring as inorganic SO_4^{2-} (Turner et al. 1980; Mitchell et al. 1992). Concentration measurements and pool estimates of total S in the soil of W5 were done in 1983 (summer before a whole-tree harvest experiment, see below). The concentration and pools of S vary among soil horizons (Figures 13 and 14) with the largest pool occurring in the Bs2 horizon, which contributed about 38,700 mol S/ha or ~ 73% of the total (Figure 14, Table 2) (Zhang et al. 1999). Of the total S in soil (about 53,000 mol S/ha) some-

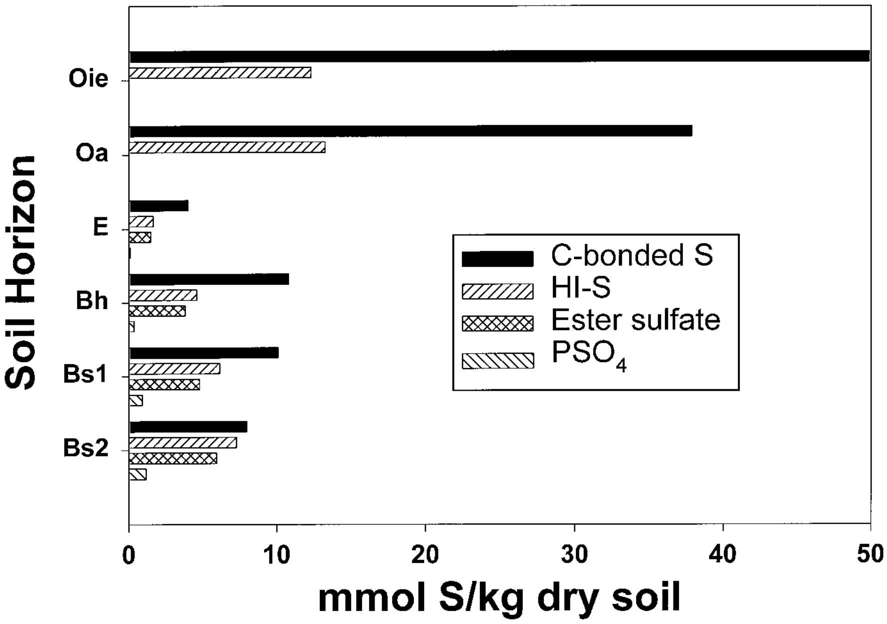

Figure 13. Concentration of S constituents in soil of W5 in 1983. (Data from Zhang et al. (1999)).

what more than 3 kmol/ha (6%) exists as phosphate-extractable SO_4^{2-} or PSO_4 (Table 2). Organic S (carbon-bonded and ester sulfates) represents some 89% of the total S in the soil at HBEF (Table 2) (Mitchell et al. 1989; Alewell et al. 1999; Zhang et al. 1999).

The forest floor (O_{ie} + Oa) S pool (4696 mol/ha) represents some 9% of the total soil pool at HBEF (Table 2). On an organic matter basis, S was 0.229%, 0.277% and 0.308% of the forest floor in 1969–1970, 1982 and 1997, respectively.

Carbon-bonded S may contain amino acids, sulfolipids and sulfonic acids as well as many poorly defined compounds. Some of these compounds are formed and stabilized by humification. The chemical forms of S in humus are largely unknown, but may include both aliphatic and aromatic structures. Both N and S amino acids have been detected as constituents of humic substances, and these amino acids may comprise a substantial portion of C-bonded S in soil. A major class of S compounds is within the HI-reducible component which constitutes some 40% of total S at HBEF (Table 2). Compounds included in the operationally-defined ester SO_4^{2-} class are those that contain the C-O-S linkage (ester SO_4^{2-}) and the C-N-S linkage (sulfamate) along with some organic sulfites. The C-O-S linkage is found in greatest quantity, with the other forms being rare. Ester sulfates generally are believed to be more labile than most of the C-bonded S constituents, especially C-bonded S that has been humified. These ester sulfates compose some 33% of total S at the HBEF (Table 2). The other major form of S in soils at the HBEF to the bottom of the B horizon is inorganic SO_4^{2-} (6% of total S; Table 2). In forest soils, inorganic SO_4^{2-} can be separated into adsorbed and water-soluble fractions. The adsorption of SO_4^{2-}

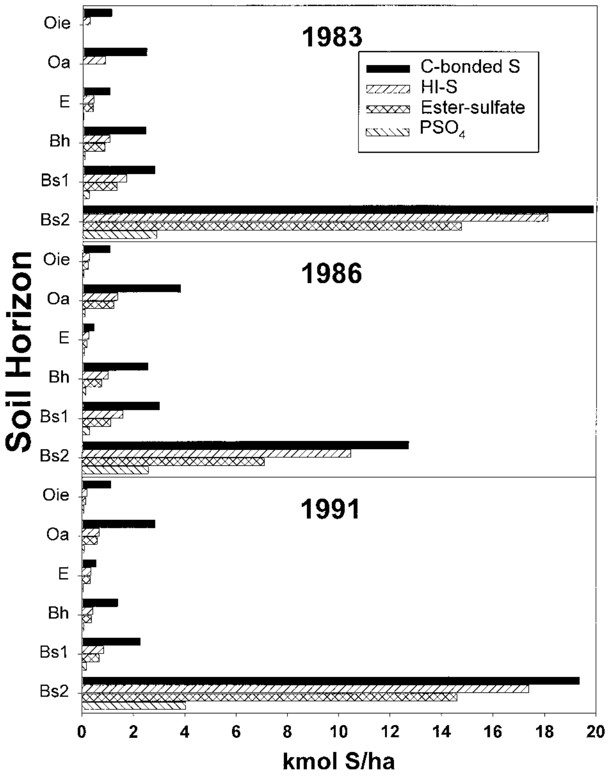

Figure 14. Content of S constituents before (1983) and after the whole tree harvest (1986, 1991) of W5. (Data from Zhang et al. (1999)).

is dependent on a variety of factors but at HBEF, pH and SO_4^{2-} concentrations in solution have been shown to be most important (Nodvin et al. 1988).

The mineralization of organic S provides SO_4^{2-} that can be taken up by plants and soil microorganisms. The role of these large organic S pools in regulating long-term changes in S storage or release at the HBEF, however, has not been clearly established, but small changes in these organic S pools could have a substantial effect on ecosystem mass balances, especially when atmospheric deposition of S is declining.

Earlier studies in North America and Europe concluded that SO_4^{2-} transport through forest soils was rather conservative, because precipitation, soil solution and stream water of forest ecosystems showed similar $\delta^{34}S$ values (Caron et al. 1986; Stam et al. 1992; Mayer et al. 1995). However, Mayer et al. (1995) showed that although $\delta^{34}S$ values are altered only slightly, the oxygen isotopic composition ($\delta^{18}O$) of SO_4^{2-} shows a depletion of several per mil indicating that biological processes were contributing to the SO_4^{2-} in soil solution. Moreover, studies from the HBEF (Zhang et al. 1998; Alewell et al. 1999) as well as from two sites in the northwestern Czech Republic and a site in northeastern Bavaria, Germany (Novac et al. 1995; Alewell 2002 (in press)) showed that $\delta^{34}S$ values of soil solutions and streams have different spatial and temporal patterns than those for precipitation or throughfall. Moreover, $\delta^{34}S$ values of SO_4^{2-} in soil solution have generally lower $\delta^{34}S$ values than SO_4^{2-} in bulk deposition and throughfall (Fuller et al. 1986b; Novac et al. 1995; Alewell et al. 1999; Zhang et al. 1998; Alewell and Gehre 1999).

Analysis of stable S isotopes during 1966 to 1994 showed significantly and consistently higher $\delta^{34}S$ values in bulk deposition (mean 4.5 and 4.2‰ at RG 22 and 11, respectively, with a higher variation (SD = 0.70 and 0.55, respectively) than in stream water (mean 3.2 and 3.7‰; SD = 0.30 and 0.28, respectively; Figure 15 Alewell et al. (1999)). Zhang et al. (1998) also showed that monthly bulk deposition $\delta^{34}S$ values were consistently higher in both growing and dormant seasons than in stream water (Figure 16). Fuller et al. (1986b) showed that $\delta^{34}S$ values of inorganic compounds were consistently higher than organic compounds at W5 (Figure 17; analysis done prior to clearcut experiment). These latter results are confirmed by other studies of forest ecosystems (for an overview see Mitchell et al. (1998)), which generally have found lower $\delta^{34}S$ values for organic sulfur than for the inorganic fractions (e.g. soil solution SO_4^{2-} and adsorbed SO_4^{2-}). Together, these results indicate that part of the stream SO_4^{2-} is derived from organic S in the soil. Thus, much of the SO_4^{2-} entering a forest ecosystem from atmospheric deposition cycles through living and dead biomass before it is released to soil solutions and stream water (Figures 16 and 18).

Also, results from the W5, whole-tree harvest experiment (see below) showed that adsorption/desorption processes play a major role in regulating net SO_4^{2-} retention for these watershed-ecosystems (Mitchell et al. 1989; Zhang et al. 1999). The whole-tree harvest of W5 resulted in some small changes in the organic S constituents, but the most dramatic changes in the soil S constituents three (Mitchell et al. 1989) and eight years (Zhang et al. 1999) after harvesting were attributed to changes in the pools of PSO_4. However, $\delta^{34}S$ values in stream waters were not affected by the experimental disturbance (Alewell et al. 1999). This result indicates that, even with major and rapid changes in soil solution and streamwater concentrations, SO_4^{2-} in stream water is released from a large and stable pool with relatively constant $\delta^{34}S$ values.

Sulfur mass balances combined with isotopic results (Figure 18) suggest that mineralization of organic S may have been an important contributor to SO_4^{2-} in stream water at HBEF during extended periods (Fuller et al. 1986b; Zhang 1994; Alewell et al. 1999). Although the isotopic results suggest the importance of S mineralization, conclusive evidence that there is net organic S mineralization has not yet been shown. Net mineralization of soil organic S would be expected in response to declines in atmospheric deposition of S. Using a model that depicts dynamics of soil organic S, we estimated that net mineralization of S in recent years (1993–1998) at HBEF to be 69 mol/ha-yr (Gbondo-Tugbawa et al. 2001).

Soil sulfate adsorption

Soil SO_4^{2-} adsorption capacity is considered an important parameter in assessments of the effects of acidic deposition (Galloway et al. 1983). Adsorption of SO_4^{2-} re-

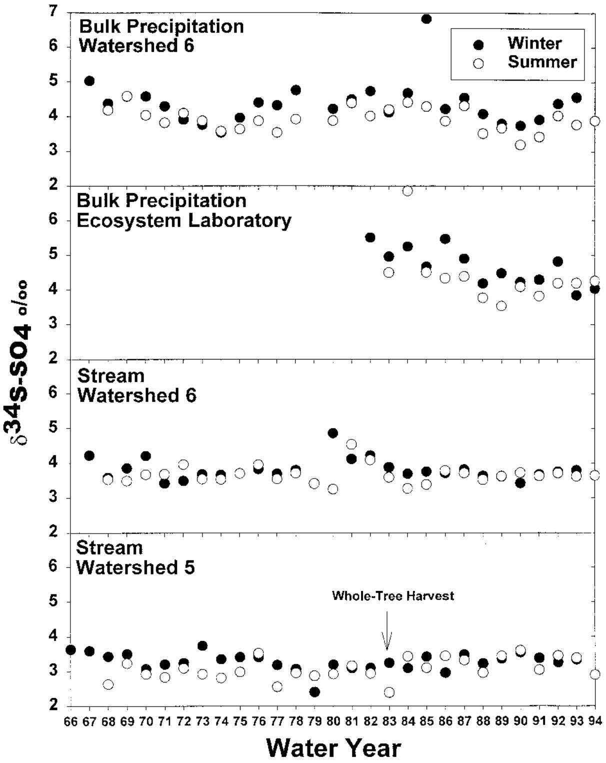

Figure 15. δ^{34}S values of SO_4^{2-} in bulk deposition collected near base of W6 and at HQ site near the Robert S. Pierce Ecosystem Laboratory and in stream samples taken just above the weir of W5 and W6 (see Figure 2). Archived samples were combined into summer (1 June through 30 Nov.) periods and winter (1 Dec. through 31 May) periods. (From Alewell et al. (2000)).

sults in the production of ANC (Johnson 1980) and increases soil cation exchange capacity (Wiklander 1980). As a result, SO_4^{2-} adsorption can alter transport of H^+, Al^{n+} and base cations from soil to surface waters. Fuller et al. (1985) investigated SO_4^{2-} adsorption relationships in soils at HBEF, and as reported by others, they found that adsorbed SO_4^{2-} was largely associated with the free Fe and Al content of the lower mineral soil. They suggested that soil was at steady-state with respect to SO_4^{2-} inputs. However, they indicated that SO_4^{2-} adsorption was an important process buffering stream SO_4^{2-} concentrations, with limited seasonal and year-to-year variability.

Several laboratory studies have investigated SO_4^{2-} adsorption of HBEF soils (Nodvin et al. (1986a, 1986b, 1988); Fuller et al. 1987). Using a Langmuir adsorption model, Driscoll et al. (1998a) reported an SO_4^{2-} adsorption capacity of 30 μeq/g for lower mineral soil at the HBEF, with a log adsorption constant of 3.32. Although SO_4^{2-} adsorption is evident in HBEF soils, the SO_4^{2-} adsorption capacity is low in comparison to advanced weathering-stage soils with higher clay content and free Fe and Al content (Johnson et al. 1980; Markewitz et al. 1998). Investigators

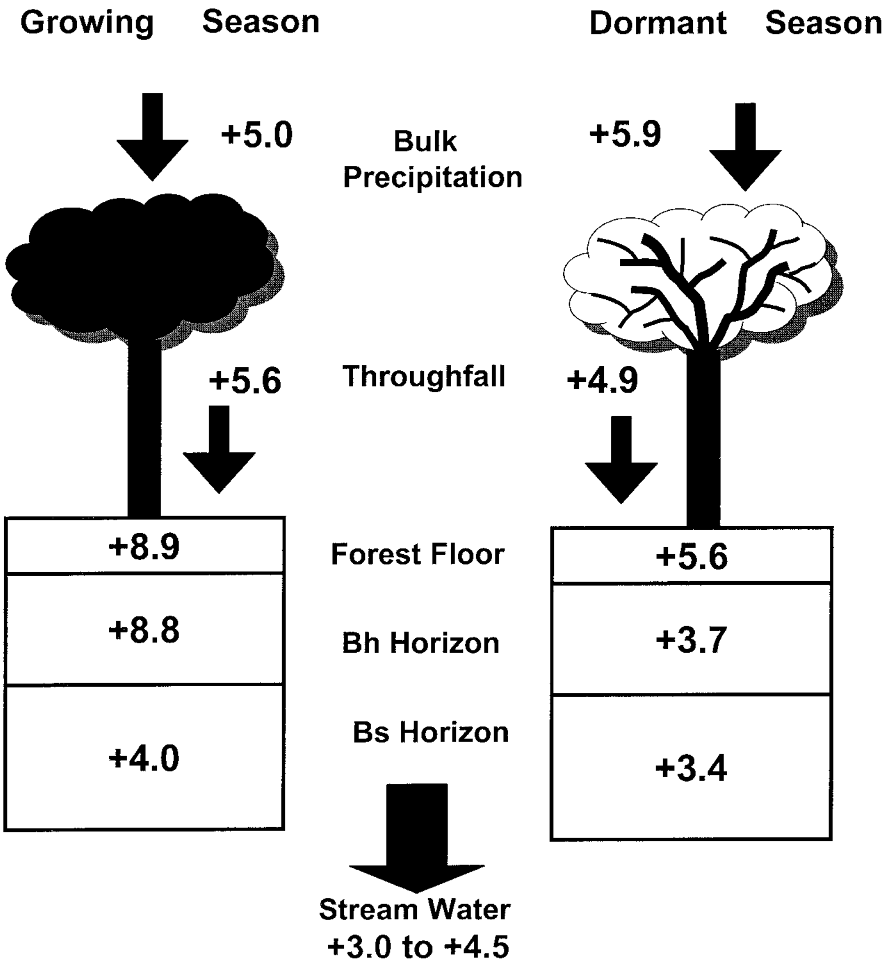

Figure 16. The average $\delta^{34}SO_4^{2-}$ values in bulk deposition, throughfall, soil-solutions and streamwater for W6 of the HBEF during the growing and dormant seasons. The units are ‰ $\delta^{34}S$ (modified from Zhang et al. (1998)).

at HBEF have noted that SO_4^{2-} adsorption is pH-dependent (Nodvin et al. (1986a, 1986b, 1988); Fuller et al. 1987). For example, phosphate extractable sulfate in the E and Bh horizons increased by 49.9 and 53.0 mol S/ha, respectively, in response to decreased pH due to enhanced nitrification after the whole-tree harvesting of W5 (Zhang et al. (1999); and see below). Soil SO_4^{2-} adsorption increases with decreases in pH, reaching a maximum near pH 4.3. At pH values below 4.3 (soil pH in distilled water), SO_4^{2-} adsorption decreases. We have attributed the pH-dependent SO_4^{2-} adsorption to the protonation/deprotonation of variable charge Fe and Al surfaces. At pH values below 4.3 elevated concentrations of solution Al form aqueous complexes with SO_4^{2-}, facilitating desorption from soil surfaces.

