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# The Role of the Ocean in the Global Atmospheric Sulfur Cycle

B. C. NGUYEN, B. BONSANG, AND A. GAUDRY

*Centre des Faibles Radioactivités, Laboratoire Mixte CNRS-CEA*

The background atmospheric  $\text{SO}_2$  concentration above the sea surface has been established at  $0.1 \times 10^{-6} \text{ g/m}^3$  (35 pptv). Several hypotheses to explain the origin of  $\text{SO}_2$  above the ocean, far from continental sources, have been discussed. We have shown that one of the mechanisms of  $\text{SO}_2$  formation is the biogenic production of reduced organic sulfur compounds in the ocean. Dimethyl sulfide (DMS) has been observed in oceanic areas, with concentrations ranging from 11 to  $1150 \times 10^{-9} \text{ g l}^{-1}$  in surface waters and from 0.2 to  $400 \times 10^{-9} \text{ g m}^{-3}$  (0.07 to 144 pptv) in marine atmosphere. This compound is emitted into the atmosphere and oxidized there by photochemically induced processes. That leads partly to  $\text{SO}_2$  formation, and subsequently, to sulfate. This hypothesis is corroborated by a correlation between atmospheric  $\text{SO}_2$  concentrations and the relation between atmospheric  $\text{SO}_2$  concentrations and biological activity. The flux of sulfur by this process (biological activity  $\rightarrow$  organic sulfides  $\rightarrow \text{SO}_2 \rightarrow \text{SO}_4^{2-}$ ) is estimated to range between 27 and  $72 \times 10^6$  tons of sulfur per year. This biogenic production is comparable to atmospheric sulfur production by sea spray, which is about  $44 \times 10^6 \text{ T S/yr}$ . Therefore, the oceanic production by these two processes could be estimated as being from 71 to  $116 \times 10^6 \text{ T S/yr}$ .

## INTRODUCTION

The global sulfur budget, particularly its atmospheric component, has been discussed by numerous authors: Eriksson [1963], Robinson and Robbins [1970], Kellogg *et al.* [1972], Friend [1973], Granat *et al.* [1976]. In all of the budgets mentioned above, known sulfur sources can account for only about one half of the recognized sinks. According to these authors, the difference, which is required to balance the budget, varies between 30 and  $170 \times 10^6 \text{ T S/yr}$ . This discrepancy indicates that natural sulfur sources are not yet well known, in particular the volcanic and oceanic sources. Several origins for this last natural source have been suggested, but data is scarce. Kellogg *et al.* proposed  $\text{H}_2\text{S}$  production above continents and coastal areas is the missing source, while Lovelock *et al.* [1972] believed organic sulfide emission from the sea surface is important. Logan *et al.* [1979], Torres *et al.* [1980], and Sze and Ko [1980] suggested that atmospheric  $\text{SO}_2$  is produced by the photooxidation of COS and  $\text{CS}_2$ , two compounds whose sources are not yet well identified. Our goal in this paper is to present data that help to elucidate the role of the ocean in the atmospheric sulfur cycle.

## EXISTENCE OF SULFUR DIOXIDE OVER THE OCEAN

### Methodology

By using an automatic "cut-out" device controlled by a weather vane system, air samples free of contamination from the ship exhaust were collected during 24 hours and analyzed for  $\text{SO}_2$  by an adaptation of the method of West and Gaeke [1956].

The lowest detectable amount of  $\text{SO}_2$  is  $0.1 \mu\text{g}$ , determined with sodium metabisulfite standard solutions. In order to lessen our detection limit we have used the preconcentrating device previously described [Nguyen *et al.*, 1974a; Bonsang and Nguyen, 1978], mainly composed of an impinger and an electromagnetic device that automatically controls the solution level.

Hence the volume of air analyzed for each sample ranges

between 4 and  $5 \text{ m}^3$ , and the detection limit is about  $0.02 \mu\text{g SO}_2/\text{m}^3$ .

### Sulfur Dioxide Over the Open Ocean

To complete our previous  $\text{SO}_2$  measurements in marine environments [Nguyen *et al.*, 1974a], three oceanographic expeditions, described in Figure 1a, were undertaken in sub-antarctic regions and in the Indian Ocean from  $5^\circ\text{S}$  to  $30^\circ\text{S}$ . In this last area the circulation of air masses is essentially zonal, from east to west;  $\text{SO}_2$  concentrations were only measured in air masses that had probably last passed over Australia several thousand kilometers away.

Figures 1b and 1c show a geographical distribution of 160 values of  $\text{SO}_2$  above the Indian Ocean sub-Antarctic region and the Atlantic Ocean (Table 1). The average concentration of 121 values of atmospheric  $\text{SO}_2$ ,  $0.1 \mu\text{g}/\text{m}^3$  in the Indian Ocean and the sub-Antarctic area (Figure 1c), is the same as the previous background already found above this region [Nguyen *et al.*, 1974a].

As the basic pH of seawater ( $\approx 8.2$ ) would prevent the direct release of dissolved  $\text{SO}_2$  to the marine atmosphere, other sources must be determined to explain the observed background concentration of  $0.1 \mu\text{g}/\text{m}^3$ . It is therefore relevant to discuss the various hypotheses for the occurrence of  $\text{SO}_2$  in the open ocean.

*Could the  $\text{SO}_2$  be carried along great distances from remote continental sources?*  $\text{SO}_2$  can be carried into the marine atmosphere either through the lower troposphere or through the upper troposphere.

Nguyen *et al.* [1975, 1978b] have determined a 17-hour residence time (12-hour half-life) for  $\text{SO}_2$  in the marine atmosphere of the boundary layer over the Mediterranean. A similar value was found by Prahm *et al.* [1976] above the North Atlantic. Furthermore, a strong decrease of  $\text{SO}_2$  concentrations has been observed over the Mediterranean. Such a decrease is due to the oxidation and dilution effects and the absorption by seawater, which represents as much as 9% to 34% of the scavenging process [Bonsang, 1980]. In fact, at 100 km from the coast this concentration is only one tenth of its mean coastal value ( $5 \mu\text{g}/\text{m}^3$ ). Even when near a polluted area such as Fos-sur-Mer, the  $\text{SO}_2$  concentrations observed 200 km out to sea were only  $0.25 \mu\text{g}/\text{m}^3$  with winds coming from

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0148-0227/83/003C-1233\$05.00

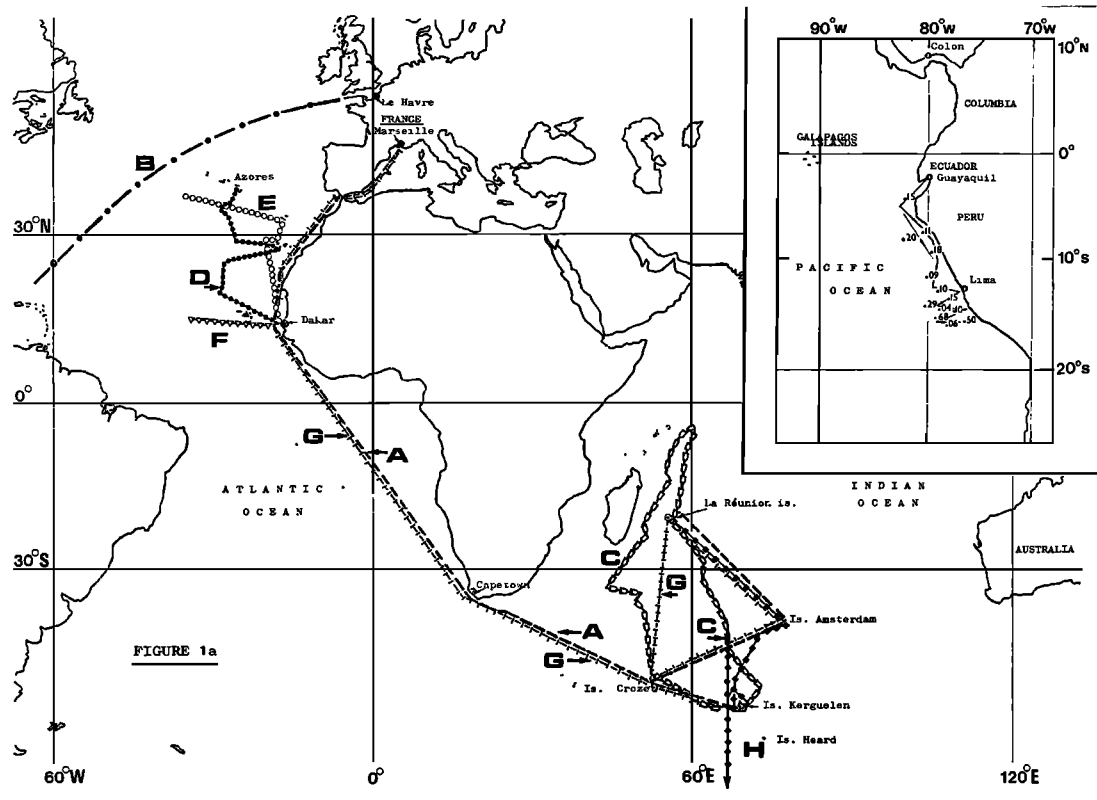


Fig. 1a.

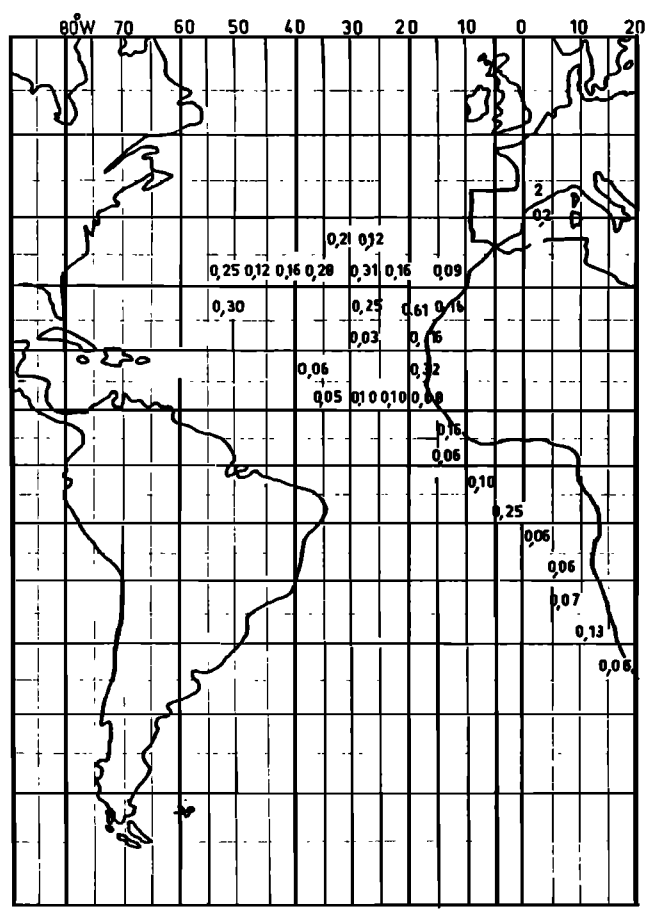


Fig. 1b.

