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Emission Survey of Biogenic Sulfur Flux from Terrestrial Surfaces

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The most critical gap in knowledge important for delineating the global atmospheric cycle of sulfur is uncertainty about the magnitude, distribution, source, and form of biogenic emissions to the atmosphere. All global sulfur budget estimates which have appeared recently in the literature require a substantial biogenic sulfur emission to balance the budget; however, the estimated magnitude of the global natural source strengths vary widely—from ~35 to ~280 TgS/yr.

Direct measurements of sulfur emission rates were made by sampling various terrestrial surfaces (water surfaces, soil, and selected vegetation) during 1978. An emission flux reactor (chamber) technique was used to determine the emission rates of sulfur compounds into the atmosphere. The sulfur gases were identified and their concentrations in the flux reactor measured with a gas chromatograph equipped with a flame photometric detector specific for S. H2S (average flux ~0.5 gS/m^2/yr), (CH3)2S (average flux ~0.4 gS/m^2/yr), COS (average flux ~0.03 gS/m^2/yr), CS2 (average flux ~0.15 gS/m^2/yr) were measured. In general, the emission rates of these gases varied over a wide range of concentrations under varying conditions of soils, soil moisture, and temperature. These results are compared with previously measured sulfur emission fluxes. Comparison is also made with global sulfur budgets, sulfur emission rates expressed as fluxes, and from calculations based on a simple mass transfer model in an abiotic environment. The mass transfer model calculations suggest that the emission rates for H2S are considerably reduced in natural biotic environments, while the reverse is the case for DMS and CS2.

Natural processes and anthropogenic activity are the two sources of the sulfur-containing compounds in the atmosphere. Natural sources are thought to constitute a large fraction (~0.1 to ~0.7) of the atmospheric sulfur burden. Only recently comprehensive experimental evidence has been reported in which earth-atmosphere fluxes of biogenic sulfur compounds were measured. Moreover, physical and chemical properties thought to influence the release of these compounds were also measured. Identification and characterization of sources of atmospheric biogenic sulfur compounds are essential for the rational formulation of emission control policies designed to limit the atmospheric sulfate burden, and for analysis of the origins of acid precipitation.

Biogenic sulfur is released from vegetation, produced by decomposition of organic matter and from bacterial sulfate reduction in the biosphere. Data on sulfur release by vegetation is scanty although some plants are known to emit hydrogen sulfide (H2S), dimethyl sulfide, and carbon disulfide. Many fungi and bacteria release sulfur compounds during organic decomposition. The principal known microbial process for generating H2S is the reduction of sulfate (SO4^-2) by bacteria of the genera Desulfinibrio and Desulfotomaculum. These anaerobes utilize sulfate and other inorganic sulfur compounds as specific hydrogen acceptors during the oxidation of organic energy sources. During this metabolic cycle, the original sulfur compounds are reduced to sulfides. Non-specific reducers may be found in anaerobic or aerobic environments. Both processes of H2S production require the presence of organic material. Regardless of type of bacterial mediation, the locale of generation is probably in aqueous medium, whether in a film of moisture in soil or within the sediments or bulk water of lakes or oceans. The chemical form of the generated compound will vary with local conditions such as pH, temperature, metallic ions, etc.

Field investigations of biogenic sulfur compounds have involved measurement of concentrations of compounds of interest in the ambient air. Comprehensive direct measurements of emission fluxes of biogenic sulfur compounds along the east coast of U.S. from tidal marshes and water surfaces have also been carried out. However inland, nonaquatic environments are also of interest especially if plants may be emitting sulfur compounds.

This paper reports estimates of sulfur emission rates into the atmosphere based on sampling various terrestrial surfaces using an emission flux reactor.

Flux Measurement Technique

An emission flux reactor (chamber) (Figure 1) for measuring earth-atmosphere fluxes of biogenic sulfur compounds was used. Under appropriate conditions the chamber technique has the important feature that the sensitivity for flux measurement is high without the necessity of measuring very
low concentrations. In addition, gas residence times in the emission flux reactor are on the order of minutes so that chemical transformations between emission and analysis may be minimized. The walls are made from 5 mil (~0.13 mm) thick FEP Teflon supported by an exterior aluminum frame. This design was chosen to afford negligible attenuation of ambient light and minimal wall reactions. A more complete design of the field experimental apparatus is shown in Figure 2.

