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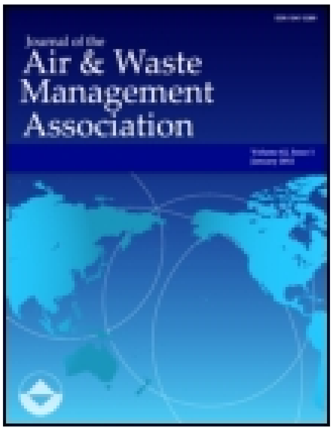

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Biogenic Sulfur Compounds and the Global Sulfur Cycle

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Biogenic Sulfur Compounds and the Global Sulfur Cycle

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Sulfur compounds of biogenic origin are thought to constitute a significant fraction of the atmospheric sulfur burden. Experimental determination of the biogenic fluxes of these compounds into the atmosphere is required to assess accurately the relative contributions of the anthropogenic and the biogenic fraction of the natural sources to such important phenomena as the atmospheric sulfate burden and acid precipitation.

A review of the literature describing field measurements of biogenic sulfur compounds at different kinds of emission locales to include both generation processes (sulfate reduction and plant decomposition) of volatile sulfur production show a great variation in the emission rate measurements associated primarily with wide variations in the surface and climatic environments of the various study sites. Although the maximum emission rate measurements balance the global sulfur cycle, the average measurement values do not, indicating the need for more experimental investigations in order to characterize the biogenic process adequately.

Field measurements describe biogenic, gaseous sulfur compounds emitted from different kinds of locales and show a great variation both in absolute concentrations and in emission rates. These variations can be explained partially by the wide differences among the surface and climatic environments. Although the maximum emission rates would appear high enough to balance the global sulfur cycle, the average measurements do not, indicating the need for more experimental investigations to characterize adequately the biogenic processes. These studies are needed for an understanding of such important phenomena as the atmospheric sulfate content and acid precipitation.

The rational development of emission control strategies for sulfur require the identification and characterization of all major sources of atmospheric sulfur compounds, both natural and anthropogenic (Figure I). Natural sulfur sources include sea spray, volcanic activity, decay of animal and plant tissue, marine algae, anaerobic microbiological activity, and other in-situ inland soil processes.

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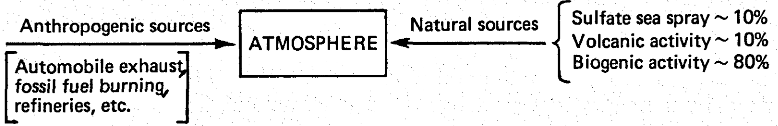

Figure 1. Sources of sulfur compounds.

Biogenic sulfur compounds originate from nonspecific bacterial reduction of organic sulfur, i.e. plant decomposition, and from specific sulfate reducing bacteria. The latter organisms are strictly anaerobic, while nonspecific reducers may be found in anaerobic or aerobic environments. Both processes require the presence of organic material and moisture. Because the biogenically produced fraction of the natural sulfur emissions has not been well characterized, either qualitatively or quantitatively, the total amount of sulfur that biogenic sources supply to the atmosphere per year has been estimated by difference. The amount of atmospheric sulfur contributed per year from anthropogenic sources, from volcanoes, and from sea spray is known. It is assumed that the sulfur content of the atmosphere does not change in the time scale of one year, and the biogenic emission rate is set equal to the source deficit usually found.

Ambient Air Concentration Measurements

Early field investigation of biogenic sulfur compounds involved measuring the concentrations of H_2S, DMS, CS_2, COS, and SO_2 in ambient air. The values for H_2S, DMS, CS_2 and COS together with their ranges are presented in Table I.[1-19] The H_2S concentrations found prior to 1970 should be treated with caution because they were obtained with unreliable sampling and analytical techniques. For these early values background concentrations have been assumed to be of the order of 0.3 $\mu g/m^3$ or less.

Prior to Natusch, analytical methods could not measure H_2S concentrations less than about 0.15 $\mu g/m^3$. In 1972, Natusch *et al.*[4] reported a fluorescence method with a sensitivity of 0.002 $\mu g/m^3$. Using this method at a remote mountain ski area in Boulder, CO under westerly wind conditions, they found H_2S concentrations averaging 0.04 $\mu g/m^3$.

Years later, Delmas *et al.*[10] employed this method of Natusch and gas chromatography and observed that the H_2S

Table I. Atmospheric concentrations of sulfur compounds.

