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Natural Sulfur Emissions into the Atmosphere

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Natural atmospheric sulfur emission rates are reviewed for important components of the sulfur cycle. A summary of emission estimates is provided for vegetation, coastal and wetland ecosystems, inland soils, and oceanic environments. A brief discussion of sea salt sulfate, aeolian sources, volcanic activity, and biomass burning is also included. The emissions from plants and inland soils, may play a significant role in global sulfur cycling and very little work has been reported covering this subject. Large uncertainties continue to exist in the identity and the emission rates of the sulfur compounds and thus it is not reasonable to extrapolate these data in an attempt to balance the global sulfur cycle. Moreover interactions of enhanced anthropogenic activity with various components of the sulfur cycle need to be considered.

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Sulfur in the atmosphere originates either from natural processes or anthropogenic activity. The natural biogenic sources are thought to constitute a large fraction (estimates as high as ~70 percent have been reported) of the atmospheric sulfur burden[1-9] (See Appendix A). As such, these natural sources may have a substantial impact on global sulfur cycling. Moreover, identification and characterization of sources of atmospheric natural sulfur compounds are essential for the rational formulation of emission control policies designed to limit the atmospheric sulfate burden, for analysis of the origins of acidic precipitation, and in exploring global climate change.

It is known that both natural and man-made sources release chemical species that can modify acidic deposition, climate, human health, ecological systems, and visibility. If a controlled reduction in man-made emissions were to occur, natural sources would continue to affect acidic deposition, climate, human health and welfare. As a result, the benefits that would be anticipated from such a controlled reduction could be erroneously optimistic if natural sources make a significant contribution to the present total acidic, climatic and atmospheric budget. Therefore, policy decisions regarding possible emission control strategies require, among other inputs, an accurate assessment of the relative importance of natural and man-made sources.

Biogenic sulfur, that is sulfur compounds which result from biological processes, is only one component of the natural sulfur cycle. The first measurements of biogenic sulfur fluxes were those of Aneja and co-workers.[10-11] Numerous studies have been published in the last decade, the most recent, a review by Aneja and Cooper,[12] which added to our understanding of the natural sulfur emissions.[13-29] This research has provided experimental data, which are helpful in refining the biogenic emission estimates necessary to develop the global sulfur cycle. These data bases, although inadequate for detailed quantitative estimates, are helpful for estimating emissions from both terrestrial and oceanic environments.

In all the early attempts at developing global sulfur budgets, natural emissions were obtained from the amount of sulfur necessary to balance the cycle. This resulted in considerable scatter in the biogenic estimates, from 34 Tg S yr^{-1},[7] to 267 Tg S yr^{-1},[2] where Tg = 10^{12} g. It is possible with the existing data to begin to make estimates of the upper and lower bounds for biogenic emissions based on direct measurements. However, additional data are necessary to assess biogenic sulfur emissions independent of other portions of the global sulfur cycle.

In making some of the flux estimates of global quantities, the area of the globe is taken to be $5.1 * 10^{14}$ m^2, with land and ocean areas being $1.5 * 10^{14}$ m^2 and $3.6 * 10^{14}$ m^2, respectively.[11]

Biogenic Sulfur Emissions from Vegetation

It is recognized that sulfur is essential for plant growth. It is used in amino acids, and many other biochemicals. The biological transformation of sulfur compounds in natural ecosystems is closely coupled to the formation of living biomass and to the subsequent decomposition and remineralization of the biomass. Plants contain an average sulfur content of 0.25 percent (dry weight basis).[30] Hence sulfur compounds may be released directly from vegetation or during the process(es) of decomposition of the organic matter. However uncertainty exists concerning the nature of the global sinks for COS; and it has been suggested[31] that vegetation may provide a global sink for COS. It is also suggested that volatile sulfur

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species may be emitted from soils/plants that are reactive or enzymatically inhibited in live tissue and therefore have so far eluded detection by conventional analytical methods such as gas chromatography. Data on sulfur released by vegetation are scanty and the mechanism(s) of release are only now being developed.[32] Ranenberg[32] has suggested that hydrogen sulfide emissions by higher plants has been observed both in the laboratory and in the field and it may provide a significant contribution to the biogeochemical cycle of sulfur. Andreae[33] has also proposed that plants may be a potential source of global COS by the photochemically initiated reactions from organic sulfur compounds present in plant tissues and molecular oxygen. A summary of available data is provided below.

