The VOTALP Mesolcina Valley Campaign 1996 - Concept, Background and some Highlights

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Abstract

The Mesolcina Valley campaign was an important part of the VOTALP project. Its main goals were the study of the effects of thermal wind systems on horizontal and vertical ozone transport over various distances, and on local production of ozone in an Alpine valley. The field measurements took place in the Mesolcina Valley in southern Switzerland in July and August 1996. The Mesolcina Valley is typical for the Alps for its size and its rural character, and contains an important traffic route. Ground-based and airborne instruments were deployed to obtain a four-dimensional chemical and physical picture of the valley atmosphere and the surroundings. Field measurements were complemented by numerical modeling studies. An overview of the campaign, its geographic background, and the measurement plan is given together with selected highlights of the results obtained so far. A synoptic-climatological approach tries to evaluate the representativeness of the observation days. It was found that during the campaign representative data for typical ozone days were collected, while extreme events did not occur.

The main results of the campaign are that very high pollutant concentrations at the Alpine crests are the effect of advective, larger-scale transport, mainly from the Alpine forelands. The valley is very effective in pumping air into elevated layers during the day, with the slope winds probably carrying the bulk of the air volume to higher levels. Up to five times the valley volume may be exported during one upwind phase. Net local production is estimated to be approximately 3 - 8 ppb h⁻¹ of ozone, but seems to be compensated by dry deposition. This indicates that the Alpine valleys may be important net sinks of air pollutants, which may lead to negative impacts on the Alpine ecosystems.

key word index: Alps, Alpine boundary layer, mountain meteorology, ozone, photochemistry

1. Introduction

The influence of the Alps on the atmosphere has been studied for more than a century (e.g. Fournet, 1840). Emphasis was put mainly upon dynamical issues. It is only in the past two decades that questions of atmospheric chemistry have become the topic of specifically designed studies in mountainous areas. Field campaigns such as TRANSALP (Ambrosetti *et al.*, 1998), Pollumet (Neininger and Dommen, 1996), ALPTRAC (Puxbaum and Wagenbach, 1998), ASCOT (Clements *et al.*, 1989), SCCCAMP 1985 (Hanna *et al.*, 1991), and Pacific'93 (Steyn *et al.*, 1997) investigated various aspects of air pollution in mountainous terrain.

Questions regarding the interaction between Alpine ecosystems and the atmosphere were brought up when air quality and its influence on the mountain environment were recognized as important factors for the sustainability of human activities in remote Alpine areas. One key species for air pollution is ozone, which may reveal its destructive influence far away from the primary emission sources. The VOTALP (Vertical Ozone Transport in the ALPs, Wotawa and Kromp-Kolb, 1999) field campaign has been performed to study the transport, production and exchange of ozone from various source regions and over different transport distances into and within the Alps. One such transport channel are valleys with their thermally-induced circulation systems (e.g., Lehning *et al.*, 1996). These wind systems exhibit a diurnal cycle with horizontal winds blowing up-valley during daytime and down-valley during nighttime if the weather is sunny and synoptic pressure gradients are not too large. Inside the Alps slope winds take over part of the vertical transport of species from the valley boundary layers to the lower free troposphere. Such wind systems have been investigated by a number of researchers, and Whiteman (1990) gives an overview of knowledge on the meteorological aspects of valley wind systems. Recent work on air quality aspects of valley wind systems has been published in Banta *et al.* (1997) and McKendry *et al.* (1997). The horizontal inflow and outflow of air through the valley mouth must be compensated by a vertical flow across the interface that separates the valley atmosphere from the free troposphere aloft. This exchange mechanism is still not well understood because of the lack of quantitative information on the magnitude of the exchange. Numerical modeling generally suffers from the lack of sufficiently resolved input data.

The valley campaign was designed to yield a dataset for the study of the exchange processes between a valley atmosphere and the free troposphere, and of the chemistry involved. Basically, three questions were addressed,

- 1) what are the effects of valley winds and slope winds with respect to ozone concentrations within and above the valley?
- 2) how important is the in-situ production of photo-oxidants in the Alpine valleys?
- 3) how important is the horizontal and vertical advection of pollutants from adjacent plains into an Alpine valley?

The VOTALP valley campaign tackled these questions with both measurements and numerical modeling. This paper gives an overview of the observations made during the valley measurement campaign, which took place in the summer of 1996. It contains the necessary information common to all Mesolcina Valley papers in this

special issue, plus a selection of highlights. Other results will be discussed more thoroughly in the subsequent papers in this issue.

2. Geographical setting

2.1. Landscape

The Mesolcina Valley in southern Switzerland (Fig. 1) was selected for this study, because of its position south of the main Alpine crest under the influence of the circulation system between the Alps and the Po Basin (Italy). It stretches from the San Bernardino Pass to the Ticino River valley near the city of Bellinzona. The Ticino River valley is on the St. Gotthard Pass route, one of the most important European north-south highway traffic routes across the Alps. Orographically, there is a direct connection from the Mesolcina Valley to Lago Maggiore to the Po Basin, along which a part of the air may be exchanged between the valley and the foreland by the valley breeze. However, the bulk of traffic follows the route directly south-north over the low hills and the Monte Ceneri Pass. In many cases polluted airmasses from the Milan metropolitan area move towards the Alps as a plume, approaching the Magadino Plain (the flat area between Bellinzona and the Lago Maggiore) and the Alpine valleys from south-east rather than along the Lago Maggiore (Prévôt *et al.*, 1997), as illustrated by the wind field in Fig. 4, with additional comments in Section 5.1. Numerical simulations show that the flow along the lake may be diverted into the valleys north of Lago Maggiore, without reaching the Mesolcina Valley (Grell *et al.*, 1999, this issue). The flow over the Monte Ceneri Pass, however, may later in the day reach the Mesolcina Valley.

