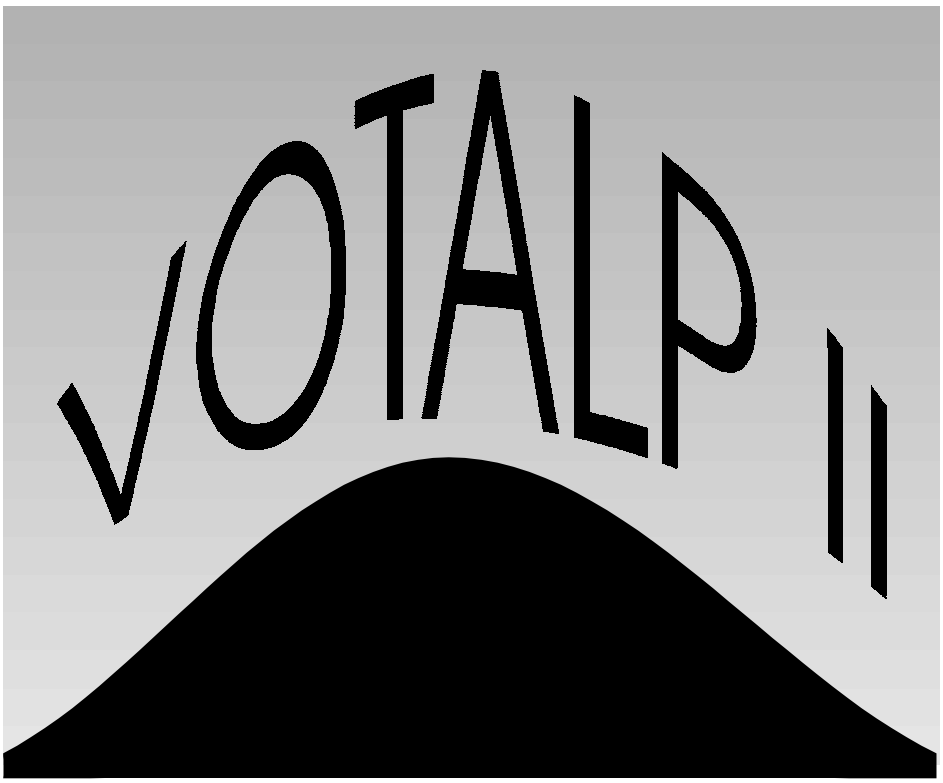

VERTICAL OZONE TRANSPORTS IN THE ALPS II

FINAL REPORT

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PART A

SUMMARY REPORT OF THE PROJECT

1. Abstract

The EU research project VOTALP II investigated the enhanced vertical exchange above the Alps as well as other processes which might be relevant for increased ozone concentrations. The role of stratospheric intrusions for mountain peaks and of horizontal advection of polluted air for the foothill area causing a high ozone abundance has been quantified for selected locations. Above the Alpine foothills a so called "injection layer" above the boundary layer was detected, into which pollutants from below are transported. The Alps also play a crucial role for transport of boundary layer air up to the mid troposphere. The upper troposphere and the tropopause region, however, seem to be less affected.

2. Executive summary

The European Union research project VOTALP II (March 1998 to February 2000) generalised the results on the effects of enhanced vertical exchange in mountainous regions obtained in VOTALP I and extended the investigation to a larger spatial and temporal scale. In searching for an answer to the fundamental question of VOTALP II "What is the effect of the strong vertical exchange over the Alps on the ozone concentrations in the Alpine region and in Europe as a whole?" measurements and model simulations on different scales were combined and results from case studies were aggregated to obtain a complete climatological picture.

Climatological analysis of continuous measurements at mountain peaks show a significant frequency (5–10% of the time) of stratospheric ozone intrusions in the Alpine area. Criteria to define stratospheric intrusions need to be defined separately for every station. Good agreement with lidar data and with in-situ measurements at mountain peaks prove simulations with FLEXPART, a Lagrangian particle dispersion model, to be a promising tool for climatological studies as well as for prognostic purposes. Some cases of elevated ozone concentrations in the upper troposphere were found to be due to intercontinental transport from North-America.

In the foothill area of the Alps a considerable transport of pollutants and of ozone into the altitude range above the boundary layer was detected. This finding is based on measurements from the campaigns performed during VOTALP II in the Milan/Como region on the southern side in 1998 as well as around Garmisch-Partenkirchen on the northern side of the Alps in 1999. Over flat terrain, the free troposphere lies immediately above the planetary boundary layer. In the Alpine area, there is another layer between the boundary layer and the free troposphere that we would like to call the "mountain injection layer". It is not as well vertically mixed as the planetary boundary layer, but this layer incorporates air and pollutant injections out of the planetary boundary layer. A typical altitude for this layer is 2000 – 4000 m ASL.

During the Garmisch campaign the Munich urban plume was detectable on Hohenpeißenberg and Bromberg, but not at Garmisch-Partenkirchen, indicating that it might not always reach the Alps. A weather pattern classification based on cluster analysis has been developed, on the basis of which a climatological analysis of Garmisch and Wank ozone data was evaluated for indications of the Munich plume. Contributions of 11% for summer were found based on data from 1990 to 1998. Available long-term data were also analysed for the plumes of Milan and Vienna.

Model calculations for two summer months revealed, that 57% of the Milan emissions are transported into the Alps and contribute significantly to the Alpine ozone budget. Emission reductions on the regional as well as on the Europe-wide scale would reduce the ozone abundance. Close to the city of Milan the ozone formation is clearly controlled by VOC (volatile organic compounds). With growing distance from the main emission sources the sensitivity to NO_x-emissions increases. However, the calculated distance for the transition from VOC- to NO_x-limitation depends strongly on model specifications like e.g. the consideration of biogenic NO_x-emissions.

Vertical ozone budgets for the Alpine region were computed for selected weather patterns and compared with budgets obtained by simulations in which the Alpine terrain was flattened. The results of these Eulerian model calculations and two further Lagrangian approaches revealed the important role of the Alps for the dispersion of boundary layer pollutants into the lower free troposphere. However, on the synoptic scale both Lagrangian calculations, one with a trajectory model and the other with a particle dispersion model, could not detect significant transport from the boundary layer into the upper free troposphere and the tropopause region above the Alps.

Summing up, ozone levels in the Alps are strongly influenced by stratospheric intrusions as well as by emissions in the surroundings of the Alps, which are horizontally advected in the boundary layer. Valleys as well as foothills pump pollutants into an "injection layer", situated above the boundary layer. As a whole the Alps play an important role for the transport of pollutants into the free troposphere, causing significantly enhanced concentrations of primary pollutants. No evidence was found for an Alpine effect in the upper troposphere.

3. General objectives

The project "Vertical ozone transports in the Alps II" (VOTALP II) continued work that was begun in VOTALP I. It was tried to generalise the results on the effects of enhanced vertical exchange in mountainous regions obtained in the previous project and to extend the investigation to a larger spatial and temporal scale. The main approach of VOTALP II was to combine measurements and model simulations on different scales and to bring together results from case studies and statistical analyses over longer periods of time to obtain a climatological picture.

The fundamental question of VOTALP II was:

What is the effect of the strong vertical exchange over the Alps on the ozone concentrations in the Alpine region and in Europe as a whole?

In the course of the project, the following different processes were studied (see figure):

I. Local ozone production in Alpine valleys

II. Climatology of ozone influx from the stratosphere

III. New aspects of vertical exchange between boundary layer and free troposphere

IV. Advection of urban plumes into the Alps

V. The Alpine effect on the European ozone concentrations

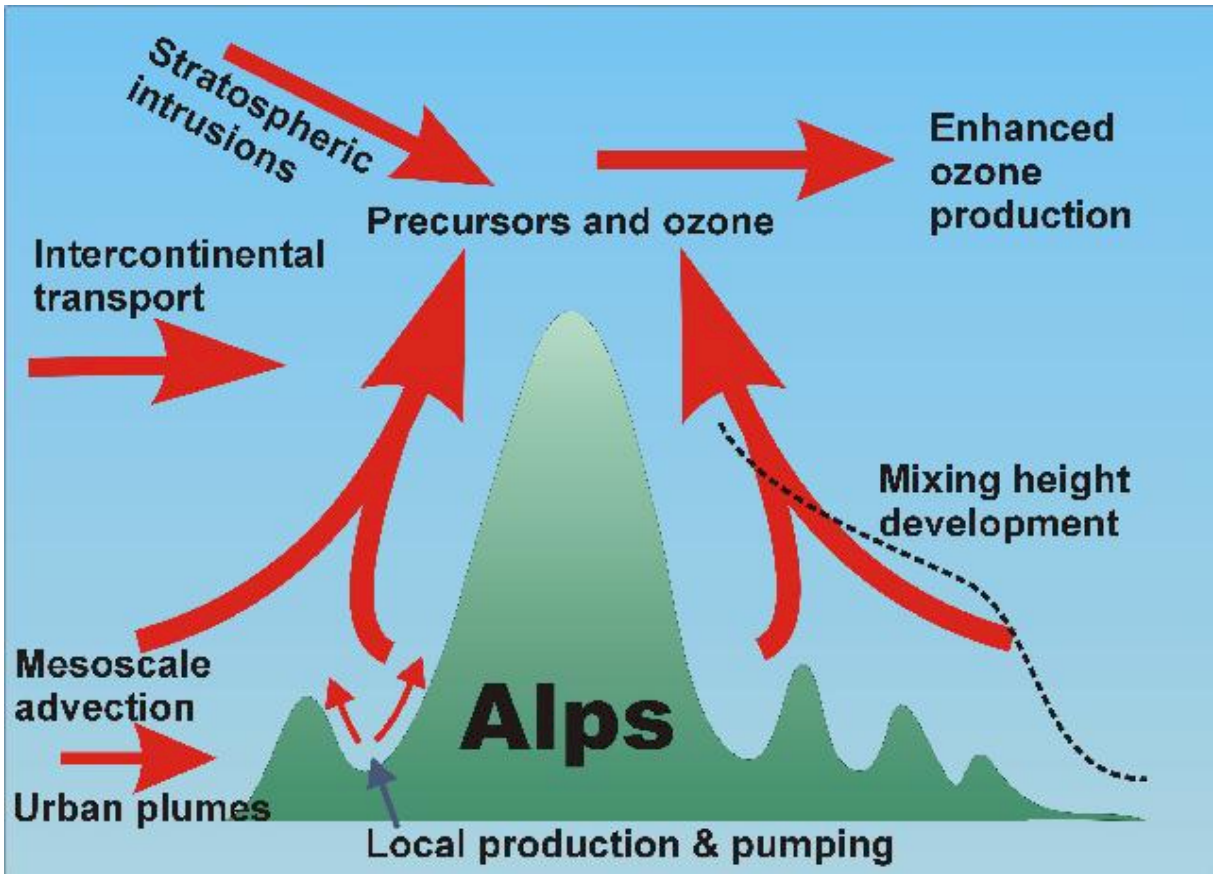

Figure 1: Schematic sketch of processes studied in VOTALP II.

Continuous measurements of several meteorological and chemical parameters at four mountain peak stations were kept up. A climatological assessment of the frequency and intensity of stratospheric intrusions based on these measurements as well as on modelling activities was established. Furthermore it was intended to develop a stratospheric intrusion index.

