SULFUR DIOXIDE AND SULFUR CYCLES

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Summary

Sulfur, which exists in the atmosphere in several chemical forms, is an essential component of our Earth - biosphere system. Sulfur compounds participate in a dynamic, cyclical exchange between the land, the oceans, and the atmosphere. Numerous natural sources combine with human emissions to supply substantial quantities of sulfur compounds to the atmosphere, where they can be transported over large distances from their source regions. Once in the air, these compounds react chemically and are ultimately delivered back to the Earth's surface by dry- and wet-deposition processes.

Specific sulfur compounds, such as sulfur dioxide, are known to cause detrimental effects on human health and vegetation. Both sulfur dioxide and sulfate ion are key contributors to wet and dry acid deposition, and sulfate aerosol is a primary contributor to visibility reduction in polluted areas. Moreover sulfate aerosol, by direct light scattering as well as by influencing cloud-reflectivity, is suspected to be an important contributor to increases in planetary albedo, thus affecting the Earth's radiation balance, resulting in climatic responses on regional and global scales.

While our knowledge of atmospheric sulfur behavior has increased substantially during the past decade, much remains to be learned before a fully satisfactory, quantitative understanding exists. Significant advances can be expected during the next ten years, particularly in the areas of air/surface exchange and global modeling.

1. Introduction: Atmospheric Sulfur Distributions, Cycles and Global Material Balances

Sulfur is an essential component of our Earth-biosphere system. As can be noted from Table 1, it is the 15th most abundant element in the Earth's crust and the 5th most abundant in its oceans. Major natural pathways for sulfur exchange between the crustal, ocean, and atmosphere reservoirs include geological weathering with subsequent runoff to the oceans, emission of gaseous and particulate sulfur species from the oceans and pedosphere to the atmosphere, and atmospheric deposition via wet and dry processes. Natural emissions to the atmosphere arise from a number of phenomena, including biological processing, dust and sea-spray entrainment, and volcanic releases; these complement the substantial sulfur emissions arising from human activity (see *Greenhouse Gases and Global Warming*, *Suspended Material / Aerosol* , *Acid Deposition*, *Formation and Effects of Smog*).

Earth's Crust		**Oceans**	
Element	**Abundance ($mg\ kg^{-1}$)**	**Element**	**Abundance ($mg\ kg^{-1}$)**
oxygen	4.61×10^5	oxygen	8.57×10^5
silicon	2.83×10^5	hydrogen	1.08×10^5
aluminum	8.23×10^4	chlorine	1.94×10^4
iron	5.63×10^4	sodium	1.08×10^4
calcium	4.15×10^4	sulfur	9.05×10^2
sodium	2.36×10^4		
magnesium	2.33×10^4		
potassium	2.09×10^4		
titanium	5.65×10^3		
hydrogen	1.40×10^3		
phosphorous	1.05×10^3		
manganese	9.50×10^2		
fluorine	5.85×10^2		

barium	4.25×10^2		
sulfur	3.50×10^2		

Table 1. Relative abundances of sulfur in the Earth's crust and its oceans. Adapted from CRC Handbook of Chemistry and Physics, 76th edition CRC Press, New York (1995)

Atmospheric sulfur occurs in a number of trace compounds representing a variety of sulfur oxidation states (Table 2), many of which have a strong affinity for water and dissolve easily in clouds and precipitation. As a result, atmospheric sulfur compounds participate in a variety of gaseous- and aqueous-phase reactions, and many are scavenged readily by wet- and dry-deposition processes. Although several of these reactions are reversible and thus enter into equilibrium (or, at least quasi-equilibrium) situations, the general reaction tendency is toward oxidation and — unless scavenged in a lower oxidation state— their ultimate product is sulfuric acid (H_2SO_4) or some form of sulfate ion (SO_4^{2-}).

