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# Dry deposition of sulfur: a 23-year record for the Hubbard Brook Forest ecosystem

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ABSTRACT

Dry deposition of S was estimated for watershed-ecosystems of the Hubbard Brook Experimental Forest from 1964–65 through 1986–87. Two approaches, a regression analysis of bulk precipitation inputs and stream outputs and a mass-balance method, gave similar average values for Watershed 6 (430 and 410 eq $SO_4^=$/ha-yr, respectively, for this 23-year period). Dry deposition contributed about 37% of total S deposition, varying from 12% in 1964–65 to 61% in 1983–84. Long-term data from "replicated" watershed-ecosystems showed that temporal variability in estimates of dry deposition was considerably greater than spatial (between watersheds) variability.

## 1. Introduction

Materials are removed from the atmosphere by the processes of wet and dry deposition. Estimates of both wet and dry deposition are vital for evaluating the atmospheric influx of chemical elements and the effects of such airborne nutrients and pollutants on terrestrial and aquatic ecosystems. Yet, current estimates of dry deposition are few and uncertain because of major methodological problems.

Wet deposition of chemicals in rain and snow is measured currently by standard techniques in national and regional networks throughout both Canada and the United States (e.g., Barrie and Hales, 1984; Dana and Easter, 1987). Estimates of dry deposition of gases and particles, however, result in only approximate values for inputs to landscapes with complex topographies (e.g., Bormann, 1983; Hicks et al., 1986; Hicks and Matt, 1988). The difficulties in making quantitative measurements of dry deposition are related to problems in measuring micrometeorological gradients especially in complex terrain, to different characteristics of potential impaction surfaces (e.g., leaves of conifer versus hardwood trees), and to uneven topography or complicated architecture of terrestrial surfaces producing variable patterns of atmospheric turbulence. Nevertheless, quantitative measurements of dry deposition for entire ecosystems are vital to assessments of the ecological effects of total inputs of nutrients and toxic chemicals. For example, dry deposition may contribute significantly to the anthropogenic acidification of landscapes (e.g., Driscoll and Likens, 1982; Norton, 1984; Schindler, 1985; Gibson, 1986; Lindberg and Garten, 1988; Schaefer et al., 1989; Shepard et al., 1990). Dry deposition also has been reported to be an important component of total N input to coastal marine ecosystems, thereby contributing to their eutrophication (Fisher et al., 1988).

## 2. Approach

For watershed-ecosystems the sum of all sources of a chemical element (wet deposition,

† Deceased

dry deposition and weathering release) must equal the sum of all losses (drainage water and gaseous losses) plus any changes in storage (net storage) within the biotic or abiotic compartments (Bormann and Likens, 1967). Thus,

wet deposition + dry deposition + weathering release = loss in drainage water + gaseous loss + net storage in biomass and soil. (1)

Because of the essentially watertight geologic substrate of the experimental watersheds of the Hubbard Brook Experimental Forest (HBEF) in West Thornton, NH, it is possible to construct quantitative mass balances for many chemical elements (see Bormann and Likens, 1967; Likens et al., 1967; Likens et al., 1977; Likens et al., 1985). Here, we use this mass-balance approach for watershed-ecosystems at Hubbard Brook to derive estimates of the dry deposition of S during a 23-year period. For comparative purposes, all of the values in the mass balance are calculated as $SO_4^=$.

By rearranging eq. (1), we obtain:

dry deposition = loss in drainage water (stream water) + gaseous loss + net storage − wet deposition − weathering release. (2)

When appropriate watershed-ecosystems are used, this method can provide realistic and direct estimates of dry deposition for large and structurally complex units of landscape. Furthermore, this method does not involve assumptions about scaling from an individual site(s) to an entire watershed-ecosystem. At the HBEF, we were able to use several "replicated" watershed-ecosystems to evaluate spatial variability and other errors associated with the watershed method. Previously, we used this approach to calculate a mean value for all undisturbed watershed-ecosystems during 1963–1974, years with a relatively large coefficient of variation (Likens et al., 1977; Eaton et al., 1978, 1980). Now based on 23 years of data, it is possible to improve our calculation for dry deposition of sulfur for these forested watershed-ecosystems and to evaluate factors that contribute to temporal and spatial variation.

