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# The distribution of sulfur dioxide over the Norwegian Arctic Ocean during summer

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ABSTRACT

Measurements of atmospheric sulfur dioxide performed during the Swedish expedition "Ymer 80" in the Arctic are presented. Wet chemical filter sampling and subsequent chemiluminescence analysis enabled detection in the low pptv range. $SO_2$ mixing ratios between 5 pptv and 100 pptv were measured. $SO_2$ values over the closed ice sheet were usually lower than over the open ocean. Possible source and sink mechanisms are discussed. The influence of atmospheric transport is shown by trajectory analysis and helicopter ascents.

## 1. Introduction

The Arctic is one of the few areas where only very limited knowledge exists on the distribution and concentration of reactive trace gases like $SO_2$. One reason for this fact is the difficulty in determining low $SO_2$ concentrations which do not permit detection by conventional methods. However, the sparse data which are available both for trace gases and aerosols indicate that the degree of pollution in the Arctic is higher during the winter season than during summer (Heintzenberg et al., 1981; Rahn et al., 1980). Rahn et al. measured high $SO_2$ values on Bear Island, an Arctic site at 74° N, 19° E, reaching daily mean concentrations of 6 $\mu$g $SO_2$ $m^{-3}$ on several events in the winter months, while during summer, values close to the detection limit (0.2 $\mu$g $m^{-3}$) were usually found. It is suggested that the different meteorological situation during the two seasons is responsible for this change. During winter, polluted air advected from industrialized countries in Europe and the North American continent may be transported directly to the Arctic, while during summer, the long-range transport seems to be of minor importance and the local sources dominate. The cruise of the icebreaker "Ymer" during the Swedish expedition "Ymer 80", as shown in Fig. 1, gave the opportunity of measuring $SO_2$ from 60° N to 82° N latitude and to deepen our knowledge on the distribution of this trace gas in the Norwegian part of the Arctic during summer.

## 2. Experimental

The measurement of atmospheric sulfur dioxide was performed by a wet chemical filter sampling method with subsequent chemiluminescence analysis.

### 2.1. *Sampling procedure*

Filter samples were collected in a laboratory container mounted on the front part of the ship. The air was taken from a 5 m long vertical air inlet of 15 cm diameter. Its application to air–chemistry measurements is described in detail by Lannefors et al. (1983). To avoid contamination of the samples from the ship's exhaust or from helicopters, the air-intake was connected to a modified wind vane and a condensation nucleus counter. As soon as the wind turned more than ±70° from the ship's direction of movement or when the number of condensation nuclei exceeded a prefixed value, the airflow was interrupted immediately. A possible influence of the air intake pipe on ambient $SO_2$ was