Oxidation State	**Compound**		**Typical Range (mixing ratio)**
	Common Name	**Chemical Formula**	
-II	hydrogen sulfide	H_2S	1–1000 ppt
	mercaptans	RSH; e.g. CH_3SH	4 ppt
	alkyl sulfides	R'SR; e.g. $(CH_3)_2S$	42–62 ppt
	carbon disulfide	CS_2	1–300 ppt
	carbonyl sulfide	OCS	500 ppt
-I	alkyl disulfides	R'SSR; e.g. $(CH_3)_2S_2$	1–500 ppt
0	alkyl sulfoxides	R'SOR; e.g. $(CH_3)_2SO$	trace
IV	sulfur dioxide	SO_2	10–10 000 ppt
	bisulfite ion	HSO_3^-	condensed phase
	sulfite ion	SO_3^{2-}	condensed phase
	hydroxymethane sulfonate ion	$HOCH_2SO_2^{2-}$	condensed phase
	methane sulfonic acid	CH_3SO_3H	1–15 ppt
VI	sulfur trioxide	SO_3	trace
	sulfuric acid	H_2SO_4	10–10 000 ppt
	sulfate aerosol (including sulfuric acid)	SO_4^{2-}	10–10 000 ppt

Table 2. Common atmospheric sulfur compounds, their oxidation states, and typical abundances in lower troposphere. Reported quantities are based on observed

abundances in both pristine and urban areas. Abundances close to emission sources can be significantly larger.

Although many of the sulfur-containing compounds listed in Table 2 are considered toxic at high concentrations and some (e.g. hydrogen sulfide) have resulted in human mortality in extreme situations, typical ambient exposures are usually insufficient to cause significant health impacts. Notable exceptions include sulfur dioxide, which is known to result in severe effects on human health and vegetation in polluted areas, and sulfate aerosol, which is considered a suspect agent in the context of fine particulate-matter health impacts. Both sulfur dioxide and sulfate ion are key ingredients leading to wet and dry acid deposition, and sulfate aerosol is a primary factor contributing to visibility reduction in polluted areas. Moreover sulfate aerosol, by direct light scattering as well as by influencing cloud-reflectivity, is suspected to be an important contributor to increases in planetary albedo, thus affecting the Earth's radiation balance and resulting in climatic responses on regional and global scales (see *Greenhouse Gases and Global Warming, Atmospheric Chemistry*).

As discussed more fully in Section 4, the continual interchange of sulfur compounds between the Earth's surface and its atmosphere is often assumed to approximate steady-state conditions globally (i.e. the sources of atmospheric sulfur are balanced roughly by deposition to the Earth's surface). Such an assumption is usually invalid, at least at smaller scales however, because of the pronounced spatial and temporal variability of emission and deposition processes. Clearly, for example, sulfur emissions from heavily industrialized areas usually will far exceed deposition within those areas; thus, some caution is mandatory whenever applying steady-state, or at least emission/deposition balance, assumptions under particular circumstances.

Much of the above discussion is reflected by Figure 1, whose numbered pathways set the structure for the discussion to follow, and can be viewed as an interchange diagram for total sulfur or for individual sulfur compounds, depending on the purpose at-hand. Numerous authors have examined the case for total sulfur on a global basis, including early work during the mid-20th century and continuing up to the present time. Table 3 summarizes salient features of several global sulfur-emission inventories published during the past decade. In viewing these numbers one should note that aeolian sulfur emissions, including sea-spray and soil-dust suspensions, also contribute substantial fluxes of sulfur to the atmosphere. These are not included in Table 3 for two reasons. First, and although exceptions such as trans-oceanic transport of suspended dust occur, aeolian suspension of these materials is usually followed by rapid deposition through saltation and other short-term processes, making source contributions to the total atmospheric burden difficult to express in meaningful quantitative terms. Second, such suspensions tend to be composed of large particles which are relatively neutral in an acid-base context, placing them in a interest category that usually is different from that of fine aerosol particles derived from atmospheric precursor gases.

