Aerological studies on the atmospheric sulfur budget

By D. JOST, *Institute of Meteorology, Geophysics, University Frankfurt/M., Frankfurt/M., W-Germany*

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ABSTRACT

Air-craft ascents for measurements of trace substances in the atmosphere permit surveillance of air pollution as well as soundings in relatively pure air when special sampling and analysing techniques are used. The concentrations of the components SO_2, NH_3, $SO_4^=$, H_2S, and heavy metals were studied under different meteorological situations and air masses. From this the influence of clouds, sun radiation e.g. on the atmospheric SO_2 concentration may be estimated. SO_2 residence time in the atmosphere ranges from about one hour to several days as it is calculated from the concentration distribution of several trace substances (SO_2, CO_2) in the troposphere. SO_2 and its reaction products are omnipresent air pollutants in the troposphere over Europe as is seen from air-craft measurements and combined trajectory studies.

Investigations of the atmospheric sulfur budget are done both by studying the chemical reactions of the participating components and by measurements of concentrations in industrial and remote areas. The studies are expedited by knowledge of the large amounts of anthropogenic SO_2 emitted, and by reports of the effects of this SO_2 in regions far from sources (Granat, 1972). These effects result in an acidification of rain water that cannot be explained by nearby sources of air pollution. The most important natural and anthropogenic factors in the atmospheric sulfur budget, together with several methods of investigation, are shown in Fig. 1. SO_2 concentration itself leads to local effects (Gudrian, 1970). H_2S apparently plays the most important role concerning the natural sulfur compounds in the atmosphere (Robinson, 1970). NH_3 and heavy metal salts support the SO_2 oxidation (Georgii, 1974; Junge, 1958), which is enhanced in clouds and rainwater after washout and rainout (Beilke, 1970). There are only few quantitative indications on the role of Ozone and other oxidants in oxidising tropospheric SO_2 (Penkett, 1974; Wilson, 1970; Stephens, 1969).

A separation of the effects of SO_2 corresponding to various time and space scales, gives an insight into the possibility of obtaining further information about the atmospheric sulfur budget by means of measurements made in the free atmosphere.

Local scale of SO_2 concentration

The SO_2 concentration (0–3 mg/m^3) on the lee side of well defined sources is to be determined (few kilometers). The dispersion is influenced by meteorological parameters. Recent measurements indicate SO_2 reactions already on this scale (Weber, 1971).

Regional scale of SO_2 concentration

The SO_2 concentration (0–3 mg/m^3) and pro ducts from SO_2 reactions are to be determined in industrialised areas (tenth of kilometers). Dispersion and chemical reactions of SO_2 are influenced by meteorological parameters. Aircraft measurements from Montreal (East, 1972) indicate that about $\frac{1}{2}$ of the SO_2 emitted in the mentioned area is already oxidised within the local and regional scale.

The reaction products of SO_2 may appear as Aitken nuclei, larger sulphate particles and H_2SO_4 containing particles. SO_2 reactions are still under investigation.

Model experiments (Scott, 1967), measure-

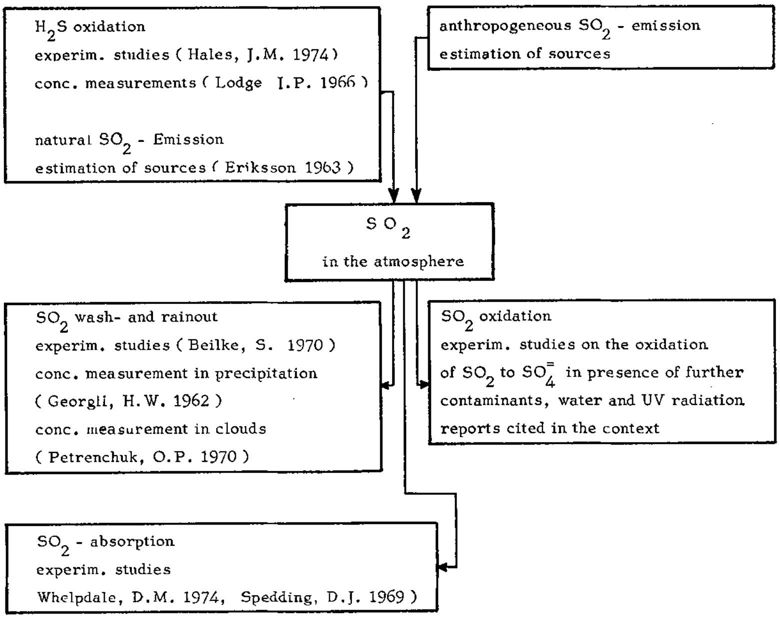


Fig. 1. Diagram of fog chamber and associated apparatus.