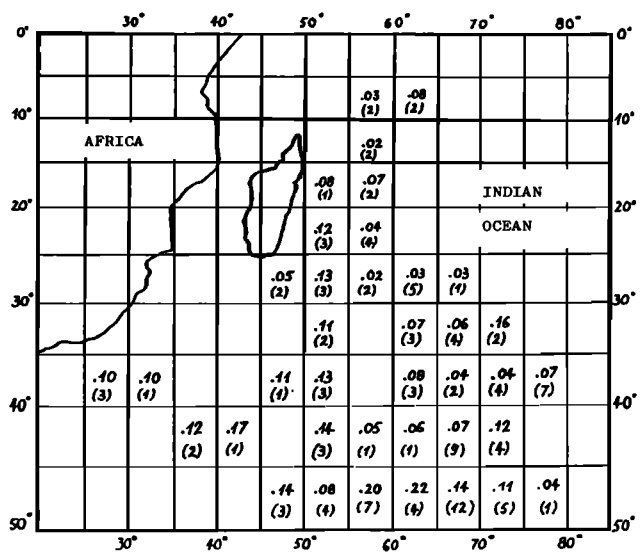


Fig. 1c.

Fig. 1. (a) Tracks for oceanographic cruises A to H in the Atlantic and Indian Ocean. Right corner: SO<sub>2</sub> concentrations during a cruise in the Peruvian Upwelling in April 1975. (b) Mean atmospheric SO<sub>2</sub> concentrations (μg/m<sup>3</sup>) above the Atlantic Ocean and (c) above the Indian Ocean and subantarctic areas. Values in parenthesis represent the number of measurements.

TABLE 1a. Atmospheric SO<sub>2</sub> Concentrations: Cruise A

Date	Latitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
March 11, 1973	42.9°N	41.6°N	0.096 ± 0.008
March 12, 1973	40.5°N	36.7°N	0.088 ± 0.007
March 13, 1973	36.7°N	33.2°N	0.055 ± 0.006
March 14, 1973	33.2°N	28.0°N	0.094 ± 0.007
March 16, 1973	22.6°N	15.8°N	0.089 ± 0.008
March 17, 1973	15.6°N	9.7°N	0.077 ± 0.007
March 18, 1973	9.6°N	4.6°N	0.220 ± 0.012
March 19, 1972	4.5°N	0.3°S	0.045 ± 0.006
March 20, 1973	0.4°S	5.4°S	0.163 ± 0.010
March 21, 1973	5.5°S	10.0°S	0.440 ± 0.020
March 22, 1973	10.2°S	15.1°S	0.082 ± 0.009
March 23, 1973	15.1°S	20.0°S	0.082 ± 0.009
March 24, 1973	20.1°S	24.7°S	0.094 ± 0.008
March 25, 1973	24.7°S	29.5°S	0.106 ± 0.010
March 26, 1973	29.6°S	34.0°S	0.077 ± 0.009
March 29, 1973	36°1'S	38.3°S	0.133 ± 0.011
March 30, 1973	38°35'S	39°7'S	0.103 ± 0.010
March 31, 1973	39°8'S	42°9'S	0.126 ± 0.010
April 1, 1973	43°0'S	46°1'S	0.066 ± 0.006
April 2, 1973	46°15'S	47°7'S	0.094 ± 0.010
<i>Crozet Island</i>			
April 3, 1973	47°7'S	49°4'S	0.098 ± 0.009
April 4, 1973	49°4'S		< 0.020
April 7, 1973			0.420 ± 0.022
April 8, 1973	<i>Kerguelen Island</i>		0.092 ± 0.008
April 9, 1973	49°9'S	48°8'S	0.071 ± 0.007
April 10, 1973	48°9'S	47°5'S	0.025 ± 0.006
April 11, 1973	47°5'S	46°20'S	0.020
<i>Crozet Island</i>			
April 13, 1973	46°20'S	44°6'S	0.084 ± 0.009
April 14, 1973	44°6'S	42°0'S	0.055 ± 0.008
April 15, 1973	41°9'S	39°2'S	0.020 ± 0.007
April 16, 1973	39°2'S	37°5'S	0.020
<i>Amsterdam Island</i>			
April 20, 1973	37°0'S	32°9'S	0.030 ± 0.005
April 21, 1973	32°9'S	27°4'S	0.025 ± 0.006
April 22, 1973	27°1'S	22°6'S	0.040 ± 0.004

the coast. As this is close to the background measured in the sub-Antarctic area at several thousand kilometers from continents, the continental SO<sub>2</sub> component transported through the lower troposphere may be considered negligible.

However, the residence time of SO<sub>2</sub> in the high remote troposphere could be rather higher than 1.5 days [Rodhe and Isaksen, 1980], and even 8 days [Logan et al., 1979], if heterogeneous reactions are neglected. Consequently, if some SO<sub>2</sub> is

TABLE 1b. Atmospheric SO<sub>2</sub> Concentrations Cruise B

Date	Latitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
April 23, 1973	18°20'N	20°40'N	0.105 ± 0.010
April 24, 1973	20°40'N	23°05'N	0.140 ± 0.010
April 25, 1973	23°05'N	25°57'N	0.555 ± 0.060
April 26, 1973	25°57'N	29°08'N	0.405 ± 0.020
April 27, 1973	29°08'N	31°56'N	0.304 ± 0.015
April 28, 1973	31°56'N	34°28'N	0.248 ± 0.015
April 29, 1973	34°28'N	36°40'N	0.121 ± 0.013
April 30, 1972	36°40'N	38°55'N	0.158 ± 0.016
May 1, 1973	38°55'N	40°35'N	—
May 2, 1973	40°38'N	42°28'N	0.276 ± 0.015
May 3, 1973	42°28'N	44°24'N	0.212 ± 0.012
May 4, 1973	44°24'N	45°48'N	0.240 ± 0.015

TABLE 1c. Atmospheric SO<sub>2</sub> Concentrations: Cruise C

Date	Latitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
<i>Reunion</i>			
April 29, 1973	17°7'S	13°5'S	0.120 ± 0.008
April 30, 1973	13°5'S	8°9'S	0.033 ± 0.006
May 1, 1973	8°9'S	5°6'S	0.100 ± 0.010
May 2, 1973	5°6'S	6°7'S	0.058 ± 0.008
May 3, 1973	6°7'S	9°1'S	< 0.020
May 4, 1973	9°1'S	11°0'S	0.035 ± 0.015
May 5, 1973	11°0'S	14°9'S	<< 0.020
May 6, 1973	15°2'S	20°0'S	0.080 ± 0.007
May 7, 1973	20°S	23°4'S	0.095 ± 0.007
May 8, 1973	23°4'S	26°6'S	0.052 ± 0.006
May 9, 1973	27°4'S	28°8'S	0.040 ± 0.007
May 10, 1973	28°8'S	32°9'S	0.148 ± 0.008
May 11, 1973	32°9'S	33°6'S	
May 12, 1973	33°6'S	33°7'S	0.200 ± 0.010
May 13, 1973	33°8'S	38°0'S	0.110 ± 0.007
May 14, 1973	38°0'S	40°0'S	0.174 ± 0.012
May 15, 1973	40°0'S	43°6'S	0.030 ± 0.007
May 16, 1973	43°6'S	45°4'S	0.110 ± 0.010
May 17, 1973	45°4'S	47°0'S	0.034 ± 0.006
May 18, 1973	47°0'S	49°7'S	0.065 ± 0.007
May 19, 1973	49°7'S	49°7'S	0.084 ± 0.008
<i>Kerguelen Island</i>			
May 21, 1973	49°7'S	47°1'S	0.140 ± 0.013
May 22, 1973	46°9'S	46°6'S	0.043 ± 0.006
May 23, 1973	46°6'S	43°7'S	< 0.020
May 24, 1973	43°7'S	42°3'S	0.088 ± 0.009
May 25, 1973	42°3'S	41°1'S	0.081 ± 0.012
May 26, 1973	38°9'S	34°3'S	0.062 ± 0.008
May 27, 1973	34°0'S	31°9'S	< 0.020
May 28, 1973	30°1'S	29°5'S	< 0.020
May 29, 1973	28°9'S	26°4'S	0.025 ± 0.004
<i>La Reunion</i>			
May 30, 1973	26°4'S	20°8'S	0.020 ± 0.007
June 1, 1973	20°8'S	20°5'S	0.197 ± 0.012
June 2, 1973	20°5'S	20°0'S	0.258 ± 0.013
June 3, 1973	20°0'S	17°8'S	0.072 ± 0.008
June 4, 1973	17°7'S	26°S	0.020 ± 0.007

carried far from the continents after its advection in the upper troposphere, it should have the same behavior as radioactive gaseous continental tracers such as <sup>222</sup>Rn. In that hypothesis the residence time of SO<sub>2</sub> would be still shorter than the residence time of <sup>222</sup>Rn (5.5 days). As the typical radon con-

TABLE 1d. Atmospheric SO<sub>2</sub> Concentrations: Cruise D

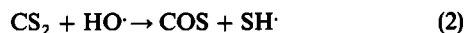
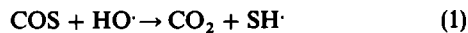
Date	Latitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
April 25, 1974	18°9'N	24°0'N	0.037 ± 0.006
April 28, 1974	24°S	24°0'N	0.036 ± 0.016
April 29, 1974	25°2'N	26°0'N	0.026 ± 0.006
May 1, 1974	26°0'N	27°9'N	0.072 ± 0.008
May 4, 1974	28°0'N	28°3'N	0.519 ± 0.055
May 5, 1974	28°3'N	28°9'N	0.224 ± 0.015
May 6, 1974	28°8'N	28°6'N	0.079 ± 0.007
May 7, 1974	28°6'N	28°6'N	0.086 ± 0.008
May 9, 1974	28°6'N	28°6'N	0.124 ± 0.010
May 10, 1974	28°6'N	28°6'N	0.980 ± 0.065
May 11, 1974	28°6'N	28°0'N	0.068 ± 0.006
May 13, 1974	28°0'N	31°1'N	0.299 ± 0.015
May 14, 1974	31°1'N	34°2'N	0.636 ± 0.050
May 15, 1974	34°2'N	34°6'N	0.087 ± 0.009
May 16, 1974	34°6'N	36°9'N	0.076 ± 0.007

TABLE 1e. Atmospheric SO<sub>2</sub> Concentrations: Cruise E

Date	Latitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
May 22, 1974	37°0'N	35°6'N	0.208 ± 0.014
May 26, 1974	36°8'N	36°0'N	0.260 ± 0.015
May 30, 1974	36°9'N	36°6'N	0.947 ± 0.070
May 31, 1974	37°0'N	36°9'N	0.314 ± 0.016
June 1, 1974	37°0'N	36°9'N	0.157 ± 0.013
June 2, 1974	37°0'N	35°7'N	0.059 ± 0.006
June 3, 1974	35°7'N	34°3'N	0.126 ± 0.011
June 4, 1974	34°3'N	32°9'N	0.157 ± 0.012
June 8, 1974	28°6'N	28°6'N	0.594 ± 0.055
June 9, 1974	28.6'N	23.7'N	0.254 ± 0.014
June 10, 1974	23°7'N	20°2'N	0.528 ± 0.040
June 11, 1974	20°2'N	15°9'N	0.745 ± 0.060

concentrations obtained during these three expeditions in the remote marine areas is generally less than 2 pCi/m<sup>3</sup> (100 to 1000 times less than the continental values), SO<sub>2</sub> from continental origin would not normally contribute to the SO<sub>2</sub> levels measured in the boundary layer of the sub-Antarctic marine atmosphere. For this region, another source is required.