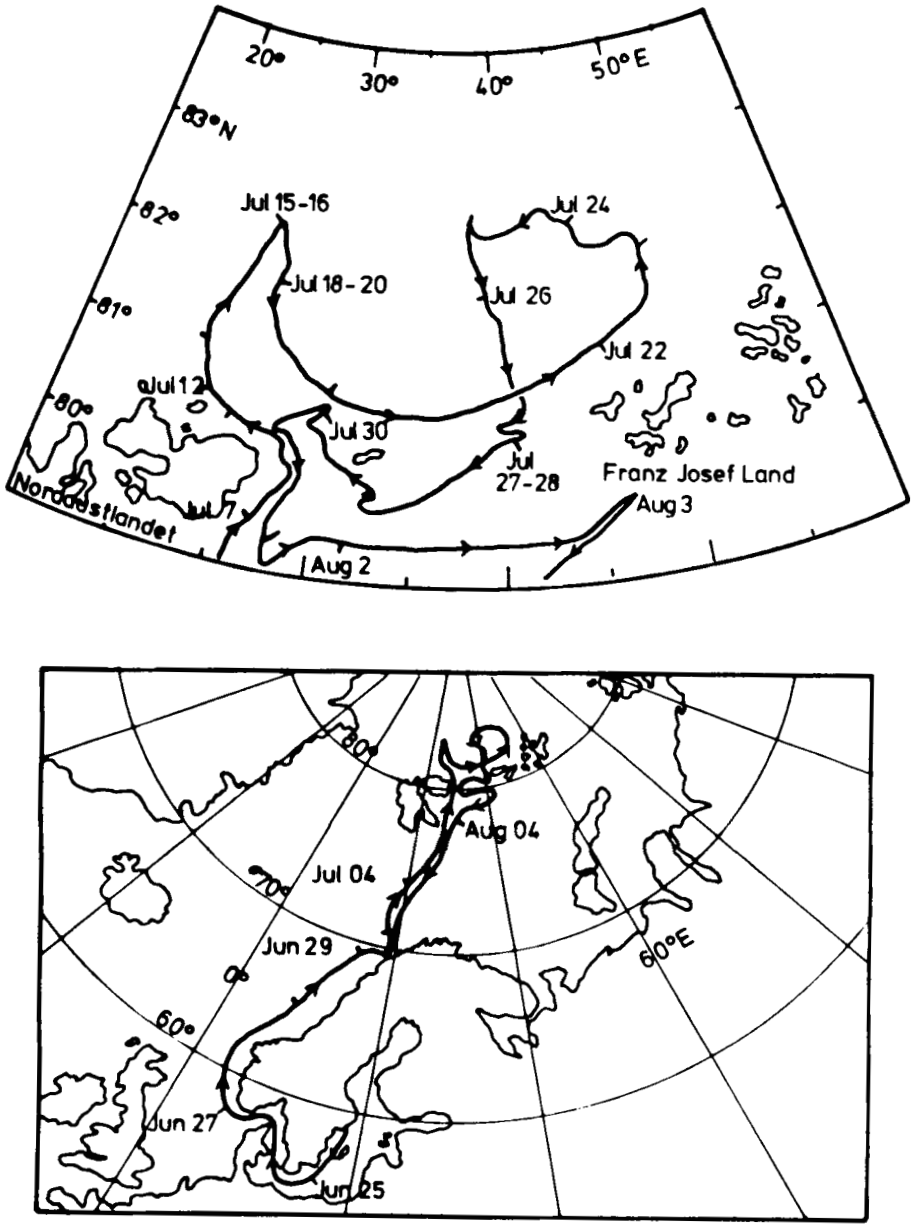


*Fig. 1.* Cruise track of HMS "Ymer" between June 24 and August 4, 1980.

tested during the first days of the cruise by simultaneous measurements. One filter was mounted in the laboratory and a second one on the roof close to the air inlet. Both measurements showed agreement within 20%, which indicates no influence of the intake-line on ambient $SO_2$. Such tests were not performed under foggy conditions. In this case, the accuracy of measurements may be affected by wetting intake lines. However, we think that due to the large dimensions of the main air intake system, its high flow rate of air and the warming of the system entering the heated con-

tainer minimized the possibility of water condensation.

For sampling on board the helicopter, a small battery-powered device was used. The air intake was mounted at the pitot-tube in the very front of the vessel. To clean the tubings from contamination caused by the take-off, they were rinsed with ambient air during the first minutes of the flight. The samples were taken at a speed of 110 km $h^{-1}$. At this speed there exists no airflow from the rotor to the lower sections of the fuselage. This provides a reasonably representative sample of the undisturbed atmosphere (Gartrell and Carpenter, 1955).

### 2.2. *Filter handling technique*

Before sampling, the filters (Delbag, Microsorban) were impregnated with an absorption liquid consisting of a tetrachloromercurate (TCM) solution. Samples of 200–300 l of air were collected at a flow rate of 8 l $min^{-1}$. Under these conditions, the absorption of $SO_2$ is quantitative. After completion of the sampling procedure, the filters were washed with 15 ml of TCM. The washing solution which is identical to the sample was then analysed by the chemiluminescence technique. A further 15 ml of TCM drawn through the filter represented the blank value of the sample.

### 2.3. *Detection method*

The analysis of the complexed sulfur dioxide is based on the following effect: $SO_2$ is oxidized to sulfate by an acid potassium permanganate solution (pH = 2.50); the oxidizing step is accompanied by chemiluminescence ($\lambda < 550$ nm). The main part of the measuring instrument is a light-proof reaction chamber with consecutive photocathode and photomultiplier. For the analysis, 5 ml of the sample and 1 ml of potassium permanganate are injected successively into the reaction chamber by automatic syringes. As soon as the mixing of both agents is initiated, photons are counted over a period of 100 s with a photoncounter system. The chamber is then emptied, a further 5 ml of the sample are injected, and the analysis is repeated. The chemiluminescence effect generates reproducible light yields with an accuracy better than 2%.

