

SULFUR CYCLE

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CURRENT ISSUES

Human activities strongly influence the tropospheric sulfur cycle in certain regions of the world, particularly in and downwind of populated areas. The literature on the reaction and transformation of SO₂ and its distribution and transport in eastern North America and western Europe is voluminous. A reading of even selected portions of the literature on sulfur cycling illustrates that measurements and models of sulfur on the regional scale are providing a relatively consistent understanding of the sources, transport, and fate of anthropogenic emissions of SO₂. However, with the possible exception of reasonably well-understood processes related to local and mesoscale impacts of anthropogenic SO₂, global sulfur cycle studies are in the infancy stage.

Among the general categories of tropospheric sulfur sources, anthropogenic sources have been quantified the most accurately, particularly for the OECD countries. Research on fluxes of sulfur compounds from volcanic sources is now in progress. However, very few generally accepted measurements are available for either concentrations or fluxes of SO₂, H₂S, DMS, DMDS, CS₂, COS, and other sulfur species derived from natural biogenic sources. Measurement techniques have been inadequate until recently; serious questions still remain concerning flux determinations. Tables 7.4, 7.5, and 7.6 summarize most of the data available in the open literature.

What do the existing data indicate in terms of interesting hypotheses and the design of future global studies? First, natural sources of reduced sulfur compounds are highly variable in both space and time. Variables, such as soil temperature, hydrology (tidal and water table), and organic flux into the soil, all interact to determine microbial production and subsequent emissions of reduced sulfur compounds from anaerobic soils and sediments. For example, fluxes of H₂S, COS, CS₂,

(CH₃)₂S, (CH₃)₂S₂, and CH₃SH can vary by several orders of magnitude on time scales of hours and space scales of meters in a coastal environment. A second interesting aspect of existing data on biogenic sources of reduced sulfur relates to the origin of relatively high SO₂ values measured in the mid-troposphere over the tropics and in the southern hemisphere during GAMETAG.

SOURCES AND DISTRIBUTIONS

Current estimates of global sources of atmospheric sulfur are based on very few data and will not be discussed in detail here. Several recent comprehensive reviews are cited at the end of this section for the reader unfamiliar with previous attempts to estimate sulfur sources. We briefly summarize available information on sources of COS, CS₂, DMS, and H₂S to the troposphere in the following paragraphs; these are the major biogenic sulfur species with a clearly identified role in tropospheric chemistry.

Carbonyl Sulfide (COS)

Carbonyl sulfide is the most abundant gaseous sulfur species in the troposphere. Concentrations of COS are approximately 500 ± 50 pptv, with no detectable systematic variations vertically or latitudinally. This constant concentration with altitude and latitude suggests a relatively long atmospheric lifetime, estimated to be around 2 years.

Current estimates of global sources and sinks of COS are summarized in Table 7.6. It is important to note that these source and sink estimates are derived by extrapolation of a very limited data base and are subject to large uncertainties. Recent data suggest that oceanic regions of high biological productivity and organic content, particularly coastal waters and upwelling areas, are a major global source of COS. Experiments in coastal waters

TABLE 7.4 Approximate Tropospheric Concentration Range of Selected Sulfur Compounds in Unpolluted Air

Location	Atmospheric Concentrations ^a (ng/m ³)				
	H ₂ S	DMS	CS ₂	COS	SO ₂
Ocean boundary layer	< 5-150	< 2-200	1200-1550	50-70	< 15-300
Temperate continental boundary layer	20-200	PD	1200-1550	PD	< 15-300
Tropical coastal boundary layer	100-9000	PD	1200-1550	PD	PD
Free troposphere	PD	< 2(PD)	1200-1550	< 10	30-300

^aPD indicates poorly determined at this review.