Because the experimental watershed-ecosystems of the HBEF have negligible losses in deep seepage, the total export of drainage water can be measured continuously as stream water at gauging weirs at the base of each watershed-ecosystem (Likens et al., 1977, 1985). Wet deposition is measured weekly as bulk precipitation at 3–5 sites within the HBEF (Likens et al., 1977). Information on sample collection and analytical procedures, and uncertainty analysis relative to mass balance components are given in Likens et al. (1977, 1984, 1985).

Eaton et al. (1980) estimated that dry deposition contributed about 5% of the $SO_4^=$ in bulk precipitation samples at the HBEF during 1975–1978. A more recent assessment also suggests that the chemistry of bulk precipitation at Hubbard Brook approximates closely that of the wet-only precipitation. Stensland et al. (1986) found that volume-weighted averages for bulk samples of $SO_4^=$ were 2.9% higher and $Ca^{++}$ were 3.4% lower than wet-only samples collected at Hubbard Brook during June 1979 through May 1982. Precipitation input and streamflow export of $SO_4^=$ have been measured in several experimental watershed-ecosystems at Hubbard Brook since 1964 (Likens et al., 1977, 1985). Precipitation inputs and stream outputs of S are primarily as $SO_4^=$. Precipitation concentrations of organic S are extremely low (M. Mitchell, personal communication) and stream concentrations of organic S range from 0.7 to 9.5 μmol/l (representing 1.5 to 15% of total S in the few samples analyzed; Mitchell et al., 1989). Because concentrations of organic S are small and neither continuous nor long-term data are available in the HBEF, they are not considered in our analysis.

Watershed 6 (13.2 ha) is the HBEF reference watershed for biogeochemical studies and data are available for 23 years (1964–87). In addition, Watershed 1 (11.8 ha), Watershed 3 (42.4 ha) and Watershed 5 (21.9 ha) have data available for 1971–87, 1973–87 and 1973–83, respectively, to provide watershed-ecosystem "replicates" during portions of the full 23-year period. The water-year at Hubbard Brook extends from 1 June to 31 May (see Likens et al., 1977).

Gaseous losses of S from this well-drained system are thought to be small (~20 eq $SO_4^=$/ha-yr; Eaton et al., 1978), and represent only 1.9% of average yearly stream outputs. Net biomass storage (living biomass above and belowground, and forest floor) has been estimated at various times since 1964 (Likens et al., 1977; Driscoll et al., 1989; T. Siccama, personal communication).

Net accumulation of organic S in the soil was calculated according to the procedures in Mitchell et al. (1989). Annual weathering release was calculated on the basis of total rock weathered (assuming complete extraction of $Ca^{++}$) and concentration of S in the rock (see Likens et al., 1977). Net $Ca^{++}$ export (stream output − bulk deposition input ± net biomass storage) was used as a measure of total rock weathered. Based on data from Watershed 6, annual, net biomass and soil organic S storage averaged about 120 eq $SO_4^=$/ha-yr (Likens et al., 1977; Driscoll et al., 1989; Mitchell et al., 1989), and annual weathering release during the 23 years averaged 40 eq $SO_4^=$/ha-yr, $s_{\bar{x}} = 1.4$. These terms are relatively small compared to long-term mean wet bulk deposition (705 eq $SO_4^=$/ha-yr; $s_{\bar{x}} = 35$) or mean streamwater loss (1040 eq $SO_4^=$/ha-yr; $s_{\bar{x}} = 49$), and are opposite in sign. Thus, the major terms in eq. (2) for Watershed 6 of the HBEF can be approximated as:

dry deposition
= stream water loss − wet deposition. (3)

This simplified relationship can be evaluated for HBEF watershed-ecosystems by linear regression analysis and provides a second approach to estimate dry deposition.