The Mesolcina Valley is characterized by its narrow cross section and its steep sidewalls with inclinations of up to 40°. It is roughly 40 km long and about 10 km wide at crest height. The flat valley floor is 1 km wide in the southern half, while practically absent in the northern part, yielding an approximate V shape there. The crest height varies between 2000 and 3000 m above mean sea level (MSL), the valley floor ascends from 240 m MSL (Moësa river mouth) to 2065 m MSL (San Bernardino Pass). At two places the valley axis is bent, so that the valley can be divided into three sections. The uppermost section from the San Bernardino Pass to Pian San Giacomo is the most complicated with regard to topography (and only marginally covered by measurements). The middle section between Pian San Giacomo and Grono is approximately NNE-SSW oriented. The third section between Grono and the Moësa river mouth is ENE-WSW oriented. The only major tributary valley is the

Calanca Valley, which branches off the Mesolcina Valley near Grono. To minimize possible influences from the Calanca Valley, measurement efforts were concentrated in the middle section. The valley floor consists mainly of grassland (pastures), while the sidewalls were covered with forests (mostly deciduous trees) up to the timberline at about 1800 m MSL. Alpine meadows and bare rock are found above timberline.

2.2. Climate

The climate is typical for a valley south of the Central Alps, where Mediterranean airmasses dominate. Summers are characterized by long-lasting fair weather periods with much sunshine and intense thunderstorm activity associated with heavy, short-duration rainfall events. Convective activity triggers the formation of clouds in the afternoon. Often haze can be observed entering the area from the south, significantly reducing the visibility. Northerly advection over the Alps leads to north foehn within the valley, which often hinders air from the Po Basin to progress northward. Typical for such situations are clear skies, high insolation, slightly higher temperatures in the lower parts of the valley and low humidity (Urfer *et al.*, 1979).

In fair weather situations with weak pressure gradients a thermal circulation system with mountain winds during the night and valley winds during the day develops. This circulation is part of a more complex and spatially more extended wind system that exchanges air between the Alpine crests and the foothills or the foreland, i.e. the Po Basin. Depending on the synoptic situation, two different appearances of the valley circulation can be distinguished (Ambrosetti *et al.*, 1998). The first appearance corresponds to the classical valley wind driven by purely thermal forces, and develops more or less independently of the weak airflow aloft, which can even be northerly. This type is called 'Inverna'. The second appearance of the valley wind, called 'Invernone', is stronger, because the thermo-topographic winds are enforced by a general south-north flow. Such situations exhibit easterly or south-easterly flow over the Po Basin. This flow is then deflected towards the Alps by synoptic pressure gradients. Inverna conditions occur far more frequently than Invernone conditions.

2.3. Air quality

Industrial activities in the valley are very sparse, so that the San Bernardino freeway provides the only significant source of anthropogenic ozone precursors within the valley. The traffic density was of the order of 900 cars per hour during the day (July 1996), reaching a broad maximum between noon and the evening rush hour around 1800 CET. Values during the night dropped to near 100 cars per hour at 0600 CET. The minimum was reached

around 0500 LST. Traffic counts in Roveredo were about twice as high as in San Bernardino. The difference between the two counts can be defined as commuter traffic. During the weekends, counts reached peak values of 1500 cars per hour, while commuter traffic remained at about a constant level of 400 cars per hour. More vehicles follow the route to the St. Gotthard Pass to the west, and contaminated air from the Ticino valley can enter the Mesolcina Valley with the up-valley winds. Calculations using emission factors from a traffic emission model (BUWAL, 1995) indicate that the local traffic emissions cause a NO_x concentration increase within the middle valley section of roughly 100 ppt h^{-1} when assuming a homogeneous distribution within the valley atmosphere.

Because most of the valley sidewalls are covered by forests, biogenic emissions of VOC are expected to contribute to the local oxidant production. Biesenthal *et al.* (1997) found a forest contribution of 13 % to the ozone production in the Lower Fraser Valley, B. C. Whether the situation is similar in the Mesolcina Valley is an objective of the follow-up project VOTALP II.

Pollutants from other sources enter the valley by advection. This can happen either from the north or from the south. Advected NO_x concentrations from the south amount to 2 ppb in the afternoon of sunny summer days (see Section 5.1). Southerly advection sometimes brings highly polluted air originating in southern Ticino or in the Po Basin. In such episodes, ozone concentrations may reach 150 ppb or more (Prévôt *et al.*, 1997). For comparison, the Swiss national air quality standard for ozone is 60 ppb. This hour-average concentration must not be exceeded more than once per year. Advection from the north normally feeds on the pollutant reservoir over the Alps and thus shows characteristics of the 'background' ozone concentration which is of the order of 50 - 60 ppb in summer (e.g. Neiningen and Dommen, 1996).

3. Experimental approach

The field campaign consisted of two parts. The *monitoring phase* lasted from July 15 through August 24, 1996. Embedded within these five weeks were two *Intensive Observation Periods* (IOPs) of three days duration each. During these IOPs all available platforms and instruments were operated to gain as much information on the valley atmosphere as possible. The first IOP took place from July 19-23 (with an interruption on July 20-21 due to unfavorable weather), the second was from August 16-18.

