The Role of the Ocean in the Global Atmospheric Sulfur Cycle

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The background atmospheric 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 SO_2 above the ocean, far from continental sources, have been discussed. We have shown that one of the mechanisms of 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 SO_2 formation, and subsequently, to sulfate. This hypothesis is corroborated by a correlation between atmospheric SO_2 concentrations and the relation between atmospheric 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 72×10^6 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 H_2S 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 SO_2 is produced by the photooxidation of COS and 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 SO_2 by an adaptation of the method of West and Gaeke [1956].

The lowest detectable amount of 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 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 SO_2 measurements in marine environments [Nguyen *et al.*, 1974a], three oceanographic expeditions, described in Figure 1a, were undertaken in subantarctic regions and in the Indian Ocean from 5°S to 30°S . In this last area the circulation of air masses is essentially zonal, from east to west; 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 SO_2 above the Indian Ocean sub-Antarctic region and the Atlantic Ocean (Table 1). The average concentration of 121 values of atmospheric 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 (≈ 8.2) would prevent the direct release of dissolved 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 SO_2 in the open ocean.

Could the SO_2 be carried along great distances from remote continental sources? 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 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 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 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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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_2 concentrations during a cruise in the Peruvian Upwelling in April 1975. (b) Mean atmospheric SO_2 concentrations ($\mu\text{g}/\text{m}^3$) above the Atlantic Ocean and (c) above the Indian Ocean and subantarctic areas. Values in parenthesis represent the number of measurements.

TABLE 1a. Atmospheric SO₂ Concentrations: Cruise A

Date	Latitude		SO ₂ µg/m ³
	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 SO₂ component transported through the lower troposphere may be considered negligible.

However, the residence time of SO₂ 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 SO₂ is

TABLE 1c. Atmospheric SO₂ Concentrations: Cruise C

	Latitude		
Date	Start	End	SO ₂ µg/m ³
Reunion			
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
Kerguelen Island			
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
La Reunion			
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 ²²²Rn. In that hypothesis the residence time of SO₂ would be still shorter than the residence time of ²²²Rn (5.5 days). As the typical radon con-

TABLE 1b. Atmospheric SO₂ Concentrations Cruise B

Date	Latitude		SO ₂ µg/m ³
	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 1d. Atmospheric SO₂ Concentrations: Cruise D

Date	Latitude		SO ₂ µg/m ³
	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 SO₂ Concentrations: Cruise E

Date	Latitude		SO ₂ , µg/m ³
	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

centrations obtained during these three expeditions in the remote marine areas is generally less than 2 pCi/m³ (100 to 1000 times less than the continental values), SO₂ from continental origin would not normally contribute to the SO₂ levels measured in the boundary layer of the sub-Antarctic marine atmosphere. For this region, another source is required.

Could the SO₂ be produced above the open ocean by the oxidation of gaseous sulfur compounds with high residence times (several months), such as CS₂ and COS? COS may be produced by the oxidation of CS₂ and may be a precursor of SO₂ 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 SO₂ by the following principal reactions [Perry et al., 1976; McElroy et al., 1980]:

TABLE 1f. Atmospheric SO₂ Concentrations: Cruise F

Date	Longitude		SO ₂ , µg/m ³
	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 SO₂ Concentrations: Cruise G

Date	Latitude		SO ₂ , µg/m ³
	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 5.7×10^{-14} cm³ molecule⁻¹ s⁻¹ [Kurylo, 1978a] and 8.8×10^{-15} cm³ molecule⁻¹ s⁻¹ [Ravishankara et al., 1980].

