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The atmospheric concentration of sulfure dioxide and sulfate aerosols over antarctic, subantarctic areas and oceans

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ABSTRACT

During several trips, measurements of sulfur dioxide and sulfate aerosols have been taken over Antarctic and Subantarctic areas and also over the Mediterranean Sea. A special application of the West Gaeke method enabled us to measure SO_2 concentrations in Antarctic and Subantarctic areas, ranging from 0.05 to 1 $\mu\text{g}/\text{m}^3$. SO_2 and sulfate aerosols concentrations in these areas are then compared with concentrations observed in other areas.

1. Introduction

Measurements of sulfur compounds have been taken mainly in industrial areas. Few of them have been performed far from urban zones, such as in oceanic regions, and even fewer over Antarctic and Subantarctic areas.

Nevertheless, oceans produce SO_4^{2-} by the bursting of myriads of sea water bubbles containing about 2.65 mg of SO_4^{2-} per gram of H_2O (Kellogg et al., 1972), and because of their large surface, oceans could also produce a non-negligible quantity of SO_2 and SO_4^{2-} by oxidization of H_2S (202.10⁶ tons/year of H_2S oceanic after Eriksson, (1959, 1960) but only 30.10⁶ tons after Robinson & Robbins (1969)). Eriksson (1959, 1960) estimates the annual production of SO_4^{2-} by sea water bubbles at 130.10⁶ tons, 10% of which passes over the continents. Recently, Lovelock et al. (1972) suggested that dimethyl sulfide (DMS) was the natural sulfur compound which played the role previously attributed to H_2S . According to Challenger (1951), DMS is produced by many living systems, especially marine algae.

Kellogg et al. (1972) believe that "Man is now contributing about one-half as much as nature to the total atmospheric burden of sulfur compounds". Likewise Friend (1973) found a

contribution to the atmosphere of 65 tons/year of pollution SO_2 and of 108 tons/year of biogenic sulfur (gaseous) and volcanic SO_2 .

In order to contribute to the determination of a natural product budget of these compounds, we decided to investigate a region where SO_2 and sulfate aerosol sources of non-oceanic origin would be minimal. Therefore, it was obvious to study the Antarctic and the Subantarctic regions which are entirely covered with ice or sea water. Thus, since 1971 we have made measurements of atmospheric SO_2 and sulfate aerosol concentrations on board oceanographic ships during Antarctic and Subantarctic expeditions.

2. SO_2 measurements

The main difficulty in these areas is due to very low SO_2 atmospheric concentrations which have been only measured by Cadle et al. (1968) and proved to be smaller than 1 to 3 $\mu\text{g}/\text{m}^3$. It was therefore necessary to build an apparatus sensitive enough to measure SO_2 atmospheric concentrations of at least 0.05 $\mu\text{g}/\text{m}^3$ for a reasonable sampling time. The use of the West Gaeke method (1956) with some care in air sampling and of a spectrophotometer of high performance (such as in our experiments: Zeiss PMQ II) made possible the measurements of

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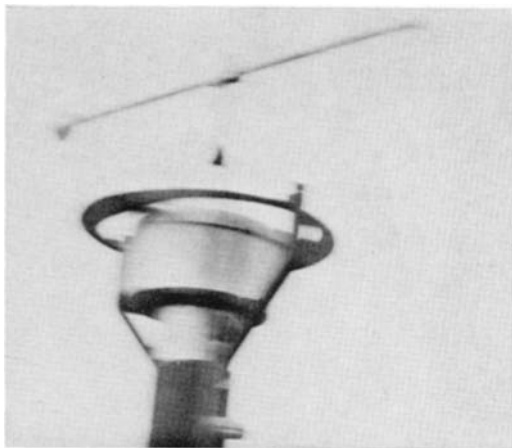


Fig. 1. System to avoid SO_2 sampling from contaminations by ship exhausts.

such low concentrations. Since this spectrometer is a laboratory fixture, the operations therefore consist of three distinct phases: sampling, sample storage and analysis.