Could the SO<sub>2</sub> be produced above the open ocean by the oxidation of gaseous sulfur compounds with high residence times (several months), such as CS<sub>2</sub> and COS? COS may be produced by the oxidation of CS<sub>2</sub> and may be a precursor of SO<sub>2</sub> via the oxidation with HO radical [Crutzen, 1976; Kurylo, 1978a; Logan et al., 1979; Sze and Ko, 1980; Torres et al., 1980].



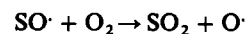
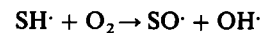
In the atmosphere, SH· radicals probably oxidize into SO<sub>2</sub> by the following principal reactions [Perry et al., 1976; McElroy et al., 1980]:

TABLE 1f. Atmospheric SO<sub>2</sub> Concentrations: Cruise F

Date	Longitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
June 21, 1974	19°1'W	22°3'W	0.104 ± 0.010
June 22, 1974	22°3'W	26°0'W	0.178 ± 0.013
June 23, 1974	26°0'W	30°3'W	0.037 ± 0.009
June 24, 1974	30°3'W	34°2'W	0.070 ± 0.007
June 25, 1974	34°2'W	35°0'W	0.045 ± 0.005
June 26, 1974	35°0'W	35°0'W	0.045 ± 0.005
June 27, 1974	35°0'W	35°0'W	0.030 ± 0.006
June 28, 1974	35°0'W	35°0'W	0.068 ± 0.006
June 29, 1974	35°0'W	35°0'W	0.090 ± 0.008
June 30, 1974	35°0'W	35°0'W	0.050 ± 0.005
July 1, 1974	35°0'W	35°0'W	0.118 ± 0.010
July 2, 1974	35°0'W	35°0'W	0.075 ± 0.007
July 3, 1974	35°0'W	35°0'W	0.137 ± 0.011
July 4, 1974	35°0'W	35°0'W	0.063 ± 0.006
July 5, 1974	35°0'W	35°0'W	0.073 ± 0.007
July 6, 1974	35°0'W	35°0'W	0.030 ± 0.005
July 7, 1974	35°0'W	35°0'W	0.020 ± 0.005
July 8, 1974	35°0'W	35°0'W	0.020 ± 0.005
July 9, 1974	35°0'W	35°0'W	0.032 ± 0.006
July 10, 1974	35°0'W	35°0'W	0.040 ± 0.006
July 11, 1974	35°0'W	35°0'W	0.050 ± 0.006
July 12, 1974	35°0'W	35°0'W	0.040 ± 0.006
July 13, 1974	35°0'W	35°0'W	0.035 ± 0.006
July 14, 1974	35°0'W	32°9'W	0.036 ± 0.007
July 15, 1974	32°9'W	28°5'W	0.020 ± 0.005
July 16, 1974	28°5'W	22°7'W	0.022 ± 0.005

TABLE 1g. Atmospheric SO<sub>2</sub> Concentrations: Cruise G

Date	Latitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
January 16, 1974	24.1°S	28.0°S	0.0 ± 0.005
January 17, 1974	28.0°S	32.0°S	0.032 ± 0.005
January 18, 1974	32.0°S	36.2°S	0.067 ± 0.006
January 19, 1974	36.2°S	Amsterdam	0.142 ± 0.011
January 21, 1974	Amsterdam Island		0.172 ± 0.014
January 22, 1974	Amsterdam	39.2°S	0.074 ± 0.007
January 23, 1974	39.2°S	40.9°S	0.080 ± 0.007
January 24, 1974	40.9°S	43.0°S	0.085 ± 0.007
January 26, 1974	45.1°S	Crozet	0.044 ± 0.006
January 27, 1974	Crozet Island		0.093 ± 0.009
January 28, 1974	Crozet Island		0.095 ± 0.009
January 29, 1974	Crozet	47.3°S	0.484 ± 0.035
January 30, 1974	47.4°S	49.0°S	0.709 ± 0.060
January 31, 1974	49.0°S	Kerguelen	0.687 ± 0.060
February 2, 1974	Kerguelen Island		0.068 ± 0.007
February 3, 1974	Kerguelen	46.9°S	0.203 ± 0.012
February 4, 1974	46.9°S	40.4°S	0.036 ± 0.005
February 6, 1974	37.8°S	35.2°S	0.037 ± 0.006
February 7, 1974	35.2°S	31.0°S	0.245 ± 0.014
November 26, 1974	Marseille	41°9'N	0.077 ± 0.007
November 27, 1974	41°9'N	37°3'N	0.188 ± 0.009
November 28, 1974	37°3'N	34°4'N	0.071 ± 0.007
November 29, 1974	34°4'N	29°N	0.071 ± 0.007
November 30, 1974	29°6'N	24°4'N	0.068 ± 0.007
December 1, 1974	24°4'N	18°2'N	0.102 ± 0.009
December 2, 1974	18°2'N	12°7'N	0.066 ± 0.006
December 3, 1974	12°7'N	7°5'N	0.094 ± 0.009
December 4, 1974	7°5'N	2°9'N	0.086 ± 0.008
December 5, 1974	2°9'N	1°7'S	0.045 ± 0.006
December 6, 1974	1°7'S	6°6'S	0.041 ± 0.008
December 7, 1974	6°6'S	11°4'S	0.055 ± 0.006
December 8, 1974	11°4'S	16°3'S	0.049 ± 0.006
December 9, 1974	16°3'S	21°2'S	0.038 ± 0.006
December 10, 1974	21°2'S	25°6'S	0.043 ± 0.006
December 11, 1974	25°6'S	29°5'S	0.149 ± 0.011
December 12, 1974	29°1'S	33°5'S	0.047 ± 0.008
December 15, 1974	36°8'S	42°3'S	0.017 ± 0.005
December 15, 1974	39°1'S	43°7'S	0.048 ± 0.008
December 17, 1974	45°6'S	46°9'S	0.170 ± 0.012
December 19, 1974	45°7'S	48°2'S	0.149 ± 0.011
December 19, 1974	46°0'S	49°0'S	0.159 ± 0.011
January 5, 1975	46°5'S	42°3'S	0.013 ± 0.004
January 6, 1974	42°3'S	38°0'S	0.014 ± 0.004
January 7, 1974	38°S	32°2'S	0.169 ± 0.012
January 8, 1975	32°2'S	26°3'S	0.019 ± 0.005
January 9, 1975	26°3'S	La Reunion	0.040 ± 0.006
January 15, 1975	La Reunion	24°1'S	0.042 ± 0.006



A great discrepancy still exists regarding the kinetic constant  $k_1$  of (1); the advanced values range between  $5.7 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [Kurylo, 1978a] and  $8.8 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [Ravishankara et al., 1980].

A larger uncertainty exists for the kinetic constant of (2);  $k_2$  varies between  $4.3 \times 10^{-12}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $1.5 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> [Kurylo, 1978a; Wine et al., 1980].

In any case the oxidation rate in (2) is faster than the oxidation rate in (1), the rate production of SO<sub>2</sub> from these sulfur compounds essentially depends on (1). Chameides and Tan [1981] have calculated concentrations increasing from  $0.5 \times 10^5$  radicals cm<sup>-3</sup> in high latitudes to  $2.5 \times 10^6$  radicals cm<sup>-3</sup> in equatorial and tropical areas. Moreover, Logan et al. [1979] have computed OH profiles where the maximum concentrations for the low troposphere was  $3 \times 10^6$  radicals

TABLE 1h. Atmospheric SO<sub>2</sub> Concentrations: Cruise H

Date	Latitude		SO <sub>2</sub> , μg/m <sup>3</sup>
	Start	End	
February 22, 1977	21.6°S	23.2°S	0.129 ± 0.011
February 23, 1977	24.0°S	25.0°S	0.054 ± 0.005
February 23, 1977	25.0°S	26.9°S	0.043 ± 0.004
February 24, 1977	27.5°S	30.4°S	0.041 ± 0.004
February 25, 1977	30.4°S	34.2°S	0.010 ± 0.003
February 26, 1977	34.4°S	35.5°S	0.127 ± 0.010
February 26, 1977	35.5°S	Amsterdam	0.015 ± 0.004
February 28, 1977	Amsterdam	39.8°S	0.058 ± 0.005
March 1, 1974	39.8°S	41.3°S	0.176 ± 0.012
March 2, 1974	41.3°S	43.0°S	0.243 ± 0.015
March 3, 1974	43.0°S	Kerguelen	0.027 ± 0.005
March 5, 1974	49.0°S	47.5°S	0.093 ± 0.009
March 6, 1974	47.5°S	46.7°S	0.119 ± 0.010
March 6, 1974	46.7°S	46.0°S	0.226 ± 0.015
March 7, 1974	46.0°S	46.0°S	0.023 ± 0.004
March 7, 1974	46.0°S	46.7°S	0.031 ± 0.005
March 8, 1974	46.7°S	48.3°S	0.022 ± 0.005
March 8, 1974	48.3°S	49.1°S	0.020 ± 0.004
March 9, 1974	49.1°S	49.8°S	0.010 ± 0.003
March 9, 1974	49.8°S	50.4°S	0.013 ± 0.003
March 10, 1974	51.3°S	52.0°S	0.033 ± 0.005
March 10, 1974	52.0°S	52.8°S	< 0.010
March 11, 1974	52.8°S	52.8°S	0.035 ± 0.005
March 11, 1974	52.8°S	53.6°S	0.017 ± 0.004
March 12, 1974	53.6°S	54.4°S	0.166 ± 0.012
March 12, 1974	54.4°S	56.3°S	0.044 ± 0.004
March 13, 1974	56.3°S	57.4°S	0.074 ± 0.007
March 14, 1974	57.4°S	58.4°S	0.093 ± 0.009
March 14, 1974	58.4°S	59.4°S	0.056 ± 0.005
March 15, 1974	59.4°S	60.4°S	0.099 ± 0.009
March 15, 1974	60.4°S	60.4°S	0.112 ± 0.010
March 16, 1974	60.4°S	61.2°S	0.022 ± 0.004
March 16, 1974	61.2°S	62.2°S	0.030 ± 0.005
March 17, 1974	62.2°S	62.2°S	0.095 ± 0.008
March 17, 1974	62.2°S	62.2°S	0.032 ± 0.005
March 18, 1974	62.2°S	59.2°S	0.011 ± 0.003
March 19, 1974	59.2°S	57.5°S	0.101 ± 0.010
March 19, 1974	57.5°S	55.3°S	0.040 ± 0.004
March 20, 1974	55.3°S	55.3°S	0.010 ± 0.003
March 20, 1974	55.3°S	55.4°S	0.157 ± 0.012
March 21, 1974	55.4°S	54.8°S	0.014 ± 0.003
March 21, 1974	54.8°S	52.6°S	< 0.010
March 22, 1974	52.6°S	50.3°S	0.18 ± 0.004
March 22, 1974	50.3°S	47.8°S	0.347 ± 0.016
March 24, 1974	47.8°S	42.9°S	< 0.010
March 24, 1974	42.9°S	42.9°S	< 0.010
March 25, 1974	42.9°S	42.8°S	0.012 ± 0.003
March 25, 1974	42.8°S	43.9°S	< 0.010
March 26, 1974	43.9°S	45.15°S	0.116 ± 0.011
March 26, 1974	45.1°S	45.2°S	0.054 ± 0.005
March 27, 1977	45.2°S	45.2°S	0.119 ± 0.011
March 27, 1977	45.2°S	46.0°S	0.052 ± 0.005
March 31, 1977	46.0°S	45.4°S	0.020 ± 0.004
March 31, 1977	45.4°S	45.4°S	0.0 ± 0.004
April 1, 1977	45.4°S	43.5°S	0.279 ± 0.015
April 2, 1977	43.5°S	39.5°S	0.010 ± 0.003
April 3, 1977	39.5°S	34.5°S	0.010 ± 0.003

