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Journal

Journal of Atmospheric Chemistry, 14(1-4)

ISSN

0167-7764

Authors

Bates, TS
Lamb, BK
Guenther, A
[et al.](#)

Publication Date

1992-04-01

DOI

10.1007/BF00115242

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Sulfur Emissions to the Atmosphere from Natural Sources

T. S. BATES¹, B. K. LAMB², A. GUENTHER³, J. DIGNON⁴, AND R. E. STOIBER⁵

¹ NOAA/Pacific Marine Environmental Laboratory, Seattle, WA 98115

² Laboratory for Atmospheric Research, Washington State University, Pullman, WA 99164

³ Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, CO 80303

⁴ Lawrence Livermore National Laboratory, Livermore, CA 94550

⁵ Department of Earth Sciences, Dartmouth College, Hanover, NH 03755

Abstract. Emissions of sulfur gases from both natural and anthropogenic sources strongly influence the chemistry of the atmosphere. To assess the relative importance of these sources we have combined the measurements of sulfur gases and fluxes during the past decade to create a global emission inventory. The inventory, which is divided into 12 latitude belts, takes into account the seasonal dependence of sulfur emissions from biogenic sources. The total emissions of sulfur gases from natural sources are approximately 0.79 Tmol S/a. These emissions are 16% of the total sulfur emissions in the Northern Hemisphere and 58% in the Southern Hemisphere. The inventory clearly shows the impact of anthropogenic sulfur emissions in the region between 35° and 50°N.

1. Introduction

The cycling of sulfur through the troposphere plays an important role in atmospheric acid-base chemistry and in the formation and growth of aerosol particles. During the past century the natural biogeochemical sulfur cycle has been seriously perturbed over many areas of the globe, resulting in highly acidic precipitation and a dramatic increase in aerosol particle populations. The significance of these anthropogenic sulfur emissions, as well as the climatic importance of the natural atmospheric sulfur cycle, are difficult to assess without first quantifying the sulfur emissions from natural sources. Attempts to estimate natural sulfur emissions have been fraught with both a paucity of data and high natural variability.

The increased awareness of the environmental consequences of acidic precipitation has resulted in many recent measurements of both the sources of sulfur to the atmosphere and the processes involved in the cycling of sulfur through the atmosphere. These additional data permit us to re-assess earlier global natural sulfur emission estimates (Andreae, 1986) and to further refine these estimates on regional scales. These regional emission estimates are vital to our understanding of sulfur cycling because the atmospheric lifetime of most sulfur species is on the order of days (Summers and Fricke, 1989). Hence, global or even hemispherical sulfur budgets can obscure the climatic and environmental significance of the atmospheric sulfur cycle. There are, for example, vast regions over the remote oceans where natural sulfur emissions account for essentially all the atmospheric non-sea-salt (NSS) sulfate (Savoie and Prospero, 1989). On the other hand, the dominance of anthropogenic over natural sulfur emissions in the northeastern United States is underemphasized if one considers that globally, natural and anthropogenic sulfur emissions are of the same order of magnitude.

In this review, we combine the data from recent studies to calculate natural sulfur emissions on global, hemispherical, and regional scales. Included in these calculations are estimates of the uncertainties and natural variability.

2. Estimates of Natural Emissions

2.1. MARINE

2.1.1. Oceanic concentrations of volatile sulfur gases. Several volatile sulfur gases are produced biologically (CH_3SCH_3 , CS_2 , CH_3SH , CH_3SSCH_3) and/or photochemically (H_2S , OCS) in the surface waters of the ocean (Andreae, 1986). Of these compounds, dimethyl-sulfide (CH_3SCH_3 or DMS) is the most abundant and is the only compound which contributes significantly to the atmospheric burden of NSS sulfate (Cline and Bates, 1983; Nguyen *et al.*, 1983; Andreae, 1986).

Haas first identified DMS emissions from the marine algae *Polysiphonia fastigiata* in 1935. The precursor of DMS, dimethyl-sulfoniopropionate (DMSP), was isolated from this species by Challenger and Simpson (1948) and the biosynthesis of DMSP from methionine has been demonstrated by Greene (1962). The occurrence of DMSP in marine phytoplankton was first documented by Ackman and coworkers (1966). The DMSP concentration within phytoplankton cells is extremely species specific (Keller *et al.*, 1989) and has been shown to contribute significantly to the intracellular osmotic pressure (Reed, 1983; Vairavamurthy *et al.*, 1985), thus serving to maintain the osmotic balance required for cell growth. DMSP is released from phytoplankton cells both during senescence (Nguyen *et al.*, 1988; Leck *et al.*, 1990) and during zooplankton grazing (Dacey and Wakeham, 1986; Leck *et al.*, 1990) and is then cleaved enzymatically to yield DMS and acrylic acid (Cantoni and Anderson, 1956; Dacey and Blough, 1987).

DMS was reported first in oceanic waters by Lovelock and coworkers (1972) and has subsequently been measured throughout the Pacific (Andreae and Raemdonck, 1983; Cline and Bates, 1983; Barnard *et al.*, 1984; Andreae, 1985; Bates and Cline, 1985; Bates *et al.*, 1987), Atlantic (Barnard *et al.*, 1982; Andreae and Barnard, 1984; Turner and Liss, 1985; Turner *et al.*, 1988; Iverson *et al.*, 1989), and Southern Oceans (Berresheim, 1987; Berresheim *et al.*, 1990). DMS concentrations vary substantially on a regional and seasonal basis, and have been recently summarized by Bates and coworkers (1987) and Cooper and Matrai (1989). Open ocean surface seawater DMS concentrations generally range from 0.5 to 5 nmol/L, and are lowest during the winter months in high latitudes and highest during the summer months at these same latitudes (Bates *et al.*, 1987). On a regional and seasonal basis, the average natural variability of DMS concentrations in the North Pacific Ocean is approximately 30% (Bates *et al.*, 1987). This includes the analytical uncertainty of approximately 10%. The natural variability in DMS concentrations can be much higher in coastal regions where concentrations can vary by an order of magnitude within a two-week period in a given area (Bates and Cline, 1985; Turner *et al.*, 1989; Leck *et al.*, 1990). The lifetime of DMS in surface waters is on the order of one day (Kiene and Bates, 1990) as it is degraded both microbially (Suylen *et al.*, 1986; Taylor and Kiene, 1989) and photochemically (Brimblecombe and Shooter, 1986) and lost to the atmosphere via air-sea exchange.

