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The input of gaseous and particulate sulfur to a forest ecosystem[1]

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ABSTRACT

Sulfate is the predominant anion in precipitation entering the Hubbard Brook Experimental Forest, a northern hardwood forest in north-central New Hampshire. Sulfur is also the dominant element in airborne particulate matter. Losses of sulfur from the ecosystem in stream water exceed inputs in precipitation plus that released from weathering. Using the ecosystem method, it is possible to estimate (by difference) that 6.1 kg/ha/yr of sulfur is obtained from dry deposition on the ecosystem. The deposition velocity for particulate sulfur is estimated to be about 0.1 cm/s and the deposition velocity for sulfur dioxide is 0.9 cm/s. Some biogeochemical relationships of sulfur for the Hubbard Brook Forest are presented.

1. Introduction

In recent years ecologists have become increasingly interested in the flow of nutrients and energy through ecological systems. This has included both an evaluation of the size and the rate of exchange between various "pools" within the ecosystem, and studies of the inputs and outputs of nutrients and energy for that ecosystem. The Hubbard Brook Ecosystem Study, a study of a northern hardwood forest ecosystem, was begun in 1963 and based on a nutrient flux and cycling model (Bormann and Likens, 1967; Likens and Bormann, 1972). This model permitted the construction of ecosystem nutrient budgets based on the measurement of chemical inputs and outputs. Further studies of the intrasystem cycles including the determination of plant biomass and productivity, litterfall, decomposition, leaching, geologic weathering, etc., allow us to quantify elemental cycles for our ecosystem.

The Hubbard Brook Experimental Forest is located in north–central New Hampshire within the White Mountain National Forest at an elevation of 200 to 1000 m. The vegetation is characterized by an uneven-aged, well-stocked, second-growth northern hardwoods forest with coniferous species occurring at the high elevations and on north-facing slopes. The major overstory tree species are sugar maple, *Acer saccharum*, American beech, *Fagus grandifolia*, yellow birch, *Betula alleghaniensis*, and red spruce, *Picea rubens*. The forest was extensively cut between 1909 and 1917, but no major cutting or fire has occurred since. Mean annual precipitation is 130 cm and mean annual streamflow is 80 cm. Detailed descriptions of the geologic, hydrologic and climatic conditions have been reported elsewhere (cf. Likens et al., 1977).

The biogeochemistry of sulfur plays a key role in the overall function of watershed-ecosystems at Hubbard Brook. Sulfate is the predominant anion entering the ecosystem in precipitation both on a mass basis and on an ionic basis (Table 1). Ammonium and calcium are the major cations in precipitation on a mass basis, whereas on an ionic basis hydrogen ion predominates. Based on 10 years of precipitation analysis, the average input of sulfate–sulfur in precipitation is 12.7 kg/ha/yr.

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Table 1. *Mean annual bulk precipitation inputs and stream-water outputs weighted for volumes of water of various elements in kg/ha and μeq/liter for undisturbed watersheds of the Hubbard Brook Experimental Forest (1963–1974) [from Likens et al., 1977]*

	Precipitation inputs		Stream-water outputs		Net gain or loss
Element	kg/ha	μeq/l	kg/ha	μeq/l	(kg/ha)
Ca	2.2	7.98	13.9	82.3	−11.7
Mg	0.6	3.29	3.3	31.3	−2.7
K	0.9	1.79	2.4	5.9	−1.5
Na	1.6	5.22	7.5	37.8	−5.9
NH_4	2.9	12.2	0.34	2.2	2.6
Al	—	—	3.4	26.6	−3.4
H	0.97	72.4	0.10	11.9	0.87
SO_4	38.0	60.3	52.8	131.	−14.8
NO_3	19.0	23.7	16.1	32.4	2.9
Cl	6.2	13.3	4.6	15.5	1.6
PO_4	0.11	.253	0.02	0.1	0.09
Si	—	—	23.7	—	−23.7

Since these ecosystems are small watersheds, the only nongaseous loss of sulfur occurs as dissolved or particulate matter in drainage water. These are the output data presented in Table 1.