Reference	Location	Atmospheric concentrations, $\mu g/m^3$			
		H_2S	DMS	CS_2	COS
Smith *et al.*[1] (1961)	U.S.	0.15–0.45			
Lodge and Pate[2] (1966)	Panama	1.0			
Axelrod *et al.*[3] (1969)	Panama	0–0.48			
Natusch *et al.*[4] (1972)	U.S. (CO)	0.04			
Breeding *et al.*[5] (1973)	U.S. (IL, MO)	0.12–0.3			
Slatt *et al.*[6] (1978)	Miami, FL	0.008–0.08			
Jaeschke *et al.*[7] (1978)	W. Germany	0.035–1.65			
Georgii[8] (1978)	Island of Sylt (North Sea)	0.1			
Delmas *et al.*[9] (1978)	Ivory Coast	0.1–8.7			
Delams *et al.*[10] (1979)	France	0.017–0.17			
Denmead[11] (1962)	Above Polluted Air New Zealand	1 × 10^3			
Graedel *et al.*[12] (1974)	Polluted Air USA	1 × 10^3			
Hitchcock *et al.*[13] (1977)	U.S. (NC) Polluted Marsh	80			
Slatt *et al.*[6] (1978)	Miami, FL polluted air	0.17–1.15			
Maroulis, Bandy[14] (1977)	U.S. (VA Coast)		0.15		
Hanst *et al.*[15] (1975)	U.S. Atmosphere				0.27–0.80
Sandall & Penkett[16] (1977)	UK Atmosphere			0.24–1.26	1.29–1.50
Maroulis *et al.*[17] (1977)	Philadelphia, PA (U.S.)				1.17 ± 0.07
Maroulis *et al.*[17] (1977)	Wallops Island, VA (U.S.)				1.21 ± 0.083
Maroulis *et al.*[17] (1977)	Lawton, OK (U.S.)				1.37 ± 0.096
Torres *et al.*[18] (1978)	Latitude Range 67°N–57°S				1.37 ± 0.16
Inn *et al.*[19] (1979)	38°N–119°W (15.2 km)				1.31–140

air concentration in the temperate zone of France was close to that in Boulder, CO; it ranged from 0.017–0.17 $\mu g/m^3$. These same investigators found that the atmospheric H_2S was much higher in the equatorial region of the Ivory Coast, ranging from 0.1–8.7 $\mu g/m^3$. It is noted that urban air in Miami, FL had an H_2S concentration much lower than this—0.17–0.15 $\mu g/m^3$.[6]

In areas where high H_2S concentrations are suspected, very high concentrations have been found. Hitchock *et al.*[13] measured H_2S in the air above a tidal marsh in North Carolina and found the concentration to be as high as 80 $\mu g/m^3$. These data may be unreliable, however, because they were possibly influenced by a nearby sewage treatment plant. At a sampling station 0.4–11.3 km away from industrial sources, Graedel *et al.*[12] measured long-term H_2S concentrations exceeding 1 × 10^3 $\mu g/m^3$. Denmead[11] found H_2S concentrations approaching 1 × 10^3 $\mu g/m^3$ above the highly polluted, shallow backwaters of a harbor.

Originally H_2S was considered to be the only biogenic form of sulfur. In 1972 DMS was found in sea water and in the headspace gas of soils and organic matter stored under several laboratory conditions.[20]

In 1975 Hanst *et al.*[15] used a cryogenic procedure for concentrating trace gases in the atmosphere and analysis by means of long-path infrared absorption spectroscopy and observed COS in the North Carolina atmosphere at concentrations of 0.49 $\mu g/m^3$. In 1977 Sandalls and Penkett[16] employed cryogenic sample concentration and subsequent gas chromatographic analysis to find atmospheric COS and CS_2 in Harwell, England at concentrations of 1.25 and 0.59 $\mu g/m^3$, respectively. In the same year Maroulis and Bandy[14] found average DMS concentrations as high as 0.15 $\mu g/m^3$ at two sites along the coast of Virginia.