The other reduced sulfur gases in surface ocean waters have been much less studied. CS_2 is present in surface open ocean waters at concentrations of approximately 16 ± 8 pmol/L (Kim and Andreae, 1987; Lovelock, 1974). The sources and sinks of this compound are largely unknown.

OCS concentrations in surface seawater range from 10 to 100 pmol/L (Rasmussen *et al.*, 1982; Ferek and Andreae, 1983; Turner and Liss, 1985; Johnson and Harrison, 1986). The concentrations can vary diurnally by almost an order of magnitude due to the photochemical production of OCS from organic matter. The source material may be particulate organic sulfur (Ferek and Andreae, 1984) which has been measured in surface seawater at concentrations ranging from 10–100 nmol/L (Matrai, 1989). The hydrolysis of OCS (Elliott *et al.*, 1987) and the decay of sulfur compounds in organic matter (Cutter and Krahforst, 1988) lead to the formation of the sulfide ion. Although the sulfide ion is clearly present in surface seawater in concentrations ranging from 0.1 to 1.1 nmol/L (Cutter and Krahforst, 1988), it is likely complexed with trace metals (Elliott, 1988; Dyrssen, 1989; Elliott *et al.*, 1989; Elliott and Rowland, 1990), and hence, not in a volatile form. The other potentially important volatile species are methanethiol (CH_3SH) and dimethyldisulfide (CH_3SSCH_3). Methanethiol is produced in anoxic marine sediments (Kiene and Visscher, 1987; Sorensen, 1988), in decomposing algal mats (Zinder *et al.*, 1977), and in coastal waters (Leck and Rodhe, 1990), but as yet has not been quantified in open ocean surface seawater. Our experience has shown that methanethiol and dimethyldisulfide can be produced as an artifact of sampling/analysis if plankton cells undergo anaerobic decomposition (Bates, unpublished data).

2.1.2. *Oceanic emissions of volatile sulfur gases.* The amount of oceanic sulfur released to the atmosphere was a major uncertainty in early atmospheric sulfur budgets. Model estimates ranged from 9 Tmol/a (Eriksson, 1963) to 1 Tmol/a (Granat, 1976) and were based solely on the amount of additional sulfur needed to balance the global budget. This wide range of emissions made it extremely difficult to assess the significance of anthropogenic sulfur emissions which were estimated during the early 1970's at approximately 2 Tmol/a (Varhelyi, 1985 and references therein). Although there are still no reliable methods of directly measuring the flux of volatile oceanic sulfur to the atmosphere (Andreae, 1985), the flux can now be calculated from measured seawater and atmospheric sulfur gas concentrations. This eliminates a great deal of the uncertainty from the early model estimates.

The flux of gases across the air-sea interface is calculated from air-sea exchange models (Liss, 1973) which predict that the flux is proportional to the product of the concentration difference across the air-sea interface and a first-order exchange coefficient ($V_{(p)}$) such that:

$$\text{flux} = V_{(p)} * \{[S] - b[S_{air}]\} \quad (1)$$

where $b[S_{air}]$ is the equilibrium solubility concentration, (b = Bunsen coefficient, $[S_{air}]$ = atmospheric partial pressure) and $[S]$ is the measured concentration of the sulfur gas in the surface ocean. For DMS, the dominant volatile sulfur compound, the concentration calculated assuming equilibrium solubility is quite small relative to the observed surface water DMS values (Cline and Bates, 1983; Barnard *et al.*, 1982), hence the flux of DMS = $V_{(p)} * [\text{DMS}]$. The exchange coefficient is a function of both wind speed (Smethie *et al.*, 1985; Liss and Merlivat, 1986) and the molecular diffusivity of the gas (Holmen and Liss, 1984; Ledwell, 1984), and has been summarized for DMS by Bates and coworkers (1987). The root mean square of the uncertainties in these flux calculations is approximately 66%, based on the standard deviation of the seasonally averaged concentrations (30%), the range of potential exchange coefficients (30%), and the calculated molecular diffusivity (50%).

The first global ocean-to-atmosphere DMS flux estimates, based on observations in the Atlantic and Eastern Tropical Pacific, suggested a value near 1 Tmol/a (Andreae and Raemdonck,

1983; Galloway, 1985; Andreae, 1986). More recent calculations, taking into account the seasonality of DMS concentrations and a much larger data base, have reduced the calculated global flux to 0.5 ± 0.33 Tmol/a (Bates *et al.*, 1987). The flux of OCS (Rasmussen *et al.*, 1982; Ferek and Andreae, 1984; Johnson and Harrison, 1986) and CS₂ (Kim and Andreae, 1987) have been estimated at 1–2% of the DMS flux. Presently, the major uncertainty in calculating the total air-sea exchange of volatile sulfur is in the flux of H₂S. Recent atmospheric measurements by Saltzman and Cooper (1988) suggest that oceanic H₂S may account for approximately 10% of the NSS sulfate in the marine boundary layer. The implication is that the flux of H₂S from the ocean to the atmosphere may be as high as 10% of the DMS flux. Also in question at this time is the calculated diffusivity of DMS, which has recently been measured at a level approximately 75% lower than previous estimates (Saltzman *et al.*, 1988; Asher *et al.*, 1990). This would result in an oceanic DMS flux of approximately 0.2–0.3 Tmol/a (Cooper and Saltzman, 1990).

The oceanic DMS flux of 0.5 ± 0.33 Tmol/a was obtained from extrapolation of regional and seasonal emissions for the North Pacific Ocean (Bates *et al.*, 1987). These emissions also can be extrapolated regionally and seasonally to the other oceans to obtain a map of oceanic DMS emissions (Table 1 and Figure 1). For the purposes of this analysis, the year has been divided

TABLE 1. Oceanic DMS fluxes

Region	winter summer		PACIFIC		ATLANTIC		INDIAN	
	emiss	emiss	winter	summer	winter	summer	winter	summer
	($\mu\text{mol S/m}^2/\text{d}$)		flux flux		flux flux		flux flux	
			-----		-(10 ⁶ mol/d)		-----	
80°–65°N	0.00	2.11	0	0	0	19	0	0
65°–50°N	1.40	6.57	8	39	8	39	0	0
50°–35°N	2.21	4.96	30	68	19	42	0	0
35°–20°N	2.15	5.14	44	105	26	63	2	4
20°–5°N	4.72	4.45	136	128	51	48	35	33
5°N–0°	4.36	4.01	45	41	16	15	14	13
0°–5°S	4.36	4.01	42	39	14	13	16	15
5°–20°S	4.72	4.45	124	117	42	40	68	64
20°–35°S	2.15	5.14	47	113	22	52	29	69
35°–50°S	2.21	4.96	40	89	24	55	37	84
50°–65°S	1.40	6.57	19	89	12	57	18	83
65°–80°S	0.00	2.11	0	11	0	6	0	3
N. Hemisphere			264	382	120	225	50	49
S. Hemisphere			271	457	114	222	168	317

Fluxes are the product of the emission rate (Bates *et al.*, 1987) and the ocean area (Levitus, 1982). Winter is defined from November to April in the Northern Hemisphere and May to October in the Southern Hemisphere.

