ANNUAL VARIABILITY OF OZONE ALONG ALPINE HILLSIDES

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ABSTRACT

Over a period of more than two years (March 1989 till June 1991) ozone and nitrogen dioxide have been monitored along twelve alpine hillsides in the Austrian alps. The profiles had a heigth-resolution of 100 m and cover a range between 400 m and 1800 m asl, that is 100 m to 1100 m above the bottom of the valleys. They were situated in remote rural areas as well as in the vicinity of polluted urban and industrial areas. Both trace gases were monitored by means of integral chemical (SAM-surface active monitor) methods with a measuring cycle of two weeks.

The concentration of ozone exhibits a substantial annual variation over the entire heigth range. In summer highest ozone levels are observed near ground and the top of the mountains, whereas in winter the maxima are found mainly in the crest regions. The overall ozone burden shows a relative maximum near the temperature inversion layer in the valleys and an absolut maximum at the crest.

1. INTRODUCTION

By the end of the 1970's there was growing recognition, that air pollution was threatening the alpine ecosystem. Reports on damaged forests were published and the public realized, that not only some regions in the vicinity of powerplants or heavy industry were effected, but more or less the whole alpine region. Acid rain was the cause identified first. Actions for a reduction of sulphurdioxide emissions were set up, but soon it became clear that other pollutants and photochemical reaction products may play a more pronounced role. Investigations of forest authorities showed, that even in remote rural areas forests were damaged at a great pace. One striking feature is that the severest problems ocurre in distinct heights.

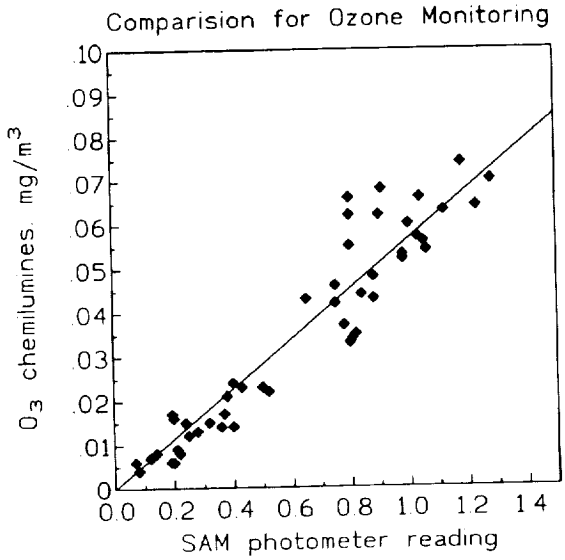
Like other alpine countries Austria has crowded populated valleys and basins combined with heavy transit traffic. More than two third of a year these basins are not ventilated very well. Although the emission controls are more rigorous nowadays we are faced with increasing air pollution.

By the mid 1980's the implementation of an air pollution monitoring network was still in its beginnings, especially in remote rural areas. Although there were indications, that Central Europe and especially the alpine regions are exposed to higher ozone concentrations as compared to other regions in Europe, the knowledge of the spatial distribution of NOx and ozone burden in inneralpine valleys was not sufficient to decide if ozone was a threat or not. Reiter et al.(1987) and Paffrath and Peter (1988) observed higher ozone concentrations in the heigth range of 400m - 1400 m above ground and Broder and Gygax (1985) and other authors investigated the gradient of ozone in northern alpine regions. All investigations were limited in time, using airborne or balloon measurements or limited in space with instruments fixed on cablecars. It was not clear if these observations can be generalized for most inneralpine valleys or not. Moreover there was and is still a lack of regional models fitting such complex

terrain to decide wether local conditions, i.e. wind systems and emissions have significant influence on vertical ozone profiles or not. For economical reasons it is impossible to gain a sufficient spatial data coverage using sophisticated instruments, therefore it is necessary to utilize inexpensive passive samplers. To study the variability of ozone with height we set up profiles ascending twelve alpine hillsides in the province of Styria in the southeastern part of Austria, ozone was monitored for more than two years starting March 1989.

