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INTERACTIONS BETWEEN AIR AND ATMOSPHERIC WATER

The pattern of the forestry damage in the Black Triangle region is established based on the forests at higher altitudes. High levels of both pollutants and liquid aerosols at higher parts of mountains are evidenced by the available data from field studies. The statement is well exemplified by the experiments conducted at a site located at Mt. Szrenica (1362 m asl, Sudeten Mts.). In this article, at first the exchange processes between air and atmospheric water are reviewed, and then some results obtained during the Szrenica field measurements are presented.

1. INTRODUCTION

Topography, meteorology, and the distribution of emission sources near the region of German–Polish border (many of these sources are tall stacks built in the 1960s and 1970s), combine to produce enhanced pollutant levels in the mountainous area in Poland. The same pollutants are transported northward through Germany. On the German side, however, due to its orography, there are better conditions for ventilation than in Poland.

The mountains act as a barrier for prevailing winds (from western, south-western and north-western directions) carrying wet air from the Atlantic Ocean. As a result of air streamline deformation produced by topography, mountain clouds are formed due to the cooling and condensation of water vapour in the air ascending the slopes. The ridges can be also immersed in stratus clouds (sub-inversion clouds associated with the high pressure system). Within a year, foggy days are also caused by frontal cloudiness. The clouds of the latter type observed in the mountains have normally their bases at the altitude of 800–1200 m asl. This means that the upper parts of the mountains are often immersed in clouds, in the zone above 1000 m asl, which leads to the very high number of cloudy or foggy days.

Because upper parts of the mountains are exposed both to pollutants and liquid aerosols of high concentrations, these locations are most suitable for studying smog (smoke–fog) interactions. The experiments carried out at Mt. Brocken (MOLLER et al. [5]) and at Mt. Szrenica (ZWOŹDZIAK et al. [16]) corroborate this opinion.

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2. CLEAN AIR SITUATION

In lower layers of the atmosphere, water is everywhere. Its unending circulation begins with evaporation of enormous quantities of water (from the surface of water and the land). Convection currents, caused by temperature differences in adjacent air masses, redistribute vertically the moist air and other atmospheric constituents. Then winds transport water vapour to other regions, where it condenses into clouds, some of which produce rain and snow.

The exchange processes between air and atmospheric water begin with the cloud formation. As saturation is approached the aerosol particles containing deliquescent or hygroscopic materials accrete increasing amount of water. As saturation is exceeded some particles become activated to form cloud droplets. Thus, many particles in clean air serve as surfaces on which water vapour can condense.

All natural atmospheres contain a substantial number of aerosol particles which makes both condensation and cloud formation much easier. These particles enter the atmosphere in a variety of ways: dust, volcano, forest fires, salt from ocean spray and sulphate particles produced by phytoplankton in oceans. Depending on their size and physical and chemical composition, some particles are much more active as condensation nuclei than the others. These different particles compete with each other for available water vapour, leading to such a range of droplet sizes within the cloud that is partly dependent on the size–composition spectrum of the original aerosol. Cloud atmosphere contains also non-nucleated "interstitial" aerosol, consisting of particles which have not entered the nucleation process. These particles may become attached to water phases by a number of individual mechanisms (e.g. impaction and interception).

The degree to which atmospheric water is affected by the pre-existing aerosol composition depends on the scavenging efficiency (the mass fraction of pre-cloud aerosol that is incorporated into cloud water by the nucleation process). In clean atmosphere, the aerosol scavenging efficiency is close to unity (JENSEN and CHARLSON [4]), but that for the aerosol concentration typical of industrial regions is not clear.

The second major process, which begins immediately after cloud formation, is the uptake of the material present initially as gaseous phase species. The rate of sorption is determined by the turbulent transport of species to the droplet surface, their molecular diffusion through the liquid water, and by the rate of chemical reaction if any.

The effective uptake of trace gases depends on their physical solubility (according to Henry's law), on the degree of their dissociation in cloud water and on the rate of their liquid phase reactions. Because of small amount of trace species in gaseous phase in clean atmosphere, these gases contribute little to cloud water composition.

The picture is quite different over industrial area compared to that of clean atmosphere: the increase in pollutant concentration in the air leads to numerous chemical reactions in aqueous phase which are responsible for the transformation of many species into acids appearing in high concentrations in the air (TANNER [12]). Thus these strong acids will be a direct contributor to cloud water composition.