Sampling

The most important thing for atmospheric SO_2 sampling on board, is to exclude from these samples any smoke from the ship. For this reason, the air inlet of the SO_2 sampling device is always placed on the fore-castle. We designed a system to cut off automatically the power of the SO_2 device as soon as the wind blows from astern (Fig. 1). An electrical control connects this system with the SO_2 sampling device (Fig. 2). To obtain a sufficient amount of SO_2 , each sampling is made during 24 hours with an air flow of 3 litres per minute. The air flows through a Millipore filter and then through a 10 cm^3 solution of sodium tetrachloromercurate, thus forming a dichlorosulfite-mercurate(II) complex. The long duration of the sampling requires the use of an electromagnetic device for automatic volume control of the solution (Fig. 3).

Storage

As we could not have a sufficiently sensitive spectrophotometer on board the ship, we had

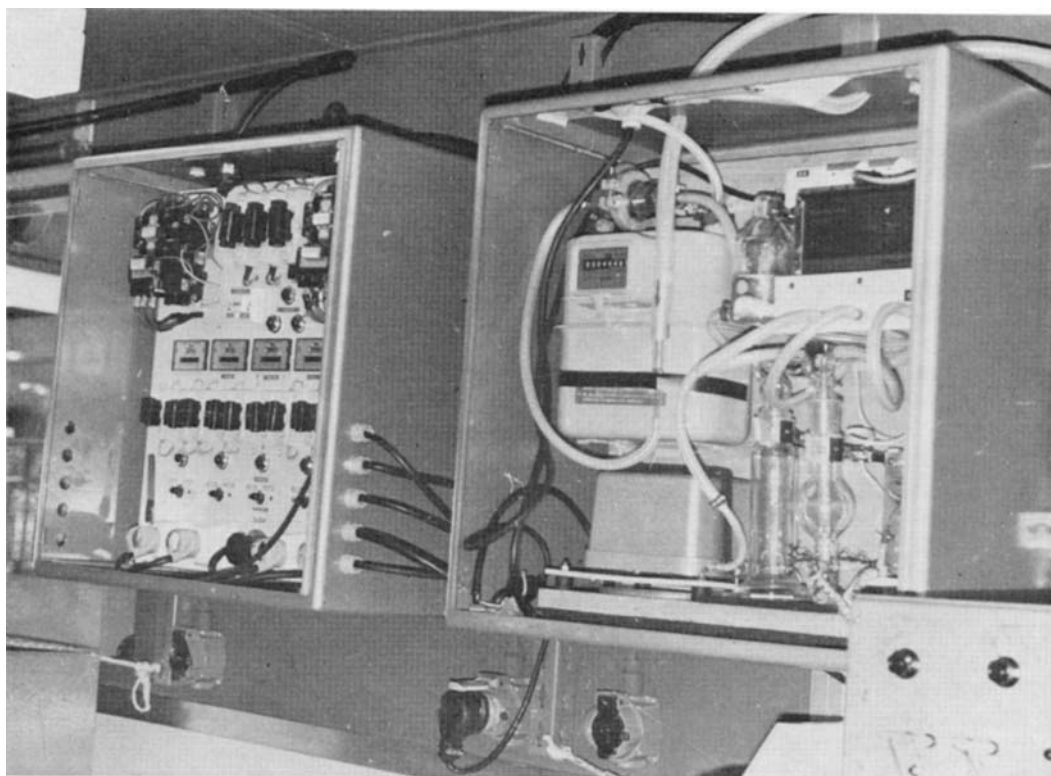


Fig. 2. Electrical control (on the left) and SO_2 sampling device (on the right).

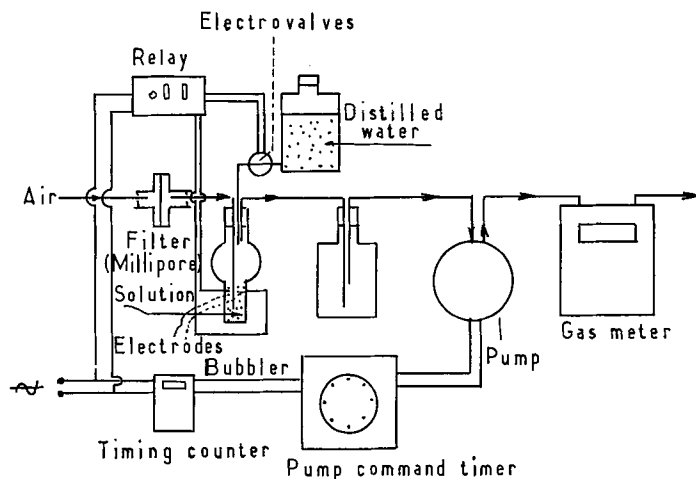


Fig. 3. Schema of SO₂ sampling device.