ments in surveillance networks, as well as studies in the free atmosphere help to clarify unknown processes. Since chemical reactions of SO_2 appeared to be dependant on the concentration of SO_2 itself as well as on the concentration of other pollutants, the problem of dispersion is important.

INTERREGIONAL SCALE OF SO_2 CONCENTRATION

SO_2 measurements (0–0.3 mg/m^3) in extended surveillance systems (few 100 km) are to be prepared. With increasing scale the SO_2 reaction products become more important. Air pollution episodes lead to increased concentration of SO_2 and related products in remote areas.

The back tracing of air pollution by aircraft measurements, and studies on special problems such as concentration enrichment in temperature inversions, lead to knowledge of the phenomena which are to be included in models describing the behaviour of sulfur compounds in the atmosphere. There are no quantitative models available, which contain the transmission of SO_2 on this scale, and the efficiency of atmospheric interactions (washout, chemical reactions) are still unknown.

Continental scale of SO_2 concentration

The SO_2 concentration (smaller than 0.03 mg/m^3) plays a minor role in this scale (1 000 km) but the reaction products and their effects are reason for scientific studies. In this scale atmospheric chemistry is more important than dispersion phenomena where SO_2 and its reaction products are concerned. Concentration measurements in extended surveillance systems including background stations are to be prepared. Aircraft measurements contribute to the knowledge of the extension of these pollutants and yield data which are to be included in models of this scale (OECD Project on long range transport of air pollutants). The SO_2 transport must be quantified by aid of trajectory studies in order to correlate concentrations in ambient air with specific emission areas, as demonstrated in Figs. 2 and 3.

Hemispheric and global scale

Measurements in this scale (10 000 km) are in preparation but there are still problems in analytical chemistry. Aircraft measurements from higher altitudes and expeditions into very

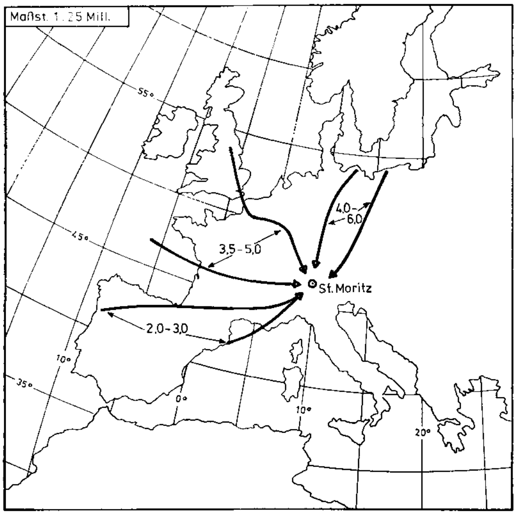


Fig. 2. Range of trajectories from several parts of Europe to the Alps. $SO_2 + SO_4^=$-Sulfur concentration ($\mu gS/m^3$). Measurements from summer 1968 in St. Moritz (Alps).

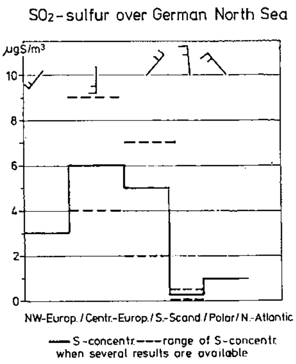
remote areas of the ocean may contribute useful results. Additional tracers such as CO_2 (Jost, 1972) and lead (Chow, 1969) may be used.

Methods used for aerological measurements

Sulfur dioxide is measured using the TCM method (West, 1956) in some modification by taking the zero values from filtered outdoor air (Jost, 1973). None of the other modifications could avoid negative values of SO_2 concentration (Scaringelli, 1968). The range of applicability of this TCM modification is indicated in Table 1 by the reproducibility (standard deviation of TCM measurements in percent of given SO_2 concentrations).