3. IMPACT OF AIR POLLUTION

Condensation nuclei are most abundant over industrial regions, where highly polluted air may contain nearly 1 million of particles per cubic centimetre. Their number decreases in a cleaner atmosphere, sometimes reaching the value lower than a few nuclei per cubic centimetre.

In a clean air, there are relatively large particles of small particle number concentration, while in a polluted one – the aerosol particles of much larger particle number concentration. The latter are generally much smaller in size.

The question of the mass fraction of pre-cloud aerosol over industrial areas that is incorporated into cloud water has been the subject of numerous investigations.

Results of field studies and model calculations have varied considerably. JENSEN and CHARLSON [4] indicate that the efficiency of nucleation scavenging is as low as 40% for the aerosol typical of urban air and for stratiform clouds. Low scavenging efficiencies are also reported by WALDMAN and HOFFMANN [13] and MUNGER et al. [7] in their study of radiation fogs. MUNGER et al. [7] and COLLETT et al. [3] have also observed high scavenging efficiencies for marine stratus and mountain clouds. Because the aerosol concentration, size distribution, and saturation conditions in clouds may be highly diversified as well as there are some inherent uncertainties in the scavenging calculations, we do not generalize these results. Also the microphysical processes that govern the liquid water content may cause a complication. They consist in condensation, evaporation, autoconversion of cloud droplets to rain -drops and collection of cloud droplets to raindrops.

Attachment of gaseous pollutant to water droplet differs from that of aerosol in several important ways. Owing to their high diffusive mobility, the advective/diffusive attachment of gas molecules dominates other mechanisms of mass transfer. Gas molecules can migrate to a water droplet surface and be absorbed within its interior, but its desorption to the gaseous phase is also possible. This is in a stark contrast to the behaviour of nonvolatile aerosol particles which remain associated with the aqueous phase unless total evaporation occurs. In a state of diffusional equilibrium, there is no net gas uptake by the aqueous phase, with absorption and desorption of molecules being in dynamic balance.

The mechanisms of pollutant gas capture often combine with chemical reactions of aqueous phase. SCHWARZ [8] reported that simultaneous mass transfer and chemical reaction rates were functions of droplets size, acidity and temperature in SO_2–O_3 and SO_2–H_2O_2 systems.

Soluble gases rapidly exchange across the air–water interface (in seconds) and sorption rate can be predicted from thermodynamic considerations (SCHWARZ and FREIBERG [9]). However, the solubility of trace gases in atmospheric water is very different. Such gaseous components as HCl, HNO_3, NH_3, NO_3, H_2O_2 are readily soluble in water.

The effective solubility of gaseous pollutants depends not only on their physical solubility, but also on the concentrations of all gaseous and particulate species in the

aqueous phase and on pH of this phase. For example, the effective solubility of SO_2 increases with a decrease in acidity caused by high NH_3 and alkaline dust concentrations. The SO_2 uptake increases in the presence of high concentration of oxidant, too. But in-cloud oxidation of SO_2 increases the acidity of the cloud droplets, modifying the dissolution of other chemical species, e.g. NH_3 and HNO_3, in the cloud droplets. In the past decade, substantial advance has been made in describing the rates of aqueous phase reactions in clouds.

We should emphasize that when many reactive gases dissolve and react in atmospheric water, the concentrations of trace gases in clouds are modified through two mechanisms:

• clouds scatter an incoming solar radiation, generally reducing photolysis rates below clouds (radiative forcing);

• during convective updrafts and downdrafts, the pollutants emitted are rapidly exchanged between the boundary layer and free atmosphere (vertical mixing).

Early studies and some recent studies of in-cloud reactions between dissolved constituents have been carried out in order to explain how sulphuric, nitric and organic acids are produced in clouds. It has been suggested that sulphuric acid is one of the more important anthropogenic acids in the atmosphere and is predominantly produced via the aqueous-phase reactions in clouds. Most acid-forming aerosol particles are usually so hygroscopic that the nucleation scavenging dominates whenever cloud-formation processes proceed.