to store our samples on board before being analysed in the laboratory about one month later. Unfortunately the dichlorosulfitomercurate complex is not very stable. The solution must therefore be kept at the temperature for which the stability is optimum. Lahmann (1969) found that stability is better at 5°C than at higher temperatures. After several laboratory experiments between +20°C and -25°C, we established that the optimum temperature is about 0°C.

The stability of this complex solution also increases with concentration. Finally, for quantities of SO₂ in the range of 0.2 to 3 µg in 10 cm³ of absorbent solution, the losses are be-

tween 31 and 14.5% after 4 weeks at 2°C (see Table 1). Experimental details will be published later.

Analysis and possible interferences

Traces of heavy metals (Fe, Mn) catalyse the SO₂ oxidization in the solution. We have eliminated this interference by adding to the absorbent solution a chelating agent (EDTA, 0.05 µg/10 cm³) (Zurlo & Griffini, 1962).

Interference from nitrogen dioxide is also eliminated by adding sulfamic acid (Pate et al., 1965).

Oxidization of SO₂ by O₃ in the absorbent solution has not yet been measured. However, recent results show that the oxidization rate of SO₂ in solution is 12.6% per hour for pH and concentration conditions (Penkett, 1972) are very similar to those encountered here. A much smaller figure was found by us for atmospheric samples. This may be explained by the following fact: the O₃ molecules are much more likely to be destroyed by the reagents present in the absorbent solution in ponderable concentration than by the SO₂ traces.

The complex formed in the absorbent solution reacts with formaldehyde and pararosaniline in acid solution to form a pararosaniline methylsulfonic acid. The intensity of the color of this compound is measured spectrophotometrically at 560 mµ.

With our spectrophotometer we can measure, for instance, with a possible error of 2%, a

Table 1. Stability (%)^a of dichlorosulfitomercurate solution after one or four weeks at various temperatures

Temperature of storage (°C)	SO ₂ concentration of 0.2 to 0.5 µg/10 cm ³ absorbent solution		SO ₂ concentration of 1.0 to 3.0 µg/10 cm ³ absorbent solution	
	After 1 week	After 4 weeks	After 1 week	After 4 weeks
+20	78.0	65.0	84.5	72.5
+ 2	87.5	69.0	90.0	85.5
-15	81.0	69.5	76.0	74.0
-25	84.0	67.5	76.0	75.0

^a Reference = 100 % for a measurement immediately after preparation of solution.

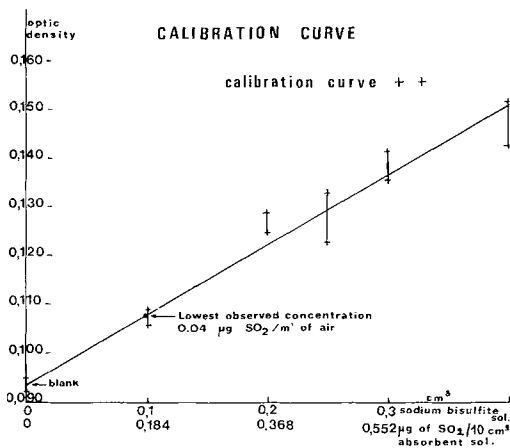


Fig. 4. Calibration curve.

concentration of $0.02 \mu\text{g SO}_2$ per cm^3 of absorbent solution, corresponding to 5 m^3 of air with $0.04 \mu\text{g SO}_2$ per m^3 . Fig. 4 shows one of our calibration curves where the lowest concentration observed in this work is indicated ($0.04 \mu\text{g}/\text{m}^3$). The optic density corresponding to this concentration is obviously higher than the blank ones.