Seawater DMS Emissions

Gmoles/degree/season

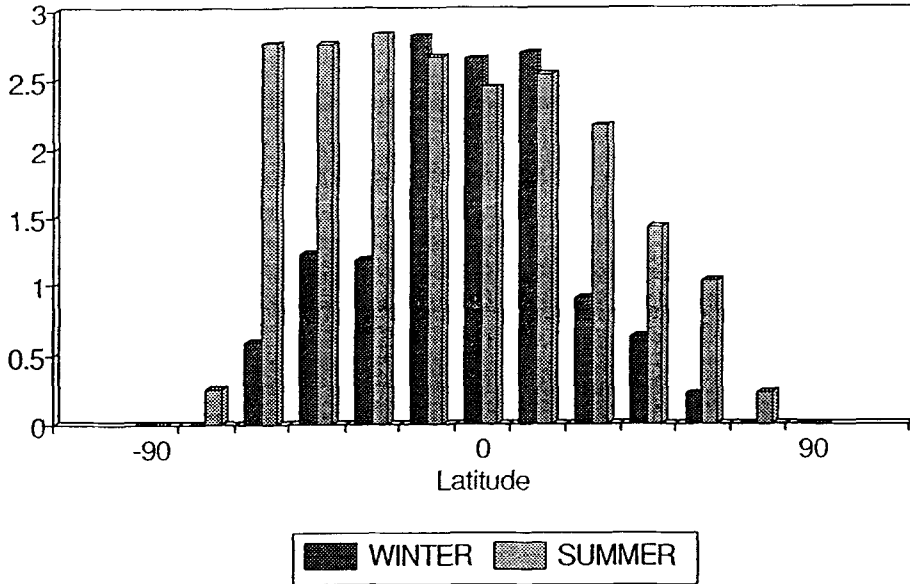


Fig. 1. Biogenic emissions of oceanic DMS to the atmosphere corresponding to the regions shown in Table 1. The equatorial regions have been combined (5°N to 5°S). The data have been plotted per degree of latitude to demonstrate the large source strength in the temperate latitudes of the Southern Hemisphere.

into two seasons, summer and winter, with the midpoints of the seasons offset from the solstices by two months to account for the lag in ocean/soil warming. The globe has been divided into 12 latitude belts (Table 1) after Bates and coworkers (1987) with the areas poleward of 80° being neglected due to snow or ice cover. For simplicity, the coastal ocean has not been separated from the open ocean. Although DMS concentrations along the coast can be appreciably higher than the open ocean with significant local impacts in regions with large continental shelves (Turner *et al.*, 1988; Turner *et al.*, 1989; Leck and Rodhe, 1990), the area of the biologically productive coastal zone with higher DMS flux is generally insignificant on a regional basis (Bates *et al.*, 1990). However, the average fluxes computed here likely underestimate the high point source emissions from coccolithophorid blooms found in the North Atlantic Ocean (Keller *et al.*, 1989).

2.1.3. *Oceanic emissions of non-volatile sulfur species.* Sea-salt particles are ejected into the atmosphere from bubbles bursting at the sea surface (Blanchard and Woodcock, 1957). The magnitude of this flux is largely a function of wind speed (Patterson *et al.*, 1980) and the height at which the flux is calculated (Blanchard, 1985). Measurements show that the mass concentration of sea-salt particles falls off rapidly with increasing height in the lower marine boundary layer, dropping by a factor of two between 20 and 30 m (Blanchard *et al.*, 1984). The

number population decreases even more rapidly, falling by three orders of magnitude between the lower marine boundary layer and the overlying free troposphere at approximately 2 km (Patterson *et al.*, 1980). Typical number populations of coarse ($D_p > 1.0 \mu\text{m}$) sea-salt particles over the open ocean at cloud height are generally $<1.0 \text{ cm}^{-3}$ (Hobbs, 1971; Patterson *et al.*, 1980; Andreae *et al.*, 1986) as opposed to several hundred cm^{-3} for submicrometer non-sea-salt sulfate particles (Bigg *et al.*, 1984). Consequently, although a sea-salt sulfur production rate of 4.1 to 8.6 Tmol/a is calculated for the layer 10 to 20 m above the sea surface (Varhelyi and Gravenhorst, 1983; Blanchard, 1985), this sulfur has a relatively short atmospheric life-time and is not mixed throughout the marine boundary layer. The uncertainties associated with sea-salt emissions are difficult to estimate since the calculations are based on rainfall rates, dry deposition rates, and aerosol concentrations that are a strong function of wind speed and height above the sea surface.

2.2. TERRESTRIAL BIOGENIC

2.2.1. Emission measurements. Terrestrial biogenic emissions are extremely difficult to quantify because they include a number of sulfur species (e.g. H_2S , OCS, CS_2 , DMS, and DMDS) and varied sources (e.g. wetlands, soils and vegetation). Unlike oceanic fluxes, which are calculated from concentration measurements and air-sea exchange models, terrestrial fluxes are measured directly using either enclosure or micro-meteorological techniques. Both techniques have their limitations. The more commonly used enclosure technique can disturb the natural habitat (e.g. damage roots or vegetation, increase the temperature in the enclosure) and cause high and erratic sulfur fluxes (Dacey *et al.*, 1987). Many early measurements which reported extremely high fluxes undoubtedly suffered from these problems. Micro-meteorological techniques require a sulfur gas gradient in the atmosphere and eddy correlation measurements of some other parameter (generally water vapor) since species specific sulfur detectors currently do not have a sufficiently fast response to directly obtain sulfur fluxes. Hence, these measurements are subject to extremely high uncertainties.