Table 1. *Reproducibility of SO_2-analyses for different concentration ranges, determined from simultaneous outdoor measurements*

SO_2 concentration ($\mu g\ SO_2/m^3$)	20	10	5	2
Reproducibility ± (%)	10	12	30	50



SO_2 in rainwater is analysed after sampling in concentrated TCM solution.

Sulfate mass concentration is measured by the nephelometric $BaCl_2$ method. Samples are taken nonisokinetic on Microsorbane filters. The retension efficiency for particles larger than $d = 0.4\ \mu$ ranges from 95 to 98%. The sulfate content of the filter material is about 2 $\mu g\ SO_4^=$ per filter, but this value has to be controlled.

The number concentration of sulfate particles is measured using a three stage impactor with slides prepared with $BaCl_2$ containing gelatine (Georgii, 1971).

Ammonia is analysed by the Indophenolblue-method (VDI 1969, Georgii, 1974) after enriching in absorption flasks, which are used for SO_2 sampling too (Georgii, 1964).

Aircraft measurements for NO_x, H_2S, and heavy metals are performed in some special cases. CO_2 is sometimes measured as a further tracer.

Mean vertical distribution

The mentioned components are considered as to their mean vertical distribution under various atmospheric conditions. Clouds and vertical turbulent exchange influence this vertical distribution.

The influence of meteorological conditions on the vertical distribution of SO_2, its reaction products, and CO_2, as a further tracer over industrialised areas, may be found using aircraft measurements (Jost, 1973). The vertical range of anthropogenic sources is strongly dependent on the wind velocity and on the temperature lapse rate. This vertical range varies from 200 m in stable conditions to about 1 500 m in lapse

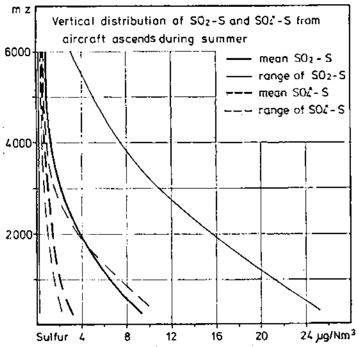


Fig. 4

and calm conditions. Nevertheless the influence of industrial sources on the vertical SO_2 distribution may be observed up to 5 000 m under special conditions like extreme updraft. In Figs. 4 and 5 the mean vertical distribution of SO_2 over Central Europe is shown together with the concentration range. Extended flights for $SO_4^=$-measurements resulted in mean distributions which are also shown in these figures. The relatively slow decrease of $SO_4^=$ compared to SO_2 points to chemical reactions which consume SO_2 and result in $SO_4^=$. This explanation is also supported by aircraft measurements concerning the size distribution of sulfate particles in different heights. The less efficient washout and rainout of particles compared to gaseous SO_2 (Beilke, 1970) is to be mentioned.

From aircraft ascents NH_3 concentrations from between 1 and 10 μg NH_3/m^3 in the free atmosphere are reported (Georgii, 1974).

Concerning heavy metals, which may play an important role in the atmospheric sulfur budget, until now only values from mountain stations may be given, as only recently the analysing methods have been developed for measurements in the free atmosphere. In Table 2 data for some relevant heavy metals are given.

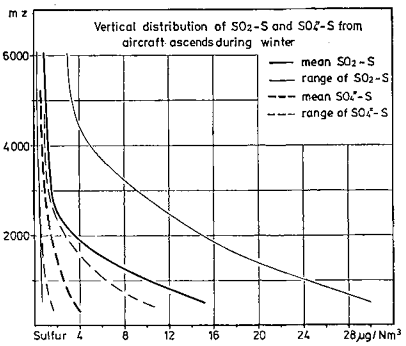


Fig. 5

Table 2. *Concentration data for metals ($\mu g/m^3$) in remote areas*

Mean values Measuring site	Pb	Fe	Mn	Cu
Kl. Feldberg, Taunus	0.20	0.51	0.03	0.47
St. Moritz Alps	0.15	0.20	0.02	0.10
Corviglia 2 500 m Alps	0.07	0.18	0.02	0.10
Corvatsch 3 300 m Alps	0.02	0.20	0.02	0.30
Sylt, Germ. North Sea	0.05	0.16	0.01	0.20