Because all sulfur species are eventually oxidized to SO_2 and sulfates, the concentration of atmospheric SO_2 gives a general indication of the original total concentration of other sulfur compounds. Therefore, instead of measuring the other sulfur compounds individually, the atmospheric reaction product SO_2 is sometimes determined. In a remote, moist equatorial forest of the Ivory Coast, Delmas *et al.*[9,10] measured the atmospheric SO_2 concentration and found it to be ~30 $\mu g/m^3$. This SO_2 is the secondary reaction product from the decomposition of organic litter and humus. The concentration is comparable to SO_2 levels in industrial zones and higher than those reported for rural zones in the U.S. and Europe. In comparison, marine concentrations of SO_2 in the air near the Ivory Coast are low (0.1–0.5 $\mu g/m^3$).

Sulfur Flux Measurements

Recently, comprehensive experimental measurements have been reported for earth atmosphere fluxes of biogenic sulfur compounds.[7,9–10,14,21–29] Table II[7,10,17,21–26,30,31] presents these measurements as published values for natural biogenic sulfur emissions from salt and fresh water marshes (i.e. by bacterial reduction of sulfate), from various inland soils and vegetative cover, and from the decomposition of tropical vegetation.

Although these measurements show wide variations from site to site, the differences may, in part, be associated with the temperature range at the time of sampling and the type of soils where the measurements were made. Some of the variations in measured fluxes may be due to the different sampling and analytical methods used by these investigators.

Measurements over Marshes, Swamps, and Intertidal Zones

The first direct measurements of emission fluxes were reported by Aneja[21] and published by Hill *et al.*[22] The latter reported that the biogenic H_2S fluxes above a Long Island salt marsh varied from below detection limit to 42 $gS/m^2/yr$ with a strong seasonal variation. When these values are corrected for seasonal (i.e. temperature) and tidal variations, the average H_2S flux is ~0.5 $gS/m^2/yr$ for this marsh. Other sulfur gases were found in the flux from this marsh. The maximum fluxes measured were: CH_3SH, 1.92 $gS/m^2/yr$; DMS, 3.84 $gS/m^2/yr$; and $(CH_3)_2S_2$, 0.81 $gS/m^2/yr$.

Hansen *et al.*[23] observed copious quantities of H_2S in two shallow, coastal areas of Denmark. Here the peak emission rates were ~89 to ~2000 $gS/m^2/yr$ with diurnal averages equivalent to ~19 to ~470 $gS/m^2/yr$. Aneja *et al.*[24] reported peak H_2S flux values from salt marshes at Cox's Landing, NC of ~100 $gS/m^2/yr$ with an average over the mud flat zone of ~0.5 $gS/m^2/yr$.

At the same locale over the *Spartina alterniflora* zone, the average DMS flux values were found to be ~0.66 $gS/m^2/yr$.[24,25] CS_2 and COS flux values were also measured from the same salt marsh by Aneja *et al.*[26–29,32] who reported the estimated emission rates as ~0.2 $gS/m^2/yr$ and ~0.03 $gS/m^2/yr$, respectively. Adams *et al.*[31] working at this location under different climatic and surface conditions and excluding emissions from tide water surfaces, observed quite different CS_2 and COS emission rates—1.13 and 6.36 $gS/m^2/yr$, respectively.

Table II. Biogenic emissions of sulfur compounds. Emission rate gS/m^2/yr.

Reference	Source	H_2S Avg.	H_2S Max.	DMS Avg.	DMS Max.	DMDS Avg.	DMDS Max.	CH_3SH Avg.	CH_3SH Max.	CS_2 Avg.	CS_2 Max.	COS Avg.	COS Max.
Aneja[21] (1975) Hill, Aneja, Felder[22] (1977)	Salt Marsh, NY	0.55	41.5		3.84		0.81		1.92				
Maroulis, Bandy (1977)	Atlantic Ocean, VA			0.006									
Aneja *et al.*[24–26] (1979)	Salt Marsh, NC	0.5	100	0.66	2.5						0.2		0.03
Aneja *et al.*[30]	Fresh Water Marsh, NC	0.6	1.27										
Adams *et al.*[31] (1979)	Salt Marsh, NC	72	381	0.093		0.004			6.56		1.13		6.36
Adams *et al.*[31] (1979)	Inland Soils U.S.	0.001		0.001		0.001				0.001		0.002	
Jaeschke[7] *et al.* (1978)	Swamps and tidal flats	0.044											
Hansen *et al.*[23] (1978)	Sediments of shallow coastal area, Denmark	~19	~2000										
Delmas *et al.*[10] (1979)	Soils of humid equatorial forests Ivory Coast (near a salt marsh)	0.07	2.6										
Delmas *et al.*[10] (1979)	Soils of temperate regions, France	0.044	0.24										

