NATURAL SULFUR EMISSIONS TO THE ATMOSPHERE OF THE CONTINENTAL UNITED STATES

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Abstract. Seasonal emissions of biogenic sulfur gases from marine and terrestrial sources were assessed for 13 regions of the continental United States. The resulting inventory was compared to volcanic and anthropogenic sulfur emissions from the same regions. Terrestrial biogenic sulfur emissions were less than 1% of the total sulfur emissions in each region. However, during the summer, marine biogenic sulfur emissions may be contributing 20–40% of the total sulfur emissions in western coastal regions.

1. INTRODUCTION

The increased awareness of the environmental consequences of acidic precipitation has prompted numerous studies of sulfur gas emissions from both anthropogenic and natural (biogenic and volcanic) sources. Quantitative estimates of these sources are needed as inputs to both regional acid deposition models and global climate models. Although sulfur emissions in the northern hemisphere are strongly dominated by anthropogenic sources [Andreae, 1990; Bates et al., 1991], natural sulfur emissions may be significant on smaller, regional scales. Global oceanic sulfur gas concentrations and terrestrial sulfur emissions have recently been reviewed [Bates et al., 1991]. In this manuscript we combine data from recent studies to calculate seasonal sulfur emissions in 13 regions of the continental United States. To facilitate comparisons of the natural sulfur emissions with the National Acid Precipitation Assessment Program (NAPAP) emissions inventory data base, the

coastline of the United States has been divided into six segments which correspond to Environmental Protection Agency regions (Figure 1).

2. MARINE EMISSIONS

Dimethylsulfide (DMS) is the most abundant reduced sulfur gas in surface seawater and generally comprises greater than 90% of the total gaseous sulfur flux to the atmosphere [Bates et al., 1991]. Measurements of oceanic DMS concentrations off the west coast of the United States (1983–1989) were used to compute seasonal average concentrations. A detailed study of the regional atmospheric sulfur cycle [Bates et al., 1990] showed that neither the biologically productive region near shore nor the surf zone contributed significantly to the onshore transport of DMS. Seasonal and regional wind speeds, seawater temperatures [Summary of Synoptic Meteorological Observations, 1975], and North Pacific Ocean DMS concentrations were used to calculate DMS fluxes (Table 1) using air-sea exchange models [Liss and Merlivat, 1986], which predict that the flux of DMS is proportional to the product of the seawater DMS concentration and a first-order exchange coefficient [Bates et al., 1987]. The calculated regional fluxes varied from 1.5 to 2.0 μmol/m^2/d in the winter (November–April) and from 3.1 to 5.5 μmol/m^2/d in the summer (May–October) and are consistent with regional open ocean DMS fluxes [Bates et al., 1987]. The root-mean-square of the uncertainties in these flux calculations is approximately 66%, based on the standard deviation of the seasonally averaged concentrations (30%), the range of potential exchange coefficients (30%), and the calculated molecular diffusivity (50%).

Once in the atmosphere, DMS is oxidized to methanesulfonic acid and sulfur dioxide/sulfate. The lifetime of each species has been estimated from regional studies of marine boundary layer biogeochemical sulfur cycles off Washington state [Andreae et al., 1988; Bates et
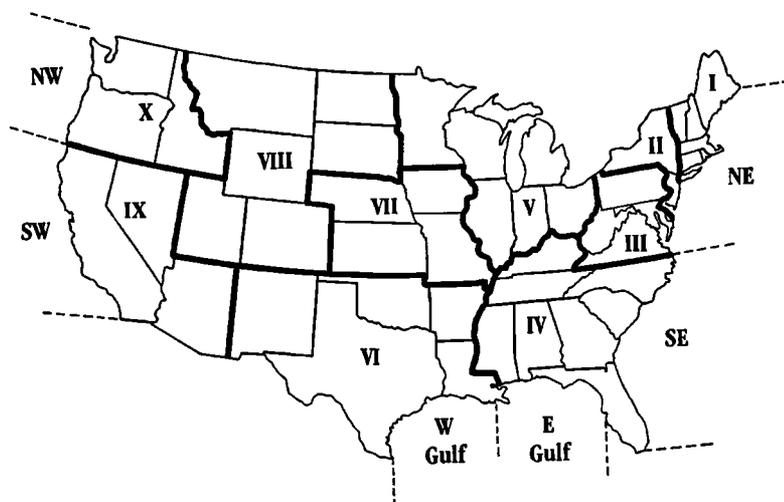
Fig. 1. Coastal divisions and EPA regions used in assessing the onshore transport of marine sulfur to the continental United States.