The first estimates of terrestrial biogenic sulfur emissions, based on measured fluxes, were done by Adams and coworkers (1981). Since then there have been many studies conducted using increasingly better measurement technology. Recently, Lamb and coworkers (1987) have compiled an extensive data base of over 300 field measurements of natural sulfur emission rates from a wide range of sources at sites in Iowa, Ohio, North Carolina, Washington and Idaho. Bare Mollisol, Histosol, and marshland soils were sampled in addition to surface areas with row crops (celery, carrots and onions) or natural vegetation. Above ground emissions were also measured from agricultural crops (soybean, corn, and alfalfa) and forest canopies (ash, oak, maple, hickory, and pine). The biogenic sulfur emission rates measured by Lamb and coworkers (1987) were from two (for H_2S) to one (other sulfur compounds) order of magnitude lower than measurements reported by Adams and coworkers (1981) at the same sites. Independent data collected simultaneously at the same sites by MacTaggart and coworkers (1987) and Goldan and coworkers (1987) are within a factor of two of the emission rates measured by Lamb and coworkers (1987). Other recently published data (Jorgensen and Okholm-Hansen, 1985; Carroll *et al.*, 1986; Cooper *et al.*, 1987a; Cooper *et al.*, 1987b; de Mello *et al.*, 1987; Andreae and Andreae, 1988; Fall *et al.*, 1988; Staubes *et al.*, 1989) are also within the range of these emission rate estimates. Biogenic sulfur emission measurements now extend from high latitude tundra sites ($0.083 \mu\text{mol/m}^2/\text{d}$ for a 150-day season, Hines and Morrison, 1989) to the tropics (see below, Andreae and Andreae, 1988). The various biogenic sources are reviewed below.

2.2.1.1. Marsh and tideland emissions. Wetlands are a major source of both DMS and H₂S to the atmosphere. DMS is the dominant species from both wet and dry vegetated sites and its emission is strongly dependent on temperature (de Mello *et al.*, 1987) and the abundance of one species, *Spartina alterniflora* (Dacey *et al.*, 1987). H₂S emissions from sediments can vary by over 5 orders of magnitude (0.045 to 4500 $\mu\text{mol}/\text{m}^2/\text{d}$) and generally can be correlated to tidal cycling (Jorgensen and Okholm-Hansen, 1985; Stuedler and Peterson, 1985; Carroll *et al.*, 1986; Cooper *et al.*, 1987a; Cooper *et al.*, 1987b; de Mello *et al.*, 1987). Ninety percent of the emissions can occur in less than 10% of the tidal cycle in a narrow region at the water's edge as the tide rises and falls (Cooper *et al.*, 1987a). Both the species dependency of DMS emissions and the large variations in H₂S emissions make it difficult to develop an emission rate algorithm for wetland emissions.

2.2.1.2. Freshwater emissions. DMS is the major volatile sulfur compound in oxic freshwater lakes (Turner and Liss, 1985), although the concentrations are much lower than that found in seawater. Nriagu and Holdway (1989) measured DMS in the Great Lakes, USA, and found surface concentrations ranging from 0.1 to 1 nmol/L during the summer. The one exception was a sample containing remnants of a diatom bloom which had a concentration near 15 nmol/L. The calculated mean DMS flux from the Great Lakes was 0.5 $\mu\text{mol}/\text{m}^2/\text{d}$ (Nriagu and Holdway, 1989), or 1/10 of the average summer temperate latitude open ocean DMS flux (Bates *et al.*, 1987).

2.2.1.3. Soil emissions. Laboratory studies have indicated that the sulfur flux from soils is not dependent on soil microorganisms leading to the speculation that sulfur compounds are desorbed from soil surfaces (Goldan *et al.*, 1987). The flux of sulfur gases from soils is exponentially dependent on the surface soil temperature (Goldan *et al.*, 1987) and is also a function of soil nitrogen content (Melillo and Stuedler, 1989), soil type, and moisture content (Goldan *et al.*, 1987; Lamb *et al.*, 1987; Staubes *et al.*, 1989). Sulfur fluxes generally range from 0.1 to 2 $\mu\text{mol}/\text{m}^2/\text{d}$ for temperatures between 20 and 30°C (Goldan *et al.*, 1987; Lamb *et al.*, 1987; Andreae and Andreae, 1988; Staubes *et al.*, 1989).

2.2.1.4. Vegetation emissions. Sulfur is an essential nutrient for all plants and is taken into the plant cells both from roots (sulfate) and leaves (SO₂ and other volatile sulfur compounds) (Rennenberg *et al.*, 1984). Plants are the largest sink for atmospheric OCS (Brown and Bell, 1986; Fall *et al.*, 1988; Mihalopoulos *et al.*, 1989), absorbing 3 to 10 Gmol S/a through their open leaf stomata (Goldan *et al.*, 1988). Laboratory studies have demonstrated that OCS uptake by plants is light dependent (Fall *et al.*, 1988). The emission of reduced sulfur gases from plants is also light dependent (Fall *et al.*, 1988) and may be a mechanism by which plants dispose of excess sulfur (Filner *et al.*, 1984; Rennenberg, 1984). Laboratory studies have demonstrated that DMS is the dominant compound emitted from crops (corn, alfalfa, wheat) with the flux increasing exponentially with temperature (Fall *et al.*, 1988). Similar results have been found in the field (Goldan *et al.*, 1987; Lamb *et al.*, 1987). This temperature dependence results in a significant seasonal cycle in biogenic sulfur emissions at higher latitudes. Measurements in the tropics, however, show no significant differences between the wet and dry seasons (Andreae *et al.*, 1990). Sulfur emissions from forests and croplands generally range from 0.4 to 4 $\mu\text{mol}/\text{m}^2/\text{d}$ for temperatures between 20 and 30°C (Goldan *et al.*, 1987; Lamb *et al.*, 1987; Andreae and Andreae, 1988). The emissions calculated below are a gross flux as measured by enclosure techniques and hence do not include OCS uptake by plants.

