The Exchange of Reduced Sulfur Gases Across the Atmosphere–Terrestrial Biosphere Interface

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Abstract

In this review, the significance of terrestrial ecosystems in the global sulfur budget has been reviewed based on the currently available databases covering the topic. In the section 1, we describe our current understanding of natural sulfur cycle in relation to most well–known natural reservoir, oceanic environment. The sections 2 and 3 provide the fundamental pictures of the terrestrial sulfur cycle with respect to the relative importance of its individual chemical components and of source components, respectively. In the section 3, previously reported flux values for several major sulfur gases are presented for each reservoir and are intercompared to derive representative fluxes for the respective environment. In the section 4, source mechanisms for volatile sulfur species are dealt for both microscale and macroscale processes leading to their productions. In the section 5, environmental factors controlling the exchange of biogenic sulfur gases across the air–surface interface have been discussed. In the section 6, environmental fate of sulfur gases released into the atmosphere has been described. Finally in the section 7, as concluding remarks, we discuss directions and suggestions to overcome various limitations encountered from previous measurement investigations of natural sulfur cycle in diverse natural ecological systems.

1. INTRODUCTION

The linkage between the atmospheric sulfur cycle and the physico–chemical conditions of the global atmosphere is relatively well-perceived with respect to climatic modification, imbalance in global radiation, high acidity in precipitation, and visibility reduction (Bates *et al.*, 1987a; Charlson *et al.*, 1987). The growing alertness to the environmental consequences of sulfur cycle has served as a driving force in evaluating the relative significance of each

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individual source in the global sulfur budget. The essential load of sulfur to the earth's atmosphere arises from both natural and anthropogenic processes. Human activities can introduce a large quantity of sulfur via combustion of fossil fuels and the associated emission of oxidized sulfur species (predominantly SO_2). The magnitude, and composition, of man–made contribution to the global sulfur budget has been estimated with reasonable consistency: 80 ± 20 Tg yr^{-1} (Tg=Teragram=10^{12} g) (Spiro *et al.*, 1992).

The extent of contribution made by the natural environment to the global atmos-

pheric sulfur budget has been a long debated subject. Estimates for natural sulfur emissions, once reported to exceed those of anthropogenic counterpart (e.g., 100 to 280 Tg yr^{-1}; Prahm et $al.$, 1976), have been several-fold downgraded over the past decades. A number of sources have been identified in the meantime to be the important components of the natural sulfur budget: oceans (Bates et $al.$, 1987b; Andreae and Raemdonck 1983); volcanoes (Millan et $al.$, 1985); soils (Adams et $al.$, 1981); vegetation (Lamb et $al.$, 1987; Filner et $al.$, 1984); and biomass burning (Andreae, 1991). Among these natural sources, the oceanic environment has been most thoroughly investigated by numerous authors. Owing to extensive field measurements and model-based calculations, the ocean's potential as a dominant compartment of the natural sulfur budget is relatively well established. Although the sea-to-air flux of sulfur was once estimated to be of the order of 30 to 40 Tg S yr^{-1} (e.g., Andreae and Raemdonck 1983), results of recent studies with reasonably low sea-to-air transfer coefficients turned out much reduced values for oceanic emissions: oceanic source strengths of approximately 2 to 5 times lower than those of earlier work have been reported by several groups (Cooper and Saltzman, 1990; Bates et $al.$, 1987b). Despite this downward revision of oceanic sulfur inventory, the ocean is still believed to represent the dominant portion of natural sulfur budget.

With the aid of numerous investigations conducted over the marine troposphere, many aspects of sulfur chemistry can now be assessed for unperturbed natural background conditions. While notable progresses have been achieved in studies of the marine sulfur chemistry, the role of terrestrial ecosystem in the global sulfur cycle remains as one of the most poorly defined subjects due to the absence of good, representative flux estimates. In addition, exchange rate data for various sulfur gases measured from terrestrial biosphere, while being scarce, have rarely been validated (e.g., Lamb et $al.$, 1987). These lack and possible inaccuracy of database can be ascribed to problems associated with both natural (large temporal and geographical variabilities) and experimental (absence of proper methodologies) unknowns. Undoubtedly, these restrictions in our knowledge of natural sulfur cycle act as a major limiting factor in precise evaluation of the global natural sulfur budget.