TABLE 7.5 Biogenic Emissions of Sulfur Compounds (emission rate in g S/m²/yr)

Location	H ₂ S		DMS		CS ₂		COS	
	Avg.	Max.	Avg.	Max.	Avg.	Max.	Avg.	Max.
Salt marsh	0.55	41.5		3.84				
	0.5	100	0.006					
	72	381	0.66	2.5		0.2		0.03
	0.6	1.27	0.093			1.13		6.36
Freshwater marsh	0.001							
Inland soils (U.S.)	0.044				0.001		0.002	
Swamps and tidal flats	~19	~2000						
Sediments of shallow coastal area	0.07	2.6						
Soils of humid equatorial forests	0.044	0.24						
Soils of temperate regions			0.106					
Open ocean								

indicate that COS is produced by photooxidation of dissolved organic matter independent of salinity, plant metabolism, or bacterial activity.

Some authors have suggested that the oceans may be a net sink for COS from the atmosphere. An intensive research program concerned with the production, distribution, and emissions of COS from coastal and oceanic environments will be required to quantify the role of the marine environment as a source of this compound.

Soils can also be a source of COS to the troposphere. Coastal salt marsh soils appear to be a "hot spot" for COS emissions, but the small area of these soils limits the role of marshes as a major global source. Measurements from a variety of soils in the United States were used to calculate the global soil source of COS shown in Table 7.6. The total absence of data on COS emissions from tropical soils introduces significant uncertainties into estimates of the global soil source. Efforts to quantify COS emissions from soils will probably be complicated by large variations in both space and time. Microbial processes that produce COS are influenced by soil moisture, nutrients, soil organic content, and other physiochemical variables.

Combustion processes are also thought to be a significant global source of COS. These processes include biomass burning, fossil fuel burning, and high-temperature industrial processes involving sulfur compounds. Again, it must be emphasized that these estimates are based on very limited data and may change significantly as new data become available.

During periods of low volcanic activity, COS may be a major source of sulfur to the stratosphere, resulting in the formation of the stratospheric aerosol layer that influences the earth's climate. The anthropogenic sources of COS identified in Table 7.6 represent approximately 25 percent of the total source strength, supporting speculations of possible effects on climate within the next century. Because of the importance of COS in the global sulfur cycle, its sources, atmospheric chemistry, and sinks are a critical scientific issue.

Carbon Disulfide (CS₂)

The abundance and distribution of CS₂ in the troposphere are not well known. Available measurements in the literature at this date show a typical range from approximately 15 to 30 pptv in surface nonurban air to 100 to 200 pptv in surface polluted air. The concentra-

TABLE 7.6 Global Sources and Sinks of Carbonyl Sulfide

	Estimate	Range
Sources (Tg/yr)		
Oceans	0.60	0.3-0.9
Soils	0.40	0.2-0.6
Volcanoes	0.02	0.01-0.05
Marshes	0.02	0.01-0.06
Biomass burning	0.20	0.1-0.5
Coal-fired power plants	0.08	0.04-0.15
Automobiles, chemical industry and sulfur recovery processes	0.06	0.01-0.3
Subtotal	1.4	≤ 3
CS ₂ -COS: CS ₂ -photochemistry and OH reactions	0.60	0-2
Total	2	≤ 5
Global burdens (Tg)	4.7	3.8-5.2
(500 pptv)		
Lifetime (yr)	2-2.5	≥ 1
Sinks (Tg/yr)		
OH reaction	0.8	0.1-1.5
Stratospheric photolysis	0.1	≤ 0.2
O reaction	0.03	—
Other	1.1	≤ 3.3

NOTES The estimated emissions are consistent with observed distributions of COS and CS₂ according to a global mass balance. All combinations of emissions within the ranges given above may not be consistent.

SOURCE. From Khalil and Rasmussen, 1984.

tion of CS₂ appears to decrease rapidly with altitude, indicating ground sources and a relatively short atmospheric lifetime. The primary removal mechanism for CS₂ in the troposphere is thought to be reaction with OH, producing COS and SO₂. The reaction rate constants for oxidation of CS₂ are poorly known, and the relative importance of CS₂ as a precursor for atmospheric COS and SO₂ is an unresolved issue.

The primary natural sources of COS and CS₂ are thought to be similar. The one available set of measurements of CS₂ in seawater indicates that concentrations are highest in coastal waters.