2.2.2. *Emission algorithms.* A high degree of variability in local natural terrestrial sulfur emissions results in large uncertainties when extrapolating to regional and global scales. While the mechanisms controlling the release of natural sulfur emissions are not well understood, field observations have demonstrated that temperature plays a dominant role and that characteristic temperature-flux patterns can be determined for individual compounds and sources. As temperatures fall below 0°C, sulfur emissions fall below the lower detection limit of the methods used by Lamb and coworkers (1987) which is approximately 45 nmol/m²/d for surface fluxes and 1.8 nmol/m²/d for vegetative emissions. The low emission rate below 0°C is not unexpected considering the minimal biological enzymatic activity which occurs at those temperatures (Tauber, 1949). Sulfur emissions tend to increase logarithmically with increasing temperature for normal ambient temperatures (10°C to 35°C) (Goldan *et al.*, 1987; Lamb *et al.*, 1987). Although biological enzymatic activity normally reaches a plateau at high temperatures, a saturation point is not always apparent in field measurements. This may be the result of temporarily increased emissions which result from the stress experienced by the vegetation enclosed within a chamber at high temperatures (above 35°C).

The emission characteristics observed in field studies suggest that the following form of the Michaelis-Menten equation can be used to mathematically represent the relationship between ambient temperatures and natural sulfur emissions:

$$\log(F) = k_a/(1 + k_b/T) + k_c \quad (2)$$

where F is the sulfur emission rate ($\mu\text{mol}/\text{m}^2/\text{d}$). T is ambient temperature ($^{\circ}\text{C}$), k_a and k_b are rate constants determined by a non-linear least squares fit to emission rate data, and k_c is a rate constant determined by the lower detection limit. Equation (2) provides an emission algorithm that predicts very low emissions near 0°C, a logarithmic increase in emissions at intermediate temperatures, and approaches a maximum emission rate at some saturation temperature. Guenther and coworkers (1989) have applied a non-linear least squares best fit technique to the emissions data collected by Lamb and coworkers (1987) to estimate k_a and k_b for OCS, CS₂, DMDS, DMS and H₂S for five surface categories which include wetland soils, organic soils, other soils, water, and agricultural crops (other than corn) and three vegetation categories which are deciduous and coniferous forest canopies and corn biomass. Additional natural sulfur compounds (e.g. mercaptans) are typically released at rates which are small (<1%) relative to the total sulfur flux.

The temperature dependent algorithms used to predict natural sulfur emissions do not account for all of the variation in observed emissions. Other important environmental parameters may include, but are not limited to, tidal flushing, availability of sulfur, soil moisture, soil pH, mineral composition, ground cover, and solar radiation. A more accurate estimation of biogenic sulfur emissions requires a better understanding of the factors which influence natural emissions and the means to extrapolate any additional parameters which are determined to be important.

2.2.3. *Global inventory of terrestrial biogenic volatile sulfur emissions.* Initial attempts to describe global biogeochemical sulfur circulation indirectly estimated terrestrial biogenic sulfur emissions by calculating the amount necessary to balance the global sulfur budget. Global average terrestrial emissions of 3.3 $\mu\text{mol}/\text{m}^2/\text{d}$ (Friend, 1973) to 63 $\mu\text{mol}/\text{m}^2/\text{d}$ (Eriksson, 1963) were required to balance global sulfur budgets. As a first step towards extrapolating actual terrestrial emission rate measurements to the global scale, the biogenic sulfur emissions algorithms developed by Guenther and coworkers (1989) are used here to generate a global emissions inventory. Climatic data compiled on a 2° latitude by 2° longitude spatial scale and

monthly temperature scale by Shea (1986) and land cover data compiled by Wilson and Henderson-Sellers (1985) on a 1° latitude by 1° longitude scale provide the temperature and source inputs required for a global inventory. The primary (>50% of the grid) and secondary (25% to 50% of the grid) land cover types were compiled into 12 simple surface types using the types and proportions given in Table 12 of Henderson-Sellers and coworkers (1986). The areas associated with each of these 12 surface types were summed by latitude band and these sums were used as the primary input into the emission calculation. It was assumed that primary vegetation covered 75% of a grid and secondary vegetation covered 25% of the grid in this summation process. Areas of open water and ice were eliminated from the summation process. For this preliminary estimate, the earth land mass was divided into the same latitudinal regions and seasons used for estimating oceanic sulfur emissions. Seasonal emission rates were calculated for five sources: cropland vegetation, wetlands, deciduous and coniferous canopies, and soils (total soil area = natural vegetation area + agricultural land areas + bare soil area).

The resulting total annual global emission estimate of 0.011 Tmol is equivalent to 0.21 $\mu\text{mol}/\text{m}^2/\text{d}$ which is only slightly higher than the estimated U.S. national average emission rate estimate of 0.18 $\mu\text{mol}/\text{m}^2/\text{d}$ (Guenther *et al.*, 1989). The tropical regions (20°N to 20°S) generate 61% of all emissions (Table 2 and Figure 2). Because of the temperature dependence

TABLE 2. Terrestrial sulfur fluxes

Region	winter emiss --($\mu\text{mol S}/\text{m}^2/\text{d}$)--	summer emiss --($\mu\text{mol S}/\text{m}^2/\text{d}$)--	winter flux --($10^6 \text{ mol}/\text{d}$)--	summer flux --($10^6 \text{ mol}/\text{d}$)--
80°–65°N	0.00	0.01	0.0	0.1
65°–50°N	0.00	0.10	0.0	2.2
50°–35°N	0.02	0.19	0.6	4.6
35°–20°N	0.16	0.33	3.6	7.6
20°–5°N	0.39	0.43	6.6	7.3
5°N–0°	0.55	0.53	3.2	3.1
0°–5°S	0.55	0.56	3.0	3.1
5°–20°S	0.36	0.43	5.3	6.3
20°–35°S	0.15	0.25	1.8	2.9
35°–50°S	0.09	0.15	0.2	0.3
50°–65°S	0.03	0.07	0.0	0.0
65°–80°S	0.00	0.00	0.0	0.0
N. Hemisphere			13.9	24.9
S. Hemisphere			10.2	12.6

Winter is defined from November to April in the Northern Hemisphere and May to October in the Southern Hemisphere.

