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# EMISSIONS OF BIOGENIC SULFUR GASES FROM ALASKAN TUNDRA

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*Abstract.* Fluxes of the biogenic sulfur gases carbonyl sulfide (COS), dimethyl sulfide (DMS), methyl mercaptan (MeSH), and carbon disulfide (CS$_2$) were determined for several freshwater and coastal marine tundra habitats using a dynamic enclosure method and gas chromatography. In the freshwater tundra sites, highest emissions, with a mean of 6.0 nmol m$^{-2}$ h$^{-1}$ (1.5-10) occurred in the water-saturated wet meadow areas inhabited by grasses, sedges and *Sphagnum* mosses. In the drier upland tundra sites, highest fluxes occurred in areas inhabited by mixed vegetation and labrador tea at 3.0 nmol m$^{-2}$ h$^{-1}$ (0-8.3) and lowest fluxes were from lichen-dominated areas at 0.9 nmol m$^{-2}$ h$^{-1}$. Sulfur emissions from a lake surface were also low at 0.8 nmol m$^{-2}$ h$^{-1}$. Of the compounds measured, DMS was the dominant gas emitted from all of these sites. Sulfur emissions from the marine sites were up to 20-fold greater than fluxes in the freshwater habitats and were also dominated by DMS. Emissions of DMS were highest from intertidal soils inhabited by *Carex subspathacea* (150-250 nmol m$^{-2}$ h$^{-1}$). This *Carex* sp. was grazed thoroughly by geese and DMS fluxes doubled when goose feces were left within the flux chamber. Emissions were much lower from other types of vegetation which were more spatially dominant. Sulfur emissions from tundra were among the lowest reported in the literature. When emission data were extrapolated to include all tundra globally, the global flux of biogenic sulfur from this biome is 2-3 x 10$^8$ g yr$^{-1}$. This represents less than 0.001% of the estimated annual global flux (~50 Tg) of biogenic sulfur and <0.01% of the estimated terrestrial flux. The low emissions are attributed to the low availability of sulfate, certain hydrological characteristics of tundra, and the tendency for tundra to accumulate organic matter.

## Introduction

Sulfur gases contribute to precipitation acidity [*Charlson and Rodhe*, 1982; *Nriagu et al.*, 1987], are involved in various important atmospheric chemical reactions, and have been implicated as potential regulators of climate by increasing global albedo [*Bates et al.*, 1987a; *Charlson et al.*, 1987]. A major question in our understanding of the natural sulfur cycle is the role of biogenic sulfur emissions in the atmosphere [*Andreae et al.*, 1990]. Although tremendous progress in delineating the sources and sinks of sulfur gases has been achieved recently, there remains considerable uncertainty as to the role of certain terrestrial environments as sources of biogenic sulfur gases [*Andreae*, 1985]. Recent work has contributed greatly to an understanding of the role of temperate soils and vegetation as sources and sinks of sulfur gases [*Goldan et al.*, 1987, 1988; *Lamb et al.*, 1987; *Fall et al.*, 1988]. Several studies have examined the emissions of sulfur gases from temperate salt marshes (see references listed in *Aneja and Cooper* [1989]) and recent studies have begun to examine the emissions of sulfur gases from tropical environments [*Andreae and Andreae*, 1988; *Andreae et al.*, 1990].

*Nriagu et al.* [1987] suggested that wetlands in Ontario, Canada, may emit quantities of biogenic sulfur which are similar in magnitude to oceanic fluxes of dimethyl sulfide (DMS). Although high latitude wetlands constitute a relatively large area of the terrestrial Earth [*Matthews and Fung*, 1987], no studies have directly determined the flux of sulfur gases from these environments. In this paper we present results of sulfur emission measurements made in freshwater and marine wetlands in Alaskan tundra during the Arctic Boundary Layer Expedition 3A (ABLE 3A) in July 1988 . These data indicated that this type of tundra emits very small amounts of gaseous sulfur and accounts for a very small percentage of the global flux of biogenic sulfur to the atmosphere.