Sulfur compounds are known to be volatilized from living plant leaves,[34] and from decaying leaves.[35] It has been estimated that sulfur emission rates from decaying leaves are about 10 to 100 times higher than those from living leaves of the same species.[35] Many fungi and bacteria release sulfur compounds[36] during plant decomposition. Some plants are known to emit H_2S.[30,32,37–39] Emission rates of H_2S from several lawns and from a pine forest on aerobic soils, in France, ranged from 0.006 to 0.25 g S m^{-2} yr^{-1}.[37] Measurements made by Adams et al.[43] from similar sources and latitudes in the continental United States have provided comparable results. However, in Ivory Coast, West Africa, emission rates of H_2S from humid forests ranged between 0.24 and 2.4 g S m^{-2} yr^{-1}.[38] However, much of the biogenic H_2S released from the plants may be recycled within the tropical rain forest.[40] It may also help explain the relatively low precipitation pH found in the remote tropical rain forest sites.[41]

Some plants including *spartina alterniflora*, oak and pine are also known to emit dimethyl sulfide (DMS), CH_3SCH_3,[14,42,43] dimethyl disulfide (DMDS), $CH_3S_2CH_3$,[10,43] methyl mercaptan, CH_3SH,[10,43] carbonyl sulfide, COS,[14,30,43] and carbon disulfide, CS_2,[14,43–48] and possible ethyl mercaptan.[47,48] Emission rates of sulfur from crops including corn, soybeans, oats, alfalfa, and miscellaneous vegetables have been measured.[27–29] The flux from crops range from 0.008 to 0.3 g S m^{-2} yr^{-1}. H_2S and DMS are the two primary sulfur species being emitted by crops. Emission rates of sulfur from a variety of plants are summarized in Table I.

Biogenic Sulfur Emissions from Wetlands

The tidal flats of marine environments are areas of extreme complexity and biological activity. They serve as both sources and sinks of a wide variety of compounds and materials. They are in a constant state of mass, energy and momentum flux with the surrounding environment. In these areas sulfur plays a major role in biological processes, principally because of the relatively high concentration of sulfate ion in marine waters.

Sulfate is a major electron acceptor for respiration in anoxic marine sediments and may account for 25 percent of the total sediment respiration in nearshore sediments, 0.3 to 3 g C m^{-2} day^{-1}. In salt marsh sediments, where total respiration rates may be 2.5 to 5 g C m^{-2} day^{-1}, sulfate ion respiration may account for up to 90 percent of the total (e.g. References 19 and 23). Because of the extensive literature in this area, for further discussion of the processes and variables affecting H_2S emissions, the reader is referred to some excellent discussions (See for example, References 19, 23, 26, 49–67).

There have been a number of studies of biogenic emissions reported in the literature. Most of these have been concerned with high productivity sources, such as salt marshes and tidal areas. The emission measurements range from undetectable to about 2000 g S m^{-2} yr^{-1}. Typical emission fluxes for various sulfur compounds are summarized in Table II. The scatter in the data is tremendous, suggesting many sources of variability and large uncertainties in the magnitude of the fluxes associated with the sulfur compounds. No systematic statistical treatment has been applied to the data collected thus far.[102]

Aneja[10] and Adams et al.[43] have reported several unidentified peaks, suggesting that perhaps other sulfur compounds still remain to be identified or that these peaks are caused by nonsulfur compounds to which the sulfur flame photometric detector is sensitive.

There are a number of physical, chemical and biological factors which affect the emission rates of biogenic sulfur from wetlands. In recent studies these have been investigated for wetlands in North Carolina[24,26,43,103] and Florida.[43,64–67,103] These physical factors are divided into spatial, temporal, seasonal, diel and tidal components. In addition, other variables which affect emissions are temperature, insolation, and soil inundation. The primary chemical factor affecting sulfur emission rate is the oxidation removal pathway. Some researchers have accounted for these factors in estimating the fluxes. However, the emission estimates obtained using these methods are highly variable, and considerable additional data are required to better refine an extend emission estimates to other environments.

