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SULPHATE AEROSOL FORMATION IN THE UPPER PARTS OF SUDETEN, POLAND

Concentrations of sulphur dioxide, total sulphur and sulphates in atmospheric aerosols were measured in a mountainous region. The percentage of particle sulphur in the total sulphur measured was higher than that reported for other parts of Europe. The highest values were recorded during the inflow of maritime-polar air masses from western directions. We conclude that sulphur dioxide in the mixing layer undergoes a rapid change resulting in formation of sulphate ions as the air ascends up the mountains. The large extent of conversion (up to 70%) observed in the periods of high humidity (above 90%), low temperature (below 10°C and persistence of non-raining strati over the summits suggest that oxidation of sulphur dioxide by hydrogen peroxide to sulphate ions tends to dominate in the region of interest.

1. INTRODUCTION

The phenomenon of sulphate formation in the atmosphere due to the oxidation of sulphur dioxide has received considerable attention in recent years [1]–[5]. It is a well established fact that sulphate aerosols are amongst the primary contributors to acid rains and regional haze. Evidence of such impact is also clear for the Sudeten in south-western Poland. Atmospheric pollutants have induced forest decline at high elevation.

In this study, consideration has been given to the different sulphur species in the atmosphere at the upper parts of the Sudeten. The percentage ratio of particle sulphur to total sulphur measured was higher than that reported in other studies conducted both in Europe [6], [7] and the United States [8].

2. EXPERIMENTAL

Twenty four-hour samples of sulphur dioxide, total sulphur and sulphate in atmospheric aerosols were collected for five days every month from April 1987 to September 1989 at three sampling sites. All of them were located in the western part of the Sudeten, where forest damage has become increasingly frequent.

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Concentrations of sulphur dioxide were determined colorimetrically, using the modified West-Geake procedure [9], [10]. Total sulphur concentrations were determined by the hydrogen peroxide/sulphate method [11]. The sampled air was passed through a slightly acidic 0.3% solution of hydrogen peroxide.

The sampling units comprised a prefilter (Whatman 41, \varnothing 47 mm) for collection of sulphates from particulate matter. The samples collected were extracted in redistilled water at ambient temperature in a mechanical shaker for 2.5 h.

The extracted solution, as well as the absorption solution (hydrogen peroxide method), were analysed for sulphate ions by the adaption of the thoron method [12], [13].

Basic meteorological data were evaluated from on-site observations, others (like mass category, height of the inversion layer, weather conditions in Central Europe, direction of air mass inflow at 850 mb) were submitted by the National Weather Service of Wrocław.

3. RESULTS AND DISCUSSION

The concentrations of all analysed species varied considerably throughout the measuring periods. Several episodes of increased concentrations, especially of total sulphur, were observed. Table 1 summarizes the results recorded in the sampling site at 1362 m a.s.l. for the summer (April–September) and winter (October–March) seasons. Table 2 provides 24-hour concentrations of sulphur dioxide, total sulphur, sulphates and relevant meteorological data for selected case studies. Concentrations of all sulphur species were calculated in terms of sulphur. Table 2 includes solely data sets for air mass flowing from the west.

Table 1

24-hour concentrations of sulphur dioxide, total sulphur and sulphates for air masses reaching the Sudeten summits during summer and winter periods (all sulphur species calculated in terms of sulphur)

Air mass category	Wind direction	Sulphur dioxide	Total sulphur	Sulphates
($\mu\text{g}/\text{m}^3$)				
Summer				
MP	S-SW-W	13 \pm 4	30 \pm 10	10 \pm 5
MP	W-NW-N	17 \pm 13	48 \pm 34	5 \pm 2
CP	E-SE-S	5 \pm 3	5 \pm 2	10 \pm 4
A	NW-N-NE	6 \pm 1	13 \pm 7	9 \pm 4
Winter				
MP	S-SW-W	4 \pm 2	20 \pm 11	3 \pm 2
MP	W-NW-N	15 \pm 6	35 \pm 10	4 \pm 1
A	NW-N-NE	5 \pm 1	7 \pm 4	6 \pm 2

MP – maritime-polar, CP – continental-polar, A – arctic.