A year later Adams *et al.*[27–29] reported a peak H_2S flux value of ~381 gS/m^2/yr with an average value of ~71 gS/m^2/yr in the intertidal salt marsh at Cox's Landing. (Incidentally, these researchers observed average CH_3SH emissions from this marsh of ~6.5 gS/m^2/yr, corroborating the earlier findings of Aneja[21] and Hill *et al.*[22])

Measurements over Land

Aneja *et al.*[30] measured H_2S flux rates from a fresh water marsh soil in North Carolina and found an emission rate varying between ~0.08 and 1.27 gS/m^2/yr with an average value of 0.6 gS/m^2/yr. Adams *et al.*[31] studied the emissions from a North Carolina histosol soil produced from an ancient, fresh-water cyprus swamp and reported an average H_2S emission of 0.018 gS/m^2/yr.

Jaeschke *et al.*[7] calculated a H_2S flux of 0.044 gS/m^2/yr for the Island of Sylt (off the shore of Denmark). This study also showed that the flux of H_2S above aerobic soils is negative, i.e. these soils are a sink for H_2S.

In a broad and diverse inland study area in the eastern and southern U.S., Adams *et al.*[27–29,31,33,34] reported H_2S fluxes consistent with Jaeschke's[7] values, ranging from 0.01–0.17 gS/m^2/yr, in addition to the fluxes of several other sulfur gases including DMS, CS_2, and COS. Although the fluxes of all of these gases are much lower than fluxes over marshes, swamps, and intertidal zones of more limited area, measurements at more than 30 sites indicate that these inland soils contribute up to 58% of the total biogenic sulfur over this inland area.

Delmas *et al.*[10] measured H_2S emitted by anaerobic soils of humid equatorial forests of the Ivory Coast and estimated the flux to be between ~0.3 and ~2.6 gS/m^2/yr. They also measured H_2S emissions from three aerobic, grass-covered (lawn) soils between 43 and 47 N latitude in France and found them to be low in contrast, varying between 0.007 and 0.24 gS/m^2/yr with an average value of 0.04 gS/m^2/yr. At five sites at the same latitude in New York, Michigan, Wisconsin, Massachusetts, and Minnesota, Adams *et al.*[34] measured sulfur fluxes and found them to be consistent with the Delmas *et al.* data.[9,10] The H_2S flux was found to range from undetectable to 0.16 gS/m^2/yr with an average flux of 0.04 gS/m^2/yr for all five sites. (These investigations were a part of the extensive Sulfate Regional Experiment Study, (SURE.[35]) In addition, the total sulfur flux from these five U.S. sites ranges from 0.013–0.33 gS/m^2/yr.[34] Thus, approximately 30–50% of the total measured sulfur flux at these five sites consists of organo-sulfur compounds—primarily CS_2, COS, and DMS, the remainder being H_2S.

The Stratospheric Aerosol Layer

In order to describe the global sulfur cycle adequately, the sulfur content of both the troposphere and the stratosphere must be taken into consideration. In 1961 Junge[36,37] suggested that sulfur could be found in the stratosphere and measurements were made to confirm its presence. Because all gaseous sulfur compounds except for COS and CS_2 are oxidized rapidly in the troposphere, it was decided that COS and CS_2 are responsible for the presence of sulfur in the stratosphere.

Two studies consider the possible contribution of COS and CS_2 from salt marshes to the stratospheric sulfate aerosol layer.[26,38] It can be calculated that CS_2 and COS from salt marshes account for more than 100% of the stratospheric sulfur. This calculation is based on the following synthesis. According to Crutzen's[39] estimate, a flux of 1.8×10^{-4} gS/m^2/yr into the stratosphere accounts for the entire stratospheric sulfate aerosol layer.

Applying Junge's[37] one-dimensional eddy diffusion model to the troposphere, and using the mean sum of CS_2 and COS maximum emission rates for global marshes (Table II) and CS_2 and COS atmospheric lifetimes (Table III),[16,40–45] the mean maximum contribution due to CS_2 and COS can be computed to be greater than 100% (Table IV). (This

Table III. Atmospheric residence times of CS_2 and COS.

Reference	Atmospheric residence time, days CS_2	Atmospheric residence time, days COS
Sandals, Penkett[16] (1977)	365	7300
Kurylo[40] (1978)		503
Atkinson *et al.*[41] (1978)		4134
Logan *et al.*[42] (1979)	60	200
Ravishankara *et al.*[43] (1980)	19290	3288
Cox, Sheppard[44] (1980)		723
Turco *et al.*[45] (1980)	45	365

Table IV. Contribution of biogenic sulfur compounds to the global sulfur cycle.