Table I. Biogenic emissions of sulfur from vegetation.

Plant	Mean sample temperature (°C)	Primary sulfur species	Emission rate g S m^{-2} yr^{-1}	Ref.
Spartina alterniflora, N.C.	30	DMS	0.66	13
S. alterniflora, N.C.	25	CS_2	0.20	14
Lawn, France	22	H_2S	0.24	37
Lawn, U.S.				
Grass, FL		H_2S	0.2	103
Grass, MI		H_2S	0.13	103
Grass, MO		H_2S	0.38	103
Pine Forest, France	10	H_2S	0.023	37
Humid Forest, Ivory Coast	25	H_2S	0.88	38
Crops				
Oats (with soil), IA	35.4	DSM, H_2S	0.007	29
Corn, IA, IO	28.9	DMS, H_2S	0.032	29
Soybeans, IA	32.8	DMS, H_2S	0.066	29
Alfalfa, WA	22.4	DMS, H_2S	0.056	29
Trees				
Deciduous, IA, OH NC	29.5	DMS, H_2S, COS	0.007	29
Coniferous, NC	29.2	COS	0.005	29
Crops				
Soybeans, IA	25.5		0.0018	27
Carrots, OH	22		0.113	27
Onions, OH	22		0.104	27
Grass, IA	25.5		0.018	27
Crops				
Soybeans	30	DMS	0.037	28
Oats	30	DMS	0.023	28
Orchard Grass	30	DMS	0.008	28
Purple Clover	30	DMS	0.007	28
Corn	30	DMS	0.273	28

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Table II. Biogenic emissions of sulfur compounds from coastal ecosystems.

Source	Month of year	Emission rate (g S m^{-2} yr^{-1}) H_2S	DMS	DMDS	CH_3SH	CS_2	COS	Ref.
Salt Marsh, NY	10/11	0.55	0.15	0.018	0.064	—	—	10, 11
Swamps and tidal flats, Denmark		0.044	—	—	—	—	—	17
Coastal area, Denmark		~19	—	—	—	—	—	58
Salt marsh, N. Carolina	7/8/9	0.5	0.66	—	—	0.2	0.03	13, 14, 59
Salt Marshes								
N. Carolina	5/7/10	0.033	0.538	0.0005	0.00026	0.035	0.012	15, 16
Delaware	8	0.096	0.48	0.00053	—	0.07	0.012	
Massachusetts	8	—	0.06	0.006	—	0.028	0.004	
Virginia		—	1.87	0.04	0.22	1.38	0.03	
Salt marsh, Virginia	8	9.5	—	—	—	—	—	60
Salt marsh, Virginia	8/9	0.0013	—	—	—	—	0.0014	61
Salt marsh, Massachusetts	1 yr.	2.32	0.16	0.25	—	0.20	0.34	62
Salt marsh, N. Carolina	8	0.5	—	—	—	—	—	26
Salt marsh, N. Carolina	8	0.33	0.083	0.00064	—	0.0017	0.052	29
Salt marsh, N. Carolina		0.05	0.1	—	0.0037	0.0032	0.0042	28
Salt marsh								
Delaware	8	0.01	0.91	0.006	—	0.125	0.02	43
N. Carolina	11	1.65	0.02	—	0.08	0.01	0.43	43

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Biogenic Emissions from Land