3.1. Measurement strategy

The vertical exchange of ozone and other chemical species between the valley atmosphere and the free troposphere can be determined with a mass budget calculation. In a simple box-model approach (referred to as ‘Mesolcina box’ hereafter), the valley sidewalls and a lid at an appropriately selected altitude define the air volume. For this volume the equation for the conservation of a species concentration is given by

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x_i} (U_i \cdot C + \overline{u_i c}) = S \quad (1)$$

where C is the concentration (mass per volume) of the constituent, U is mean wind speed, S is the source or sink strength. Capital letters denote ensemble averages, lowercase letters are turbulent quantities. The index i runs from 1 through 3, and Einstein’s summation convention applies. The terms in (1) are either measured or estimated with models. The solution requires continuous measurements to resolve temporal variations, as well as an appropriate spatial coverage to resolve the spatial gradients. Such requirements could only be partly fulfilled. Continuous measurements were made with conventional ground-based weather instruments (some located on meteorological towers) and chemical samplers. They provided the time gradients and to some degree spatial gradients of U and C at the lower boundary. Attempts to measure the turbulent term in (1) were only partly successful. In-volume measurements were obtained with remote-sensing equipment operating continuously (sodar, scintillometer/DOAS - differential optical absorption spectroscopy - systems, lidar) or episodically with in-situ techniques (radiosoundings, instrumented aircraft). The instrumentation used for this approach is described in the next section.

3.2. Instrumentation

Monitoring was achieved with ground-based instruments that did not require frequent or continuous surveillance. The monitoring platforms delivered data averaged over 10 or 30 min. During the *IOPs* additional parameters were measured in-situ or remotely with higher temporal resolution. A list of stations with their acronyms and equipment is given in Table 1. These acronyms will subsequently be used whenever data from a particular station is mentioned. Data routinely collected by the Swiss Meteorological Institute (SMI) and the Amt für Umweltschutz of the Canton of Grisons (AfU), as well as the radiosoundings of Milano were added to the database.

a) Surface measurements

Surface measurements were obtained with portable 10-m towers, and vans equipped with commercial and other sensors. The different sites were not equally instrumented. Meteorological parameters measured were 2D or 3D wind, temperature, relative humidity, and global radiation. Chemical measurements included O₃, NO, NO₂, and VOC (C₅-C₁₀). Ozone was measured with a UV absorption method (instrument built by PSI), NO with a chemiluminescence method (Ecophysics), NO₂ with photolytic converters (Ecophysics) and luminol chemiluminescence (Scintrex). O₃ and NO_x measurements were calibrated with a mobile calibration platform mounted on a trailer. Turbulence measurements were obtained with Solent ultrasonic anemometers (Gill Instruments) combined with thermocouples and fast KH20 hygrometers by Campbell Scientific Ltd., and with a 3D propeller anemometer together with a thermocouple. Fluxes were computed with the eddy-covariance method. Continuous VOC monitoring was performed at GRK with an Airmotec gas chromatograph (GC, Prévôt *et al.*, 1999, this issue). VOC cartridge samples were taken during IOP-1 at SMA and SAL and, during IOP-2, at SMA and SOZ. The samples were later analyzed in the laboratory.

b) Profile measurements

Information on the vertical structure of the valley atmosphere were obtained with different methods. A Remtech PA-2 sodar provided wind data at SVT in the lower part of the valley up to about 700 m above ground level (AGL). The aerosol lidar of IfU measured the 3D aerosol distribution up to 5000 m AGL at GRK (July 16-19; Carnuth and Trickl, 1999, this issue). A Radian Corporation LAP-3000 (1290 MHz) radar wind profiler operated by the Swiss Meteorological Institute was located in Cadenazzo in the Magadino Plain and measured wind profiles up to 4000 m AGL. Temperature and humidity profiles were obtained with a VIZ-9000 radiosounding system at GRN. This system also measured wind profiles at times, but reception of positional data proved to be difficult in the valley, and many wind profiles were lost. Slope wind information in the upper part of the valley was provided by a mini-sodar at PS2 built by IMP Vienna. Additional ozone soundings were performed in the Po Basin at the Italian station San Pietro Capofiume.

c) Aircraft measurements

During the IOPs, daytime measurements of meteorological and chemical parameters were made with two instrumented light aircraft. Both were able to fly close to the slopes and up to 5000 m MSL. Typical flight

tracks were usually flown twice per day. A curtain-like pattern perpendicular to the valley axis at different heights was flown near Grono to determine the situation at the lower end of the 'Mesolcina box'. Three legs, two along the valley sidewalls and one at the center of the valley, at three or four different altitudes provided information on the interior and the borders of the box. Circumferential and transverse flights over the crests of the Mesolcina Valley complemented the in-valley flights. Traverses over the crests of both the Mesolcina and Calanca valleys were flown to collect data on the vertical exchange produced by thermals. Parameters measured by the first aircraft include air temperature, dew point temperature, pressure, position, wind, NO₂, O₃, particles, NMHC (C₄-C₁₀), H₂O₂, organic peroxide and video images. NMHC were analyzed with the on-board GC of Airmotec. The other, usually higher flying aircraft, measured NMHC (C₂-C₇) with a grab-sampling method, NO₂, O₃ and standard meteorological parameters. These air samples were later analyzed on a Varian laboratory GC.

d) Scintillometer/DOAS measurements

To obtain continuous measurements of wind and chemical constituents at different elevations within the valley both during day and night, several scintillometer/DOAS systems built by PSI were used. The scintillometers measured the average crosswind speed, while the DOAS measured path-averaged concentrations of O₃ and water vapor. From the measurements, advective fluxes of O₃ and water vapor could be determined. Scintillometers are optical instruments consisting of two components. A transmitter generates a pulsed infrared light beam. The receiver measures the intensity of this light beam with two sensors as a function of time. When computing the covariance of the intensity time series of the two sensors, information of the average wind component across the light beam can be obtained (see, for example, Wang *et al.*, 1981; Furger *et al.*, 1995). Concentrations of chemical constituents of the atmosphere can be obtained from DOAS measurements, where the absorption of light by molecules in the light path is determined. DOAS are similar to scintillometers with respect to transmitter and receiver units, and hence, using a scintillometer and a DOAS parallel to each other with the light beams pointing across the valley was the approach chosen for VOTALP. Five systems were deployed, four of them pointing across the valley at SMA, CAS, PRA and SEI, and the fifth of them along the valley sidewall at STA. Beam lengths ranged from 925 m to 2725 m.