	Mean average	Mean maximum
Biogenic emissions of total sulfur species (ΣS) gS/m^2/yr (Table II)	~10.7	~373.1
Biogenic contribution of (ΣS) to the troposphere ton/yr	~4.1 × 10^6	~142 × 10^6
Biogenic contribution of COS + CS_2 to stratospheric sulfate aerosol layer	~1%	>100%

calculation assumes zero CS_2 and COS concentrations at 15 km height.)

The Biogenic Contribution

It is interesting to speculate on the possible role of biogenically produced H_2S, DMS, DMDS, CH_3SH, CS_2, and COS in the sulfur cycle of the troposphere and the stratosphere. The estimated biogenic contribution to balance the global sulfur cycle ranges from 40 × 10^6–230 × 10^6 tons of gaseous sulfur per year.[36,46–51] It has been assumed that the real value may lie somewhere between these limits. Measurements of sulfur removed from the troposphere by rainwater (as sulfate) indicate that 100 × 10^6 tons of gaseous sulfur, put into the atmosphere by biogenic processes, is removed from the troposphere by rainwater.[48]

It has been calculated that the contribution from salt marshes is mean ~4.1 × 10^6 ton/yr and maximum ~142 × 10^6 ton/yr by making the following assumptions:

- All salt marshes emit uniformly.
- The total salt marsh area is 3.8 × 10^5 km^2.[52]
- The total sulfur (ΣS) emission rate for salt marshes is mean arithmetic average ΣS = ~10.3 gS/m^2/yr and mean arithmetic maximum ΣS = ~361 gS/m^2/yr. Using a total annual turnover of 100 × 10^6 ton of biogenic sulfur, it can be seen that marshes contribute mean ~4% and maximum ~100% of the biogenic sulfur compounds.

In conclusion, when biogenic sulfur compounds from both sulfate reduction and plant decomposition generation processes are considered, there is a great variation in the measured emission rates for different kinds of locales. While the maximum emission rate measurements from salt marshes certainly make a significant contribution to the global sulfur cycle, the mean average values do not. Adams[34] reported that nearly 58% of the biogenic sulfur emissions from the SURE study area originated from inland soils which represent nearly 90% of the study area. Obviously, additional field measurements at carefully defined locales are needed to characterize global processes adequately. A large body of biogenic sulfur flux data is becoming available for the temperate zone, particularly in the northern hemisphere. However, very limited data are available from the tropics which may be the greatest source of biogenic sulfur gases due to the tropical wetlands, the high biomass, and the high ambient temperatures.

Methods for Measuring Flux

Two methods are used to measure earth-atmosphere fluxes of gases. In the chamber method (Figure 2, direct measurement), an open-bottom chamber is placed over the surface to capture the gases emanating from the surface. A carrier gas is introduced into the chamber and mixed with these gases. The effluent gas is sampled and analyzed for the compounds of interest and the flux is estimated by mass balance.

In the micrometeorological method (Figure 3, indirect measurement), the concentration of the gas of interest is measured at various altitudes above the source along with the wind speed and direction. Estimates of flux are made by applying turbulent diffusion theory to the concentration profile data.