2. MAJOR CHEMICAL COMPONENTS OF TERRESTRIAL SULFUR CYCLE

Sulfur gases of natural origin are generally called as 'biogenic', 'reduced' or 'volatile' sulfur compounds because of their involvement in biological activity, low oxidation states, or high volatility, respectively. In various settings of natural environment including terrestrial biosphere, the most important biogenic sulfur compounds are often found out to be: dimethyl sulfide (DMS or $(CH_3)_2S$), hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2). (Such species as methyl mercaptan (CH_3SH), dimethyl disulfide (DMDS or CH_3SSCH_3) can also be included as minor components of sulfur budget.) Hence, our discussions of chemistry of reduced sulfur species will be in most cases confined to the above-mentioned four major chemical components. Numerous models have been developed and used to estimate the emission strengths of these natural sulfur gases since the early 60's. In those days, more emphasis focused on H_2S, as it was believed to be the sole component of the natural tropospheric sulfur budget (Junge, 1963). More

recent studies, however, confirm that its contribution is of minor importance on global scale based on the following findings: (1) low background concentrations of H_2S in the remote marine atmosphere (Saltzman and Cooper, 1988) and (2) its tendency to form stable complex with surface water metallic ions (Elliot and Rowland, 1990). In fact, it turned out that DMS, instead of H_2S, represents the single predominant contributor to the natural sulfur budget. The major portions of those DMS input to the atmosphere is accounted for by its emissions from the surface waters of the world oceans (e.g., Bates et al., 1987b).

The emissions of the four most predominant sulfur gases (DMS, H_2S, COS and CS_2) and other minor organosulfur compounds have been documented from most of the major reservoirs of terrestrial biosphere including: soil, marshes, and vegetations (e.g., Adams et al., 1981). Although relative significance of DMS appears to be reduced to a degree in terrestrial biosphere (e.g., relative to the marine systems), it is by far the most dominant sulfur gas emitted to the atmosphere from most ecological systems. In some cases, however, the emissions of H_2S exceeds, or are as significant as, that of DMS (Steudler and Peterson, 1985). Nevertheless, generalization of its emission trend in the terrestrial biosphere suffers from substantial variabilities both geographically and temporally (e.g., Cooper et al., 1987). Due to its inertness with atmospheric reactants and lengthy tropospheric lifetime of approximately $1 \sim 2$ yrs, COS is found to be the most abundant and evenly dispersed S-containing gas in the remote troposphere (around 500 pptv; WMO 1986). COS is also well-known for its contribution to the formation of stratospheric sulfate layer, especially during volcanically quiescent periods. The atmospheric chemistry of CS_2 has attracted a great deal of attention due mainly to its unique oxidation pathway leading to the production of SO_2 and COS (Kim and Andreae, 1987). While the strength of CS_2 emissions over terrestrial systems is quite variable, similarly to H_2S, relatively little is known about the biochemical processes responsible for its formation (Andreae, 1990).

3. MAJOR SOURCE COMPONENTS OF THE TERRESTRIAL SULFUR CYCLE

3. 1 Soils

A summary of available field measurement data for biogenic sulfur fluxes over various inland soil environments is presented in Table 1. Despite their areal predominance, relative significance of inland soils has rarely been examined until the studies of Delmas et al. (1980); they conducted pioneering measurements of soil fluxes of volatile sulfur gases from three inland sites in France. The first comprehensive measurements of biogenic sulfur fluxes were made over a wide variety of terrestrial ecosystems in the eastern and southeastern United States during the Electric Power Research Institute/Sulfate Regional Experiment (EPRI/SURE) project (Adams et al., 1981). Interestingly enough, among numerous inland sites investigated by Adams et al. (1981), two of those sites which include Celeryville, Ohio and Ames, Iowa have been thoroughly reexamined on a comparative purpose during a joint campaign conducted by three independent research groups (Goldan et al., 1987; Lamb et al., 1987; MacTaggart et al., 1987). Although Adams et al. (1981) reported pronouncingly high fluxes of H_2S (ranging up to 280 Tg S yr^{-1}) relative to other species, such trends were no longer apparent from the results reported by the joint project study.

Table 1. Previous measurements of the soil-to-air fluxes of reduced sulfur gases over mollisol and histosol soil.*

Location	Time (Month)	DMS	H₂S	COS	CS₂	Reference
			1. Mollisol Soil			
Iowa, US	July	6	280	32	30	Adams *et al.*(1980)
Iowa, US	July	0.9	0.6	2.8	0.6	Goldan *et al.*(1987)
Iowa, US	July	0.9	0.4	5.5	0.4	Lamb *et al.*(1987)
			2. Histosol Soil			
Ohio, US	July	6	89	23	11	Adams *et al.*(1980)
Ohio, US	July	0.8	17.2	28	0.07	Lamb *et al.*(1987)
Ohio, US	July	0.6	4.6	6.9	1.4	Goldan *et al.*(1987)
Germany	May–Oct.	5.1~92	–	7.4~57	1.2~4.7	Taubes *et al.*(1989)

* All units for the soil fluxes are expressed in ng S kg^{-1} min^{-1}.