3.3. Weather situation

a) IOP-1

The first IOP (19-23 July, 1996) was conducted during in a period of northwesterly advection at higher levels, with weakening pressure gradients close to the ground (Fig. 2). Hence, the thermal circulation could develop (Inverna). At the 850 hPa level an airmass boundary was located over the southern Alps. On the 20th the pressure gradient weakened and convection started. A heat low developed over the Alps on 20 July and on the following two days around noon, providing the driving force for the thermal circulation between the foreland and the valleys. Fog within the valley and thunderstorms in the evening forced an interruption of the IOP, which was resumed on the 22nd. High ozone concentrations (up to 100 ppb at ROM) measured during this IOP were associated with significant transport of polluted air from the Po Basin towards the Mesolcina Valley, sometimes even reaching the Alpine crest late in the evening (Invernone). The maximum O₃ concentration, observed at SBP, was 106 ppb at 0200 CET on 23 July 1996.

b) IOP-2

The second IOP (16-18 August, 1996), conducted during a period of fair weather and strong insolation south of the Alps, was governed by northerly advection aloft, which decreased in strength and turned towards east over the course of the IOP (Fig. 2). This northerly flow aloft affected the local circulation systems by opposing the up-valley wind during the day (Inverna). Consequently, the up-valley wind in the Mesolcina Valley developed relatively late in the day. The up-valley wind increased in strength from day to day, as the daytime heat low became better centered over the Alps. Ozone was transported into the valley, but with a maximum of 70 ppb at SBP the values never reached the levels of IOP-1. The second IOP was conducted in a 3-day window of mild, sunny weather, which was bracketed by unsettled weather. The maximum O₃ concentration, observed at ROM, was 90 ppb.

4. Modelling approaches

To get continuous distributions of all variables in space and time the models listed below were applied. These models were either purely meteorological, purely chemical or combined. All scales were covered from synoptic (5000 km) to local (10 m).

MCCM, the IFU Meteorology Chemistry Climate Model (Grell *et al.*, 1997), a combined Eulerian model which is based on MM5 and the RADM2 chemistry mechanism, was executed to model three days of IOP-2. The simulation started with a coarse grid (54 km grid width) run for the whole of Europe. Nests with subsequently increasing horizontal resolution were inserted in further model runs to show the balance between advection of ozone and local production of ozone in Alpine valleys in greater detail. The finest nest had a horizontal grid width of 1 km, and an example of a model output is shown in Fig. 3.

The simulations with MCCM showed the overall influence of the synoptic situation on the air currents at the southern flank of the Alps. On the first day, northerly flow prevailed. On the second and third day the pressure gradient weakened and the wind turned towards east and southeast. On these two days thermally driven winds between the Po Basin and the southern flank of the Alps developed. The distribution of trace substances shows tongues of ozone and other pollutants advected into the lower parts of the main Alpine valleys from the Po Basin. Eulerian simulations with higher spatial resolution are possible if the necessary input data is available. This has only been the case for the Grisons part of the domain. Results of MCCM simulations are presented in Grell *et al.*, 1999, this issue). Besides simulating the key features of the valley circulation, the model calculations also reproduced some of the peculiarities of the airflow in a valley that is bending.

Wotawa and Kröger (personal communication) simulated transport towards the valley on the meso- β scale by means of Lagrangian tracer dispersion calculations applying the particle diffusion model FLEXPART (Stohl *et al.*, 1998), and by means of Lagrangian box model calculations along boundary layer trajectories, applying the IMPO photochemical trajectory model (Wotawa *et al.*, 1998). These calculations were based on the wind fields of the operational German/Swiss limited-area weather prediction model (SM/DM) with a horizontal resolution of approximately 14 km available during the whole monitoring phase. Transport processes from the main emission regions of the Po Basin proved to be of high relevance to explain elevated ozone concentrations along the crests and at the pass. Differences in the characteristics of such episodes - at times, the high ozone values reached the mid-section of the valley at Santa Maria, but never reached the San Bernardino Pass - were well reproduced by the tracer model. The performance of the O₃ simulations was generally poor, except for the area near the pass, where the correlation between measured and modeled daily maximum O₃ concentrations amounted to 0.63. A large underprediction of O₃ maxima during episodes was observed, which cannot be explained solely by transport simulation errors. Applications of the same model in less complex terrain (see, e.g. Wotawa *et al.*, 1998) showed a significantly better performance.

Thermodynamic aspects of the valley atmosphere were studied with ALPTHERM (Liechti and Neininger, 1994), a 1-dimensional model which includes the area-height distribution of the topography (Steinacker, 1984). Reasonable thermodynamic profiles could be simulated mainly by considering variations in the Bowen ratio with distance up the sidewalls. Key features like the stable stratification of the boundary layer and its diurnal development were well reproduced with this model.

Chemical aspects were investigated with the Harwell photochemical trajectory model HPT-M (Derwent and Jenkin, 1990), which was operated in a photostationary state. The chemical mechanism in the HPT-M model was modified by using Atkinson *et al.*'s (1993) compilation of rate constants for inorganic reactions.