The sulfur compounds were analyzed by a gas chromatograph equipped with a flame photometric detector. A 394 nm interference filter made the detector sensitive to sulfur compounds. A 36 ft (~11 m) FEP Teflon column (1/8 in. (0.32 cm) o.d.) packed with 40-60 mesh Teflon coated with 5% polyphenyl ether (PPE) and 0.5% phosphoric acid (H3PO4) was used at 50°C to separate gaseous sulfur species. The carrier gas was nitrogen with a flow rate of ~80 ml/min. The column and operating conditions gave good resolution of peaks of H2S + COS (H2S and COS not separated, retention time = 1.5 min), SO2 (retention time = 3.1 min), CH3SH (retention time = 5.0 min), DMS (retention time = 12.2 min), and CS2 (retention time = 14.5 min). The overlapping DMS and CS2 peaks were manually resolved into separate contributions. The separation of H2S + COS was obtained by incorporating a second 19 ft (5.8 m) FEP Teflon column (1/8 in. (0.32 cm) o.d.) packed with 50/80 mesh Porapak QS in parallel with the first. The two columns were incorporated in the flow lines separately by a pneumatically controlled switching system. The carrier gas for the second column was nitrogen with a flow rate of ~40 ml/min. The retention time for COS under these conditions is ~8 min, which allows a good separation from H2S (retention time ~5.5 min); however, this column did not transmit CS2. The gas chromatographic was calibrated for both columns in the laboratory and in the field using a dilution system and bag samples.

**Emission Flux Measurements**

Measurements were made for biogenic sulfur species at various coastal and inland sites in North Carolina representing a variety of emission surfaces ranging from (a) coastal, saline marsh through (b) dry inland soils to (c) fresh water marsh. Sampling was conducted during daylight conditions during summer and fall, 1978.

Soils were classified wet or dry on the basis of moisture analysis. At each site 4 or 5 soil core samples were taken at the surface. They were 1 in. (2.54 cm) in diameter and 2 in. (5.08 cm) long. The cores were mixed together and ~100 g of soil was weighed. This subsample was dried for 24 hr in a ~100°C oven, surface. They were 1 in. (2.54 cm) in diameter and 2 in. (5.08 cm) long. The cores were mixed together and ~100 g of soil was weighed. This subsample was dried for 24 hr in a ~100°C oven, cooled, and reweighed. The moisture content was thus ascertained. The moisture content for soil beneath a water column was not measured.

Moisture content of dry soils ranged from 6-16%. In 81 samples taken in the inland sites (these experimental sites were in the Research Triangle Park, NC region and in all cases the soil was covered with grass), no sulfur containing gases were detected (Table I). This result seems consistent, as far as H2S is concerned, since the process of biogenic H2S production requires an aqueous medium such as a film of moisture in soil, interstitial water in sediments, or the bulk water of natural water bodies.

### Table 1. Average sulfur flux from various terrestrial surfaces.

<table>
<thead>
<tr>
<th>Sampling surface</th>
<th>Average sulfur flux, gS/m²/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2S</td>
<td>DMS</td>
</tr>
<tr>
<td>Dry inland soil</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Fresh water marsh with water column</td>
<td>0.6</td>
</tr>
<tr>
<td>Fresh water marsh mud</td>
<td>0.1</td>
</tr>
<tr>
<td>Fresh water marsh grass</td>
<td>0.1</td>
</tr>
<tr>
<td>Saline marsh with water column</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Saline marsh mud flat</td>
<td>0.5</td>
</tr>
<tr>
<td>Saline marsh Spartina alterniflora</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

a Based on the H2S, DMS and COS detectable limit of the instrument, the corresponding emission rate is <0.01 gS/m²/yr.
b Based on the CH3SH, CH3SH and DMDS detectable limit of the instrument, the corresponding emission rate is <0.05 gS/m²/yr.

The moisture content of fresh water marsh soil, in the absence of a water column, was between ~50 to 60%. The sediment temperatures ranged between 21°C to ~29°C. H2S was the only specie detected in all the locales of fresh water marsh soil. Emission rate of H2S ranged from a high of ~1.27 gS/m²/yr in the soil covered with a thin layer of water to a low of ~0.08 gS/m²/yr over grass which was clipped to about 1 in. above ground level. The mean emission rates are given in Table I. Adams20 also observed principally H2S emissions from a North Carolina fresh water swamp.