## Methods

### Sampling Locations

The freshwater sites studied were located near Bethel, Alaska, in the Yukon-Kuskokwim delta (Figure 1). In this area, flux measurements were made in various types of upland tundra vegetation including regions dominated by graminoids, labrador tea (*Ledum palustre*), *Sphagnum* mosses, and lichen species and in wet meadow sites dominated by *Sphagnum* spp., grasses (*Eriophorum* spp.) and sedges (*Carex* spp.). The wet meadow sites contained standing water while the upland sites were moist without standing water. Emissions from a lake surface were also measured.

In addition to the freshwater sites, emission measurements were made in a coastal area of the Delta at the mouth of the Tutakote River near Angyoyaravak Bay on the Bering Sea (Figure 1). Here, emissions were measured in an intertidal mud flat, an intertidal area inhabited by the sedge *Carex subspathacea*, and two supralittoral sites in monospecific stands of *Carex ramenskii* and *Elymus arenarius*. *Carex subspathacea* is grazed extensively by geese, and emission measurements were made in the presence and absence of goose feces. Samples and equipment were transported via float plane.

### Sampling and Analysis

Net emission measurements were made using 30 x 30 x 30 cm dynamic FEP Teflon flux chambers placed on Teflon-lined aluminum collars which had been deployed previously in the various habitats. For the lake samples, chambers were placed on collars which were attached to Styrofoam floats. Three chambers were deployed simultaneously, each over a different vegetation mixture. Compressed synthetic air was used for sweep air at 2.0 L min$^{-1}$ and 5.0 L gas samples were removed at 500 mL min$^{-1}$ and trapped in Teflon loops immersed in liquid N$_2$. Laboratory studies demonstrated no measurable breakthrough of sulfur gases at this sampling rate [*Morrison*, 1988]. However, these tests were conducted using higher concentrations of sulfur gases than those encountered in the present study so it is possible that the rates reported here are underestimated. Oxygen condensation within loops was prevented by trapping gases under a slight vacuum. Rates of sweep air flow and sample air collection were regulated using
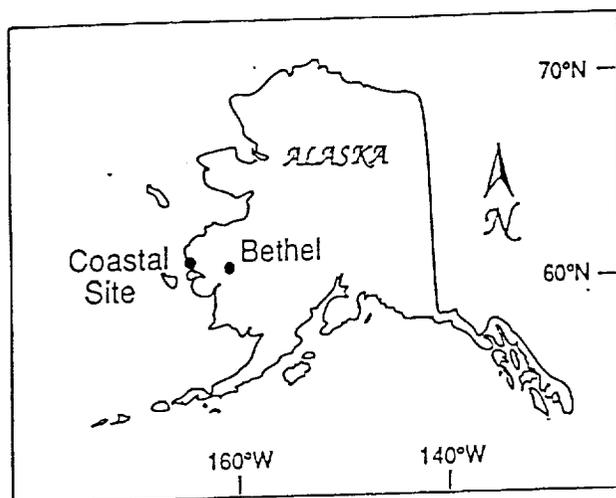
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Fig. 1. Location in Alaska of the freshwater sampling site in Bethel and the coastal sampling site near Angyoyaravak Bay (165°36'W, 61°20'N).

mass flow controllers. Sample size was determined by integrating meter output. Samples were collected every 30-60 min for several hours. Diel experiments were not conducted. However, this area of Alaska in July receives sunlight for approximately 20 hours each day. For comparison, in some instances static chambers, which entrapped ambient air, were employed. Samples were collected every 30 min.

Sample loops were transported to a laboratory, where they were analyzed within at least 5 hours. In laboratory tests, samples could be stored in loops under liquid $N_2$ for over 8 hours without loss [Morrison, 1988]. Sulfur gases were remobilized by heating loops in a hot water bath, separated on a column packed with 1.5% XE-60, 1% $H_3PO_4$, 60/80 Carbopack B (Supelco) and quantified by a sulfur-doped flame photometric detector. Calibration was conducted using sulfur gases liberated from gravimetrically calibrated permeation devices maintained in a permeation oven. The minimum fluxes that could be detected under the conditions used were

0.15, 0.2, 0.25 and 0.3 nmol m$^{-2}$ h$^{-1}$ for carbonyl sulphide (COS), methane thiol [$CH_3SH$, (MeSH)], DMS and carbon disulfide ($CS_2$), respectively. Hydrogen sulfide ($H_2S$) could be detected but could not be quantified because it elutes on the tail of negative peaks due to hydrocarbons and carbon dioxide. For further analytical details, see Morrison and Hines [1990].