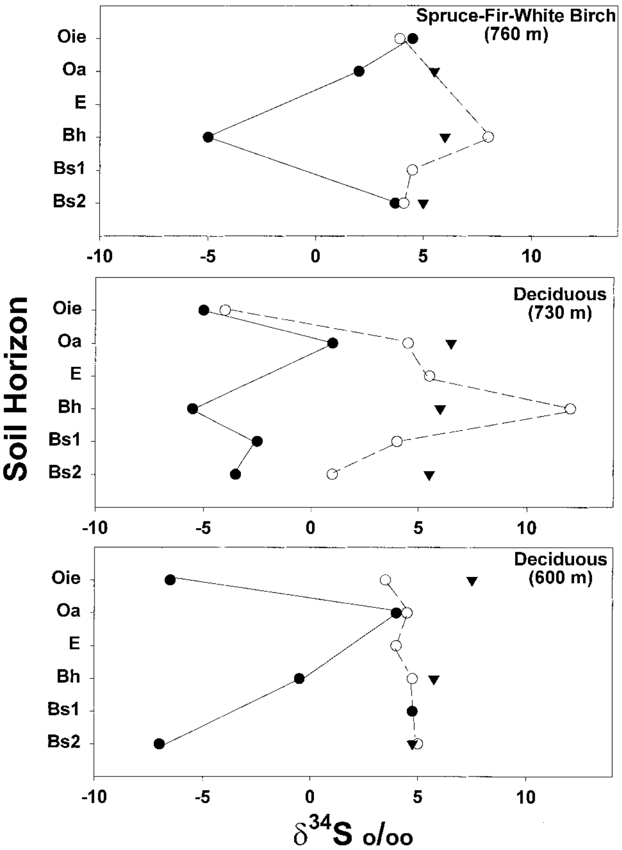

Figure 17. Values of δ^{34}S for both organic and inorganic fractions in the soil as well as SO_4^{2-} in soil water along an elevational gradient at the HBEF. Soil organic sulfur (-●-); soil SO_4^{2-} (-○-); soil water (-▼-) (from Fuller et al. (1986b)).

Desorption of SO_4^{2-} would be expected in response to declines in SO_4^{2-} in soil solution. Using a model of soil chemistry that includes SO_4^{2-} adsorption and desorption, we estimate that S desorption in recent years (1993–1998) at HBEF to be 32 mol S/ha-yr (Gbondo-Tugbawa et al. 2001).

Losses of sulfur from the watershed-ecosystem

Dissolved losses in stream water – concentrations, trends and patterns

The long-term, volume-weighted mean concentration of SO_4^{2-} in stream water is 55.3 μmol/liter (5.31 mg SO_4^{2-}/liter). Annual, volume-weighted mean concentrations of SO_4^{2-} in stream water have ranged from a low of 42.3 μmol/liter in 1996–1997 to a high of 66.1 μmol/liter in 1970–1971 (Figure 3, Table 8). Overall, there was a statistically significant and large decrease (31%) in streamwater concentrations of SO_4^{2-} with time (Figure 3; $p < 0.001$; $r^2 = 0.87$).

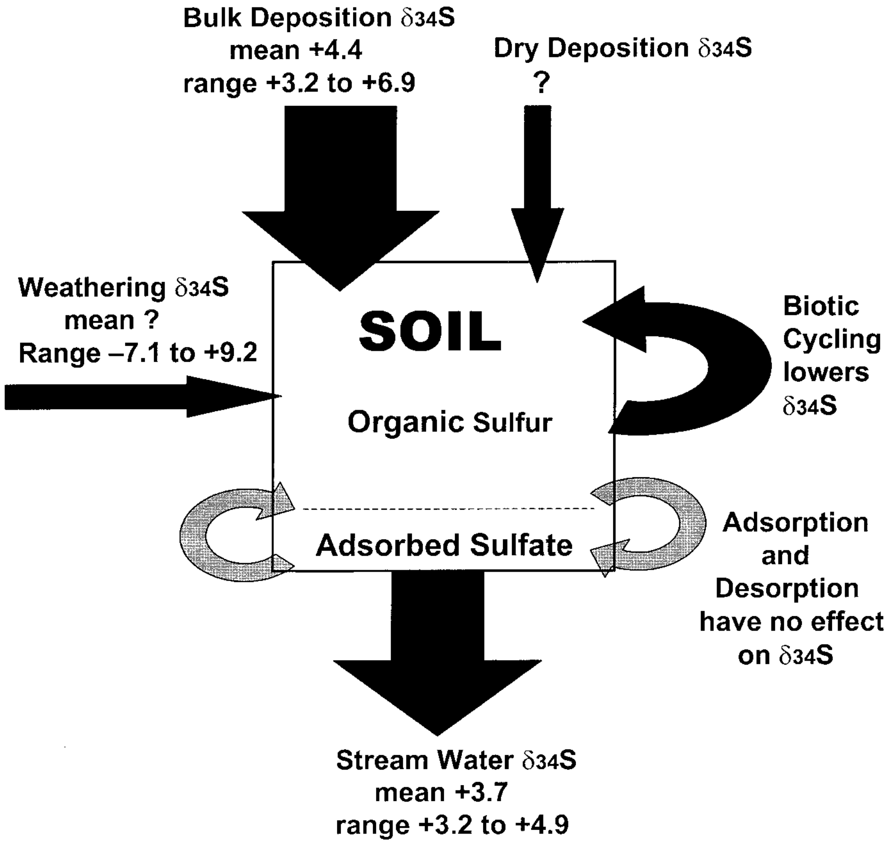

Figure 18. Generalized diagram of inputs, soil pools, processes and outputs with $\delta^{34}S$ values for W6 at HBEF from 1968 through 1993. Units are ‰ $\delta^{34}S$ (modified from Alewell et al. (1999)).

As observed for bulk deposition, concentrations of SO_4^{2-} in stream water were linearly and statistically correlated ($r^2 = 0.75$; $p < 0.001$) with emissions of SO_2 during 1964 through 1998 (Figure 5A). Also streamwater output of SO_4^{2-} was significantly correlated ($p < 0.001$) with emissions of SO_2 from the source area for HBEF ($r^2 = 0.13$; Figure 5B).

We have only limited data on the contribution of dissolved organic S to streamwater loss. In W5 and W6, organic S concentrations ranged from 0.7 to 9.5 μmol/liter during 1986 and constituted some 2 to 15% of the total S in stream water (Mitchell et al. 1989).

Average monthly concentrations of SO_4^{2-} in stream water are at a minimum during April and peak during late summer–early autumn (Figure 6). The major output of SO_4^{2-} in streamflow occurs during the snowmelt period, high runoff months of March, April and May, with a secondary peak in November (Figure 6). Average streamwater outputs of SO_4^{2-} are higher than inputs in bulk deposition during October through May. Monthly streamwater SO_4^{2-} concentrations have no statistically

Table 8. Annual volume-weighted average sulfate concentrations in streamwater at HBEF for south-facing watersheds

Water – year	W1	W2	W3	W4	W5	W6	Mean[a]	±sd
1964–1965	NA	68.0	NA	NA	NA	62.2	NA	NA
1965–1966	NA	71.0	NA	67.5	NA	64.9	NA	NA
1966–1967	NA	40.1	NA	66.5	NA	63.3	NA	NA
1967–1968	NA	38.5	NA	65.9	NA	63.8	NA	NA
1968–1969	NA	44.7	NA	61.9	NA	59.8	NA	NA
1969–1970	NA	46.6	NA	58.3	NA	56.3	NA	NA
1970–1971	71.5	68.8	NA	66.8	NA	66.1	NA	NA
1971–1972	72.5	82.9	63.3	57.0	59.5	64.5	66.8	4.1
1972–1973	73.3	80.4	71.7	59.0	63.6	63.1	69.4	4.5
1973–1974	68.6	71.7	67.3	58.9	61.9	60.6	65.5	3.5
1974–1975	69.5	72.1	69.2	62.3	63.6	62.6	67.1	3.2
1975–1976	67.9	68.6	68.0	62.0	62.1	61.9	65.9	2.8
1976–1977	58.9	65.8	62.9	59.6	57.8	56.8	59.5	2.5
1977–1978	65.0	61.3	62.2	58.5	58.9	58.0	61.8	2.9
1978–1979	62.9	58.7	60.0	56.6	58.6	57.3	60.0	2.3
1979–1980	61.0	60.1	58.8	57.5	57.7	56.0	58.6	2.0
1980–1981	64.8	63.3	62.4	62.1	59.8	57.6	61.6	3.0
1981–1982	63.3	60.7	60.9	59.0	58.5	56.3	60.2	2.9
1982–1983	62.7	58.8	59.5	57.9	58.3	56.5	59.6	2.6
1983–1984	57.6	53.4	54.9	54.7	52.9	52.4	55.0	2.1
1984–1985	58.2	54.7	55.9	56.6	39.0	54.0	56.0	1.7
1985–1986	55.3	51.7	53.7	53.2	41.1	51.1	53.4	1.7
1986–1987	55.0	53.4	54.4	53.7	48.9	49.3	52.9	2.5
1987–1988	55.4	54.3	54.8	56.0	55.9	51.4	53.8	1.8
1988–1989	57.1	56.3	55.9	58.5	58.8	52.6	55.2	1.9
1989–1990	54.8	53.8	54.7	55.0	57.3	49.8	53.1	2.4
1990–1991	53.4	52.3	53.5	52.7	53.2	49.7	52.2	1.7
1991–1992	54.9	52.4	53.4	53.7	54.1	51.1	53.1	1.6
1992–1993	52.7	50.9	51.9	52.6	50.4	48.5	51.0	1.8
1993–1994	53.1	50.2	52.5	53.4	52.7	50.0	51.9	1.3
1994–1995	52.7	51.6	53.2	52.8	53.3	50.0	52.0	1.4
1995–1996	48.9	47.8	48.2	48.8	50.5	44.5	47.2	1.9
1996–1997	44.8	42.0	43.9	42.8	46.1	42.3	43.7	1.0
1997–1998	44.5	42.8	44.9	44.2	46.5	43.1	44.2	0.8
Individual ANNUAL MEAN (μmol/L)	59.3	57.3	57.5	57.2	54.8	55.5	56.7	
±sd	7.8	10.9	6.8	5.6	6.3	6.4	6.7	

Underlined = Values from years during experimental treatments.

[a] Mean and ±sd for W1, W3, and W6 only from data after 1970–1971

significant seasonal pattern whereas bulk deposition does (Figure 6). As a result, net monthly gains and losses result from differences in hydrology (lowest flow in summer) and concentrations (highest bulk deposition concentrations in summer) (Figure 6). However, it is apparent from these data (Figure 6) that the "cross-over" pattern for monthly SO_4^{2-} flux is not determined exclusively by water flux (see May–June and September–October). Undoubtedly, it is ecologically important that these cross-over periods coincide with periods of major biological activity in the forest (e.g. leaf out and leaf fall). Also, the accumulation of snow and its melting seasonally play a major role in the uneven output of SO_4^{2-} in streamflow during the year.

Annual outputs of SO_4^{2-} in stream water generally increased from 1964–1965 to the mid 1970's, peaking during the wet year of 1973–1974. Overall, however, outputs decreased significantly during the 34-yr period, and particularly after 1974. Relatively large outputs occurred during the wet year of 1995–1996 (Figure 3, Table 9).

Annual gross outputs of SO_4^{2-} in stream water consistently exceeded bulk deposition inputs except for 1964–1965 (Figure 3). No relation of SO_4^{2-} concentration in bulk deposition or stream water to amount of precipitation or to streamflow was observed on an annual basis (Figures 7 and 19A). Thus, gross annual inputs in bulk deposition and outputs of SO_4^{2-} in stream water were positively and significantly (r^2 of 0.13 and 0.70, respectively) related to amount of annual precipitation and streamflow, respectively, during 1964–1965 to 1997–1998 (Figures 7 and 19B). Also, net annual loss of SO_4^{2-} was significantly related to annual streamflow (Figure 19C; $r^2 = 0.80$). The 1973–1974 year was the wettest year at HBEF, but its net annual loss was exceeded by the loss during 1995–1996, 1983–1984 and 1975–1976 (Figure 20, Table 9).

As was the case for Ca (Likens et al. 1998), the relationship between gross output of SO_4^{2-} and annual streamflow has changed significantly with time (Figure 21). During the first decade of study (1964–1975) gross output of SO_4^{2-} was strongly related to annual streamflow (slope = 0.59; $r^2 = 0.97$), but during the most recent decade (1986–1997), the slope has decreased to 0.39 and the r^2 to 0.91). Thus, 1400 mm of streamflow in 1964–1969 would have produced an SO_4^{2-} output of 826 mol/ha-yr, whereas the same discharge in 1986–1997 would have exported 546 mol/ha-yr, or 0.2 mol/ha-yr less per mm of streamflow (33.9% decrease) (Figure 21).

Changes in anion composition of stream water

Sulfate contributes some 80% of the total anion charge in stream water (Figure 8B). This contribution has increased slightly but significantly during the study (+ 0.36%/yr; $r^2 = 0.32$; $p < 0.001$), primarily because NO_3^- concentrations in stream water have declined markedly (–0.44%/yr; $p < 0.001$; $r^2 = 0.36$) since the mid 1970s (Figure 8B). Sulfate concentrations were positively correlated with NO_3^- concentrations in W6 stream water during 1964–1998 ($r^2 = 0.32$; $p = 0.0004$).

Elevational patterns in streamwater chemistry

The two upper-elevation sites sampled (750, 730 m MSL) drain a SFWB zone. The two middle elevation sites are located in reaches within the high elevation hard-

Table 9. Annual stream output of sulfate from HBEF for south-facing watersheds

Water – Year	W1	W2	W3	W4	W5	W6	Mean[a]	±sd
1964–1965	NA	339	NA	NA	NA	309	NA	NA
1965–1966	NA	566	NA	507	NA	491	NA	NA
1966–1967	NA	480	NA	558	NA	535	NA	NA
1967–1968	NA	475	NA	615	NA	606	NA	NA
1968–1969	NA	518	NA	574	NA	536	NA	NA
1969–1970	NA	514	NA	510	NA	490	NA	NA
1970–1971	523	678	NA	544	NA	548	NA	NA
1971–1972	496	689	452	455	413	479	476	18
1972–1973	699	862	690	636	627	649	679	22
1973–1974	918	1090	896	902	852	849	888	29
1974–1975	529	648	522	552	500	507	520	9
1975–1976	807	897	806	817	731	736	783	33
1976–1977	511	613	505	566	489	483	500	12
1977–1978	618	650	562	610	551	571	583	25
1978–1979	512	521	491	493	474	489	497	11
1979–1980	435	452	407	417	405	398	413	16
1980–1981	488	490	458	478	444	449	465	16
1981–1982	679	690	651	665	592	579	636	42
1982–1983	507	480	478	478	449	460	481	19
1983–1984	579	554	548	567	506	526	551	22
1984–1985	377	356	362	376	312	362	367	7
1985–1986	488	467	462	486	382	467	472	12
1986–1987	415	424	432	424	387	411	419	9
1987–1988	392	384	393	417	409	395	393	1
1988–1989	358	369	359	377	404	371	363	6
1989–1990	530	579	551	570	611	525	535	11
1990–1991	562	599	579	578	606	559	567	9
1991–1992	436	465	447	463	487	441	442	5
1992–1993	435	450	454	465	458	432	440	10
1993–1994	420	440	447	474	473	455	440	15
1994–1995	306	294	301	310	334	312	306	5
1995–1996	639	662	617	654	693	620	625	10
1996–1997	499	497	485	498	559	504	496	8
1997–1998	314	316	317	310	345	333	321	8
Total (mol/ha)	14472	18507	13673	17344	13492	16876	13661	
ANNUAL MEAN (mol/ha-yr)	517	544	506	526	500	496	506	
±sd	139	167	134	123	126	112	130	

Underlined = Values from years during experimental treatments.

[a] Mean and ±sd for W1, W3, and W6 only from data after 1970–1971

wood zone (700, 660 m MSL), and the two lowest elevation sites are in the low

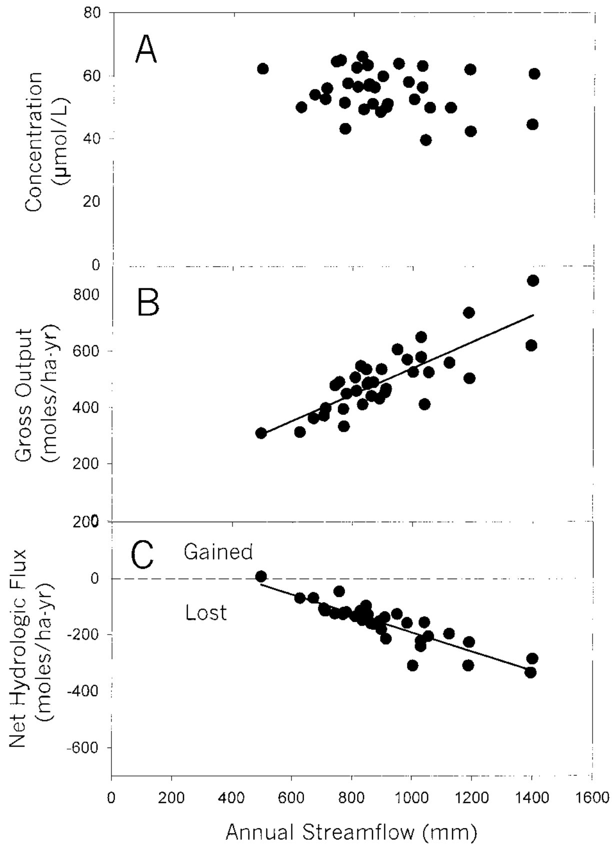

Figure 19. Relationship between the: **A.** Annual volume-weighted concentration of SO_4^{2-} in stream water and amount of annual streamflow. **B.** Annual gross output of SO_4^{2-} in stream water and amount of annual streamflow. The probability for a larger F-ratio for the regression line for 1964–1997 is $p < 0.001$; $r^2 = 0.70$, and **C.** Net hydrologic flux for SO_4^{2-} (streamwater output minus bulk deposition input) for W6 at HBEF during 1964–1998. Negative fluxes indicate that the watershed-ecosystem lost SO_4^{2-}.

elevation hardwood zone (600, 540 m MSL). Despite this gradient in elevation, no longitudinal pattern in stream SO_4^{2-} concentrations was evident during the measurement period (Figure 22). The mean SO_4^{2-} concentration at the highest elevation site was 51.4 μmol/liter, while the concentration at the gauging station was 51.7 μmol/liter during 1982–1998.