al., 1990], the equatorial Pacific [Andreae, 1986] and the southern ocean [Berresheim, 1987]. From these studies it appears that the average atmospheric residence time of a DMS-derived sulfur atom is approximately 5 days. This residence time, coupled with the speed and frequency of onshore winds, the coastline length, and DMS fluxes (Table 1) was used to calculate the regional and seasonal transport of marine sulfur to the continental United States (Table 1). The calculated transports ranged from 0.72 x 10^6 to 7.7 x 10^6 mol/d.

The transport calculations add another element of uncertainty to the DMS emission estimates, because estimates of the residence time of sulfur in the atmosphere range from 2 to 8 days. This uncertainty (60%), added to

uncertainties in the natural concentration variability, flux calculations, and DMS diffusivity, result in a root-mean-square uncertainty of 90%.

3. TERRESTRIAL EMISSIONS

Guenther et al. [1989] have used the emissions algorithms based on the data collected by Lamb et al. [1987] to develop a U.S. national biogenic sulfur (H_2S, OCS, CH_3SCH_3, CS_2, and CH_3SSCH_3) emissions inventory with a county spatial scale and monthly time scale. Using information available in the Geoecology Data Base [Olson, 1980] and U.S. Department of Interior (USDI) National Atlas [USDI Geological Survey, 1970], surface areas of wetland, organic and other soils (categorized by soil map unit chemical and

TABLE 1. Regional Chemical (DMS Concentrations), Physical (Frequency of Onshore Winds), and Meteorological (Wind Speed and Seawater Temperature) Data and Calculated Sulfur Fluxes and Transport

	Area					
	NW	SW	West Gulf	East Gulf	SE	NE
	Summer					
Wind, m/s	5.6	7.0	5.4	4.9	6.2	5.5
SW temperature, °C	16	20	28	28	26	22
DMS concentration, nmol/L	2.2	2.2	2.2	2.2	2.2	2.2
Flux, μmol/m^2/d	3.2	5.5	4.1	3.1	5.0	3.6
Frequency onshore, %	26	35	51	27	39	24
Transport, 10^6 mol/d	1.6	7.1	3.8	1.3	7.7	2.5
	Winter					
Wind, m/s	8.5	7.0	6.3	6.2	7.1	7.2
SW temperature,°C	12	17	25	25	22	16
DMS concentration, nmol/L	0.66	0.66	0.72	0.72	0.72	0.66
Flux, μmol/m^2/d	1.8	1.5	1.7	1.6	2.0	1.6
Frequency onshore, %	37	33	42	23	29	19
Transport, 10^6 mol/d	2.0	1.9	1.5	0.72	2.3	1.1

The coastlines in kilometers are as follows: NW, 800; SW, 1300; West Gulf, 800; East Gulf, 800; SE, 1200; and NE, 1400.

physical characteristics), croplands, natural vegetation, and inland waters were determined for all counties in the contiguous United States. Deciduous and coniferous forest surface area estimates were converted to leaf biomass estimates using the relationships developed by Zimmerman [1979]. Leaf biomass densities tend to be uniform throughout a vegetation association and are relatively insensitive to site-specific variables [Satoo, 1967]. Sulfur emissions from deciduous biomass were calculated only for the period between the last spring frost and the first fall frost. Data reported in the Geoecology Data Base and in the USDI National Atlas were used to make estimates of mean frost dates. Because of the observed high emission rates, emissions from corn were estimated separately from other crops. Estimates of corn biomass were based on the agricultural yield estimates reported on a county basis in the Geoecology Data Base and converted to total plant dry weight using relationships reported by Cooper [1975]. Corn was assumed to grow or increase biomass linearly through

the growing season with periodic harvests. The amount of biomass present during each month increases monthly by a fraction of the total annual yield [Guenther et al., 1989]. Mean monthly temperatures compiled in the Geoecology Data Base provide the temperature input required for the calculations.