In conclusion, it should be emphasized that a water droplet formation in the atmosphere and parallel processes of pollutant capture are highly dependent on physical processes. In the vicinity of pollution sources, when NO_x and SO_2 concentrations are high, aqueous reactions can significantly promote the formation of acidic aerosols and suppress an ozone formation.

4. THE SZRENICA FIELD CAMPAIGNS

A number of intensive field campaigns took place at the Szrenica mountain located in the Sudety Mountains on the border between Poland and the Czech Republic, where the degradation processes in the forests, manifested by reduced growth of trees and their death, have begun since the early 70-ties (ZWOŹDZIAK and ZWOŹDZIAK [14], [15]; ZWOŹDZIAK et al. [16], [17]). The air masses reaching this mountainous site come from heavily polluted regions, thus this region seems appropriate to study the interactions of many pollutants in aqueous and gaseous phases.

However, the experimental evidence accumulated to 1994 indicated that there was no simple answer the question, under what ambient conditions one could expect the highest concentrations of both primary and secondary pollutants to occur in the mountains (ZWOŹDZIAK and ZWOŹDZIAK [14], [15]; ZWOŹDZIAK et al. [16]). At first we analysed these cases by considering the impact of industrial centre located upwind in the NW and SW directions as the maxima of pollutant concentrations were ob-

served in those sectors. Afterwards we tried to explain these observations based on various meteorological factors as well as physical and chemical transformations of pollutants. High pollutant concentrations were strongly correlated with westerly, south-westerly or north-westerly flows; however, these winds were not always associated with high pollutant concentrations. Other meteorological conditions promoting the formation of pollution episodes were high pressure systems, with moderate winds, which were centred over central or eastern Europe (ZWOŹDZIAK et al. [16], [17]). But a full understanding of the processes responsible for the concentration variations in the Karkonosze Mts. required the analysis of local and regional meteorology and transport mechanisms, layering processes and their effects on the formation of air pollution episodes. These processes were studied in detail within the framework of EASE (Emission Abatement Strategies and the Environment) Project (ApSIMON et al. [1]). Theoretical studies were supported by routine monitoring and extensive field campaigns. The first experimental campaign was conducted in the Karkonosze Mts. during September/October 1995. The next ones ran in August 1996, July 1997, August 1998 and July 1999.
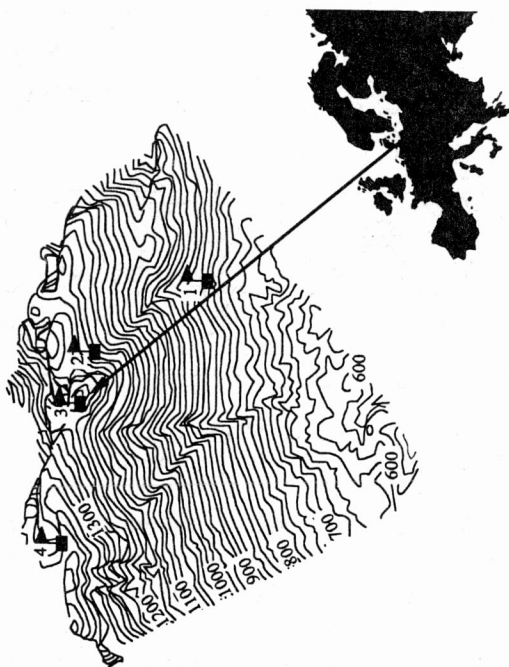

Fig. 1. Monitoring sites during the field campaign, 1995

The main site of the measurement campaigns was in the vicinity of Mt. Szrenica (1362 m asl) in the Karkonosze Mts., the first highly placed site exposed to the air masses coming from the central and western Europe. Figure 1 shows the location of measuring sites. Three of them at the altitudes of 840, 1165, 1332 m asl are referred to