This finding was unexpected as atmospheric deposition of SO_4^{2-} is thought to increase with increasing elevation in the northeastern U.S. (Lovett et al. 1999). However, we did not observe significant changes in SO_4^{2-} concentration in bulk deposition with elevation (252 to 550 m MSL; Martin et al. (2000a)) and only a 17% increase in amount of precipitation over this elevation range. The elevation of W6 ranges only from about 550 to 795 m MSL; Figure 2). Moreover, the streamwater pattern was consistent with the absence of an elevational pattern in through-

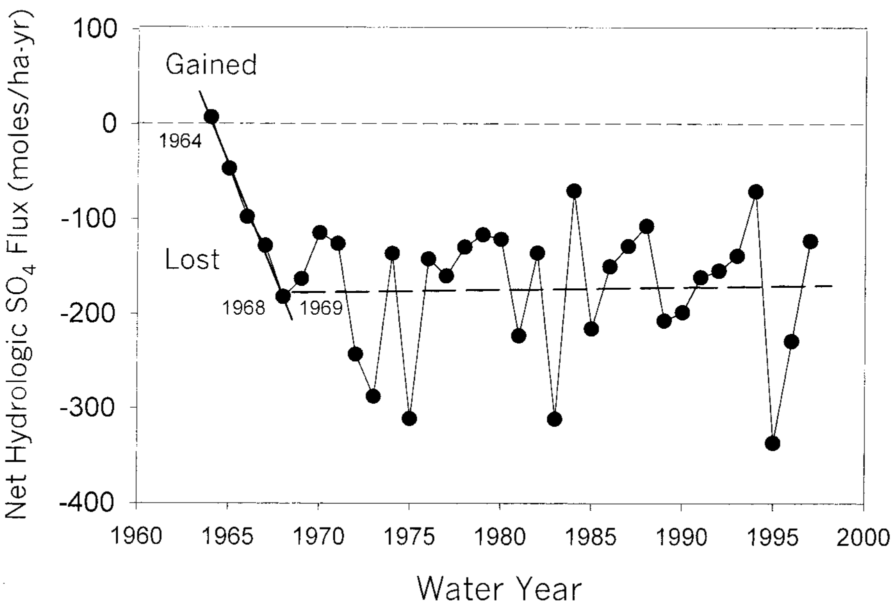

Figure 20. Net hydrologic flux (streamwater output minus bulk deposition input) of SO_4^{2-} for W6 of the HBEF during 1964–1998. The r^2 for 1964–1968 is 0.99; slope = –45.92. The slope for the 1969–1998 line is not significantly different from zero.

fall fluxes of SO_4^{2-} in the northern hardwood forest of W6 (Lovett et al. 1996). Over a larger range of elevation in the Catskill Mts. of New York, Lovett et al. (1999) found an increase in SO_4^{2-} deposition and Lawrence et al. (1999) found a corresponding increase in streamwater SO_4^{2-} concentration.

Particulate losses in stream water

The particulate matter transported from watershed-ecosystems at HBEF was partitioned into three categories: (1) suspended and bed load materials collected in the ponding basin at the mouth of the gauged watershed-ecosystem; (2) suspended material collected in a 1-mm mesh net from water passing through the gauging weir; and (3) suspended material collected on a 0.45-μm pore filter from samples collected after the water passed through the net at the weir (Bormann et al. 1969). During an 8-yr period (1965–1966 through 1972–1973), material collected in the ponding basin represented more than 77% of the total particulate matter. Organic particulate matter comprised some 33% of the total particulate matter transported (Likens and Bormann 1995). We assume that these proportions were similar throughout 1964–1998 and that S was transported accordingly.

The amount of particulate matter transported from hillslopes at HBEF is highly dependent upon stormflow events (e.g. Bormann and Likens (1979) and Bormann et al. (1969, 1974), Likens and Bormann (1995). Losses of S in particulate matter, both organic and inorganic, were very small compared to those in dissolved form. During 1965–1966 through 1969–1970 streamwater losses of S in particulate mat-

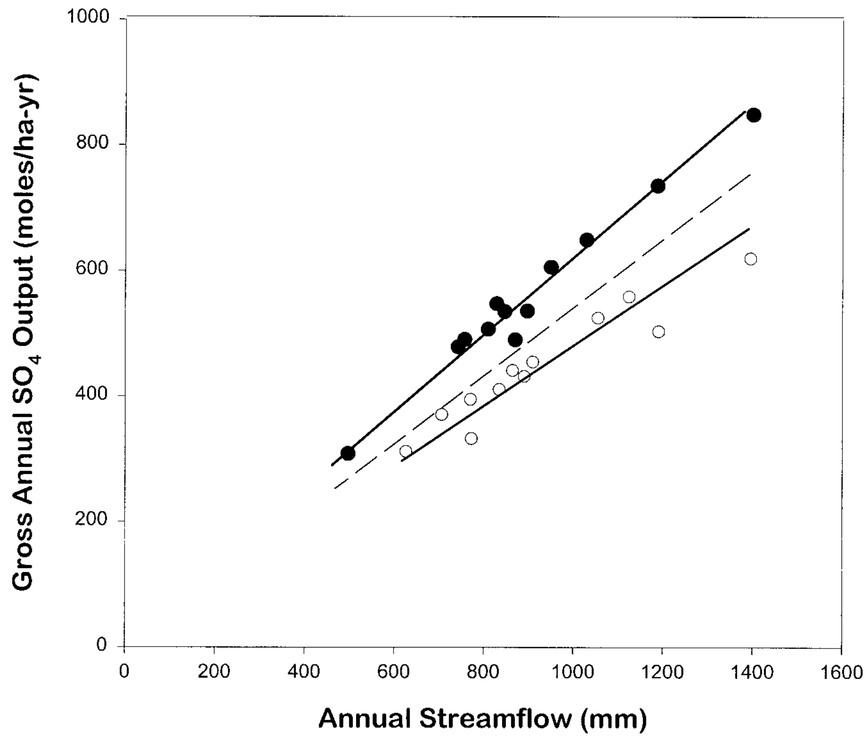

Figure 21. Changing relationship between the gross, annual output of SO_4^{2-} in stream water and the amount of annual streamflow for W6 at HBEF during 1964–1998. Symbols: -●- is 1964–1965 to 1974–1975 and -○- is 1986–1987 to 1997–1998; the dashed line is the regression for all data, 1964–1965 to 1997–1998.

ter were about 0.94 mol S/ha-yr, whereas the NHF of SO_4^{2-} was 140 mol S/ha-yr. Some 30% of the particulate matter loss of S was as inorganic particulate matter (Bormann et al. 1974).

Gaseous S loss

Certainly sulfurous gases such as H_2S or CH_3SCH_3 can be emitted from natural ecosystems, resulting in loss of S. Unfortunately, we do not have any quantitative measures of this potential flux at HBEF. Because there are limited wetlands or boggy areas within the south-facing, experimental watersheds at HBEF, we believe the loss of S by this pathway is quite small relative to other inputs and outputs for the watershed-ecosystem.

Biotic flux

Burton and Likens (1975) reported that the standing crop of S was 0.076 mol/ha in salamanders and 0.123 mol/ha in birds (no data are available for mammals) at HBEF during the early 1970s. These values are very small compared with S pools in vegetation and soils (Figure 23). Sturges et al. (1974) estimated that the maxi-

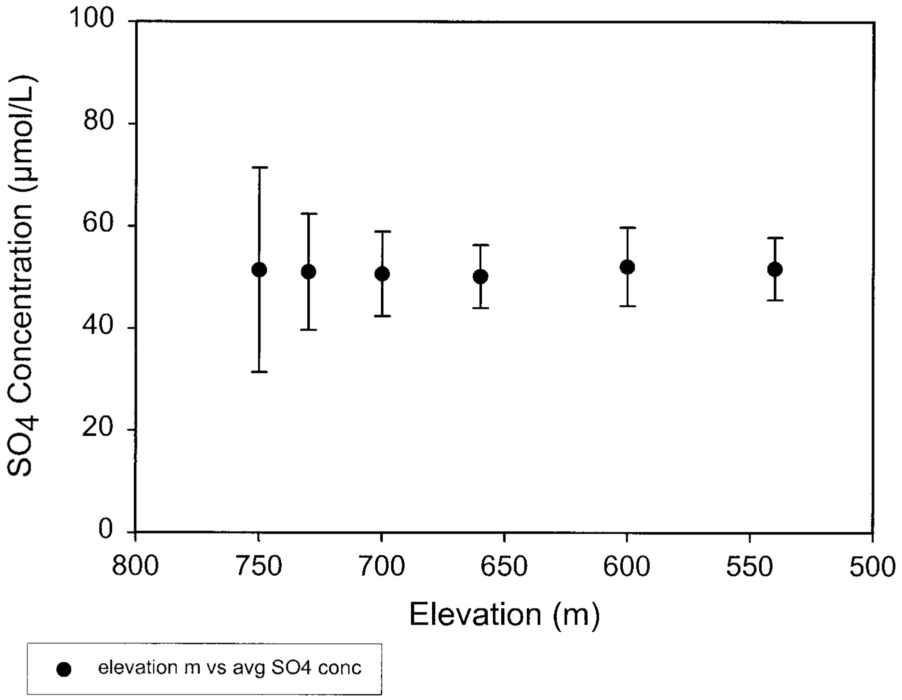

Figure 22. Mean concentrations of SO_4^{2-} and standard deviations in stream water along an elevational gradient in W6 of the HBEF.

mum net loss of S from watershed-ecosystems via birds during 1969 and 1970 was 0.056 mol/ha-yr as compared to a net streamwater loss of 109 mol/ha-yr and 0.94 mol/ha-yr in dissolved and particulate S, respectively, during this rather average hydrologic period (Figure 3). The bird population during this period was relatively large (see Holmes and Sherry (2001)). Thus, the transport of S across watershed-ecosystem boundaries at HBEF by animals is probably very small (e.g. Sturges et al. (1974)).

General discussion

The biogeochemistry of forest watershed-ecosystems has been a central theme of the Hubbard Brook Ecosystem Study since its inception in 1963. The utility of the watershed-ecosystem approach for constructing quantitative, mass-balance analyses for chemical elements has been described elsewhere (e.g. Bormann and Likens (1967, 1979) and Schindler (1980), Likens (1992, 1985), Likens et al. (1994), Likens and Bormann (1995)). The relatively water-tight nature of the bedrock in these watershed-ecosystems, limiting deep seepage (Likens and Bormann 1995), make

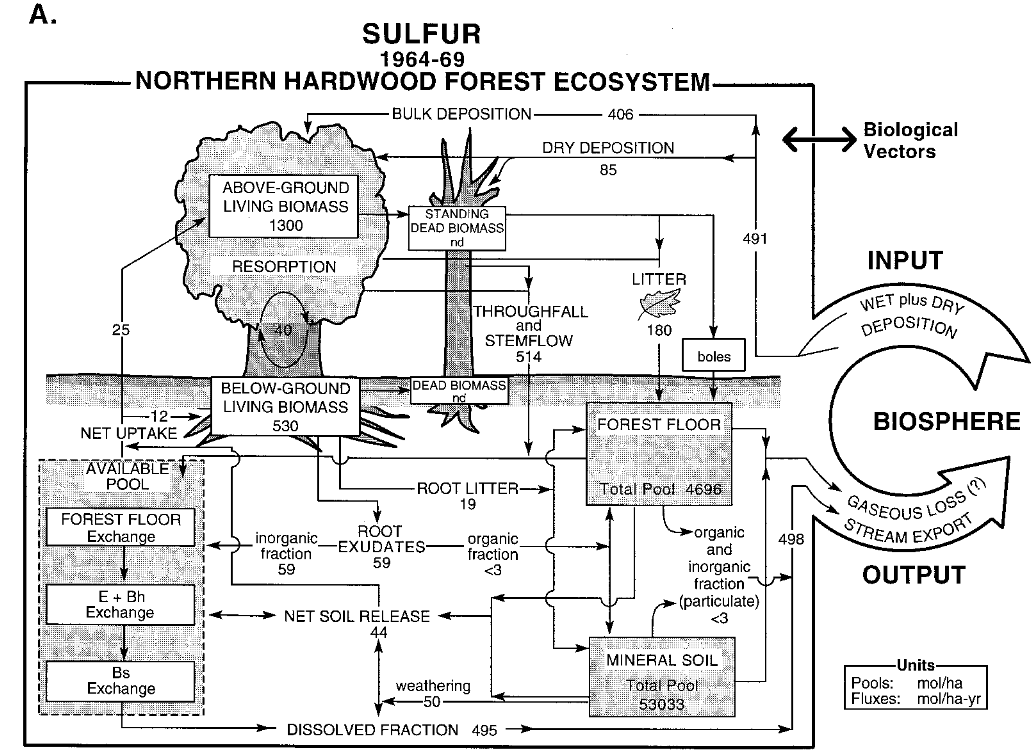

Figure 23. Ecosystem pools (boxes) and fluxes (arrows) of S for W6 at HBEF. Average values in mol/ha or mol/ha-yr for periods specified. Values for 1964–1969 are shown in [**A**] values from Likens and Bormann (1995), except for bulk deposition, dissolved fraction output, soil pools and net soil release; while [**B**] shows values for 1993–1998; above- plus belowground biomass is for 1997; root and aboveground litter, and root exudates assumed to be same as in 1964–1969; net uptake values based on difference in biomass storage between 1982 and 1998; Forest floor pools and total mineral soil pool for both periods from Zhang et al. (1999) as estimated for W5 in 1983.

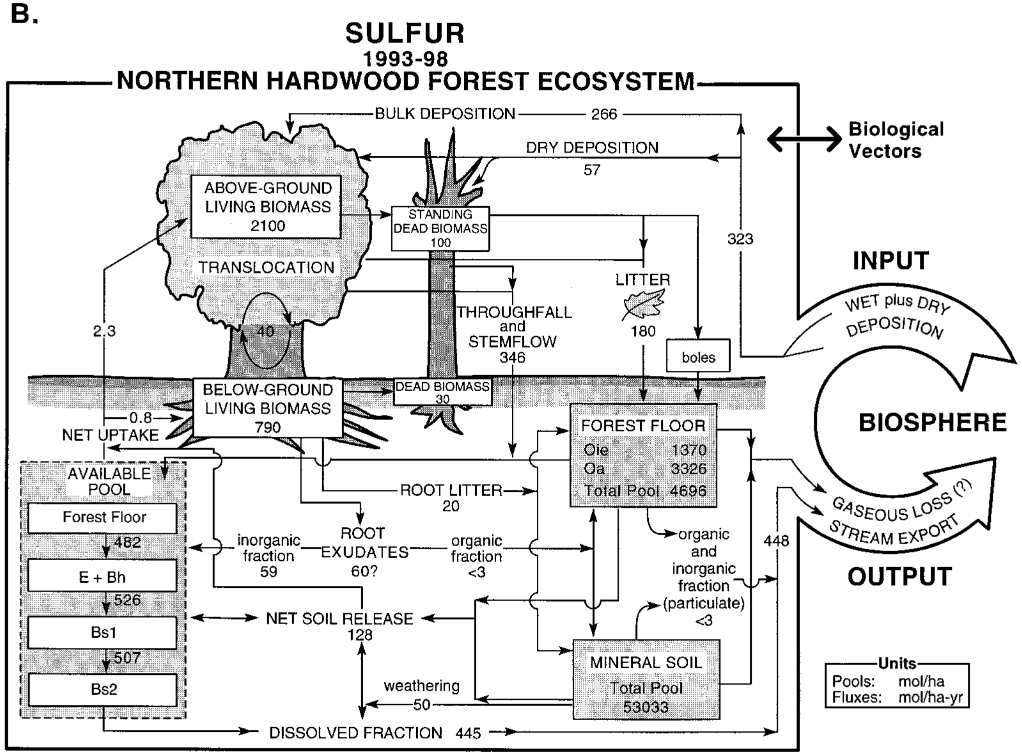

Figure 23. Continued.

such attempts particularly meaningful at HBEF. Watersheds also integrate heterogeneity in ecosystem processes across landscape scales.

