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On the vertical distribution of sulphur compounds in the lower troposphere

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ABSTRACT

The aim of this paper is to discuss the results of aircraft measurements of atmospheric sulphur dioxide made over Hungary and to compare the sulphur dioxide profile with the vertical distribution of sulphate particles based on earlier sulphate measurements over Hungary. It is shown that atmospheric SO_2 concentration decreases more rapidly with height than sulphate concentration. Finally, some data on the vertical as well as the horizontal change of the atmospheric SO_4^{2-}/SO_2 ratio as a function of the distance from anthropogenic sources are presented.

1. Introduction

For a better understanding of the global sulphur cycle as well as the role of atmospheric sulphur compounds played in several atmospheric processes, it is important to know their vertical profiles in the atmosphere. It is well known that the concentration of an air pollutant at a given height depends on a number of factors, first of all on the source characteristics at the ground surface below and the effect of distant sources by advection. The vertical exchange processes in the lower atmosphere are limited by the tropopause, so most air pollution emitted at the ground surface is accumulated in the trophosphere. The height to which an atmpspheric component penetrates is a function of its atmospheric turnover time. In the case of SO_2 this height is low because SO_2 is transformed into sulphate in a short time, and having high water solubility, it may be removed from the atmosphere by precipitation. Thus it is probable that the bulk of atmospheric SO_2 will be found in the lower layers of the troposphere and the fraction of atmospheric sulphur that is present as SO_2 will decrease with altitude. In order to determine the vertical atmospheric concentration profile of SO_2 20 aircraft measurements were carried out over Hungary in the period 1975–76. The method and the results of these aircraft measurements are presented in this paper and the SO_2 data are compared with the vertical sulphate distribution measured also over Hungary (Mészáros and Várhelyi, 1975). Based on these data, the vertical distribution of tropospheric sulphur content in the forms of SO_2 and sulphate particles is discussed.

2. Experimental

In order to measure the vertical distribution of atmospheric SO_2, 20 flights were made at heights of 500, 1000, 2000 and 3000 m over Hungary. A Morava type aircraft was equipped with the sampling system which consisted of a Venturi tube for maintaining the sampling rate at 400 l/h and a frame fixing the fritted glass bubbler (Cauer impinger) containing 5 ml sampling solution. The air flow was measured by means of a rotameter. The measurements were carried out over a flat rural area between Budapest and Szeged in the midday hours. The distance between these two towns is 180 km. The sampling period of about 1.5 hours included a flight from Budapest to Szeged and back. As one sampling was made during one flight, the obtained concentration values can be regarded as average above the given area of Hungary. The direction of the flights corresponded to the wind direction prevailing over Hungary. The SO_2 concentration was determined by the West–

Gaeke method (West and Gaeke, 1956) with some modification of the volume of the reagents.

3. Vertical sulphur dioxide profile over Hungary

The results of the aircraft measurements are summarized in Table 1. As some negative error may occur in the measurements probably because of the presence of ozone (Stauff and Jaeschke, 1975) in spite of the time delay used as suggested in Federal Register (1971), all data found below 0.2 μgm^{-3} were taken to be 0.2 μgm^{-3} (the uncertainty of the values is about ± 0.1 μgm^{-3}). The yearly average vertical profile of atmospheric SO_2 over Hungary calculated on the basis of these data is given in Fig. 1. The ground surface concentration in Fig. 1 is the mean SO_2 concentration measured at Kecskemét–Komlósi telep in the years 1974–76. This background station is practically situated on route of the aircraft measurements, about halfway between Budapest and Szeged. Fig. 1 shows that the decrease of SO_2 concentration with height is most rapid in the lower levels of the troposphere. The SO_2 concentration decreases by about 90% in the lowest 1000 m layer. Concentration values similar to those measured over Hungary above 2000 m were found by Jaeschke et al. (1976) in the upper troposphere which means that the SO_2 concentration is probably constant above this height. Based on these results, by taking a constant tropospheric mixing ratio of SO_2 above 3000 m, the total SO_2 mass in a vertical column in the troposphere over Hungary was calculated to be 4014 μgm^{-2} SO_2–S. The scale height of SO_2 obtained as the ratio of the total tropospheric SO_2 content (μgm^{-2}) and the average ground surface SO_2 concentration (μgm^{-3}) is 608 m. This value is lower than those reported for Sweden (Rodhe, 1972) and Great Britain (Garland and Branson, 1976).