2. Passive Samplers for Ozone Monitoring

It is obvious that monitoring of air pollutants at a large number of sites to cover a large region with a dense grid could not be performed with sophisticated instruments due to the high costs of each device. Simple and therefore inexpensive techniques were developed to cover this demand. One possibility is the use of passive samplers. One particular type belongs to the group of the socalled surface active monitors (SAM). Based on the very specific reaction of ozone with the blue dye indigo to the red isatin, we developed such a sampler (Remler and Kosmus, 1988). The preparation is very simple. 2 g of indigo are dispersed in distilled water by means of an ultrasonic bath and with this dispersion of very fine dye particles chromatographic paper is impregnated two times. In between and at the end of this procedure the paper is dried at 80° C in an oven. This paper of about 10 x 10 cm in size is fixed on the surface of a cylindrical body and is exposed to the ambient air during a period of several days. The whole device is covered by a bell shaped shelter to protect it from rain. Ozone molecules reaching the surface of this paper can react with the exposed indigo. Constant deposition velocity assumed this amount should be proportional to the number of molecules in the volume of ambient air or in other terms, the number of deposited molecules should be proportional to the concentration (mg) of ozone per volume (m^3). This proportionality is given by the amount of the reaction product isatin. After exposure the paper is extracted with ethanol and the isatin is measured photometrically. The validation of this method consists mainly of the exposure of SAM's in the vicinity of permanent instrumental monitors based on chemiluminescence. The mean of the measured ozone concentration during the exposure period is compared with the photometric absorption of the isatin concentration. The following figure 1 shows such an comparision. This is a result for a 2-week exposure at two different monitoring sites for 24 periodes. For higher ozone concentrations the period has to be shortened to one week or the paper has to be soaked in a mixture of glycerol-phosphate buffer at the beginning to reduce the reaction rate. There are many advantages to apply SAM's in a large number, such



as simplicity and no maintenance and power is required, but with the loss of real time data, only average concentrations are given over the whole sampling period. The precision is mainly lost with rapidly changing or even fluctuating concentrations. It depends on the analytical problem if this could be accepted.

3. Observations and Results

The profiles have a resolution in altitude of 100 m and cover a range between 400 m and 1800 m above sea level, that is from the bottom of the valley up to the crest, which is in most cases 1100 m above ground. They are situated in remote rural areas as well as in the vicinity of polluted urban and industrial areas. Nearby continuous measuring instruments based on chemilumenescence supply additional data for comparison and verification. A measuring cycle of two weeks was applied, therefore our method can not exhibit short term variations. Apart from the changing weather pattern (global radiation, wind, humidity, precipitation, temperature etc) and smallscale meteorological effects (local valley wind systems), micrometeorological conditions due to varying deposition environment such as vegetation and snowcover play an important role for the quantification of the results. Because it is out of the scope of this short paper to discuss the characteristic pattern of each individual profile, some common behaviour concerning annual variability and dependence with height could be deduced.

As an example the following figure 2 shows the time series from one specific hillside. Near ground we

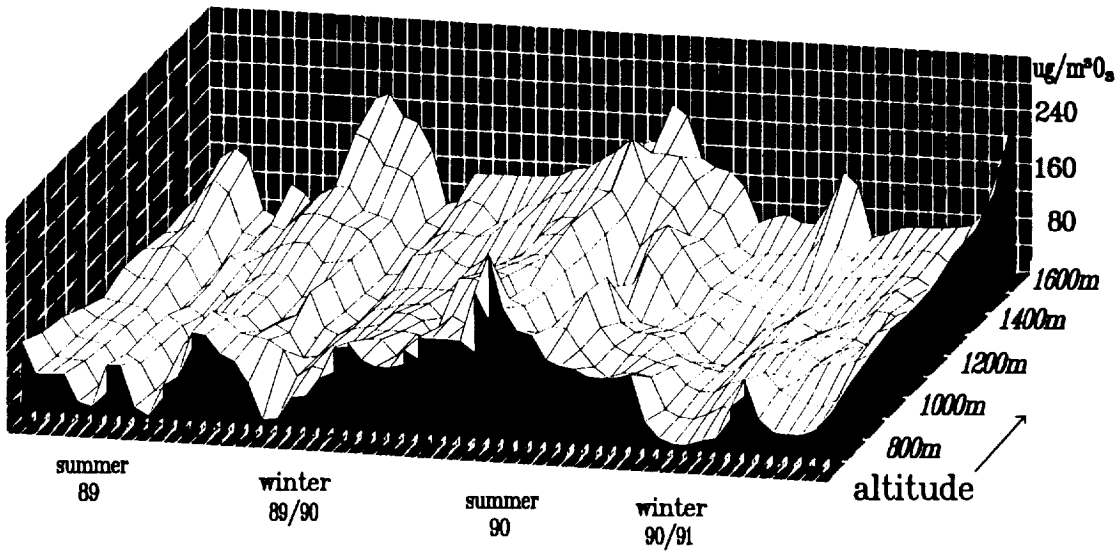


Fig. 2. Seasonal behaviour and dependence with height (asl) of ozone concentration.