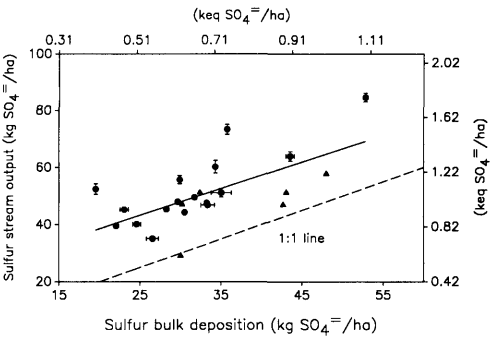


*Fig. 1.* Relationship between the average annual input of $SO_4^=$ in bulk wet precipitation and annual output in stream water for Watersheds 1, 3, 5 and 6 of the Hubbard Brook Experimental Forest during 1964–65 to 1985–86. Data on stream water $SO_4^=$ exist as follows: Watershed 1, 1971–87; Watershed 3, 1973–87; Watershed 5, 1973–83; and Watershed 6, 1965–87. The regression line (——) is $Y = 0.934X + 413$ (the probability for a larger $F$-value = 0.0007, $r^2 = 0.428$). ▲ indicate data for Watershed 6 only (1964–1969), thus annual values for these years are not replicated. ● indicate the mean value for all watersheds available ($n = 2$ to 4) with standard error bars (for some of these mean values the s.e. was very small and cannot be differentiated from the dot).

## 3. Results

Average annual stream water export of $SO_4^=$ increased linearly with increasing annual bulk precipitation input of $SO_4^=$ for Watersheds 1, 3, 5 and 6 (Fig. 1). The relationship is highly significant ($p < 0.0007$; $r^2 = 0.43$), with a slope of 0.93 (s.e. = 0.24; $p < 0.0007$) and a $Y$-intercept of 410 eq $SO_4^=$/ha-yr (s.e. = 170; $p < 0.03$). The slope is not statistically different from 1.0 ($p > 0.2$; $t$-test) suggesting that, on average, changes in precipitation inputs of $SO_4^=$ result in proportional changes in stream water outputs (Fig. 1). Furthermore, all but one annual observation (1964–65) fell above the line where $SO_4^=$ inputs from bulk precipitation equal $SO_4^=$ outputs in stream water (1:1 line in Fig. 1), suggesting that sources of S other than wet deposition are quantitatively important for the ecosystem (eq. (2)).

Using data from all watersheds and from all years, the intercept with the $Y$-axis in Fig. 1 (410 eq $SO_4^=$/ha-yr) can be used to estimate dry deposition of S during the 23-year period (eq. (3)) by adding to it the mean difference between net storage and weathering release during 1964–65 through 1986–87 (80 eq $SO_4^=$/ha-yr). Thus, the average long-term dry deposition value for all watersheds based on this $Y$-intercept approach was 490 eq $SO_4^=$/ha-yr. In comparison mean dry deposition for Watershed 6 only (23 years of record) using the $Y$-intercept method was 430 eq $SO_4^=$/ha-yr.

An alternative, and more detailed, analysis of S dry deposition can be obtained by evaluating the mass balance for S each year (eq. (2)) for Watershed 6 during 1964–65 through 1986–87 (full 23-yr period). The mean dry deposition value for Watershed 6 for this period using this mass balance approach was 410 eq $SO_4^=$/ha-yr ($s_{\bar{x}} = 34$, $n = 23$).

Annual estimates of dry deposition for Watershed 6 based on the mass balance approach are given in Fig. 2. Estimated values increased generally until about 1968–69, and then fluctuated