In addition, the absolute fluxes of other sulfur species, while being consistent within each group of the joint study, were noticeably lower than those of Adams *et al.*

Goldan *et al.*(1987) suggested that the observations of systematically higher fluxes of Adams *et al.*, were due to the accumulation of sulfur gases within the chamber caused by insufficient flushing prior to the initiation of experiment. It is also interesting to note that, unlike the findings of Adams *et al.*, both datasets from Goldan *et al.*(1987) and Lamb *et al.*(1987) generally show high fluxes from hostisol soils relative to mollisol soils; that was in fact consistent with the general expectation based on the potentials of soil type. Similarly to the observations from this joint study, Staubes *et al.*(1989) reported comparitibly lower bound fluxes from their measurements over 12 different soil types in Germany. The likelihood of lower fluxes of sulfur across the soil/atmosphere interface is further extended by field measurements made in the Amazon rain forests (Andreae *et al.*, 1990) as well as in the African rain forests (Bingemer *et al.*, 1992). The global emissions of reduced sulfur gases across the soil-air interface are estimated to be of the order of 0.05 to 0.2 Tg S yr^{-1} (Pham *et al.*, 1995; Bates *et al.*, 1992; Spiro *et al.*, 1992). Taking into account the characteristically high variabilities in emissions of sulfur gases, the general consensus among most of recent studies appear quite promising. Agreement between recent studies suggests that biases between different measurement techniques of different research groups must have been reduced to a great degree.

3. 2 Plant/Vegetation

Measurements of exchange rates of biogenic sulfur gases have actively been made from the terrestrial biosphere since the late 1970s (Table 2). Although often treated as a pair with soil system, vegetation system acts alone as one of the most significant inventories for terrestrial sulfur fluxes. It is acknowledged that reduced sulfur gases are emitted from various plants/crops. In fact, it is found that the total source strengths of plant system can exceed those of soil system by factor of 2 (Bates *et al.*, 1992) to 17 (Spiro *et al.*, 1992). However, vegetation tends to interact with sulfur gases in more complicated manners than soil. The complexity arises from the fact that plant surfaces can act not only as the prominent source, but also as the major sink of atmospheric sulfur gases (see below): in comparison, source mechanisms of

Table 2. The sulfur gas fluxes quantified previously over various vegetative surfaces.*

Type of Plants	Time (Month)	DMS	H₂S	COS	CS₂	Reference
Corn		120	21	NR**	NR**	Lamb *et al.* (1987)
Corn		520	32	ND***	NR**	Goldan *et al.* (1987)
Soybeans		70	42	−35	NR**	Goldan *et al.* (1987)
Oats		43	10	−5	NR**	Goldan *et al.* (1987)
Orchard Grass		15	10	−30	NR**	Goldan *et al.* (1987)
Purple Clover		13	5	−13	NR**	Goldan *et al.* (1987)

*All units for the soil fluxes are expressed in ng S kg⁻¹ min⁻¹.
** and *** denote not reported (NR) and non-detectable (ND), respectively.

soil are much more eminent than its counterpart. It is found that the emissions of sulfur across the plant-air systems are dominated by that of DMS under most natural settings (Filner *et al.*, 1984; Lovelock *et al.*, 1972). Similar results have also been reported from measurements made using various crop species (Kanda and Minami, 1992). The total emissions of sulfur gases from the plant system are approximated to be 0.2 to 1.0 Tg S yr⁻¹ (Bates *et al.*, 1992).

3. 3 Wetland Ecosystems

Because of their intense signal of sulfur emissions, much of earlier interests on the terrestrial sulfur cycle have centered on wetland soils, coastal marsh areas (Steudler and Peterson, 1985) and intertidal mudflats (Adams *et al.*, 1981). A summary of previous flux measurements conducted over wetland ecosystems is presented in Table 3. In a good analogy to the case of inland soil studies, several sites investigated by Adams *et al.* (1981) were revisited not only by those researchers involved in the joint project but also by many other research groups. The results of these wetland systems generally exhibit substantially larger flux values than those of inland sites by up to several orders of magnitude: Adams *et al.* (1981) even measured H₂S fluxes approaching 1 mg S m⁻² min⁻¹ from Cox Landing, North Carolina. When fluxes measured from a given locale by different authors

were intercompared, both compatible and noncompatible patterns emerged. For example, while fluxes measured by Goldan *et al.*, or Lamb *et al.*, during their August 1985 measurements over Cedar Island, North Carolina are analogous to the May or October values of Adams *et al.*, they are notably smaller than the July fluxes of Adams *et al.*, of particular those of DMS. Observations of both resemblance and difference in the magnitude of measured fluxes between earlier studies and more recent ones suggest that these reported fluxes may represnt actual temporal and spatial variabilities in sulfur gas exhange processes.

When the exchange rates of simultaneously measured sulfur species are compared, relative dominance of DMS and H₂S over other sulfur species is apparent in most cases. The close relationship between the amount of DMS released and the population density of a marsh grass, Spartina alterniflora has been documented from several previous studies (e.g., Goldan *et al.*, 1987). Since S. alterniflora is a major grass species in the marsh area, most measurements made over this grass site are expected to exhibit higher DMS fluxes. Most of field measurements clearly confirm the potential of wetland soils as a strong source of biogenic sulfur gases. Biogenic sulfur emissions from wetland ecosystems are unlikely to be important on a global scale,

Table 3. The sulfur gas fluxes measured previously over various wetland systems.*