cm<sup>-3</sup>. By using this last value, which leads to maximum SO<sub>2</sub> production, the residence time of COS should comprise between 67 days and 1.2 years and the residence time of CS<sub>2</sub> between 8 days and 7 years. Even taking into account the faster reaction rate for k<sub>1</sub>, which corresponds to the 67-day residence time for COS; a COS mixing ratio of 500 pptv [Torres et al., 1980]; and a 0.7-day residence time for SO<sub>2</sub>, and by considering a steady state, we could only explain a 5 pptv of SO<sub>2</sub> (15 × 10<sup>-9</sup> g m<sup>3</sup>) produced by the oxidation of COS. Rodhe and Isaksen [1980] also found that the contri-

bution of COS to the concentration of SO<sub>2</sub> in the low troposphere is less than 5 pptv of SO<sub>2</sub>.

This value is much lower than the 65 pptv theoretical value coming from both COS and CS<sub>2</sub> oxidation [Logan et al., 1979]. But this calculation refers to a concentration at a 6-km altitude where the residence time of SO<sub>2</sub> is probably larger than in the boundary layer.

An experimental determination of SO<sub>2</sub> concentration has been performed in a particular region where no sources other than long-lived gaseous precursors may interfere.

In collaboration with the "Laboratoire de Glaciologie de Grenoble (France)," SO<sub>2</sub> has been sampled at dome C in the Antarctic continent (74°40'S, 128°50'E; elevation, 3200 m; distance from the coast, 1070 km). The samples have been collected with the same device used by Nguyen et al. [1974a] in marine regions, except that it was enclosed in a temperature-controlled box at +20°C.

The SO<sub>2</sub> concentrations of the 30 samples collected were all less than our detection limit of 0.02 μg/m<sup>3</sup>.

From these data in the Antarctic area we can propose the two following alternatives: either both of the low-temperature conditions and low HO· radical concentrations lessen the SO<sub>2</sub> production efficiency, or this process alone cannot account for more than 0.02 μg/m<sup>3</sup>, which corresponds to 20% of the background SO<sub>2</sub> we measured above the ocean.

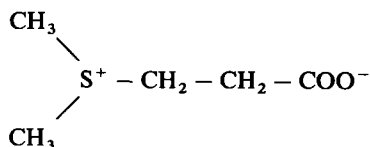
Could the SO<sub>2</sub> be produced over the open ocean from oxidation of H<sub>2</sub>S? The occurrence of atmospheric H<sub>2</sub>S over the open ocean could come from the transfer of this compound from sediment, where its production is important, to the sea surface. This hypothesis is unlikely because the half-life of H<sub>2</sub>S in seawater is on the order of several minutes [Ostlund and Alexander, 1963].

H<sub>2</sub>S could also be carried from coastal areas or be locally produced either from a biogenic process at the sea surface or by the recombination of radicals issued from the oxidation of COS and CS<sub>2</sub> [McElroy, 1980].

For instance, H<sub>2</sub>S has been observed in the air by Delmas and Servant [1982], who found 13 pptv, at a 500-km distance from the coast, in the Guinea Gulf. Moreover, Slatt et al. [1978] measured concentrations ranging between 5 and 50 pptv at the coast of Florida, at Barbados, and at Sal Islands. However, these islands may not be considered as representative of open-ocean conditions, since a possible local H<sub>2</sub>S production may occur along the littoral by the organic matter degradation. Furthermore, an atmospheric residence time for H<sub>2</sub>S, ranging between 6 and 24 hours, has been determined by Cox [1975]. Unfortunately, no data is available in remote sub-Antarctic open ocean, but if concentrations comparable to those found by Delmas et al. [1980] occur in such remote areas, H<sub>2</sub>S may be considered as a possible precursor of SO<sub>2</sub>.

Could the SO<sub>2</sub> be produced above the ocean by the oxidation of reactive sulfur compounds other than H<sub>2</sub>S? Other sulfur compounds already have been observed as well in seawater as in the marine atmosphere and could also be possible precursors of this SO<sub>2</sub> residual concentration. Considering this hypothesis by using known results and new data, we obtained

1. The marine organic sulfides: (a) In seawater. Armstrong and Boalch [1960] have noted the occurrence of organic sulfides in seawater which, although unidentified, could include dimethylsulfide. According to Schiff [1962], the production of dimethylsulfide by various marine algae (*Polysiphonia lanosa*) may be due to an enzymatic action such as degradation of dimethyl propiothetin:

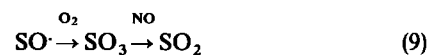
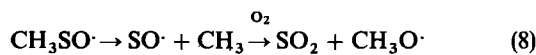
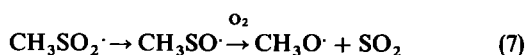
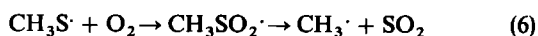
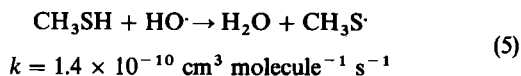
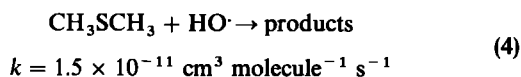
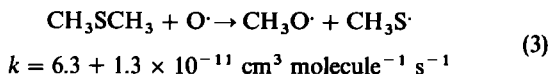


Furthermore, the degradation of methionine leads to methanethiol. *Rasmussen* [1974] has observed organic sulfides such as dimethylsulfide, diethyl disulfide, and methanethiol emitted by laboratory cultures of various marine algae. *Andreae* [1980] has presented a scheme for the marine cycle of sulfur compounds of biological origin which relates DMS and dimethylsulfoxide (DMSO) production to phytoplankton activity. *Lovelock et al.* [1972] have observed a mean concentration of DMS in the surface water of the Atlantic Ocean of about  $12 \times 10^{-9}$  g/l. *Nguyen et al.* [1978a, b] have reported DMS concentrations from 11 to  $580 \times 10^{-9}$  g/l in surface waters of the Atlantic and Indian oceans and the Mediterranean Sea. More recent data obtained in the surface water of the Pacific Ocean during an oceanographic cruise from Panama to Hobart (Tasmania) show higher DMS concentrations reaching  $1150 \times 10^{-9}$  g/l (B. C. Nguyen et al., unpublished manuscript, 1983). Likewise, *Barnard et al.* [1982] have observed DMS concentrations in the surface seawater of the Atlantic Ocean that range from 34 to  $1440 \times 10^{-9}$  g/l with a mean value of  $176 \times 10^{-9}$  g/l.

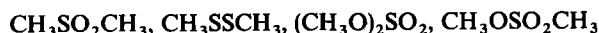
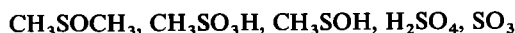
Depth distributions of DMS often show maxima within the upper 50 meters in the euphotic zone [*Barnard et al.*, 1982] associated with boundary water masses of different densities [*Nguyen et al.*, 1978a]. Also, it seems that DMS does not only originate from phytoplankton activity because high concentrations may be observed at depths as great as 2000 m (B. C. Nguyen et al., unpublished manuscript, 1983).

(b) In marine atmosphere. The dimethylsulfide produced in seawater may be released to the atmosphere from the sea surface because of its low solubility. *Maroulis and Bandy* [1977] have determined DMS concentrations of 0 to 62 pptv ( $0$  to  $170 \times 10^{-9}$  g/m<sup>3</sup>) by cryogenic sampling in a littoral zone. *Barnard et al.* [1982] found 4 to  $88 \times 10^{-9}$  g m<sup>-3</sup> of DMS above the Atlantic Ocean. More recently we found, above the Pacific Ocean, DMS concentrations ranging from 0.2 to  $400 \times 10^{-9}$  g m<sup>-3</sup>, from Panama to Hobart (B. C. Nguyen et al., unpublished manuscript, 1983).

2. SO<sub>2</sub> formation above the ocean: (a) Mechanisms. Organic sulfides released from the ocean surface are rapidly oxidized in the marine atmosphere. *Bentley et al.* [1972], *Cox* [1975], *Slagle et al.* [1976], *Kurylo* [1978b], and *Grosjean and Lewis* [1982] proposed several likely oxidation mechanisms by O<sup>•</sup> and OH<sup>•</sup> photochemically produced in the atmosphere. The following reactions summarize how SO<sub>2</sub> may be produced from DMS and methylmercaptan:



Furthermore, other pathways lead to different gaseous or particulate sulfur compounds qualitatively identified by *Bentley et al.* [1972], *Hatakeyama et al.* [1982], and *Grosjean and Lewis* [1982], such as:



From *Hatakeyama et al.* [1982], only 21% of the DMS is oxidized into SO<sub>2</sub>, whereas greater yields are obtained by *Bentley et al.* [1972], who found 31%, and by *Grosjean and Lewis* [1982], who found 35 to 73%. Thus, SO<sub>2</sub> is always a product of the photooxidation of DMS but with a yield closely depending on the laboratory conditions, particularly in the initial contents in DMS (several orders of magnitude greater than the natural atmospheric contents).