Table 2. SO_2 atmospheric concentration

Location	Concentration ($\mu\text{g}/\text{m}^3$)	Reference
<i>Urban</i>	$\sim 40-1\ 500$	
New York	280-1 500	Greenburg-Jacobs (1956)
Freiburg	40	Neuwirth (1958)
England (industrial area)	50-180	Meetham (1959)
Frankfurt/Main (Winter)	443	Georgii (1960)
Frankfurt/Main (Summer)	87	Georgii (1960)
<i>Rural</i>	$\sim 0.6-50$	
Sweden: offer	0-13	Egner-Eriksson (1955)
Sweden: Alnarp	6-42	Egner-Eriksson (1955)
Florida	3	Junge (1956)
England (rural area)	20	Meetham (1959)
Zugspitze (3 000 m)	47	Georgii (1960)
St. Moritz (August)	< 10	Georgii (1960)
Panama	< 3-15	Lodge-Pate (1966)
Colorado	0.6-2.3	Georgii (1970)
<i>Marine</i>		
Close to continent	$\sim 0.2-9$	
Atlantic Ocean	< 0.5-4	Georgii (1970)
Mediterranean Sea	0.2-9	Present work
Far from all continents	$0.04-1.0$	
Antarctic	< 1.5-5	Cadle et al. (1968)
Antarctic area	0.05-0.5	Present work
Subantarctic area	0.04-0.9	Present work

SO_2 results

SO_2 atmospheric concentrations measured in the present work are shown in Table 2 together with the results obtained by other authors. It may be pointed out that these concentrations vary from approximately 40 to $1\ 500 \mu\text{g}/\text{m}^3$ in urban zones; from 2 to $50 \mu\text{g}/\text{m}^3$ in rural zones; from 0.2 to $9 \mu\text{g}/\text{m}^3$ in marine areas close to continents and from 0.04 to $1 \mu\text{g}/\text{m}^3$ in marine areas far from all continents.

Fig. 5 shows that over the Mediterranean Sea except between Greece and Turkey SO_2 atmospheric concentrations are as low as 0.2 to $1 \mu\text{g}/\text{m}^3$, i.e. much lower than the typical European values.

Thus, off the Italian coast, at a distance of about 200 km , SO_2 concentrations vary between 0.2 and $0.4 \mu\text{g}/\text{m}^3$, whereas they are of the order of 5 to $40 \mu\text{g}/\text{m}^3$ over Europe. Hence the residence time of SO_2 appears to be very small over the sea, e.g. only a few hours.

Fig. 6 shows the values measured over oceanic areas in the southern hemisphere during the 1971 and 1972 expeditions. Three main regions should be distinguished after the order of magnitude of the encountered concentrations.

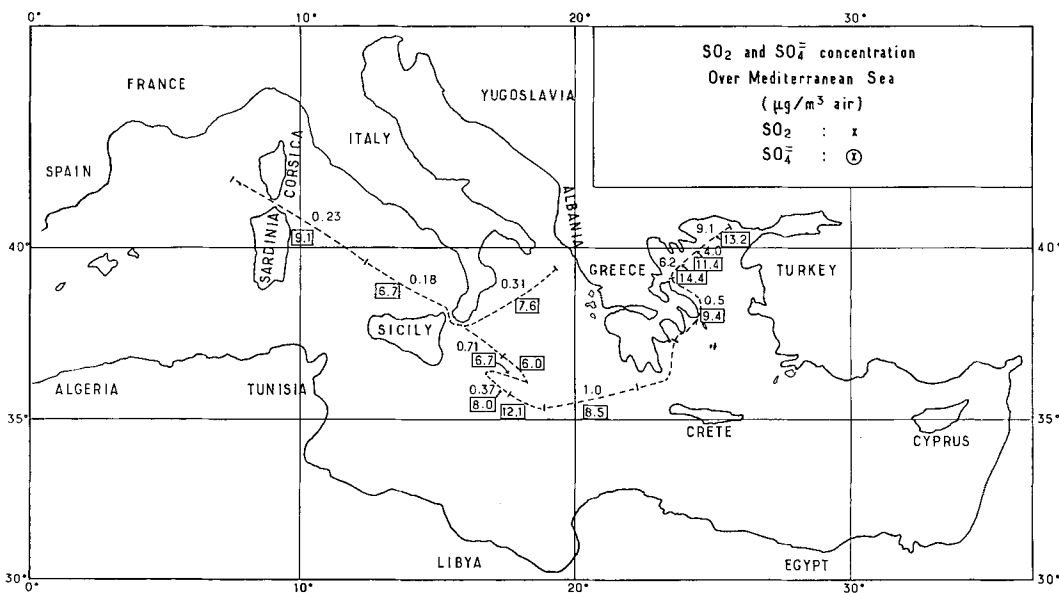


Fig. 5. SO_2 and SO_4 atmospheric concentrations over Mediterranean Sea

North of 30°S , despite the proximity of Madagascar to the West, the concentrations come down to $0.04 \mu\text{g}/\text{m}^3$. Such low concentrations

could be explained by the generally easterly wind in this area together with the position of the ship extremely far from Australia.