The importance of the advection of urban plumes into the Alps was investigated by analysing measurement data and model results. Two measurement campaigns, one on the southern and one on the northern side of the Alps, were devoted to the improvement of the understanding of enhanced vertical exchange above the Alpine foothills and of the advection of urban plumes into the Alps.

The effects of emission reduction scenarios on the ozone concentrations in the Alpine region were assessed in single cases using high-resolution 3D model simulations of chemistry and transport, and climatologically by performing Lagrangian box model calculations along air trajectories.

Vertical ozone budgets above the Alps for different weather patterns were computed with a Eulerian model and these budgets were compared with budgets obtained during simulations where Alpine terrain is flattened. Furthermore, a long-term Lagrangian particle dispersion model simulation of anthropogenic nitric oxides and carbon monoxide emissions was performed.

4. Specific objectives for the reporting period

The most important objectives of VOTALP II during the second period of VOTALP II were:

I: Local ozone production in Alpine valleys

- Case study of flow and chemical processes in an Alpine valley with a high-resolution Eulerian model. Validation of model results with measurement data from the VOTALP I field campaign in the Mesolcina Valley. Comparison with measured VOC data. Emission reduction scenarios
- Climatological investigation of transport and ozone formation for an Alpine valley with a Lagrangian model approach. Establishing, testing and evaluating a suitable model concept. Emission reduction scenarios

II: Climatology of ozone influx from the stratosphere

- Measurements of meteorological and chemical parameters at the four mountain peak stations Mt. Cimone, Sonnblick, Zugspitze and Jungfraujoch, calculation of back trajectories for these stations, ozone lidar measurements at Garmisch-Partenkirchen, data analyses
- Climatology of stratospheric intrusion events (frequency and intensity) based on measurements and model results, budget calculations
- Stratospheric intrusion index (diagnostically by measurements, prognostically by model)
- Seasonal variation and climatological importance of stratosphere–troposphere exchange.
- Intercomparison exercise of ^{7}Be measurements at the four stations Jungfraujoch, Mte. Cimone, Sonnblick, and Zugspitze.

III: New aspects of vertical exchange between boundary layer and free troposphere

- Field campaign between Munich and Garmisch-Partenkirchen in the foothills north of the Alps, data evaluation and analyses
- Budget calculations for the boundary layer, analysis of vertical pollutant fluxes

IV: Advection of urban plumes into the Alps

- Analysis of existing data: a) aircraft measurements around Milan, Vienna and Munich from 1991 onwards, transformation of aircraft data into uniform data format, b) ground-based Garmisch-Wank data from 1990 onwards
- Calculation of back trajectories, weather pattern classification
- Analysis of field campaign data (WP III) concerning the advection of urban plumes from Milan and Munich
- Long-term emission reduction scenarios in the Milan area and the Po Basin with a Lagrangian photochemical model. Comparison with the effect of emission reduction within the valley
- Budget calculation with a Eulerian model for a case of advection from Milan, emission reduction scenarios

V: The Alpine effect on the European ozone concentrations

- Calculation of summer ozone budget for the Alps for different weather situations
- Sensitivity study with flattened topography of the Alps
- Long-term particle dispersion model simulation with parameterised vertical transport in the Alps
- Synthesis and open questions
- Maintaining the VOTALP data base

5. Main results

I: Local ozone production in Alpine valleys

The August 1996 valley campaign performed in the Mesolcina Valley during VOTALP I was simulated with the IFU coupled Eulerian model MCCM (Meteorology Chemistry Climate Model), using a grid scale of 1 km. Substantial improvements of the model were necessary to reach satisfactory results in this orographically complex area. Although validation work is not yet completed, it seems that one of the results of VOTALP I can be confirmed by the model calculation: The advection by valley winds does not transport photo-oxidants from the industrial region around Milan to the upper part of the Mesolcina Valley within one day. Thus the ozone concentration in inner-Alpine valleys is mainly dominated by turbulent vertical exchange between the boundary layer and the reservoir layer above.

Simulations with a Lagrangian box model intended to model climatological aspects of the local ozone production in the Alpine valleys were not satisfactory and thus discontinued.

II: Climatology of ozone influx from the stratosphere

The ozone flux reaching the 3000 m level (Zugspitze) in direct intrusions (i.e. stratospheric air descending into the troposphere directly over Europe) was determined to amount to 8.2% of the total amount of ozone accumulated over the year. The fraction for the period April to September is just 5.5%, for October to March 11.8% of the respective half-year average mixing ratio. The annual input due to direct intrusions at 3000 m would, therefore, correspond to 4.0 ppb of ozone. If one assumes a non-anthropogenic background of the order of 10 to 15 ppb (based on measurements in the nineteenth century) and the existence of a significant contribution also from indirect intrusions (which are mostly not accessible by the measurements) one arrives at an estimate of the contribution of stratospheric ozone to the natural component in the lower troposphere exceeding the 50% level. Of course, a large uncertainty results from the fact that the natural background might have changed since pre-industrial times and the indirect intrusion events have not yet been quantified.

The modelling activities were extended to a few more case studies. Again, good agreement was found in direct comparison with the measurements. This adds to the confidence in modelling as a tool to study also aged stratospheric air intrusions descending into the troposphere outside Europe and being subsequently advected towards Europe. Budget calculations with the EURAD model showed that the net chemical production in the intrusion zones is slightly negative. Therefore, treating stratospheric ozone as a passive tracer seems to be acceptable on a time scale of a few days as used by the climatological Lagrangian particle simulations. A five-year (1995-1999) model run was carried out with the FLEXPART model, and reproduced the average seasonal cycles of the four mountain stations as obtained from the measurement data. There is a steep vertical gradient in the contribution from stratospheric

intrusions to the ozone budget. Whereas it is almost negligible at sea level, it increases to approximately 5 to 10 ppb at the level of the peak stations. This accounts for all intrusions occurring within the modelling domain (50°W to 50°E and 25°N to 80°N).

As already found during VOTALP I the intrusion frequency distribution exhibits a summer minimum for the three stations near 3000 m and below. For the higher-lying Jungfraujoch (3580 m ASL) no such pronounced summer minimum exists in both the model results and the measurements, in agreement with the results from the TOR (Tropospheric Ozone Research) project. This is due to a less deep penetration of the stratospheric air into the lower troposphere in summer, which affects the lower-lying stations, but not Jungfraujoch.

The measurements at the four peak stations Jungfraujoch, Zugspitze, Sonnblick and Mte. Cimone were continued and delivered continuous data on ^{7}Be, O_3, humidity and (in part) CO. An intercomparison exercise between the four laboratories measuring ^{7}Be at the peak stations showed that all ^{7}Be results were within twice the standard deviation of the mean. This indicates that the ^{7}Be data do not depend on the procedures applied. Stratospheric intrusions were identified based on measurement data of ozone, relative humidity and ^{7}Be. This identification was supported by calculated three-dimensional backward trajectories. The climatology of stratospheric intrusions was extended almost to the full period of VOTALP I and II.

Different procedures were applied to establish climatologies of stratospheric intrusions. A diagnostic stratospheric intrusion index was defined based on measurements of ozone, relative humidity (and beryllium-7). As shown in VOTALP I, the combined criteria "$^{7}Be > 8$ mBq m^{-3} AND rel. humidity (RH) < 40%" was fulfilled at Zugspitze for about 5% of the time during 1996-1997. In order to account for the long-term behaviour of ^{7}Be at Zugspitze with a significant decrease of the monthly means at the beginning of the 90s, a variable, statistically determined threshold value was preferred. The 85th percentiles of the annual ^{7}Be data were finally chosen, keeping in mind the drawback that this means a predetermination of the number of cases. However, for most of the years the 85th percentiles were close to 8 mBq m^{-3}.

Another intrusion index, based on the criteria "$^{7}Be > 8$ mBq m^{-3} AND RH < 40% AND $O_3 > 1.1 \times$monthly mean" was applied to the three stations Jungfraujoch, Sonnblick and Zugspitze. It was found that these criteria are suitable for Sonnblick and Zugspitze, but overestimated the intrusion frequency at Jungfraujoch. Stratospheric intrusion indices are thus station-specific and can hardly be used to compare intrusion frequencies at different stations. In view of these difficulties and the successful simulations with the Lagrangian particle dispersion model it is suggested, that the FLEXPART model is used, rather than an intrusion index. The model is a public domain model with modest requirements regarding computer space and time, which can be run with ECMWF meteorological input.

As an important by-product the lidar measurements yielded the first detection of the North-American ozone plume over Europe. During several of the stratospheric episodes high ozone values were observed in the upper troposphere which could not be ascribed to stratospheric air. The transport pathway was unambiguously identified by calculations with the FLEXTRA and FLEXPART models. Polluted air from the boundary layer of the eastern United States is exported off-shore, lifted to heights near 10 km in a warm conveyor belt and subsequently rapidly transported to Europe with the jet stream. Such episodes have been observed for periods as long as four days. Since, in addition, the ozone mixing ratios consistently ranged between 80 and 100 ppb a significant contribution of the intercontinental transport to the European background ozone concentration must be expected.

III: New aspects of vertical exchange between boundary layer and free troposphere

Substantial pollutant concentration increases could be found during the VOTALP II campaigns at altitudes above the boundary layer in the hilly areas north of Milan and south of Munich, proving that foothills contribute to vertical transport. Comparing concentrations up- and down-wind the hills in the Como area at around 2000-2100 m MSL, concentration increases of 30-40% were found for e.g. HCHO, aerosols and water vapour. Similarly, concentrations in the Garmisch hills significantly increased at 2300 m MSL, yielding around 40% concentration increase of the primary pollutants and water vapour. However, compared to deep Alpine valleys, in the Alpine foothills pollutants are not injected to those very high altitudes like 3000-4000 m MSL as observed above the Mesolcina Valley during VOTALP I.

The lidar measurements of aerosol and ozone in the Como region, indicated that the pollutants are typically only transported up to around 2200 m MSL. Combining results from VOTALP II with VOTALP I, we believe that the foothill findings can serve as a model for the processes over the whole Alps. Convergent flow is expected in the boundary layer, divergent flow at high altitudes. This yields a net average vertical wind speed of 0.03 – 0.1 m/s into a layer with substantial concentration increases. Over flat terrain, the free troposphere lies above the planetary boundary layer. In the Alpine area, there is another layer between the boundary layer and the free troposphere that we would like to call the "mountain injection layer". It is not as well vertically mixed as the planetary boundary layer, but this layer incorporates air and pollutant injections out of the planetary boundary layer. Typical altitudes of the layers over the core of the Alps are: planetary boundary layer : 200 - 2000 m MSL, injection layer: 2000-4000 m MSL, free troposphere: 4000 m MSL up to the tropopause.

The acceleration of the winds at high altitudes from the Alps to the plain in the Garmisch area might be one of the best proofs ever that thermally induced anti-valley winds exist and can be substantial. In the boundary layer, winds from the plain to the Alps were found during the day. It was often postulated that compensating anti-valley winds should exist at high altitudes from the Alps back over the plain. This is usually very rarely observed because this thermally induced flow is weak compared to the mean flow at these altitudes. Evidence for anti-valley winds has so far been found only by statistical wind analyses over longer time periods.

Aerosol lidar measurements at Garmisch-Partenkirchen in the past two years have revealed a distinct mountain injection layer, which was clearly separated in structure and, thus, indicative of a reverse flow in the height range up to 4000 m. However, this was only observed under conditions of low (5 m/s) synoptic winds from southerly to south-easterly directions.