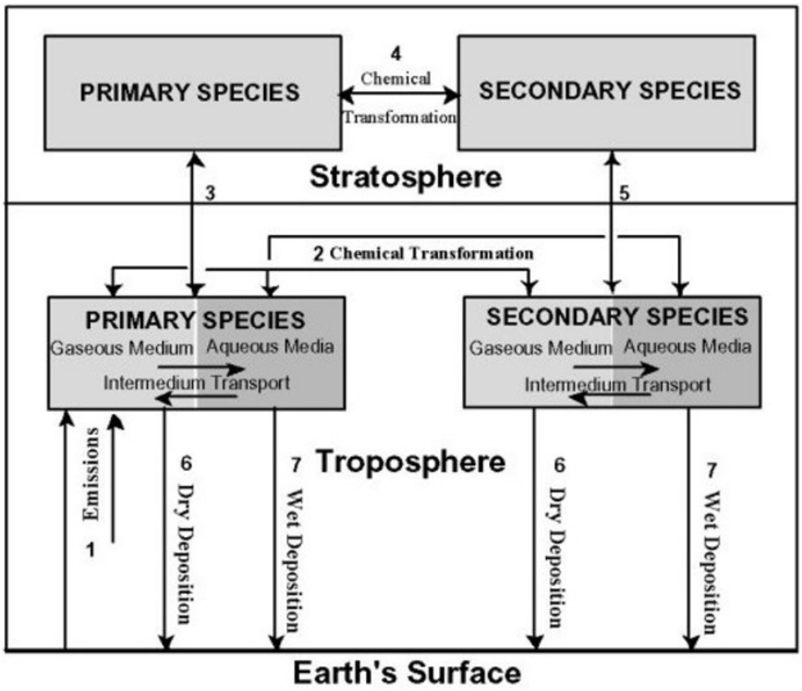

Figure 1. Approximate schematic of atmospheric sulfur-compound reservoirs and exchange pathways

Sulfur Source to Atmosphere	**Emission in Tg of sulfur per year**					
	Spiro, et al.[e]	**Charlson, et al.**[b]	**Bates, et al.**[c]	**Berresheim, et al.**[d]	**IPCC**[e]	**GEIA**[f]
Industrial and utility activities	71	not estimated	76.8	71-77	76	67
Biomass burning	2.3	not estimated	2.2	2.2-3.0	2.2	not estimated
Volcanoes	9.6	23	9.3	9.3-11.8	9.3	not estimated
Biogenic emissions from land areas	0.9	18	0.35	0.26-2.78	1.0	not estimated
Biogenic emissions from oceans	11.9	39	15.4	15–25	24	not estimated
Total anthropogenic emissions	**71**	not estimated	**79**	**73–80**	**78.2**	**67**
Total natural emissions	**22.4**	**80**	**25**	**24.5-39.6**	**34.3**	not estimated
Total emissions	**93.4**	not estimated	**104**	**97.5-119.6**	**112.5**	not estimated

[a] Spiro P.A., Jacob D.J., Logan J.A. (1992). Global inventory of sulfur emission with a 1° × 1° resolution. *Journal of Geophysical Research* **97,** 6023–6036.

[b] Charlson R.J., Anderson T.A., McDuff R.E. (1992). The sulfur cycle. *Global Biogeochemical Cycles*, (eds. Butcher S.S., Charlson R.J., Orians G.H., Wolfe G.V.), 285-299. London, UK: Academic Press.

[c] Bates T.S., Lamb B.K., Guenther A., Dignon J., Stoiber R.E. (1992). Sulfur emissions to the atmosphere from natural sources. *Journal of Atmospheric Chemistry* **14**, 315–337.

[d] Berresheim H., Wine P.H., Davis D.D. (1995). Sulfur in the atmosphere. *Composition, Chemistry, and Climate of the Atmosphere*, (ed. H.W. Singh), 251-307. New York, USA: Van Nostrand Reinhold.