Biocycling

In an attempt to summarize and integrate the diverse information from this study, we compare all known fluxes and pools of S at HBEF during two five-year periods (pentads) at the beginning and at the end of the study period (Figure 23). Biomass and soil pools of S are large relative to atmospheric inputs and streamwater losses (Figure 23). Currently most (94.6%) of the S in the forest ecosystem is associated with the soil, with 5.4% bound in living and dead biomass (Figure 23B). Current inputs to the available nutrient compartment are dominated by atmospheric sources and are partitioned as follows: atmospheric bulk deposition (50%), net soil release (24%), dry deposition (11%), root exudates (11%) and canopy leaching (4%) (Figure 23B).

During 1993–1998, we estimate the gross uptake of S in trees to be approximately 286 mol/ha-yr, based on estimates of root exudation (60 mol/ha-yr; Smith (1976) and Likens and Bormann (1995)), root litter (20; Likens and Bormann (1995)), aboveground litterfall (180), canopy leaching (23), and net biomass accrual (3) (Figure 23B). In comparison, gross uptake of S (excluding root exudation and turnover) in 11 eastern U.S. forests ranged from 22–499 mol S/ha-yr, with a mean of 203 mol S/ha-yr (Johnson and Lindberg 1992). Of the annual gross uptake by vegetation at HBEF, only about 1% is stored while the other 99% is returned to the soil. Gross uptake (318 mol/ha-yr) during 1964–1969 was ∼11% greater than in 1993–1998, and net biomass storage represented about 12% of gross uptake of S.

The gross uptake of S provides a measure of the importance of vegetation to the S cycle. Approximately 1.6 times more S was lost from the watershed-ecosystem in stream water each year than was cycled through trees in 1964–1969. In 1993–1998, annual streamwater loss of S exceeded annual gross tree uptake by about 160 mol S/ha. Annual net uptake of S by forest vegetation decreased by more than an order of magnitude from 1964–1969 to 1993–1998 (Figure 23). Thus, total annual streamwater output was >13× greater than net biomass accretion in 1964–1969, and 145× greater in 1993–1998. Also, the gross uptake represented about 0.5% of the entire S pool in the soil (53,033 mol S/ha).

Turnover

Laboratory studies of soils from HBEF, including the use of radioactive ^{35}S, have shown that both S mineralization and immobilization rates are rapid (Fuller et al. 1986a; Schindler et al. 1986; Schindler and Mitchell 1987). However, a substantial portion of this organic S, especially a large percentage of the carbon-bonded S in soil, is fairly recalcitrant and thus only a relatively small portion of the total organic S pool turns over relatively quickly.

In natural ecosystems, differences in the relative abundance of stable S isotopes can be used to draw inferences about sources as well as about biological turnover

Table 10. Content and inputs to forest floor, residence time (yr) and fractional annual loss of S in W6 in the mid 1990s

Forest floor content (mol S/ha)[a]	Litter (mol S/ha)[b]	Bulk deposition (mol S/ha)[c]	Net stemflow + throughfall (molS/ha)[d]	Residence time, T_n (yr)	Annual fractional Loss
4696	191	266	80	8.7	0.11

[a] Zhang et al. (1999)

[b] Gosz et al. (1976) for aboveground; 60% of root litter for belowground

[c] This paper

[d] T_n = forest floor content/litter + bulk deposition + net stemflow and throughfall

of S. Zhang et al. (1998) determined that bulk deposition $\delta^{34}S$ values were higher in the dormant season ($\delta^{34}S = 5.9 \pm 0.6‰$) than in the growing season ($\delta^{34}S = 5.0 \pm 0.6‰$), but throughfall growing-season values were higher $\delta^{34}S = 5.6 \pm 0.6‰$) than for the dormant season ($\delta^{34}S = 4.9 \pm 0.7‰$) at HBEF. In soil solution, $\delta^{34}S$ values were higher in the growing season than in the dormant season in the forest floor as well as the B-horizons of the soil. These seasonal differences in various compartments at HBEF point to the importance of biological turnover. Although results from stable isotopes cannot be used to draw quantitative conclusions about turnover rates the dynamics of stable S isotopes indicate that an important part of the atmospherically deposited SO_4^{2-} cycles through the biomass.

Using the approach of Gosz et al. (1976) we calculated the average residence time (yr) or Turnover (T_N) for HBEF soils during the mid 1990s. Residence time for S in the soil was about 9 yr with an annual fractional loss of 0.11 (Table 10).

Budgetary considerations – watershed mass balances

Net Hydrologic Flux (NHF)

Despite recent declines in concentrations, SO_4^{2-} has been the dominant anion in both bulk deposition and stream water at HBEF since measurements began in 1964 (Likens and Bormann 1995). Concentrations of SO_4^{2-} in bulk deposition have decreased from an average of 31.5 μmol/liter (input of 406 mol/ha-yr) during 1964–1969, to 18.3 μmol/liter (input of 266 mol/ha-yr) during 1993–1998 (Figure 23). Likewise, average streamwater concentrations of SO_4^{2-} have decreased from 62.8 μmol/liter (output of 495 mol/ha-yr) in 1964–1969, to 46.0 μmol/liter (output of 445 mol/ha-yr) in 1993–1998 (Figure 23). Sulfate represented 71% and 53% of bulk deposition anions in 1964–1965 and 1997–1998, respectively, and 80% and 87% of streamwater anions in 1964–1965 and 1997–1998, respectively. During the full period, 1964–1965 to 1997–1998, streamwater outputs of SO_4^{2-} for W6 averaged 496 ± 112 SD mol/ha-yr (Table 9), whereas bulk deposition inputs averaged 336 ± 78 SD mol/ha-yr (Table 3).

Annual atmospheric inputs and streamwater outputs for all of the south-facing watershed-ecosystems at HBEF are given in Tables 3 and 9. Annual streamwater outputs of SO_4^{2-} typically exceed atmospheric inputs throughout the year (Figure 3B). During the drought year 1964–1965, however, the watershed-ecosystem gained slightly more SO_4^{2-} via bulk deposition than was lost in stream water (Figure 20, Table 11). Then, during the next 4 years the watershed-ecosystem lost progressively more SO_4^{2-} in stream water each year than was gained from bulk atmospheric deposition (Figure 20). Since about 1971–1972, this net NHF has been variable, but averaged 174.8 ± 72.8 (SD) mol/ha-yr (Figure 20, Table 11). These changing relations in NHF clearly are linearly related to amount of annual streamflow (Figure 19C), which varies annually but shows no long-term trend (e.g. Figure 3C). Based upon a one-way ANOVA, the average NHF of SO_4^{2-} for W1 and W3 were not significantly different ($p = 0.092$), but the average NHF for W6 was slightly, but significantly less ($p < 0.001$) than for W1 and W3 (Table 11) during 1971–1972 to 1997–1998.

Although variable on an annual basis, there is a strong relationship between both concentration and flux of SO_4^{2-} in stream water vs. bulk deposition (Figures 23 and 25). The statistically significant long-term decrease in annual streamwater output with time is highly variable (Figure 3B) and is dependent on amount of streamflow (Figure19B). During 1964–1965 to 1972–1973, streamwater S output generally increased, then declined until 1980 or so following the pattern for annual streamflow (Figure3). Streamwater outputs were smallest during the drought year of 1964–1965 and largest during the four wettest years of 1973–1974, 1975–1976, 1990–1991 and 1995–1996. In contrast, decreases in streamwater SO_4^{2-} concentrations were much more regular (Figure 3A). As a result, much less of the annual variability in streamwater outputs was explained by bulk deposition inputs than was the case for concentration (Figures 24 and 25).

The largest bulk deposition input (562 mol S/ha-yr) and largest streamwater output (848 mol S/ha-yr) of SO_4^{2-} occurred in 1973–1974, the wettest year during the study (Figure 3, Tables 3 and 9). In contrast, 1995–1996 the second wettest year on record with precipitation and streamwater values approximately equal to 1973–1974 (Figure 3), had a relatively low bulk deposition input (284 mol S/ha-yr; 23rd largest out of 34 yr) and a relatively high streamwater output (620 mol S/ha-yr; 4th largest out of 34 yr), resulting in the largest negative NHF on record (−336 mol S/ha-yr) (Figure 20, Table 11). The lowest bulk deposition input occurred in 1997–1998 (211 mol S/ha-yr) and the lowest streamwater output occurred in 1964–1965 (309 mol S/ha-yr) (Tables 3 and 9). The 1983–1984 year was characterized by several large, relatively clean storms originating from the east (marine source) and a summer drought, when SO_4^{2-} concentrations usually peak (Figure 6A), producing an unusually low input of 215 mol S/ha-yr (Table 3, Figure 26, Likens et al. (1990b)).

The strong relation to hydrology is clear. In general, the more precipitation, the greater the bulk deposition input (Figure 7B); the more streamflow, the greater the streamwater output (Figure 19B); and the more streamflow the greater the NHF (Figure 19C) of SO_4^{2-} at HBEF.

Bulk deposition inputs of SO_4^{2-} averaged about 65% of streamwater outputs during the period, but were an appreciably larger percentage during the early part

Table 11. Net hydrologic flux (NHF) of sulfate from HBEF south-facing watersheds

Water – Year	W1	W2	W3	W4	W5	W6	Mean[a]	±sd
1964–1965	NA	−34	NA	NA	NA	7	NA	NA
1965–1966	NA	−141	NA	−72	NA	−46	NA	NA
1966–1967	NA	−64	NA	−132	NA	−97	NA	NA
1967–1968	NA	−21	NA	−154	NA	−128	NA	NA
1968–1969	NA	−191	NA	−233	NA	−182	NA	NA
1969–1970	NA	−206	NA	−195	NA	−163	NA	NA
1970–1971	−119	−275	NA	−131	NA	−114	NA	NA
1971–1972	−161	−355	−116	−121	−72	−125	−137	19
1972–1973	−304	−466	−294	−244	−229	−242	−282	27
1973–1974	−363	−539	−349	−345	−296	−287	−333	33
1974–1975	−161	−281	−149	−182	−125	−136	−149	10
1975–1976	−409	−502	−409	−419	−330	−311	−381	46
1976–1977	−186	−288	−182	−238	−159	−142	−171	20
1977–1978	−227	−260	−172	−218	−157	−159	−189	30
1978–1979	−173	−183	−150	−148	−127	−129	−152	18
1979–1980	−166	−184	−140	−142	−131	−116	−141	20
1980–1981	−178	−181	−146	−160	−124	−121	−149	23
1981–1982	−332	−346	−298	−306	−236	−222	−284	46
1982–1983	−200	−177	−170	−161	−130	−135	−168	27
1983–1984	−378	−354	−347	−356	−294	−311	−344	28
1984–1985	−109	−88	−92	−92	−27	−70	−89	16
1985–1986	−253	−232	−227	−239	−135	−215	−230	16
1986–1987	−168	−177	−185	−166	−127	−150	−166	14
1987–1988	−146	−140	−143	−160	−150	−128	−139	8
1988–1989	−110	−121	−111	−120	−145	−107	−109	2
1989–1990	−226	−277	−248	−255	−296	−206	−226	17
1990–1991	−213	−250	−230	−218	−246	−198	−212	13
1991–1992	−168	−197	−180	−184	−208	−161	−168	8
1992–1993	−163	−178	−177	−185	−178	−154	−164	10
1993–1994	−120	−139	−148	−165	−160	−138	−134	11
1994–1995	−72	−62	−66	−69	−92	−70	−69	3
1995–1996	−372	−396	−348	−375	−412	−336	−351	15
1996–1997	−235	−235	−221	−219	−282	−228	−226	6
1997–1998	−113	−116	−115	−103	−136	−122	−116	4
Cumulative total (mol/ha)	−5824	−7655	−5410	−6508	−5005	−5441	−5279	
Annual mean (mol/ha-yr)	−208	−225	−200	−197	−185	−160	−196	
±sd	90	125	87	85	87	75	82	

Underlined = Values from years during experimental treatments.

[a] Mean and ±sd for W1, W3, and W6 only from data after 1970–1971

of the study (1964–1967) (Figure 27). Large excursions in this relation occurred in

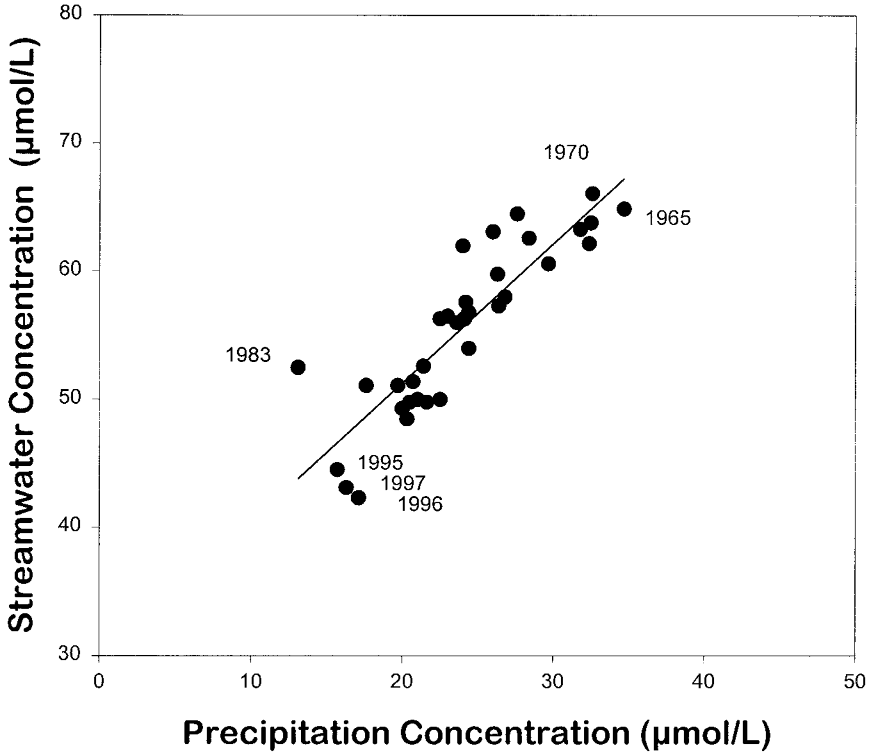

Figure 24. Relation between streamwater and bulk precipitation concentration for W6 of the HBEF during 1964–1998. ($p < 0.001$; slope = 1.09; $r^2 = 0.77$).

1964–1965, the drought year, 1983–1984 an unusually low input year (discussed above) and 1995–1996, a very wet year (Figure 27). Although changes in the ratio between bulk deposition inputs and streamwater outputs during 1983–1985 were large, they still tended to oscillate around the mean rather than initiate some new trend.

Overall, streamwater outputs of SO_4^{2-} have tended to increase relative to bulk deposition inputs since 1964 (Figure 27) suggesting a net discharge/release of accumulated SO_4^{2-} from the ecosystem. Interestingly, this rate of "discharge" was highest during the early part of the study (1964–1969).

During 1964–1965 to 1997–1998, a total input of 11,435 mol/ha in bulk deposition and an output of 16,876 mol/ha in stream water occurred, giving a NHF of −5441 mol/ha of SO_4^{2-} at HBEF (Tables 3, 9 and 11). Adding dry deposition input at 71 mol/ha-yr (11,435 × 0.21/34), still leaves a net loss of 3040 mol/ha for the period. The long-term mean bulk deposition input of SO_4^{2-} was 336 mol/ha-yr and the long-term, mean dissolved streamwater output was 496 mol/ha-yr giving a NHF during the 34 yrs of −160.0 ± 75.3 SD mol/ha-yr (Table 11) (−89 if dry deposition inputs are included).

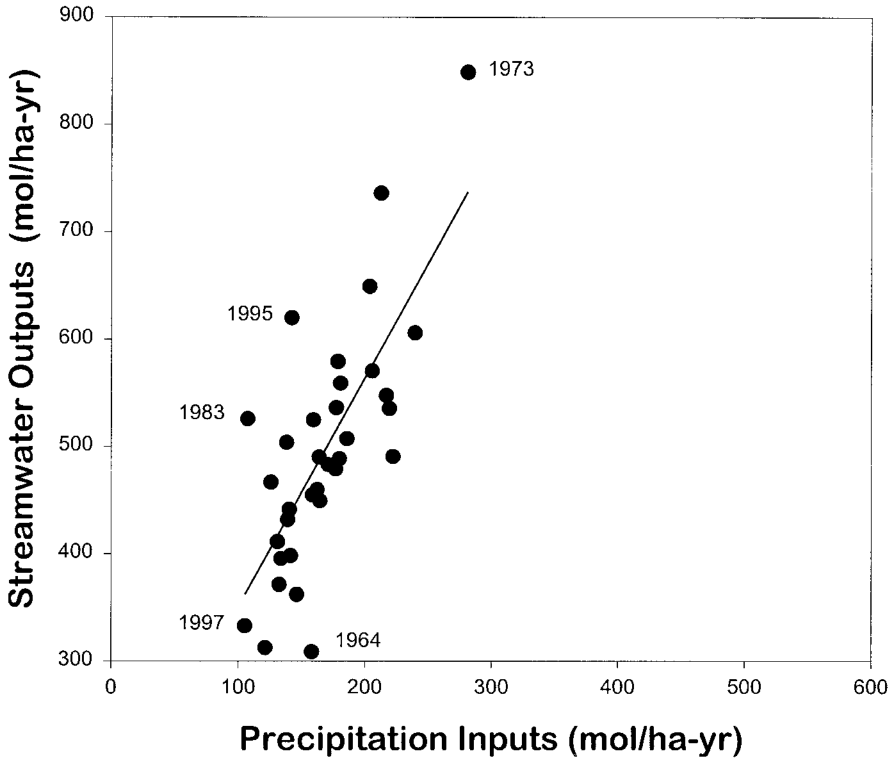

Figure 25. Relation between streamwater outputs and bulk precipitation inputs for W6 of the HBEF during 1964–1998. ($p < 0.001$; slope = 2.14; $r^2 = 0.55$).