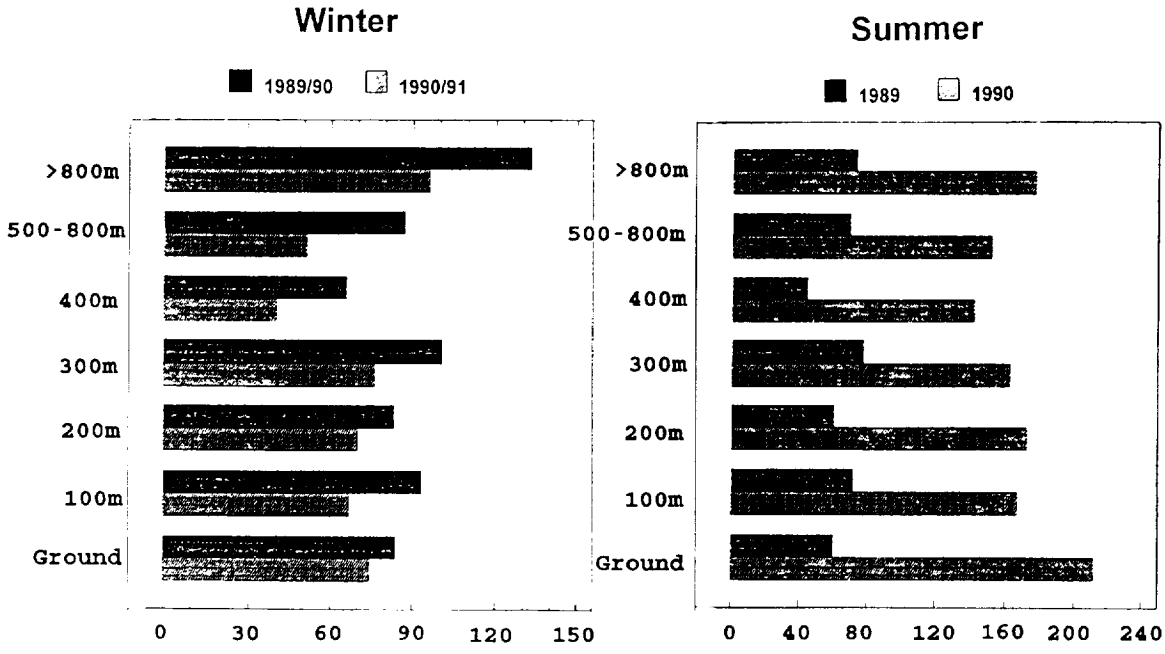


Fig. 3. Overall ozone burden ($\mu g/m^3$) in different altitudes for winter and summer

observe the highest values during autumn 1989 and summer 1990 which is attributed to the exceptional high sunshine duration in both seasons. The differences between the two summers 1989 and 1990 is attributed to a very rainy summer in the first year. The relative high values in winter 1989/90 might also be due to the exceptional hight sunshine duration, a record since more than a century, leading to high local traffic to skiing resorts. The increased emission of ozone precursors results in an accumulation of ozone in high altitudes.

To demonstrate the different course of ozone with altitude more precisely we show in figure 3 the average ozone burden in two different seasons, winter and summer 1989 and 1990 from the same hillside. For the winter seasons we observe an increase from the ground up to a local maximum at about 300m above ground. From the minimum at 400m the concentration of ozone increases up to a maximum at the top of the mountain. The minimum coincides with the average height of the temperature inversion layer in alpine valleys. In the summer we observe the maximum at or near the bottom of the valley, a minimum around 400 m or 500 m above and again a maximum at the crest. The height of the minimum varies sligthly from one hillside to the other, depending on local conditions, local wind systems, etc.

In spring and autumn the profiles exhibit either winter or summer behaviour, depending on the prevailing weather pattern. It is interesting to add, that the intervariance of the height-profiles is a minimum in winter 89/90 and summer 1990, i.e. low variabilty between individual heights, time and sites and a maximum in summer 1989 and winter 90/91. This shows the over all dominant influence of macroscale high pressure systems over central Europe for the production of ozone. In periodes which are dominated by low pressure systems, increased convection and rapid changes of air masses the differences between the individual profiles appear more pronounced. For this investigation and even more general for the whole alpine region we have take into account that the mountain barrier acts as a weather divide. As a result we can distinguish for the ozone different behaviour for inner alpine basins, valleys at the northern and southern part.

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