[e] International Panel on Climate Change (1996). *Climate Change 1995.* (eds. Houghton J.T., Meira Filo L.G., Callander B.A., Harris N., Kattenburg A., Maskell K.), Cambridge, MA, USA: Cambridge University Press.

[f] Information on the UN Global Emissions Inventory Activities working group (GEIA) is available on http://www.ortech.ca/cgeic

Table 3. Recent global sulfur emission estimates

Some of the apparent disagreement between the various inventories for anthropogenic emissions appearing in Table 3 stems from the dates, which range from the mid 1980s to the early 1990s, to which the individual inventories apply. As can be noted from Figure 2, a significant upward trend in anthropogenic sulfur emissions occurred during this period and undoubtedly continues at the present time. It is also noteworthy that decreases in North American emissions during the seventies and eighties have been offset by increases in other regions, particularly Asia. The rather wide ranges in estimated natural emissions, reflected in both Table 3 and Figure 2, reflect the difficulty of measuring these emissions, as well as in consolidating them over the widely varying ranges of sources and ambient conditions involved.

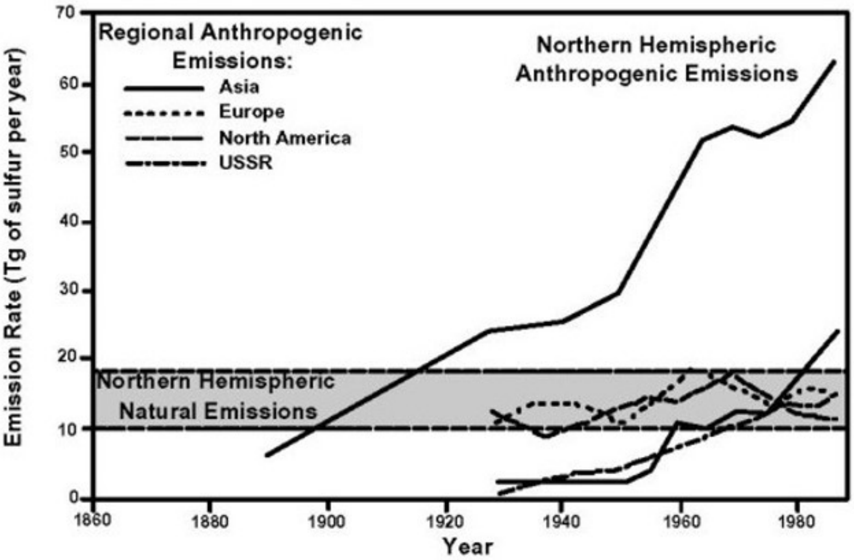

Figure 2. Time-trend estimates of sulfur emissions in the Northern Hemisphere. Adapted from International Panel on Climate Change (1996). *Climate Change 1995.* (eds. Houghton J.T., Meira Filo L.G., Callander B.A., Harris N., Kattenburg A., Maskell K.), Cambridge, MA, USA: Cambridge University Press.

2. Sources, Concentrations, and Chemistry of Sulfur Compounds in the Atmosphere

2.1. Initial Considerations

Considerations of atmospheric fate and residence times often are complicated by the fact that many atmospheric sulfur compounds are emitted as primary species, as well as generated by chemical conversion of other atmospheric sulfur-containing compounds. Accordingly, it is appropriate to discuss sources and atmospheric chemistry of sulfur in the same context. The following subsections discuss sources and chemistry for each of the compounds whose primary emissions are considered to be of atmospheric significance, beginning with the lowest oxidation level and proceeding upward.

2.2. Oxidation State –II: Hydrogen Sulfide, Mercaptans, Alkyl Sulfides, Carbonyl Sulfide, and Carbon Disulfide

2.2.1. Hydrogen Sulfide and Mercaptans

The simplest sulfur compounds in oxidation-state -II, hydrogen sulfide $(\mathrm{H_2S})$ and mercaptans $(\mathrm{RSH, R}$ denoting an alkyl group such as methyl, ethyl, . . . $)$ are emitted mainly from natural sources, although industrial processes such as pulping, petroleum refining, and smelting contribute as well. Methyl mercaptan $(\mathrm{CH_3SH})$ is the most common of the alkyl mercaptans, but usually is far less abundant than hydrogen sulfide in the atmosphere. Naturally emitted hydrogen sulfide originates mainly from anaerobic decomposition processes but is also present in volcanic plumes, which can become a dominant source when major eruptions occur.