5. Selected highlights

5.1. Observed vertical structure of the valley atmosphere

The vertical structure of a valley atmosphere substantially influences the vertical exchange of air between the valley and the overlying layers. Thermodynamic profile measurements by aircraft and radiosondes are available during the day only, while wind profiles were measured day and night. Fig. 4 shows the diurnal variation of the wind field in Cadenazzo (outside the Mesolcina Valley, Fig. 1a). One of the key features revealed by the measurements is a multilayer structure with varying stability. Basically there are three layers. Layer 1 below about 2000 m MSL could be characterized by the up- and down-valley flow with a wind speed maximum a few hundred meters above ground. This is the typical valley wind regime where in weak gradient situations air flow is generated by thermal processes. The upper boundary of this layer was clearly within the valley, i.e. below the valley rim. Above, at heights between 2000 m and 3500 m MSL was layer 2 with weak winds most of the time blowing from NE, but sometimes rotating counterclockwise from the up-valley wind direction to the synoptic-scale flow aloft, which remained persistently northerly or northwesterly above about 3500 to 4000 m MSL. The uppermost layer 3 could be considered as the free troposphere and was also clearly depicted by a low water vapor and aerosol content. The heights indicated were not fixed, but varied with time over a couple of hundred meters. The wind and temperature structure was in good agreement with aerosol lidar observations on the pre-IOP days (Carnuth and Trickl, 1999, this issue). While layers 1 and 3 can easily be understood, layer 2 is more complicated because it is a transition layer. The air contained in layer 2 originated in the north at times of north

foehn, or in the south or east at times with weak synoptic gradients. Antiwinds (Buettner and Thyer, 1966) might also be found in this layer, but this would require a more detailed analysis.

Thermal stability was greatest close to the ground during the night, and at the boundary between layers 2 and 3. During the day layer 2 was only slightly stable or even neutrally stratified in most of the cases. An exception to this was 22 July, when layer 2 was stable all day. This restricted vertical exchange in the center of the valley (but not in the slope wind layer). As an example for 22 July, profiles of ozone, NO₂ and VOC, each averaged over one flight and in vertical bins of 100 m, are shown in Fig. 5. The profiles indicate, besides the diurnal variation, the absence of a well-mixed valley atmosphere.

5.2. Exchange caused by thermal circulation systems

Vertical exchange of pollutants between the Alpine atmospheric boundary layer and the free troposphere in weak pressure gradient situations is strongly connected to the thermally-driven valley circulation. An air mass budget for the Mesolcina box was calculated for those days when aircraft data were available (Prévôt *et al.*, 1998a). The volume of the box (reaching up to 2000 m MSL) was determined to be 100 km³. Volume fluxes were computed by calculating the differences between inflow through the Grono cross-section and outflow through the Pian San Giacomo cross-section. The net vertical export amounted to 270 to 580 km³ during the day (Table 2), corresponding to an injection of 40 to 80 t of ozone into the atmospheric layer aloft. The volume exported vertically is of the order that would be expected when assuming an up-slope wind layer of 100 m thickness surrounding the whole valley section, with a wind speed of 2 to 3 m s⁻¹, within the uncertainties of the assumptions. This simplistic approach explains the order of magnitude of the net export considering only thermodynamic processes.

We expect dynamic processes to contribute to vertical exchange as well. For example, we observed on some days that part of the export occurs via direct venting of the up-valley wind at the valley end. Such a process also occurs at the bends of the valley axis near Pian San Giacomo (Fig. 1c) and east of Grono. Minisodar measurements at PS2 indicate that during the day the up-valley wind impinges onto the slope where it is deflected mostly up-slope and to a lesser degree up-valley, thereby eroding much of the slope wind layer, which attains a thickness of less than 20 m. The setting of PS2 in a place where the valley bends seems to produce this peculiar effect in which the separation of valley wind and slope wind is difficult. We hypothesize that the vertical exchange happens mainly in the layer adjacent to the slopes. Aircraft measurements did not reveal significant

convection in the center of the valley. During the course of the day asymmetries in flow and layer depth between the valley sidewalls due to the varying distribution of insolation have been observed.

The stable multi-layered stratification of the valley atmosphere observed during the day does not seem to influence strongly the export caused by the slope winds, but probably suppresses the exchange in the centre of the valley. If the quantity of ozone exported by the slope winds is dispersed in a 2 km thick north wind layer (layer 2) above the valley atmosphere which is itself advected by the gradient wind with a speed of 5 m s^{-1} , a concentration increase of 2 to 3 ppb would result there. The resulting airmass deficit in the valley must be compensated by horizontal advection.

The injection of valley air into layer 3 is a good example of air venting from the valley atmosphere into elevated layers, a process sometimes called mountain venting (see, e.g., Kossmann *et al.*, 1999, and references therein; Wakimoto and McElroy, 1986). The formation of clouds above the crests as a consequence of the up-slope flow was observed especially in the afternoon. However, no clouds formed over the valley itself, indicating that the main vertical exchange happened along the slopes. The process we observed may be termed mountain-cloud venting. The injection of 300 to 500 km³ of air containing primary pollutants such as NO_x and VOC into layer 2 can lead to additional photochemical production of ozone in this elevated layer. The increase of the ozone concentration due to the export of primary pollutants from layer 1 could be of a similar magnitude as the exported ozone amount (Jacob *et al.*, 1993; Flatøy *et al.*, 1995). Once the air has been mixed into layer 2 it will be transported with the gradient wind, leaving the area above the valley. The reservoir created in this way will be advected elsewhere, and may never return to its origin unless the gradient wind shifts appropriately. The reversed thermal circulation at night will then bring air from a different origin into the valley. VOC measurements in GRK showed distinct morning minima when the winds at SBP blew from the north during the night, while no remarkable concentration drop was observed when winds at the pass blew from the south. In the north wind cases, down-valley winds fill the valley with cleaner air originating north of the Central Alps. This air is mixed into the polluted surface layer as soon as convective mixing develops in the morning. In contrast, southerly winds fill the valley atmosphere with polluted air, and downmixing will not reduce local VOC levels (Prévôt *et al.*, 1998b). A more detailed discussion can be found in Prévôt *et al.* (1999, this issue).