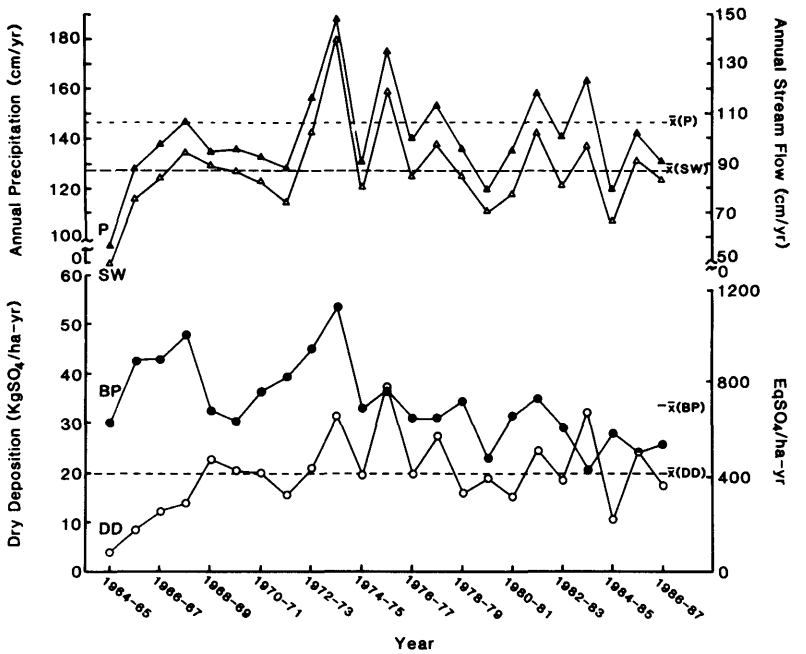


*Fig. 2.* Annual precipitation (P), streamflow (SW), wet bulk deposition (BP) of $SO_4^=$, and dry deposition (DD) of $SO_4^=$ for Watershed 6 of the HBEF during 1964–65 through 1986–87. Annual dry deposition values are calculated by the mass balance method (see text).

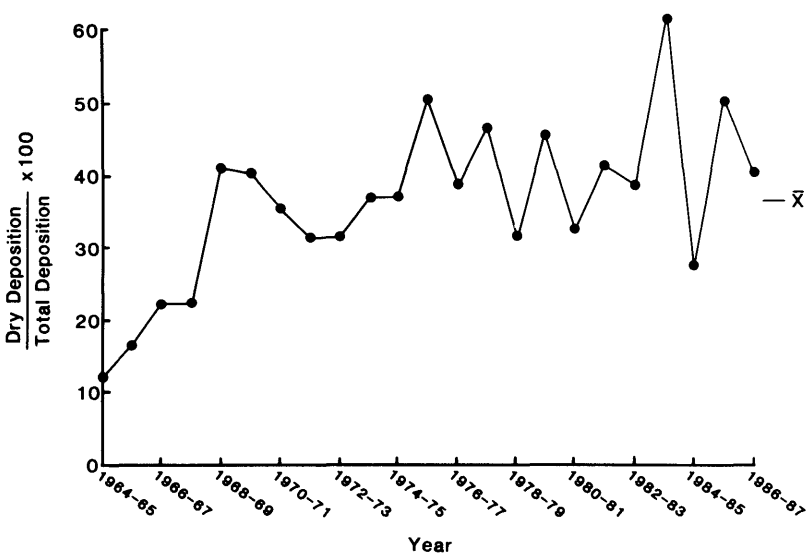


*Fig. 3.* Annual dry deposition as a percent of annual total deposition of $SO_4^=$ for Watershed 6 of the HBEF during 1964–65 through 1986–87.

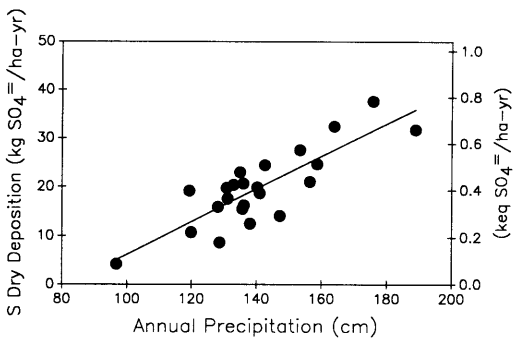


*Fig. 4.* Relationship between annual dry deposition of $SO_4^=$ and annual amount of precipitation for Watershed 6 of the HBEF during 1964–65 through 1986–87. The regression is $Y = 0.34X - 570$; $r^2 = 0.70$, $p = < 0.0001$, where $Y$ = dry deposition of $SO_4^=$ in eq/ha-yr and $X$ = precipitation in cm/yr.

about the mean value through 1987 (Fig. 2). In contrast, significant decreases in bulk wet deposition of $SO_4^=$ occurred during the period of study (Fig. 2; Likens et al., 1984; Hedin et al., 1987; Driscoll et al., 1989). As a result, annual estimates of dry deposition represented a relatively small percentage (10–25%) of the total S deposition at the HBEF during the first 4 years of the study. During the last two decades, however, our estimates of dry deposition have ranged from about 30 to 60% of the total S deposition (Fig. 3).

The annual values that are farthest from the regression line in Fig. 1 tend to represent extreme years hydrologically at Hubbard Brook. In fact, year-to-year variability in estimates of dry deposition of S was strongly related to amount of precipitation (Fig. 4), which in turn was directly related to streamflow (Fig. 2). Factors affecting this annual variability within the overall relationship will be discussed below.