## Results and Discussion

Rates of sulfur gas emissions were low at all of the freshwater sites (Table 1). Carbonyl sulfide was emitted from all sites and was the most dominant sulfur gas in many instances. Dimethyl sulfide emissions were also important and this gas was the dominant sulfur gas emitted from the wet meadow areas. Carbon disulfide was found less frequently and MeSH was detected only rarely at low concentrations and is not presented. Hydrogen sulfide was detected routinely but could not be quantified.

The data in Table 1 include replicate measurements from the same chamber made on the same day as well as measurements made on separate days. The collars remained in place throughout the experiment so the exact location could be sampled on several days. In most instances, variation within one day at one site was less than a factor of two. Fluxes were most variable in the upland sites. Fluxes increased from July 11 to 16, 1988. The highest increase of eightfold occurred in the lichen-dominated area, while emissions increased 2.8- to 4.5-fold in the wet meadow/slough areas. During this period the weather was unusually warm and dry. The midday ambient temperature ranged from 19 to 25° C throughout the experiment.

When employing the flow-through dynamic flux chambers, COS fluxes were 0.23 to 12 nmol m$^{-2}$ h$^{-1}$ with highest fluxes in the upland sites and lowest fluxes in the wet meadow (Table 1). These higher rates are rapid enough to double the COS concentration in an hour in our static chambers. However, when static chambers were used over an upland site, ambient COS concentrations decreased exponentially over time (data not shown) indicating that tundra vegetation was consuming COS. Others have reported the uptake of COS by photosynthesizing vegetation [Fall et al., 1988; Goldan et al., 1988].

TABLE 1. Summary of Sulfur Gas Emissions From Freshwater Tundra Near Bethel, Alaska

| Site | Emissions, nmol S m$^{-2}$ h$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | COS | | DMS | | CS$_2$ | |
| | Range* | Mean | Range* | Mean | Range* | Mean |
| Wet meadow grass and sedge | 1.3-5.2 | 2.7 | 2.7-10 | 6.1 | 0-1.1 | 0.22 |
| Wet meadow moss† | 0.23-8.9 | 4.9 | 1.5-9.5 | 5.7 | 0-3.3 | 0.6 |
| Upland mixed‡ | 2.3-12 | 7.6 | 0-5.0 | 2.6 | 0-1.2 | 0.4 |
| Upland Labrador Tea§ | 2.9-10 | 6.5 | 0.5-8.3 | 3.5 | 0 | 0 |
| Upland moss§ | 3.3-8.4 | 5.8 | 0-7.6 | 2.0 | 0 | 0 |
| Upland lichen§ | 11-12 | 12 | 0.8-1.1 | 0.9 | 0 | 0 |
| Lake¶ | 2.9 | 2.9 | 0.7-0.8 | 0.8 | 0-1.1 | 0.5 |

Methyl mercaptan (MeSH) was detected occasionally.
*All values including daily replicates and measurements made on separate days.
†Mixed with grass and sedge.
‡Variety of species including dwarf birch, graminoids, lichens, labrador tea, and mosses.
§Mixed tundra dominated by this type of vegetation.
¶Emission chamber floating on lake surface.

Emissions of COS measured using dynamic chambers did not vary significantly with time once equilibrium was established (~1.5 h). This indicated that the tundra soil was a source of COS since COS emissions, i.e., COS concentrations within the chamber, would have decreased with time if the only source of COS was that which was in equilibrium with the atmosphere. In addition, using the following equation [Liss and Slater, 1974], we calculated the expected flux of COS from water when the aqueous COS concentration was in equilibrium with the atmosphere and then the atmosphere was suddenly replaced by COS-free air:

$$F = k\Delta C \qquad (1)$$

where F is flux in nmol $m^{-2}$ $h^{-1}$, k is piston or exchange velocity in m $h^{-1}$ and $\Delta C$ is COS concentration gradient. Since the atmosphere in the dynamic chamber was devoid of COS, $\Delta C$ equals the concentration of COS in water that is in equilibrium with ambient air. This concentration of COS in water was 9.2 pM as calculated as the quotient of an atmospheric concentration of COS of 500 ppt(v) divided by the Henry's law constant of COS in seawater at 20° C of 2.22 [Johnson and Harrison, 1986]. Hence, using equation (1), the flux of COS expected in the absence of COS production when COS-free sweep air is used is ~0.18 nmol $m^{-2}$ $h^{-1}$. This is an underestimate, since the Henry's law constant used was determined for seawater. However, this emission rate is substantially lower than the rates actually measured using the dynamic chambers. This fact and the finding that the COS emission rates in dynamic chambers did not decrease over time indicated that these tundra soils were producing COS.

