Forest ecosystem SO$_4$–S input-output discrepancies and acid rain: are they related?

Bruce Haines


The SO$_4$–S inputs exceed SO$_4$–S outputs in rain forests at San Carlos de Rio Negro, Amazonas, Venezuela and at La Selva, Costa Rica. Hypotheses to explain excess of inputs over outputs include: 1) accumulation of S in biomass, 2) accumulation of S in soil, 3) conversion of SO$_4$–S to organic S compounds which leave the system in drainage water, 4) conversion of SO$_4$–S to volatile S compounds which leave as gases, and 5) estimation errors. Acid rain occurs at both sites. If the S were volatilized out of the forest, oxidized in the atmosphere to SO$_4$ (4 above) then washed out of the atmosphere by rain, the resulting quantity of H$_2$SO$_4$ would be sufficient to account for the rainfall acidity observed in the field in Costa Rica.

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**Input-output discrepancies for SO\(_4\)-S**

The inputs and outputs of SO\(_4\)-S have been estimated by various workers for seven terrestrial ecosystems in the Americas (Tab. 1). Two of the systems showed an excess of outputs over inputs. Five of the systems, an agricultural watershed, and two deciduous forests in the Southeastern United States, and a Central and a South American rainforest had an excess of inputs over outputs. In these studies the inputs of S in rain water and the outputs of S in stream water or in lysimeter water were measured as SO\(_4\)-S. The discrepancies reported from these independent investigations were -2.7 and -4.9 kg ha\(^{-1}\) yr\(^{-1}\) for the systems showing net S losses while values were between +4 and +11 kg ha\(^{-1}\) yr\(^{-1}\) for systems showing apparent net S accumulation.

This paper considers the five systems showing an excess of SO\(_4\)-S inputs over outputs. Alternative hypotheses to account for these discrepancies are 1) S is being accumulated in new forest growth at a faster rate than it is being released through death and decay, 2) S is being stored in the soil, 3) S is being converted to organic-S compounds or to inorganic S compounds such as H\(_2\)S which leave the forest in streamwater, 4) S is being reduced to H\(_2\)S, dimethylsulfide or other volatile S compounds which leave the forest as gases, or 5) there are errors in one or more of the estimated variables and the direction and magnitudes of these errors are the same in the five independent studies reporting the discrepancies (Tab. 1).

**Acid rain**

Acid rain is a subject of concern to environmental scientists in Europe and North America (Hutchinson and Havas 1980) where it is thought to result at least in part from the scavenging of oxides of N and S from the atmosphere by rain. These oxides are formed during the burning of fossil fuels (Likens 1976, MacCracken 1978, Glass et al. 1979). The occurrence of acid rain of pH 4.6-4.7 at San Carlos de Rio Negro, Venezuela (Clark et al. 1980, Haines et al. 1982) and at Manaus, Brazil, Anon. 1972, Ungemach 1970) remote from sources of industrial pollution, and rain of pH 4.66 in a Costa Rican rain forest (Johnson 1979) call into question the industrial pollution model as an explanation for all acid rain.

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**Tab. 1. Annual sulfur budgets for tropical and temperate research sites expressed in kg S ha\(^{-1}\) yr\(^{-1}\) and predicted pH based on rainfall amount and S discrepancy.**