As mentioned above, the HBEF is not unique in having an imbalance in the NHF of S. Many watersheds show this same pattern (e.g. Driscoll et al. (1998a) and Mitchell et al. (2001)) indicating that the processes controlling it may be a general feature of the S cycle in these watershed-ecosystems.

Net Ecosystem Flux (NEF)

In an attempt to summarize the long-term NEF for HBEF, all sources and sinks of SO_4^{2-} were apportioned (Figure 28) from 1964 to the present. Sulfate release from weathering was assumed to be constant throughout the period at a value of 50 mol/ha-yr (see section on *Supply of S from weathering release and sulfate desorption*). The rate of storage of S in biomass from 1964 to 1970 was assumed to be a constant accumulation (37.0 mol S/ha-yr; Likens and Bormann (1995)). The net increase in biomass accumulation between 1970 and 1981 was estimated from a straight line fitted to data from 1970–1982, and biomass storage during 1981 to 1998 was taken as 3.0 mol S/ha-yr. For bulk deposition inputs, we used measured values. Bulk deposition samplers underestimate the dry portion of total atmospheric deposition (e.g. Lovett (1994)), but no quantitative, temporal data on dry deposition are available to enable us to estimate values throughout the period 1964 to

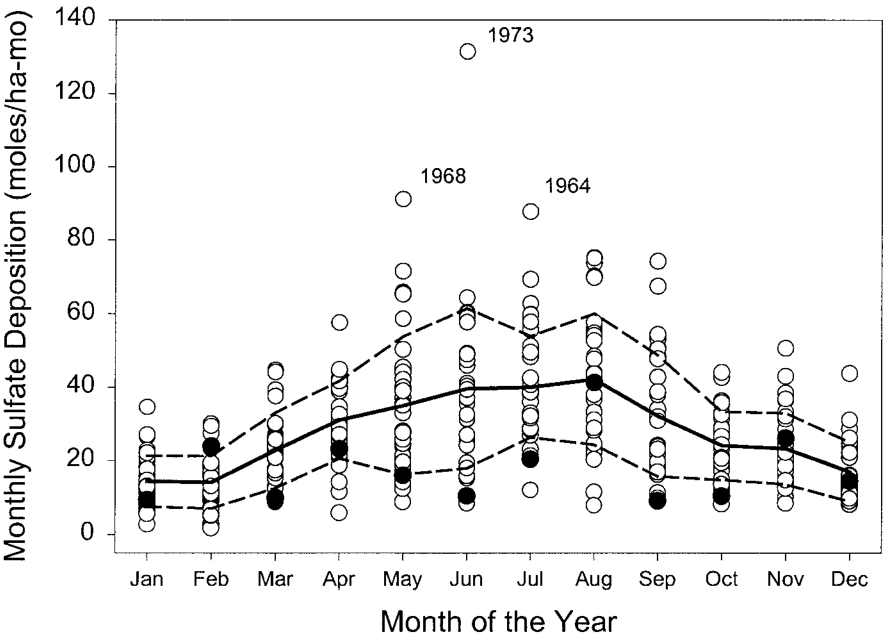

Figure 26. Atmospheric SO_4^{2-} input: individual monthly bulk deposition values during 1964–1998 (○): many values overlap; average monthly deposition (—) ±SD (- - -) during the 36 months of 1964–1998, and monthly deposition values during the 1983–1984 water-year (●).

1998. Thus, we calculated dry deposition as 21% of bulk deposition values for this period. For streamwater SO_4^{2-} output we used measured values.

Based on these values, NEF varied between +86.8 mol S/ha-yr in 1964–1965, a drought year, and −229.5 mol S/ha-yr in 1995–1996, and averaged −54.3 ± 72.9 (SD for the year-to-year variability) during 1964–1965 to 1997–1998 at HBEF (Figure 28). [**Note**: the large negative NEF value in 1983–1984 (−219.1 mol S/ha-yr) was driven by relatively small atmospheric inputs and in 1995–1996, a wet year (−229.5 mol S/ha-yr) by a relatively large streamwater output (Figure 28).]

Annual NEF values for SO_4^{2-} were significantly ($p < 0.001$) related to annual streamflow ($r^2 = 0.70$), annual outputs of dissolved silica ($r^2 = 0.57$) H^+ ($r^2 = 0.55$) and Na^+ ($r^2 = 0.49$) and other base cations. The more negative the NEF, the larger the values for streamflow, dissolved silica, etc. Annual NEF of SO_4^{2-} was not correlated with annual streamwater outputs of NH_4 $^+$ or NO_3^- during 1964–1965 to 1997–1998. The positive annual NEF of SO_4^{2-} during 1964–1965 to 1967–1968 may reflect a period of net adsorption of SO_4^{2-} or net retention of S in soil organic matter or in accumulating forest biomass during and following the severe drought of 1963–1965 (Likens and Bormann (1995); Figure 3C. The potential sources and variability regarding loss and gain in these annual, mass balances and their overall unbalanced nature are discussed below.

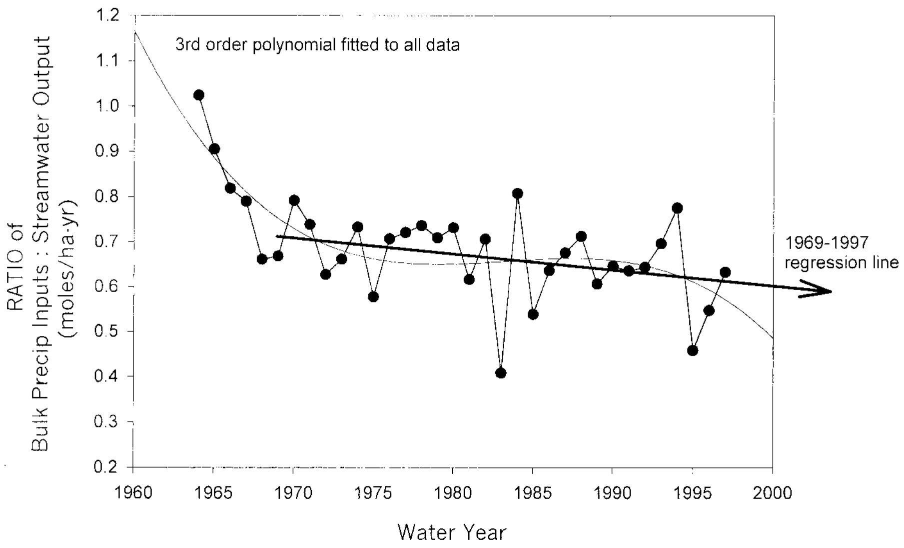

Figure 27. Ratio of bulk deposition inputs to streamwater outputs of SO_4^{2-} during 1964–1998 for W6 of the HBEF. The third-order polynomial regression is statistically significant ($r^2 = 0.45$). The 1969–1998 regression line has a slope of –0.0035 ($r^2 = 0.10$; $p < 0.087$).

Net loss hypotheses for the unbalanced, mass balance (NEF)
Although the average NHF was large and negative (–160 mol S/ha-yr) during 1964–1965 to 1997–1998, the average imbalance in the NEF was much smaller (–54.3 mol S/ha-yr). This difference in average flux calculation between NFH and NEF illustrates clearly the value of the ecosystem approach in evaluating this complex issue for watershed-ecosystems. The NEF has been negative during most years since 1968. It averaged –76.0 ± 101.5 SD (range + 27.7 to –229.5) mol S/ha-yr during the most recent pentad, 1993–1998 (Figure 28). For this most recent pentad, the difference between the NHF (–178.9 mol S/ha-yr) and the NEF (–76.0 mol S/ha-yr) can be accounted for by our estimates of weathering release (+50 mol S/ha-yr), dry deposition (+56) and net biomass storage (–3).

Although valuable, it would be very difficult to do a formal analysis of the errors associated with the NEF value using the data available. We give a standard deviation (SD) and range for mean NEF-values presented, which provide a measure of the variation in annual values, but do not reflect the errors associated with the calculation of a given annual NEF value. In an attempt to make the potential for error accumulation in the calculation of NEF more transparent, we provide the following evaluation of each component. Admittedly and unfortunately, this analysis is only semi-quantitative.

The uncertainty for amount of annual precipitation and streamflow, measured by gauges at HBEF, is estimated at 5% or less (Winter 1981) and analytical precision for SO_4^{2-} in these solutions is ~ 5% (Buso et al. 2000). Thus, uncertainties for bulk deposition and streamwater fluxes of SO_4^{2-} are taken as ± 5% of the annual measured value. Dry deposition is assumed to have an uncertainty of ± a factor of 2, or

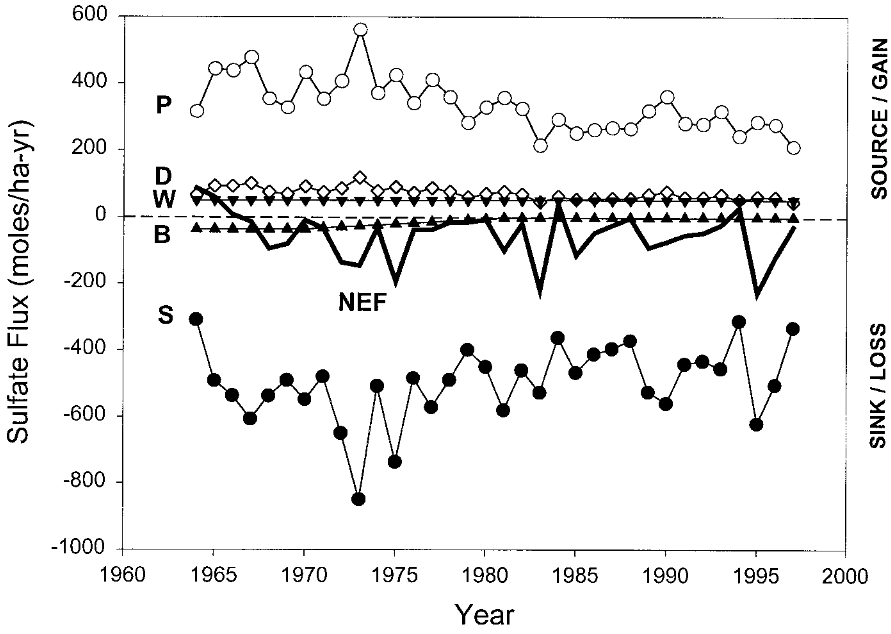

Figure 28. Annual fluxes of S for W6 of the HBEF during 1964–1998. P (○) is bulk deposition input, W (▼) is weathering release, S (●) is streamwater loss, B (▲) is net biomass storage and D (◇) is dry deposition and NEF (—) is net ecosystem flux obtained by difference.

from 30 to 120 mol S/ha-yr. Net biomass storage is assumed to have an uncertainty range of 0 to 30 mol S/ha-yr for the entire period, 1964 to 1998 (0 to 74 mol S/ha-yr during 1964–1982 and 0 to 6 mol S/ha-yr during 1983 to 1998). We assume a range from 20 to 50 mol S/ha-yr for weathering release.

Using these values and assumptions, we can calculate minimum and maximum NEF values: for the 34-yr average NEF value (−54.3) the uncertainty might range from −28 to −102 mol S/ha-yr; for the 1964–1969 pentad, the average NEF value (+9.3) might have an uncertainty range of +3 to −35 mol S/ha-yr; and for the 1993–1998 pentad, the average NEF value (−76.0) the uncertainty might range from −23.8 to −119.9 mol S/ha-yr.

There are four hypotheses that might account for the observed average NEF of −54.3 mol S/ha-yr during 1964–1965 to 1997–1998 (Figure 28) from these watershed-ecosystems: underestimates of (1) dry deposition, (2) SO_4^{2-} desorption from soil pools, (3) additional S weathering release, and (4) net mineralization of organic S. Several observations about the net S loss can be used to help distinguish among these possibilities. First, we know that the NEF of S is consistent across watersheds at HBEF. Second, we know that there is no consistent temporal trend in the NEF since 1969 or so at HBEF (Figure 20) – in contrast to the record of bulk deposition, which shows a significant decrease since 1964–1965 (Figure 3). Third, we know that the NEF is proportional to streamflow. Fourth, we know that the ^{34}S ratio is lower in streams than in bulk deposition, and that it is remarkably stable

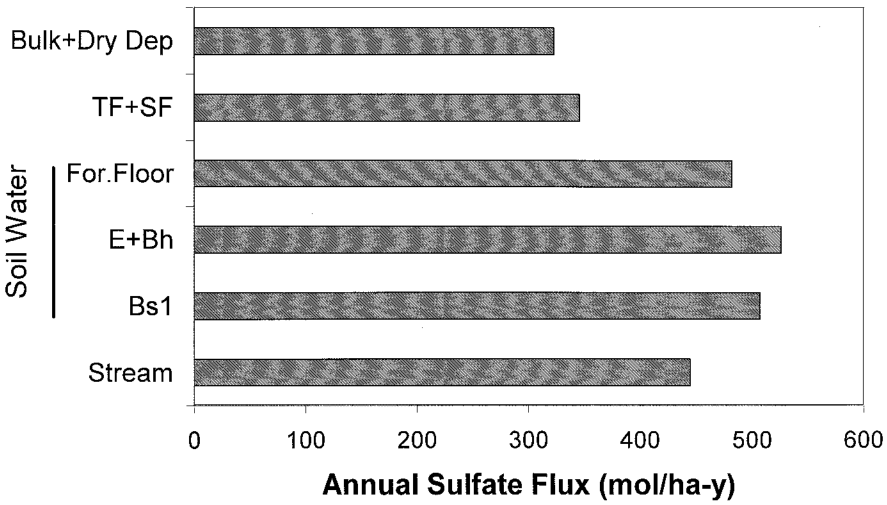

Figure 29. Annual flux of S in solutions passing through the ecosystems of the HBEF during 1993–1998.

over time (Figure 13). Fifth, we have independent estimates, although admittedly crude, for dry deposition, desorption, and weathering release. Lastly, we know that most of the increase in S flux for the watershed-ecosystem arises as soil water passes through the forest floor (Figure 29).

Our ecosystem data are well within range of similar data available to us for other forests (Table 12). Unfortunately, these data are not adequate for a full NEF analysis as we have done at HBEF.

We evaluated the consistency of each of these observations with the proposed hypotheses for the source of the negative NEF (Table 13). The dry deposition hypothesis is consistent with a uniform signal across watersheds, but we would expect to see decreases over time in dry deposition as a result of reductions in SO_2 emissions. If, (1) unaccounted dry deposition inputs were the principal cause of the NEF imbalance, (2) if dry deposition inputs were declining with time and (3) if the underestimate were a constant proportion of the dry deposition input, then the NEF would decline with time. It did not (Figure 28). In addition, the ^{34}S isotope ratios in stream water are lower than those in atmospheric deposition, indicating some microbial processing of S within terrestrial and/or aquatic ecosystems. This result suggests at least that any dry deposition that ends up at the weir in stream water did not pass conservatively through the watershed, but rather was adsorbed/desorbed and/or cycled through biota en route. Thus, some of the additional input of S could be due to an underestimate of dry S deposition, occurring directly to the forest floor.

We may have underestimated the dry deposition of S, because dry deposition fluxes are notoriously difficult to measure. The models used for inferential estimates are difficult to test and are theoretically inappropriate for complex terrain like HBEF. On the other hand, our inferential and throughfall estimates of dry deposi-

Table 12. Sulfur budget data for various forests throughout the world (data from Johnson and Mitchell (1998)

	Forest floor (mol S/ha)	Mineral soil (mol S/ha)	Vegetation (mol S/ha)	S deposition bulk (mol S/ha)	TF+SF (mol S/ha)
Solling (Spruce), Germany	4586	45328	2995	NA	1912
Solling (Beech; American beech), Germany	3806	28544	1497	NA	761
ORNL (Tower; red spruce), TN	7830	38752	5010	1107	1036
ORNL (Becking), TN	7393	30438	5035	NA	805
ORNL (loblolly pine), TN	NA	34762	2873	471	387
ORNL (American Beech), TN	752	42458	2957	NA	386
Walker Branch (Oak), TN	1373	47917	1329	799	814
Hubbard Brook (northern hardwoods)*	4700	53033	2890	266	346
Whiteface Mt. (conifers), NY	NA	33941	2998	549	518
Duke Forest (loblolly pine), NC	1644	56309	1494	527	586
Turkey Lakes (northern hardwoods), Ontario	2808	34191	1482	381	387
Nordmoen (Norway spruce), Norway	2561	NA	1157	331	296
COWEETA (southern hardwoods), NC	764	44423	3703	NA	278
COWEETA (White Pine), NC	624	22461	4461	268	262
Huntington Forest (northern hardwoods), NY	2187	36780	1616	243	271
Findley Lake (fir hemlock), WA	1828	43737	3123	NA	221
Thompson Forest (red alder), WA	4630	20777	2096	162	90.5
Thompson Forest (Douglas Fir), WA	1173	20527	1132	159	115
Bago, NSW (Douglas Fir), Australia	842	24957	1965	NA	28.1

* 1994–1998, this paper. NA = not available.