(b) DMS and SO<sub>2</sub> concentrations over a high-productivity area; evidence of an "in situ" photooxidation of DMS. Two different experiments were performed in a coastal site of Guissey (Brittany, France), which is rich in algae (*Poly-siphonia lanosa* and *laminaria*), known to produce important amounts of DMS (Figure 2).

During the first experiment, previously described by *Bonsang et al.* [1976a], SO<sub>2</sub> was sampled at site B, 200 meters inland in the direction of the dominant wind flowing above the algae beds (Figure 2).

We observed a diurnal effect in the SO<sub>2</sub> production; the atmospheric SO<sub>2</sub> concentration during the day reached values as high as 6 μg/m<sup>3</sup>, while concentrations at night varied between 0.2 and 1.8 μg/m<sup>3</sup> [*Bonsang et al.*, 1976a], (Figure 3). Diurnal maxima were observed at the low-tide hours and increased with the tidal coefficient.

Furthermore, the SO<sub>2</sub> concentrations were sharply correlated with the Aitken nuclei production, which reached values close to 10<sup>6</sup>/cm<sup>3</sup> at low-tide hours [*Paugam et al.*, 1977].

The atmospheric SO<sub>2</sub> concentration seems to increase with both the uncovered algae areas and the sunlight intensity, these experiments in coastal areas near important sources of dimethylsulfide argue persuasively that the SO<sub>2</sub> production is photochemically mediated.

In a second experiment, in February 1978, we simultaneously measured DMS on site B previously described and on site A at about 30 cm above the algae beds shown in Figure 2. The atmospheric concentration of DMS at sites A and B in February 1978 were  $80 \times 10^{-9}$  g/m<sup>3</sup> and  $2.7 \times 10^{-9}$  g/m<sup>3</sup>, respectively. Such a decrease in DMS concentration between sites A and B (factor of 30) confirms a local DMS production.

It may be suggested that the diurnal SO<sub>2</sub> effect previously observed is very likely caused by this biogenic local production of DMS or of other sulfide compounds not yet investigated. However, to explain SO<sub>2</sub> concentrations as high as 6 μg/m<sup>3</sup>, we have to admit very fast oxidation rates for these particular conditions, since the transport time between the source of sulfide compounds (site A) and the SO<sub>2</sub> measurement (site B) do not exceed 2 min (wind speed < 5 m s<sup>-1</sup>).

The occurrence of high concentrations of DMS in open oceanic areas, as well as these last experiments in a coastal site, suggest that DMS could be the predominant precursor for marine SO<sub>2</sub>. This hypothesis is apparently only consistent

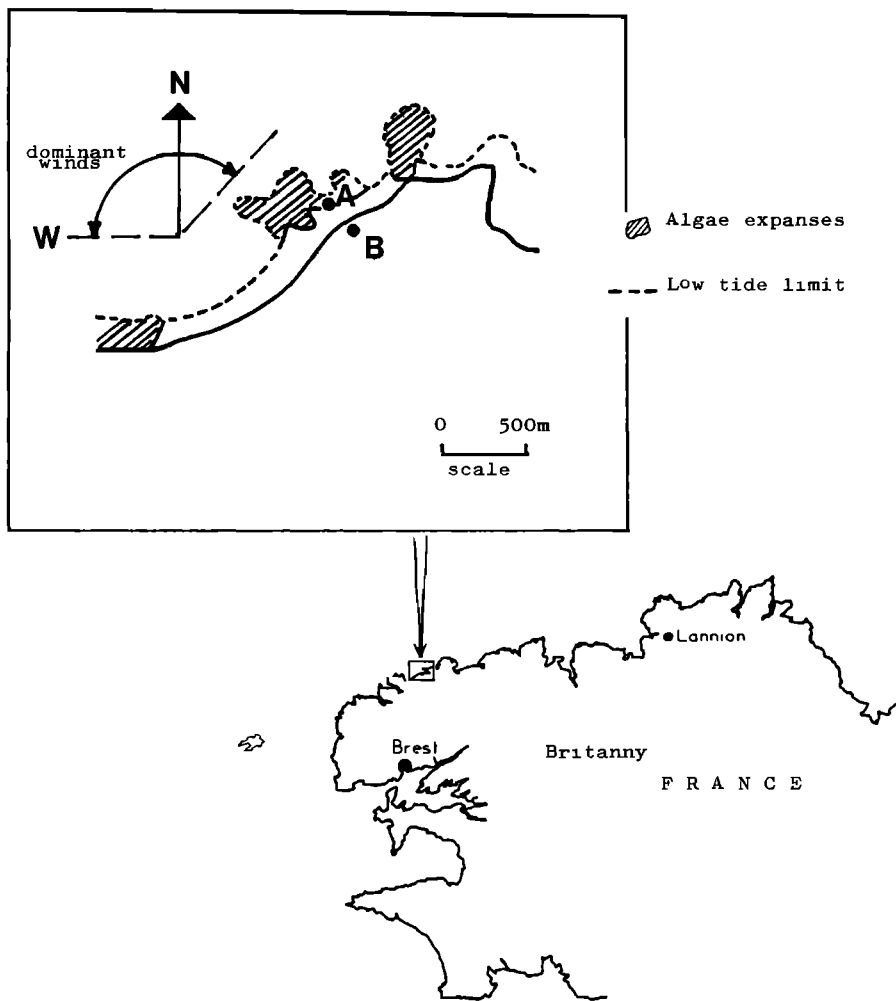


Fig. 2. Site of Guisseny (Brittany, France).

with a rate of oxidation of DMS that is higher than current laboratory measurements suggest. However, other organic sulfur compounds, more reactive than DMS, cannot be discarded as potential precursors of  $\text{SO}_2$ . Field data as presented could now corroborate both these hypotheses.

#### THE INFLUENCE OF THE BIOLOGICAL ACTIVITY ON THE PRODUCTION OF SULFUR DIOXIDE IN THE MARINE ATMOSPHERE

1. *Atmospheric concentration of  $\text{SO}_2$  in upwelling and convergence areas.* It is well known that upwelling areas have high levels of biological activity. Two cruises, A and G (Figure

1a), were made in the Gulf of Guinea upwelling area.  $\text{SO}_2$  concentrations observed in March 1973 and December 1976 between Dakar and Capetown were always higher than the mean  $0.1 \mu\text{g SO}_2/\text{m}^3$  ocean value and ranged from 0.2 to  $0.45 \mu\text{g}/\text{m}^3$  inside the upwelling area; lower values, from 0.04 to  $0.10 \mu\text{g}/\text{m}^3$ , were found outside the main upwelling area.

A third cruise in the Peruvian upwelling (Figure 1a) confirmed these results:  $\text{SO}_2$  concentrations ranged from 0.2 to  $0.7 \mu\text{g}/\text{m}^3$  in the upwelling area and from 0.1 to  $0.15 \mu\text{g}/\text{m}^3$  outside [Bonsang *et al.*, 1976b; Bonsang, 1980]. In addition, the influence of biological activity on atmospheric  $\text{SO}_2$  con-

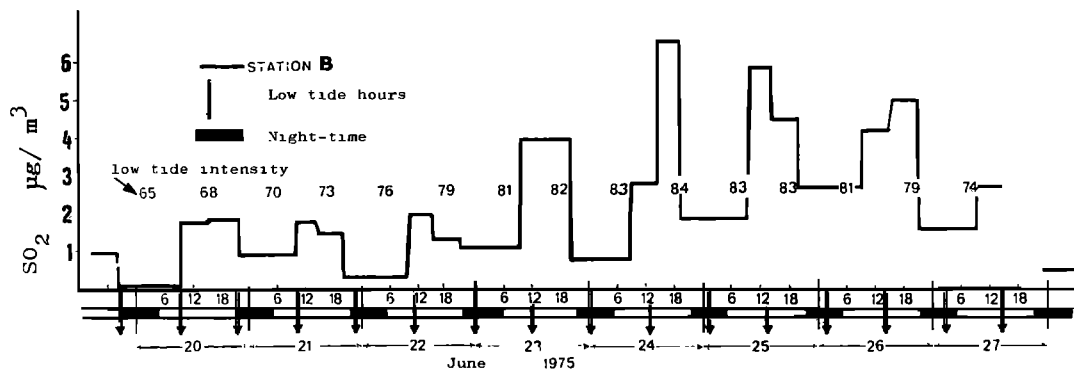


Fig. 3. Atmospheric  $\text{SO}_2$  concentrations at Guisseny (site B), June 1975.



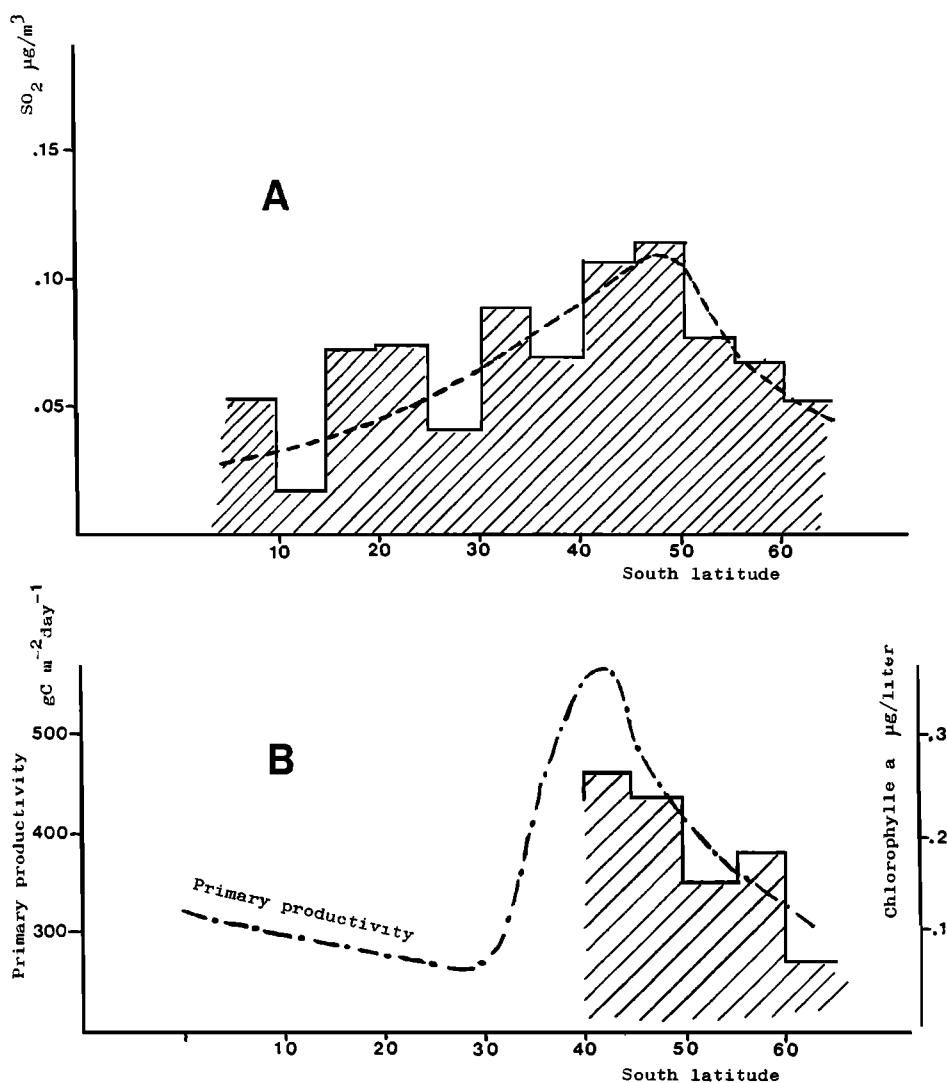


Fig. 4. (a) Atmospheric  $\text{SO}_2$  concentration ( $\mu\text{g}/\text{m}^3$ ) versus latitude in the southern part of the Indian Ocean between  $55^\circ\text{E}$  and  $75^\circ\text{E}$ . (b) Simultaneous record of chlorophyll "a" (solid line). Also shown is primary productivity observed above the  $70^\circ\text{E}$  meridian at the same time of year (late summer), from Krey [1973] (dashed line).