Type of vegetation**	Time (Month)	DMS	H_2S	COS	CS_2	Reference
1. Cedar Island, North Carolina, USA							
SA(+JR)	May-78	76	38	19	17	Adams et al. (1981)
SA(+JR)	Jul.-78	2,990	304	38	114	Adams et al. (1981)
SA(+JR)	Oct.-77	13	38	4	NR***	Adams et al. (1981)
SA	Jul.-78	2,480	362	NR	NR	Aneja et al. (1979)
JR(+SA)	August	200	100	8	6	Goldan et al. (1987)
SA+JR+DS	August	93	29	15	2	Lamb et al. (1987)
2. Wallops Island, Virginia, USA							
SA	?	3,560	NR	57	2,630	Adams et al. (1981)
SA	July	NR	5,700~30,460	NR	NR	Goldberg(1981)
SA+SP	Aug.-Sept.	NR	2.5	2.7	NR	Carrol(1986)
3. Cox Landing, North Carolina, USA							
	Jul.-78	3,370	956,800	1,670	1,850	Adams et al. (1981)
	Nov.-77	NR	265,400	12,100	NR	Adams et al. (1981)
	Sept.	343	76	NR	NR	Aneja et al. (1979)
4. Other locations(All in the United States)							
SA(Lewes, DE)		910	183	25	130	Adams et al. (1981)
SA(E. Wareham, MA)		1,140	NR	8	50	Adams et al. (1981)
(N. Carolina)	Jul.-Aug.	762	19	57	285	Aneja et al. (1979)
SA(Falmouth, MA)	1Yr	5,470	3,900	572	305	Steudler & Peterson(1985)
SA(Strathan, NH)	Jun. & Aug.	430~9,590	NR	−13~−21	NR	Morrison & Hines(1990)
SP(Strathan, NH)	Jun. & Aug.	0~69	NR	5.3~19	NR	Morrison & Hines(1990)

* All units for the soil fluxes are expressed in ng S kg^{-1} min^{-1}.
** SA=S. alterniflora; SP=S. patens; JR=Juncus romerianus; DS=Distichlis spicata
***denotes not reported(NR).

however, owing to their limited areal coverage.

3.4 Volcanic Activities

Since a strong volcanic eruption can inject substantial quantities of sulfur directly into the stratosphere, its influences on the earth's climate is expected to be quite significant. Emissions of sulfur gases via volcanic activity occur, however, during both eruptive and noneruptive periods; interestingly, emissions during the latter sometimes are found to be more important quantitatively than the former (Berresheim & Jaeschke, 1983). Thermodynamic equilibrium calculations of anoxic magma indicate that SO_2 is dominant under high temperature condition, while H_2S becomes more important with decreasing temperature (Heald et al., 1963). In line with this expectation, field measurements confirm that sulfur dioxide is the predominant component of volcanic gases accompanied by such minor components as H_2S and COS (e.g., Stoiber et al., 1987). Although there have been consider-

Table 4. Annual emission of sulfur due to volcanic activity.

The amount of sulfur emission (Tg S yr^{-1})	Reference
0.5~0.75	Kellogg et al., 1972; Berresheim & Jaeschke, 1983
1.5~3	Friend, 1973; Granat et al., 1976; Migdisov et al., 1983
9.2~9.6	Spiro et al., 1992; Pham et al., 1995
34.0	Barteles, 1972

able disagreements on the relative significance of volcanic contribution to the atmospheric sulfur burden, recent studies indicate that the global volcanic fluxes of sulfur approximate little less than 10 Tg S yr^{-1} (See Table 4).

3. 5 Biomass Burning

Biomass burning, while acting as intense sources of volatile sulfur species, is characterized to be of local and of short-term nature. Strictly speaking however, its occurrences related to the man-made activities (e.g. controlled forest management burning, wood as a source of fuel, and agricultural practices etc.) out-number those associated with purely natural activities (e.g. wild fires) by approximately 20 times (Aneja, 1990). On dry weight basis, plants contain an average sulfur content of about 0.2% (Bowen, 1979): if a burning of dry matter is assumed to amount to 8,700 Tg yr^{-1}, then the potential sulfur flux is computed to be about 17 Tg S yr^{-1}. Roughly up to 50 percents of this sulfur are to be released into the atmosphere during the course of burning, while the remainders being retained as the ash (Delmas, 1982). Although SO_2 and COS are thought to be the primary components of these combustion processes, the chemical forms with which sulfur gases are emitted via burning appear to be quite complicated.

However, since massive emissions of CO_2 and CO are accompanied by emissions of SO_2 and COS, respectively, the source strengths of these sulfur gases are commonly deduced from their molar ratio relationships. Estimates of sulfur emissions due to biomass burning range from 2 (Andreae et al., 1990) to 3.5 Tg S yr^{-1} (Delmas and Servant, 1983). In comparison to the global emissions of sulfur from the land and ocean biota, biomass burning may be a minor component of the global atmospheric sulfur budget. Previous observations made in Africa (Lacaux et al., 1988) and Amazonia (Andreae et al., 1990) regions suggest that biomass burning can act as a significant source of sulfur gases at least on local scale.