Table 2

24-hour concentrations of sulphur dioxide, total sulphur, sulphates and some meteorological parameters for selected case studies at the 1362 m a.s.l. sampling point (all sulphur species calculated in terms of sulphur)

Date	Inflow direction (deg)	Temperature (°C)	Relative humidity (%)	Sulphur dioxide	Total sulphur	
					($\mu\text{g}/\text{m}^3$)	
11/12.08.87	290	3.3	98	23.5	74.2	5.7
13/14.08.87	300	5.0	97	10.0	58.7	6.4
15/16.09.87	280	5.0	93	6.6	66.6	7.1
14/15.10.87	230	2.1	95	1.9	42.1	2.9
10/11.02.88	270	-8.0	99	10.1	21.4	10.3
08/09.03.88	280	-7.5	98	5.4	34.4	5.2
12/13.04.88	250	2.0	65	4.2	23.1	5.4
19/20.04.89	250	1.0	86	10.6	48.2	6.3
28/29.06.89	280	8.2	85	7.3	29.4	5.6

Comparison of the total sulphur concentrations with the concentrations of sulphur determined on the basis of sulphur dioxide analysis shows considerable differences between the two data sets. A paired *t*-test has revealed that they fail to be statistically similar. Therefore, we adopt the hypothesis that the bubbler which contains acidic hydrogen peroxide solution is likely to include not only sulphates obtained via oxidation of sulphur dioxide, but also some other compounds containing sulphate ions. This indicates that a portion of fine particles (assumed to contain sulphate ions) penetrates the filters when the total load is low (small volume air sampled, clear atmosphere). To test it, third sampling line was introduced, in which the sulphates penetrating the filter were absorbed in acidic distilled water (pH = 4.6). It was found that the difference in the total sulphur and sulphur dioxide concentrations was statistically similar (at the 95% confidence level) to the sulphur concentrations determined in acidic distilled water.

The work reported previously supports our observations [14], [15]. Aerosol samples described in the papers were collected on electron microscopic screens and then examined with TEM. Numerous fine particles were found in the smallest size fraction (below 0.1 μm).

Distinct differences in total sulphur and dioxide sulphur concentrations were recorded during the inflow of maritime-polar (MP) air masses from western directions. During inflow of continental-polar (CP) air from eastern Poland and Arctic (A) air from northern Poland and Germany only sulphate sulphur displayed increased concentrations. Sulphate particles from filter analysis represented the most stable portion of atmospheric aerosol.

We assume that the difference in the total sulphur and sulphur dioxide (calculated in terms of sulphur) concentrations is equivalent to the sulphur associated with fine sulphates, and so the highest concentrations of sulphur dioxide and fine sulphates approach 40 $\mu\text{g S}/\text{m}^3$ and 90 $\mu\text{g S}/\text{m}^3$, respectively. This gives the percentage of fine particle sulphur in

total sulphur (the extent of conversion) close to 70%. The application of sole filter analysis to measurements of sulphate concentration has led to a considerably lower percentage of particle sulphur in the total sulphur measured, which ranged from 15 to 30%. These values are consistent with the data reported by OTTAR [16] and ALTSHULLER [8].

Results of the field investigations lead to the conclusion that in the Sudeten the extent of conversion is substantially higher than at other sites, which might have been the result of intensive particle formation. The most favourable conditions for these processes occur when air is flowing from the west. The explanation would be that the air masses from western directions are more polluted than those from other directions. This finding was confirmed by the measurements of nitrogen oxides, total particulate matter, trace metals and PAH concentrations [16]. A substantial increase in these concentrations occurred during the exposure of Sudeten to inflow of air from SW-NW directions. But it is difficult to understand how such large numbers of very small particles could have been transported directly into the region of interest. It is more likely that the upward transport of the influent air masses, sulphur dioxide from the mixing layer undergoes rapid change resulting in sulphate-ion formation. An example is provided by the measurements presented in table 2.

The extremely high concentrations of total sulphur were measured in August 1987 and in September 1987. At that time the meteorological conditions were influenced alternately by cyclonic and anticyclonic weather conditions. There was inflow of cold and humid MP air masses from W-NW directions. Air temperature in the mountains dropped from 10 to 15°C. The summits were above the strati. Sulphur dioxide from the mixing layer might have been converted to sulphate ions during its entrainment into upper atmospheric layers where there is enhanced air humidity and lower temperature. Equally high concentrations of sulphuric acid droplets (smaller than 0.1 μm) in clear atmosphere were reported by SHOW [17]. SHOW [17] concluded that the formation of a substantial fraction of new particles (assumed to be droplets of sulphuric acid) can take place only in humid pre-cleaned air mass system.