concentrations has been studied in convergence areas, where primary productivity is higher than in tropical regions. This influence is illustrated in Figure 4, which shows the mean atmospheric  $\text{SO}_2$  concentration in each  $5^\circ$  of latitude between  $5^\circ\text{S}$  and  $62^\circ\text{S}$ . This figure was obtained from 138 measurements in the Indian Ocean performed during cruises of the R/V *Marion Dufresne* from 1973 to 1977. We can observe that the  $\text{SO}_2$  concentration reaches a maximum of  $0.12 \mu\text{g}/\text{m}^3$  near the Antarctic convergence zone ( $45\text{--}50^\circ\text{S}$ ) and decreases to  $0.05 \mu\text{g}/\text{m}^3$  both southward and northward.

This latitudinal dependence of atmospheric  $\text{SO}_2$  concentrations is thus very well related to the general variation of primary productivity. Particularly between  $40^\circ\text{S}$  and  $60^\circ\text{S}$ , we can observe the same trend of variation between atmospheric  $\text{SO}_2$  concentrations and the chlorophyll "a" concentrations simultaneously measured in sea surface water. (Collaboration with the Laboratoire Arago at Banyuls-sur-Mer, G. Jacques and G. Neveu). The large variation of  $\text{SO}_2$  measurements is also quite reasonable, since the concentrations should be greatly influenced by chemical factors producing and destroying  $\text{SO}_2$  and, perhaps, meteorological factors diluting the substance.

## 2. Atmospheric $\text{SO}_2$ concentrations versus primary productiv-

ity in several oceanic areas. From 162  $\text{SO}_2$  measurements we can represent the atmospheric  $\text{SO}_2$  concentration above different oceanic areas versus primary productivity in the sea surface water (Figure 5). We observe that the weak productivity areas, such as the tropical Indian Ocean (primary production less than  $36 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) correspond to a low  $\text{SO}_2$  concentration of  $0.03 \mu\text{g}/\text{m}^3$ ; areas with an intermediate primary productivity between 36 and  $90 \text{ g cm}^{-2} \text{ yr}^{-1}$  have an atmospheric  $\text{SO}_2$  concentration of about  $0.1 \mu\text{g}/\text{m}^3$ ; regions of highest production (convergence and upwelling areas greater than  $90 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) correspond to  $0.2\text{--}0.3 \mu\text{g SO}_2/\text{m}^3$ .

## FLUX OF SULFUR COMPOUNDS FROM THE OCEAN TO THE ATMOSPHERE

At high altitude the  $\text{SO}_2$  concentrations observed in the marine atmosphere can be considered as resulting from a steady state balance between the oxidation of reduced sulfur compounds and the oxidation of  $\text{SO}_2$  to sulfate by gas-to-particle conversion. The flux of sulfur compounds from the ocean to the atmosphere can be calculated from the atmospheric  $\text{SO}_2$  profile and its residence time above the ocean. Numerous  $\text{SO}_2$  profiles have been established above the polluted mid-latitude European continents and show an ex-

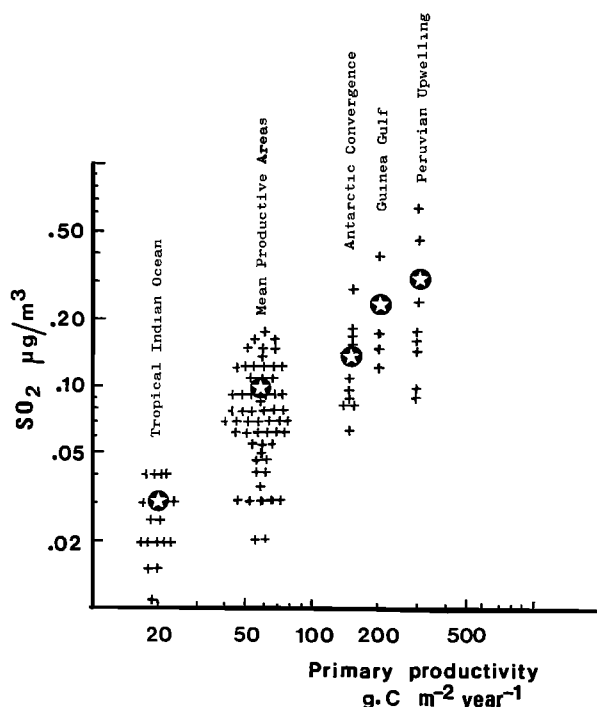


Fig. 5. SO<sub>2</sub> concentration variations with respect to primary productivity in several oceanic regions.

ponential decrease versus the altitude [Rodhe 1972; Jost, 1974; Jaeschke et al., 1976; Varhelyi, 1978], whereas SO<sub>2</sub> profiles above the oceans are very sparse.

However, such a profile has been established by Georgii and Meixner [1980] above the Atlantic, close to the west of France. This profile shows a practically constant mixing ratio of SO<sub>2</sub> (100 pptv or 0.27 μg SO<sub>2</sub>/STD m<sup>3</sup>) from 1000 to 6500 m. Such values were later confirmed by Maroulis and Bandy [1980], who indicated in the free troposphere a mean concentration level of 122 pptv in the northern hemisphere and 90 pptv in the southern hemisphere.

In the lower marine atmosphere, scavenging processes of SO<sub>2</sub> are much more efficient than in the free troposphere because the ocean surface acts as a sink for this gas [Beilke

and Lamb, 1974]. Consequently, the SO<sub>2</sub> concentration may decrease toward the ocean atmosphere interface. Both the average SO<sub>2</sub> concentration of 35 pptv, measured at the sea level by Nguyen et al. [1974a, b], and the slightly higher mean concentration of 57 pptv in the boundary layer, reported by Maroulis et al. [1980], tend to confirm that effect.

Hence, we can consider two different cases:

1. For an oceanic source of SO<sub>2</sub>, caused by the oxidation of reduced sulfur compounds outgassed from the sea surface, the atmospheric concentration of SO<sub>2</sub> would increase up to altitude *h*<sub>1</sub> and then decrease exponentially (Figure 6, curve A), according to the profile proposed by Logan et al. [1979]. Indeed, our previous study [Nguyen, 1968; Nguyen and Lambert, 1970] concerning the exchanges between the stratosphere and the troposphere suggests that similar mixing conditions occur for gases and particles beyond the boundary layer of both oceanic and continental areas; therefore, SO<sub>2</sub> concentrations should decrease exponentially over the oceans as well as over continents.

2. For meteorological situations typical of the tropics and, possibly, portions of the midlatitudes, SO<sub>2</sub> could be produced at low altitude and transported, as well as its precursors, throughout the troposphere [Chatfield and Crutzen, 1981]. Their vertical profiles depend on the presence of cumulonimbus clouds scattered through a region occupying about 20% of a larger synoptic region, more or less as is observed. Hence the vertical mixing ratio of SO<sub>2</sub> can increase up to 1000 or 2000 meters of altitude and stay almost constant up to 10,000 meters (curve B).

Since the experimental values are located between these two extreme cases, we will consider them in developing an estimate of the SO<sub>2</sub> budget.

*Case 1:* Increase of SO<sub>2</sub> concentration from 0.1 μg/m<sup>3</sup> STD at sea level to 0.16 μg/m<sup>3</sup> STD at altitude *h*<sub>1</sub> (close to 1500 m), then exponential decrease.

*Case 2:* Same variations versus altitude in the low troposphere up to altitude *h*<sub>1</sub>, then the mixing ratio remains constant from altitude *h*<sub>1</sub> to 10 km.

Hence from sea level to altitude *h*<sub>1</sub> the SO<sub>2</sub> mixing ratio follows the general law:

$$(SO_2)_h = (SO_2)_0 e^{\beta h}$$

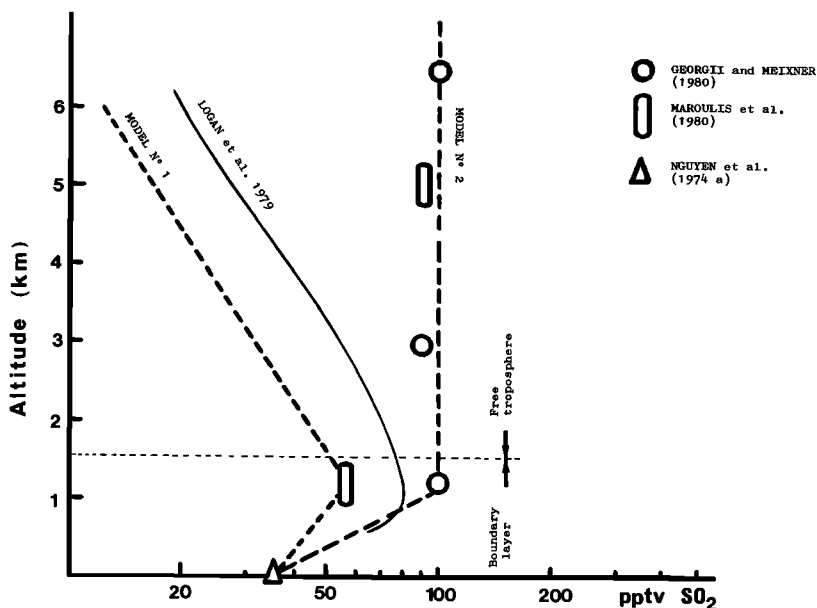


Fig. 6. Profiles of SO<sub>2</sub> concentration above the ocean.

Beyond altitude  $h_1$ , the  $\text{SO}_2$  mixing ratio varies according to

$$(\text{SO}_2)_h = (\text{SO}_2)_{h_1} e^{-\alpha(h-h_1)}$$

( $\alpha = 0$  in model 2).