Monthly emissions of OCS, CS_2, dimethyl, disulfide, and H_2S were calculated by Guenther et al. [1989] for each of 3071 contiguous U.S. counties. The annual national flux of 5.0×10^8 moles of sulfur was broken down by source, month, compound, and region by Guenther et al. [1989] and is summarized here by season and region (Table 2).

Above ground biomass was estimated to generate slightly more than one half of the national annual total flux. Coniferous canopies are the largest above ground biomass type and emitted 30% of the total, while low-organic content soils were the largest surface source with 22% of all natural sulfur emissions. Although organic and wetland soils have higher per area emission rates, they each contributed only

TABLE 2. Seasonal Sources of Sulfur to the Continental United States

Marine Region	Continental Region	Marine Biogenic	Terrestrial Biogenic	Anthropogenic,[a] %	Natural Anthropogenic
		Summer[b]			
NW	X	1.6	0.13	10	18%
NW	coast[c]	1.6	0.09	8	21
SW	IX	7.1	0.23	38	19
SW	coast	7.1	0.10	9	80
W Gulf	VI	3.8	0.44	94	4.5
W Gulf	coast	3.8	0.27	73	5.6
SE	IV	9.0	0.41	200	4.6
SE	coast	9.0	0.34	130	7.1
NE	I-III	2.5	0.28	180	1.5
NE	coast	2.5	0.21	72	3.8
	VIII	0.0	0.24	28	0.9
	VII	0.0	0.29	66	0.4
	V	0.0	0.35	276	0.1
		Winter[b]			
NW	X	2.0	0.027	10	21
NW	coast	2.0	0.023	8	25
SW	IX	1.9	0.070	38	5.2
SW	coast	1.9	0.037	9	22
W Gulf	VI	1.5	0.12	94	1.7
W Gulf	coast	1.5	0.080	73	2.2
SE	IV	3.1	0.11	204	1.6
SE	coast	3.1	0.10	132	2.4
NE	I-III	1.1	0.023	181	0.6
NE	coast	1.1	0.017	72	1.6
	VIII	0.0	0.018	28	0.1
	VII	0.0	0.020	66	<0.1
	V	0.0	0.013	276	<0.1

Regions are shown in Figure 1. Sources are expressed in 10^6 mol/d.
[a] Anthropogenic emissions for 1985 from U.S. EPA [1989]. The tabulated emissions ignore the 1–2% seasonal variability in anthropogenic emissions.
[b] Winter: November–April; Summer: May–October,
[c] Coast: coastal states only.

7% of the total as a result of their smaller share of the total U.S. land area. Noncorn crops contributed less than 4% of the total emissions on an annual basis. The total summertime flux was predicted to account for 84% of the annual total. This is not unexpected considering the strong temperature dependence of the emission functions.

Calculated terrestrial biogenic sulfur emissions in the United States were dominated by OCS (38%), DMS (35%), and H_2S (21%). Emissions of CS_2 and DMDS together represented about 6% of the total. On a regional basis, two thirds of the total national flux originated in regions 4, 5, 6, and 7 which are in the southeast and midwest portions of the United States. This encompasses about one half of the total land area. Regional-averaged fluxes ranged from about 0.09 $\mu mol/m^2/d$ in region 8 to about 0.27 $\mu mol/m^2/d$ in region 4, in comparison to the national average of 0.18 $\mu mol/m^2/d$. In general, the highest county-averaged flux rates were predicted for the agriculturally intensive midwestern corn belt region, the New England deciduous forests, and over the wetlands and organic soils along the Atlantic and Gulf Coasts and the Mississippi river valley. The lowest flux rates were predicted for the Rocky Mountain region.