IV: Advection of urban plumes into the Alps

The role of urban plumes for the air quality in the Alpine foothill area has been investigated during VOTALP II by means of measurements, evaluation of available data and by model calculations for three cities. The pollutant plumes of all three cities – Milan, Munich, and Vienna – are advected into the Alps under certain conditions.

During a one-month period in summer 1998 about 57% of the emissions of the Milan area were transported into the Alps, as was shown by a Lagrangian particle dispersion model (FLEXPART). The model results compared well with aircraft data available for several case studies from the VOTALP II Milan campaign in 1998 (in collaboration with the EUROTRAC-II subproject LOOP).

A statistical evaluation of operational surface measurements from 1990 to 1999 at Mendrisio also confirmed the Milan contribution to the pollutants in the foothill area. In July on 17.4%

of the days ozone enhancements could be attributed to Milan. In northerly Foehn situations (6% of the days in all seasons), however, free tropospheric air is brought down to the boundary layer of the Alpine foothills. The concentrations are low in summer, high in winter during these cases. In summer the mean ozone concentrations in Mendrisio have considerably decreased in the 1990ies. Benzene concentration levels are relatively low in comparison to the total VOC load in the Po Basin due to Italian gasoline composition regulations. Isoprene, on the other hand, considerably contributes to the OH-reactivity, as it does in other regions around the Alps.

Contributions to the ozone level at Garmisch-Partenkirchen and Wank of 11% in summer and 4% in winter were calculated for advection from the northeast sector (1990 – 1998), which includes contributions from the Munich plume. A case study for May 1999 from the VOTALP II Garmisch campaign indicated an increase of about 10 ppbv ozone registered at Bromberg and Hohenpeißenberg, which could be attributed to the Munich plume. The presence and orientation of the plume was well captured by the measurements. In this case study, however, the plume reached the Alpine foreland too late to be completely sucked into the Loisach valley and to Garmisch-Partenkirchen.

Anthropogenic as well as biogenic concentrations of volatile organic compounds (VOC) are higher at lower levels (Bromberg near Munich and Alpe del Vicere near Milan) than at the elevated sites Wank and Monte Boletto. A high correlation between benzene derivatives at most measuring sites indicates that traffic is the predominant emission source in the pre-Alpine area.

One of the important topics of discussion in VOTALP II, but also and much more so in LOOP, was the extent of the VOC- and/or NO_x-limitation around Milan. The problem has not been completely solved so far. While simulations with the Lagrangian photochemical column model IMPO (based on FLEXTRA trajectories) for a period of two months indicate predominant VOC-limitation within the whole area including the foothills, most modelling groups within LOOP and also the EURAD model claim VOC-limitation only in a more limited area around Milan and a transition to NO_x-limitation before the plume reaches the foothills. However, these model calculations are based on an emission inventory, which does not include biogenic NO_x-emissions as does the IMPO model, and the LOOP calculations were basically made just for one case study and not for a period of two months. Some further model comparisons and data analyses are necessary to obtain a clear picture of the situation.

The outcome is of great importance when discussing emission reduction scenarios. Applying the Lagrangian photochemical model results a reduction of VOC-emissions in the area would lead to a stronger ozone reduction than a reduction of NO_x-emissions. Furthermore, Europe-wide reduction of both, VOC and NO_x would additionally improve the air quality in that region.

V: The Alpine effect on the European ozone concentrations

The hypothesis behind the fundamental VOTALP II question "What is the effect of the strong vertical exchange over the Alps on the ozone concentrations in the Alpine region and in Europe as a whole?" proved to be correct: The Alps increase vertical exchange and thus lead to enhanced pollution transport into the mid-troposphere, enhancing net ozone production at levels between 3000 and 4500 m. There is very strong agreement between measurement-based data analyses, the long-term tracer simulation and the episodic CTM simulations that the Alps influence the free troposphere above Europe up to heigths of up to 4500 - 5000 m.

Our long-term tracer simulation (4 months) shows that there is an 4-month averaged net upward flow above the Alps across levels of 3000 to 4500 m. We showed that, on the average, the Alps cause an increase of 5-10% of the vertical transport towards the mid-troposphere above Europe. This yields to an averaged mid-tropospheric excess concentration of NO_x of approximately 10 ppt in the lower to middle free troposphere over Europe, presumably increasing the vertical extent of the region where O_3 is photochemically produced.

Photochemical model calculations done with the EURAD model for four case studies, weighted by the frequency of the relevant weather patterns, confirmed that the Alps are a region with enhanced vertical transport. On the average, pollutants (e.g. NO_x and PAN) in the lower free troposphere (~700 hPa) are enhanced by a factor of more than 2 over the Alps than over the rest of Europe. They would be significantly lower (about 70%) in this region without the topography related processes. Moreover, in base-case calculations including the topography a net O_3 production of about 1.3 ppb/day was found, whereas in the case without topography, the same region proved to be a net O_3 sink of the same order of magnitude. Vertical transport is the most important among these processes, but local anthropogenic emissions at high altitudes do also play an important role.

While the Alps clearly play a role for vertical exchange between surface and the mid-troposphere, they do not seem to play a role in deep vertical exchange (surface to upper troposphere). Pollutant fluxes across 6000 m are only slightly enhanced, fluxes across 8000 m and 10000 m not at all.

On hemispheric to global scales, vertical exchange above Europe is weak, compared with the regions off the coast of the southern USA and Asia, but also compared with the continental USA as a whole. This generally leads to comparatively lower pollutant concentrations and presumably to reduced summertime O_3 production in the free troposphere above Europe, but in return to higher concentrations in the lower troposphere.

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PART B:

INDIVIDUAL REPORTS OF THE CONTRACTORS AND SUBCONTRACTORS

Final Report of IMP

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1. Objectives for the reporting period

Besides the co-ordination of the project, the main objectives pursued during the reporting period were:

- Climatological investigation of transport and ozone formation for an Alpine valley with a Lagrangian model approach. Establishing, testing and evaluating a suitable model concept. Emission reduction scenarios
- A measurement- and model based climatology of stratospheric intrusions resulting in a diagnostic and prognostic stratospheric intrusion index
- Analysis of existing aircraft measurements from Milan, Vienna and Munich together with additional data to get an overview of the contribution of urban plumes to the Alpine region. Combination of the data analysis with air trajectory studies and particle model simulations of anthropogenic emissions
- Lagrangian box model simulations of ozone formation and transport towards the Alps making use of new emission and measurement data available from the EUROTRAC-II subproject LOOP
- Long-term particle diffusion model simulations of the Alpine effect on vertical exchange of pollutants above Europe and analysis of the model results
- Maintaining the VOTALP data base
- Integration of the results of all work packages and provision of answers to the fundamental question posed in the objectives of VOTALP II

2. Main results obtained (methodology, results, discussion)

I: Local ozone production in Alpine valleys

Long-term model simulations for an Alpine valley

As it is not possible to make reliable climatological assessments of transport and formation of ozone in an Alpine valley (e.g. the Mesolcina Valley), using high-resolution Eulerian models, due to limitations in the availability of computer resources, an attempt was made to do this using a Lagrangian approach. Three scales of the transport processes have to be considered, namely i) the transport towards the Alpine region, ii) the transport across the foothills to the valley entrance and iii) the transport within the valley. It had been shown in VOTALP I, that a Lagrangian photochemical box model approach yielded plausible results for transport calculations towards the Alps even when it is based on coarse wind fields (ECMWF, 1°×1° spatial and 3h temporal resolution). In the complex terrain of the Alpine foothill region as well as in the Alps such a horizontal resolution is too coarse. Higher resolved wind fields are available from the operational weather forecast model of MeteoSchweiz (SM model) with 0.125°×0.125° (approx. 14 km×14km) horizontal and 1h temporal resolution. However, comparisons of vertical wind profiles from the SM model with measured ones by a wind profiler at Seregno (Po Basin, north of Milan, Mai-June 1998) and Cadenazzo (complex terrain, July-August 1996) for a period of more than one month yielded that the SM model gives quite satisfying results within the Po Basin, whereas in the Alps much less correspondence was found. Vector correlation increased towards higher altitudes and during daytime when advection from the South was predominant. Nevertheless, a higher resolution than that available is needed for a sound simulation within the Alps.

Two different models – VALDRIFT and ALPTHERM – were considered for simulations within the valley, but both, partly due to conceptual caveats, partly due to organisational and proprietary problems, proved unsatisfactory. A totally different concept would have been needed, the development of which was not feasible within VOTALP II. Instead, more emphasis was put on the investigation of the advection of urban plumes towards the Alps performing a long-term Lagrangian particle dispersion model (LPDM) simulation for Milan, that had not been promised in the workprogram.

II: Climatology of ozone influx from the stratosphere

Climatology of stratospheric intrusions

In order to develop a climatology of stratospheric intrusions in the Alps, we used two independent approaches: one based on measurement data, the other based on model calculations. Both methods have been described in detail by Stohl et al. (2000) and have been updated for this report.

Observational climatology: In our screening algorithm of measurement data a day is considered to be an "intrusion day" if (i) the ^{7}Be concentration is higher than 8 mBq m^{-3}, (ii) the daily minimum RH is lower than 30%, and (iii) the daily maximum O_3 concentration is at least 10% above the monthly mean concentration. Although the results are highly sensitive to the choice of the thresholds the shape of the annual cycle is stable against variations of these thresholds with most frequent stratospheric intrusions during the winter season and a minimum during the summer.

The average frequency of intrusions detected at Zugspitze during the period 1991 to 1998 is 6.0%, consistent with values reported by Scheel et al. (1999) for 1996 and 1997 only.

Intrusions are most frequent in October (11%), with a secondary maximum in winter and early spring. A deep early summer minimum (<3%) during April through July is found (Figure 1). Using the same selection criteria, the average intrusion frequency at Sonnblick during the period June 1996 through June 1999 (7.1%) is a little higher than that at Zugspitze[1]. As at Zugspitze, intrusions are most frequent in autumn and late winter and feature a summer minimum. The summer minimum is even more pronounced at Sonnblick, with no intrusion days at all in June and August.

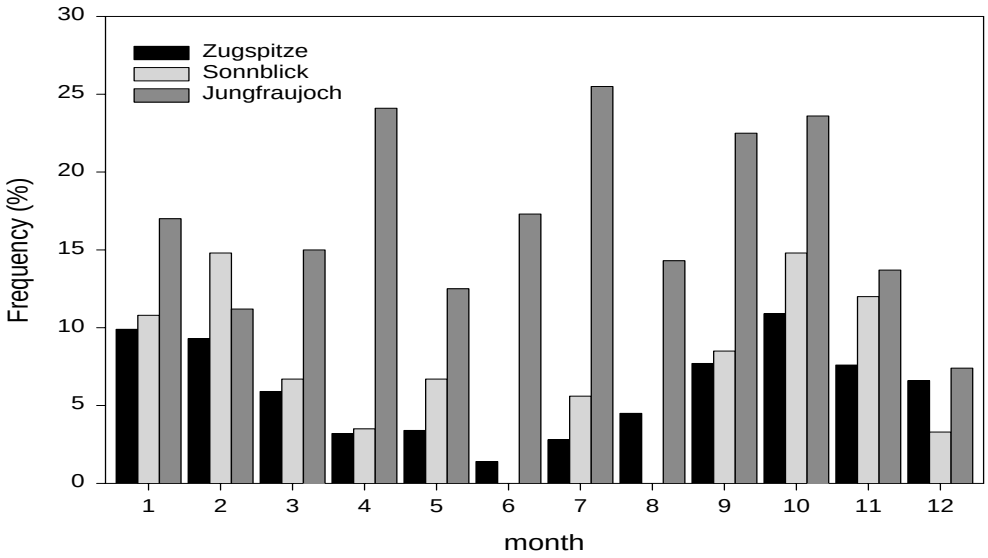

Figure 1: Seasonal variation of the frequency of stratospheric intrusion days at the sites Zugspitze (1991 through 1998), Sonnblick (June 1996 through June 1999) and Jungfraujoch (April 1996 through August 1999) as obtained with the observational detection algorithm.