Typical sulfur flux measurements from various inland locations are summarized in Table III. In three inland soils in France, the H_2S flux data ranged for 0.019 to 0.24 g S m^{-2} yr^{-1}.[37,68] Aneja et al.[69] surveyed various terrestrial surfaces. In a broad and diverse inland study area in the United States[15,16,103], in the latitudes of ~47°N to ~25°N, 27 soils were examined, and total sulfur flux reported from 0.013 to 0.33 g S m^{-2} yr^{-1}. The average flux from these inland soils is ≤0.02 g S m^{-2} yr^{-1}. The primary sulfur species was H_2S (accounting for ~65 percent of total sulfur) and the flux ranged from undetectable to 0.16 g S m^{-2} yr^{-1}. However, several other gases accounted for, CS_2 (~13 percent), COS (~13 percent), DMS (~7 percent) and DMDS (~2 percent), were observed in some locales. Fluxes between 0.001 and 1.1 g S m^{-2} yr^{-1} were reported from marshland soils in the Enis River region of northern Germany.[17] However mean annual fluxes from tropical soils in the Ivory Coast[37] are much higher than those in the U.S. and European soils, ranging between 0.3 to 0.9 g S m^{-2} yr^{-1}.

Several recent studies have reported additional data from the earlier U.S. site for the emission rates of biogenic sulfur species. The sites and the season were chosen specifically because they had been characterized by previous studies.[13-16] Lamb and co-workers[29] measured emission rates and observed H_2S, COS and DMS, during the summer of 1985. The total flux of the sulfur species can be summarized for two soils, mollisol and histisol, averaging 0.008 and 0.114 g S m^{-2} yr^{-1}, respectively. Goldan and co-workers[28] measured sulfur fluxes from bare soils, also during the summer of 1985. The principal sulfur species were COS, H_2S, DMS, and CS_2, all of which were strongly correlated with air temperature inside the flux-chamber. The emission rate of the sulfur species ranged from 0.003 to 0,008 g S m^{-2} yr^{-1}.

The newer data by Lamb et al.[29] and Goldan et al.[28] seem to suggest that the sulfur flux appears to have decreased[70] from measurements made earlier.[15,16,71] Such a conclusion cannot be arrived at definitively based on the small data set. There are many steps in determining natural emissions,[102] primary among them being: field sampling, calibration of the analytical device, sample collection, sample analysis, extrapolation to area estimates, and extrapolation to temporal estimates. Error in each category needs to be evaluated to allow an estimation of global error analysis. Moreover there exists wide spatial and temporal variations in biogenic sulfur emissions. With our limited understanding, there may be a 1000-fold difference between two samples taken in series or between two flux chambers placed close to each other. Hence the reported differences between the emissions are perhaps statistically non-significant.

Biogenic Emissions for Oceanic Environments

Oceans and the marine environment are now thought to be the major source of biogenic sulfur compounds.[72-76] The reasons for this are the generally abundant phytoplankton in surface oceans and the great extent of these waters. Dimethyl sulfide is the primary sulfur compound present in open ocean waters[20,22,77] and may account for ~90 percent of the flux of biogenic sulfur from the ocean to the atmosphere.[78] Other compounds, especially COS,[79,80] CS_2[81] and methyl mercaptan[33] may account for the remaining 10 percent, suggesting that their contribution to the global atmospheric sulfur budget is small. DMS is produced in oceanic waters by benthic and to a greater extent by planktonic marine algae,[82] suggesting that it is ubiquitous in the surface

Table III. Biogenic emissions of sulfur compounds from inland soils.

Source	Month of year	Emission rate ($g\ S\ m^{-2}\ yr^{-1}$) H_2S	DMS	DMDS	CH_3SH	CS_2	COS	Ref.
Equatorial forest, Ivory Coast	1/10 11/12	0.3–0.9	—	—	—	—	—	37
Lawn, France	4/5/6/11/12	0.07	—	—	—	—	—	37
Marshland soils, N. Germany	7,8	0.001 to 1.1						17
Dry inland soil, N. Carolina	8/9/10	<0.01	<0.01	<0.05	<0.05	<0.05	<0.01	69
Mollisol, Iowa	7	0.15	0.0032	—	—	0.017	0.017	15, 16
Histosol, Ohio	7	0.047	0.0032	—	—	0.006	0.012	15, 16
Inceptisols, Ohio	7	0.04	0.002	0.0007	0.001	0.01	0.003	15, 16
Histisols, eastern U.S.		0–94.7	1.7–92.8	0–8.7	—	0.5–68.2	5.8–34.8	43
Mollisol, Iowa	7	0.0003	0.0005	—	—	0.0003	0.0015	28
Histisol, Ohio	7	0.0024	0.0003	—	—	0.0007	0.0036	28
Mollisol, Indiana	7	0.0002	0.0005	—	—	0.00023	0.0029	29
Histisol, Ohio	7	0.009	0.0004	—	—	0.00004	0.015	29