3. 6 Other Sources

Emission of volatile sulfur species can occur from innland freshwater systems like lakes and rivers. With the rate of water flow and the quantity of water body highly variable, riverine systems were however rarely investigated for volatile sulfur species. By far, riverine data sets with the most extensive areal coverage appear to be those made as a colaborative work by Iverson et al. (1989) and Kim and Andreae (1992) for the respective measurements of DMS and CS_2 during several transects across a number of estuarine sites along the eastern coast of US.

According to these studies, DMS, being present in a few nanomolar levels, seems to be the dominant volatile sulfur species in riverine environment. However, emission strengths of riverine waters in general are unlikely to be important in quantity: significant positve correlations were commonly observed between DMS concentrtrations and salinity, implying systematic reductions in DMS levels of riverwater with decreasing salt contents. Similarly to the case of riverine system, the lake system also suffers significantly from the lack of data. While only a limited number of data are available, the existing ones indicate that DMS is the major component of sulfur emissions from oxic freshwater lakes (Turner and Liss, 1985). However, total quantity of reduced sulfur emission from lake system is again of minor significance not only by its limited areal coverage on earth

but also by weak source strengths. From their investigations of DMS in the Great Lakes of US, Nriagu and Holdway (1989) reported that unless supported by planktonic activities, DMS concentrations were found typically on sub-nanomolar ranges in surface lake waters.

In addition to the freshwater systems, desert is the one comprising the minor portions of the terristrial ecosystem. However due to highly oxic condition, no reduced sulfur gases are known to exist and to be emitted. Although emissions in the form of reduced status are of little interest in the desert system, wind blown erosion may act as a significant process to transport massive quantities of sulfur associated with aeolian dusts. Early estimates of the aeolian sulfur emission were on the order of 0.2 Tg S yr^{-1} (Granat et al., 1976). More recently, Aneja (1990) reported the values for such input process to range on the order, 20 ± 10 Tg S yr^{-1}.

4. SOURCE MECHANISMS OF REDUCED SULFUR GASES

Although being released into the atmosphere in their reduced forms, they return to the terrestrial biosphere via wet and dry deposition primarilly in the forms of oxidized sulfur species, SO_2, H_2SO_4, and/or methane sulfonic acid (MSA). Microbial process that may lead to the reduction of oxidized sulfur species is hence considered to be the driving force of the biogeochemical sulfur cycle within and across the biosphere and atmosphere interface. Since the formation of reduced sulfur gases is affected by the activities of microorganisms and plants (including algae), any physico-chemical factors that exert controls over their activities will affect their production rates. As the mechanisms involved in such processes

are very complicated, many unknowns still need to be resolved. With this respect, we discuss here several reductive pathways leading to the production of reduced sulfur species.

4. 1 Reduction of Sulfur by Microorganims

There are two metabolism pathways for microorganisms to produce reduced sulfur gases: (1) using oxidized sulfur as terminal respiratory electron acceptor, i.e. dissimilatory reduction and (2) degradation of reduced sulfur-containing substances that were formed by assimilatory reduction.

4. 1. 1 Dissimilatory reduction

In dissimilatory reduction, sulfate reducing bacteria use SO_4 (or partially S_2O_3 and elemental S) as an electron acceptor and form H_2S to use as an electron donor in the course of metabolizing organic matter. Being strictly anaerobic, this process serves in fact as the major pathway for the production of H_2S (Andreae and Jaeschke, 1992): the processes are known to occur in massive scale from stratified, anoxic water basins and sediment of wetlands. Under favourable conditions, the rate of dissimilatory reduction to produce H_2S can be considerably high, ranging up to 100 mmol m^{-2} day^{-1} or even higher in such environment as salty wetland system (Howarth, 1984). In the presence of oxygen, H_2S and other reduced sulfur compound can be used as excellent substrates for microbial oxidation during which certain bacteria can obtain a substantial amount of energy (Howarth, 1984). Hence, such microorganisms tend to be present in high abundances at the oxic/anoxic interface. As those processes are highly efficient, H_2S can be removed completely even from a water column of a few millimeter thickness (Jorgensen and Revsbech, 1983).

The fluxes of sulfur gases from dissimilatory reduction are influenced by those basic environmental factors such as temperature, pH, and moisture. However, there are other factors that are also known to be important in controlling the enzyme activities. If anoxic condition is maintained, oxidized compounds (e.g., NO_3, CO_2, and potentially reducible Mn and Fe) generally compete with SO_4 for electron acceptor, which in turn causes a decrease in its reduction capacity. Sulfate concentration can also be important as a regulating factor. In the marine environment, SO_4 concentration is so high that SO_4 reduction rates are independent of its concentration. However where SO_4 concentration occurs typically below 1 to 2 mM, e.g., in some lakes and soils, bacteria reduction can occur as a first order reaction with respect to SO_4 concentration (Lovely and Klug, 1986). In laboratory experiments using cultured soils, total S gas production from both dry and fresh soils was found to be strongly correlated with soil SO_4 concentrations (Kanda and Minami, 1992). It is also well-known that the rate of bacterial reduction of SO_4 can be stimulated by eutrophication (Cook, 1984). The effect of organic carbon supply on bacterial reduction appears to be considerably large, if one compares the reduction rates between eutrophic and oligotrophic lakes (Cook and Schindler, 1983). However, only small proportion of H_2S produced by this process is likely to be emitted to the atmosphere: its escape from the ecosystem will be basically limited however either by reoxidization at the oxic/anoxic interface or by precipitation mainly in the form of iron sulfide.