At Jungfraujoch (period April 1996 to August 1999), the average intrusion frequency (17%) is much higher than at Zugspitze and Sonnblick. Also in contrast to the other stations, there is little seasonal variation. At present, the reason for the high frequency of observed intrusions at Jungfraujoch remains unclear. Possibly the detection algorithm, which was set up by studying intrusions mostly for Zugspitze, is less suited for Jungfraujoch. At that altitude, tropospheric air may more often show signatures (low RH, high ^{7}Be concentrations) that at lower levels are characteristic for stratospheric intrusions. In fact, average ^{7}Be concentrations at Jungfraujoch are much higher than at the other stations. However, while using a higher threshold level for ^{7}Be (12 mBq m^{-3}) brings the average intrusion frequency into agreement with Sonnblick and Zugspitze, it does not change the annual variation which remains in contrast to the other stations.

Model climatology: Ozone behaves almost like a passive tracer over timescales of a few days. Therefore, on these timescales, it is possible to simulate intrusions of ozone from the stratosphere using a passive tracer model. For this, we used a special version of the stochastic Lagrangian particle model FLEXPART. The model setup has been described by Stohl et al. (2000). The model climatology now covers almost five years (January 1995 through August 1999).

[1] In contrast to Stohl et al. (2000), relative humidity at Sonnblick was determined from the dewpoint measurements rather than relative humidity measurements because of many missing relative humidity data in 1998 and 1999. This resulted in a somewhat lower frequency of stratospheric intrusions.

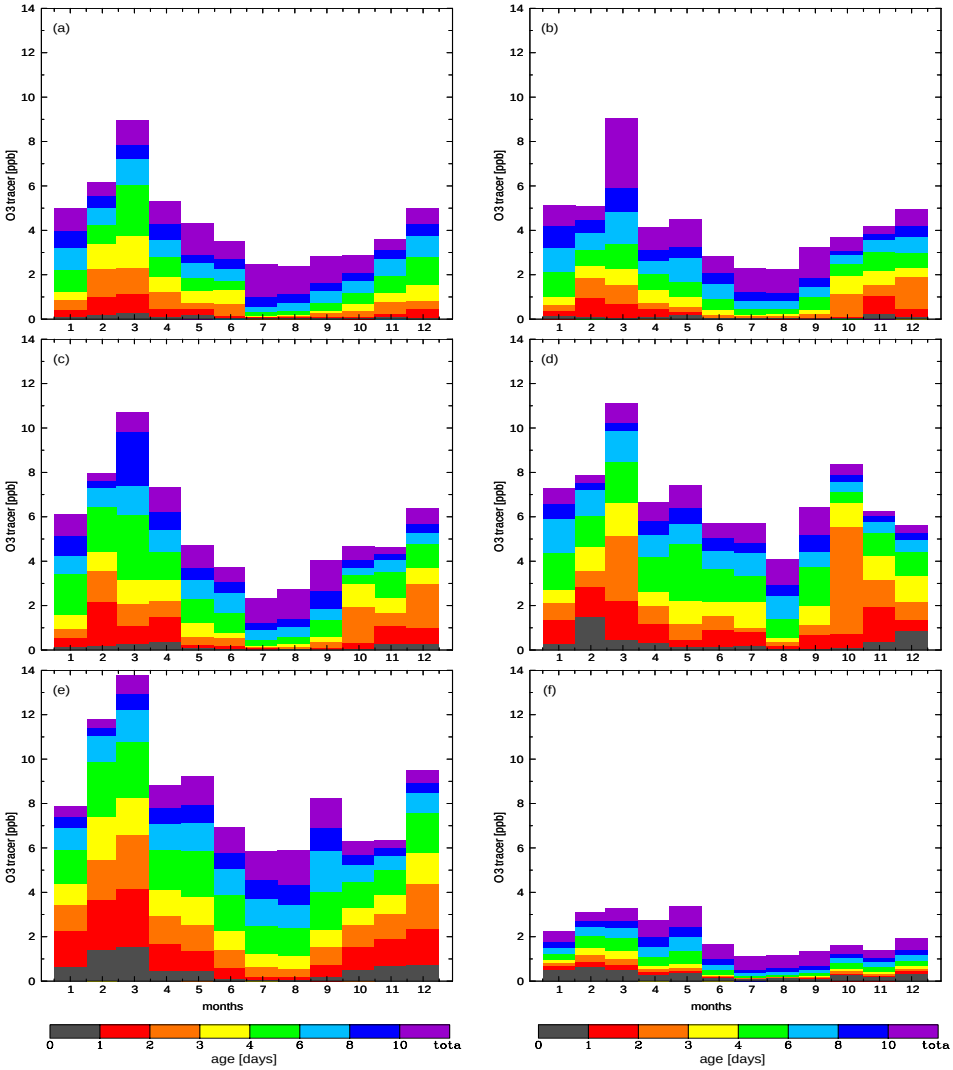

Figure 2: Seasonal variation of the modelled ozone tracer mixing ratios at Mt. Cimone (a), Zugspitze (b), Sonnblick (c), Jungfraujoch (d), at 3500-4000 m in the European box (e), and at the surface in the European box (f).

Figure 2 shows the seasonal variation of the O_3 tracer, averaged over nearly five years, at the mountain peaks and in the highest and lowest layer of a European-scale box. A strong seasonal variation is evident at all sites, with a minimum in mid-summer and a maximum in late winter/early spring. At the highest station, Jungfraujoch, the variation is weakest and a secondary October maximum appears. This seasonal variation is in good agreement with that shown in Figure 1 as obtained from the observational climatology. In both climatologies, there is a deep summer minimum at Zugspitze and an even deeper one at Sonnblick. Although O_3 tracer concentrations at Jungfraujoch are somewhat higher than at the other two sites, the difference is much less than in the observational climatology. In both the model climatology and the observational climatology, however, the seasonal variation of stratospheric intrusions is much weaker at Jungfraujoch. Obviously, this is due to the higher altitude of this site, because stratospheric intrusions penetrate less deep into the troposphere in summer than in winter.

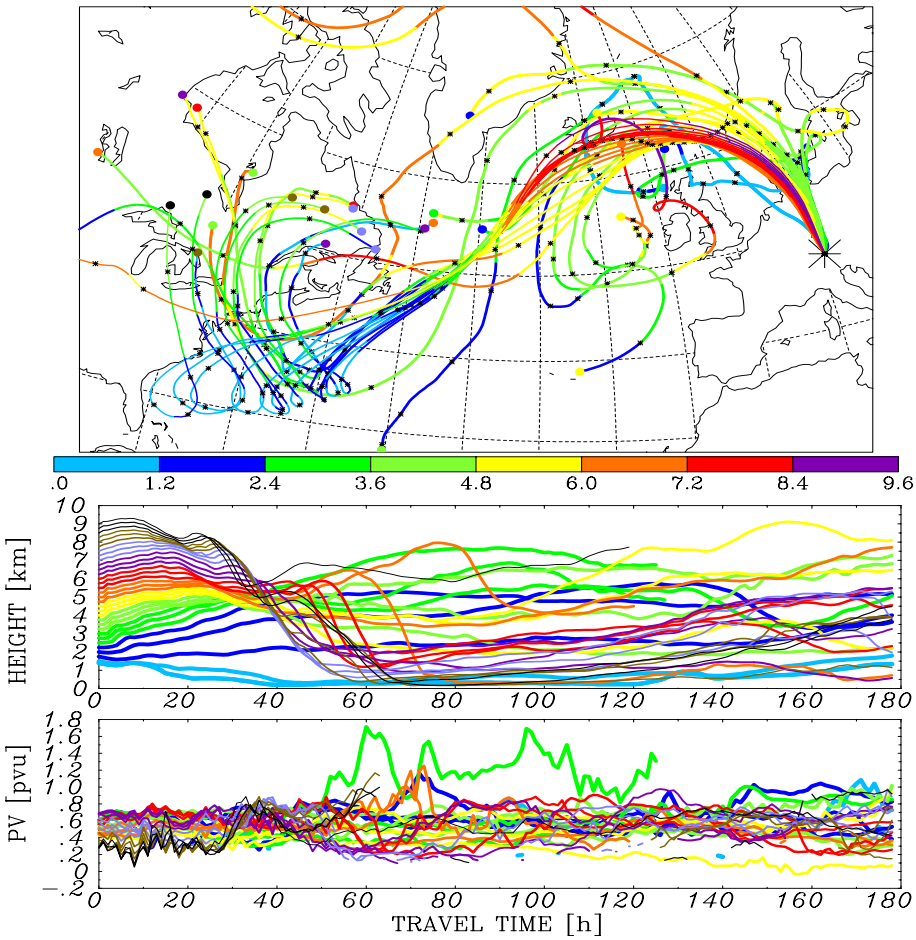

Figure 3: 178 h three-dimensional backward trajectories terminating at the lidar measurement site every 250 m in height on 29 May 1997 at 9 UTC (corresponding to 34 h in the measurement time series): the top figure shows a horizontal projection of the trajectories, with the colour-coding according to the label bar referring to the actual heights (in km ASL); positions are marked with asterisks every 24 h. The dots at the trajectory starting points indicate the heights where the trajectories terminated along the lidar profile, with the colour code of the dots corresponding to the middle figure. The same information is also provided by the line widths (thinner lines representing trajectories terminating at higher levels). The middle figure shows time-height profiles of the trajectories with both colour and line width indicating their ending height at T=0. The bottom figure represents PV along the different trajectories with both the line colour and line width corresponding to the middle figure. PV data is sometimes missing in the boundary layer in unstable situations. Some of the trajectories were terminated because they exited the computational domain. Note that time is backward along the trajectories.

An interesting result is the almost complete absence of direct intrusions with a tropospheric age of less than four days in mid-summer. Direct stratospheric intrusions deliver 4-25 times more O_3 tracer to our receptor boxes during February through April than during June through August. This strong seasonal variation is only partly due to the initialisation of the O_3 tracer in relation to PV. Mainly it is caused by differences in the circulation patterns of the atmosphere.