During our present study, the calibration of the method was accomplished daily with liquid sulfite standards. The detection limit defined by the blank values and their standard deviation was 5 pptv.

The precision of the whole method (sampling and analysis) was tested extensively with a dynamic gas dilution system and, under field conditions, in comparison with other methods (Meixner and Jaeschke, 1981). The error of the method was found to be below 20%.

## 3. Results

### 3.1. *On-ship measurements*

Figs. 2 and 3 show the $SO_2$ data measured during the expedition. A few samples were taken during the first part of the cruise from June 27 to 30 over the North Sea (Fig. 2). These measurements reflect $SO_2$ concentrations of marine air, and the mixing ratios are comparable to the values which were measured over the Atlantic Ocean in the same year (Ockelmann et al., 1984). The samples between July 3 and August 4 (Fig. 3) were taken north of Tromsoe in the Arctic region between Spitsbergen and Franz Josef Land. From the individual data, it can be seen that the sulfur dioxide concentration varied by more than one order of magnitude between the detection limit of the method (5 pptv) and more than 100 pptv, both over the open ocean and the ice covered Arctic. Such large fluctuations sometimes occurred within one day; examples are July 22 and August 4. In general, however, the mixing ratio was extremely low. Only 20% of the data gained in the Arctic exceeded 30 pptv. Besides short-period fluctuations which were caused to some extent by fog, it is

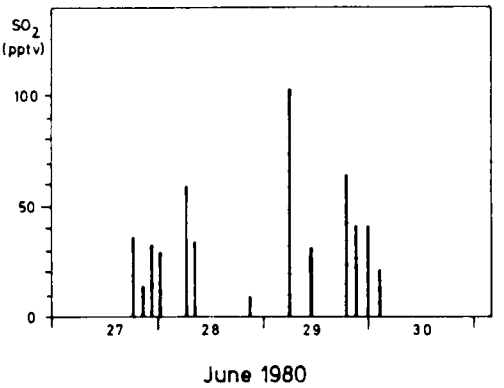


*Fig. 2.* $SO_2$ mixing ratios over the Atlantic between 60° N and 70° N.