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ocean.[20,72–74,77,83,84] Its concentrations in oceanic waters appears always to be much greater than the concentrations expected at atmospheric equilibrium.[22,35] Its distribution has been characterized by "hot spots" with high DMS concentrations superimposed on more or less constant levels of approximately 1–3 nM in the surface waters. The high concentrations—hot spots—may be the result of blooms of e.g. *Phaeocystis poucheti*, which are known to produce DMS. Keller et al.[85] performed the most comprehensive survey relating DMS and its precursor DMSP (dimethylproprionosulfonate) to marine phytoplankton, analyzing over 120 phytoplankton clones. A summary of the emission rates of DMS, the major biogenic sulfur species in marine environments is presented in Table IV. Estimates are included which were determined directly and from model calculations.

The first report of DMS in the ocean appeared in 1972.[35] The authors suggested that DMS might be more important than H_2S as a biogenic sulfur source for balancing the global sulfur budgets. Preliminary estimates of DMS sea-to-air flux based on the limited data were made by Liss and Slater.[86] However its first direct emission rate measurements from the marine environment were reported in 1975.[10]

Estimates of DMS flux from oceanic environments have resulted from direct measurements of DMS concentrations in surface waters[22] and from model calculations.[87,88] At this time it is not possible to determine which of the numbers are correct, or if any of the numbers are correct, however, there is little doubt that the marine environment is one of the major sources of biogenic sulfur.

There is considerable debate and little relevant data regarding the marine environment and the possibility that it is a major source of H_2S. In a coastal area, integrated over tidal and diel cycles, a rate of H_2S of 0.10 g S m^{-2} yr^{-1}, has been reported.[26]

Oceanic Emission of Sea Salt Sulfate

The most commonly identified marine source of sulfur is the sulfate component of sea spray. For the most part, this source is thought to have little impact on land areas, even though significant amounts of sea salt containing sulfate enter the atmosphere as sea spray. This source of sulfur has been addressed thus far in only a limited manner, and there appears to be considerable debate in emission estimates (Table V).

The initial estimates of sulfate flux of 0.122 g S m^{-2} yr^{-1} is still commonly cited.[2] It was based on the assumption that the ratio of sulfate in sea salts redeposited to the ocean and transferred to continents is the same as that in moisture evaporated over the ocean (i.e. 9:1). This assumption has been questioned recently as being unreasonable to assume that these ratios should be the same for water vapor and aerosols.[8] Hence such an approach underestimates the magnitude of marine sulfate emission. Other data seem to suggest that sulfate flux is much higher, ranging from 0.361[89] to 1.944 g S m^{-2} yr^{-1}.[90] However, more recently, a study has been reported with estimates of 0.833 g S m^{-2} yr^{-1}.[91] Additional data are required before more refined estimates are possible.

Table IV. Biogenic emissions of DMS from open oceans and the marine environment.

Environment	Emission ($g\ S\ m^{-2}\ yr^{-1}$)	Reference
Open ocean[a]	0.02	86
Ocean	0.075	77
Ocean	0.106	23
Ocean[a]	0.022	87
Gulf of Mexico[a]	0.037	88

[a] Based on model calculations.

Aeolian Sulfur Emission from Continental Surfaces

This component of the natural sulfur cycle is the least understood process. Flux estimates of sulfur by aeolian weathering pathways has been ignored in most global atmospheric cycles including the most recent by Warneck.[9] Granat and coworkers[7] estimate the aeolian sulfur emission to be 0.2 Tg S yr^{-1}. More recently,[8] estimates of aeolian sulfur were reported to be 20 ± 10 Tg S yr^{-1}. Clearly this is one area which requires further study to better estimate emission flux.