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>Years of record</th>
<th>Input</th>
<th>Output</th>
<th>Net change</th>
<th>Rainfall (m)</th>
<th>Predicted pH (I)</th>
<th>Observed pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rainforest, La Selva, Costa Rica (A)</td>
<td>1</td>
<td>12.5</td>
<td>0.8</td>
<td>+11.7</td>
<td>3.4</td>
<td>4.66</td>
<td>4.66</td>
</tr>
<tr>
<td>Rainforest, San Carlos de Rio Negro, Amazonas, Venezuela (B, C)</td>
<td>1</td>
<td>15.16</td>
<td>11.22</td>
<td>+4</td>
<td>3.5</td>
<td>5.1</td>
<td>4.6 (J)</td>
</tr>
<tr>
<td>Agricultural ecosystem, Little River, Tifton, GA (D)</td>
<td>1</td>
<td>24.81</td>
<td>16.99</td>
<td>+7.82</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Deciduous hardwood forests</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Coweeta Hydrologic Laboratory North Carolina (E, F)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Undisturbed watersheds</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watershed 2</td>
<td>3</td>
<td>9.6</td>
<td>1.40</td>
<td>+8.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watershed 14</td>
<td>2</td>
<td>12.04</td>
<td>1.63</td>
<td>+10.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watershed 18</td>
<td>3</td>
<td>10.66</td>
<td>1.38</td>
<td>+9.27</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watershed 32</td>
<td>2</td>
<td>14.62</td>
<td>2.52</td>
<td>+12.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watershed 34</td>
<td>2</td>
<td>13.15</td>
<td>1.50</td>
<td>+11.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average for undisturbed watersheds</td>
<td></td>
<td></td>
<td></td>
<td>+10.33</td>
<td>2.16</td>
<td>4.52</td>
<td>4.3-4.5</td>
</tr>
<tr>
<td>2. Walker Branch, Tennessee (G)</td>
<td>3</td>
<td>18.1</td>
<td>11.5</td>
<td>+6.6</td>
<td>1.51</td>
<td>4.56</td>
<td>4.2</td>
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<tr>
<td>3. Hubbard Brook, New Hampshire (H)</td>
<td>11</td>
<td>12.66</td>
<td>17.59</td>
<td>-4.93</td>
<td>1.25</td>
<td>4.13</td>
<td></td>
</tr>
<tr>
<td>Coniferous forest, (Douglas fir plantation), Thompson, Washington (A)</td>
<td>1.2</td>
<td>4.1</td>
<td>6.1</td>
<td>-2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A. Cole and Johnson 1977, Johnson et al. 1979
B. Jordan et al. 1980
C. Jordan, pers. comm.
D. Todd 1980
E. Swank and Douglass 1975
F. Swank and Douglass 1977
G. Shriner and Henderson 1978
H. Likens et al. 1977
I. Rainfall pH predicted from sulfur discrepancy = 1/log ((net change in S)/(Equiv. wt)/(Rain volume))
J. Clark et al., Haines et al. 1982
Sulfur accumulation in biomass and in soils and loss of reduced sulfur compounds in drainage water

Accumulation of S in forest biomass (Hypothesis 1) seems unlikely to explain S input-output discrepancies in the eastern US. The production of new tissue balances the decay of old tissue (Jordan et al. 1980). The soil at La Selva was demonstrated, in laboratory studies, to adsorb SO\(_4\) (Johnson et al. 1979, Johnson et al. 1980). The soil at La Selva may be accumulating in the soil but they also say that they cannot account for the conversion of SO\(_4\) to H\(_2\)S in the soil. Any H\(_2\)S could have been lost through the atmosphere.

The soils from the Walker Branch, Coweeta, Hubbard Brook, and Thompson sites (Tab. 1) can also adsorb SO\(_4\) in short term laboratory equilibrations (Johnson et al. 1980). Whether adsorption occurs at a sufficient rate in the field in the presence of microbial activity to account for the magnitude of the SO\(_4\)-S input-output discrepancies at these sites is less clear. The most direct evidence for long term SO\(_4\)-S accumulation in soil is from the Walker Branch site where Johnson et al. (1981) found significantly more insoluble SO\(_4\)-S within the 0-15 cm layer of soil exposed to wet and dry atmospheric inputs than in adjacent soil protected from such inputs by a house for the last 90 yr.

The possible loss of organic-S compounds or H\(_2\)S in water draining the ecosystems (Hypothesis 3) at San Carlos de Rio Negro, La Selva, Tifton, and Coweeta has yet to be measured.

Proposed relationship between sulfur discrepancies and acid rain

For the rainforest at La Selva, Costa Rica (Tab. 1), if Hypothesis 4 above were correct, the total input 12.5 kg S ha\(^{-1}\) yr\(^{-1}\) entering the forest as bulk precipitation would be comprised of a "background" component of 0.8 kg S ha\(^{-1}\) yr\(^{-1}\) derived from soil dust and possibly combustion products and a "recycled" component of 11.7 kg S ha\(^{-1}\) yr\(^{-1}\) resulting from the volatilization of S compounds from the forest, the oxidation of these compounds to SO\(_4\), and their return in rain. If for example 11.7 kg (1.17 g S m\(^{-2}\) yr\(^{-1}\)) of SO\(_4\)-S were volatilized, oxidized to H\(_2\)SO\(_4\), and returned in the 3.4 m of annual rainfall, the resulting volume weighted annual average concentration of each S and H would be 2.15 x 10\(^{-6}\) equivalents l\(^{-1}\). The corresponding pH would be 4.66. The pH reported by the authors was also 4.66. They attribute the acidity to the activity of a local volcano, Volcan Irazu, but this seems unlikely because the prevailing trade winds at La Selva come from the east off of the Gulf of Mexico (Goode and Espenshade 1957) while the volcano lies to the south of La Selva. For La Selva, the authors suggest that SO\(_4\)-S is accumulating in the soil but they also say that they cannot account for the conversion of SO\(_4\) to H\(_2\)S in the soil. Any H\(_2\)S could have been lost through the atmosphere.