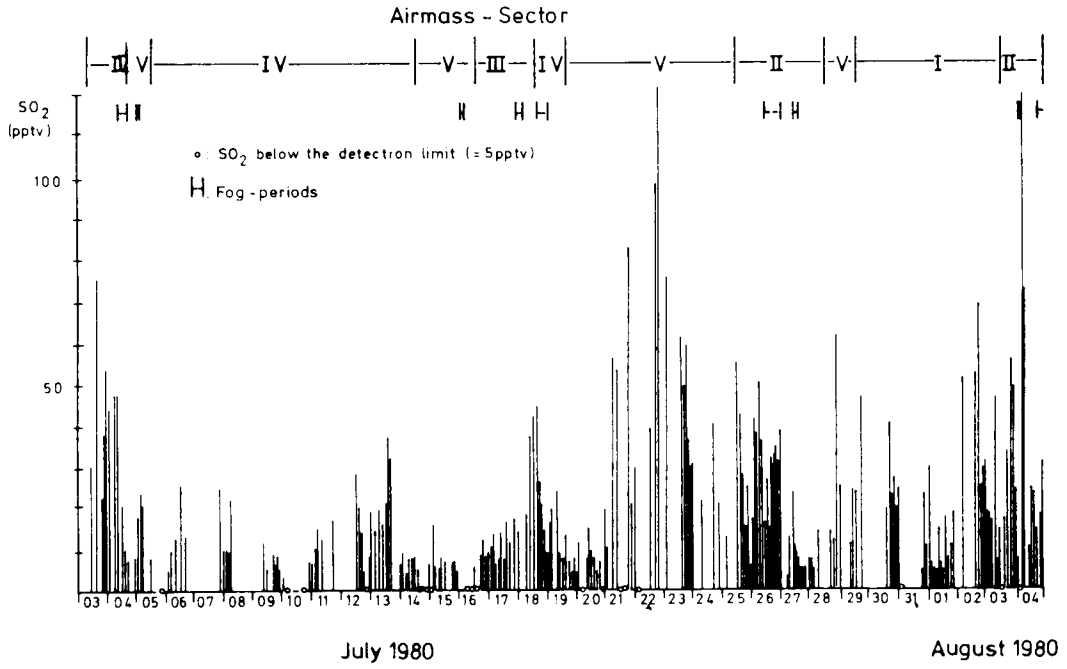


*Fig. 3.* $SO_2$ mixing ratios measured over the Arctic Ocean. Fog periods (visibility lower than 1 km) are marked with dashed lines.

obvious from Fig. 3 that temporal variations of the order of several days also exist, which may be related to changes of advection.

## 4. Discussion

### 4.1. *Surface level trajectories*

To distinguish between local and distant sources and to evaluate the pathway of air parcels, a trajectory analysis was performed. Trajectories starting at 00.00 and 12.00 GMT were calculated backwards for 48 h in 12-h steps. In the present case, surface level trajectories were favoured since the stratification of Arctic air was generally stable (Jaenicke and Schütz, 1982). In order to gain our main results on the importance of atmospheric transport processes, we divided the area covered by the trajectories into 5 sectors (see Fig. 4). The classification was characterized by presumed $SO_2$ sources which are in particular:

— Arctic settlements on Greenland (Sector I) and Siberia (Sector III);
— The ocean (Sector II) and northern Europe which includes possible long-range transport from continental sources over the ocean;
— The region of the North Pole (Sector VI) where we assumed a lack of $SO_2$ sources;
— Local sources (Sector V) including Spitsbergen

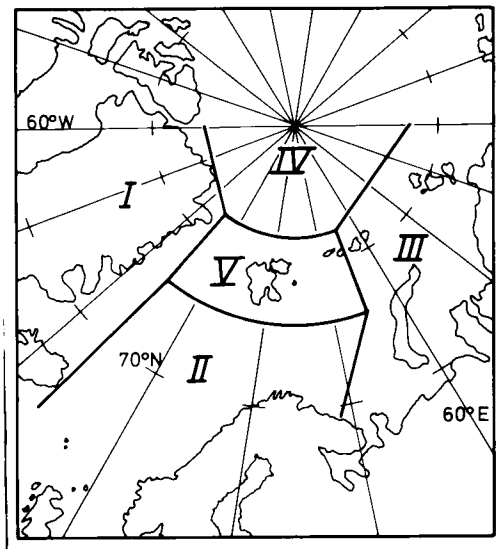


*Fig. 4.* Selection of 5 air-mass sectors characterizing atmospheric transport from different regions.

and the ship's route. At low wind speeds and frequent changes in the ship's course, it cannot be excluded that the ship may have crossed its own plume.

In order to assess the influence of advection from different directions, the $SO_2$ data are given in their mean concentration and standard deviation for every transport episode within one sector (Fig. 5).

4.1.1. *Clean arctic air.* The polar region is expected to be without any $SO_2$ sources. However, sulfur dioxide was detected in most cases when the air was advected from the pole (Sector IV). One exception is July 10 (see Fig. 3) with extremely low values: 2 measurements were below and 2 at or a little above the detection limit of 5 pptv. The aerosol size distribution measured during this day showed a well-aged aerosol with particles below 0.01 $\mu$m radius completely absent (Jaenicke and Schütz, 1982). This is a clear indication that gas-to-particle conversion did not occur. The fact, however, that $SO_2$ was detected in most cases suggests a long $SO_2$ residence time in the Arctic region.

4.1.2. *The contribution of Arctic settlement.* Although anthropogenic emissions in the Arctic are lower by orders of magnitude compared to Europe, they may be significant for the $SO_2$ levels which are present in Arctic air. Our data in Sectors I and III show that $SO_2$ concentrations in air parcels which were transported from Greenland and Siberia are higher by a factor of about 1.5 compared to air which had been advected directly from the pole. This indicates that Arctic settlements are of minor importance for the pollution of the Arctic.