Dimethylsulfide (CH₃)₂S

Dimethylsulfide (DMS) is the most abundant volatile sulfur compound in seawater with an average concentration of $\sim 100 \times 10^{-9}$ g/l. This compound is produced by both algae and bacteria. The evidence for a biogenic origin for DMS has come from laboratory measurements of emissions produced in pure, axenic cultures of marine planktonic algae and field measurements of emissions from soils, benthic macroalgae, decaying algae, and corals. Extensive oceanographic studies have shown direct correlations between DMS concentrations in seawater and indicators of phytoplankton activity. The vertical distribution, local patchiness, and distribution of DMS in oceanic ecozones exhibit a pattern very similar to primary productivity. Selected groups of marine organisms such as coccolithophorids (i.e., a type of marine planktonic algae) and stressed corals are particularly prolific producers of DMS. The calculated global sea-to-air flux of sulfur as DMS is ~ 0.1 g S/m²/yr, which totals to approximately 39×10^{12} g S/yr. A more limited set of measurements has been made in coastal salt marshes with DMS emissions commonly in the range of 0.006 to 0.66 g S/m²/yr.

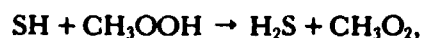
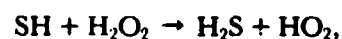
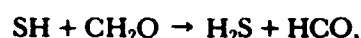
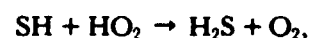
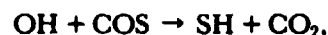
Hydrogen Sulfide (H₂S)

Knowledge of natural sources of H₂S to the troposphere is still rudimentary. Preliminary studies have shown that anaerobic, sulfur-rich soils (e.g., coastal soils and sediments) emit H₂S to the atmosphere, albeit with strong temporal and spatial variations. Hydrogen sulfide fluxes at a single location can vary by a factor of up to 10⁴ depending on variables such as light, temperature, Eh, pH, O₂, and rate of microbial sulfate reduction in the sediment. The presence of active photosynthetic organisms or a layer of oxygenated water at the sediment surface can reduce or stop emissions due to rapid oxidation of H₂S.

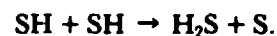
Agricultural and forest soils can also be a source of H₂S to the atmosphere. Measurements by several inves-

tigators suggest that maximum emissions from nonmarine soils are associated with wet tropical forest soils. It is likely that many soils that appear to be aerated contain anaerobic microhabitats suitable for microbial sulfate reduction; the magnitude of H₂S emissions will depend on the net effects of many processes that influence production, transport in the soil, oxidation rates, and exchange at the soil-air interface.

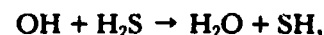
Photochemical sources for atmospheric H₂S have been proposed to occur through a combination of the following reactions:



and



Removal of H₂S is thought to be accomplished by



resulting in a lifetime of approximately 1 day. In situ photochemical production from COS and CS₂ precursors is the most likely source of H₂S measured in remote ocean air. Atmospheric concentrations of H₂S in continental air are highly variable, resulting from a complex interaction of factors determining ground emissions, in situ photochemical production, and atmospheric lifetime.

TRANSFORMATIONS AND SINKS

The oxidation of SO₂ to H₂SO₄ can often have a significant impact on the acidity of precipitation, currently an issue of national and international concern. A schematic representation of some important transformations and sinks for selected sulfur species is illustrated in Figures 5.11, 5.13, and 7.5. The oxidation of reduced sulfur compounds, such as H₂S, CS₂, (CH₃)₂S, and others, leads to the production of acids or acid precursors such as SO₂, SO₄²⁻, and CH₃SO₃H. Subsequent oxidation steps involving a combination of homogeneous and heterogeneous reactions lead to the production of H₂SO₄, which is removed from the atmosphere by wet and dry deposition processes (see Chapter 5). Carbonyl sulfide appears to be relatively inert in the troposphere and is primarily destroyed in the stratosphere.