Sulfate concentration influenced by clouds

There are considerable deviations from the mentioned mean distributions caused by clouds as it has been already tentatively shown from measurements of the sulfate mass concentration in the free atmosphere (Georgii, 1968). The sulfate concentration near clouds is to be seen in more detail from measurements of the sulfate particle number concentration for different particle sizes. In Fig. 6 the number of sulfate particles from measurements below and beside

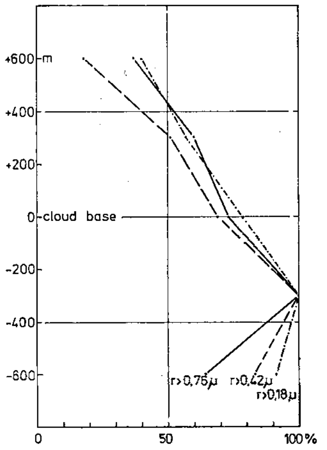


Fig. 6. Sulfate particle concentration normalized to maximum concentration below cloud base. Height (m) relative to cloud base.

Table 3. *SO_2 from TCM method and $SO_4^=$ both in rainwater measured immediately after precipitation*

Concentrations in μg S SO_2 air ($\mu g/m^3$)	SO_2 rain (μg/ml)	$SO_4^=$ rain (μg/ml)	SO_2 sulfur $SO_4^=$ sulfur
55	0.32	3.4	0.1
27	1.70	7.2	0.2
40	0.30	2.6	0.1

cumuli formed clouds is indicated for sulfate particles with radius $r > 0.18$ μ, $r > 0.42$ μ and $r > 0.76$ μ. Below clouds these particles occur with relatively high concentrations. The distribution shown in Fig. 6 is normalized to the $SO_4^=$-particle concentration measured 300 m below the visual cloud base. As all flights were due to limited flight conditions, no flights beneath the clouds were prepared. There are no measurements from inside the clouds. The increase of concentration below clouds is more pronounced for the larger particles than for the smaller ones. As these particles are measured proportional to their sulfate content this maximum cannot be due to particle growth by water uptake. The maximum of the sulfate particle concentration below clouds could be caused by an increased oxidation of SO_2 to $SO_4^=$ inside the clouds. With the assumption that these particles originate from cloud droplets and that each particle contains 0.3×10^{-12} to 12×10^{-12} g sulfate sulfur, cloudwater contains 0.2 to 0.8 μg sulfate sulfur/ml (Georgii, 1962) the corresponding droplets should have radii from 40 to 250 μ, that is to say the larger ones should have a downward velocity relative to the cloud. These particles may remain in the atmosphere as invisible clouds even after the water cloud has diminished. An increase of sulfate particle concentration was only measured below clouds, and there was in no case a maximum lateral to clouds. Thus the maximum of large $SO_4^=$ containing particles may be explained from $SO_4^=$ containing droplets which evaporated during falling relatively to the cloud. It is to be noticed that these $SO_4^=$ containing particles showed an absolute maximum in the vertical distribution below clouds and not only a relative maximum compared to the air besides the clouds which shows low sulfate concentration.

The reactivity of SO_2 in cloud and rainwater is indicated by results from SO_2 ($SO_3^=$) and $SO_4^=$-analyses in rainwater given in Table 3.

Cloud water in the polluted area of Frankfurt–Taunus Mountains contains 0.3 to 3.0 μg S/ml. The total sulfur content of rainwater in Frankfurt/Main ranges from 2 to 20 μg S/ml analysed as $SO_4^=$. The difference of 1.7 to 17 μg S/ml (sulfur in rain water minus sulfur in cloud water) is due to washout beneath clouds in polluted areas. The SO_2 concentration in rainwater diminishes during the first hour after precipitation. As pointed out by Beilke (Beilke, 1970), in a polluted atmosphere 3/4 of the sulfur content of rainwater has been captured by rain droplets from SO_2 falling from the cloud base to the ground. From the measurements noted in Table 3 it is to be seen that the larger part of this sulfur is already oxidized to sulfate when the rain reaches the ground and only a smaller part is oxidized by slower reactions.