Ozone transport from North-America

As a by-product of the VOTALP stratospheric intrusion studies, Stohl and Trickl (1999) have identified the first ozone episode over Europe that was unambiguously caused by transport from the North-American boundary layer. The ozone, photochemically produced at the American east coast, was uplifted in a warm conveyor belt over the Atlantic Ocean. A MOZAIC airplane, flying through this warm conveyor belt at an altitude of 10700 m ASL in the middle of the Atlantic Ocean recorded ozone concentrations of up to 100 ppb, positively

correlated with water vapour. Behind and above a stratospheric intrusion, the warm conveyor belt air was then transported to Europe. Lidar measurements in Garmisch-Partenkirchen (see contribution from IFU) showed pockets of high (80-100 ppb) ozone concentrations above a filament that descended from the stratosphere. Radiosoundings showed that the air in the ozone pockets, in contrast to the stratospheric filament, was very moist.

Trajectory calculations established the pathway of the air from North-America to the lidar site (Figure 3). While trajectories ending in the stratospheric filament at approximately 3 km ASL descended, those ending in the moist ozone maxima at higher levels ascended from the North-American seaboard. A background measurement station in Virginia also measured ozone concentrations of around 100 ppb, in agreement with the MOZAIC and lidar observations along the paths of the trajectories.

Work package 4, Activity 1: Analysis of existing data

"Historical" MetAir aircraft data of several campaigns near and in the Alps from 1991 onwards were transformed into one uniform data format, the VOTALP data format. Analysing the suitability of the data, it turned out that a thorough investigation of the advection of urban plumes towards the Alps was most promising using the aircraft data around Milan and the Ticino region from the 1998 LOOP/VOTALP campaign. In addition to the workprogram a long-term LPDM simulation was performed to investigate the impact of Milan on pollutant concentrations in the Alps. This is described in more detail in "IV, Modelling the contribution of urban plumes". The results of the simulation were compared with the aircraft data and pollutant fluxes were calculated.

The climatological study of the contribution of urban plumes performed by IFU using existing pollutant measurement data from Garmisch, and Wank in southern Germany was supported by trajectory calculations and the classification of general weather patterns.

An analysis of data measured between 1990 and 1995 at the station Exelberg near Vienna revealed, that in cases when the wind direction led to transport from the city, ozone and NO_x were significantly higher in summer than in cases of other wind directions. In winter, air from the city showed lower ozone values. Wind from the direction of the city was observed in about 25% of all cases. Figure 4 shows the averaged diurnal course of ozone and NO_2 in July at the station Exelberg.

As Exelberg is located quite close to Vienna, at the easternmost part of the Alps, tracing the Vienna plume to Exelberg might not suffice to define plume transport to the Alps. Indeed, most of the case studies for which aircraft data are available, show the urban plume moving around the Alps to the north or the east. However, some cases are documented, which confirm direct transport of the Vienna plume into the Alps. In this respect, these results agree with those of other groups within VOTALP II for Munich and Milan, showing the influence of the big cities on the pollutant concentrations in the Alps.

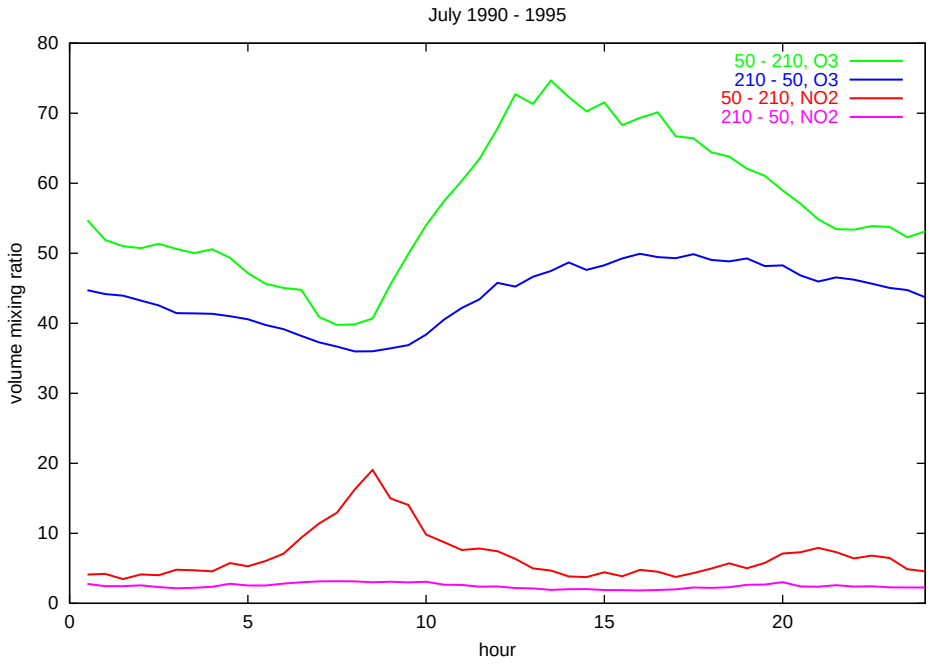

Figure 4: Diurnal course of ozone and NO_2 at Exelberg near Vienna in July, derived from data measured between 1990 and 1995. Green: ozone with wind from sector 50º to 210º (Vienna), blue: ozone with wind from other directions, red: NO_2 with wind from sector 50º to 210º (Vienna), magenta: NO_2 with wind from other directions.

IV: Advection of urban plumes into the Alps

Modelling the contribution of urban plumes

Lagrangian box model calculations were performed for the months of May and June 1998 for several stations in the forelands south of the Alps. The calculations are based on air trajectories computed with wind fields from the MeteoSchweiz weather forecast model (SM model) with a horizontal resolution of $14\,km \times 14\,km$ (Majewski, 1991). The available Lagrangian column model was extended by the photochemical RACM mechanism, which is intended to be valid for remote to polluted conditions and from the Earth's surface through the upper troposphere (Stockwell et al., 1997). A new emission inventory made available from the EUROTRAC-II subproject LOOP was also introduced into the model. Using the new inventory, emission reduction scenarios were calculated.

The model had been validated with trace gas measurements obtained during the VOTALP/LOOP-1998 campaign. The comparisons showed, that its application is only feasible at a certain number of stations, since the SM model did not resolve local wind structures, like e.g. slope winds, which might advect fresh air from above towards the measuring station at night. At some other stations (mainly in the foothills) the diurnal course of the trace gas contribution is strongly influenced by such phenomena. Therefore the model was only applied for locations, at which the diurnal course of the measured wind direction resembled that of the SM model. As examples for the further calculations the stations Bresso (near Milan), Lugano and Magadino (in the foothills) were chosen. Scenario calculations of the full months May and June 1998 for Bresso, Lugano and Magadino, in which either the NO_x- or the VOC- emissions or both were reduced by 35% in the whole of Europe as well as in the limited local area of the LOOP-emission-inventory around Milan (162 km × 141 km), showed, that the area is more sensitive to reductions of VOC than to NO_x-reductions. Local

reductions in the Milan area have a strong effect on the foothill area in cases of southerly winds. However, Europe-wide reductions are generally more effective. The following table shows the effect of the reductions on the average volume mixing ratio of O_3 and NO_2 as well as the AOT40 and AOT60 values for the months May and June 1998.

Table 1: Average results of emission scenario calculations for Lugano, May and June 1998.

	Meas.	0%	35% NO_x	35% VOC	35% both
Reductions in the area around Milan:					
O_3 averages / ppb					
All values	50.3	49.9	52.6	46.9	50.8
Daytime	56.5	59.6	61.6	56.3	59.4
Night-time	38.2	38.1	41.7	36.0	40.5
AOT40[2] / ppb h					
Sum	20654	17861	18952	15215	17194
/ day	338.6	292.8	310.7	249.4	281.9
/ hour	22.6	19.4	20.6	16.6	18.7
AOT60[2] / ppb h					
Sum	12441	7064	7418	5068	6022
/ day	204.0	115.8	121.6	83.1	98.7
/ hour	13.6	7.7	8.1	5.5	6.6
NO_2 averages / ppb					
All values	17.0	11.8	7.9	12.3	8.1
Daytime	18.1	7.5	5.0	7.8	5.2
Night-time	17.4	15.8	10.5	16.3	10.7
Europe-wide reductions:					
O_3 averages / ppb					
All values	50.3	49.9	51.2	44.9	48.2
Daytime	56.5	59.6	59.8	54.0	56.4
Night-time	38.2	38.1	40.7	34.3	38.5
AOT40[2] / ppb h					
Sum	20654	17861	17513	13533	14847
/ day	338.6	292.8	287.1	221.9	243.4
/ hour	22.6	19.4	19.1	14.7	16.2
AOT60[2] / ppb h					
Sum	12441	7064	6334	4133	4445
/ day	204.0	115.8	103.8	67.8	72.9
/ hour	13.6	7.7	6.9	4.5	4.8
NO_2 averages / ppb					
All values	17.0	11.8	7.4	12.4	7.7
Daytime	18.1	7.5	4.6	8.0	4.8
Night-time	17.4	15.8	10.0	16.5	10.4

[2] Accumulated ozone exposure above a threshold of 40 ppbv (AOT40) and 60 ppbv (AOT60). Only values at daytime (solar elevation > 0°) were considered. Normally these values are calculated from daytime hourly means over a period of 3 months (May - July for AOT40) and 6 months (April - September for AOT60). In this work the values noted sum are the averages over 2 months (May and June). In addition the averaged values over the considered days and the considered hours are given in the table.

A reduction of NO_x-emissions by 35% leads in all cases to an increase of the averaged ozone mixing ratio. At night-time this obviously is caused by the reduced efficiency of the ozone destruction reaction with NO. Also at daytime small increases of the ozone mean due to NO_x-reduction can be observed. However, also single situations were found when ozone decrease together with NO_x-reduction occurs. In the case of emission reductions only in the Milan area, the 35% NO_x case also shows an increase of the AOT40 and AOT60 values (AOT40 = Accumulated Ozone over a Threshold of 40 ppbv) by 6.1% and 5.0%, respectively, indicating, that the area is VOC controlled. In contrast, when the emissions are reduced all over Europe, the 35% NO_x-reduction causes a reduction of AOT40 and AOT60 by 2.0% and 10.4%. This is, however, not as strong as the reductions caused by VOC control of 24.2% and 41.5%, respectively, or by reductions of both, NO_x and VOC, of 16.9% and 37.1%, respectively. The difference in the behaviour of the two reduction scenarios can be explained with the atmospheric lifetime of NO_x which is in general shorter than that of VOC. Therefore, emission reductions tend to show higher VOC-sensitivity only in the vicinity of the source.

The high VOC-sensitivity at Lugano calculated with the Lagrangian column model seems to be in contrast to several Eulerian calculations, including the EURAD model, which predict a transition from VOC- to NOx-control at a closer distance to Milan. However, these models do not consider biogenic NOx-emissions as does our model. This difference alone might cause the disagreement. A second uncertainty lies in the treatment of biogenic VOCs like isoprene, which differs considerably between the models. Further research is needed to find out about the reasons for the contradicting model results. Comparisons with other models and studies about the influence of biogenic emissions on NOx/VOC-control are necessary for a detailed and complete answer.

The emission of ozone precursors in Europe and in particular in the vicinity of the Alps contribute to the ozone concentration in the Alpine foothills. If the Lagrangian model simulations presented here prove right VOC control on local emissions results in a stronger efficiency in reducing the ozone abundance. Considering emissions on a European scale, reductions of both, NO_x and VOC emissions, would be effective.