## 4. Discussion

Our two long-term, watershed-ecosystem estimates of dry deposition using the $Y$-intercept and mass balance methods are similar in magnitude (430 and 410 eq $SO_4^=$/ha-yr, respectively, for Watershed 6). Thus, the average total (wet + dry), annual deposition of $SO_4^=$ for Watershed 6 of the HBEF during the past 23 years was 1125 eq/ha-yr ($s_{\bar{x}} = 48$) of which, on average, 37% was contributed by dry deposition. Other studies have suggested that dry deposition can contribute up to 60% of total inputs of sulfur to forest and lake ecosystems (e.g., Likens et al., 1977; Eaton et al., 1978, 1980; Grennfelt et al., 1985; Hultberg, 1985; Lindberg et al., 1986; Barchet, 1987; Norton et al., 1988; Shepard et al., 1990). This fraction probably changes with distance from major emission source areas (Gibson, 1986) and with different time periods studied.

Even though annual inputs of S in bulk precipitation showed a statistically significant decline during this period at Hubbard Brook (Likens et al., 1984; Hedin et al., 1987; Driscoll et al., 1989) no long-term, linear trend was apparent in our annual estimates of dry deposition (Fig. 2). There was a significant curvilinear trend to these data (dry deposition = 15.3 year − 0.10 year$^2$ − 565.4; $r^2 = 0.38$; $p < 0.009$), mainly due to low values in the first 4 years of the study. Thus, dry deposition currently represents a larger fraction of the total S deposition than it did 23 years ago, although since 1968–69 there has been no trend with values fluctuating around the long-term mean (Fig. 3). In fact, since 1975–76 there has been no significant difference ($p < 0.05$) between the long-term mean bulk precipitation input and the mean dry deposition input of S at the HBEF (Fig. 2).

Annual total deposition values for Watershed 6 ranged from a low of 710 in 1964–65 to a high of 1770 eq $SO_4^=$/ha-yr in 1973–74; dry deposition values (mass balance method for Watershed 6) ranged from 87 in 1964–65 to 780 eq $SO_4^=$/ha-yr in 1975–76. These values are similar to those measured by other methods at various sites in the northeastern US (see Barchet, 1987).

Long-term data from forested watershed-ecosystems at Hubbard Brook provide a unique opportunity to evaluate spatial (between watersheds) and temporal (between years) variability associated with the dry deposition of S. During the past 23 years in Watersheds 1, 3, 5 and 6, streamwater outputs have been greater than, but proportional to, bulk precipitation inputs, suggesting that S is relatively conservative in these ecosystems (Fig. 1). The four watersheds behave very similarly through time, and most of the variability seen in Fig. 1 is due to actual changes in inputs and outputs of $SO_4^=$ between different years. For example, only 2% of the variance in $SO_4^=$ output can be attributed to

differences between watersheds, while 97% of the variance is due to differences between years (ANOVA; $p < 0.0001$). These year-to-year variations appear to be related to the variability in amount of precipitation and streamflow, which themselves are coupled closely at the HBEF (Fig. 2; Likens et al., 1977). This relationship with hydrologic parameters holds for both the deviations from means for the mass balance method (Fig. 2), as well as for the residuals from the *Y*-intercept method (Fig. 1). The only annual value below the 1:1 line in Fig. 1 was the driest year on record (1964–65). 6 of the 7 points (years) above the regression line in Fig. 1 occurred during the wettest years on record at the HBEF.

For years when the records for the different watershed-ecosystems overlap, the variance in either mean annual input or output is small (Fig. 1). Because the variability in Fig. 1 is due largely to temporal differences between years, it follows that estimates of dry deposition by the *Y*-intercept method may be sensitive to the choice of years used in the analysis. This observation is true for the HBEF watersheds. For example, *Y*-intercepts of individual regressions from each of the four watersheds ranged from 130 to 350 eq $SO_4^=$/ha-yr ($\bar{x} = 246$; s.e. = 45.8; $n = 4$), depending upon the exact period for which data were available for each watershed. For example, the smaller *Y*-intercept value of the regression for W5 (130 eq $SO_4^=$/ha-yr) was obtained because data for 1964–65 to 1971–72 and 1984–85 to 1986–87 were not available or not included (Watershed 5 was manipulated experimentally in 1983–84), and these were relatively dry years at the HBEF (see Fig. 2). Thus, for a given period of record all watershed-ecosystems give similar estimates of dry deposition, but estimates vary when different time periods are used. To minimize this effect of differences in time periods on our long-term average estimate of S dry deposition, we based our analysis in Fig. 1 on as many years as possible ($n = 23$), giving equal weight to each year in the regression. Note, however, that for four years (1964–65 to 1967–68; indicated by triangles in Fig. 1) the annual values are based on Watershed 6 only.