In contrast to a large week-to-week variation in precipitation chemistry, the stream-water sulfate concentrations as well as other chemical constituents of stream water at Hubbard Brook are relatively constant during the year even though the discharge of water may range over four to five orders of magnitude. On a mass basis (kg/ha) sulfate and dissolved silica are the dominant substances in stream water, whereas on an ionic basis, sulfate and calcium dominate. The predominance of sulfate is striking. The average annual gross output of sulfate–sulfur is 17.6 kg/ha which represents 36% of the average total dissolved substance.

Knowing chemical inputs in precipitation and losses in stream water, it is possible to calculate net budgets for these watershed-ecosystems for all chemicals except those which have a prominent gaseous phase. It is apparent from this type of a budget that there is a significant net loss of calcium, magnesium, sodium, aluminum, sulfur and dissolved silica (Likens et al., 1977). The primary source of these element losses is the weathering of primary and secondary minerals. However, there is relatively little sulfur in the parent soil material at Hubbard Brook. Therefore, this net loss of sulfur cannot be accounted for unless there is an input to the ecosystem other than that measured in bulk precipitation.

Utilizing the ecosystem approach (Fig. 1), the integration of the various specialized, sometimes diverse, studies at Hubbard Brook contribute in a meaningful way to our understanding of sulfur in the northern hardwood ecosystems.

2. Sulfur diagram

Our current understanding of the biogeochemistry of sulfur within the northern hardwood ecosystem is given in Fig. 1. The boxes within the ecosystem represent pools of sulfur in kg/ha. The arrows between the boxes are annual fluxes in kg/ha/yr. The forest is an aggrading ecosystem with an annual net accumulation of biomass (Whittaker et al., 1974). The annual rate of sulfur accumulation in the biomass is presented in parentheses within each box.

The above and below ground living biomass pools along with the current rate of biomass accumulation were calculated using dimension analysis (Whittaker et al., 1974). Sulfur in the biomass was calculated by combining these biomass values with the sulfur analyses of the various plant parts (Likens and Bormann, 1970). The living biomass within the ecosystem contains