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References

1. A. F. Smith, D. G. Jenkins, D. E. Cunningworth, "Measurements of trace quantities of hydrogen sulfide in industrial atmosphere," *J. Appl. Chem.* **11:** 317 (1961).
2. J. P. Lodge, J. B. Pate, "Atmospheric gases and particulates in Panama," *Science* **153:** 408 (1966).
3. M. C. Axelrod, J. H. Cary, J. E. Bonelli, J. P. Lodge, Jr., "Fluorescence determination of sub parts per billion hydrogen sulfide in the atmosphere," *Anal. Chem.* **41:** 1850 (1969).
4. D. F. S. Natusch, M. B. Klonis, H. D. Axelrod, R. J. Teck, J. P. Lodge, Jr., "Sensitive method for the measurement of atmospheric hydrogen sulfide," *Anal. Chem.* **44:** 2067 (1972).
5. R. J. Breeding, J. P. Lodge, Jr., J. B. Pate, D. C. Sheesley, H. B. Klonis, B. Fogle, J. A. Anderson, T. R. Englert, P. L. Haagenson, A. F. Wartburg, "Background trace gas concentrations in the central United States." *J. Geophys. Res.* **78:** 7057 (1973).
6. B. J. Slatt, D. F. S. Natusch, J. M. Prospero, D. L. Savoie, "Hydrogen sulfide in the atmosphere of the northern equatorial Atlantic Ocean and its relation to the global sulfur cycle," *Atmos. Environ.* **12:** 981 (1978).
7. W. Jaeschke, H. M. Georgii, H. Claude, H. Malewski, "Contributions of H_2S to the atmospheric sulfur cycle," *Pure and Appl. Geophys.* **116**(2/3): 463 (1978).
8. H. W. Georgii, "Large-scale spatial and temporal distribution of sulfur compounds." *Atmos. Environ.* **12:** 681 (1978).
9. R. Delmas, J. Bandet, J. Servant, "A demonstration of the natural sources of sulfate in a moist tropical environment," *TELLUS* **30:** 158 (1978).
10. R. Delmas, J. Bandet, J. Servant, R. Baziard, "Emissions and Concentration of Hydrogen Sulfide in the Air of the Tropical Forest of the Ivory Coast and of Temperate Regions in France," Fourth International Conference of the Commission of Atmospheric Chemistry and Global Pollution, University of Colorado, Boulder, CO, 1979.
11. C. F. Denmead, "Air Pollution by Hydrogen Sulfide from a Shallow Polluted Tidal Inlet, Auckland, New Zealand," in

$$\text{Emission rate, } n = \frac{F \cdot \Delta C}{A}$$

F=Steady volumetric flow rate of gas through the chamber
ΔC=Concentration increase
A=Area of emitting surface covered by the chamber

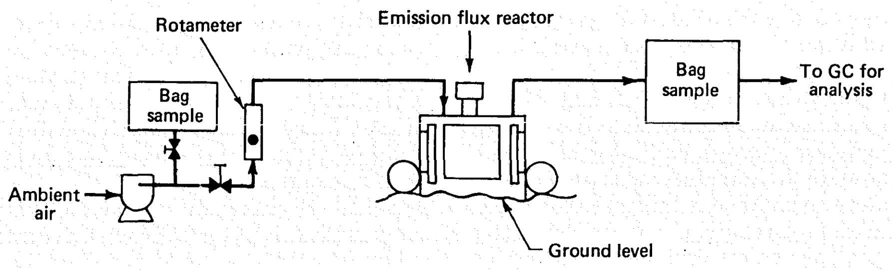

Figure 2. Layout of field experiment using emission flux reactor with ambient air carrier gas.[24]

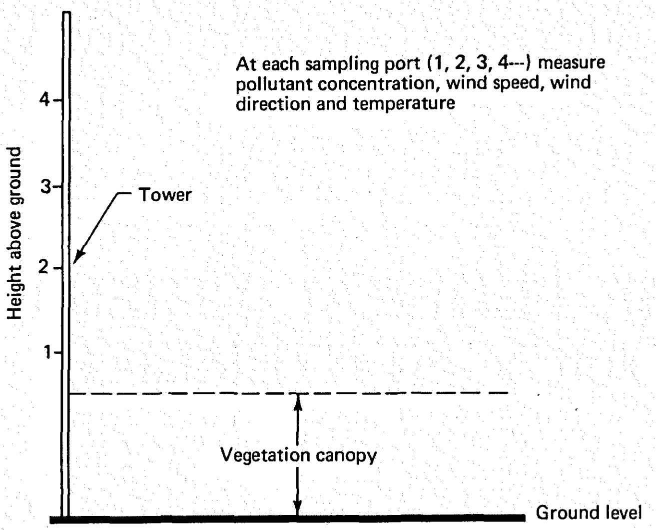

Figure 3. Micrometeorological method. Emission rate $n = K_Z \cdot \Delta C / \Delta Z$, where K_Z = vertical diffusivity and $\Delta C / \Delta Z$ = vertical pollutant concentration gradient.

Proc. Clean Air Conference, University of New South Wales, Paper No. 4, First Technical Session, 1962.