### 4.1. *Variability in annual input/output budgets*

Our estimate of dry deposition is based upon 23 years of data. Not only are these long-term data robust (e.g., Fig. 1), but they also provide an opportunity to evaluate factors affecting year-to-year variability associated with these long-term estimates. Appreciable scatter occurs in the annual values ($r^2 = 0.43$). The variability between years associated with the long-term estimate of dry deposition (Fig. 1) was highly correlated with amount of annual precipitation (Fig. 4). This variability could be a direct or indirect effect of either of the two major input terms (wet deposition and weathering release) or changes in storage in the mass balance equation (1).

*4.1.1. Weathering sources of sulfur.* Changes in rates of weathering release related to hydrologic variability could produce discrepancies in the annual S balance leading to variations in annual dry deposition estimates (eq. (1)). We do not believe, however, that annual variations in weathering release during the last 23 years at the HBEF are large enough to cause significant variation in the annual dry deposition estimates. Based upon our calculations, annual weathering release of $SO_4^=$ is small for Watershed 6, varying between 25 and 58 eq $SO_4^=$/ha-yr ($\bar{x} = 40$, $s_{\bar{x}} = 1.4$ eq $SO_4^=$/ha-yr) during 1964–65 through 1986–87. Also, an examination of stable S isotope ratios in precipitation, bedrock, soil, soil solutions and stream water confirms that inputs of $SO_4^=$ to the Hubbard Brook ecosystem from weathering sources are low (Fuller et al., 1986). Even if the weathering release values were underestimated

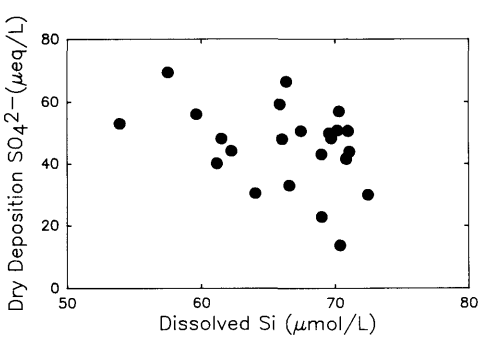


*Fig. 5.* Relationship between the concentration of dry deposition of $SO_4^=$ (DD) in stream water (SW), (DD/SW), and the dissolved Si concentration in stream water for Watershed 6 of the HBEF during 1964–65 through 1986–87.

by a factor of two they would not alter the relationship evident in Fig. 4. In addition, several investigators have used successfully stream concentrations (efflux) of dissolved Si to assess weathering in small catchment studies (e.g., Siegel and Pfannkuch, 1984; Clayton, 1986). The relationship between annual, volume-weighted stream $SO_4^=$ concentration derived from dry deposition (annual calculated flux of $SO_4^=$ from dry deposition divided by annual stream discharge) and annual volume-weighted stream concentrations of dissolved Si for Watershed 6 show a negative relationship (slope = −0.99 (s.e. 0.54); $r^2 = 0.14$; $n = 23$; Fig. 5). The lack of a positive relationship between the discrepancy in the annual S balance and dissolved Si in stream water suggests that the annual S discrepancy is not associated with weathering release.

*4.1.2. Changes in sulfur storage.* Changes in soil pools of S could contribute to the annual variability shown in Fig. 1. These changes may be related either to changes in hydrologic flowpaths or to changes in mineralization/immobilization of organic S or adsorption/desorption of $SO_4^=$, which in turn are related to hydrologic variations. For example, there could be greater retention of atmospheric S within the soil profile in dry years and less during wet years when subsurface drainage is more channelized by cracks, animal burrows, old root paths, etc. (macropore flow, e.g., Likens, 1984) resulting in less contact between soil water and mineral soil.

Mitchell et al. (1989) have estimated that pools of S in the soil at Hubbard Brook are about 85 keq of organic S/ha, with a current net accumulation rate of 32 eq organic S/ha-yr in the mineral soil. Rates of organic matter accumulation in the forest floor at Hubbard Brook during the past two decades are thought to be negligible (T. Siccama, personal communication). Such soil contents are the result of accumulations of organic matter over at least the past 4000–6000 yr (Davis et al., 1985). This annual rate of accumulation of organic S in the soil at Hubbard Brook is small, however, relative to the annual variability (Fig. 1).