Table 13. Evaluation of whether the observations of the behavior of net ecosystem flux (NEF) of S are consistent (C) or inconsistent (I) with four hypotheses to explain the observed unbalanced, mass balance at HBEF. NA = not applicable

Observation	Hypotheses Additional dry deposition	S desportion	Additional weathering release	S net mineralization
Consistent loss across watersheds	C	C	I?	C
No consistent temporal trend	I?	C?	C	C?
Loss proportional to streamflow	?	C	C	C?
Low ^{34}S ratio in stream	NA	NA	C?	C
Independent estimates	I	I	I	None
Fluxes of SO_4 in throughfall, soil water and stream water	C?	I	I	C

tion are more or less consistent with one another. For the 1993–1998 pentad, our best estimate of the dry deposition flux (57 mol S/ha-yr) would need to be more than doubled if all of the NEF imbalance during this pentad (−76 mol S/ha-yr) were assumed to be from dry deposition. Therefore, although the amount of dry deposition is very difficult to measure and could conceivably account for the imbalance in the NEF, our best estimates of dry deposition indicate that this is unlikely.

Desorption of SO_4^{2-} from the mineral soil could occur as a result of declining inputs of SO_4^{2-} in atmospheric deposition, if SO_4^{2-} adsorption had been enhanced during earlier, higher deposition periods. This mechanism would give a consistent signal across watersheds and may not produce an observable temporal trend. Loss of desorbed SO_4^{2-} would also be expected to be proportional to stream flow. Our model calculations (Driscoll et al. (1998a, 1998b); Gbondo-Tugbawa et al. 2001) of desorption of S given the decline in SO_4^{2-} concentrations in atmospheric deposition indicate that this mechanism could account for as much as 32 mol S/ha-yr during the 1993–1998 pentad. The observed decrease in the δ^{34}S value from bulk deposition to stream water is inconsistent with this mechanism, however, since adsorption does not result in fractionation of S isotopes.

Some of the most compelling information we have to test the hypothesis that net desorption of SO_4^{2-} contributes to the NEF pattern is derived from soil water and stream fluxes of SO_4^{2-} (Figure 23B, 29). Area-weighted soil water SO_4^{2-} fluxes were based on data collected from the three elevational zones. These fluxes suggested that there is relatively uniform transport of SO_4^{2-} through the mineral soil profile, from 482 ± 144 mol/ha-yr draining the forest floor to 507 ± 89 mol/ha-yr exported from the lower mineral soil. These fluxes of SO_4^{2-} are greater than bulk deposition inputs (323 mol/ha-yr), throughfall plus stemflow inputs (346 mol/ha-yr) and slightly greater than stream water exports from the watershed (448 mol/ha-yr). This pattern suggests there is an input of S that occurs above the mineral soil (Figure 29) that is larger than the discrepancy in the S mass balance. Because the adsorbed SO_4^{2-} pool (PSO_4) occurs mainly in the lower mineral soil (Figure 14, Table 2), the solution profile (Figure 29) is inconsistent with a large net source from SO_4^{2-} desorption.

Weathering release of S could potentially account for the net SO_4^{2-} loss from the watershed-ecosystems. Although we might expect high variability in streamwater loss of S among watersheds because of heterogeneous distribution of soils, rock fragments and bedrock with variable S concentrations within the HBEF, this is not the case (Tables 9 and 11). Unfortunately, we have only limited quantitative data on the S distribution in soils, rock fragments and bedrock within the HBEF. With weathering release as a major source of S, we would expect an increase in SO_4^{2-} flux through the soil profile and in stream water as S is released from S minerals in soil and glacial till. Moreover, we would anticipate an increase in SO_4^{2-} concentrations with decreases in elevation as drainage water contacts soil and surficial materials of increasing depth. Further, if we assume that there were an increasing proportion of deeper, older water contributing to streamflow with increasing size of the drainage area and that S inputs from weathering are more likely to occur deeper in the solum where minerals are less depleted, then it could be argued that relatively constant streamwater SO_4^{2-} concentration implies a relatively small contribution of weathering to the overall export of SO_4^{2-} from the watershed-ecosystem. The relatively uniform pattern of SO_4^{2-} transport through the soil profile and elevationally in stream water would seem to eliminate weathering release as the missing source of S (Figures 22 and 29).

We attempted to bound our weathering release estimates based on possible conditions in the absence of anthropogenic sulfur deposition. Using average hydrologic fluxes for HBEF, and solute concentrations from literature values for precipitation and streamwater chemistry in areas remote from human activity, we derived a range of probable annual S fluxes. Scenarios that resulted in stoichiometrically impossible ionic relationships or unreasonable NEF values were rejected. This “sensitivity analysis” suggested that the weathering release of S did not and should not exceed 50 mol/ha-yr for the HBEF during the last 200 yr or so.

Finally, net mineralization of S bound in soil organic matter could be the source of the net S loss. The large organic S pool potentially represents an important source or sink for SO_4^{2-} in forest soils (Swank et al. 1984; Strickland et al. 1984; Alewell et al. 1999). Constituents such as ester SO_4^{2-} in soil have shown small increases following experimental additions of SO_4^{2-} (David et al. 1990; Mitchell et al. 1989), but detecting changes under field conditions is very difficult because of the relatively large size of the pool and the heterogeneity of forest soils (Johnson and Mitchell 1998). A net mineralization of only about $< 0.2\%$ per year of the total organic S pool in the soil would easily account for the discrepancy in the S mass balance. Laboratory studies using HBEF soils have found rates exceeding this value

(Fuller et al. 1986a; Schindler et al. 1986), but it is very difficult to extrapolate these laboratory results to natural field conditions (Alewell et al. 1999).

Net mineralization of S could occur without net loss of organic C if the C:S ratio were lower in soil organic matter being mineralized than in soil organic matter being formed currently. Given the decline in S bulk deposition to the ecosystem, recent increases in the C_{org}:S_{org} ratio of soil organic matter are likely. This hypothesis is consistent with a similar signal across watersheds, and may be consistent with the lack of a temporal trend in the net loss. It is also consistent with the reduced ^{34}S ratios in stream water, which indicate that the S being exported has been cycled through the biota (Alewell et al. 1999). At this time, we have no independent measures of net mineralization of organic S, and particularly how this rate may have changed with time. The increased flux of S in soil water from the forest floor (Figure 29) would seem to be consistent with organic S mineralization, but inconsistent with weathering and sulfate desorption. It could be consistent with dry deposition directly to the forest floor.

Our model calculations (Gbondo-Tugbawa et al. 2001) of net mineralization of soil organic S, given declines in atmospheric deposition of S, indicate that this process could contribute some 69 mol S/ha-yr during the 1993–1998 pentad.

It is possible that several or all of the mechanisms discussed above contribute to the small, but ecologically significant net loss of S from the watershed-ecosystem. As atmospheric deposition of S has decreased in recent years, it appears likely that net desorption of SO_4^{2-} from soil and net mineralization of soil organic S contributes to the observed NEF imbalance. If our model estimates of SO_4^{2-} desorption are correct, then desorption can explain 32 of the 79 mol S/ha-yr of NEF imbalance for the most recent pentad. Based upon the summary in Table 13, net mineralization of organic S appears to be the most likely mechanism to explain the remaining 50 mol S/ha-yr net loss from W6. The behavior of net S mineralization is not inconsistent with any of the observations.

Sulfur biogeochemistry and acidic deposition

Deposition and effects of SO_4^{2-} in the forest ecosystem

Anthropogenic acid rain *per se* began about 1950–1955 in the northeastern U.S. (e.g. Cogbill and Likens (1974)), and this issue has been debated heatedly and extensively in North America since 1972 (Likens 1992). Federal regulations to control acid rain directly were initiated for the first time in the U.S. through the 1990 Amendments to the Clean Air Act (CAAA).

The volume-weighted annual pH of bulk precipitation at HBEF has varied from 4.05 to 4.3 during 1963–1998, with minimum values for individual storms as low as 2.85. The average pH of rain during May through September of 1964–1965 was 3.94, whereas during 1997–1998 it was 4.32.

Sulfate is the major component of acidic deposition in the eastern U.S., but other ions also are important. Nitric acid is a major contributor (Galloway and Likens 1981) and has been increasing in importance at HBEF since 1964 (Figure 8A). Also, atmospheric inputs of base cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) are important components of the overall acid rain impact by contributing significantly to the acid/base status of the soil (Likens et al. (1996, 1998)).

Although SO_4^{2-} is the dominant anion in both bulk deposition and throughfall, the cations which balance it change markedly as the water passes through the forest canopy. The H^+ and NH_4^+, which are associated with atmospheric SO_4^{2-}, are partially retained in the canopy, primarily through an exchange reaction on canopy surfaces and in the leaf apoplasm (Eaton et al. 1973; Lovett and Hubbell 1991; Lovett et al. 1996). This cation exchange strips Ca^{2+}, Mg^{2+} and K^+ from the canopy in amounts greater than in non-acidic precipitation (Wood and Bormann 1975; Lovett and Hubbell 1991; Lovett et al. 1996). The loss of foliar cations may have deleterious effects on some trees, for instance, red spruce, where Ca^{2+} depletion appears to be related to foliar susceptibility to freezing damage (DeHayes et al. 1999).

Decreased inputs of atmospheric Ca^{2+} and large atmospheric inputs of strong acids have markedly depleted labile pools of Ca^{2+} and other base cations from the soil at HBEF during the past 50 yr or so (Likens et al. (1996, 1998)). Sulfate, and to a lesser extent NO_3^-, are the major strong acid anions associated with the loss of these base cations from the ecosystem in stream water. It has been estimated that Ca^{2+} depletion from the exchangeable pools in the soil at HBEF was > 21,125 mol/ha, or a decline in the available Ca pool of ~50% during the last 50 years (Likens et al. (1996, 1998); Driscoll et al. 2001). As a result, the forest ecosystems at HBEF are much more sensitive to continuing inputs of acidic deposition than prior to this depletion (Likens et al. (1996, 1998)). Likewise, data from long-term experimental studies of forest plots in Sweden showed that additions of both sulfuric acid and sulfur acidified the soil and depleted it of Ca^{2+} and Mg^{2+} (Tamm and Popovic 1995). The depleted base cations were largely replaced aluminum.

Effects of recent decreases in S emissions

Realized effects of the 1990 CAAA did not occur until 1995 when Phase I of Title IV of the Act was implemented. At that time, U.S. emissions of SO_2 declined by about 40% of the overall reduction proposed by the 1990 CAAA. Emissions then increased somewhat during 1996 and 1997. Implementation of Phase II of the Act intends to cap national utility emissions of SO_2 at 8.1 Mg × 10^6/yr by 2010, a reduction of ~50% from 1980 values (Likens et al. 2001). These large changes in national SO_2 emissions have affected both the bulk deposition and streamwater chemistry at HBEF, but need to be placed in the context of changes that have occurred during the preceding 3 decades as well (Figure 3, Likens et al. (2001)).

Phase I of the 1990 CAAA continued the reduction in SO_2 emissions and bulk deposition concentrations of SO_4^{2-} at HBEF [because of the robust relation between annual SO_2 emissions and SO_4^{2-} concentrations (Figure 5)]. Nevertheless, the long-term data at HBEF (Figure 3A, B) indicate that decreases in SO_4^{2-} since 1990 were neither unusual nor large relative to the long-term trend beginning in 1964 (Likens et al. 2001). Moreover, these changes have not translated into significant decreases in acidification for many sensitive ecosystems in the northeastern U.S. (Driscoll et al. 2001).

The decline in bulk deposition of SO_4^{2-} at HBEF is related to decreases in SO_2 emissions ($r^2 = 0.57$) but annual variations in SO_4^{2-} deposition are also significantly related to amount of precipitation ($r^2 = 0.14$) and other factors, such as air-mass trajectory (Likens et al. 2001). Because of the strong relation between emissions of SO_2 and SO_4^{2-} concentrations in bulk deposition, it is expected that further reductions in SO_2 emissions will further decrease SO_4^{2-} concentrations in atmospheric deposition, thus alleviating the inputs and the impact of acid rain on sensitive ecosystems. Other factors, however, such as increasing importance of NO_3^- and changing base cation concentrations, are also critical to the overall trends and impacts of acid deposition.

Although there have been marked decreases in atmospheric deposition of S over the past 30 years in response to SO_2 emission controls following the 1970 and 1990 CAAAs, there has been little recovery of soil and surface waters in base-poor regions, such as the northeastern U.S. (Likens et al. 1996; Stoddard et al. 1999; Driscoll et al. 2001). Moreover, there is particular interest in assessing the response of these acid-sensitive forest ecosystems to future decreases in atmospheric deposition of S, in anticipation of additional emission controls beyond the 1990 CAAA. In this regard, the model PnET-BGC has been developed to simulate forest net primary productivity, element cycling and dynamics by vegetation and soil and water balances (Gbondo-Tugbawa et al. 2001). The PnET models have been used extensively at the HBEF to investigate the effects of disturbance (e.g. forest cutting, climatic disturbance, air pollution) on forest and aquatic resources. (Aber et al. 1997; Aber and Driscoll 1997; Gbondo-Tugbawa et al. 2001). Recently, Driscoll et al. (2001) used PnET-BGC to evaluate the response of W6 to potential changes in atmospheric deposition. In these calculations four scenarios of future conditions of SO_4^{2-} deposition were considered: (1) “business as usual,” which represents constant deposition onward from 1992 values, (2) S deposition following implementation of the 1990 CAAA, (3) S deposition following the 1990 CAAA with 40% cuts in utility SO_2 emissions in 2010 and (4) S deposition following the 1990 CAAA with 80% cuts in utility SO_2 emissions in 2010. These latter two scenarios represent the full range of emission reductions currently being considered in legislative bills proposed in the U.S. Congress. As utility sources are only a portion of the total SO_2 emissions for the U.S., these reductions (40 and 80%) would result in reductions of approximately 22 and 44% in total S deposition.

As anticipated, model calculations show that additional decreases in atmospheric S deposition will result in beneficial changes in water chemistry at the HBEF (Figure 30). The 1990 CAAA will result in modest improvements in stream water chemistry at the HBEF for the period 1994–2005. Specifically SO_4^{2-} will decrease by 7.6 μeq/liter, ANC will increase by 3 μeq/liter and pH will increase slightly by about 0.1 unit. Additional reductions in SO_2 emissions, such as those suggested in current legislative proposals, should accelerate recovery of soil and water chemistry. Model predictions indicate that a 22% decrease in atmospheric S deposition in 2010 beyond levels anticipated from the 1990 CAAA (40% reduction in utility emissions) will decrease stream SO_4^{2-} concentrations by about 8 μeq/liter by 2025, compared to no controls beyond the 1990 CAAA. In contrast, a 44% decrease in S deposition (80% decrease in utility SO_2 emissions) would result in a 15 μeq/liter decrease in stream SO_4^{2-} concentrations by 2025. Despite marked reductions in atmospheric S deposition over the last 34 years (Figure 3B; Likens et al. (2001)), stream ANC at the HBEF remains below 0 μeq/liter. Due to loss of available soil nutrient cations from decreases in atmospheric inputs of Ca^{2+} and increase in deposition of atmospheric S during the last century, the recovery of stream ANC following decreases in strong acid loading has been delayed (Likens et al. (1996, 1998)). For the scenario of no controls beyond the 1990 CAAA, the model predicted rate of ANC for 2010 to 2025 is 0.13 μeq/liter-yr. A 22 and 44% decrease in atmospheric S deposition in 2010 increases the predicted rate of ANC change to 0.19 and 0.28 μeq/liter-yr, respectively. Model projections suggest that a 44% decrease in atmospheric S deposition in 2010 beyond the 1990 CAAA will result in positive stream ANC by 2023, while a 22% reduction will delay recovery of stream ANC to positive values to a much later date (2038). Model predictions also suggest that a 44% reduction in S deposition beyond the 1990 CAAA will facilitate an increase in stream pH to values exceeding 5.5 by 2050. Unfortunately, these model calculations indicate that the chemical changes predicted for these scenarios would probably not allow for significant recovery of aquatic biota from the effects of acid and associated biogeochemical stress (Driscoll et al. 2001).

Response of S biogeochemistry to forest deforestation

The northern hardwood forest ecosystem may be disturbed by natural factors, such as climatic changes, weather events, insect outbreaks, or by anthropogenic disturbances such as acidic deposition, land-use changes and forest cutting (e.g. Aber et al. (1978) and Bormann and Likens (1979), Johnson and Todd (1987), Mann et al. (1988), Hendrickson et al. (1989)). We have studied different forest cutting practices at HBEF for many years (e.g. Bormann and Likens (1969) and Likens et al. (1970), Martin and Hornbeck (1989), Martin et al. (2000b)), and these vegetation removal experiments have been very useful in understanding S biogeochemistry.