Terrestrial Biogenic Sulfur Emissions

Gmoles/degree/season

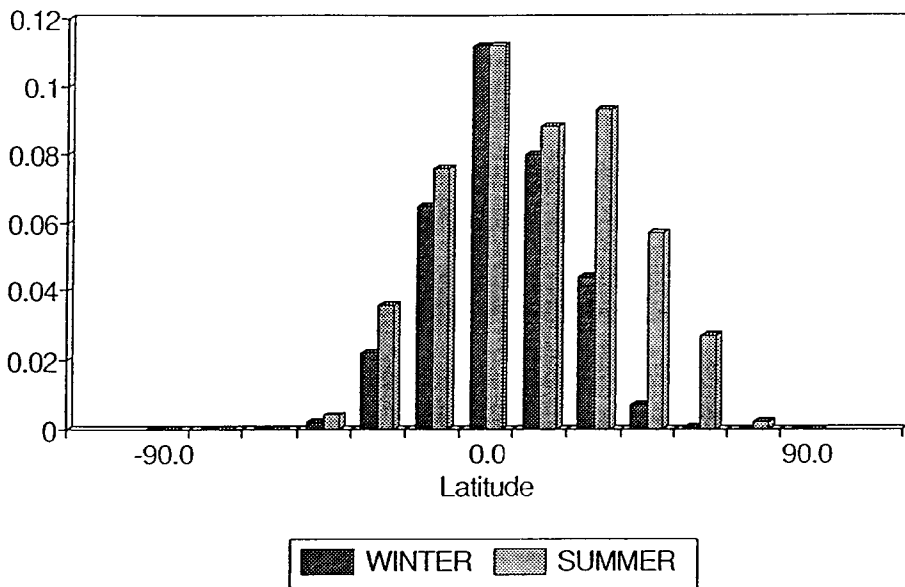


Fig. 2. Biogenic emissions of terrestrial sulfur compounds to the atmosphere. The data have been plotted per degree of latitude to demonstrate the uneven distribution between the northern and southern hemispheres.

of the emission algorithms, the summertime (May to October in the Northern Hemisphere, November to April in the Southern Hemisphere) emissions contribute 61% of the global annual flux. Seasonal emissions are nearly constant in the equatorial region. The predicted emissions are primarily OCS (47%), DMS (27%), and H₂S (20%). CS₂ and DMDS each contribute about 3% on a global scale but as much as 10% in individual regions (Table 3). Emissions estimated for the northern hemisphere are 70% greater than those predicted for the southern hemisphere. Emissions from deciduous canopies dominate (58%) the total emission rate with soils (29%) and coniferous canopies (9%) contributing the majority of the remainder (Table 4). Coniferous canopies are important (>27%) at high latitudes (>35°N or S) and predominate in the northern boreal biome. Croplands and wetlands together account for 4% of the annual global flux. The areas used to calculate the emissions by source are shown in Table 5.

The global terrestrial emission inventory described in this paper is a conservative estimate. A low sulfur emission rate, representative of alfalfa and row crops, was applied to all croplands. Cropland emissions may be considerably higher if significant portions of croplands contain plants, such as corn, which have much higher sulfur emission rates. If, for example, 25% of the world's croplands were corn (or crops with similar sulfur emission rates) then the estimated annual sulfur emission rate for croplands would increase from 1.6×10^8 to 1.8×10^9 moles. Similarly, a low

TABLE 3. Terrestrial sulfur fluxes by compound

Region	OCS ¹	CS ₂	DMDS --(10 ⁶ mol/d)--	DMS	H ₂ S
80°–65°N	0.03	0.01	0.01	0.01	0.00
65°–50°N	0.65	0.07	0.05	0.16	0.18
50°–35°N	1.35	0.13	0.09	0.57	0.46
35°–20°N	2.48	0.22	0.15	1.68	1.08
20°–5°N	3.03	0.23	0.15	2.17	1.34
5°N–0°	1.51	0.09	0.06	0.80	0.66
0°–5°S	1.43	0.09	0.06	0.79	0.63
5°–20°S	2.82	0.19	0.13	1.45	1.20
20°–35°S	1.15	0.09	0.07	0.59	0.46
35°–50°S	0.13	0.01	0.01	0.04	0.04
50°–65°S	0.00	0.00	0.00	0.00	0.00
65°–80°S	0.00	0.00	0.00	0.00	0.00
N. Hemisphere	9.05	0.75	0.51	5.40	3.72
S. Hemisphere	5.54	0.38	0.27	2.86	2.33

¹ Fluxes are a gross flux as measured in enclosures and hence do not take into account OCS uptake by vegetation. 82% of the flux listed above is from natural vegetation and crops.

emission rate was applied to all soils other than wetlands. If 10% of the world's soils emit sulfur at a rate similar to the organic histosol soils measured by Lamb and coworkers (1987), then the estimated annual sulfur emission rate for non-wetland soils would increase from 3.4×10^9 to 6.9×10^9 moles. Because of the exponential relationship between temperature and emissions, higher emissions would also be calculated if smaller spatial or temporal resolution were used. For example, Guenther and coworkers (1989) have estimated that using monthly average instead of daily average temperatures underestimates biogenic sulfur emissions by up to 25%. Another simplification in the methodology used to calculate this global inventory, the use of a constant peak biomass, overestimates emissions by assuming that all biomass is present at all times while in reality deciduous canopies and croplands have very little biomass at certain times of the year. The importance of this overestimated biomass is probably minimal since cold temperatures, resulting in a very low biomass emission rate, correspond with the periods of overestimated biomass.

It is possible that an improved inventory methodology (e.g. better resolution and more specific source types) would result in a global emission rate estimate that is as much as a factor of two greater than our preliminary estimate of 0.011 Tmol/a. This would still be one or two orders of magnitude less than the 0.16 to 3.4 Tmol/a required to balance the early global sulfur budgets (e.g. Eriksson, 1963; Friend, 1973; Granat *et al.*, 1976).

TABLE 4. Terrestrial sulfur fluxes by source

Region	conifers	deciduous	crops	soils	wetlands
	--(10^6 mol/d)--				
80°–65°N	0.02	0.02	0.00	0.02	0.00
65°–50°N	0.49	0.32	0.05	0.22	0.02
50°–35°N	0.69	0.97	0.15	0.69	0.10
35°–20°N	0.51	2.52	0.15	2.11	0.30
20°–5°N	0.44	3.95	0.07	2.30	0.15
5°N–0°	0.08	2.36	0.00	0.66	0.02
0°–5°S	0.07	2.24	0.00	0.65	0.04
5°–20°S	0.32	4.01	0.00	1.39	0.06
20°–35°S	0.21	1.36	0.02	0.76	0.01
35°–50°S	0.06	0.12	0.00	0.05	0.00
50°–65°S	0.00	0.00	0.00	0.00	0.00
65°–80°S	0.00	0.00	0.00	0.00	0.00
N. Hemisphere	2.24	10.15	0.43	6.01	0.59
S. Hemisphere	0.67	7.73	0.03	2.85	0.11

TABLE 5. Terrestrial areas by source (areas of open water and ice are eliminated from totals).