The total amount of adsorbed $SO_4^=$ (phosphate extractable) that occurs in HBEF soils (~5.5 keq $SO_4^=$/ha; Mitchell et al., 1989), is large relative to the year-to-year variability in our annual estimates of dry deposition, SD = 0.16 keq $SO_4^=$/ha-yr; Figs. 2 and 4). Furthermore, experimental studies by Nodvin et al. (1986, 1988) have documented that temporal changes in S pools occur due to adsorption/desorption reactions of $SO_4^=$ in HBEF soils. Sulfate adsorption increases with decreases in soil solution pH to a maximum near pH 4.0. Therefore, although the total capacity for sorption in HBEF soils is low compared to many other soils (Johnson et al., 1980), the remaining variability in annual estimates of dry deposition (Fig. 1) may be a result of slight year-to-year differences in adsorption/desorption of $SO_4^=$ related to changes in hydrology (Fig. 4). A clearcutting experiment at the HBEF provides some limits, however, on the amount of $SO_4^=$ adsorption/desorption that could occur. For example, following whole-tree harvest of Watershed 5 in 1983–84, marked acidification (from pH 5.2 to 4.6) and increased amounts of drainage water resulted in a net adsorption of $SO_4^=$ of about 85 eq/ha-yr during a 3-year period (Mitchell et al., 1989). This change, however, even under these extreme conditions, is well within the range of variability for our annual estimates of dry deposition (Figs. 1, 4).

Emissions of $SO_2$ peaked in the United States during the early 1970s and have declined recently (Placet and Streets, 1987). Elevated atmospheric inputs of $SO_4^=$ could have resulted in some immobilization of S into both inorganic and organic soil pools during the early part of this century. With recent decreases in $SO_4^=$ loading, soil S pools may no longer be at steady-state, resulting in a net loss (e.g., desorption) of $SO_4^=$ from the ecosystem to drainage water. If this process were to occur, soil losses likely would increase with increasing streamflow, and thereby contribute to the positive relationship between dry deposition and hydrology (Fig. 4).

*4.1.3. Surface wetness.* A final possible explanation for the variability in the annual estimate for dry deposition of S (Fig. 1) includes direct effects associated with amount and distribution of precipitation. It might be anticipated that as the period of wet conditions increases (generally coinciding with higher amounts of precipitation) stomatal resistance to $SO_2$ uptake decreases due to reduced water stress. This response may lead to increased rates of gaseous S dry deposition during wet years. In addition, wet surfaces (e.g., leaves) may enhance dry deposition rates, par-

ticularly for gaseous sulfur (Fowler, 1980; Fowler and Unsworth, 1979). On average, precipitation (rain or snow) occurs on 111 days per year or about twice per week at the HBEF (Likens et al., 1977). Thus, there are ample, unique periods for both wet and dry deposition to occur even if precipitation amount were to change appreciably from year to year. (Annual precipitation has varied by two-fold during the past 32 years; Likens et al., 1977, 1985.) Yet given the large temporal variability in other meteorological parameters, such as $SO_2$ concentrations (see, e.g., Barchet, 1987; Shepard et al., 1990), it appears unlikely that surface wetness alone could produce the strong relationship shown in Fig. 4.

The atmospheric sources for wet and dry deposition of $SO_4^=$ undoubtedly are different with changing meteorological conditions. For example, Rahn and Lowenthal (1985), and Rahn (1986) have suggested for sites in the northeastern US that about 45% of the particulate S collected on air-flow filters came from distant midwestern sources, whereas 85% of the S in samples of rainwater came from these distant sources. Moreover, long-term reductions in emissions of $SO_2$ have coincided with decreases in wet deposition of $SO_4^=$ at the HBEF (Likens et al., 1984; Hedin et al., 1987; Butler and Likens, 1990), but not with long-term trends in dry deposition of S.