as Kamienczyk, Ski-hut and Szrenica. Site 4, Labska Bouda, a national monitoring site of the Czech Republic, is located in the lee of the summit at the height of 1220 m asl. In figure 2, for example, the time series of SO_2, O_3 and NO_2 mixing ratios (30 minute averaged) measured at these sites are presented. It is well seen that in the air pollution monitoring stations the enhanced levels of SO_2, NO_2 and ozone are episodically measured.
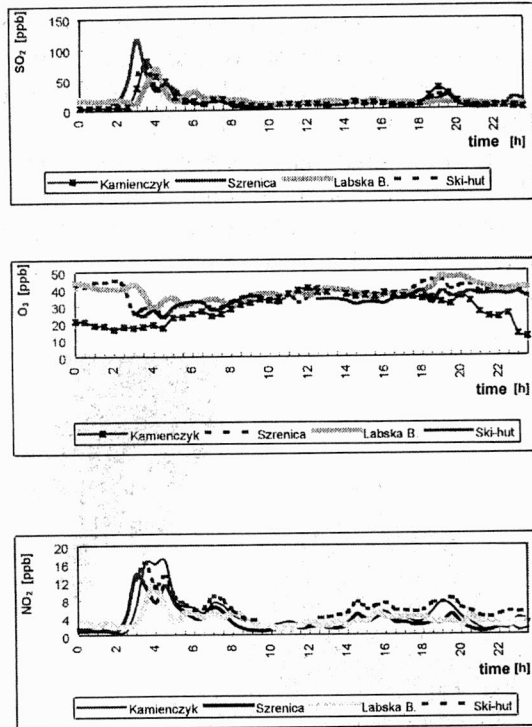

Fig. 2. Sequences of 30-min SO_2, O_3 and NO_2 mixing ratios
for different monitoring sites on September 23, 1995

The air masses reaching this region contain pollutants from different sources, local and regional, including industrial facilities, thermal power plants and motor vehicles. Since a long time back trajectories have been a standard tool of characterising source –receptor relationships in air pollution field campaigns (SEIBERT [10]; STOHL [11]). However, it should be kept in mind that trajectories do not always resemble exactly the actual path of the air mass. Trajectories with a length of several days can be subject to considerable errors, resulting from uncertainties in the wind fields, interpolation procedure in space and time, and from numerical errors (SEIBERT [10]). Thus, the use of back trajectories to identify surface source regions for regional or long-range transport is suitable only for a rough approximation rather than an exact source –receptor meteorological link.

The coordinates of air masses arriving at Mount Szrenica every 12 h were calculated back to their origin 48 h earlier for the whole period studied in September/October, 1995. Figure 3 shows back trajectories for 1–4 October, 1995. The bold line represents the "dirty" air mass. According to MOY et al. [6] we selected two distinct classifications for our study. The air mass was "dirty" if the SO_2 episode was observed (SO_2 episode was characterized by 30-minute averaged SO_2 concentrations higher than 15 ppb at least at two monitoring sites); otherwise the air mass was "clean". It also happened that at the same type of back trajectories "clean" and "dirty" air masses arrived. Thus, we tested the hypothesis that the variability of pollutant levels observed in the mountains is highly dependent not only on the synoptic-scale weather patterns, but also on the layering of pollutants prior to their arrival to the monitoring stations. The transport and concentrations of pollutants are also strongly influenced by clouds.
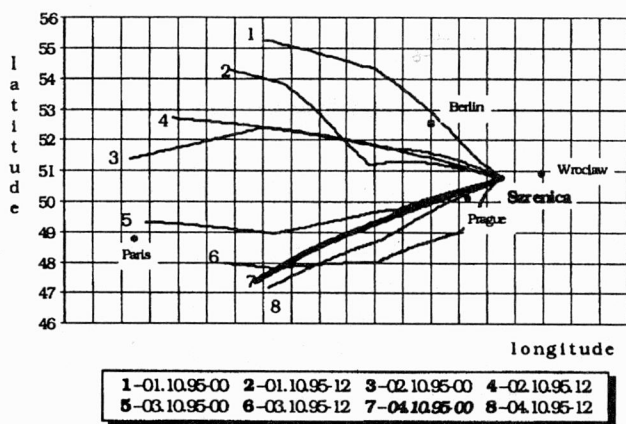

Fig. 3. 48-back trajectories for October 1–4, 1995, Szrenica Mt.