Volcanic and Fumarole Emissions

Volcanic and fumarole sulfur emissions into the atmosphere are sporadic in nature. Sulfur compounds emitted from volcanic activity are mainly sulfur dioxide, some hydrogen sulfide, and smaller amounts of sulfur trioxide, carbon disulfide, and carbonyl sulfide; together with various sulfates and elemental sulfur. Based on thermodynamic equilbrium calculations performed for anoxic conditions at high

Table V. Emission of sea salt sulfate from oceanic environments.

Sulfate emission ($g\ S\ m^{-2}\ yr^{-1}$)	Reference
1.944	90
0.122	2
0.361	89
0.833	91

temperatures of the magma, SO_2 is the preferred specie; while at low temperatures for the same system, H_2S may be predominant.[92] However, there is considerable disagreement on the relative contribution of sulfur compounds of volcanic origin to the atmospheric sulfur burden. This is in part brought about by the use of incomplete data sets, different assumptions utilized in computing the emission, and/or lack of adequate analytical techniques to distinguish compounds of volcanic origin, plus sampling and analysis errors. Since 1972, the volcanic plume has been analyzed directly for sulfur compounds using remote-sensing techniques and by means of airborne monitoring.

In a recent comprehensive analysis, Berresheim and Jaeschke[93] review world-wide volcanic emissions measurements between 1961 and 1979. They identified five categories of volcanic activities with further subdivisions for differing intensities. They conclude that SO_2 emissions are 8 Tg S/yr and 1 Tg S/yr during noneruptive and eruptive categories respectively. The contribution from other categories (extraeruptive, preruptive and intraeruptive phases) may be either neglected or discarded. During the time period analyzed, by integrating over the categories and intensities, they found an average emission rate of 0.5 Tg S/yr. The flux of sulfur due to volcanic and fumarole activity is presented in Table VI.

Sulfur Emissions from Biomass Burning

Plants contain an average sulfur content of ~0.25 percent (dry weight basis).[30] It is thought that about 50 percent of this sulfur content may be released into the atmosphere during combustion, the remaining being retained in the ash.[42] Combusted biomass may be the result of either anthropogenic (e.g. controlled forest management burning, wood as a source of fuel, and agricultural practices etc.) or natural (e.g., wild fires) origin, the former contributing sulfur significantly more than the latter.

SO_2 is assumed to be the primary sulfur compound emitted during the combustion of biomass, although COS, H_2S and sulfate aerosol have also been identified during biomass burning. Uncertainties exist in the identity of all the sulfur compounds, their relative contribution and emission rates into the atmosphere during combustion sulfur emissions from biomass burning has been estimated to be ~7 Tg S yr^{-1}.[33]

Emission Flux Measurement Methods

To complete an overview on sulfur emissions, a brief discussion of methods used to estimate emissions is appropriate. There are primarily two methods that may be used to measure earth-atmosphere flux of gases. In the dynamic chamber method,[10,11] an open-bottom chamber is placed over a surface of interest such as mud, soil, or water, with or without vegetation, to capture the gases emanating from the surface. A carrier gas is introduced into the chamber and mixed with the natural gases. The carrier gas is usually, but not necessarily free of the species being detected. The effluent gas from the chamber is sampled and analyzed for the compounds of interest and the flux is estimated by mass balance. While this technique is easy to use, there are indications that care should be taken to minimize the changes which the chamber itself may exert upon the emitting surface.[99]

In the second method, the micrometeorological method[100,101] (vertical gradient), the concentration of the gas of interest is measured at various altitudes above the source along with the wind speed and direction. To determine their vertical concentration profile, samples obtained simultaneously at various elevations on a tower must be analyzed at low (~ppt) concentrations. This requires the ability to determine very small differences in concentrations among the vertical samples. Hence the detection method must have great precision at low ppt concentrations. Estimates of flux are made by applying turbulent diffusion theory to the concentration profile data. This method, although reasonably simple in concept, is very difficult in practice and requires considerable supporting micrometeorological data.