12. T. E. Graedel, B. Kleiner, C. C. Patterson, 1974. "Measurements of extreme concentration of tropospheric hydrogen sulfide," *J. Geophys. Res.* **79:** 4467 (1974).
13. D. R. Hitchcock, L. L. Spiller, W. E. Wilson, "Biogenic Sulfides in the Atmosphere in a North Carolina Tidal Marsh," Paper presented at the New Orleans American Chemical Society Meeting, March 1977.
14. P. J. Maroulis, A. R. Bandy, "Estimate of the contribution of biologically produced dimethyl sulfide to the global sulfur cycle," *Science* **196:** 647 (1977).
15. P. L. Hanst, L. L. Spiller, D. M. Watts, J. W. Spence, M. F. Miller, "Infrared measurements of fluorocarbons, carbon tetrachloride, carbonyl sulfide, and other atmospheric trace gases," *JAPCA* **25:** 1220 (1975).
16. F. J. Sandalls, S. A. Penkett, "Measurements of carbonyl sulfide and carbon disulfide in the atmosphere," *Atmos. Environ.* **11:** 197 (1977).
17. P. J. Maroulis, A. L. Torres, A. R. Bandy, "Atmospheric conditions of carbonyl sulfide in the south-western and eastern United States," *Geophys. Res. Lett.* **4:** 510 (1977).
18. A. L. Torres, P. J. Maroulis, A. B. Goldberg, A. R. Bandy, "Measurement of Tropospheric COS on the 1978 GAMETAG Flights," *EOS-Trans. Amer. Geophys. Union* **59:** 1082 (1978).
19. E. C. Y. Inn, J. F. Vedder, B. J. Tyson, "COS in the stratosphere," *Geophys. Res. Lett.* **6:** 191 (1979).
20. J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, "Atmospheric dimethyl sulfide and the natural sulfur cycle," *Nature* **237:** 452 (1972).
21. V. P. Aneja, "Characterization of Sources of Biogenic Atmospheric Sulfur Compounds," M.S. Thesis, Department of Chemical Engineering, North Carolina State University, Raleigh, NC, 1975.
22. F. B. Hill, V. P. Aneja, R. M. Felder, "A technique for measurement of biogenic sulfur emission fluxes," *Environ. Sci. Technol.* **13:** 199 (1978).
23. M. H. Hansen, K. Ingvoren, Jorgensen, "Mechanisms of hydrogen sulfide release from coastal marine sediments to the atmosphere," *Limnology Oceanology* **23**(1): 66 (1978).
24. V. P. Aneja, E. W. Corse, L. T. Cupitt, J. C. King, J. H. Overton, Jr., R. E. Rader, M. H. Richards, H. J. Sher, R. J. Whitkus, "Biogenic Sulfur Sources Strength Field Study." Northrop Services, Inc. Report No. ESC-TR-79-22, Research Triangle Park, NC, 1979, p. 189.
25. V. P. Aneja, J. H. Overton, Jr., L. T. Cupitt, J. L. Durham, W. E. Wilson, "Direct measurements of emission rates of some atmospheric biogenic sulfur compounds," TELLUS **31**(2): 176 (1979).
26. V. P. Aneja, J. H. Overton, Jr., L. T. Cupitt, J. L. Durham, W. E. Wilson, "Carbon disulfide and carbonyl sulfide from biogenic sources and their contribution to the global sulfur cycle," *Nature* **282**(5738): 493 (1979).
27. D. F. Adams, "Estimates of Natural Source Strengths," Chapter in *Atmospheric Sulfur Deposition: Environmental Impact and Health Effects*, Ed. D. S. Shiner, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1980.
28. D. F. Adams, S. O. Farwell, E. Robinson, M. R. Pack, "Assessment of Biogenic Sulfur Emissions in the SURE Area," EPRI Final Report, No. EA-1516, Electric Power Research Institute, Palo Alto, CA, Sept. 1980.
29. D. F. Adams, S. O. Farwell, E. Robinson, M. R. Pack, "Biogenic sulfur gas emissions from soils in eastern and southeastern United States," *JAPCA* **31:** 1083 (1981).
30. V. P. Aneja, J. H. Overton, A. P. Aneja, "Emission survey of biogenic sulfur flux from terrestrial surfaces," *JAPCA* **31:** 256 (1981).
31. D. F. Adams, S. O. Farwell, M. R. Pack, W. L. Bamesberger, "Preliminary measurements of biogenic sulfur-containing gas emissions from soils," *JAPCA* **29:** 380 (1979).