Nighttime processes were less well studied due to the absence of vertical ozone and temperature profiles. The northerly flow penetrated into the valley down to at least 900 m MSL, i.e., to the altitude of SMA (Furger *et al.*,

1997). In these cases, the upper cross-section at PS1 was largely within the upper level flow, and the budget volume was altered substantially. DOAS measurements indicated nocturnal ozone concentration minima of 60 ppb or more at SEI at 60 m and at PRA at 250 m above ground. These values corresponded well with the surface values at SBP and the summer background ozone concentration for the Alps of 50 – 60 ppb. Within the stable surface layer, ozone was destroyed by dry deposition and titration, as can be seen at ROM where ozone mixing ratios dropped to 10 ppb (Fig. 6). Downward mixing of clean air from elevated layers (McKendry *et al.*, 1997) can be excluded as a cause for such low concentrations because SBP never showed values below 40 ppb. Both DOAS and surface measurements at SMA had similar concentrations (about 60 ppb) as were observed at PS1. Downward advection of relatively clean air should have been observable at some of the elevated stations. Their absence supports our view of the importance of dry deposition and titration for the destruction of ozone in the surface layer.

The effects of slope winds have also been studied at SOZ. This station showed marked effects of shadowing by the valley sidewalls. Sunset was about 2 hours earlier than at other sites, and the subsequently developing slope wind layer led to a distinctly different behavior at this site compared to the others. Shadowing effects also led to considerable asymmetries between the opposing valley sidewalls with respect to chemical species concentrations, especially in the morning when up-slope winds on the sunlit side brought cleansed, ozone-poor air from the valley floor to higher elevations. Such asymmetries were confirmed by asymmetries in aerosol data obtained from lidar measurements (Carnuth and Trickl, 1999, this issue).

5.3. Local production and deposition

No net ozone production was observed in the valley when comparing measured ozone concentration profiles taken by aircraft near Grono and Pian San Giacomo, respectively. Local production and destruction/deposition of O₃ seem to balance each other.

To determine the local ozone production a photostationary state calculation was applied with the Harwell model (Derwent and Jenkin, 1990). Concentrations of VOC, ozone and NO₂ were held constant at their measured values. Aldehydes and PAN were treated as variables, which were left to reach a steady state concentration. Calculations were performed for ground level, and at 700 and 2000 m MSL. Ozone production, which is strongly dependent on formaldehyde concentration, ranges between 7 and 10 ppb h⁻¹ at 700 m MSL for early afternoon hours. Including dry deposition with a deposition rate of 0.5 to 1 cm s⁻¹ yielded a net ozone production of 3 - 8 ppb h⁻¹. The lower

value is in agreement with measurements, given the experimental uncertainties. The upper value could be explained by a higher deposition rate in the valley atmosphere compared to rates determined over flat areas.

5.4. Relevance of regional transport

Ozone measurements obtained at SBP in July and August 1996 exhibited several significant concentration maxima above 100 ppb (Fig. 7). These maxima occurred at night and were always associated with southerly airflow. We conclude that more than one full daytime up-valley wind phase is needed to bring high ozone values from the Po Basin to the Mesolcina Valley end and the main Alpine crest. The maxima at the pass occurred a few hours after those at ROM. Since photochemistry is switched off during the night, concentrations increasing with time are indicators for the advection of a concentration gradient. In July 1996 this happened during 6 nights.

Regional southerly advection was also identified as the source of extreme ozone concentrations by MCCM model simulations (Grell *et al.*, 1999, this issue). An analysis of regional (meso- β -scale) transport processes by means of trajectories, Lagrangian particle simulations and Lagrangian photochemical box model simulations was performed by Wotawa and Kröger (personal communication). Their results support the data analysis findings reported here.

6. Climatological evaluation

The summer of 1996 was unusual with respect to the persistence of the weather in southern Switzerland, but not so much with respect to climatological average values of the standard parameters, which often came close to long-term averages. The Azores high did not establish its influence in the Alps in July, and the expected long-lasting fair weather periods were absent. The weather was quite variable and unsettled as a consequence of increased frontal activity. Although it was generally wetter than normal in the southern Alpine valleys (e.g., SBE with 174 % of the 30-year average precipitation in July), the sunshine duration was close to normal. A decrease in precipitation was observed from the Alpine crest towards the Po Basin. High values of global radiation, sunshine duration and persistent fair weather are important for the formation of ozone.

The methods of synoptic climatology provide a tool for an evaluating the weather situations in July and August 1996. We used the synoptic weather situations of the Alpine Weather Statistics ('Alpenwetterstatistik', AWS, Wanner *et al.*, 1998) for July and August 1987-96. In AWS each day is assigned to one of 40 weather situations, according to a set of parameters obtained from measurements and synoptic weather charts. These 40 weather

situations are grouped into 8 synoptic groups for more convenience, each group representing typical synoptic situations in the central Alps (see Wanner *et al.*, 1998, for details on terminology, methodology and applicability of the AWS). The 8 groups can further be combined into the 3 classes, ‘convective’, ‘advective’ and ‘mixed’, which give an indication of the prevailing pressure gradient. It becomes evident from the frequencies of occurrence of individual synoptic groups in Fig. 8 that in 1996 a strong predominance of indifferent weather situations occurred, and that anticyclonic situations were remarkably underrepresented. While in the 10-year period the synoptic group I (indifferent) occurs in 35 % of all cases, its frequency in 1996 was 47 %. Group A (anticyclonic) at the same time comprised only 8 % instead of 34 %. Such an imbalance could be felt during the campaign planning phase, when it proved difficult to find a consecutive 3-day period of fair weather. Persistence was not high for the southern valleys, because the Alps were under the influence of a succession of fronts such that no weather situation lasted for more than 4 days. The IOP days are classified in Table 3. From the AWS data it becomes evident that convective activity was high, and that cloudiness often reduced the amount of sunshine received within the valleys and hence the local formation of ozone. Furthermore, days with northerly advection were about twice as frequent in 1996 as in the 10-year period. Weak northerly flow leads to reduced cloudiness south of the Alpine crest and thus favors the generation of thermal circulations which transport polluted air into the valleys. Strong northerly flow may delay or completely suppress the formation of the up-valley winds.