The high extent of conversion in the mountains under study, low temperature and high humidity suggest that in aqueous solution an oxidation of sulphur dioxide by hydrogen peroxide rather than conversion of homogeneous gas to particles might have been responsible for the high total sulphur concentrations [4], [18]. This suggestion supports the MIDDLETON et al. [1] and SAXENA and SEIGNEUR [4], [19] models. According to the SAXENA and SEIGNEUR model [4], the reaction of dissolved sulphur dioxide and hydrogen peroxide is highly dependent on temperature, thus contributing appreciably to the total sulphate formed at 5°C. A theoretical investigation of sulphate formation in clouds by SEIGNEOUR and SAXENA [19] has shown that in non-raining strati, oxidation of sulphur dioxide by hydrogen peroxide in aqueous solution dominates, although the gas-phase reaction of sulphur dioxide and OH \cdot radicals also contributes to sulphate formation in the mixing layer. Likewise, the gas-phase reaction with OH \cdot radicals is temperature dependent [19], [20]. At low temperatures (which prevail in the area of interest) the concentrations of OH \cdot radicals seem to be very low.

Other mechanisms of sulphate formation, e.g., reactions of dissolved sulphur dioxide with ozone, do not seem to contribute significantly to sulphate formation in the region of interest. The aqueous-phase oxidation of sulphur dioxide with ozone beco-

mes significant at comparatively high pH [21]–[23]. The atmospheric aerosols in Sudeten are highly acidic [16].

We can also adopt the mechanism of oxidation of sulphur dioxide by oxygen catalysed by trace metal [21]. Such reactions occur in the airborne particles, and they are likely to contribute to the formation of sulphate sulphur which is efficiently retained by the filter. Water extracts from filter samples contained iron and manganese ions (from trace amounts to $640 \mu\text{g}$ of Fe^{2+} /g of particulate and from trace amounts to $120 \mu\text{g}$ of Mn^{2+} /g of particulate, respectively). Likewise, no trace metals were found in the hydrogen peroxide solution.

4. CONCLUSIONS

Differences in total sulphur and sulphur dioxide (in terms of sulphur) concentrations, the results of microscopic examinations, as well as literature reports suggest that the production of particles containing sulphate ions takes place in the upper parts of the Sudeten.

A rapid formation of sulphate ions during the upward transport of the influent air masses is a more likely explanation of high concentrations of total sulphur measured far away from the emitter. The phenomenon may also explain the forest damage which originates in the higher parts of the mountains.

Under conditions typical of the mountains, formation of sulphate ions in the atmosphere through reactions in aqueous solution may be of great significance.

A high extent of conversion was recorded during the inflow of cold and humid maritime-polar air masses from south-western to north-western Europe. At that time air temperature in the mountains dropped below 10°C , humidity was above 90% and the summits were above the base of strati.

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TWORZENIE SIĘ AEROZOLU SIARCZANOWEGO W WYŻSZYCH PARTIACH SUDETÓW ZACHODNICH

Przedstawiono pomiary stężenia dwutlenku siarki, siarki całkowitej i siarczanów w aerozolu atmosferycznym w wyższych partiach Sudetów Zachodnich. Wyliczony stopień konwersji był wyższy niż podany przez uczonych z innych części Europy. Najwyższe wartości stężeń rejestrowano podczas napływu chłodnych i wilgotnych mas powietrza polarno-morskiego z kierunków zachodnich. Z badań wynika, że dwutlenek siarki podlega gwałtownym przemianom do jonów siarczanowych podczas wznoszenia się napływających mas powietrza wzdłuż zboczy. Ze względu na wysoki stopień konwersji (do 70%) rozważa się głównie przebieg procesu utleniania z udziałem nadtlenu wodoru. Sprzyja temu niska temperatura, duża wilgotność oraz niskie pH aerozolu atmosferycznego.

ОБРАЗОВАНИЕ СУЛЬФАТНОГО АЭРОЗОЛЯ В ВЫСШИХ ПАРТИЯХ ЗАПАДНЫХ СУДЕТОВ

Представлены измерения концентрации двуокиси серы, полной серы и сульфатов в атмосферном аэрозоле в высших партиях Западных Судетов. Вычисленная степень конверсии была выше, чем данная учеными из других районов Европы. Самые большие значения концентраций зарегистрированы во время притока прохладных и сырых массов полярно-морского воздуха с западных направлений. Из исследований вытекает, что двуокись серы подвергается турбулентным превращениям к сульфатным ионам во время подъема притекающих массов воздуха вдоль скатов. Из-за большой степени конверсии (до 70%) рассуждено, в основном, протекание процесса окисления с участием перекиси водорода. Этому содействует низкая температура, большая влажность и малое pH атмосферного аэрозоля.