## 5. Comparisons with other estimates of dry deposition

Dry deposition has been estimated at other specific sites in the northeastern US by micrometeorological approaches (multiplying a measured averge air concentration by an estimate of the deposition velocity). Values $\bar{x} = 253$ eq $SO_4^=$/ha-yr; $s_{\bar{x}} = 107$; $n = 6$) derived in this way for sites within about 480 km of Hubbard Brook for 1987 (Barchet, 1987) were not significantly different from the value (364 eq $SO_4^=$/ha-yr) that we derived at Hubbard Brook for 1986–87 with the watershed-ecosystem approach.

Measurements of stemflow (SF) and throughfall (TF) fluxes also have been used to estimate dry deposition of S in some forest ecosystems (e.g., Parker et al., 1980; Lovett and Lindberg, 1984; Lindberg and Garten, 1988; Schaefer et al., 1989). At the HBEF the SF + TF during June through October of 1969 was 1630 eq $SO_4^=$/ha (Eaton et al., 1973). Subtracting bulk precipitation during this same 5-month period (320 eq $SO_4^=$/ha) yields a net value for SF + TF of 1310 eq $SO_4^=$/ha. Using S isotopes Lindberg and Garten (1988) found that >85% of the $SO_4^=$ in net TF below three tree species in eastern Tennessee was due to dry deposition. Comparing our combined (*Y*-intercept + mass balance) average, long-term estimate of dry deposition (420 eq $SO_4^=$/ha-yr) or the mass balance estimate for 1969–70 (430 eq $SO_4^=$/ha-yr) to the 5-month measure of net SF + TF at the HBEF (1310 eq $SO_4^=$/ha) would suggest that about 32–33% (420/1310 or 430/1310) of the S in SF + TF at Hubbard Brook was due to dry deposition.

The estimate of dry deposition at the Tennessee site was more than two-fold higher than our estimate for the HBEF, and the proportion of particulate S was much greater in Tennessee. Some 70% of the dry deposition of S was attributable to $SO_2$ at the Tennessee site (Lindberg et al., 1986), whereas $SO_2$ deposition contributed 95% of the total at the HBEF (Eaton et al., 1978). The poor agreement between our long-term estimate of dry deposition and that based on net SF and TF may be because the SF + TF contain large amounts of biologically recycled S, which then is leached from the plant tissues by incident rainfall, or it may be due to the limited data base from 1969.

The dry deposition values based on the mass-balance approach are annual estimates, whereas most of the dry deposition occurs during the summer at the HBEF when the deciduous canopy is leafed out, aerosol concentrations of $SO_4^=$ are highest and $SO_2$ deposition is occurring at maximum rates (Eaton et al., 1978). Mean concentrations of $SO_4^=$ in TF and SF may be 6× more concentrated than that in incident precipitation during the summer (Likens et al., 1977). In contrast, 52% of the annual stream water loss of $SO_4^=$ occurs during March to May as the accumulated snowpack melts (Likens et al., 1977). Thus, although major, seasonal inputs and outputs are out of phase with each other (see Fig. 26 in Likens et al., 1977) the annual fluxes of S reflect the overall, long-term biogeochemistry quite well.

## 6. Conclusions

(1) Dry deposition of S can be estimated for structurally complex units of terrestrial landscapes (watershed-ecosystems).

(2) Using long-term data from Watershed 6 of the HBEF, annual dry deposition was estimated to be 420 eq $SO_4^=$/ha-yr (average of *Y*-intercept and mass balance methods). Annual values based on the mass balance approach ranged between 87 and 780 eq $SO_4^=$/ha-yr during the last 23 years ($\bar{x} = 410$ eq $SO_4^=$/ha-yr, $s_{\bar{x}} = 34$).

(3) Differences in annual estimates of dry deposition between adjacent watershed-ecosystems were small, but differences between years may be substantial because of changing hydrologic conditions. Therefore when using the mass-balance method for estimating dry deposition, short-term (a few years) estimates of S dry deposition may be influenced by hydrology and must be interpreted with caution.

(4) No long-term, linear trend in dry deposition of $SO_4^=$ was observed at the HBEF during the last 23 years, despite a 40% reduction in wet deposition of $SO_4^=$ and a similar decrease in emissions of $SO_2$ in the northeastern US (see Likens et al., 1984; Hedin et al., 1987; Butler and Likens, 1990). These differences in deposition trends may be due to differences in source areas for wet and dry deposition; and have policy implications relative to regulation of anthropogenic emissions.

(5) Net stemflow and throughfall data from 1969 did not provide a good estimate of S dry deposition at the HBEF.

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