Ozone concentrations did not reach extreme levels in 1996, given that the maximum concentration of 116 ppb at SBP on 12 July 1996 is considerably lower than the aircraft measurements of up to 150 ppb obtained from earlier studies further south (Prévôt *et al.*, 1997). Average concentrations are given in Table 4. The gross features of the Table are that in August ozone levels were roughly 10 ppb lower than in July. In 1996 the averaged diurnal variation showed maxima that were below the 1991-96 average by 5 ppb in July and 10 ppb in August. Both IOPs exhibited ozone levels above the monthly average.

Even more illustrative for the general ozone characteristics of the Mesolcina Valley is the diurnal variation. Fig. 9 shows scatterplots of ozone measurements as a function of time of day for the two stations ROM close to the valley floor, and SBP at the upper end of the valley. Each graph contains one month of data. IOP data are represented by black asterisks. Both IOPs fit well into the general diurnal behavior of ozone concentrations, with above-average ozone concentrations, but without representing extreme events. IOP-2 shows better internal consistency than IOP-1, which caught one episode of regional transport.

7. Conclusions

The VOTALP Mesolcina Valley campaign generated a dataset for the study of meteorological and chemical aspects of a valley atmosphere. With respect to its size, shape and population density the Mesolcina Valley is typical of a medium size Alpine valley, while on the other hand the freeway in the valley is one of the most important traffic routes in the Alps, producing above-average emissions.

The summer of 1996 was remarkable with respect to a rather low persistence of anticyclonic conditions. The Azores high never really stretched into the continent, and the general weather development was characterized by a succession of fronts moving over central Europe. Northerly flow advecting relatively cool air prevailed on many days. This reduced or suppressed pollutant transport towards the Alps from the south. This strong variability also limited the build-up of very high ozone concentrations. Hence, the measurements can be regarded as representative for average (not severe) summer ozone situations.

An airmass budget calculation based on measurements estimated the amount of air exported to the free troposphere. *Net vertical outflux* of the polluted boundary layer was found to be on the order of three to six times the whole valley volume during one up-valley wind phase of a typical bright summer day. Vertical transport by slope winds was estimated to be sufficient to compensate the difference between horizontal inflow through the valley mouth and outflow at the upper end of the valley, though identification of the relevant processes needs further study.

Regional transport of polluted air from the Alpine forelands into the Alps was a key process leading to extreme ozone concentrations in the Alps, especially at elevated sites. In contrast, *local production* proved to be important for keeping the ozone levels high within the valley, but would never yield levels comparable to those resulting from regional advection. This is in part the consequence of enhanced dry deposition at the valley floor and in the slope wind layer at the valley sidewalls, which compensates production to a large degree. Hence, most Alpine valleys can be regarded as a net sink of photo-oxidants with negative consequences for the local ecosystems. The budget estimates further indicate that Alpine valleys act as very efficient pumps venting large quantities of (polluted) air into elevated atmospheric layers. Therefore, they can be regarded as an important mechanism for transporting pollutants from the atmospheric boundary layer into the free troposphere in Central Europe. Consequently, considering, for example, scenarios of future traffic development in the Alps, the mechanisms discussed here will significantly enhance air pollution in high Alpine areas and the impact of pollutants on those

fragile ecosystems. Given this scenario, reductions of primary pollutants will be necessary for the protection of the Alps.

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Tables

Table 1: Measurement sites. X (east) and Y (north) coordinates are in the Swiss km coordinate system. Types of measurements are indicated in the lettered columns, M = meteorology, O = ozone, N = NO_x, V = VOC, T = turbulence, S = scintillometry/DOAS, A = special measurements, with instrumentation indicated in the rightmost column.

ACR	NAME	X East (km)	Y North (km)	Height (m MSL)	M	O	N	V	T	S	A	Remarks
<i>VOTALP stations</i>												
CUP	Cupeis	736.00	144.30	1507	+	-	-	-	-	-	-	
SAL	Salec	737.20	143.10	1180	+	+	+	+	-	-	-	
PS1	Pian San Giacomo PSI	738.00	142.40	1280	+	+	-	-	+	+	-	
PS2	Pian San Giacomo IMP	738.00	142.40	1280	+	+	-	-	+	+	+	Minisodar
PRA	Pradiron	736.70	142.30	1440	+	+	-	-	-	+	-	
SEI	Sei	737.20	142.25	1220	-	-	-	-	-	+	-	
STA	Stabi	739.20	140.75	1420	+	+	-	-	-	+	-	
MES	Mesocco	737.90	139.00	800	+	-	-	-	-	-	-	
SOZ	Soazza	737.25	136.21	620	+	+	+	+	-	-	-	
LOS	Lostallo	735.30	129.70	400	+	-	-	-	-	-	-	
GRN	Grono Nationalstrasse	731.85	122.85	315	-	-	-	-	+	-	+	Radiosoundings
GRK	Grono Kraftwerk	732.20	122.75	315	+	+	+	+	-	-	+	Lidar
GDO	Grono Druckleitung Oben	732.70	122.05	900	-	-	-	-	-	+	-	
GDM	Grono Druckleitung Mitte	732.60	122.30	700	-	-	-	-	-	+	-	
SMA	Santa Maria	731.70	124.65	940	+	+	-	+	-	+	-	
CAS	Castaneda	731.55	124.25	740	-	-	-	-	-	+	-	
SVT	San Vittore	728.15	121.76	269	+	-	-	-	-	-	+	Sodar
<i>Stations of the Amt für Umweltschutz, Grisons (AfU)</i>												
SBP	San Bernardino Pass AFU	733.19	149.26	1930	+	+	-	-	-	-	-	
CAA	Castaneda AFU	731.32	124.23	770	+	+	-	-	-	-	-	
ROM	Roveredo Municipio AFU	730.21	121.97	320	-	+	-	-	-	-	-	
ROS	Roveredo Stazione AFU	730.30	122.04	298	+	-	+	-	-	-	-	
<i>Stations of the Swiss Meteorological Institute (SMI)</i>												
SBE	San Bernardino SMA	734.12	147.27	1639	+	-	-	-	-	-	-	
HIR	Hinterrhein SMA	733.90	153.98	1611	+	-	-	-	-	-	-	
CIM	Cimetta SMA	704.37	117.52	1672	+	-	-	-	-	-	-	
COM	Comporvasco SMA	715.00	146.44	575	+	-	-	-	-	-	-	
COV	Corvatsch SMA	783.16	143.53	3315	+	-	-	-	-	-	-	
GUE	Guetsch SMA	690.14	167.59	2287	+	-	-	-	-	-	-	
LOC	Locarno Monti SMA	704.16	114.35	366	+	-	-	-	-	-	-	
LUG	Lugano SMA	717.88	95.87	273	+	-	-	-	-	-	-	
MAG	Magadino SMA	711.16	113.54	197	+	-	-	-	-	-	-	
STO	Stabio SMA	716.04	77.97	353	+	-	-	-	-	-	-	
WFJ	Weissfluhjoch SMA	780.60	189.63	2690	+	-	-	-	-	-	-	