The discrepancy in the COS data between the dynamic and the static chambers was probably due to the uptake of ambient COS by vegetation when static chambers were employed. In the dynamic chambers, the concentration of COS, and, hence, the calculated flux, was a net result of emission from soils and consumption by vegetation. When using dynamic chambers, the most rapid COS emissions were from the lichen and other dry areas while COS fluxes were slower in the areas which were wet and contained much more biomass. These latter results suggested that the lower COS fluxes measured using dynamic chambers were not due to a smaller flux from wet meadow areas but to a faster rate of consumption. A similar conclusion was derived from our recent study of a temperate salt marsh [Morrison and Hines, 1990]. Therefore, we believe that the emission data for COS from these tundra sites, which were derived from dynamic chambers, do not represent the actual fluxes from the habitats and that it is possible that tundra is a net sink for COS. Unfortunately, since we only employed the static chambers on one occasion at two dry sites to test the utility of the dynamic enclosures for this gas, we were unable to quantify the uptake the COS thoroughly to make conclusions about the role of tundra in regulating atmospheric COS. We have included the COS flux data from dynamic chambers in Table 1 for comparison to other published COS emission data, most of which were derived from dynamic chamber deployments. In addition, it appears that of the sulfur gases quantified, DMS was the dominant S gas emitted from these habitats rather than COS.

Emissions of sulfur gases from the freshwater sites were highest in the wet meadow areas and slightly lower in most of the upland tundra sites (Table 1). Sulfur emissions were very low from upland areas dominated by lichens, and these fluxes were similar in magnitude to those from a lake surface.

Sulfur fluxes at the coastal sites were more rapid than the inland areas in most instances (Table 2). In addition, we were able to detect MeSH emissions from most of these sites. We did not utilize static chambers with ambient COS concentrations to test whether COS fluxes were artificial so the COS emission data, like those presented in Table 1, are suspect. Highest rates were noted in the intertidal area inhabited by C.

TABLE 2. Summary of Sulfur Gas Emissions at the Coastal Site on the Tutakote River, Alaska

| Site | Range of Emissions, nmol S $m^{-2}$ $h^{-1}$ | | | |
| --- | --- | --- | --- | --- |
| | COS | MeSH | DMS | CS2 |
| Carex subspathacea | 5.7-10 | 1.6-2.6 | 70-81 | 5.0-9.7 |
| C. subspathacea +feces | 4.3-8.2 | 2.4-4.5 | 150-250 | 5.9-6.9 |
| C. ramenskii | 11-16 | 0-0.7 | 0-1.7 | 1.6-8.4 |
| Elymus arenarius | 18-21 | 1.2-2.7 | 75* | 4.3-7.8 |
| Mud flat | 9.3-11 | <0.2 | 10-16 | 2.1-4.2 |

All measurements made on July 18, 1988.
*Only one measurement.

subspathacea, and fluxes of DMS in this area more than doubled when goose feces were left within the flux chambers. Fluxes of DMS from C. subspathacea were six (vegetation alone) to 15 (vegetation plus feces) times faster than from the adjacent mud flat which was devoid of vegetation. The quantity of emergent biomass of C. subspathacea was low at ~10 g dry weight $m^{-2}$.

Fluxes of sulfur gases from E. arenarius were similar in magnitude to those from C. subspathacea. Although we did not measure the biomass of E. arenarius, it was dense and over 30 cm tall and appeared to be at least 20 times more abundant in emergent biomass than C. subspathacea.

Except for CS2, the rates of sulfur emissions from C. ramenskii were extremely low, even less than most of the inland freshwater sites examined (Tables 1 and 2). These low fluxes were surprising since the stand studied was only 2-3 m from the C. subspathacea site and, due to its close proximity to the ocean, this region must receive considerably higher inputs of sulfur than the Bethel sites. The C. ramenskii was dense, bright green, ~15 cm tall and we observed large areas of C. ramenskii from the air.