4. 1. 2 Assimilatory reduction and degradation

The oxidized sulfur taken in by microorganisms can be incorporated into organic substances in its reduced forms via assimilatory reduction. While animals can meet their sulfur requirements from their food supply, microbes can obtain sulfur from assimilatory sulfate reduction through the synthesis of organosulfur compounds. Since most of the reduced sulfur gases are fixed by the intracellular assimilation process, the dominant fraction of them is unlikely to be released during their lifetime. However upon organisms' death, escape of sulfur into the atmosphere proceeds via decompostion of S-containing amino acids. As with sulfides formed from assimilatory sulfate reduction, the sulfides released during decomposition are chemically unstable in oxic environment. Hence, they tend to be re-oxidized into sulfate with aids of a variety of microorganisms. The species as well as the amount of S release depend strongly on the types of sulfur-containing material and the factors affecting enzymatic activities. Minami *et al.* (1993) showed that the evolution of sulfur gases is quite dependent on substances and that the amounts of S evolved were in most cases

Table 5. Microbial degradation of organic matter under aerobic and anaerobic conditions as sources of reduced sulfur gases in the soil layer (Mianmi *et al.*, 1993; Warneck, 1988)

Sulfur Compounds	Biochemical Precursors
H_2S	sulfate, proteins, polypeptides, cystein, cystine, gluthathione
CH_3SH	methionine, methionine sulfoxide, methionine sulfone, S-methyl cysteine
CH_3SCH_3	methionine, methionine sulfoxide, methionine sulfone, S-methyl cysteine, homocysteine
CH_3SSCH_3	same as CH_3SH
CS_2	cysteine, cystine, homocysteine, lanthionine, djenkolic acid, thiosulfate
COS	lanthionine, djenkolic acid cystine, cysteine, thiocyanate

significantly correlated with the contents of total S in the tested matrix.

Many studies also focused on finding the precursors of volatile sulfur species. The formation of MeSH was confirmed by adding methionine into anoxic sediments of a lake (Zinder and Brock, 1978) as well as of a salt marsh (Kiene and Visscher, 1987). Efforts to identify biochemical precursors of volatile sulfur gases has also been made using artificial cultures (Kadota and Ishida, 1972) and incubation of natural/amended soils (Bremner and Steele, 1978). It is revealed that the addition of S-containing amino acids in the soil layer can give rise to several reduced sulfur compounds via microbial breakdown (Minami and Fukushi, 1981). A compilation of most prominent biochemical precursors for volatile sulfur species that tend to be produced during microbial degradation processes under both aerobic and anaerobic conditions is provided in Table 5.

4. 2 Reduction of Sulfur by Macroorganisms –Plants and Crops

As were the cases for microorganisms, living plants can also release large quantities of reduced sulfur gases. Their patterns for sulfur reduction and for the following emission are likely to be dependent on (1) the factors associated with the plants and their physiology which include: the types of plant species, the part of plant body under consideration, nutritional effect, and photosynthetic CO_2 fixation, and (2) the surrounding environmental conditions which include: ambient SO_2 concentration, light intensity, temperature, and humidity. Emissions of the reduced sulfur compounds can also be accounted for as regulatory steps of plants to balance the sulfur pools of their body, for their physiological demand of sulfur is subject to vary during ontogenic development.

The dominant sulfur species emitted from various tree species is known to be DMS. Its emission from tree species is likely to be affected by photosynthetic assimilation processes. Based on sulfur gas flux measurements of a mid-latitude tree Quersus petrea, one of the typical European oak species, Kesselmeir et al.(1993) reported the existence of a significant correlation between DMS emission and photosynthetic CO_2 assimilation. Like trees, the fluxes of sulfur gases from diverse crop species (e.g., corn, rice, alfalfa, wheat, etc.) are generally dominated by DMS: a large quantity of DMS is known to be emitted from rice fields, sometimes reaching as high as 90% of the total S fluxes (Kanda et al., 1992). The DMS emission rates from rice fields were likely to be influenced by the rice plant activity such as growth rate and respiration rate. It was seen that the emission rate increased with the growth of rice plants. The maximum emissions were observed immediately after the heading day which was followed by subsequent decrease. In case of MeSH, evidence is also available that its emission from various plant species is influenced by their uptake of amino acids.