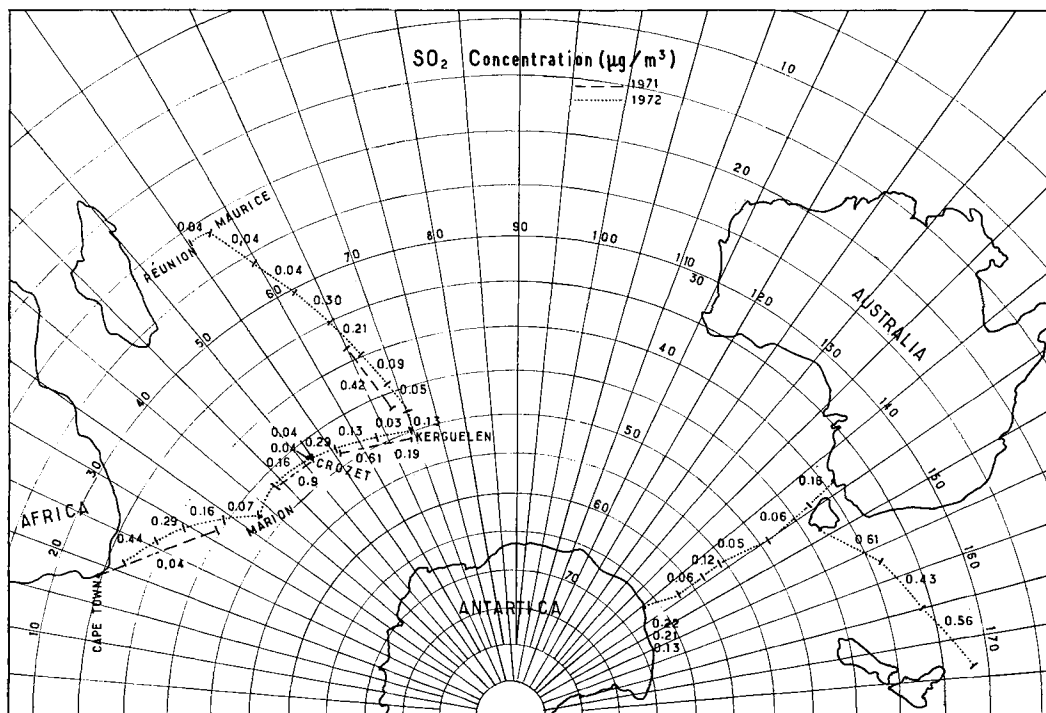


Fig. 6. SO_2 atmospheric concentration over Subantarctic and Antarctic areas

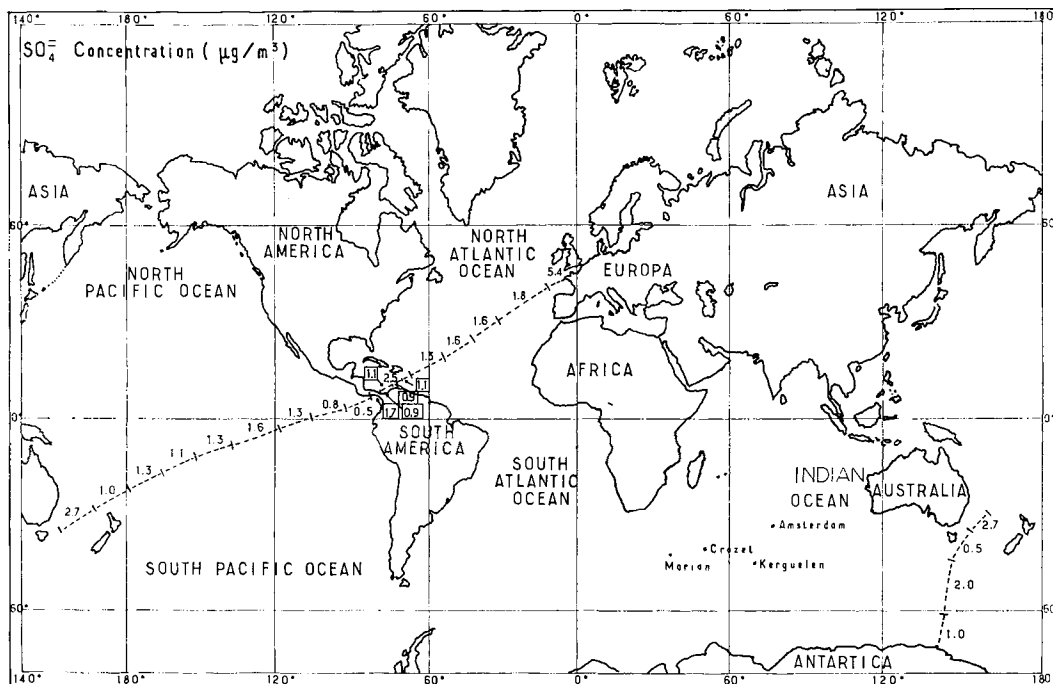


Fig. 7. Atmospheric sulfate aerosol concentration over the Atlantic and the Pacific.

South of 30°S , the wind is mainly westerly, sometimes northwesterly: this could explain SO_2 concentrations generally ranging from 0.04 to $0.9\ \mu\text{g}/\text{m}^3$.

In the Tasmanian Sea, i.e. leeward of Australia, the concentrations are again the same range as in the Mediterranean Sea: from 0.4 to $0.6\ \mu\text{g}/\text{m}^3$.

However, these general considerations on air mass trajectories cannot by themselves account for SO_2 concentration variations over the Antarctic and Subantarctic areas.

It seems probable that, allowing for the very short residence time of SO_2 over the oceans (i.e. a few hours) remote continental influences should be practically negligible over central and southern Indian Ocean and in Antarctic regions.

There, the wide concentration range (0.04 to $0.9\ \mu\text{g}/\text{m}^3$) should be accounted for only by local considerations.

It is reasonable to think that the ocean could play the part both of a source and a sink of SO_2 . If this is so, the variations in atmospheric concentration observed should reflect some local chemical and biological changes of the

superficial sea water and possibly of the meteorological parameters.

3. Sulfate aerosol measurements

During Mediterranean and Antarctic expeditions, we also made sulfate aerosol samplings.