However, in salt water locales, not only was H2S detected, but also DMS, COS, and CS2. In the present study the measured fluxes of H2S of ~0.5 gS/m²/yr in saline marshes over mud flats were comparable to earlier direct emission rate measurements.8-10 DMS, the predominant specie over *Spartina alterniflora* zone10 had an emission rate of ~0.4 gS/m²/yr, consistent with results reported earlier.10 However, the measured DMS emission rates over *Spartina* exceeded the indirectly-measured20 values. COS flux in saline marsh locales was ~0.03 gS/m²/yr while CS2 predominantly over the

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**Figure 1.** Emission flux reactor. Source: Aneja, et al.21

**Figure 2.** Layout of field experiment using emission flux reactor with ambient air carrier gas. Source: Aneja, et al.21 Emission rate, $n = F \cdot \Delta C / A$, where $F =$ steady volumetric flow rate of gas through the chamber; $\Delta C =$ concentration increase; and $A =$ area of emitting surface covered by the chamber.
Table II. Maximum desorption fluxes of SO₂, H₂S, DMS, and CS₂ from turbulent water bodies.a

<table>
<thead>
<tr>
<th>pH</th>
<th>SO₂</th>
<th>H₂S</th>
<th>DMS</th>
<th>CS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.14 × 10⁻²</td>
<td>5.51</td>
<td>1.0 × 10⁻²</td>
<td>7.2 × 10⁻⁴</td>
</tr>
<tr>
<td>6</td>
<td>2.15 × 10⁻³</td>
<td>5.50</td>
<td>1.0 × 10⁻²</td>
<td>7.2 × 10⁻⁴</td>
</tr>
<tr>
<td>7</td>
<td>2.15 × 10⁻³</td>
<td>5.42</td>
<td>1.0 × 10⁻²</td>
<td>7.2 × 10⁻⁴</td>
</tr>
<tr>
<td>8</td>
<td>2.15 × 10⁻³</td>
<td>4.76</td>
<td>1.0 × 10⁻²</td>
<td>7.2 × 10⁻⁴</td>
</tr>
</tbody>
</table>

a Total bulk liquid [CS₂] = 5 × 10⁻¹³ g/mL and no dissociation in liquid.²⁸ Air [CS₂] = 0.0 ppb.

Sparsita zone had an emission rate over that zone of ~0.15 gS/m²/yr (Table I).¹¹

The average sulfur flux of different sulfur species for various sampling locales are summarized in Table I. Temperature (seasonal) effect corrections have not been applied. Climatic and environmental factors play an important role in natural emission phenomena. Aneja et al.²⁴ and Adams et al.²⁵ observed the temperature correlation for sulfur emission rates from numerous sites.

Soil moisture is an important factor in the release of biogenic sulfur species. However, the presence of a water column above the bacterial muddy zone of production may only serve to transform various biogenic gaseous sulfur species to non-volatile forms by several processes, including oxidation by dissolved oxygen and by various kinds of bacteria, and precipitation as an insoluble metal sulfide leading to lower emission rates of sulfur compounds.

It is interesting to compare the fluxes reported in the present work with other values of biogenic fluxes, such as those derived from global sulfur budgets and those derived from a mass transfer calculation. The fluxes reported in the present work are ~0.5 gS/m²/yr, when corrected for diurnal and tidal changes from fresh and saline marshes. In making estimates of global quantities the area of the globe was taken to be 5.1 × 10²⁷ cm² and 3.6 × 10²³ cm², respectively.² Average terrestrial fluxes calculated from recent global atmospheric sulfur budgets¹⁷ range from 0.4 to 0.7 gS/m²/yr (based on surface area of the land), while marine fluxes derived in the same way range from 0.1 to 0.5 gS/m²/yr (based on surface area of the ocean).³

Estimates of mass transfer rates across the air-sea interface have been made by Liss and Slater.²⁵ Their approach is used here to estimate fluxes of CS₂ from water to air under conditions corresponding to the air-sea interface. Fluxes under similar conditions are reported for H₂S and SO₂ and DMS.²⁵ Data used in the calculation and the results are given in Table II.

Comparing the flux values in an abiotic environment (Table II) with the biotic environment (Table I), we see that the emission rates for H₂S are considerably reduced in natural biotic environments due to either microbial or oxidation effects in the water column, while the reverse is the case for DMS and CS₂.

Acknowledgments

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References