4.1.3. *Atlantic air masses.* The ocean is known as a source of biogenic sulfur compounds especially of dimethylsulfide which is produced by marine algae (Barnard et al., 1982; Nguyen et al., 1978). These reduced sulfur compounds are emitted into the atmosphere where they react with OH radicals forming $SO_2$ (Atkinson et al., 1978). The ocean is therefore not only a sink (Georgii and Gravenhorst, 1977) but also a secondary source of $SO_2$. An average $SO_2$ mixing ratio for the marine atmosphere deduced from measurements over the Atlantic between 54° N and 30° S is about 30–40 pptv (Ockelmann et al., 1984). The $SO_2$ measurements during the Ymer expedition in June 1980 (41 pptv) and between July 3 and 4 (38 pptv) and August 4 (30 pptv) which were made over open water are comparable with these findings and show that similar $SO_2$ values can be found even close to the ice border. The $SO_2$ mixing ratio found over the ice-covered ocean, however, was lower by a factor of 2 at least compared to mixing ratios over the open ocean. We conclude that the ice cover

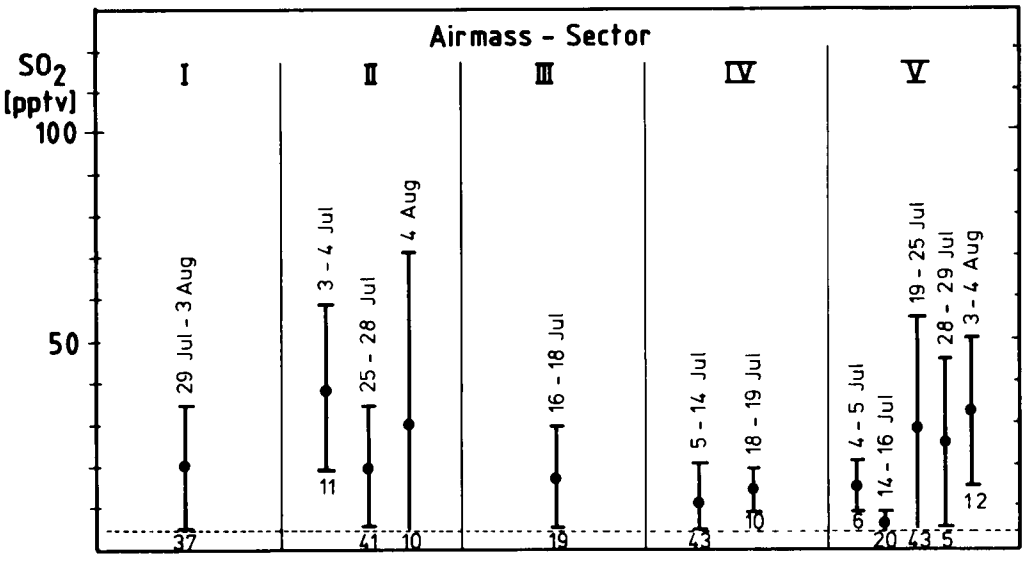


*Fig. 5.* $SO_2$ data attached to the different air-mass sectors mean and standard deviation). The numbers of data are given for each period.

interrupts the gas exchange between ocean and atmosphere and consequently leads to lower $SO_2$ concentrations in the boundary-layer above the ice sheet.

### 4.2. *Measurements by helicopter*

Three ascents were made by helicopter to study the vertical distribution of $SO_2$. The helicopter permitted measurements up to 2000 m height and a total sampling time of 60 min, allowing up to 3 samples to be taken during each flight. The results are shown in Fig. 6 together with a measurement made on the ship shortly before or after the flight. Trajectories are shown for the surface and 850 and 700 mb.

During the three flights, the atmospheric condition was stable with an inversion between 500 and 1000 m during the first two ascents and isothermal conditions up to 1000 m during the third flight. Three quite different $SO_2$ distributions were found which will be discussed on the basis of the trajectories.