At San Carlos there is also evidence for the loss of volatile phosphorus from the water logged forest soils. Herrera (1979) placed pairs of polypropylene vessels containing 5 N HNO\(_3\) under inverted polypropylene containers on the forest floor. One vessel of each pair was closed to the atmosphere and served as a blank while the other was covered with a screen to exclude insects. Pairs of vessels were maintained on the forest floor for periods ranging from 1 to 30 d. The P concentrations were determined and the differences between blank and open vessels were plotted against exposure time. The slope was 0.14 µg P m\(^{-2}\) d\(^{-1}\) (r = 0.92). Although the trapping efficiency of the method is not known and the emission rate could account for only 53 µg P m\(^{-2}\) yr\(^{-1}\) (5 x 10\(^{-6}\) eq m\(^{-2}\) yr\(^{-1}\)), qualitatively at least it demonstrates the loss of volatile P compounds from the forest floor. Phosphorus volatilization might also contribute to acid rain.

Sulfur compounds are known to be volatilized from living plant leaves (Spaleny 1977), from decaying leaves (Lovekock et al. 1972), and from soils (Bremner and Steele 1978, Farwell et al. 1979). Emission rates from decaying leaves were 10 to 100 times higher than from living leaves of the same species (Lovekock et al. 1972). Rates of sulfur biogenesis are variable and appear to increase from temperate to tropical sites. Sulfur biogenesis from fresh water swamp and upland soils in the eastern US ranged from 0.002 to 0.36 g S m\(^{-2}\) yr\(^{-1}\) but reached 152 g S m\(^{-3}\) yr\(^{-1}\) in a coastal salt marsh (Adams et al. 1979, 1980). In France, emissions of H\(_2\)S from several lawns and from a pine forest on aerobic soils ranged from 0.006 to 0.22 g S m\(^{-2}\) yr\(^{-1}\) (Delmas et al. 1980). Except for the salt marsh, which is enriched with seawater SO\(_4\), these annual emission rates for the
eastern US and French soils are between 1 and 50 times smaller than the 4 and 11 kg S ha\(^{-1}\) yr\(^{-1}\) (0.4 and 1.1 g S m\(^{-2}\) yr\(^{-1}\)) discrepancy in the S balance for the Amazon and Costa Rican rainforests. However, in Ivy Coast, West Africa, emissions of H\(_2\)S from humid forests ranged between 0.24 and 2.4 g S m\(^{-2}\) yr\(^{-1}\) (Delmas et al. 1980). This range brackets the magnitude of the S discrepancy in the American rainforests. Henry and Hidy (1980) estimate that microbial sulfate reduction in carbon poor fresh water sediments should release about 7.2 kg S ha\(^{-1}\) yr\(^{-1}\) (0.72 g S m\(^{-2}\) yr\(^{-1}\)) which is of the same magnitude as the S discrepancies for the Amazon and Costa Rican rainforests. Volatilization of H\(_2\)S from Amazon floodplain lakes near Manaus was reported by Brinkmann and Santos (1974) who argue that emitted S is recycled back to the forest on a local or regional scale by convective rainstorms. Evidence for the volatilization of both S and P from the rainforest at Manaus, Brazil was derived from studies of aerosol chemistry by Lawson and Winchester (1979).

Decomposing litter may be an important site for volatilization. Emission rates were positively related to soil organic matter by Farwell et al. (1979). Compared to soils, decomposing plant residues, animal manures and sewage sludge have higher rates of emission of S compounds (Bremner and Steele 1978). In Ivy Coast, emissions of H\(_2\)S from humid forests were calculated from H\(_2\)S profiles for the whole forest (Delmas et al. 1980) thus they involve potential emissions from decomposing leaf litter as well as from the soil.