Region	Total Area	Natural Vegetation	Soil Area	Agriculture Area	Wetland Area
	--(10^{12} m ²)--				
80°–65°N	9.8	9.0	9.5	0.0	0.3
65°–50°N	21.6	15.5	20.5	2.7	1.0
50°–35°N	24.5	17.7	23.2	4.7	1.3
35°–20°N	23.1	19.2	22.4	2.7	0.7
20°–5°N	16.8	14.7	16.6	1.0	0.2
5°N–0°	5.8	5.5	5.7	0.0	0.0
0°–5°S	5.4	5.1	5.4	0.1	0.1
5°–20°S	14.6	13.4	14.5	0.1	0.1
20°–35°S	11.6	10.9	11.6	0.4	0.1
35°–50°S	1.9	1.8	1.9	0.1	0.0
50°–65°S	0.1	0.1	0.1	0.0	0.0
65°–80°S	0.0	0.0	0.0	0.0	0.0
N. Hemisphere	101.5	81.6	98.1	11.1	3.4
S. Hemisphere	33.7	31.3	33.5	0.6	0.3

2.3. VOLCANIC

Sulfur gases are emitted to the atmosphere from both erupting and non-erupting degassing volcanos with the more violent eruptions constituting the major source of sulfur to the stratosphere (Pinto *et al.*, 1989). The major sulfur compound emitted from volcanos is SO₂ with SO₄⁼ and H₂S generally comprising less than 1% (Stoiber *et al.*, 1987) and OCS less than 0.1% (Khalil and Rasmussen, 1984; Belviso *et al.*, 1986) of the total sulfur emissions. The most recent estimate of annual SO₂ emissions to the atmosphere by volcanos is 0.29 Tmol/a (Stoiber *et al.*, 1987). This estimate is based on an extrapolation of direct measurements of volcanic SO₂ and include 0.11 Tmol/a from 102 degassing volcanos and 0.18 Tmol/a from approximately 60 erupting volcanos. The estimate of the number of volcanos is an average over the past 400 years.

Not all of this sulfur is emitted to the troposphere. Volcanoes with a Volcanic Explosivity Index (VEI) of 4 or greater produce approximately 7% of the total sulfur emitted from volcanoes (Stoiber *et al.*, 1987) and have eruption cloud columns which can reach the stratosphere. During the period 1975–1985 seven of the eight volcanoes with VEI of four or greater were located in the northern hemisphere (McClelland *et al.*, 1989) and are evident in the stratospheric aerosol mixing ratio (Hofmann, 1990).

Unlike biogenic sulfur emissions which have relatively small emission rates over large areas, volcanism is concentrated in small segments of the Earth's crust, generally related to plate boundaries. Two-thirds of the world's known volcanos are in the northern hemisphere and only 18% are between 10°S and the South Pole (Simkin *et al.*, 1981; Simkin and Siebert, 1984). The emission rate of SO₂ from any one volcano is episodic and varies with eruptive activity (Malinconico, 1987), making it extremely difficult to calculate the uncertainty of the estimates.

2.4. OTHER NATURAL SOURCES

2.4.1. Biomass Burning. The burning of forests, grasslands, and agricultural wastes can not necessarily be considered a "natural" sulfur emission since as much as 95% of global burning is thought to be human initiated (Hileman, 1990). However, biomass burning is a significant source of SO₂ to the atmosphere. Field measurements of sulfur gases and sulfate aerosol particles have been made in prescribed burns of chaparral and brush near Los Angeles, California (Hegg *et al.*, 1987) and in the Amazon basin (Andreae *et al.*, 1988). The molar ratio of total sulfur emissions to CO₂ emissions ranged from 0.00021 (Hegg *et al.*, 1987) to 0.00032 (Andreae *et al.*, 1988). These emission ratios can be used with global estimates of CO₂ emissions from biomass burning (Seiler and Crutzen, 1980; Hao *et al.*, 1989; Dignon and Penner, 1990; Hileman, 1990; Logan *et al.*, 1990) to calculate a total sulfur emission of 0.045 to 0.092 Tmol S/a. Based on the sulfur content of dry matter before and after a fire, Delmas and Servant (1988) calculated an emission of 0.11 Tmol S/a from biomass burning, a value very similar to that calculated here. Delmas (1982) proposed a range of 0.013 to 0.038 Tmol S/a for total annual emissions from savanna fires. Dignon and Penner (1990) have estimated that savanna fires may account for 50 to 60 percent of global biomass burning emissions. Thus, the total sulfur source based on the savanna estimates of Delmas (1982) would yield roughly 0.026 to 0.063 Tmol S/a. The estimates presented by Delmas (1982) and later by Delmas and Servant (1988) are similar to the range presented here.

Most of the burning occurs during the dry season in the tropics with roughly 80 percent of the emissions between 25°N and 25°S (Dignon and Penner, 1990). Based on the work of Hao *et al.* (1989) and Lacey *et al.* (1982) it is estimated that less than 20 percent of the biomass burning

in the southern hemisphere occurs in summer. In the northern hemisphere, tropical burning is predominantly in winter while at higher latitudes, summer is the dominant burning season. Since most burning area estimates are known to no better than $\pm 50\%$ (Robinson, 1989), and there are few emission measurements for sulfur species, these estimates are expected to have a considerable uncertainty. The only aspect of biomass burning that is certain at this time, is that the amount of burning has accelerated greatly in the past few decades with detrimental environmental consequences (Hileman, 1990).

2.4.2. Aeolian dust. Massive quantities of dust are transported throughout the troposphere due to wind blown erosion. Although the dust carried across the tropical North Atlantic-Ocean from the Sahara desert is associated with approximately 60% of the mean total concentration of sulfate reaching Barbados, this sulfate is most likely associated with anthropogenic as opposed to crustal Saharan material (Savoie *et al.*, 1989). Like sea-salt-sulfate, the sulfur derived from soils is principally contained on larger ($>1 \mu\text{m}$) particles.