Global emission rates of methyl mercaptan and particularly hydrogen sulfide have been the subject of substantial uncertainty over the past decades, a fact that is reflected in the widely varying estimates of their magnitudes. Although some measurements have suggested that hydrogen sulfide fluxes contribute significant fractions of overall sulfur emissions from soils as well as tidal and estuary environments, it is now generally accepted that hydrogen sulfide emissions constitute a significant, but secondary, sulfur source on a global basis. Recent estimates indicate global hydrogen sulfide emissions to range between one-half and slightly more than 3 Tg of sulfur per year, depending on volcanic activity.

As indicated by the reaction sequence in Figure 3, the primary degradation pathways for both hydrogen sulfide and methyl mercaptan are direct attack by hydroxyl (HO) and nitrate $(\mathrm{NO_3})$ radicals to form HS and RS radicals, respectively. In reaction-sequences dashed arrows will indicate complex reaction pathways that are not characterized explicitly. These radicals react rapidly with either oxygen, ozone, or nitrogen dioxide in a variety of rather complex reactions to ultimately form sulfur dioxide and associated reaction products.

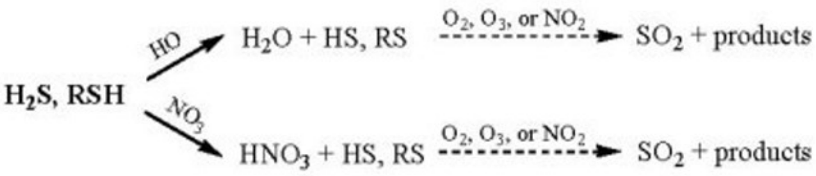

Figure 3. Primary atmospheric degradation pathways for hydrogen sulfide and mercaptans

Table 4 gives the second-order rate coefficients at 298 K for the hydroxyl- and nitrate-radical reactions associated with hydrogen sulfide and methyl mercaptan, along with estimated half lives associated with typical ambient radical concentrations. In viewing the half lives shown here, one should observe that hydroxyl radicals will be largely absent at night whereas the converse is true for nitrate radicals; thus the reported half lives should be adjusted, depending on the portions of the diurnal cycle being considered.

Species	**Rate Coefficient ($cm^3 molecule^{-1} s^{-1}$)**		**Reaction Half Life**	
	HO	**NO_3**	**HO**	**NO_3**
H_2S	4.8×10^{-12}	$<10^{-15}$	2.4 days	>1 year
CH_3SH	3.3×10^{-11}	9.2×10^{-13}	8 hours	12 hours
CH_3SCH_3	6.5×10^{-12}	1.1×10^{-12}	2 days	10 hours
CS_2	4.7×10^{-12}	no data	2.5 days	no data
COS	2×10^{-15}	no data	16 years	no data
CH_3SSCH_3	2.3×10^{-10}	no data	1.2 hours	no data
SO_2	9×10^{-13}	no data	13 days	no data

Table 4. The second-order rate coefficients and lifetimes associated with gas-phase hydroxyl- and nitrate-radicals attack on selected reduced sulfur compounds. Adapted from Finlayson-Pitts B.J., Pitts J.N. (2000). *Chemistry of the Upper and Lower Atmosphere*. 969 pp. New York, USA: Academic Press. Estimated lifetimes are based on assumed HO and NO_3 radicals concentrations of 10^6 and 2.5×10^7 radicals per cubic centimeter, respectively.