Watershed 2 (W2) was experimentally deforested in the winter of 1965–1966 without removal of forest products, and regrowth was inhibited with herbicides until the summer of 1969 (Bormann and Likens 1979). This experimental manipulation was designed to quantify the role of vegetation in the biogeochemistry of forest ecosystems. Other clearcutting experiments done at HBEF include a progressive strip-cut of W4 (Likens and Bormann 1974b), a block clear-cut of W101 and whole-tree harvest of W5 (Likens and Bormann 1974b; Hornbeck et al. 1986; Lawrence et al. 1987; Martin and Hornbeck 1989; Johnson et al. 1990; Martin et al. 2000b). In W4, 25-m wide strips were cut along elevational contours. The first third was cut in 1970, the second in 1972, and the final third in 1974, all with timber removal. A narrow band of trees was uncut on either side of the stream channel. Watershed 101, an ungauged watershed, was commercially harvested in 1970, and W5 was logged by a commercial, whole-tree harvest in 1983–1984, both with timber products removed.

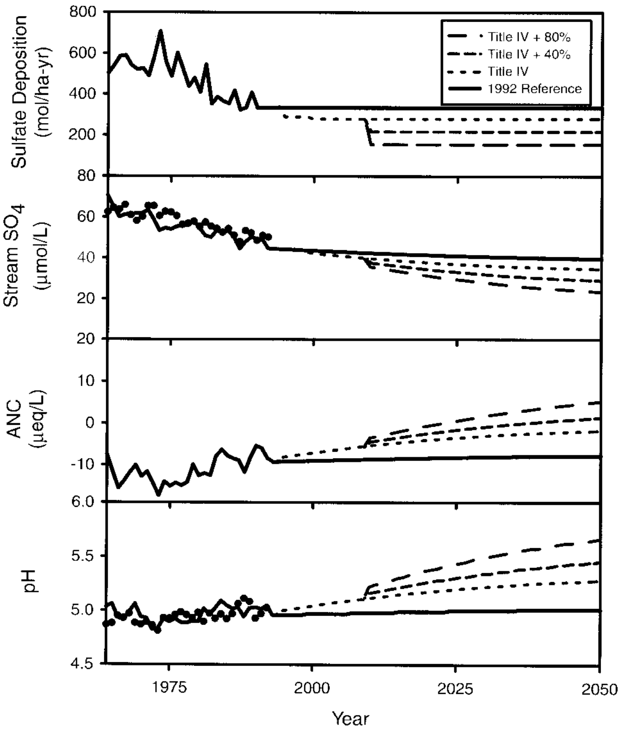

Figure 30. Predictions of SO_4^{2-} in atmospheric deposition (a), and SO_4^{2-} (b), acid-neutralizing capacity (ANC) (c) and pH (d) in stream water draining W6 of the HBEF using the model PnET-BGC. Model predictions of annual volume-weighted SO_4^{2-} and pH are compared to measured values (●). Four future scenarios of atmospheric S deposition are considered (a): (*1*) constant deposition from 1992 values, (*2*) S deposition following implementation of Title IV of the 1990 CAAA, (*3*) S deposition following the 1990 CAAA with 40% cuts in utility SO_2 emissions in 2010 and (*4*) S deposition following the 1990 CAAA with 80% cuts in utility SO_2 emissions in 2010 (modified from Driscoll et al. (2001)).

Stream chemistry response to forest disturbance

Changes in streamwater SO_4^{2-} in response to deforestation and subsequent vegetation regrowth in W2 were particularly interesting. During the devegetation period all other streamwater solutes increased except SO_4^{2-}. Streamwater concentrations of SO_4^{2-} decreased in response to deforestation (W2), strip-cut (W4) and whole-tree harvest (W5) treatments and then increased above reference values (W6) during regrowth, particularly during the first decade or so in W2 and W5 (Figure 31).

Volume-weighted, average annual streamwater concentrations of SO_4^{2-} in W2 initially decreased from ~70 μmol/liter before the experiment to ~40 μmol/liter in 1966 and were less than the reference values (W6) for 4 years following deforestation (Figure 31). After vegetation recovery, streamwater concentrations of SO_4^{2-} in W2 increased to values higher than in W6 for some 12 yr. Since the early 1980s, concentrations have been approximately the same in the deforested (W2) and uncut reference (W6) watersheds (Figure 31). Streamwater concentrations of NO_3^- in W2

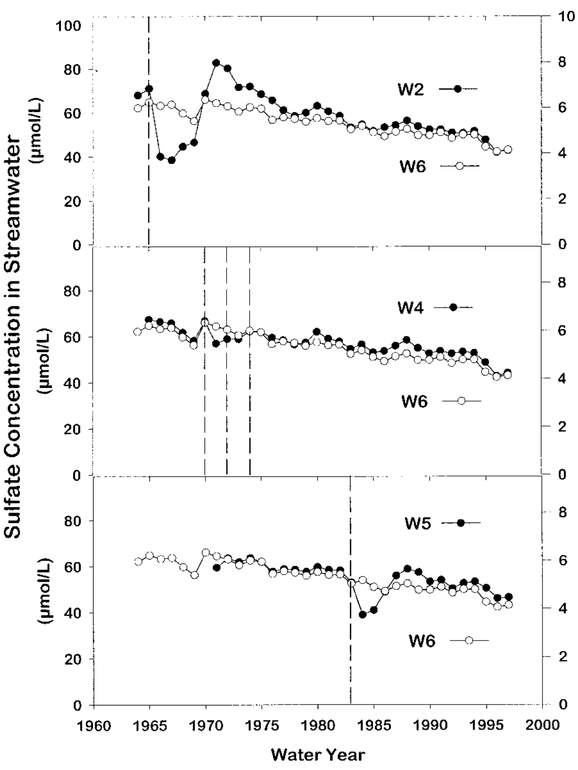

Figure 31. Concentrations of SO_4^{2-} in stream water in experimentally treated Watersheds 2, 4 and 5 (-●-), and uncut W6 (-○-) at HBEF (see text for details of treatments).

peaked at ~ 1300 µmol/liter in October 1967, compared to pre-deforestation values of ~ 20 µmol/liter and remained high through 1971 (Nodvin et al. 1988).

Some of the concentration decrease of SO_4^{2-} immediately following deforestation was due to dilution by the increased streamflow from W2 relative to the precutting period and relative to W6 (Likens et al. 1970). Because streamwater output values take the dilution effect into account (the product of volume-weighted concentration times discharge), it is significant that SO_4^{2-} output from W2 decreased below that for W6 during 1966 and 1967, when W2 was still devegetated and streamflow was elevated, but in 1968 and 1969 (regrowth began in 1969) matched W6 in SO_4^{2-} outputs (Figure 32). Beginning about 1970, W2 outputs exceeded W6 outputs until approximately 1982.

During the first 4 full years following deforestation (1966–1967 to 1969–1970), the NHF from W2 was −483 mol S/ha in stream water, whereas W6 lost −569 mol S/ha. During the next 4 yr (1970–1971 to 1973–1974) the NHF from W2 was −1635 mol S/ha and −768 from W6. During the 11 years after 1966–1967 the NHF from W2 was −3384 mol S/ha and from W6 −1989 (Table 11). Concurrently, very large losses of NO_3^-, H^+, Al^{n+} were measured in drainage water from W2 during the three years after deforestation when regrowth was suppressed (1966–1969),

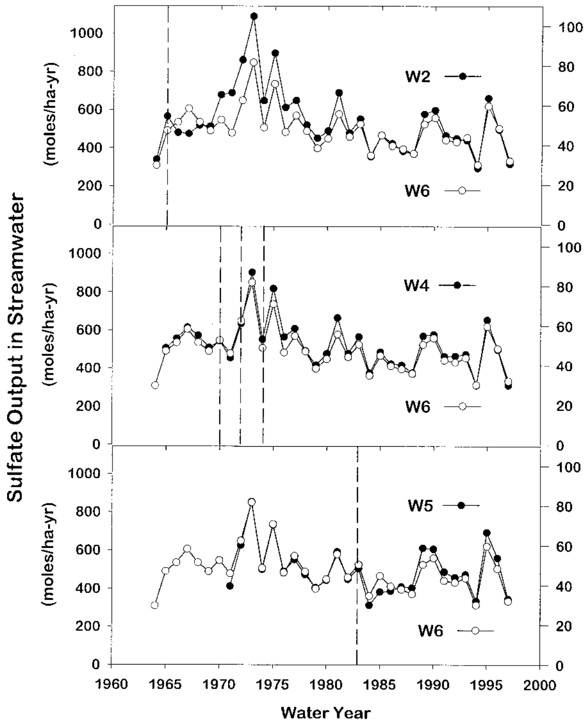

Figure 32. Outputs of SO_4^{2-} in stream water from experimentally treated Watersheds 2, 4 and 5 (-●-), and uncut W6 (-○-) at HBEF (see text for details of treatments).

primarily as a result of increased decomposition and nitrification in the soil (e.g. Bormann et al. (1968) and Likens et al. (1969, 1970, 1978), Bormann and Likens (1979)).

Organic plus inorganic particulate losses of S during 1965–1966 to 1969–1970 were about 3.43 mol/ha-yr for W2 and 0.94 mol/ha-yr for W6, a 3.7-fold difference (Bormann et al. 1974). The NHF of S during the same period was 140 mol/ha-yr for W6 and 123 mol/ha-yr for W2, only a 1.14-fold difference (Bormann et al. 1974). While this particulate matter loss is a striking ecosystem response to disturbance, its magnitude is too small to account for the difference in total S output before and after 1970.

Between the winter of 1965–1966 and summer of 1969, plant growth on W2 was inhibited while decomposition and mineralization were accelerated by the combination of microclimatic and soil moisture change. This disturbance was illustrated dramatically by the behavior of N (large streamwater loss of NO_3^- during this period; Likens et al. (1978). A possible prediction would be that the devegetation and herbicide treatment would facilitate the mineralization of organic S in soil to SO_4^{2-}, which if not taken up by vegetation, would lead to increased outputs of S as was evidenced for N. In fact, a pattern of decreased SO_4^{2-} output was observed immediately following the treatment. Regrowth began in 1969, accelerating until about

Table 14. Sulfur content of vegetation of W2, Hubbard Brook Experimental Forest, through succession. Aboveground data are means of 70 plots distributed evenly across the watershed. Belowground data are estimated as fixed percentages of aboveground nutrient contents as follows. Trees and saplings belowground = 41% aboveground, shrubs = 53%, Herbs = 14%. Data are in moles S/ha.

	Year 1 (1969)			Year 2 (1970)			Year 3 (1971)		
Stratum	Above	Below	Total	Above	Below	Total	Above	Below	Total
Herbs	6	1	7	12	2	13	16	2	18
Shrubs	3	2	5	8	4	12	20	11	31
Saplings	0	0	0	3	1	5	26	11	37
Trees	0	0	0	0	0	0	0	0	0
Total	9	3	12	23	7	30	62	24	86

	Year 5 (1973)			Year 11 (1979)			Year 20 (1988)		
Stratum	Above	Below	Total	Above	Below	Total	Above	Below	Total
Herbs	28	4	32	23	3	26	26	4	29
Shrubs	33	18	51	21	11	32	8	4	11
Saplings	86	35	121	150	61	211	98	40	138
Trees	0	0	0	89	36	125	296	121	418
Total	147	57	204	282	112	395	428	169	597

1973, then continuing at a more or less regular rate until the last published measurement in 1988 (Table 14, Reiners (1992)). We might predict that during this period of rapid plant uptake and reconstitution of litter, these pools would enhance ecosystem retention of S so that streamwater output would be diminished compared with previous years and compared with W6. Again, the reverse occurred – outputs continued to increase from W2, reaching a maximum difference with W6 in 1973–1974 (Figure 32, Tables 9 and 11).

The annual plant biomass increment (Table 14) for W2 was small compared with the NHF (Figure 33; Note: *The biomass increment values are at a different scale to clarify trends*.) Calculations show that the biomass increment was greatest during the period of greatest NHF, and amounted to 8.3% of net loss rate at maximum.

Clearly, other processes dominated the S balance in W2 during this period of disturbance and early recovery. These processes worked in reverse of processes controlling the initial NHF, and then in the net uptake of organic S in living and dead organic pools. The most probable of these controlling processes is enhanced adsorption of SO_4^{2-} in the B horizon of the soil during deforestation and initial regrowth. Enhanced nitrification during this period lowered soil and soil solution pH, protonating sesquioxide surfaces and increasing SO_4^{2-} adsorption during that time. Thus, SO_4^{2-} derived from atmospheric inputs and mineralization of soil organic S may have been retained as adsorbed SO_4^{2-} (PSO_4) during that period. Later, around 1970 (Figure 32), it is likely that desorption occurred, as SO_4^{2-} losses increased un-

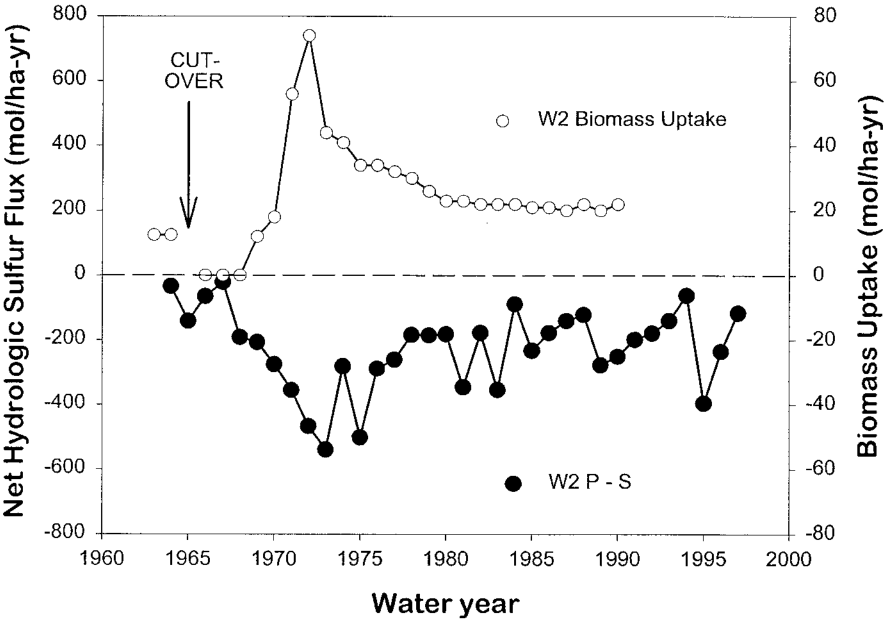

Figure 33. Changes in the S balance (●) and biomass increment (○) multiplied by 10, during 1966–1989 in W2 of the HBEF. The biomass increment values for 1963 and 1964 are for W6. P = bulk deposition input and S = streamwater output. Annual biomass increment was calculated from Table 3 in Reiners (1992).

til they were greater than those from W6. This shift in the adsorbed SO_4^{2-} pool from a net sink to a net source of S was brought about by a cessation in high rates of nitrification and associated acidification. Net discharge from this pool, augmented perhaps, by higher weathering rates, led to greater NHF from W2 than W6 until about 1982. Since then, the combination of processes has brought these two watersheds into about equal rates of net S loss (Figure 32).

The whole-tree harvesting of W5 resulted in some similar, but less pronounced effects on streamwater chemistry than for the W2 experiment. Stream water NO_3^- concentrations increased to ~450 μmol/liter in autumn 1994, but by 1996–1997 were <100 μmol/liter and in subsequent years returned to concentrations equal to or even less than those of W6 (Dahlgren and Driscoll 1994). With this increase in NO_3^- concentrations there was an increase in H^+ and a decrease in SO_4^{2-} from ~60 to ~40 μmol/liter (Figure 31). The same temporal patterns in solute concentrations were found in the soil solution as that for the stream water of W5. The stronger retention of NO_3^- in W5 associated with immediate vegetation regrowth coincided with increases in pH of soil and soil solutions. This process facilitated the deprotonation of SO_4^{2-} adsorption sites on sesquioxides in the lower mineral soil and decrease in the SO_4^{2-} adsorption capacity.

The W4 experiment had an even smaller effect on NO_3^- generation. Hence, changes in SO_4^{2-} concentrations in stream water were smaller, but of the same pattern, as in the other deforested watersheds (Figure 31). There was little effect on streamwater output of SO_4^{2-}, however, due to the progressive harvest and buffer strip of living trees left along the stream channel (Figure 32).

Soil solutions and soils

No differences were found in the organic S concentrations in soil solutions or streams between W5 and W6 in 1986 following the whole-tree harvest (Mitchell et al. 1989). Average organic S concentrations decreased from 6.6 μmol/liter to 4.7 μmol/liter as soil solution passed from the Oa to the Bs2 horizons, respectively, suggesting that dissolved organic S was retained in the mineral soil. Similar results were reported by Homann et al. (1990). This decrease was used to calculate an accumulation of organic S in the mineral soil of about 16 mol/ha-yr (Mitchell et al. 1989).

The whole-tree harvest of W5 increased total S concentrations in the Bh horizon and decreased total S concentrations in the Bs2 horizon of the soil. It also increased the amount of PSO_4 in the E and Bh horizons. Eight years after whole-tree harvesting, a relationship between SO_4^{2-} concentration and elevation was evident in the mineral soil, with higher PSO_4 concentrations in the upper elevations of W5 (Figure 34). This relationship was the result of differences in desorption and adsorption of SO_4^{2-} at different elevations in W5, which differed in both soil and vegetation characteristics. The whole-tree harvest of W5 in 1983–1984 increased soil SO_4^{2-} adsorption (i.e. increase in PSO_4) in 1986. By 1991, considerable desorption of SO_4^{2-} was observed at the lower elevations of W5 while at the upper elevations SO_4^{2-} adsorption continued due to high concentrations of SO_4^{2-} and H^+ in soil water, the latter enhanced by elevated nitrification (Zhang et al. 1999).