For some plant species, emission of H_2S can become the most important in quantity, as long as the supply of surplus sulfur can be maintained (Rennenberg et al., 1991). Its emission from plant leaves appears to be a light-dependent process: the rate of release is found to be proportional to the intensity of light flux such that emission becomes insignificant in the absence of light (Filner et al., 1984). Its emission can also be activated by several other factors which include: developmental stage of plants, root injury, concentrations of atmospheric SO_2, and the contents of soil-

water sulfate or bisulfite. In some cases, the developmental stage of plants plays a key role in determining their emission behavior. For example prior to and during bud break, spruce tree exhibited the highest emission of H_2S which was also accompanied by significant emissions of CS_2 and COS (Rennenberg *et al.*, 1991): those gases were otherwise deposited during the rest of the year. H_2S emission in young spruce trees were also stimulated when branches were wounded, detached from the tree, or exposed to SO_2 in moderate concentrations.

Transformation among reduced sulfur species can also serve as their sources. In oxic water, hydrolysis of carbonyl sulfide is identified to be a quantifiable source that is capable of maintaining the hydrogen sulfide at picomolar or upper level (Elloitt *et al.*, 1989).

$$COS + H_2O = CO_2 + H_2S$$
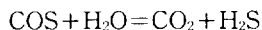
In addition, DMDS is known to occur as an oxidation product of MeSH (Tanzer and Heumann, 1992).

5. ENVIRONMENTAL FACTORS GOVERNING THE EXCHANGE OF REDUCED SULFUR GASES

To adequately explain process-level significance of sulfur gas exchange across the air-surface interface, the relationships between the fluxes and environmental parameters need to be accurately understood. It is accepted that the magnitude of as well as chemical composition of exchange processes is influenced by the combined effects of various factors which include: surface soil temperature, N content of soil, soil moisture, light intensity, plant physiology, and seasonal climatology. The importance of these environemntal parameters is described below.

The emission of reduced sulfur gases from plants is light-dependent (Filner *et al.*, 1984). The fluxes of DMS in coastal wetland areas have been found to be positively correlated with the intensity of solar radiation (Cooper *et al.*, 1987). Kanda and Minami (1992) also showed similar relationships from their measurements conducted over a paddy field. The effects of temperature on the emission behavior of sulfur species are also well-documented (Goldan *et al.*, 1987). A general consensus can be drawn from data sets reported previously in defining the relationships between temperature and fluxes. Those data indicate that, as a genral rule, the increase in temperature is reflected by the increase in the sulfur gas fluxes on logarithmic scale. The emission of reduced sulfur gases from plants and soils is also highly dependent on specific plant and soil type, and thus are highly variable geographically, often on a small scale. Kanda and Tsuruta (1995) investigated 42 types of high plant species with respect to their capacity of sulfur gas emissions. According to their study, most plants are capable of releasing sulfur gases, but species and amounts of such release are highly variable. The activities of plant can also greatly influence sulfur emission. The emission of sulfur gases from some plants can be explained as a mechanism of removing excess sulfur accumulated in their body. For example, uptake of nutrition can be accelerated by removing SO_4 from the rhizosphere which otherwise would inhibit such processes. There is evidence that sulfur emissions of the plants may have potentials to offer multiple advantages at varying stages of their growth (Haines *et al.*, 1989). There are also some indications that the application of nitrogen fertilizer and organic manure usually resulted in increases

in the plant biomass and the activities of the soil microorganisms. They in turn help increase the emissions of reduced sulfur gases from soil ecosystem (Yang et al., 1996; Kanda et al., 1992). Melillo and Steudler (1989) have shown that the addition of nitrogen to forest soils activated the emissions of both COS and CS_2.

Results of a few studies also indicate that the production of reduced sulfur compounds may be positively affected by the SO_4 concentration or sulfur content in soil (Crozier et al., 1995). However, there is no simple correlation between the emission of reduced sulfur gases and the content of total sulfur in soil (Yang et al., 1996). The above-mentioned factors, used to predict sulfur exchange patterns, do not necessarily account for all of the variabilities associated with sulfur gas exchange processes. To understand more accurately those exchange processes, one needs to establish better descriptions of the relationships between different factors and parameters that are influential to their exchange processes.

6. ENVIRONMENTAL FATE OF VOLATILE SULFUR GASES

Observations as well as model-based predictions of the distribution and behavior of atmospheric sulfur species suggest that most of sulfur gases emitted from terrestrial ecosystems (with an exception of COS) may actively participate in various atmospheric reactions. For example, DMS of which atmospheric reactions are most intensively investigated is known to be subject to fast oxidative destruction processin the lower troposphere which is of the order of a few hours to a few days (Hatakeyama et al., 1985). For such destruction reactions, hydroxyl radical (OH) is identified to be the predominant atmospheric oxidant in the

background environment (Yin et al., 1986). In some cases, nitrate (NO_3) radicals are also demonstrated to be an effective reactant for DMS (e.g., during nighttime) as long as streams of polluted air masses are to be supplied (Andreae, 1990).