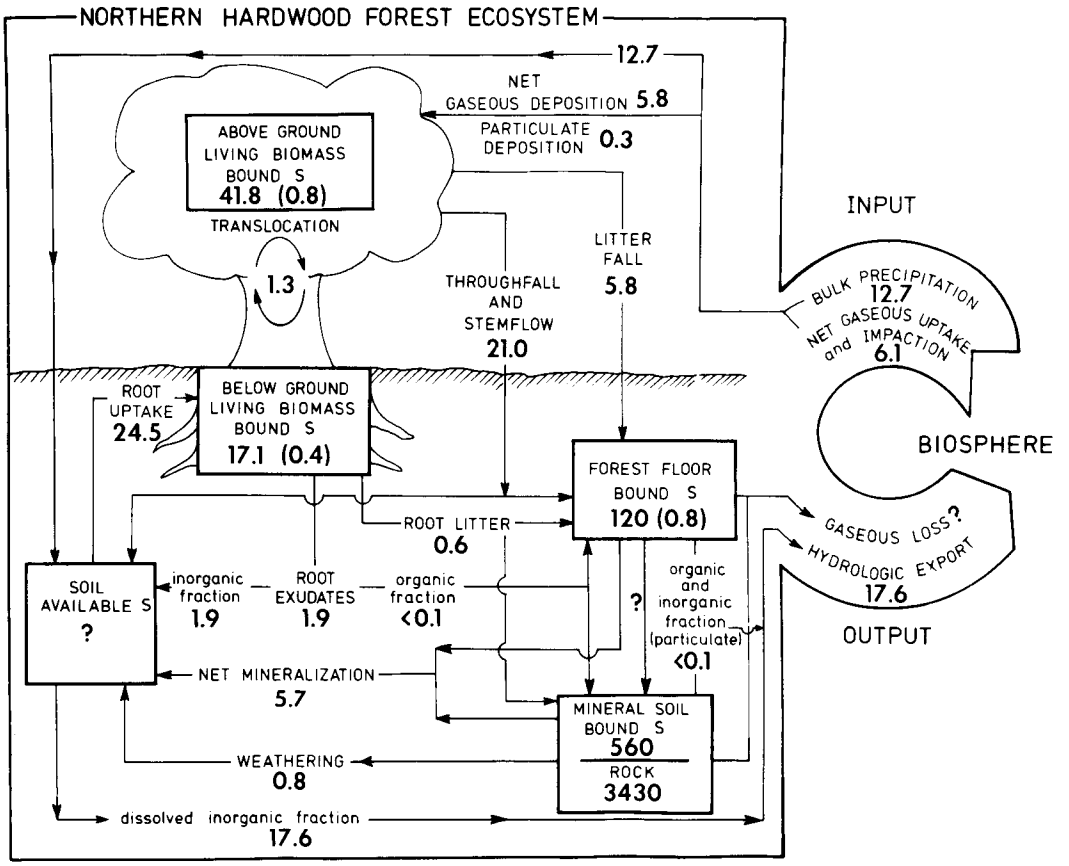

Fig. 1. Annual sulfur budget for an aggrading forested ecosystem at Hubbard Brook. Standing crop values are in kg/ha and sulfur fluxes are in kg/ha/yr. Values in parentheses represent annual accretion rates (modified from Likens et al., 1977).

approximately 59 kg/ha of sulfur (41.8 kg/ha above ground and 17.1 kg/ha below ground). At the present time the accretion rate for sulfur within the living biomass is in excess of 1 kg/ha/yr.

The amount of sulfur in the forest floor has been measured and the rate at which sulfur is accumulating on the forest floor was estimated from a successional sequence of northern hardwood stands ranging in age from 3 to 200 years (Covington, 1976). The amount of sulfur bound in the dead organic matter on the forest floor to a depth of 8.9 cm is 120 kg/ha or almost twice that found in the living biomass.

The amount of sulfur in the soil, including organic matter below 8.9 cm and to a depth of 45 cm, unquestionably dominates the various pools within the ecosystem. The living biomass contains only 1.4% of the sulfur in the ecosystem, the forest floor contains 2.9% and the underlying soil contains almost 96% of the sulfur. However, based on a weathering rate of 1.5 metric tons of bedrock per hectare per year (Likens et al., 1977), the rate at which this sulfur is released to the available sulfur pool through weathering is very slow. We calculate that weathering contributes 0.8 kg/ha/yr or only about 2% of all sulfur taken up by the vegetation annually.

The cycling of sulfur in stemflow, throughfall, root exudates, and above ground litter has been measured, and estimates of root litter have been made (Eaton et al., 1973; Smith, 1976; Gosz et al., 1972; and Whittaker et al., 1974).

The annual uptake of sulfur by plants from the soil was calculated by adding the annual ac-

cumulation of sulfur in biomass to the sulfur transferred annually from living vegetation to the soil through stemflow and throughfall minus particulate deposition, root exudates, and above and below ground litter.

The direct absorption of atmospheric SO_2 by plants is well known, particularly for agricultural crops (e.g., Olsen, 1956; Hoeft et al., 1972). It is also known that airborne particulate matter can be deposited on surfaces such as plants. Although leaching is a recognized source, the large amounts of sulfur in throughfall and stemflow at Hubbard Brook (Eaton et al., 1973) suggest that sulfur aerosols are being deposited on the vegetation surfaces, particularly during the summer.