Analyses of the data of our interest collected during following field investigations have revealed that pollution episodes occur due to development of a multi-layer structure over a larger area as it is shown in figure 4. Ascending of pollutants within a nocturnal residual layer to the boundary of anticyclonic subsidence inversion resulted in the overnight appearance of the episodes in the upper parts of the mountains (sub-inversion fog was observed). It is noteworthy that during that event the SO_2 concentrations meandered (in time) from peak to peak amplitude of up to 20–30 ppbv at the top sites and to lesser extent at Kamienczyk. Fluctuations in pollutant concentrations ("waves") during this episode probably were caused by relatively unstable air beneath the inversion layer. The existence of small turbulence in stable conditions due to even slight irregularities in the surface height was described by CHIMONAS and NAPPO [2]. When the air is flowing over the mountains, it is likely for some air from aloft to be mixed downward and thus contributing to a drop in SO_2 and NO_2 concentrations at the top sites.
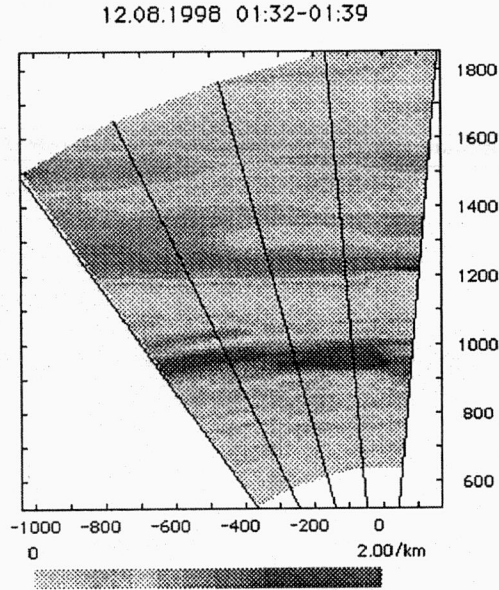
12.08.1998 01:32-01:39

Fig. 4. Vertical profile of extinction coefficient measured at the Kamienczyk site
on 25 July, 1997 between 01:01–01:27 LT

It was also confirmed that the same type of episode could be related to a slight ascent of mixing height during the day allowing the pollutants previously trapped below the layer to mix up to higher elevations. But this kind of episode was documented when the vertical transport was limited by the existence of a strong upper inversion layer. The second type of episodes, which was identified only during the night time, was associated with the regional/local transport of "freshly emitted plume" being not effectively diluted. In these periods the atmosphere was also structurally differentiated. The whole process involved plume penetration up to stable layer and subsequent transport in this layer, or more likely it was as follows: pollutants from high stacks began to accumulate in the upper part of a nocturnal residual layer, i.e. at its boundary with a stable zone, simultaneously a radiative cooling progressed near the surface. Due to a slow transport of these polluted air masses towards the mountains (light winds were the crucial parameters) high levels of pollutants were monitored at the upper parts of the Karkonosze Mts.

The episodes of the "fresh plume" were associated with the decrease in ozone concentration by several tens of parts per billion (ppb), while the episodes of the "aged plume" were accompanied by the changes in ozone concentrations by several or, rarely, more than ten ppb.

The experimental data suggested that daily photochemical formation of ozone from its precursors could approach maximally a dozen ppb during the study; this can be added to the "background value" ranging from 30 to 40 ppb for the layer above the layer of nocturnal inversion. It was also noticeable that the rise in ozone concentration

corresponded both to the diurnal photochemical activity and (to the same extent) to transport mechanisms (vertical movements and advection). Spatial variation in ozone concentrations was estimated by merging the information about the LIDAR data (figure 5) with the results from monitoring stations at different altitudes (figure 6).
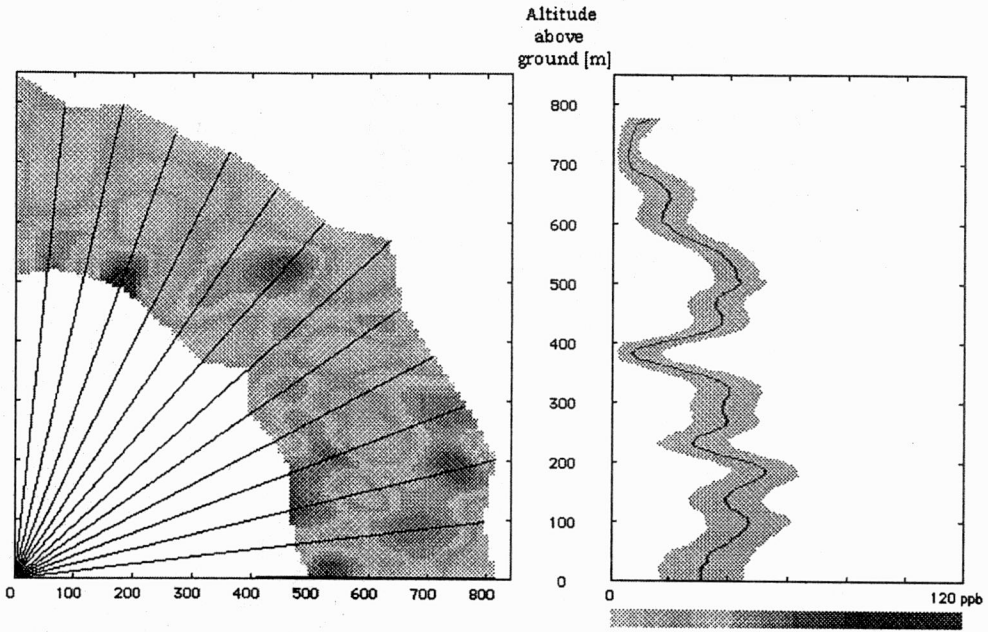