Table 1. *The concentration of SO_2 over Hungary at different heights and in different half-years*

	Height [m]			
	500	1000	2000	3000
Summer	0.8	2.3	0.3	0.2
	1.0	0.7	0.2	0.2
	0.5	2.1	0.2	
	1.9	1.1	0.2	
		0.2		
Average	1.0	1.3	0.2	0.2
Winter	9.1	1.4	0.8	
	5.3	2.4		
Average	7.2	1.9	0.8	
Yearly average	4.1	1.6	0.5	0.2

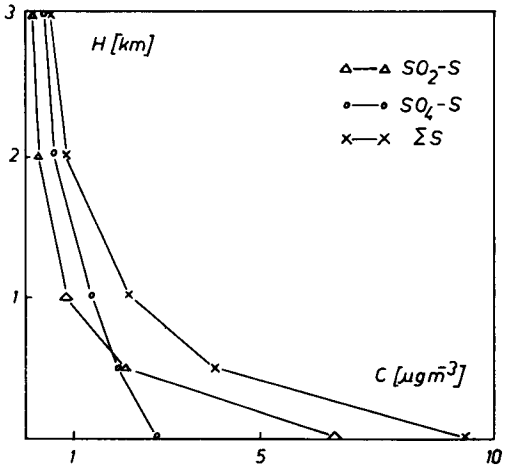

Fig. 1. Concentration profiles of atmospheric sulphur compounds in the lower troposphere over Hungary.

4. Vertical distribution of tropospheric sulphur as SO_2 and sulphate

The average sulphate mass concentration profile measured over Hungary also between Budapest and Szeged in 1972–74 (Mészáros and Várhelyi, 1975) is shown together with the SO_2 profile in Fig. 1. The particles were captured by means of a filter and analyzed by nephelometric method. One can see in Fig. 1 that the sulphate concentration decreases more slowly with height than SO_2. This is in good agreement with the results of Georgii (1970). The scale height of sulphate aerosol over Hungary is nearly 2000 m, about three times greater than the scale height of SO_2.

The total sulphur amount in the troposphere over Hungary calculated on the basis of the SO_2 and sulphate data is about 9400 μgm^{-2}. More than 50% of it was found in the lowest 1000-m layer of the troposphere. The distribution of the

Table 2. *Distribution of the sulphur content of the troposphere over Hungary in the forms of SO_2–S and sulphate-S as a function of height* [μgm^{-2}]

H[m]	$M_{SO_2\text{-}S}$	$M_{SO_4\text{-}S}$	M_S
0–1000	2850	2050	4900
1000–2000	500	1000	1500
2000–3000	200	500	700
3000–10,000	464	1850	2314
0–10,000	4014	5400	9414

Table 3. *The SO_4^{2-}/SO_2 ratio as a function of height*

H[m]	SO_4^{2-}/SO_2
0	0.6
500	1.5
1000	2.6
2000	3.6
3000	6

Table 4. *Variation of SO_4^{2-}/SO_2 ratio with increasing horizontal distance from anthropogenic sources*

Scale of SO_2 pollution processes	SO_4^{2-}/SO_2
Local pollution (towns)	0.025
Regional pollution	0.25–0.53
Continental pollution	1
Maritime areas	5

tropospheric sulphur content as SO_2 and sulphate aerosol is given in Table 2. In the calculation of the tropospheric sulphur content, only the species of oxidized state were considered. Taking into account a vertical H_2S profile estimated from the data of Georgii (1978), the total tropospheric sulphur content in an air column may be about 10,200 μgm^{-2}. Other atmospheric sulphur compounds can probably be neglected.

If we compare the variation of atmospheric SO_4^{2-}/SO_2 ratio with vertical and horizontal distance from the main SO_2 sources, a similar change can be shown. The SO_4^{2-}/SO_2 ratio as a function of height is given in Table 3. These data show that there is an increase with altitude of the SO_4^{2-}/SO_2 ratio which is caused mainly by the oxidation of SO_2 into sulphate. A similar vertical change of atmospheric SO_4^{2-}/SO_2 ratio was recently found by Trägårdh (1978) over Sweden. At the same time some typical values of the SO_4^{2-}/SO_2 ratio for areas with different pollution characteristics taken from the papers by Georgii (1978) and Mészáros (1978) are summarized in Table 4. It can be seen that about the same atmospheric SO_4^{2-}/SO_2 ratio can be found over the oceans as at heights of 2000–3000 m above continental areas. Considering the fact that sulphate particles have a significant source other than oxidation from SO_2 in maritime areas, this may be an indirect proof of a certain SO_2 amount coming from the surface of the oceans, probably by oxidation of some reduced sulphur species.

5. Conclusions

Based on the results of aircraft measurements, the conclusion can be drawn that atmospheric sulphur plays an important role in the global atmospheric processes in the form of sulphate particles, and SO_2 takes part mostly in an indirect way by transforming into sulphate. In order to get more reliable information on the question discussed, further research is needed. It will be necessary to carry out measurements with shorter sampling time as well as to extend them to higher levels of the atmosphere.

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О ВЕРТИКАЛЬНОМ РАСПРЕДЕЛЕНИИ КОМПОНЕНТ СЕРЫ В НИЖНЕЙ ТРОПОСФЕРЕ

Целью статьи является обсуждение результатов самолетных измерений двуокиси серы в атмосфере, выполненных над Венгрией и сравнение профиля концентрации двуокиси серы с вертикальным распределением частиц сульфатов, основанным на более ранних измерениях. Показано, что концентрация SO_2 в атмосфере уменьшается с высотой более быстро, чем концентрация сульфатов. В конце представлены некоторые данные как о вертикальных, так и горизонтальных изменениях отношения SO_4^{2-}/SO_2 как функции расстояния от антропогенных источников.