SO_2 and sulfate concentration influenced by temperature inversions

Besides scavenging of SO_2 by clouds and rain the most obvious meteorological situation influencing the vertical distribution of SO_2 and $SO_4^=$ containing particles is the temperature lapse rate. For SO_2 and NO_2 maxima of the vertical concentration distribution were already reported (Georgii, 1964). Above inversions and in the middle and upper troposphere sulfur is present in almost equal amounts of sulfur dioxide and sulfate. Above inversions the smallest analysed $SO_4^=$ containing particles ($r > 0.18$ μ) tend to decrease slower than the larger ones. In unpolluted atmosphere sulfate exceeds SO_2 at these heights as it is to be seen from the lines in Figs. 4 and 5, which indicate the lower limits of sulfur concentration.

Conclusions

The mentioned parameters; emission, cloudiness, atmospheric stability, contribute to yearly variations of the SO_2 and $SO_4^=$ concentration in the troposphere. Summing up the concentration relation $SO_4^=$ sulfur/SO_2 sulfur will show specific variations from summer to winter. These variations are given in Table 4.

Table 4. *Concentration relation $SO_4^=$ sulfur/SO_2 sulfur in summer and winter*

Factor influencing SO_2 and $SO_4^=$	Effect on SO_2 and $SO_4^=$ concentration
1. Increasing $SO_4^=$ emission	Increasing $SO_4^=$ concentration by factor 2 (Georgii, 1966). Larger gradient of sulfate concentration
2. Increasing SO_2 emission	Increasing SO_2 concentration by factor 4 in rural and city area. (Pilotstation Frankfurt 1972). Larger gradient of SO_2 concentration
3. Decreasing O_3 concentration	Smaller gradient of SO_2 concentration. Larger gradient of $SO_4^=$ concentration
4. Decreasing NH_3 concentration	Smaller gradient of SO_2 concentration. Larger gradient of $SO_4^=$ concentration
5. Decreasing sun radiation	Smaller gradient of SO_2 concentration. Larger gradient of $SO_4^=$ concentration
6. Increasing cloudiness	Larger gradient of SO_2 concentration. Smaller gradient of $SO_4^=$ concentration
7. Decreasing height of cloud base	Same as above

The frequency of inversions shows no clear variation from summer to winter, this is true also for the concentration of heavy metals in air masses which are not polluted by nearby sources.

From Table 5 a stronger vertical SO_2 decrease during winter than during summer is evident whereas the $SO_4^=$ decrease remains almost constant.

That is to say the effects by the factors noticed under 1, 6 and 7 counterbalance and even exceed the effects of those noted under 2 to 6.

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Table 5. *Comparison of SO_2 and $SO_4^=$ concentration in 500 m and 1 500 m from the averaged vertical concentration distributions (Figs. 4, 5)*

	SO_2–S ($\mu g/m^3$)	$SO_4^=$–S ($\mu g/m^=$
Summer 500/1 500 m	8:6 = 1.3	2.5:1.9 = 1.3
Winter 500/1 500 m	16:6 = 2.7	3.3:2.3 = 1.4

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АЭРОЛОГИЧЕСКИЕ ИССЛЕДОВАНИЯ БЮДЖЕТА АТМОСФЕРНОЙ СЕРЫ

Подъемы самолета для измерений концентраций трассеров в атмосфере дают возможность регистрировать загрязнения воздуха и производить зондирование в относительно чистом воздухе, если используются специальная техника забора проб и их анализа. При различных метеорологических ситуациях и воздушных массах изучались концентрации SO_2, NH_3, SO_4, H_2S и тяжелых металлов. Отсюда можно оценить влияние облаков, солнечной радиации, например, на концентрации SO_2. Время его жизни в атмосфере находится в пределах от, примерно, одного часа до нескольких дней, как это вычислено из распределений концентраций нескольких трассеров (SO_2, CO_2) в тропосфере и продукты его реакций являются всегда присутствующими загрязнителями атмосферы в тропосфере над Европой, как это видно из самолетных измерений в комбинации с исследованиями траекторий воздушных масс.