The principle sources of error in terrestrial sulfur emission calculations include the uncertainties in the analytical procedures used to determine sulfur fluxes and the extrapolation of the limited data base to obtain generalized flux distributions. Overall, the uncertainty in the biogenic sulfur emissions estimated for terrestrial sources in the United States is approximately a factor of 3 [Lamb et al., 1987; Guenther et al., 1989].

4. VOLCANIC EMISSIONS

Within the continental United States there are seven active volcanos [Macdonald, 1972] along the Cascade Range, with Mount St. Helens being the most eruptive during the past century. The total mass of sulfur released during the major eruption of Mount St. Helens on May 18, 1980, was estimated at between 0.0075 [Stoiber et al., 1981] and 0.034 Tmol S [Millan et al., 1985]. During the active period following the major eruption (May 26, 1980, through December 1982), 0.0066 Tmol S were emitted from the volcano [Casadevall et al., 1983]. Since that time, there has been no major volcanic activity and current sulfur emissions are estimated at 0.17 x 10^6 mol/d (Kenneth McGee, U.S. Geological Survey, personal communication, 1990). An unusually high percentage (35–100) of the sulfur emissions from Mount St. Helens was H_2S, especially in the early stages (March–June, 1980) of volcanic activity [Hobbs et al., 1982]. Further analysis of the data showed that H_2S was the dominant gas released from the melt (H_2S/SO_2 = 100), while SO_2 was the dominant sulfur gas measured in the plume and in the low-temperature fumaroles [Casadevall and Greenland, 1981]. The lack of H_2S in the plume and in the stratosphere suggest that the H_2S was rapidly oxidized shortly after release from the magma [Casadevall and Greenland, 1981]. The current emissions from Mount St. Helens are approximately 4% of the natural sulfur emissions in region X (Figure 1) of the United States.

5. A COMPARISON WITH ANTHROPOGENIC EMISSIONS

The major difficulty in comparing the onshore transport of marine sulfur with natural terrestrial and anthropogenic emissions is in estimating the depositional area of the marine sulfur [Bates and Cline, 1985]. In Table 2 the onshore transports (East Gulf and SE marine sources are combined) are compared with the natural terrestrial and anthropogenic emissions from both the adjacent Environmental Protection Agency regions (Figure 1) and the coastal states [U.S. EPA, 1989]. Marine transport dominates the natural sulfur sources in all regions. Along the gulf and east coasts, biogenic sulfur sources are at most equal to 7% of the anthropogenic SO_2 emissions. This is probably an upper limit since it is likely that the marine sulfur is carried further inland in these areas than just the coastal states. Along the west coast, however, much of the marine sulfur is likely deposited in rainfall on the western slopes of the Cascade/Sierra Nevada Mountains [Bates and Cline, 1985]. In these coastal states, marine sulfur could be as much as 80% of the amount of the anthropogenic SO_2 emitted during the summer (Table 2).

The EPA 1985 anthropogenic emission inventory has estimated an annual SO_2 flux of 0.33 Tmol or 120 $\mu mol/m^2/d$. In comparison, terrestrial natural emissions are predicted to be 0.0005 Tmol which corresponds to 0.15% of the combined natural and anthropogenic total. Anthropogenic SO_2 emissions are relatively constant throughout the year in the United States, while biogenic sulfur emissions decrease substantially during the winter months. As a result, the national average contribution of natural emissions ranges from 0.04% in winter to 0.26% in summer. Natural sulfur emissions are from very diffuse sources spread over large areas while anthropogenic sources are point or concentrated area sources. The diffuse natural emissions are expected to have a negligible impact on urban sites but may make significant contributions to sulfur concentrations in remote areas.

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