Table 2: Daytime volume flux estimates for the Mesolcina Valley.

	July 19	July 22	Aug 16	Aug 17	Aug 18
Horizontal flux (km ³ /day) for Grono cross section	650	600	300	500	600
Horizontal flux (km ³ /day) for Pian San Giacomo cross section	70	150	30	100	140
Net vertical outflux (km ³ /day)	580	450	270	400	460

Table 3: Characterization of IOP days according to the Alpine Weather Statistics, adapted from Wanner *et al.*, (1998).

Date	AWS Synoptic Class	AWS Synoptic Group	AWS Synoptic Weather Situation	Description
19 JUL 1996	advective	N	24	baroclinic, northerly flow with above normal pressure aloft
22 JUL 1996	convective	I	8	indifferent, with weak northerly flow aloft
23 JUL 1996	advective	W	17	barotropic, westerly flow with above normal pressure aloft
16 AUG 1996	advective	N	23	barotropic, northerly flow with below normal pressure aloft
17 AUG 1996	convective	I	8	indifferent, with weak northerly flow aloft
18 AUG 1996	advective	N	22	barotropic, northerly flow with above normal pressure aloft

Table 4: Selected ozone statistics (in ppb) for Roveredo-Municipio (ROM) and San Bernardino Pass (SBP).

Ozone (ppb)	Roveredo (ROM)	San Bernardino Pass (SBP)
July 96 average	42.9	66.8
IOP 1 average	53.4	77.5
July 96 Maximum	106.3	116.3
August 96 average	33.0	57.3
IOP 2 average	41.7	62.7
August 96 Maximum	95.1	107.1

Figure Captions

Fig. 1: a) Map of the larger study area. The rectangle marks the area depicted in b. b) Map of the Mesolcina Valley, with measurement sites. The lower left edge corresponds to the geographical coordinates 46.1702° N, 9.0588° E. Acronyms of the station names correspond to Table 1. Black lines indicate scintillometer/DOAS paths. The Mesolcina box is between Grono (GRN) and Pian San Giacomo (PS1/2). c) Height profile along the Moësa river (thick solid line) from the San Bernardino Pass (0 km) to the river mouth (41 km). Thin solid line: Crest height on the eastern side. Dashed line: Crest height on the western side. Crest positions are projected onto the valley axes. Notice the Calanca Valley at 33 km on the western side. (Digital terrain model data reproduced with the permission of the Swiss Federal Office of Topography, dated 24 September 1998.)

Fig. 2: 12 UTC geopotential height analyses for 22 July 1996, a) 500 hPa, b) 1000 hPa, and for 17 August 1996, c) 500 hPa, d) 1000 hPa. The thick lines indicate 5760 m MSL (500 hPa) and 160 m MSL (1000 hPa). Maps from the European Center for Medium Range Forecasting.

Fig. 3: Numerical simulation with MCCM: Horizontal cross section at 1.8 km MSL. Displayed is O_x (= sum of O_3 and NO_2) concentration in ppb (colors), horizontal wind barbs (full barb = 2 m s^{-1}), and terrain (black isolines) at 1400 UTC, 17 August 1996. The map corresponds roughly to the lower two thirds of Fig 1a. The Mesolcina Valley is located about one-third from the top right corner towards the left.

Fig. 4: Wind profiler measurements in Cadenazzo for 17 August 1996.

Fig. 5: Averaged O_3 , NO_2 , and VOC profiles for 22 July 1996 from the Stemme and Dimona aircraft measurements. O_3 and NO_2 data has been binned to 100-m height intervals and averaged. VOC data are 10-min averages. Data from the shuttle flight between the airport and the valley have been excluded.

Fig. 6: Ozone time series measured at Pian San Giacomo (PS1), Santa Maria (SMA) and Roveredo (ROM).

Fig. 7: Time series of ozone concentration for July 1996 at Roveredo-Municipio (ROM, thin line) and San Bernardino Pass (SBP, thick line). The upper part indicates wind directions at SBP (dots). IOP days are shaded.

Fig. 8: Relative frequencies of occurrences of the 8 weather groups in July and August, a) for the years 1987-96, b) for 1996. A = anticyclonic, I = indifferent, C = cyclonic, W = westerly, N = northerly, E = easterly, S = southerly, M = mixed.

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Figures

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Fig. 1b

Fig. 1c)

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a)

b)

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