Each sampling was carried out during 24 hours with a "Poelmann Schneider" filter. The air flow was $12\ \text{m}^3/\text{hour}$. As far as smoke protection is concerned the same precautions were taken as in the case of SO_2 sampling.

The soluble sulfates were extracted by ultrasound cleansing from previously calcinated filters. Their concentrations were measured by the turbidimetric barium sulfate method. The background level was $25\ \mu\text{g}$ of sulfates which is comparable to the smallest sample collected, i.e. $72\ \mu\text{g}$ for a $0.3\ \mu\text{g}/\text{m}^3$ atmospheric concentration.

Atmospheric sulfate aerosol concentrations over the Atlantic and the Pacific (Fig. 7) range from 2 to $5\ \mu\text{g}/\text{m}^3$ close to continents and from 0.5 to $1.8\ \mu\text{g}/\text{m}^3$ in the middle of oceans.

These figures are in agreement with those

Table 3. Atmospheric concentration of sulfur dioxide and sulfate aerosols

Location	SO ₂ (μg/m ³)	SO ₄ ⁻ (μg/m ³)	SO ₂ /SO ₄ ⁻
Antarctic (60° S – 70° S) area	0.13	1.57	0.08
Subantarctic (40° S – 60° S) area	0.18	1.68	0.11
South Pacific Ocean (20° S – 40° S)	0.12	1.15	0.10
North Atlantic Ocean (50° N – 8° N)		2.33	
Mediterranean Sea	2.27	8.43	0.27
Boulder, Colorado			
Ground	2.1	1.7	1.3
5.2 km (above ground) ^a	0.4	0.1	4.0
Germany	(μg/Nm ³)	(μg/Nm ³)	
Ground to 1 600 m	4–25	3–7	5–3
(unpolluted area) at ≈ 2 800 m ^a	~ 1	~ 4	0.25
Sweden	SO ₂ -S	SO ₄ ⁻ -S	SO ₂ -S/SO ₄ ⁻ -S
400–2 800 m		(μg/kg)	
Unpolluted area (30 flights) ^b	1–7	0.1–1.6	10–4

^a Georgii (1970). ^b Rodhe (1972).

found by Junge (1969) and Georgii (1970) in similar places.