Summing the net fluxes between compartments and across the ecosystem boundary in Fig. 1 enables us to estimate that 6.1 kg/ha of sulfur is added to the ecosystem each year from dry deposition and direct absorption of SO_2. To the best of our knowledge, this is the first time that the inputs of sulfur by dry deposition have been estimated for an entire ecosystem. Our estimate would indicate that the forested ecosystem at Hubbard Brook is receiving 32% of its sulfur by this means.

The major factors which determine the precision of this calculation are the accretion rates for both the living and dead biomass and the flux rates across the ecosystem boundary. The accretion rate for the living biomass is based on an average of two periods, 1956–1960 and 1961–1965. The accretion rate for the first 5-yr period (1956–1960) was 1.48 kg S/ha/yr and for the second (1961–1965) was 0.83 kg S/ha/yr. The average is 1.2 kg S/ha/yr (Fig. 1) with a range spanning 0.6 kg S/ha/yr. Accretion rate for dead biomass in the forest floor was determined from a regression analysis of data for a 30-yr period (from 30 to 60 years following clear cutting of the forest; Covington, 1976). *The mean and standard error of the regression coefficient* for these data was 0.8 $\pm$ 0.48 kg S/ha/yr. Precipitation input and stream-water output values (kg/ha/yr) for sulfur in Fig. 1 represent averages weighted for volume of water for a 10-yr period (Likens et al., 1977). The arithmetic means and standard errors for weighted annual values during this period, were 12.5 $\pm$ 0.8 kg S/ha/yr for precipitation and 17.5 $\pm$ 1.4 kg S/ha for stream water. Thus, net annual losses of sulfur were 5.0 $\pm$ 0.9 kg/ha/yr. We have no error estimate for the weathering rate. However, very appreciable errors in this weathering rate would be necessary to seriously affect the overall balance. Therefore, we believe that the gaseous and particulate deposition of sulfur, which was determined by difference in Fig. 1 is essentially correct with a standard error probably less than 35% of the value.

We have not measured gaseous loss of sulfur from the ecosystem. If this loss were significant, our estimate of particulate and gaseous inputs would be a *net* input and would be conservative. R. A. Rasmussen (personal communication) has estimated that the gaseous losses from the ecosystem might be in the order of 1 kg/ha/yr. This is in line with the estimates of dimethyl sulphide loss from forest litter (Lovelock et al., 1972). These gaseous losses from our ecosystem would increase our estimate of gaseous and particulate inputs to about 7 kg/ha/yr.

For a period of two years, lead candles were used in an attempt to characterize the sulfur dioxide concentrations in the atmosphere at Hubbard Brook. We are aware of the inherent problems of measuring SO_2 with lead candles; however, it is apparent from Fig. 2 that there is a strong seasonal relationship in the SO_2 concentration, with a summer low and winter high. These data along with a few SO_2 analyses using the West–Gaake method would indicate that ambient SO_2 concentrations range between 0.5 and 10 $\mu g/m^3$ with an annual mean of 2.5 $\mu g/m^3$. Sulfur dioxide monitoring at Whiteface Mountain, New York, a remote site in north-central New York State, also indicate that the levels of SO_2 are below 10 $\mu g/m^3$ (V. Mohnen, personal communication).

Bulk precipitation collectors are probably inefficient in collecting aerosols, particularly those smaller than 1 μm. Atmospheric particulates and aerosols, therefore, have been collected at Hubbard Brook for more than two years with a modified two-stage Lundgren impactor with after filters. With this device, particle sizes can be separated into the ranges of 0.1 to 0.65 μm, 0.65 to 3.6 μm, and 3.6 to 20 μm. These samples were chemically analyzed at the Crocker Nuclear Laboratory at the University of California, Davis, using ion-excited X-ray emission.