The total quantity  $Q$  of  $\text{SO}_2$  in an air column of unit area above the ocean is then equal to

$$Q = Q_1 + Q_2$$

with

$$Q_1 = \int_0^{h_1} C_0 e^{\beta h} \frac{\rho(h)}{\rho_0} S dh$$

$$Q_2 = \int_{h_1}^{h_2} C_{h_1} e^{-\alpha(h-h_1)} \frac{\rho(h)}{\rho_0} S dh$$

where  $\rho(h)$  is the air density at altitude  $h$ , i.e.,  $\rho(h) = \rho_0 e^{-h/H}$ , where  $\rho_0$  is the air density at level 0, and where  $H$ , the scale height constant is 7936 m.  $S$  is the total surface of the oceans,  $360 \times 10^{12} \text{ m}^2$ ;  $C_0 = 0.1 \text{ } \mu\text{g}/\text{m}^3$  (this study);  $\beta$  is calculated as  $\beta = 1/h_1 \text{ Ln}(C_{h_1}/C_0)$ ;  $C_{h_1} = 0.16 \text{ } \mu\text{g}/\text{m}^3$  [Maroulis et al., 1978], (model 1);  $C_{h_2} = 0.27 \text{ } \mu\text{g}/\text{m}^3$  [Georgii and Meixner, 1980], (model 2); and  $h_1$  is taken as 1500 m.

An average  $\alpha = 3.95 \times 10^{-4}/\text{m}$  is calculated from nine profiles of  $\text{SO}_2$  concentration observed by Georgii [1970, 1978], Rodhe [1972], and Jost [1974] by the relation

$$\alpha = \frac{1}{h} \text{Ln} \frac{C_h}{C_{\text{ground}}}$$

The flux of gaseous sulfur compounds from the ocean to the atmosphere is then

$$F = \frac{Q_1}{\tau_1} + \frac{Q_2}{\tau_2}$$

where  $\tau_1$  and  $\tau_2$  are the respective residence times of  $\text{SO}_2$  in the boundary layer and the free troposphere.  $Q_1$  and  $Q_2$  are equal to 3.1 and  $4.6 \times 10^{10} \text{ g S}$  in model 1 and 4.1 and  $21.0 \times 10^{10} \text{ g S}$  in model 2, respectively.

The flux of  $\text{SO}_2$  ( $Q/\tau$ ) produced from the ocean surface depends on the residence time  $\tau$  of this gas in a given reservoir. In the low atmosphere we have determined a value  $\tau_1$  close to 0.7 day [Nguyen et al., 1975], resulting from both sulfate oxidation and direct absorption by seawater. In the upper troposphere, above the boundary layer, only the oxidation of  $\text{SO}_2$  into sulfate is the dominant process. Unfortunately, no experimental data for  $\text{SO}_2$  residence time is available in the free troposphere.

The data of Prahm et al. [1976] and Smith and Jeffrey [1975] indicate an oxidation rate of  $\text{SO}_2$  comprising between  $1.1 \times 10^{-2} \text{ h}^{-1}$  and  $2.1 \times 10^{-2} \text{ h}^{-1}$ . Our previous works suggest an oxidation rate close to  $4 \times 10^{-2} \text{ h}^{-1}$  deduced from  $\text{SO}_4/\text{SO}_2$  ratio in the marine atmosphere [Bonsang et al., 1980]. Hence we can admit an average value of the order of  $2.3 \times 10^{-2} \text{ h}^{-1}$  for the oxidation rate of  $\text{SO}_2$  into sulfate, which leads to a residence time close to 1.5 days in the free troposphere.

This last value seems reasonable for the free troposphere between 2- and 6-km altitudes, and it has been also used by Rodhe and Isaksen [1980]. This can be argued by the fact that heterogeneous oxidation processes occur in the cloudy layer as well as at the marine boundary.

Thus models 1 and 2 lead to fluxes of 27 and  $72 \times 10^6$  tons of sulfur per year, respectively, outgassed from the ocean to the

atmosphere. The only experimental profile in marine atmosphere is better described by model 2. If such a profile was confirmed, the flux of biogenic marine sulfur would be close to the highest value of our estimate.

## CONCLUSIONS

Many questions still remain about the sulfur cycle in marine areas, which cover three quarters of the earth's surface. In particular, sulfur compound altitude profiles above remote oceanic areas could add a lot to the knowledge about the sulfur cycle. In spite of these problems we believe that it is possible to draw from this study the following conclusions:

1. A background concentration of  $0.1 \text{ } \mu\text{g}/\text{m}^3$  (35 pptv) of  $\text{SO}_2$  has been confirmed above different oceanic areas far from any continental influences.

2. Several possible origins for  $\text{SO}_2$  have been advanced. Instead, we have shown here that this background comes principally from oceanic biological activity, which produces volatile sulfur compounds, mainly  $\text{CH}_3\text{SCH}_3$  and probably also  $\text{CH}_3\text{SH}$  and  $\text{CH}_3\text{SSCH}_3$ , outgassed at the ocean surface. In turn these are partly oxidized in the atmosphere to  $\text{SO}_2$  and sulfate by various photochemically mediated mechanisms, as outlined in Figure 7.

Among these organic sulfides, dimethylsulfide (DMS) has been made conspicuous in the ocean water at all depths (10 to several hundreds of  $10^{-9} \text{ g/l}$ ) as well as in the atmosphere above the water ( $0.2$  to  $400 \times 10^{-9} \text{ g}/\text{m}^3$ ). Other sulfur compounds, such as COS and  $\text{CS}_2$ , occurring in the marine atmosphere could not explain more than 20% of the measured  $\text{SO}_2$ . Concerning  $\text{H}_2\text{S}$ , no data exist in the very remote subantarctic areas, and it cannot be excluded that this compound remains a possible precursor of this marine  $\text{SO}_2$ .

3. The emission of sulfur compounds produced by biological mechanisms has been estimated from 27 to  $72 \times 10^6$  tons of sulfur per year. This estimate, based on the vertical profile of atmospheric  $\text{SO}_2$ , may be considered as an approximation because of the lack of data in marine atmospheres. More data is needed to support our results.

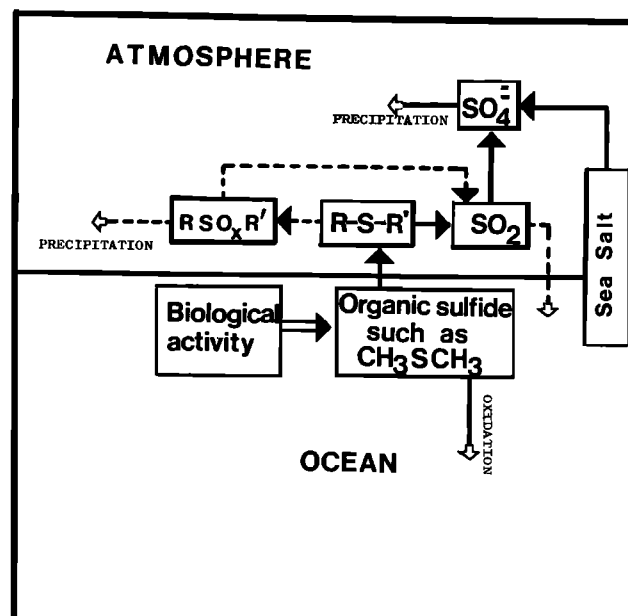


Fig. 7. Scheme for sulfur compound exchange between the ocean and the atmosphere leading to sulfate production by gas-to-particle conversion. Units are  $10^6$  tons of sulfur/year.

According to Woodwell *et al.* [1978], the primary production for the whole ocean is  $25 \times 10^{15}$  g of carbon per year, which corresponds to a mean productivity of  $70 \text{ g cm}^{-2} \text{ yr}^{-1}$ . By referring to Figure 5, this value does correspond to the mean  $\text{SO}_2$  concentration of 35 pptv, which we found and which appears reasonable in our flux calculations.

This flux is of the same order as the sea spray production of  $44 \times 10^6$  tons of sulfur per year [Eriksson, 1960] and anthropogenic inputs ( $50\text{--}80 \times 10^6 \text{ T S/yr}$ ); [Robinson and Robbins, 1970; Kellogg *et al.*, 1972; Friend, 1973; Granat *et al.*, 1976; Rodhe and Isaksen, 1980], but is much greater than the flux from volcanos ( $2\text{--}3 \times 10^6 \text{ T S/yr}$ ) [Stoiber and Jepsen, 1973; Granat *et al.*, 1976]. Therefore, the contribution of the ocean could be estimated within  $71$  and  $116 \times 10^6 \text{ T S/yr}$ .

4. Concerning the oceanic emission of sulfur compounds, the sea spray production leads to the formation of aerosols of relatively great size which quickly fall back into the sea or on the continent near the coast. Besides, biological sources lead to the formation of submicronic aerosols by gas-to-particle conversion [Bonsang *et al.*, 1980].

The simultaneous increase of  $\text{SO}_2$  and Aitken nuclei concentrations, which we observed at low tide above an algae bed contribute to reinforce that hypothesis.

These particles could have long enough residence times in the atmosphere to feed the high troposphere and, perhaps, the stratospheric reservoir. Moreover, because of their hygroscopicity, sulfate aerosols produced by this process could play an important role as condensation nuclei in the formation of clouds. Biological activity could thus have an indirect influence on climate.