LPDM simulation: The impact of Milan, pollutant fluxes towards the Alps

A Lagrangian particle dispersion model simulation with FLEXPART based on SM-model wind fields was performed to investigate the impact of Milan on pollutant concentrations in the Alps. From the model results pollutant fluxes from Milan and the Po Basin towards the Alps were calculated. The simulation covered the period from 4 May to 14 June 1998. Particles were released as passive tracer (no chemical reactions, no deposition) according to NO_x emissions from the EMEP-1992 emission inventory of $14\text{km} \times 14\text{km}$ resolution and the LOOP-Pipapo-1998 emission inventory with spatial resolution of $3\text{km} \times 3\text{km}$ and temporal resolution of 1 hour. To differentiate between different emission regions particles were especially marked according to their release area: Milan, Po Basin and the rest of Europe. Each particle carries masses of NO_x and CO taken from the emission inventories. Within the whole model domain 1.2-1.5 mio. particles where released per day depending on the day of the week. Calculated tracer concentrations were compared with aircraft and ground measurements performed during the LOOP/VOTALP II campaign between Milan and the Alps (see example of 4 June 1998 in Figure 5).

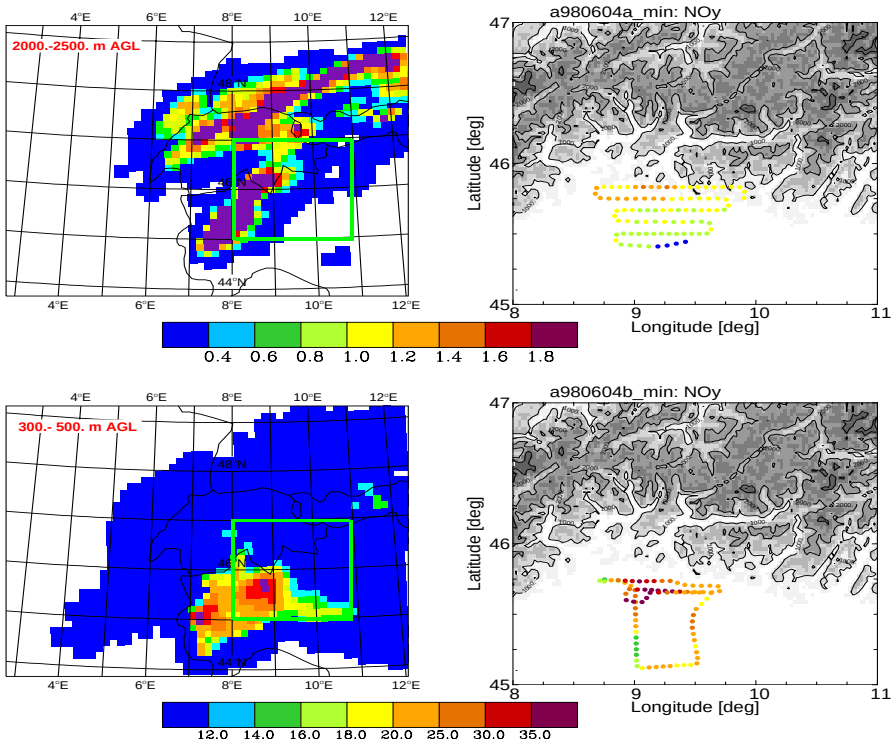

Figure 5: Concentrations [µg m^{-3}] of Milan and Po Basin tracer (left) and of NOy measured by aircraft (right) on 04 June 1998 for the morning flight (top; 9–11 UT, 2700 mASL) and the afternoon flight (bottom; 15–16:30 UT, 400–500 mASL). Note that the measurements cover only part of the model domain (green box).

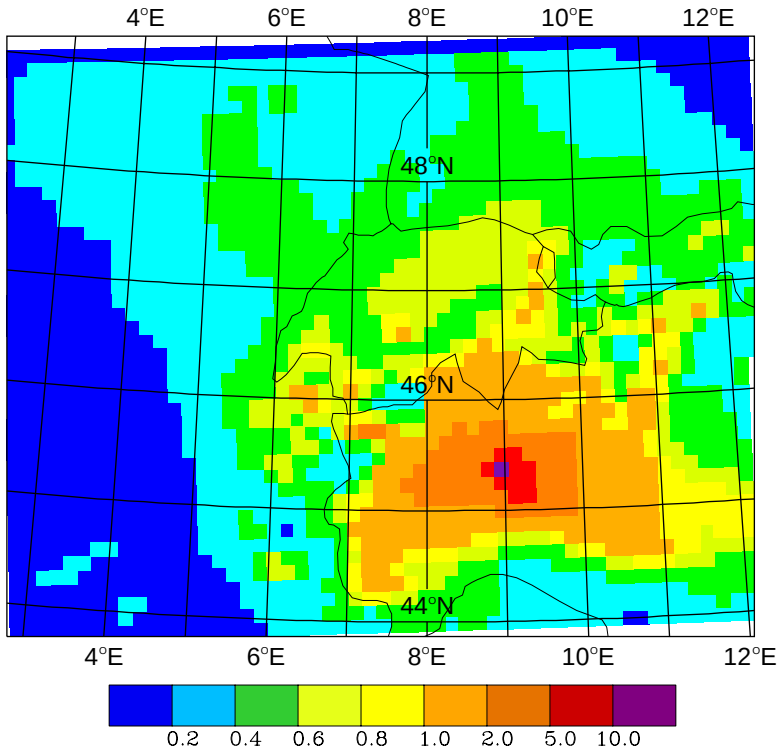

Figure 6: Average concentration of Milan tracer [µg m^{-3}] between model ground and 3500 mAGL for the period 10 May to 14 June 1998.

From the model calculations it becomes obvious, that Milan contributes to a significant extent to pollutant concentrations in the Alps. The mean vertically averaged (0 – 3500 mASL) Milan plume clearly extends into the Alps, as is shown in Figure 6. Tracer fluxes were calculated from 3D concentration fields and wind fields from the SM model. This is possible for any vertical or horizontal cross section within the model domain. The integrated meridional flux of Milan tracer through a vertical cross section between Milan and the Alps for the period of 10 May to 14 June yielded that 79% was advected northwards into the Alps. 22% of this amount was recirculated again southwards, resulting in a net percentage of 57% of Milan tracer transported northward into the Alps.

V: The Alpine effect on the European ozone concentrations

Ascending airstreams in the northern hemisphere

Mountain ranges can cause air to ascend either on their upwind (e.g. foehn) or downwind (e.g. lee-waves) side, possibly exporting air pollution from the boundary layer into the (upper) free troposphere. These are relatively large-scale effects, not directly related to smaller-scale processes like convection, and are at least partly captured by global models (e.g. ECMWF). It was interesting to study whether the Alps (or, more generally, also other mountain ranges of the northern hemisphere) cause airstreams to ascend more frequently than over other areas with less complex topography.

To do this, we calculated forward trajectories that were started on a 1° ×1° grid covering the whole northern hemisphere north of 5° N with height intervals of 1000 m between 500 m and 13500 m above sea level every day at 12 UTC over the period 1 April 1997 to 3 April 1998 (433.000 trajectories every day; 160 million trajectories totally). Calculations were carried out with the FLEXTRA model (Stohl et al., 1995; Stohl and Seibert, 1998; Stohl et al., 2000), driven with wind fields from the European Centre for Medium-Range Weather Forecasts at a resolution of 1°. Analysis fields were used every six hours and three-hour forecast fields every other three hours.

Employing this trajectory dataset we can apply suitable criteria to select ascending trajectories. Because mountain waves or foehn act on relatively short time-scales, we used trajectories of only 24 hours duration. In case studies it was found that mountain waves can cause rapid upward transport of several thousand meters downwind of the Alps. Therefore, we selected those trajectories that ascended by 3000 m or more during 24 hours. All results were averaged in 2ºlatitude ×3º longitude grid cells.

Figure 7 shows the relative frequency of the trajectories ascending by 3000 m within 24 hours relative to all other airstreams starting from the respective grid cell for the four seasons. The dominant signal throughout the whole year are the high frequencies of ascending trajectories in the mid-latitude stormtracks over the Atlantic and Pacific Oceans. The frequencies are particularly high at the eastern seaboards of North-America and Asia. These maxima are related to warm conveyor belts, which were found within VOTALP to cause intercontinental ozone transport (Stohl and Trickl, 1999). Surprisingly, in this scale, no strong signal is found close to major mountain ranges. The smaller maxima south of the Himalayas in spring and summer are related to the monsoon flow, which is enhanced by the presence of the mountain range. Over North-America a maximum of upward flow is found to the east of the Rocky Mountains in summer, probably due to lee-waves triggered in the westerlies. However, no signal at all is found over the Alps. Obviously, the Alps, because of their west-east orientation

and much lower altitude cause little large-scale ascent, at least when compared to the more important ascent regions on a global scale.

It must be noted that these results are quite stable and do not depend on the particular criteria used for selecting ascending airstreams. Similar results are also found for 48 hour and 72 hour trajectories, for stronger and weaker criteria for ascent (varying them from 1000 m to 8000 m) and other starting levels of the trajectories (from 500 m ASL to 7500 m ASL). With none of the above experiments was a region of frequent ascent identified over the Alps.

Therefore, our conclusion is that ascending airstreams rarely originate over Europe. Not even the Alps seem to cause any regional-scale maxima with more frequent ascent. Of course, convection is not accounted for in these calculations.