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Bates T.S., Lamb B.K., Guenther A., Dignon J., Stoiber R.E. (1992). Sulfur emissions to the atmosphere from natural sources. *Journal of Atmospheric Chemistry* **14**, 315–337. [These authors estimate geographical distributions of naturally emitted sulfur gases. In addition, they compile a global sulfur emission inventory for these compounds.].

Berresheim H., Wine P.H., Davis D.D. (1995). Sulfur in the atmosphere. *Composition, Chemistry, and Climate of the Atmosphere,* (ed. H.W. Singh), 251-307. New York, USA: Van Nostrand Reinhold. [This chapter presents an account of atmospheric sulfur compounds, which is especially recommended for readers interested in further pursuit of this topic. It provides a more detailed discussion of sulfur emissions and atmospheric chemistry, as well as analyses of climatic impact and removal processes.].

Butcher S.S., Charlson R.J., Orians G.H., Wolfe G.V. (1992). *Global Biogeochemical Cycles.* 379 pp. London, UK: Academic Press. [This book contains a number of chapters by different authors, covering the global sulfur cycle, general atmospheric behavior in a biogeochemical exchange context, and discussions of atmospheric residence times and transport scales].

Chin, M., Rood R.B., Linn S-J., Müller J-F, Thompson A.M. (2000). Atmospheric sulfur cycle simulated in the global model GOCART: Model description and global properties. *Journal of Geophysical Research* **105**, 24671–24687. [This article describes sulfur-chemistry simulations by the GOCART model, one of the several global-chemistry models currently in operation. In addition, it compares model outputs with those of a number of those other models, providing a good summary of global modeling activity over the past decade.].

Finlayson-Pitts B.J., Pitts J.N. (2000). *Chemistry of the Upper and Lower Atmosphere.* 969 pp. New York, USA: Academic Press. [This book is the most comprehensive and modern account of atmospheric sulfur chemistry currently available. It forms the basis for much of the discussion in Section 2, and provides much more extensive and detailed discussion of the mechanisms for sulfur-compound reactions than given here.].

NAPAP (1991). *Acidic Deposition: State of Science and Technology. Volume I: Emissions, Atmospheric Processes, and Deposition*. 1508 pp. National Acid Precipitation Assessment Program. Washington, DC, USA: US Government Printing Office. [Volume 1 of a four-volume series, this publication provides a comprehensive review of North American pollution emissions (natural and anthropogenic) and chemical deposition. In addition, it gives comprehensive overviews of air chemistry as well as the physicochemical processes responsible for precipitation scavenging and dry deposition of acidic pollutants from the atmosphere.].

Slanina S. (ed.) (1997). *Biosphere–Atmosphere Exchange of Trace Gases and Pollutants in the Troposphere.* 528 pp. Berlin, Germany: Springer-Verlag. [This book contains a number of scientific contributions from the EUROTRAC project, addressing natural emissions from the biosphere, dry-deposition, and their measurement. Behavior of selected sulfur compounds as well as a number of other important trace gases is described.].

Biographical Sketch

Dr. Hales is a principal and owner of Envair, an unincorporated association dedicated to research in the environmental and earth sciences. He is currently serving as Management Coordinator of the NARSTO program, a private/public partnership involving the US, Canada, and Mexico and addressing the joint management of regional and urban pollution in North America.

Prior to joining Envair, Dr. Hales served as Manager of the Atmospheric Sciences Department at Battelle-Northwest, where he worked as an engineer and atmospheric scientist. His primary areas of research focus are air-quality and atmospheric sciences, including coordination of combined monitoring, modeling, and data analysis programs, meteorological/pollution model development and application, and interpretive analysis of air-chemistry, cloud-physics, and pollutant-removal processes.

Dr. Hales received his B.Sc. in chemical engineering from the University of Washington in 1960 and his Ph.D. in chemical engineering from the University of Michigan in 1968. Between degrees he served in the Division of Air Pollution in the US Public Health Service. Dr. Hales is the author of over one hundred journal articles, book chapters, and technical reports dealing with various aspects of air pollution and atmospheric chemistry.