Fig. 5. Vertical profile of O_3 mixing ratio measured at the Kamienczyk site
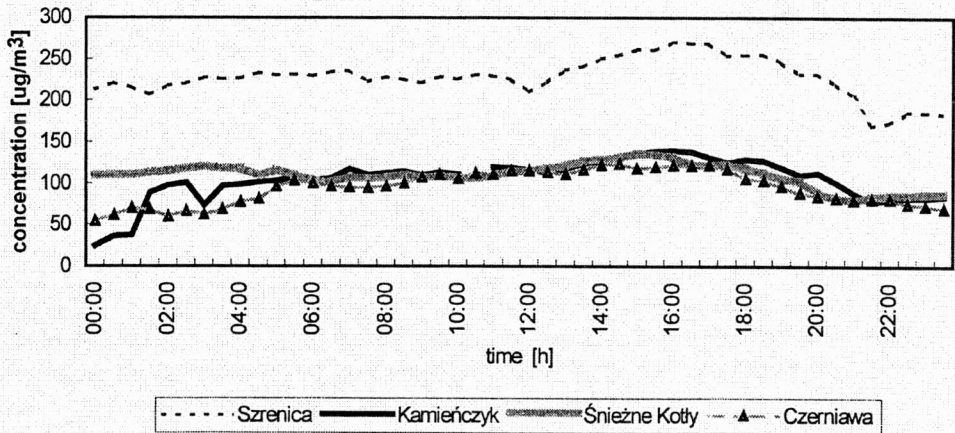on 24 July, 1997 between 23:01-23:27

Fig. 6. Time series of 30-min O_3 mixing ratio and temperature
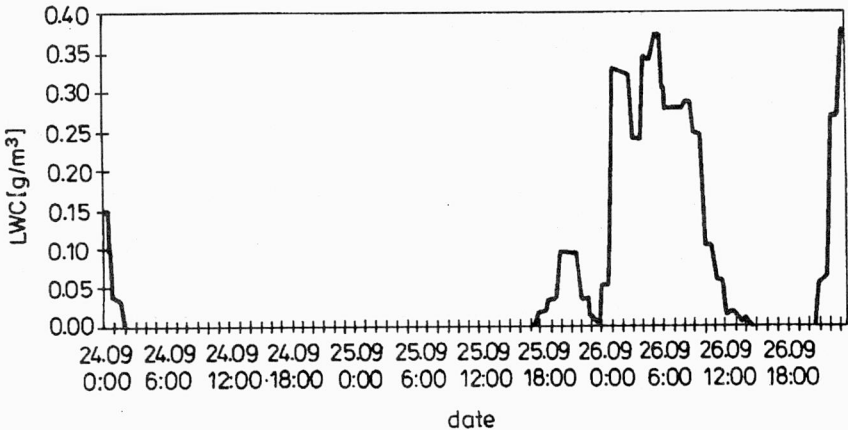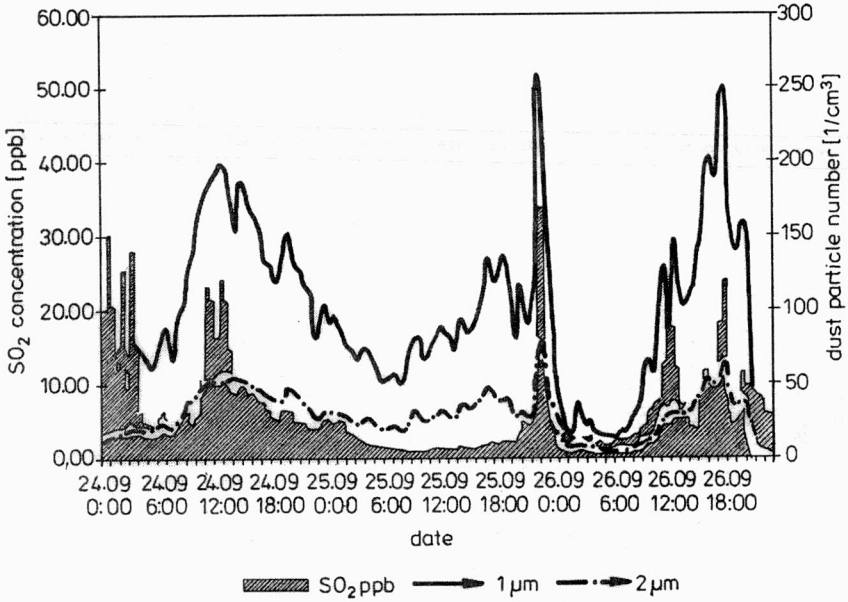for different monitoring stations on 24 July, 1997