A larger uncertainty exists for the kinetic constant of (2); k_2 varies between 4.3×10^{-12} cm³ molecule⁻¹ s⁻¹ and 1.5×10^{-15} cm³ molecule⁻¹ s⁻¹ [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 SO₂ from these sulfur compounds essentially depends on (1). Chameides and Tan [1981] have calculated concentrations increasing from 0.5×10^5 radicals cm⁻³ in high latitudes to 2.5×10^6 radicals cm⁻³ in equatorial and tropical areas. Moreover, Logan et al. [1979] have computed OH profiles where the maximum concentrations for the low troposphere was 3×10^6 radicals

TABLE 1h. Atmospheric SO₂ Concentrations: Cruise H

Date	Latitude		SO ₂ , μg/m ³
	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⁻³. By using this last value, which leads to maximum SO₂ production, the residence time of COS should comprise between 67 days and 1.2 years and the residence time of CS₂ between 8 days and 7 years. Even taking into account the faster reaction rate for *k*₁, 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 SO₂, and by considering a steady state, we could only explain a 5 pptv of SO₂ (15 × 10⁻⁹ g m³) produced by the oxidation of COS. Rodhe and Isaksen [1980] also found that the contri-

bution of COS to the concentration of SO₂ in the low troposphere is less than 5 pptv of SO₂.

This value is much lower than the 65 pptv theoretical value coming from both COS and CS₂ oxidation [Logan *et al.*, 1979]. But this calculation refers to a concentration at a 6-km altitude where the residence time of SO₂ is probably larger than in the boundary layer.

An experimental determination of SO₂ 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)," SO₂ 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 SO₂ concentrations of the 30 samples collected were all less than our detection limit of 0.02 μg/m³.

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 SO₂ production efficiency, or this process alone cannot account for more than 0.02 μg/m³, which corresponds to 20% of the background SO₂ we measured above the ocean.

Could the SO₂ be produced over the open ocean from oxidation of H₂S? The occurrence of atmospheric H₂S 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 H₂S in seawater is on the order of several minutes [Ostlund and Alexander, 1963].

H₂S 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 CS₂ [McElroy, 1980].

For instance, H₂S 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 H₂S production may occur along the littoral by the organic matter degradation. Furthermore, an atmospheric residence time for H₂S, 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, H₂S may be considered as a possible precursor of SO₂.

Could the SO₂ be produced above the ocean by the oxidation of reactive sulfur compounds other than H₂S? Other sulfur compounds already have been observed as well in seawater as in the marine atmosphere and could also be possible precursors of this SO₂ 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 12×10^{-9} g/l. *Nguyen et al.* [1978a, b] have reported DMS concentrations from 11 to 580×10^{-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 1150×10^{-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 1440×10^{-9} g/l with a mean value of 176×10^{-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 170×10^{-9} g/m³) by cryogenic sampling in a littoral zone. *Barnard et al.* [1982] found 4 to 88×10^{-9} g m⁻³ of DMS above the Atlantic Ocean. More recently we found, above the Pacific Ocean, DMS concentrations ranging from 0.2 to 400×10^{-9} g m⁻³, from Panama to Hobart (B. C. Nguyen et al., unpublished manuscript, 1983).

2. SO₂ 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[•] and OH[•] photochemically produced in the atmosphere. The following reactions summarize how SO₂ 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 SO₂, 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, SO₂ 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 SO₂ 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 (*Polysiphonia lanosa* and *laminaria*), known to produce important amounts of DMS (Figure 2).

During the first experiment, previously described by *Bonsang et al.* [1976a], SO₂ 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 SO₂ production; the atmospheric SO₂ concentration during the day reached values as high as $6 \mu\text{g}/\text{m}^3$, while concentrations at night varied between 0.2 and $1.8 \mu\text{g}/\text{m}^3$ [*Bonsang et al.*, 1976a], (Figure 3). Diurnal maxima were observed at the low-tide hours and increased with the tidal coefficient.

Furthermore, the SO₂ concentrations were sharply correlated with the Aitken nuclei production, which reached values close to $10^6/\text{cm}^3$ at low-tide hours [*Paugam et al.*, 1977].

The atmospheric SO₂ 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 SO₂ 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 80×10^{-9} g/m³ and 2.7×10^{-9} g/m³, 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 SO₂ 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 SO₂ concentrations as high as $6 \mu\text{g}/\text{m}^3$, 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 SO₂ measurement (site B) do not exceed 2 min (wind speed $< 5 \text{ m s}^{-1}$).

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 SO₂. 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 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 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. 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: 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 SO_2 con-

Fig. 3. Atmospheric SO_2 concentrations at Guisseny (site B), June 1975.