On July 22, with a nearly constant but high mixing ratio, the height of the inversion was found with 97 pptv at the surface and 100 pptv at 500 m. This indicates a well-mixed air column. Above 500 m, $SO_2$ decreased sharply and reached a value of 39 pptv at 1000 m. The surface trajectory shows that the air travelled slowly from the north-pole direction, and there were no indications of a long-range transport of trace-substances. We explain the high $SO_2$-concentration by the ship crossing its own aged plume. The data of July 24 show that $SO_2$ increased between 500 and 1000 m altitude from 15 pptv to more than 30 pptv. The strong increase of the temperature from $-1\,°C$ at the surface to $+4\,°C$ at 1000 m is remarkable. The trajectories clearly show that the influence of Arctic air continued at the surface while at the 850 and 700 mb level temperate Atlantic air was advected. The mixing ratios of 34 pptv at 1 km and 26 pptv at 2 km agree well with measurements which were performed in Atlantic air masses (Georgii and Meixner, 1980; Meixner and Jaeschke, 1981). The measurements made on July 31 show an extremely low mixing ratio of 5 and 6 pptv at the detection limit of the method. In contrast to the other two cases, the air was advected directly from Greenland in all three levels.

These three ascents demonstrate clearly the

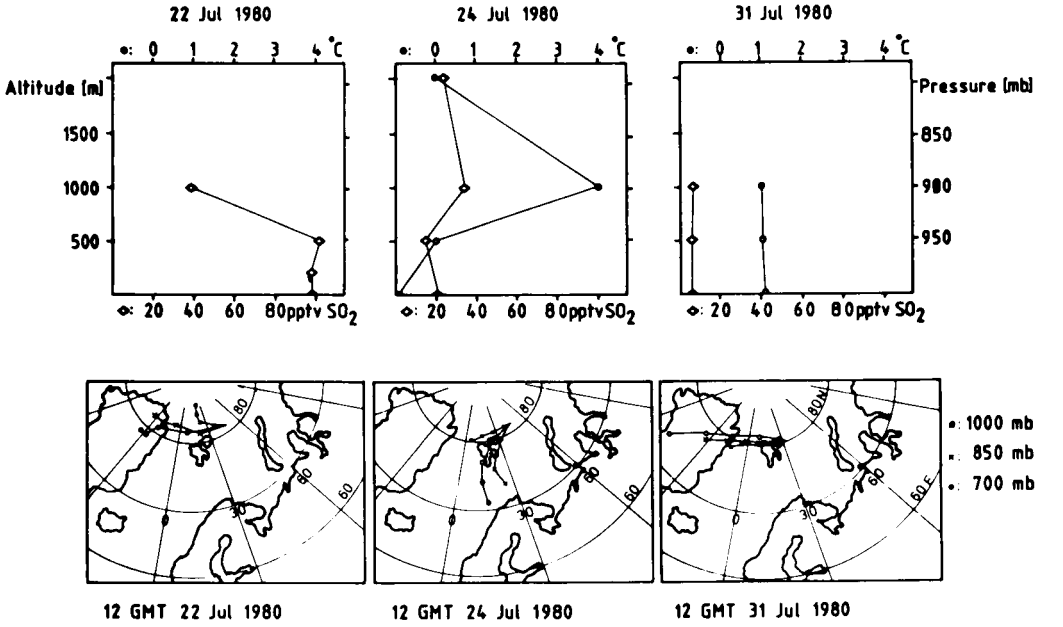


*Fig. 6.* Vertical $SO_2$ distribution in the lowest 2 km and trajectories at the surface, 850 and 700 mb level for each ascent.

strong influence of the direction of air-mass transport on the vertical $SO_2$ distribution.

## 5. Conclusion

During the whole cruise of the "Ymer" in the Arctic, $SO_2$ was found in detectable concentrations between 5 and 100 pptv. The higher values can be attributed to transport from distant sources while the low concentrations indicate a general polar background. This background concentration in an area without any significant sources can only be explained by a long residence time of $SO_2$ over the ice-covered Arctic ocean. In air masses advected from the pole, the lack of aerosol particles in the submicron range excludes the transformation of gaseous sulfur components into particles and excludes by this the existence of an important $SO_2$ sink. The low precipitation rates and the lack of heavy metal-aerosols acting as catalysts for the heterogeneous $SO_2$ oxidations reduces the efficiency of wet sulfur deposition. Further, the stable thermal stratification of the Arctic air reduces the deposition velocity of $SO_2$ and by this the dry sulfur deposition. It is suggested that these effects extend the atmospheric residence time of $SO_2$ in the Arctic region above the ice-covered ocean.

## 6. Acknowledgement

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