In terms of experiments to elucidate the fast photochemistry of this system, measurement schemes will be

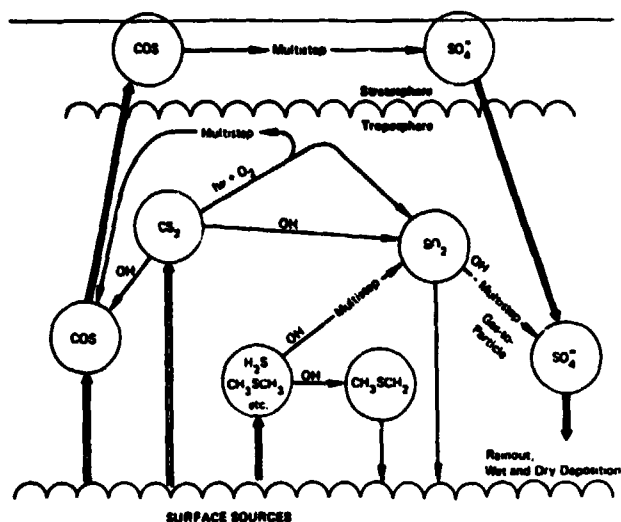


FIGURE 7.5 A tentative scheme for the oxidation and removal of atmospheric sulfur species.

needed to verify the chemical pathways by which reduced sulfur species are oxidized to SO_2 and SO_4^{2-} . It is probable that it will be useful to carry out these experiments in a variety of different environments, including areas of intense sulfur emissions (e.g., swamps, tidal flats, and marshes) as well as remote marine areas. Unfortunately, present understanding of the distributions of atmospheric sulfur species and the elementary chemical reactions involved in the previously described oxidation chains is quite poor. In addition, the instrumentation necessary to measure many of the key atmospheric constituents has yet to be developed. Once this task is completed, it will be possible to design specific fast-photochemistry experiments to selectively study various facets of the atmospheric sulfur system.

In the case of H_2S oxidation, for instance, it is believed that oxidation is initiated by reaction with OH , i.e.,



and is followed by an as yet unconfirmed reaction sequence that produces SO_2 as an end product. The lifetime of H_2S in the atmosphere seems highly variable based on limited field measurements. In situ studies of H_2S oxidation kinetics in a variety of environments (e.g., swamps, salt marshes, and mangroves) would be extremely useful to improved understanding of the sulfur cycle.

Recent studies of DMS photooxidation provide important data on reaction mechanisms and products. The major gas-phase sulfur product produced in outdoor smog chamber experiments was SO_2 . Substantial formation of light-scattering aerosol particles was

observed, with inorganic sulfate and methane sulfonic acid as major components of the aerosol. Fourier transform infrared methods have been used to quantify products of the reaction of $\text{HO} + \text{CH}_3\text{SCH}_3$ in the presence of $\text{C}_2\text{H}_5\text{ONO}$ and NO . Methyl thionitrite (CH_3SNO) was observed as an intermediate product, with SO_2 and $\text{CH}_3\text{SO}_3\text{H}$ as major products. These studies serve as models of important photooxidation sinks for reduced sulfur species.

ROLE OF CLOUDS AND AQUEOUS-PHASE CHEMISTRY

As indicated in Chapter 5 of this report, aqueous-phase chemistry (i.e., in cloud and raindrops) plays a major role in the oxidation of SO_2 to H_2SO_4 . Current thinking also suggests that clouds may be the dominant transport conduit for movement of SO_2 and other relatively short-lived reduced sulfur species to mid-tropospheric altitudes. Sulfur dioxide produced below cloud base may be injected directly into the free troposphere by updrafts associated with clouds or may dissolve or react with cloud droplets, depending on a variety of poorly quantified physical and chemical variables. Evaporation of cloud droplets may produce small sulfate-rich aerosol particles that subsequently act as cloud condensation nuclei. If the transport and reaction mechanisms mentioned in this paragraph are active over large areas of the nonurban troposphere, they contribute to explanations for acid rain in remote oceanic regions and higher SO_2 in the free troposphere than in underlying ocean boundary layer air. Once in the middle to upper troposphere, SO_2 may have a much longer lifetime with potential for long distance transport beyond the synoptic scale.

Future field experiments will need to measure a variety of species including SO_2 , $(\text{CH}_3)_2\text{S}$, H_2O_2 , and methane sulfonic acid in gas, liquid, and solid phases where appropriate. Combined ground and aircraft measurements focused on the role of cloud and aqueous-phase processes are a high priority.

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