Over the Mediterranean the concentrations are shown in frames in Fig. 5. These high concentrations (from 6 to 13 μg/m³) are very close to the concentrations of 3 to 10 μg/m³ observed in Germany by Georgii (1970) below 2.8 km altitude. Such high values of sulfate aerosol concentrations prove that over the Mediterranean most of these aerosols come from Europe. This origin is confirmed by the radon measurements over the Mediterranean Sea where the concentration of this nuclide is intermediate between continental and oceanic figures (Nguyen Ba Cuong, 1968). Moreover the lifetime of sulfate aerosols in the lower atmosphere is certainly long enough (2 or 3 days) to let them reach the Mediterranean Sea (Lambert et al., 1972).

4. Comparison of SO₂ and SO₄⁻ concentrations

Table 3 indicates the average concentrations of SO₂, SO₄⁻ and their ratio for regions investigated in the present work and in papers by Georgii (1970), and Rhode (1972). This table shows that in Antarctic, Subantarctic and Central Pacific areas in the absence of anthropogenic sulfur compounds, the ratio SO₂/SO₄⁻ is

about 0.1. A small anthropogenic influence increases this ratio up to 0.27 e.g. over the Mediterranean sea and at 2 800 m altitude over Germany. Below this altitude over Europe, this ratio rises by 10 to 100 times.

Conclusion

Two main conclusions may be drawn from our preliminary marine measurements

(a) Since Antarctic and Subantarctic areas are remote from all continents where anthropogenic sulfur compounds are important, SO₂ atmospheric concentrations of 0.04 to 0.9 μg/m³ and sulfate aerosol concentrations of 0.5 to 1.6 μg/m³ measured in these areas could be representative of SO₂ and sulfate aerosol oceanic background of the Earth's surface.

(b) Although the air concentration in sulfates and radon over the central Mediterranean Sea is characteristic of Continental inhabited areas, the SO₂ concentrations have been found very low and almost comparable to Subantarctic concentrations. A situation more or less similar is also observed in the Tasmanian Sea. Several explanations could be suggested. However, we have shown in another work that 95% of SO₂ is quickly absorbed by buffer solutions having the same pH as sea water.¹ A faster disappear-

¹ To be published.

ance of SO₂ in oceanic atmosphere could mean that we have there simultaneously oxidation of SO₂ and direct absorption by sea water.

It therefore seems that the oceans should act as both a source of SO₂ and of sulfates (e.g. the Pacific, Indian and Antarctic oceans) and a sink (e.g. the Mediterranean and Tasmanian seas). It appears very likely that the same process of absorption by sea water also exists in the oceans so that the concentration we measured should be a result of a combination of these two effects. The variations of Oceanic SO₂ concentrations indicate how the different processes are de-

pendent on biochemical and meteorological conditions.

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АТМОСФЕРНЫЕ КОНЦЕНТРАЦИИ ДВУОКСИ СЕРЫ И СУЛЬФАТНЫХ
АЭРОЗОЛЕЙ НАД АНТАРКТИКОЙ, СУБАНТАРКТИЧЕСКИМИ
ОБЛАСТЯМИ И ОКЕАНАМИ

Во время нескольких рейсов были приняты измерения SO_2 и сульфатных аэрозолей над Антарктикой и субантарктическими областями, а также над Средичемным морем. Специальное применение Вест Гейк метода позволило измерить концентрации SO_2 в

Антарктике и субантарктических областях и получить значения от 0,05 до 1 $\text{мкг}/\text{м}^3$. Концентрации SO_2 и сульфатных аэрозолей в этих областях затем сравниваются с другими концентрациями, наблюдаемыми в различных областях.