If most of the volatile S loss were from litter, are the sulfur fluxes in falling litter of sufficient magnitude to account for the S input-output discrepancy? At San Carlos de Rio Negro, for forest on oxisol soil, the average annual litter fall is 579 g m\(^{-2}\) yr\(^{-1}\) (Jordan and Murphy 1982). Assuming a foliar S content of 0.2% (Shriner and Henderson 1978, Haines unpubl.), an estimated S flux in litter would be 1.1 g S m\(^{-2}\) yr\(^{-1}\) or 11 kg S ha\(^{-1}\) yr\(^{-1}\) which is greater than the 0.4 g S m\(^{-2}\) yr\(^{-1}\) input-output discrepancy. Similar calculations can be made for Coweeta using the annual litter fall of leaves, stems, fruits, flowers and debris from Cromack and Monk (1975) of 437 g m\(^{-2}\) yr\(^{-1}\) in conjunction with sulfur concentrations given in Shriner and Henderson (1978) to provide an estimate of 0.8 g S m\(^{-2}\) yr\(^{-1}\) which is close to the average 1.03 g S m\(^{-2}\) yr\(^{-1}\) input-output discrepancy. At Walker Branch the S flux in litterfall of 0.84 g S m\(^{-2}\) yr\(^{-1}\) is of the same order of magnitude as the 0.66 g S m\(^{-2}\) yr\(^{-1}\) input-output discrepancy (Shriner and Henderson 1978).

Estimation of rainfall pH based on the assumption that the sulfur volatilization hypothesis (hypothesis 4) is correct can only be an approximation. While rain pH may be influenced by volatile phosphorus, the hydrolysis of NH\(_3\) to NH\(_4^+\) will change the pH by consuming H\(^+\) (Garrels et al. 1975). The magnitudes of NH\(_4^+\) volatilizations from Costa Rican and Venezuelan rainforests are presently unknown but seem likely to be much less than the few rates determined in temperate agricultural regions where fertilizer NH\(_3\) and the decomposition of animal urine and manure are sources of volatile NH\(_3\). Annual estimates of ammonia volatilization from a mosaic of pasture, cropland and forest in Germany and from pasture in Australia approached 8 and 100 kg ha\(^{-1}\) respectively (Lenhard and Gravenhorst 1980, Denmead et al. 1974). Junge (1958) found NH\(_4^+\) content of rain to be negatively related to soil acidity. He claimed that below soil pH of 6, loss of volatile NH\(_3\) did not occur, thus soil pH largely controls the NH\(_4^+\) content of rain. Because the partial pressure of NH\(_3\) decreases both with increasing relative humidity and with increasing solution acidity (Stelson and Seinfeld 1982) low NH\(_3\) volatilization rates are expected from the very humid and acid Venezuelan and Costa Rican rain forests which have soil solution pH values of 3.7 (Haines unpubl.) and 5.66 (Johnson et al. 1979) respectively.

Because pH is a log scale the predicted rainfall pH values are relatively insensitive to changes in the magnitude of the S input-output discrepancy. For the tropical rainforest at La Selva, if the discrepancy were reduced by half from 11.7 kg to 5.85 kg, the resulting pH at La Selva would increase to about 4.9 while for the deciduous forest at Coweeta and Walker branch, the value would increase to pH 4.8. Doubling the S discrepancy for the rainforest would decrease the pH to 4.4 and for the temperate forests to 4.3.

If the S discrepancy is the result of S biogenesis then our understanding of the gas phase of the global S cycle would be changed. Indeed, Henry and Hidy (1980) argue for direct measurement of biogenic sulfur emissions "... especially in the tropics ..." along with improved estimates of anthropogenic emission to better characterize the global sulfur budget. In a review of the photochemistry of COS, CS\(_2\), CH\(_3\)SCH\(_3\), and H\(_2\)S, Sze and Ko (1980) conclude that reliable quantitative estimates of emission rates of reduced sulfur compounds from a diversity of ecosystems are still lacking. They call for long term measurements to clarify our understanding of the global sulfur cycle.

Quantification of S emissions is potentially significant for our understanding of the magnitude of biogenic S emissions from tropical forests and for causes of acid rain in remote areas where S biogenesis may partially explain acid rain. The possibility also exists that acid rain in the region of the eastern deciduous forest is the result of combined effects of biogenic sulfur and pollution from the burning of fossil fuels.

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References


Cromack, K., Jr. and Monk, C. D. 1975. Litter production, decomposition and nutrient cycling in a mixed hardwood forest ecosystem. - Progress report. Submitted to the US National Science Foundation.