Fig. 7. Time series of liquid water content (LWC), aerosol number
and SO₂ concentrations at Mt. Szrenica on September 24–26, 1995

The time-dependent variations of SO_2 concentrations, aerosol particle number concentrations and LWC have shown that aerosol particles of the diameters exceeding 1 μm are very efficiently scavenged by liquid aerosols (figure 7). The increase in aerosol particle number concentration has appeared to be pronounced for no cloud or fog events. The behaviour of SO_2 was fairly similar, except for the events with low LWC (sub-inversion fogs or clouds during the dissipation stages). Concentrations of sulphate and nitrate ions higher than 100 μeq/dm³ were found routinely, and the

maximum concentration reached the value of 2631 $\mu eq/dm^3$ and 1194 $\mu eq/dm^3$, respectively.

Droplet deposition can be the dominant process for the input of sulphur and nitrogen species at highly elevated sites that are frequently affected by clouds. However, the deposition estimates of this process are uncertain. The interesting result from the short-term studies is the occurrence of increasing concentrations of nitrates in cloudwater samples during cloud events with the low LWC. This finding needs further investigation. In order to estimate the influence of chemical interactions in cloudwater, meteorological variables such as liquid water content (LWC), pressure or temperature must be specified.

Our recent studies carried out in order to answer the question whether acidifying and related species are taken up by cloud water from the surrounding (interstitial) air during atmospheric transport. As a result, the precise measurements of all relevant parameters like gaseous compounds, aerosol concentrations, meteorological conditions at the site are obtained. This will allow us to specify boundary conditions for the laboratory experiments and furnish chemical data for the numerical model.

5. CONCLUSIONS

The investigation presented above covers a wide range of scientific problems, which can only be satisfactorily studied by the application of very specialised techniques. Obviously, no single laboratory is capable of answering several questions concerning the influence that aerosols and clouds have on air quality in an industrialized background area. Only a close collaboration between different research groups which carry out field, laboratory and modelling studies ensure the success of such investigations.

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PROCESY WYMIANY MIĘDZYFAZOWEJ W ATMOSFERZE

Zniszczenia lasów na terenie Czarnego Trójkąta obejmują przede wszystkim wyższe piętra Sudetów. Wynika to faktu, że w wysokich partiach gór są okresowo rejestrowane zarówno duże stężenia zanieczyszczeń gazowych, jak i aerozoli kropelek cieczy. Dlatego uważa się, że te obszary najlepiej nadają się do oceny oddziaływań między gazami i mgłą, czego przykładem są badania terenowe przeprowadzone na Szrenicy (1362 m n.p.m.).

Najpierw omówiono główne zagadnienia związane z procesami wymiany między zanieczyszczeniami gazowymi, aerozolami i chmurami, a następnie przedstawiono niektóre wyniki pomiarów przeprowadzonych na Szrenicy.