3. Conclusions

The biogenic sulfur emissions calculated above are summarized by latitude in Table 6 and Figure 3. By comparing these values with estimates of anthropogenic sulfur emissions, we can

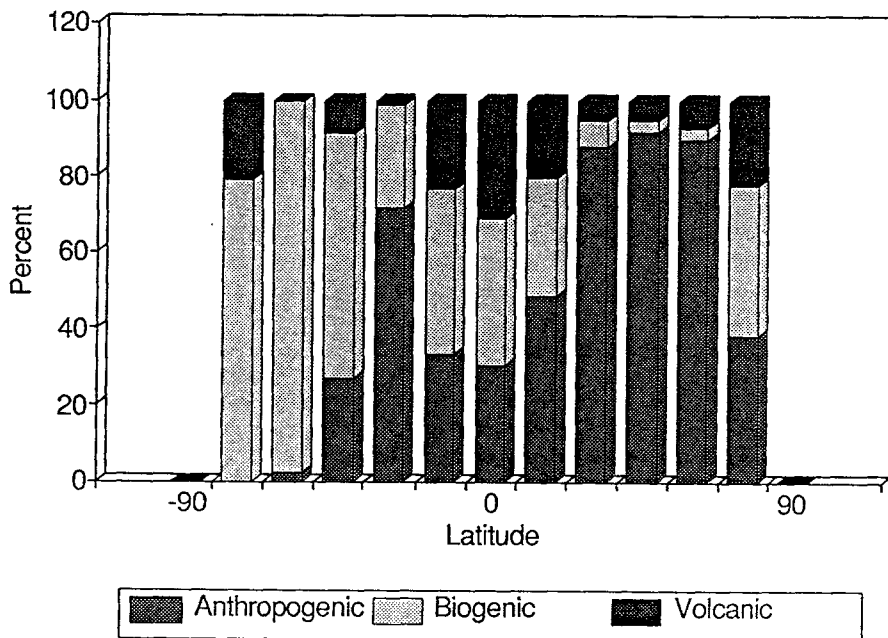


Fig. 3. Global emissions of anthropogenic (includes biomass burning), biogenic (marine and terrestrial), and volcanic sulfur.

begin to assess the magnitude of the anthropogenic perturbation to the natural atmospheric sulfur cycle. Hameed and Dignon (1990) estimate anthropogenic sulfur emissions for fossil fuel burning at 2.0 Tmol S for the year 1986. This is an update of their earlier 1980 estimates (Hameed and Dignon, 1988; Dignon and Hameed, 1989). Varhelyi (1985) has made sulfur emission estimates for the industrial sector of 2.5 Tmol S/a with 78% emitted in the northern hemisphere and 22% in the southern hemisphere. The estimates of Varhelyi can be scaled latitudinally with the fossil fuel source of Hameed and Dignon (1990) to create a global mapping of anthropogenic sulfur emissions (Dignon, 1990). In Table 6 the global anthropogenic source of 2.5 Tmol S/a is presented by latitude.

The biomass burning source is presented by latitude in Table 6 and is based on the 1×1 degree vegetation map of Matthews (1982) and the biomass burning inventories of Dignon and Penner (1990) and Logan *et al.* (1990). Volcanic sources have been apportioned by latitude based on the eruption data between 1975 and 1985 (McClelland *et al.*, 1989). During this period there were 149 erupting volcanoes and for the purposes of this latitudinal comparison, we assume that the number of volcanoes which erupted in each region between 1975–1985 is directly proportional to the sulfur emitted by active volcanoes in these regions.

TABLE 6. Sulfur emissions from natural and anthropogenic sources expressed in 10^9 mol/a

Region	Oceanic	Terrestrial	Volcanic	biomass burning	Anthropogenic	Biogenic/total ¹	Natural/total ²
80°–65°N	4	0.02	2	0.4	3	40%	62%
65°–50°N	19	0.40	43	2.3	534	3	10
50°–35°N	31	0.95	53	3.3	942	3	8
35°–20°N	46	2.05	37	7.1	598	7	12
20°–5°N	79	2.52	54	20.7	106	31	52
5°N–0°	26	1.14	17	4.2	18	41	67
0°–5°S	25	1.10	27	3.6	16	36	73
5°–20°S	82	2.11	45	17.3	47	44	67
20°–35°S	60	0.86	2	9.2	153	27	28
35°–50°S	60	0.08	8	0.7	24	65	73
50°–65°S	50	0.00	0	0.2	1	98	98
65°–80°S	4	0.00	1	0.0	0	79	100
N. Hemisphere	200	7.1	210	38	2200	8	16
S. Hemisphere	280	4.1	83	31	240	45	58
Global	480	11.	290	69	2400	15	24

¹ (Marine + Terrestrial)*100/(Marine + Terrestrial + Volcanic + Anthropogenic + Biomass burning).

² (Marine + Terrestrial + Volcanic)*100/(Marine + Terrestrial + Volcanic + Anthropogenic + Biomass burning).

It is clear from these data that the region between 35° and 50°N is seriously impacted by anthropogenic emissions with only 8% of the total sulfur emissions coming from natural sources. Natural sulfur emissions are still a significant fraction (30–100%) of the total sulfur emissions in the tropical latitudes of the northern hemisphere (0–20°N) and in all latitude belts of the southern hemisphere. Although there are certainly smaller regions in the southern hemisphere where anthropogenic sulfur emissions dominate over natural emissions, 90% of the anthropogenic sulfur emissions occur in the northern hemisphere while natural sulfur emissions are more evenly divided between the two hemispheres.

Terrestrial biogenic sulfur emissions may be important in localized regions (Andreae and Andreae, 1988), but are insignificant on the latitudinal scales compiled here. Volcanic and oceanic emissions, however, are a significant fraction of the total sulfur flux to the atmosphere and make up 58% of the total sulfur emissions in the southern hemisphere.

These data provide both seasonal and latitudinal distributions of the major sources of sulfur to the atmosphere. Although the latitudinal comparisons of the various sources provide an insight into the magnitude of the anthropogenic perturbations to the natural cycle, it is difficult to assess the climatic impacts of these perturbations with the data presented here since the lifetimes of the various sulfur species are too short to mix the sulfur species throughout the latitudinal bands. However, these data do provide input for global circulation-climate models and studies of the climatic effect of sulfur emissions (Charlson *et al.*, 1987; Charlson *et al.*, 1990; Erickson *et al.*, 1990; Penner, 1990). These modelling efforts are certainly limited by available data and critically need further field studies of both sulfur emissions and the processes that drive the atmospheric biogeochemical sulfur cycle.

Acknowledgments. We thank G. Allwine and M. Maring for the terrestrial sulfur calculations, H. Berresheim for comments on volcanic emissions, F. Fehsenfeld for his encouragement to write this manuscript, and the NOAA National Acid Precipitation Assessment Program (NAPAP) for support. This is contribution 1229 from the Pacific Marine Environmental Laboratory.

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