The highest sulfur emissions recorded in the freshwater tundra sites (exclusive of COS) were ~4% of those recorded for the average open ocean [Barnard et al., 1982; Andreae, 1986; Bates et al., 1987b], ~10% of fluxes from upland soils in the Amazon Basin during the dry season [Andreae and Andreae, 1988] and ~3.5% of estimates of sulfur emissions from waters in wetlands of southern and central Ontario, Canada [Nriagu et al., 1987]. These must be considered lower estimates, since we were unable to quantify H2S, which was always present. Fluxes of DMS from freshwater tundra were similar in magnitude to fluxes of DMS from decaying cattails, and native grasses in Ohio [Goldan et al., 1987], fluxes of DMS from organic-poor soils in Germany [Staubes et al., 1989], the lowest detectable rates of sulfur emissions from a freshwater wetland in southern Florida [Cooper et al., 1987], and rates of emission of DMS from upland soils in the Amazon Basin during the wet season [Andreae et al., 1990].

Although the sulfur emissions from the coastal sites were considerably higher than from the freshwater locations examined, the highest fluxes from the coastal sites were up to 100-fold lower than sulfur fluxes from stands of temperate salt marsh grasses [Steudler and Peterson, 1984; Aneja and Cooper, 1989; Morrison and Hines, 1990]. The biomass of C. subspathacea was only ~10 g $m^{-2}$, so the ratio of flux to biomass of 8-20 was similar to the ratio for temperate S. alterniflora of 10 (Morrison and Hines [1990] and our unpublished biomass data).

The enhanced DMS flux in the presence of C. subspathacea and the similarity between flux and biomass for this species

and *S. alterniflora* suggested that *C. subspathacea* produces a sulfonium compound like dimethylsulfonioproprionate (DMSP), a known precursor of DMS [*Dacey et al.*, 1987]. The only marsh species that have been previously shown to produce significant quantities of this compound are *Spartina alterniflora* [*Dacey et al.*, 1987] and *S. anglica* [*Larher et al.*, 1977]. The increased DMS flux in the presence of goose feces was probably due to the decomposition of DMSP after ingestion of *C. subspathacea* by geese. This is similar to the enhancement of DMS emissions when DMSP-producing marine phytoplankton are grazed by zooplankton [*Dacey et al.*, 1987] or when *S. alterniflora* is decomposed by microbes [*Kiene and Visscher*, 1987]. However, validation of the supposition that *C. subspathacea* is indeed a DMSP-producing macrophyte remains to be conducted. Despite the higher fluxes of sulfur gases from the coastal sites, the abundance of *C. ramenskii* and the fact that the coastal region is small relative to the freshwater wetlands in Alaska indicated that only the freshwater areas are of importance when considering the role of tundra in affecting the atmospheric sulfur cycle.

During the period of this study (July 1988), the wet deposition of sulfur in Bethel averaged 0.21 mg S m$^{-2}$ d$^{-1}$ (76 mg m$^{-2}$ yr$^{-1}$) [*Talbot et al.*, this issue]. Hence, the measured loss of sulfur as gaseous efflux represented only 0.5% of the input during that period as compared to estimates of 30% for the Amazon Basin during the dry season [*Andreae and Andreae*, 1988].

There are several reasons why the fluxes of sulfur gases from Alaskan tundra are small. First, the supply of sulfate must be low since the rate of atmospheric deposition of sulfur to this locale is small even when compared to other remote areas [*Andreae and Andreae*, 1988]. The Canadian wetlands areas studied by *Nriagu et al.* [1987] were subjected to relatively high levels of pollutant sulfur with deposition rates up to 40-fold higher than those encountered in our Alaskan study. It is interesting that the calculated rates of sulfur emission from the Ontario bogs studied by *Nriagu et al.* [1987] were ~40-fold higher than those measured by us in Alaska. Hence, even when the rate of sulfur deposition is very low, the percentage that is re-emitted appears to be similar to areas experiencing higher deposition rates. Too few data are available to discern if this is a common phenomenon for high latitude wetlands or . if reemission percentages are commonly high in tropical environments like those studied in the Amazon dry season.