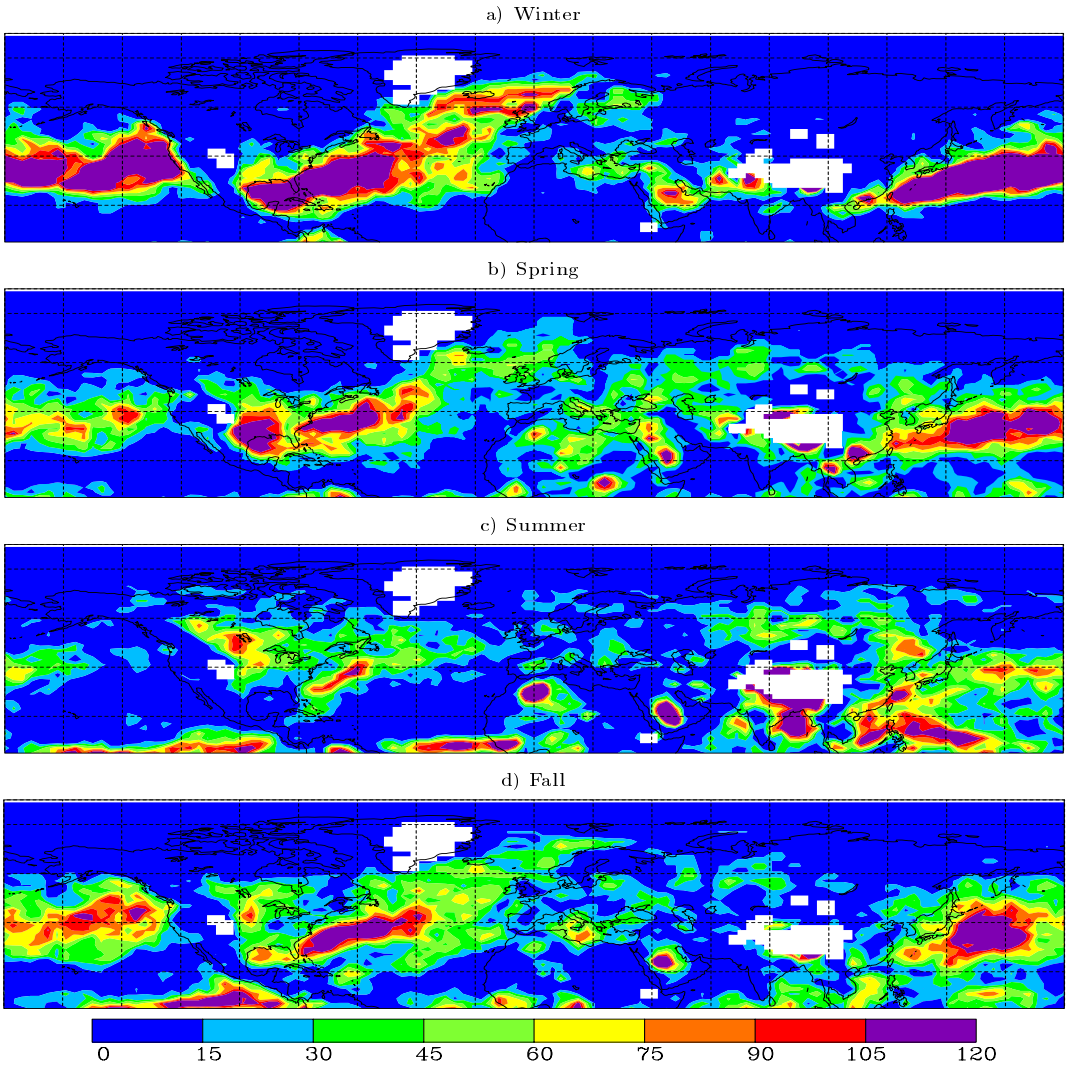

Figure 7: Frequency (‰) of airstreams starting from 1500 m ASL and ascending more than 3000 m within 24 hours relative to all other airstreams starting at this level. The white areas over Greenland, the Himalayas and the Rocky Mountains are due to high topography.

Long-term LPDM simulation for the Alps

To investigate the "climatology" of air parcels heaved into the free troposphere (FT) above the Alps, a four-month (April – July 1998) Lagrangian model simulation with a continuous particle release across large parts of western, southern and central Europe was performed

applying the Lagrangian particle dispersion model FLEXPART (Stohl and Thomson, 1999). Anthropogenic emissions of carbon monoxide (CO) and nitrogen oxides (NO_x) as specified in the EMEP-1992 inventory were simulated. CO was treated as inert tracer (no chemical reactions, no deposition), but a maximum particle lifetime of 14 days was assumed. In the case of NO_x, a first-order decay of NO_x to nitric acid (HNO_3) and dry plus wet deposition of both species was considered. The meteorological input data for the transport simulation were taken from analyses with a 0.4° (~30 km) resolution above Europe provided by the European Center for Medium Range Weather Forecasts (ECMWF, 1995). The particle masses were sampled on a 0.5° output grid with the lowest box between surface and 150 m and the highest between 9000 m and 11000 m. A simple parameterisation of convective mass fluxes was introduced into the model.

The European-scale tracer run was validated with CO measurements at the European background stations Zugspitze and Mace Head, Ireland. At Mace Head, two months (May, June) showed significant influence from Europe. During these two months, the correlation between measured and modelled daily afternoon CO concentrations was 0.69 and 0.76. At Zugspitze, the influence from the European boundary layer also varied from month to month. The correlation between modelled and measured daily averaged CO concentrations varied between 0.44 and 0.55. Since both stations are influenced by variations of the continental background CO concentrations and, at least as Zugspitze is concerned, also by subgrid-scale transport processes, the general correspondence between measurements and model results is reasonable and confirms the validity of the simulation.

During the 4-month period, approximately 1% of the emissions (300 kt CO) were transported across 10000 m. A summertime study above North-America showed an integrated flux across 10500 m of 5% of the emissions (Wotawa, 2000), with even higher percentages above a comparable area in the central USA. This is in good agreement with the results of the trajectory evaluation (Figure 7), yielding a much weaker vertical exchange above Europe compared with other parts of the world. The 4-month run showed a pronounced variability of integrated pollutant mass fluxes above Europe. In April, fluxes were generally highest above north-western Europe. In May, vertical exchange increased considerably during weather patterns with northerly flow across Europe. During this time, we saw high CO concentrations in the FT above the Mediterranean region with very high vertical upward fluxes along the coastlines. In June, the exchange rates decreased again, and the pattern of high CO fluxes shifted towards the continent. In July, we saw almost unchanged exchange between lower and mid FT, but considerably increased deep exchange. In total, high average CO concentrations in the mid-FT above Europe predominated above the continental areas east of the Alps (see Figure 8). However, while mean vertical fluxes showed strong regional variability throughout the year, we observed increased flux rates above the Alpine region during all months (4-months averaged vertical fluxes are presented in Figure 9).

Above the Alpine region, we found increased CO flux rates in the mid-FT (3100 m - 6000 m AGL), but no higher fluxes towards the upper FT. We compared the 4-months integrated fluxes at different model levels above three different regions (see Table 2), namely the Alps (4°E-18°E, 43°N-50°N), northwestern Europe (4°W-14°E, 50°N-56°N) and southeastern Europe (18°E-30°E, 37°N-44.5°N). All three regions make up less then 10% of the whole model domain. We found that 15-20% of the vertical CO fluxes across 3100 m, 4250 m and 6000 m take place above the Alpine region. The respective integrated fluxes above the Alps are more than two times higher then those above northwestern Europe or southeastern Europe. Fluxes across 8000 or 10000 m, however, are not significantly increased above the Alps. If one quantifies the effect of the Alps with the integrated flux rates above the expected limit

(15-20% instead of 10%), we see that the pollutant fluxes into the lower to middle FT above Europe are increased by 5-10% due to the existence of the Alps. This translates to excess mid-tropospheric CO concentrations of approximately 1 ppb and excess NO_x concentrations of approximately 10 ppt. Since 40 ppt of NO_x are considered as limit for photochemical O_3 production, and since average NO_x levels in the FT above Europe were found to be low due to weak vertical exchange (80 ppt between 3500 m and 5000 m, 30 ppt between 5000 m and 7000 m), this contribution can significantly increase the vertical extent of net summertime O_3 production above the continent. Particularly high averaged free tropospheric CO concentrations, especially between 3500 and 5000 m, were found south of the Alps (Po Basin). These concentrations belong to the highest above all over Europe, and this model result is strongly supported by CO measurements at Jungfraujoch, where a number of episodes with highly enhanced CO concentrations, all of them connected with Po-Basin crossing trajectories, were identified in 1998.

The dependency of the results on model resolution was investigated with an additional FLEXPART simulation for 14 – 30 April, 1998, fed with data from a nonhydrostatic nested-grid MM5 model prediction (Grell et al., 1994). A resolution of 6 km was chosen for the innermost grid covering parts of the Alps, and the whole Alpine region was covered in a resolution of 18 km.

By comparing the ECMWF-based 0.4 model simulation with our high-resolution model simulation, we found no strong differences in vertical exchange. Averaged vertical CO profiles (normalised with the surface concentrations) above the whole model area as well as above the Alps showed no significant deviations. At least for the two-week period of the mesoscale model run, our results do not depend strongly on the model resolution.

Table 2: 4-month integrated vertical CO fluxes [kt] across predefined tropospheric levels above Europe in total and above certain regions. The Alps make up 9.7% of the total area, northwestern Europe (NWEur) 9.4% and southeastern Europe (SEEur) 9.9%. The anthropogenic CO emissions during the simulation amounted to 28000 kt. See text for definition of the areas.

H AGL	Europe	Alps	% of Eur.	NWEur	% of Eur.	SEEur	% of Eur.
3100	10768	2189	20.3	853	7.9	967	9.0
4250	6220	1168	18.8	478	7.8	544	8.7
6000	2734	423	15.5	242	8.9	220	8.0
8000	1036	109	10.5	89	8.6	69	6.7
10000	292	25	8.6	19	6.5	20	6.8

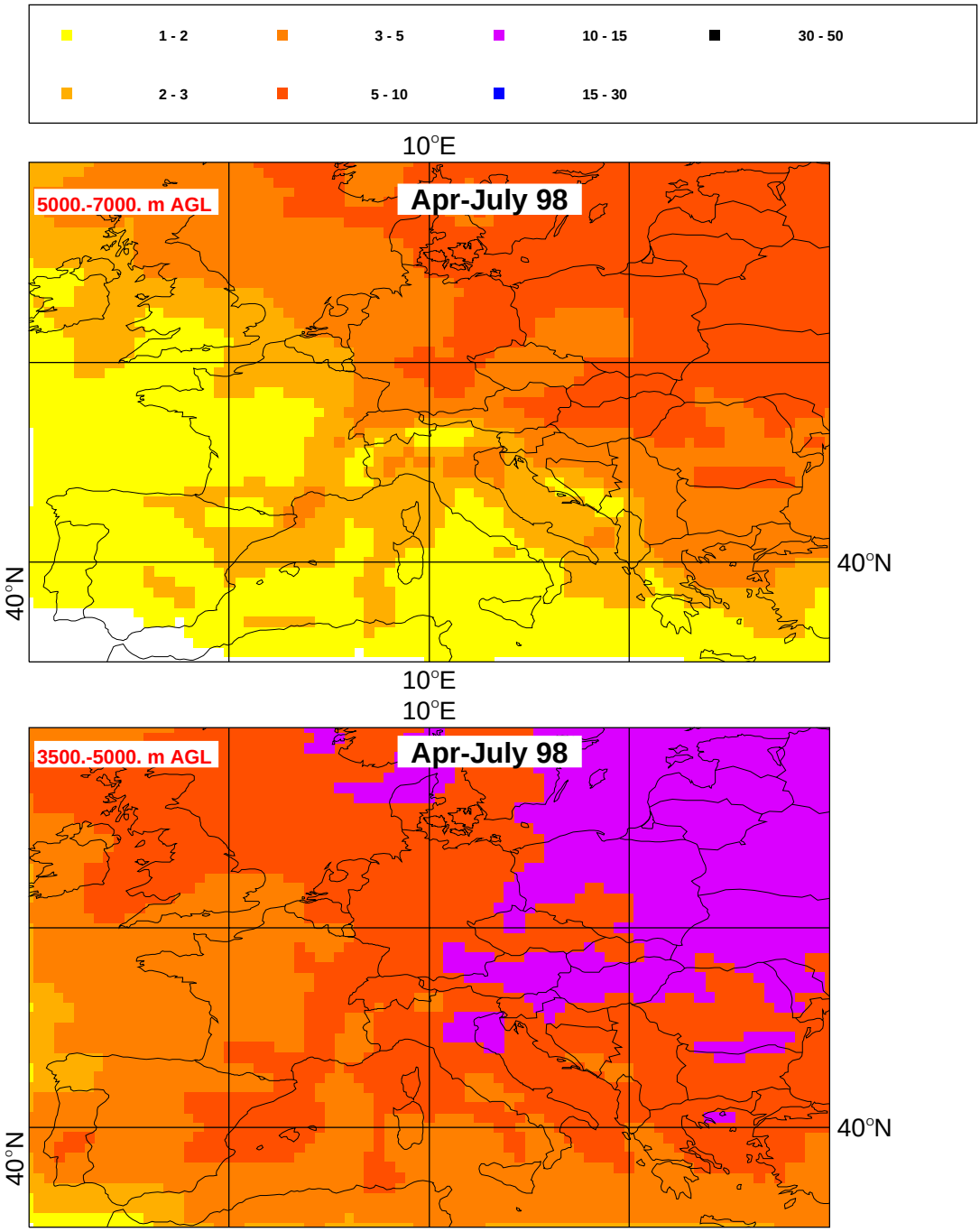

Figure 8: 4-month averaged free-tropospheric CO concentrations [ppb] above Europe from European sources only (without background) . High concentrations predominate above the continent.