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#### REFERENCES

- Andreae, M. O., Dimethylsulfoxide in marine and freshwater, *Limnol. Oceanogr.*, **25**, 1054–1063, 1980.
- Armstrong, F. A. J., and G. T. Boalch, Volatile organic matter in algae culture media and sea water, *Nature*, **185**, 761–762, 1960.
- Barnard, W. R., M. O. Andreae, W. E. Watkins, H. Bingermer, H. W. Georgii, The flux of dimethylsulfide from the oceans to the atmosphere, *J. Geophys. Res.*, **87**, 8787–8793, 1982.
- Beilke, S., and D. Lamb, On the absorption of  $\text{SO}_2$  in ocean water, *Tellus*, **26**, 268–271, 1974.
- Bentley, M. D., I. B. Douglass, J. A. Lacadie, and D. R. Whittier, The photolysis of dimethyl sulfide in air, *J. Air Pollut. Contr. Assoc.*, **22**, 359–363, 1972.
- Bonsang, B., Cycle atmosphérique du soufre d'origine marine, Ph.D. thesis, Univ. Picardie, St. Quentin, France, 1980.
- Bonsang, B., and B. C. Nguyen, Sulfur dioxide measurements in marine atmosphere at concentrations lower than ppb, Proceedings of 13th International Colloquium, Paris, in *Atmospheric Pollution 1978*, edited by M. M. Benarie, pp. 77–79, Elsevier, New York, 1978.
- Bonsang, B., B. C. Nguyen, and J. Y. Paugam, Sur la formation de gaz sulfurés et de noyaux d'Aitken dans l'atmosphère le long du littoral, *C. R. Acad. Sci. Paris, Ser. D*, **283**, 1285–1288, 1976a.
- Bonsang, B., B. C. Nguyen, and G. Lambert, Biological activity influence on atmospheric  $\text{SO}_2$  of marine origin, paper presented at Joint Oceanographic Assembly, Edinburgh, 1976b.
- Bonsang, B., B. C. Nguyen, A. Gaudry, and G. Lambert, Sulfate enrichment in marine aerosols due to biogenic gaseous sulfur compounds, *J. Geophys. Res.*, **85**, 7410–7416, 1980.
- Chameides, W. L., and A. Tan, The two-dimensional diagnostic model for tropospheric OH: An uncertainty analysis, *J. Geophys. Res.*, **86**, 5209–5223, 1981.
- Chatfield, R. B., and P. J. Crutzen, Marine sulfur emissions,  $\text{SO}_2$  in the clean upper troposphere, and the global sulfur budget, paper presented at 3rd Scientific Assembly, IAMAP, Hamburg, Fed. Repub. Ger., 1981.
- Cox, R. A., Atmospheric photo-oxidation reactions: The gas phase reaction of OH radicals with some sulfur compounds, *U.K. At. Energy Res. Estab., Rep. 8132*, 1–10, 1975.
- Crutzen, P. J., The possible importance of OCS for the sulfate layer of the stratosphere, *Geophys. Res. Lett.*, **3**, 73–76, 1976.
- Delmas, R., and J. Servant, The origins of sulfur compounds in the atmosphere of a zone of high productivity (Gulf of Guinea), *J. Geophys. Res.*, **87**, 11,019–11,026, 1982.
- Eriksson, E., The yearly circulation of chloride and sulfur in nature; Meteorological, geochemical, and pedological implications: Part 2, *Tellus*, **12**, 63–109, 1960.
- Eriksson, E., The yearly circulation of sulfur in nature, *J. Geophys. Res.*, **68**, 4001–4008, 1963.
- Friend, J. P., The global sulfur cycle, in *Chemistry of the Lower Atmosphere*, edited by S. I. Rasool, pp. 177–201, New York, 1973.
- Georgii, H. W., Contribution to the atmospheric sulfur budget, *J. Geophys. Res.*, **75**, 2365–2371, 1970.
- Georgii, H. W., Spatial and temporal distribution of sulfur compounds, International Symposium on Sulfur in the Atmosphere, Dubrovnik (Yugoslavia), *Atmos. Environ.*, **12**, 681–690, 1978.
- Georgii, H. W., and F. X. Meixner, Measurement of the tropospheric and stratospheric  $\text{SO}_2$  distribution, *J. Geophys. Res.*, **85**, 7433–7438, 1980.
- Granat, L., H. Rodhe, and R. O. Hallberg, The global sulfur cycle, *Ecol. Bull.*, **22**, 89–134, 1976.
- Grosjean, D., and R. Lewis, Atmospheric photooxidation of methyl sulfide, *Geophys. Res. Lett.*, **9**, 1203–1206, 1982.
- Hatakeyama, S., M. Okuda, and H. Akimoto, Formation of sulfur dioxide and methane sulfonic acid in the photooxidation of dimethyl sulfide in the air, *Geophys. Res. Lett.*, **9**, 583–586, 1982.
- Jaeschke, W., R. Schmitt, and H. W. Georgii, Preliminary results of stratospheric  $\text{SO}_2$  measurements, *Geophys. Res. Lett.*, **3**, 517–519, 1976.
- Jost, D., Aerological studies on the atmospheric sulfur budget, *Tellus*, **26**, 206–212, 1974.
- Kellogg, W. W., R. D. Cadle, E. R. Allen, A. L. Lazrus, and E. A. Martell, The sulfur cycle, *Science*, **175**, 587–596, 1972.
- Kurylo, M. J., Flash photolysis resonance fluorescence investigation of the reaction of OH radicals with OCS and  $\text{CS}_2$ , *Chem. Phys. Lett.*, **58**, 238–242, 1978a.
- Kurylo, M. J., Flash photolysis resonance fluorescence investigation of the reaction of OH radicals with dimethyl sulfide, *Chem. Phys. Lett.*, **58**, 233–237, 1978b.
- Logan, J. A., M. B. McElroy, S. C. Wofsy, and M. J. Prather, Oxidation of  $\text{CS}_2$  and COS: Sources for atmospheric  $\text{SO}_2$ , *Nature*, **281**, 185–188, 1979.
- Lovelock, J. E., R. J. Maggs, and R. A. Rasmussen, Atmospheric dimethyl sulfide and the natural sulfur cycle, *Nature*, **237**, 452–453, 1972.
- Maroulis, P. J., and A. R. Bandy, Estimate of the contribution of biologically produced dimethyl sulfide to the global sulfur cycle, *Science*, **196**, 647–648, 1977.
- Maroulis, P. J., A. L. Torres, A. B. Goldberg, and A. R. Bandy, Measurements of tropospheric background levels of  $\text{SO}_2$  on Project GAMETAG, *Eos Trans. AGU*, **59**, 1081, 1978.
- McElroy, M. B., S. C. Wofsy, and N. D. Sze, Photochemical sources for atmospheric  $\text{H}_2\text{S}$ , *Atmos. Environ.*, **14**, 159–163, 1980.
- Nguyen, B. C., Etude par les traceurs radioactifs des échanges entre les diverses zones de l'atmosphère au-dessus des continents et des océans, Ph.D. thesis, Fac. Sci. Paris, 1968.
- Nguyen, B. C., and G. Lambert, Geographic variations of the large-scale vertical exchange speed, *J. Geophys. Res.*, **75**, 2877–2884, 1970.
- Nguyen, B. C., B. Bonsang, and G. Lambert, The atmospheric concentration of sulfur dioxide and sulfate aerosols over antarctic, subantarctic areas and ocean, *Tellus*, **26**, 241–249, 1974a.
- Nguyen, B. C., B. Bonsang, J. L. Pasquier, and G. Lambert, Composantes marines et africaines des aérosols de sulfates dans l'hémisphère sud, *J. Rech. Atmos.*, **8**, 831–844, 1974b.
- Nguyen, B. C., B. Bonsang, G. Lambert, and J. L. Pasquier, Residence

- time of sulfur dioxide in the marine atmosphere, *Pure Appl. Geophys.*, **123**, 489–500, 1975.
- Nguyen, B. C., A. Gaudry, B. Bonsang, and G. Lambert, Reevaluation of the role of dimethyl sulphide in the sulphur budget, *Nature*, **275**, 637–639, 1978a.
- Nguyen, B. C., and B. Bonsang, Transport of continental sulfur compounds over the Mediterranean, in *Atmospheric Pollution 1978*, edited by M. M. Benarie, pp. 201–205, Elsevier, New York, 1978b.
- Ostlund, H. G., and J. Alexander, Oxidation rate of sulfide in seawater, A preliminary study, *J. Geophys. Res.*, **68**, 3995–3997, 1963.
- Paugam, J. Y., B. C. Nguyen, B. Bonsang, and S. Fongang, Production de noyaux aitken et de composés soufrés dans l'air au-dessus d'une zone littorale, *Chemosphere*, **6**, 333–339, 1977.
- Prahl, L. P., U. Torp, and R. M. Stern, Deposition and transformation rates of sulphur oxides during atmospheric transport over the Atlantic, *Tellus*, **28**, 355–372, 1976.
- Rasmussen, R. A., Emission of biogenic hydrogen sulfide, *Tellus*, **26**, 254–260, 1974.
- Ravishankara, A. R., N. M. Kreutter, R. C. Shak, and P. H. Wine, Rate of reaction of OH with COS, *Geophys. Res. Lett.*, **7**, 861–864, 1980.
- Robinson, E., and R. C. Robbins, Gaseous atmospheric pollutants from urban and natural sources, in *Global Effects of Environmental Pollution*, edited by S. F. Singer, D. Reidel, Hingham, Mass., 1970.
- Rodhe, H., Measurements of sulfur in the free atmosphere over Sweden 1969–1970, *J. Geophys. Res.*, **77**, 4494–4499, 1972.
- Rodhe, H., and I. Isaksen, Global distribution of sulfur compounds in the troposphere estimated in a height/latitude transport model, *J. Geophys. Res.*, **85**, 7401–7409, 1980.
- Schiff, J. A., Sulfur, in *Physiology and Biochemistry of Algae (Sulfur Halogens)*, edited by R. A. Lewin, pp. 239–246, Academic, New York, 1962.
- Slagle, I. R., R. E. Graham, and D. Grutman, Direct identification of reactive routes and measurements of rate constants in the reactions of oxygen atoms with methanethiol, ethanethiol, and methylsulfide, *Int. J. Chem. Kinet.*, **8**, 451–458, 1976.
- Slatt, B. J., D. R. Natush, J. M. Prospero, and D. L. Savoie, Hydrogen sulfide in the atmosphere of the Northern Equatorial Atlantic Ocean and its relation to the global sulfur cycle, *Atmos. Environ.*, **12**, 981–991, 1978.
- Smith, F. B., and G. H. Jeffrey, Airborne transport of sulfur dioxide from the UK, *Atmos. Environ.*, **9**, 643–659, 1975.
- Stoiber, R. E., and A. Jepsen, Sulfur dioxide contribution to the atmosphere by volcanos, *Science*, **182**, 577–578, 1973.
- Sze, N. D., and M. K. W. Ko, Photochemistry of COS, CS<sub>2</sub>, CH<sub>3</sub>SCH<sub>3</sub>, and H<sub>2</sub>S: Implications for the atmospheric sulfur cycle, *Atmos. Environ.*, **14**, 1223–1234, 1980.
- Torres, A. L., P. J. Maroulis, A. B. Goldberg, and A. R. Bandy, Atmospheric carbonyl sulfide measurements on Project GAME-TAG, *J. Geophys. Res.*, **85**, 7357–7360, 1980.
- Varhelyi, G., On the vertical distribution of sulfur compounds in the lower troposphere, *Tellus*, **30**, 542–545, 1978.
- West, P. W., and G. C. Gaeke, Fixation of sulfur dioxide as disulfito-mercurate (II) and subsequent colorimetric estimation, *Anal. Chem.*, **28**, 1816–1819, 1956.
- Wine, P. H., W. L. Chameides, and A. R. Ravishankara, Potential role of CS<sub>2</sub> photooxidation in tropospheric sulfur chemistry, *Geophys. Res. Lett.*, **8**, 543–546, 1981.
- Woodwell, G. M., R. H. Whittacker, W. A. Reiners, G. E. Likens, C. C. Delwiche, and D. B. Botkin, The biota and the world carbon budget, *Science*, **199**, 141–144, 1978.

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B. Bonsang, A. Gaudry, and B. C. Nguyen, Centre des Faibles Radioactivités, Laboratoire Mixte CNRS-CEA, 91190 Gif-sur-Yvette, France.

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