Summary

The biogeochemical cycling of sulfur and its circulation through the atmosphere continues to be an area of intense investigation for it has so far eluded an adequate explanation. One of the primary areas of uncertainties lies in the measurements made thus far in biogenic sulfur emissions, and the possibility of living plants being a large source of H_2S and COS. Therefore, it is very difficult, if not hopeless, with our current understanding, to perform extrapolation with any degree of known accuracy of the measurements of natural flux data to global fluxes; this is because of the lack of knowledge regarding the overall uncertainty from the combined propagation of both systematic and indeterminate errors. I believe that, currently, we can only estimate a range of emissions once we know the range of all of the uncertainties in the natural sulfur emissions.

The sulfur budgets continue to have large disagreements in their various components (See Appendix A). To some extent this is to be expected since enhanced anthropogenic activity leading to increasing sulfur emissions will perturb various components of the sulfur biogeochemical cycle including natural sulfur emissions. The time constant of interaction between anthropogenic activity and other components of the global sulfur cycle is unknown and requires further study.

The goal of developing estimates of natural sulfur emissions based upon direct measurements is far from being accomplished. With improved analytical methods and a better understanding of the factors affecting natural emissions, improved estimates are being obtained. Natural emissions remain a major area of interest where information is required on anthropogenic impacts on ecosystems and for refining methods of global sulfur cycling.

Table VI. Annual emission of sulfur due to volcanic and fumarole activity.

Volcanic emission $Tg\ S\ yr^{-1}$	Fumarole emission $Tg\ S\ yr^{-1}$	Reference
0.75		5
2.0		6
34.0		94
3		7
	3.5	95
	15.0	96
	13.5	97
1.45	26.6	98
0.50		93

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Appendix A. Fluxes (TgS/yr)[a] of the global atmospheric sulfur cycle.

Emission source or sink	Eriksson[2] (1960)	Junge[3] (1963)	Robinson and Robbins[4] (1968)	Kellog[5] et al. (1972)	Friend[6] (1973)	Granat[7] et al. (1976)	Ryaboshapko[8] (1983)	Moller[104] (1984)	Smil[105] (1985)	Warneck[9] (1988)
Gaseous emissions										
Anthropogenic emissions	39	40	73	50	65	65	101(84–118)[e]	75	98(82–112)	103[e]
Biogenic emissions, total	267	230	98	90	106	32	41(8–77)	70	140(70–175)	43
From oceans	190[b]	160	30[b]	—	48[b]	27[b]	24(3–45)	35	75(40–95)	36
From soils	77	70	68	—	58	5	17(5–32)	35	65(30–80)	7
Volcanic gases	—	—	—	1.5	2	3	28(14–42)	2	10(5–30)	7
Particulate sulfate emissions										
Seaspray	44	—[c]	44	44	44	44	140(77–203)[f]	175	45(40–60)	150
Mineral dust	—	—	—	—	—	0.2[d]	20(10–30)	—	—	?
Anthropogenic SO_4^{2-}	—	—	—	—	—	—	12(10–14)	—	—	3
Wet and dry deposition										
SO_2 over the oceans	70	70	25	[g]	25	16[h]	11(5–17)			15
SO_2 over the continents	77	70	26	15	15	44[h]	17(7–27)	30		71
Excess SO_4^{2-} over oceans	102		31	29	31	17[h]	107(70–145)			28
Excess SO_4^{2-} onto continents	57	70	90	96	102	23[h]	67(44–92)			42
Seasalt over ocean	40	60[c]	40	44	40	41	125(69–180)	157		135
Seasalt onto continents	4		4	—	4	3	15(–23)	18		15
Sum of fluxes										
Total budget	350	270	215	185	217	144	342(203–484)	322	293(197–377)	306
Flux from continent to ocean	—	—	26	—	8	17	100(50–150)	—	—	11
Flux from ocean to continents	15	—	4	—	4	15	20(10–30)	—	—	18

[a] 1Tg = 10^{12}g.
[b] Resulting as a balance in the cycle.
[c] Junge calculated excess sulfate.
[d] Only submicron fraction of aerosols is considered.
[e] Includes 3 (1–5) Tg S/yr of reduced sulfur.
[f] From the balance of fluxes in the marine atmosphere.
[g] Included in excess SO_4^{2-}.
[h] Not originally presented in this form, but calculated from the data given.

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