Due to its massive presence in most environmental settings, the destructive pathway of DMS via production of more oxidized sulfur species is of environmental interest. The major oxidation products of such pathway include both SO_2 and MSA. While SO_2 can undergo further oxidation reactions to form species with higher oxidation states, e.g., sulfuric acid or sulfate, MSA is rather stable chemically (Li and Barrie, 1993). To accurately apportion contribution from various sink processes leading to the destruction of DMS, information on its branching between different oxidized species, i.e., SO_2 and MSA is prerequisite. According to Li and Barrie (1993), its branching is rather complicated, while being temperature-dependent: using the data obtained from the Arctic environment, Li and Barrie found that SO_2 was dominant over MSA under higher temperature condition, but that the pattern became reversed with decreasing temperature. Bandy et al. (1992) reported the idea that sulfur dioxide (SO_2) may not necessarily be the dominant oxidation product of DMS under natural background environmental conditons, but evidence opposing those suggestions also exist (e.g., Saltzman et al., 1983). Although many things concerning DMS destruction still remains to be resolved, various by-products produced from such reactions are removed from the atmosphere either by being scavenged with aerosols or dissolved into precipitation water (rain or cloud-water). Other volatile sulfur gases emitted to the atmosphere are likely to be subject to similar removal pathways.

Contrary to those well-known source mechanisms of plant/vegetation, Taylor et al. (1983) also demonstrated their opposing role as the sink of the reduced sulfur gases. They showed that, under controlled-laboratory conditions, all of the sulfur gases used in their study (ie. DMS, COS, CS_2, MeSH, and SO_2) were removed from air on to plant surfaces. Such removal mechanism of reduced sulfur species, while maybe insignificant for most other sulfur species, is suspected to be the main sink mechanism of COS on global scale (Chin and Davis, 1993). Field data obtained by flux measurements over a meadow indicate that there are close relationships between plant uptake of COS and evapo-transpiration (Bartell et al., 1993). The existence of a compensation point (i.e. emission=deposition) in the exchange of COS is also well-known. The compensation point depends on numerous environmental factors like ambient concentration of the gas, light, temperature, developmental stage of the plant, and the soil type. In springtime, COS compensation points for young plants of corn, rape and wheat were found at about 144 pptv (Kesselmeier et al., 1993), 90 pptv (Kesselmeier and Merk, 1993) and 160 pptv (Schroder, 1993), respectively. These values are in line with the findings of Goldan et al. (1988). According to Goldan et al. (1988), the uptake resistence of soybean increases when ambient COS concentration are below 200 pptv. It is thus likely that COS uptake may otherwise approache zero at concentrations below 200 pptv. These findings thus suggest that under normal atmospheric conditions ([COS]~550 pptv), COS should always be taken up by the plants. The need to critically assess the interaction of volatile sulfur species with the vegetation system may be more pressing in light of potential links between the na-

tural sulfur cycle and the physico-chemical climate of the global troposphere (Charlson et al., 1987).

7. CONCLUSIONS

Despite remarkable advances made in our understanding of sulfur gas exchange processes in the terrestrial environemnt, there still remain many difficulties in accurate descriptions of its significance on global scale. Many factors contributing to its uncertainties can be summarized as follows: Among other factors, the inherent diversities of terrestrial sulfur cycle, represented by the involvement of various chemical components (e.g., H_2S, COS, CS_2, MeSH, DMS and DMDS) and of various source components (e.g., wetland, soil, vegetation, and freshwater etc.), contribute to its complicatedness. The inadequate coverage of geographical and temporal scale for the existing data is a serious problem: most crucial part of such problems is the lack of knowledge on diurnal, seasonal and annunal variations. There is also a logistical problem of obtaining representative measurement data from several important regions, especially if one considers the variabilities associated with climatical and microbiological circumstances of the chosen measuring sites, such as from forest and brush ecosystem. Hence, high degrees of variabilities in measured data from a given locality can result in large uncertainties, if the data are used for extrapolation over regional and/or global scales.

In addition to the inherent limitations and logistic problems, there are also problems with technical aspects, e.g., accurate quantifications of their concentrations and fluxes. Improving techniques for their sampling and analysis from various terrestrial reservoirs is essential to obtain reli-

able flux data. For example, the loss of reduced sulfur during sampling and storage can be quite significant due possibly to their reaction with strong oxidants collected simultaneously (Davison and Allen, 1994). Many attempts have been made recently to effectively remove oxidants from the sample. While their fluxes are commonly quantified using either enclosure chamber or micrometeorological techniques, both techniques have several limitations. Especially the more commonly used enclosure chamber techniques tend to suffer from the disturbance of the micrometeorological condition (Dacey et al., 1987). Most of earlier measurements with extremely high flux values are undoubtedly related to these problems. Micrometeorological techniques, although reasonably simple in concept, is very difficult in practice: application of such technique requires concurrent measurements of sulfur gas gradients in the atmosphere and their eddy correlation parameters for well-defined chemical species (e.g., water vapor or CO_2). The goal of accurately quantifying estimates of natural sulfur emissions based on direct measurements is far from being accomplished. Thus, more efforts need to be directed toward the improvement of sensitive and reliable measurement techniques and toward establishing a number of logistical approaches to derive representative flux values at various scales.

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