32. V. P. Aneja, J. H. Overton, Jr., L. T. Cupitt, J. L. Durham, W. E. Wilson, "Measurements of emission rates of carbon disulfide from biogenic sources and its possible importance to the stratospheric aerosol layer," *Chem. Eng. Communications* **4**(6): 721 (1980).
33. D. F. Adams, S. O. Farwell, M. R. Pack, E. Robinson, "An Initial Emission Inventory of Biogenic Sulfur Flux from Terrestrial Surfaces," Paper No. 78-16 Presented at the Annual Meeting of PNWIS/APCS, Portland, OR, 1978.
34. D. F. Adams, S. O. Farwell, E. Robinson, M. Pack, W. L. Bamesburger, "Biogenic Sulfur Source Strength," Paper No. 81-15.3 Presented at the Annual Meeting of APCA, Philadelphia, PA, 1981.
35. R. M. Perhac, "Sulfate regional experiment in northeastern United States: The "SURE" program," *Atmos. Environ.* **12:** 641 (1978).
36. C. E. Junge, *Air Chemistry and Radioactivity*, Academic Press, New York, 382 pp.
37. C. Junge, 1963, "Sulfur Budget of the Stratospheric Aerosol Layer," in *Proceedings of the International Conference of Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations*, Melbourne, Australia, 1974.
38. V. P. Aneja, "Direct Measurements of Emission Rates of Some Atmospheric Biogenic Sulfur Compounds and Their Possible Importance to the Stratospheric Aerosol Layer," Chapter in *Atmospheric Sulfur Deposition: Environmental Impact and Health Effects*, Ed. D. S. Shriner, Ann Arbor Science Publishers, Inc., Ann Arbor, MI 1980.
39. P. J. Crutzen, "The possible importance of COS for the sulfate layer of the stratosphere," *Geophys. Res. Letters* **3**(2): 73 (1976).
40. M. J. Kurylo, 1978. "Flash photolysis resonance fluorescence investigation of the reactions of OH radicals with COS and CS_2," *Chem. Phys. Lett.* **58:** 238 (1978).
41. R. Atkinson, R. A. Perry, J. N. Pitts, Jr., 1978. "Rate constant for the reaction of OH radicals with COS, CS_2, and CH_3SCH_3 over the temperature range 299–430K," *Chem. Phys. Lett.* **54:** 14 (1978).
42. J. A. Logan, M. B. McElroy, S. C. Wofsy, M. J. Prather, "Oxidation of CS_2 and COS: sources for atmospheric SO_2," *Nature* **281:** 185 (1979).
43. A. R. Ravishankara, N. M. Kreutter, R. C. Shah, P. H. Wine, 1980. "Rate of reaction of OH with COS," *Geophys. Res. Letters* **7**(11): 861 (1980).
44. R. A. Cox, D. Sheppart, "Reactions of OH with gaseous sulfur compounds," *Nature* **284:** 330 (1980).
45. R. P. Turco, R. C. Whitten, O. D. Toon, E. C. Y. Inn, P. Hamill, "Stratospheric hydroxyl radical concentrations: new limitations suggested by observations of gaseous and particulate sulfur," to be published.
46. E. J. Conway, "Mean geochemical data in relation to ocean evolution," *Proc. Royal Irish Academy, A*, **48:** 119 (1943).
47. E. Eriksson, "The yearly circulation of sulfur in nature," *J. Geophys. Res.* **68:** 4001 (1963).
48. E. Robinson, R. C. Robbins, "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants," SRI Project Report PR-6755, prepared by American Petroleum Institute, New York, 1968, 123 pp.
49. W. W. Kellogg, R. D. Cadle, E. R. Allen, A. L. Lazrus, E. Martell, "The sulfur cycle," *Science* **175:** 587 (1972).
50. J. P. Friend, "The Global Sulfur Cycle," in *Chemistry of the Lower Atmosphere* S. I. Rasool, Ed., Plenum Press, New York, 1973. pp. 221–241.
51. L. Granat, R. O. Hallberg, H. Rodhe, 1976. "The Global Sulfur Cycle," in B. H. Svensson and R. Soderlund, Eds.—*Nitrogen, Phosphorus and Sulfur-Global Cycles*, SCOPE Report 7. Ecol. Bull Stockholm **22:** 39 (1976).
52. G. M. Woodwell, P. M. Rich, C. A. A. Hall, 1973. "Carbon and the Biosphere," E. M. Woodwell and E. V. Pecan, Eds., AEC Symposium, 30, U.S. Department of Commerce, 1973. pp. 221–241.