Preliminary analysis of the impactor data indicates that sulfur and silicon are the two most abundant elements in these aerosols (Table 2). Sulfur concentrations range between about

200 ng/m³ and 2000 ng/m³ with an annual mean of 980 ng/m³. The majority (73%) of the particulate sulfur was found in the smaller aerosols (0.1 to 0.65 μm). Whereas, 25% was found in the 0.65 to 3.6 μm size range and only 2% was found in the 3.6 to 20 μm size range. Our data indicate that the highest concentrations of particulate sulfur occur during mid-summer, and the lowest concentrations occur during the winter. This pattern is similar to the sulfate concentrations in precipitation, which has a summer maximum (Likens et al., 1972; Hornbeck et al., 1976; Likens et al., 1977), but unlike the pattern we see for sulfur dioxide concentrations (Fig. 2).

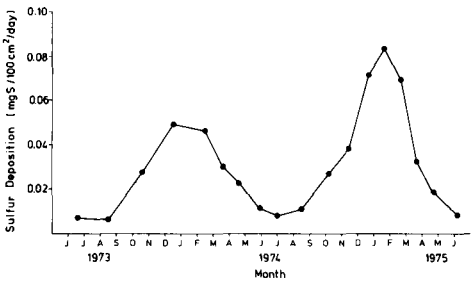

Fig. 2. Atmospheric sulfur collected by lead peroxide candles at Hubbard Brook, New Hampshire.

Using the mean concentration of 2.5 μg/m³ for SO_2 and 1 μg/m³ for particulate sulfur and assuming an ecosystem loss of 1 kg/ha as sulphides, it is possible to calculate an average deposition velocity of 0.64 cm/s for the airborne sulfur to the Hubbard Brook ecosystem. However, Chamberlain (1966) has shown that the deposition velocity for small atmospheric aerosols on grass is much less than this. Therefore, if we calculate the deposition velocity for only the particulate sulfur using Chamberlain's deposition velocities and our known particle size classes, we obtain a mean deposition velocity of 0.10 cm/s for the particulate sulfur at Hubbard Brook. This calculation also indicates that the particulate matter inputs may be much less

Table 2. *Mean annual concentration of various elements in aerosols at the Hubbard Brook Experimental Forest together with the percentage within each of three size classes. Sampling took place 1.5 m above the ground within a clearing in the forest between 1974 and 1976*

	Percent			
Element	Stage 1 (3.6–20 μm)	Stage 2 (0.65–3.6 μm)	Stage 3 (0.1–0.65 μm)	Mean annual concentration (ng/m³)
S	2	25	73	982
Si	43	17	40	592
Na	28	32	40	168
Al	58	20	22	146
Fe	43	26	31	136
K	34	19	47	133
Ca	44	21	35	98
Pb	3	14	83	89
Mg	21	21	58	63
Ba	8	4	88	53
Cl	57	17	26	53
Zn	13	37	50	29
Ti	41	20	39	25
V	5	6	89	23
Br	0	40	60	17
Cr	7	5	88	16
Mn	19	17	64	16
Ni	17	5	78	12
Cu	28	10	62	11

than the gaseous inputs contributing only about 0.3 kg S/ha/yr. It was then possible to calculate a deposition velocity of 0.9 cm/s for the SO_2 alone. This value agrees well with previously published estimates of deposition of gaseous sulfur (see, for example, Garland, 1976).

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ВВОД СЕРЫ В ГАЗОВОЙ И ДИСПЕРСНОЙ ФАЗЕ В ЛЕСНУЮ ЭКОСИСТЕМУ

Сульфаты являются основным анионом в осадках над экспериментальным лесом Хаббард Брук, северным строевым лесом в северной части центрального Нью-Хэмпшира. Сера является также доминирующим элементом твердой фракции аэрозоля. Потери серы из экосистемы с потоками воды превышают ее приток с осадками и путем выветривания. С помощью экосистемного метода можно оценить по балансу, что сухое отложение серы в экосистеме составляет 6,1 кг/га в год. Скорость осаждения для серы в дисперсной фазе оценивается в 0,1 см/с, а для двуокиси серы—в 0,9 см/с. Представлены некоторые биогеохимические соотношения для серы в исследуемом лесу.