Fig. 4. (a) Atmospheric SO_2 concentration ($\mu\text{g}/\text{m}^3$) versus latitude in the southern part of the Indian Ocean between 55°E and 75°E . (b) Simultaneous record of chlorophyll "a" (solid line). Also shown is primary productivity observed above the 70°E meridian at the same time of year (late summer), from Krey [1973] (dashed line).

centrations 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 SO_2 concentration in each 5° of latitude between 5°S and 62°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 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 SO_2 concentrations is thus very well related to the general variation of primary productivity. Particularly between 40°S and 60°S , we can observe the same trend of variation between atmospheric 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 SO_2 measurements is also quite reasonable, since the concentrations should be greatly influenced by chemical factors producing and destroying SO_2 and, perhaps, meteorological factors diluting the substance.

2. Atmospheric SO_2 concentrations versus primary productiv-

ity in several oceanic areas. From 162 SO_2 measurements we can represent the atmospheric 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 $36 \text{ gC m}^{-2} \text{yr}^{-1}$) correspond to a low SO_2 concentration of $0.03 \mu\text{g}/\text{m}^3$; areas with an intermediate primary productivity between 36 and $90 \text{ gC m}^{-2} \text{yr}^{-1}$ have an atmospheric SO_2 concentration of about $0.1 \mu\text{g}/\text{m}^3$; regions of highest production (convergence and upwelling areas greater than $90 \text{ gC m}^{-2} \text{yr}^{-1}$) correspond to $0.2\text{--}0.3 \mu\text{g}/\text{m}^3$.

FLUX OF SULFUR COMPOUNDS FROM THE OCEAN TO THE ATMOSPHERE

At high altitude the 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 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 SO_2 profile and its residence time above the ocean. Numerous SO_2 profiles have been established above the polluted mid-latitude European continents and show an ex-

Fig. 5. SO_2 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_2 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_2 (100 pptv or $0.27 \mu\text{g SO}_2/\text{STD m}^3$) 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_2 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_2 concentration may decrease toward the ocean atmosphere interface. Both the average SO_2 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_2 , caused by the oxidation of reduced sulfur compounds outgassed from the sea surface, the atmospheric concentration of SO_2 would increase up to altitude h_1 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_2 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_2 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_2 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_2 budget.

Case 1: Increase of SO_2 concentration from $0.1 \mu\text{g}/\text{m}^3$ STD at sea level to $0.16 \mu\text{g}/\text{m}^3$ STD at altitude h_1 (close to 1500 m), then exponential decrease.

Case 2: Same variations versus altitude in the low troposphere up to altitude h_1 , then the mixing ratio remains constant from altitude h_1 to 10 km.

Hence from sea level to altitude h_1 the SO_2 mixing ratio follows the general law:

$$(\text{SO}_2)_h = (\text{SO}_2)_0 e^{\beta h}$$

Fig. 6. Profiles of SO_2 concentration above the ocean.

Beyond altitude h_1 , the 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 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 ρ_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); β 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 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 τ_1 and τ_2 are the respective residence times of 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 SO_2 (Q/τ) produced from the ocean surface depends on the residence time τ of this gas in a given reservoir. In the low atmosphere we have determined a value τ_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 SO_2 into sulfate is the dominant process. Unfortunately, no experimental data for 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 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 SO_4/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 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 72×10^6 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 SO_2 has been confirmed above different oceanic areas far from any continental influences.

2. Several possible origins for 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 CH_3SCH_3 and probably also CH_3SH and CH_3SSCH_3 , outgassed at the ocean surface. In turn these are partly oxidized in the atmosphere to 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} 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 CS_2 , occurring in the marine atmosphere could not explain more than 20% of the measured SO_2 . Concerning H_2S , no data exist in the very remote subantarctic areas, and it cannot be excluded that this compound remains a possible precursor of this marine SO_2 .

3. The emission of sulfur compounds produced by biological mechanisms has been estimated from 27 to 72×10^6 tons of sulfur per year. This estimate, based on the vertical profile of atmospheric 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 25×10^{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 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 44×10^6 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 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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