Second, the biologically active component of the tundra peat is a relatively thin section near the surface. Sulfur-containing waters which percolate through this region probably do not remain in contact with the active zone long before draining into deeper layers just above the permafrost (~50 cm). The upland tundra sites studied here were never saturated with water during the study period and meteoric waters must have drained into lower, wet meadow regions. These wetter areas are sites of increased nutrient accumulation because of drainage of nutrients from upland areas [*Matthes-Sears et al.*, 1988]. Wet meadows probably tend to accumulate more sulfur than upland areas as well and this may explain the higher fluxes of sulfur in the wet meadow sites. The wet meadow sites exhibited fluxes of methane which were approximately 100-fold higher than in the upland, drier sites [*Bartlett et al.*, this issue].  . Substrate anoxia, which appears to enhance methane flux from the wet meadow areas did not enhance fluxes of sulfur gases similarly. During early spring thaw, a large portion of the precipitation runs off tundra rather quickly while flow is retarded during summer [*Matthes-Sears et al.*, 1988]. This surface flow probably also removes a large portion of any pollutant sulfur which is deposited during late winter by Arctic haze.

Third, tundra communities are characterized by organic matter accumulation with slow decomposition rates [*Chapin et al.*, 1978]. Tundra vegetation is active during the short summer season and tends to strongly sequester needed elements from the environment. Our flux measurements were made during the most productive period of the year and it is possible that sulfur emissions increased as plants began to senesce in August. Increases in DMS emissions in salt marsh soils in the fall have been reported [*Steudler and Peterson*, 1984]. In addition, there was a large increase in emissions from tundra during the final five to eight days of the experiment as the ecosystem became warmer and drier suggesting that emission rates are quite variable throughout the growing season. Others have reported good correlations between the log of sulfur emissions and enclosure temperatures with emissions increasing ~10-fold when temperature increase from 10 to 30° C in sites in Ohio [*Goldan et al.*, 1987; *Fall et al.*, 1988]. Unfortunately, too few emission data were collected and temperatures did not vary enough during our Alaska study to determine more than a semi-quantitative relationship between these variables. However, sulfur gas emissions from these tundra sites increased more per degree C than the increases reported for temperate sites [*Goldan et al.*, 1987].

If the global tundra area is 9 x 10$^{11}$ m$^2$ (estimate for nonforested bog [*Matthews and Fung*, 1987]) and the active season is 100-150 days, then we estimate that the global flux of biogenic sulfur from tundra is 2.1-3.2 x 10$^8$ g yr$^{-1}$. This represents slightly less than 0.001% of the estimated global flux of biogenic sulfur (~50 Tg yr$^{-1}$) [*Möller*, 1984]. This value is probably smaller still since a large percentage of tundra is covered by lakes which we found emit very little sulfur compared to the vegetated terrestrial surfaces. Extrapolation of our data to northern wetlands in general, including both nonforested and forested bogs [*Matthews and Fung*, 1987], would increase this contribution by only a factor of ~3 which is still an insignificant contribution to the global atmospheric sulfur burden. *Andreae et al.* [1990] recently estimated the annual terrestrial flux of biogenic sulfur as ~4.2 Tg, making the tundra flux ≤0.01% of the global terrestrial emissions of biogenic sulfur. If our emission data were  · underestimated by as much as a factor of 10, the flux of biogenic sulfur from this ecosystem would still be very low. It should be pointed out that we were not able to quantify emissions of H$_2$S. If H$_2$S is a major component of the sulfur emissions from tundra, then these estimates of the importance of this ecosystem to the atmospheric sulfur burden may be significantly low.

There appears to be insufficient atmospheric sulfur input to expect a large increase in biogenic sulfur emissions from tundra and even a 100% recycling of atmospherically-deposited sulfur would contribute only slightly (<0.1%) to the global atmospheric sulfur burden. Although areas which receive high inputs of sulfur, such as coastal regions or locations subjected to anthropogenically derived sulfur, certainly contribute considerably more recycled sulfur to the atmosphere, the bulk of tundra globally, such as in Siberia and Alaska, probably emits too little biogenic sulfur to significantly affect the global atmospheric sulfur budget.

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