There was some variation in the S mass estimates in the soil among the years when samples were taken including the summer of 1983, before the whole-tree harvest, and in 1986 and 1991 after the harvest (Figure 14). This variation was attributed to differences in estimating the depth of the Bs2 horizon (Zhang et al. 1999). There was an increase of the PSO_4 pool in the E-horizon from before the cut (15.6 mol/ha) to 65.5 mol/ha in 1986, and this increase was maintained through 1991 (53.0 mol/ha). This increase in PSO_4 determined SO_4^{2-} was consistent with the decreases in SO_4^{2-} in soil solution and stream water after the whole-tree harvest of W5.

Long-term responses

To evaluate the longer-term response of the watershed-ecosystems to deforestation disturbance, we calculated cumulative mass balances for the 10 yr immediately following the experimental manipulations of W101, W4 (modified after Hornbeck et al. (1986)), W2 and W5 (Figure 35). Bulk deposition inputs of SO_4^{2-} were compared to stream losses of SO_4^{2-} and biomass removal of S (for W101, W4 and W5). Fluxes for the deforested watersheds were compared to mean values for W6 for the entire study, prorated to correspond to a 10-yr period. Stream losses of SO_4^{2-} for the 10 yr of analysis greatly exceeded S loss associated with export of S in biomass. All watersheds showed a pattern of stream losses of SO_4^{2-} exceeding bulk

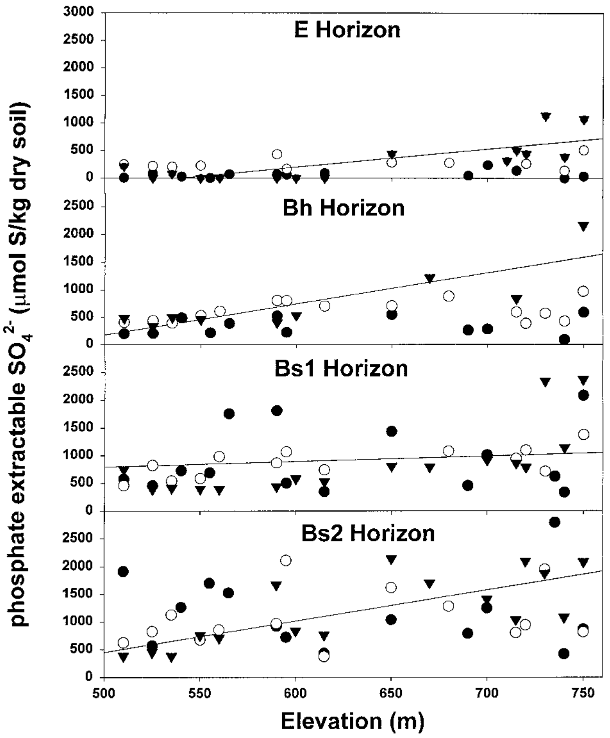

Figure 34. Phosphate extractable SO_4^{2-} (PSO_4) concentrations in E, Bh, Bs1 and Bs2 soil horizons with increasing elevation before (● – 1983), three (○ – 1986) and eight (▼ – 1991) years after whole-tree harvesting of W5. Significant linear relationships (—) between elevation and SO_4^{2-} concentrations were found only for 1991 (from Zhang et al. (1999)).

deposition inputs over the periods of interest. The differences between stream and bulk deposition flux of SO_4^{2-} for the cut watersheds for the 10-yr intervals exceeded the value for the reference watershed (W6). These values also varied markedly across the deforested watersheds, with W2 showing the greatest NHF for the 10-yr interval, followed by W101, W4 and W5. It is difficult to evaluate the mechanism(s) responsible for the watershed to watershed differences in SO_4^{2-} losses. The rank order of NHF (i.e. W2 = −3356 mol/ha > W101 = −2685 mol/ha > W4 = −2240 mol/ha > W5 = −1672 mol/ha) corresponds to both the chronological order of cutting as well as the mass of S in bulk deposition. Some of this difference, however, can be attributed to the extent of biomass removal from the watersheds following cutting. When considering stream SO_4^{2-} output plus biomass S removal less bulk SO_4^{2-} deposition input, the differences between watersheds narrowed considerably (i.e. W2 = −3356 mol/ha, W101 = −3091 mol/ha, W4 = −2802 mol/ha, W5 = −3233 mol/ha). Over the longer term, it appears that cutting results in a net loss of S from these watershed ecosystems, despite the fact that there is net retention of SO_4^{2-} associated with the enhanced adsorption of SO_4^{2-} immediately following deforesta-

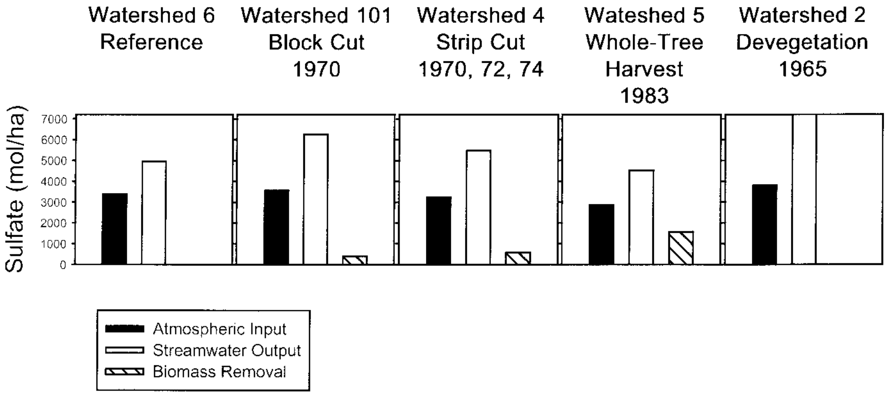

Figure 35. Comparison of inputs of SO_4^{2-} in bulk deposition, stream outflow of SO_4^{2-} and biomass removal of S over a 10-yr period immediately following devegetation of experimental watersheds at the HBEF. The S mass balances for the experimentally devegetated watersheds are compared with the reference watershed (W6). Inputs of SO_4^{2-} in bulk deposition and stream outflow of SO_4^{2-} were average values over the entire study prorated for a 10-yr interval.

tion disturbance. This net loss is probably associated with the long-term mineralization of logging debris and decaying roots.

Overall, vegetation destruction and/or removal, on the experimental watersheds resulted in increased rates of organic matter decomposition and nitrification, a lowering of the pH of soil water and stream water and enhanced SO_4^{2-} adsorption (Likens et al. 1970; Fuller et al. 1987; Nodvin et al. (1986a, 1986b, 1988)). The effect of H^+ generation in protonating anion adsorption sites and enhancing the soil adsorbing capacity of SO_4^{2-} have been shown to be an important process within other forest soils as well (Mitchell et al. 1992). These results suggest a direct linkage of SO_4^{2-} retention with accelerated nitrification causing protonation of pH-dependent anion exchange sites.

The experimental deforestation of W2, W4 and W5 clearly demonstrated the importance of SO_4^{2-} adsorption/desorption in regulating SO_4^{2-} loss in stream water. In these experiments the reduction of vegetation demand for nitrogen resulted in increased availability of N ($NH_4{}^+$) for microbial processes including nitrification. This effect was most notable in W2 due to the use of herbicides which repressed vegetation regrowth for three years, whereas in W4 and W5 this effect was more transitory since the vegetation was allowed to regenerate immediately (Mitchell et al. 1989).

As the vegetation became reestablished in W2 and W5, NO_3^- and H^+ concentrations decreased and SO_4^{2-} concentrations increased. For some 10 yr, streamwater SO_4^{2-} concentrations in W2 remained higher than those in W6 (Figure 31). These increased SO_4^{2-} concentrations were due partly to the desorption of SO_4^{2-} that had been adsorbed during the earlier period of low soil pH. Analyses of soil S constituents sampled in W5 before (1983) and after (1986 and 1991) harvest confirmed that adsorbed SO_4^{2-} pools changed after the experiment. These changes in soil pools give further support to the importance of pH-dependent SO_4^{2-} adsorption and desorption in regulating stream water SO_4^{2-} chemistry at HBEF (Mitchell et al. 1989; Zhang et al. 1999).

Watershed-ecosystem, landscape-scale dynamics

The spatial patterns of biogeochemistry are important determinants for developing ecological insights and for generating management perspectives and policies (e.g. Driscoll and Likens (1982) and Likens (1992, 1999), Johnson et al. (2000). In spite of the potential for increasing complexity with increasing watershed size, the fundamental chemical signature for stream water in the Hubbard Brook Valley is essentially established in headwater tributaries (e.g. Likens et al. (1998) and Likens (1999)). For example, ambient SO_4^{2-} concentrations in stream water, as well as their decreases with time, were strikingly similar in both W6 (13.2 ha) and the main Hubbard Brook (3000 ha) during 1973–1998 (Figure 36). Surprisingly, gross annual output of SO_4^{2-} per unit area is essentially the same over approximately 4 orders of drainage area size, from 3 to 3000 ha, within the Hubbard Brook Valley (Figure 37). While SO_4^{2-} concentration and output remain constant, acidity does not. The acidity near the source of the headwater tributaries (W6) averages about pH 4.0, is about 5.0–5.5 at the weir and is about 6.0–6.5 in the fifth-order main Hubbard Brook at the base of the Valley.

Summary and conclusions

- Significant declines occurred in annual, volume-weighted concentrations in bulk deposition (−0.44 μmol/liter-yr) and stream water (−0.64 μmol/liter-yr), and bulk deposition inputs (−5.44 mol/ha-yr) and streamwater outputs (−3.74 mol/ha-yr) for SO_4^{2-} at the HBEF during 1964–1965 to 1997–1998.
- On an annual basis, streamwater outputs of SO_4^{2-} exceeded bulk deposition inputs. On average, monthly inputs of SO_4^{2-} exceeded streamwater outputs during June, July, August and September.
- Much of the SO_4^{2-} entering HBEF in atmospheric deposition cycles through vegetation and microbial biomass before being released to the soil and stream water.
- Temporal trends in atmospheric concentration and inputs, and streamwater concentration outputs of SO_4^{2-} are significantly related to SO_2 emissions from the HBEF source area.
- Sulfur dominates aqueous chemistry at HBEF; SO_4^{2-} is the major anion in bulk deposition, soil water and stream water, although NO_3^- has greatly increased in percent of total anionic charge in bulk deposition since 1964; and acid deposition continues to impact adversely terrestrial and aquatic ecosystems at HBEF.
- Dry deposition of S is estimated at 21% of bulk deposition, although dry deposition is difficult to measure accurately.

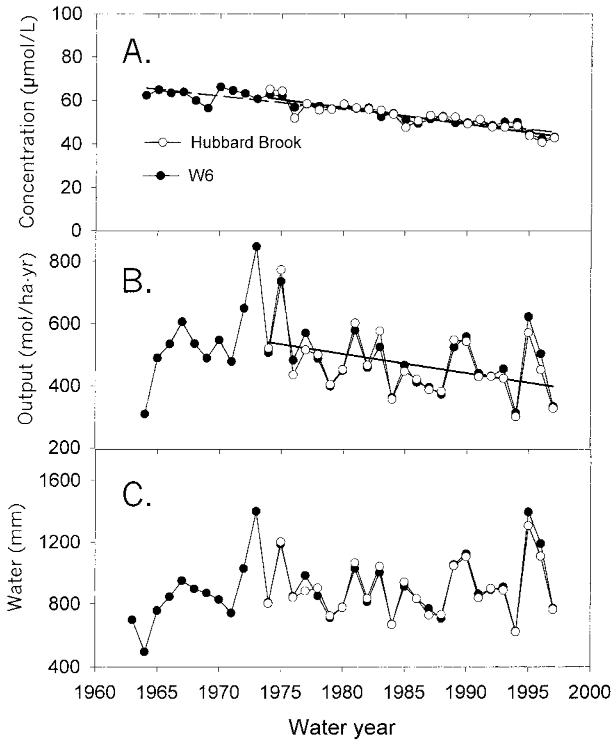

Figure 36. Long-term changes in SO_4^{2-} in stream water from W6 (-●-) and from Hubbard Brook (-○-), near the mouth (235 m MSL elevation) of the Hubbard Brook Valley. Annual volume-weighted concentration (A) and gross output (B) of SO_4^{2-} in stream water and amount of streamflow (C) with time. For (A): W6 slope −0.61, $r^2 = 0.87$, $p < 0.001$; Hubbard Brook slope −0.75, $r^2 = 0.78$, $p < 0.001$ (after Likens (1999)).

- The greater the annual precipitation amount the greater the bulk deposition, although the relationship is weak; the greater the streamflow the greater the gross and net streamwater output.
- Vegetation uptake of S and return to the soil by above- and belowground litter and microbial processes are major components of intrasystem cycling.
- The pool of S in living biomass increased from 1965 to 1982, and remained relatively constant thereafter.
- The flux of S by biological vectors across watershed-ecosystem boundaries is negligible at HBEF.
- Gaseous emissions of S from the watershed-ecosystem are unquantified, but estimated to be very small.
- Comparing ecosystem cycling of S for 1964–1969 to 1993–1998, atmospheric bulk deposition decreased by 34%, stream output decreased by 10%, net annual biomass storage decreased by 92%, and net soil release increased by 191% of the 1964–1969 values. These changes are correlated with decreased emissions of SO_2 from the source area for the HBEF.

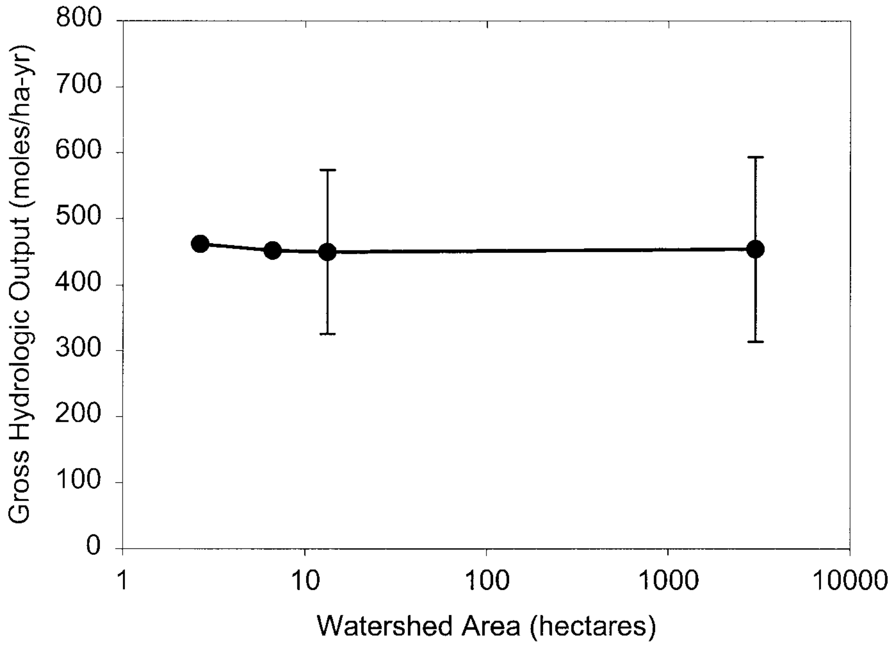

Figure 37. Annual gross streamwater output of SO_4^{2-} with changing watershed area of the Hubbard Brook Valley. Points represent average annual values for 1982–1992; error bars are ± one standard deviation of the mean (modified from Likens (1999) and Johnson et al. (2000)).

- Current inputs of SO_4^{2-} to the available nutrient compartment of the forest ecosystem are dominated by atmospheric sources: bulk deposition, 50%; net soil release, 24%; dry deposition, 11%; root exudates, 11%; and 4% from canopy leaching.
- In contrast to the long-term NHF of S for W6, the long-term, average annual NEF of S was much smaller, mostly negative and highly variable (i.e. that losses of S exceed inputs by 54.3 mol S/ha-yr (NEF range = +86.8 to −229.5) during 1964–1965 to 1997–1998). While several mechanisms may explain this small but ecologically significant discrepancy, the most likely are net desorption of S and net mineralization of organic S largely associated with the forest floor. Our best estimates indicate that additional S from dry deposition and weathering release is probably small and that desorption accounts for about 37% of the NEF imbalance and net mineralization probably accounts for the remainder. Additional inputs from dry deposition would result from unmeasured inputs directly to the forest floor. The source of this additional S input has important implications for the recovery of soils and streams in response to decreases in inputs of acidic deposition.
- Forest destruction or disturbance associated with harvesting caused increased rates of organic matter decomposition and nitrification, a lowering of soil and streamwater pH and enhanced SO_4^{2-} adsorption on mineral soil. As a result,

stream concentrations and losses of SO_4^{2-} decreased. During vegetation regrowth this adsorbed SO_4^{2-} was released from soil, increasing concentrations and fluxes of SO_4^{2-} in drainage water.

- Gross annual streamwater output of SO_4^{2-}/ha is essentially the same over approximately 4 orders of drainage area, from 3 to 3000 ha in size, within the Hubbard Brook Valley.

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