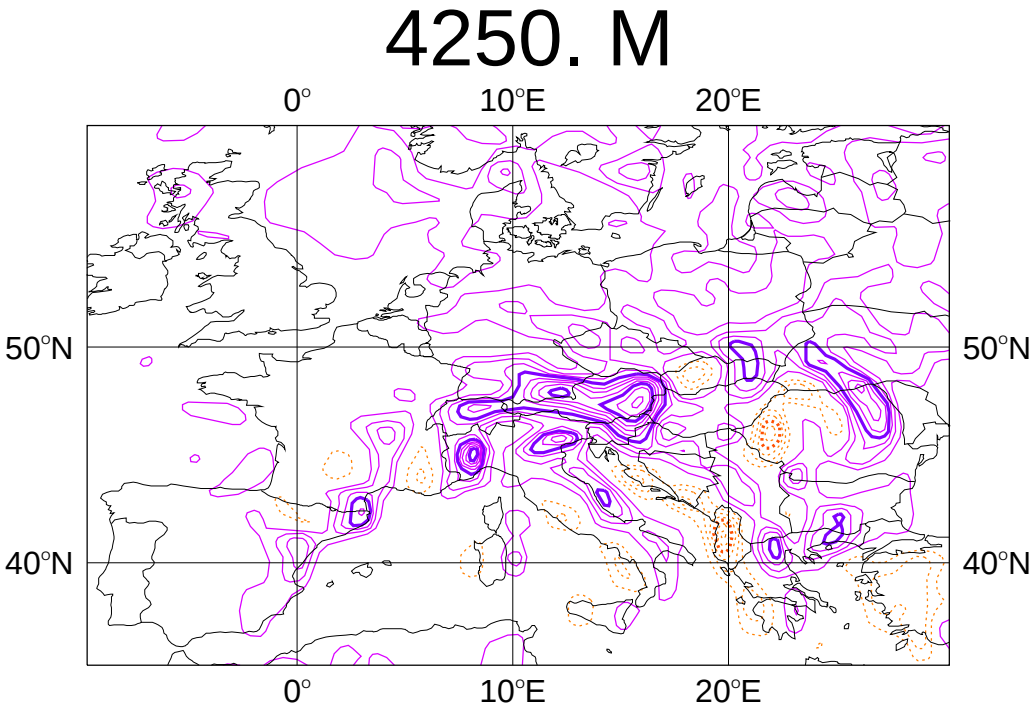

Figure 9: 4-month averaged vertical net CO flux rates [0.01 µgm^{-2}s^{-1}] across 4250 m AGL above Europe. Positive (upward directed) net fluxes are marked with solid purple isolines, negative (downward directed) net fluxes with dashed orange isolines. High average upward fluxes predominate above the Alpine area.

Maintenance of the VOTALP data base

All data collected during the two VOTALP II campaigns, by the measurements on the mountain tops and other data like the weather pattern classification or historical data collected were combined in a uniform format in the VOTALP data base, accessible by all VOTALP II participants. In addition, the data base contained the data from the VOTALP I project. The server was also used as communication medium between the participants.

For a further use of the data by the participants the data base will be held up to date for another year by the project co-ordinator. Parts of the data, like the isotope measurements at the peak stations will be transferred to the similar data base of the EU-project STACCATO.

3. Deviations from technical annex and reasons

- Two different models – VALDRIFT and ALPTHERM – were considered for simulations within the valley, but both, partly due to conceptual caveats, partly due to organisational and proprietary problems, proved unsatisfactory. A totally different concept would have been needed, the development of which was not feasible within VOTALP II.
- The statistical analysis of historical aircraft data was extended by the calculations with the Lagrangian particle dispersion model. The measured data were used for a validation of the model results and the model output was used to determine pollutant flux rates into the Alps.
- In addition to the planned work the statistical analysis of data from Exelberg near Vienna was performed.

- The long-term passive tracer simulation for a study of the vertical exchange above the Alps was restricted to four months instead of six. A planned future publication of the results will be based on a 6-months simulation. In addition to what was promised, however, we conducted a high resolution model simulation of two weeks with the same underlying emission inventory and the same transport model to investigate the scale dependency of our results.

4. Conclusions

From the work of the IMP the following conclusions can be drawn:

- In addition to a diagnostic stratospheric intrusion index based on measurements of ozone, relative humidity (and beryllium-7) a Lagrangian particle dispersion model can successfully be applied as analysis tool for stratospheric intrusions.
- Both, model results and measurements correspondingly show a frequency distribution of stratospheric intrusions which exhibits a summer minimum for the three stations near 3000 m and below. For the higher-lying Jungfraujoch (3580 m ASL) no such pronounced summer minimum exists. This is due to a less deep penetration of the stratospheric air into the lower troposphere in summer.
- Episodes over Europe were analysed, in which the high ozone concentration originated from the North American boundary layer and was transported across the Atlantic.
- During the summer season air in the plume of Vienna, which might be transported further into the Alps, shows considerable higher concentrations of ozone and NO_2 than air not originating in the city. In winter the advected city plume contains less ozone.
- The Alpine foothill area north of Milan is affected by pollution from the Po Basin. First model results indicate that a reduction of VOC emissions in the area would lead to a stronger ozone reduction than a reduction of NO_x emissions. However, Europe-wide reduction of both VOC and NO_x would further improve the air quality in that region. Contradicting results obtained with different models require further research.
- The mean Milan plume clearly extends into the Alps. About 57% of the emissions of Milan are transported northward into the Alps.
- Long-term averaged vertical pollutant fluxes above the Alps are two times higher than above other areas in Europe. Even averaged all over Europe, the Alps cause increased vertical transport between the boundary layer and the lower to mid free troposphere (and thus the average pollutant concentrations above Europe) by 5-10%. This translates to a 4-month averaged middle free tropospheric excess concentration of NO_x of approximately 10 ppt over Europe, increasing the vertical extent of the region where O_3 is photochemically produced. However, vertical exchange above Europe is weak compared with other regions. This generally leads to lower pollutant concentrations and presumably to reduced summertime O_3 production in the upper free troposphere above Europe.

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Final Report of IGM-K

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Leading scientist: Prof. Dr. A. Ebel

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The EURAD group of the University of Cologne made contributions to the work packages II, IV and V of VOTALP II. The tool used for these calculations is the 3-dimensional Eulerian EURAD model (EURopean Air pollution Dispersion model). This model describes the meteorological fields as well as the development of the chemical components over Europe. The model has been applied to several episodes of special interest for the project.

1. Objectives for the reporting period; aims

II: Climatology of ozone influx from the stratosphere

Episodic studies of stratospheric intrusion events have been performed. The aim was to study the transport and chemistry of ozone during tropopause foldings. The validity of some assumptions (stratospheric ozone as a passive tracer) which were necessary for the simulations with the FLEXPART model (IMP, TUM) - were checked.

IV: Advection of urban plumes into the Alps

The intensive measurement campaigns of the VOTALP/LOOP Milano campaign (May/June 1998) have been simulated in a high resolution mode (horizontally and vertically). An analysis of the relevant processes leading to an intensive ozone production in this region has been performed. The transports of pollutants towards the Alps and the vertical mixing processes over the Po plane, the Alpine foothills and Alps were of special interest. To identify what kind of abatement strategies would be more efficient within this region, VOC and NOx reduction scenarios have been calculated according to the indicator species approach of Sillman (1995).

V: The Alpine effect on the European ozone concentrations

Four episodes covering 34 days have been simulated with the EURAD model on different scales (Europe: grid size 90km, Central Europe: 30km, Alps: 10km). A weather pattern classification (provided by IMP) was used for the selection of suitable episodes. Budget calculations were performed for the selected periods. Most important was the quantification of the pollutant transport from the boundary layer to the free troposphere.

To give an estimate of the importance of the Alps on the vertical pollutant transport a sensitivity study has been performed. Within this study a flat topography has been assumed.

2. Main results obtained (methodology, results and discussion)

II: Climatology of ozone influx from the stratosphere

The main tool to simulate stratospheric intrusion events during VOTALP2 is the FLEXPART model (TUM, IMP, Stohl et al., 2000). This Lagrangian type particle model is a very efficient tool especially for long term and large scale applications. FLEXPART as a particle model treats ozone as a passive tracer. The results have to be checked carefully to avoid misleading results due to the missing chemistry. Two episodes have been studied intensively with the EURAD model (Feldmann et al., 1999).

The episodes are:

VI1	25 May - 3 June 1996
VI2	25 May - 3 June 1997

Base case simulations and several sensitivity studies were performed (Feldmann et al., 1999). Main results from the experiments were:

- Budget calculation showed that the net chemical production in the intrusion zones is slightly negative. Therefore, the assumption to treat stratospheric ozone as a passive tracer seems to be acceptable on a time scale of a few days.
- Anthropogenic emissions did not play a role for the ozone concentrations in the tropopause fold.
- The intercomparison with the FLEXPART results showed that both models were able to simulate the transport pattern of stratospheric intrusions.
- Stratospheric air may remain for several days in the lower free troposphere. The air from the folding zone crossed the Alps at least twice during both episodes.
- After the passage of the tropopause fold high pressure systems established over Europe. This led to an increase of the ozone boundary layer concentrations. The ozone originating from the stratosphere increased the low level concentrations slightly.
- The transcontinental transport events discovered in the Garmisch lidar profiles (IFU) and the trajectory calculations (TUM) could be identified in the EURAD model results. The model prognoses for such events were rather low concentrations. The western boundary of the model is placed over the eastern Atlantic. Therefore, the source region of the elevated ozone levels is outside the EURAD domain. To improve the treatment of the model boundaries further research is needed and should be part of future projects.

IV: Advection of urban plumes into the Alps

The focus of the IGM-K group within this work package was the simulation of the VOTALP/LOOP Milan campaign. The selected episodes are:

VM1	8. - 15. May 1998
VM2	1. - 10. May 1998

Special emphasis is laid on the 13 May, when north of Milan ozone concentrations at about 200 ppb were observed. The simulation data were made available the model groups within the

EUROTRAC2 subproject LOOP. Several groups used the EURAD data as initial and boundary values for their simulation.

It could be shown (see figure 1), that the region around Milan and the Milan plume are strongly VOC limited. The Alpine foothills and the Alps tend to be NOx limited.

On 13 May the urban plume is advected northward to the Alps. For this plume the calculated ozone production rates are above 10ppb/h around noon. There is a strong vertical transport of ozone and precursors above the boundary layer over the Alpine foothills and the mountains. The EURAD results do also indicate an injection layer downwind of the updraft regions (see also reports on work package III: mixing over the Alpine foothills). The availability of these precursors in this injection layer causes an efficient ozone production. These effects have been studied in a more general way in work package V.

V: The Alpine effect on the European ozone concentrations

The weather pattern classification provided by IMP distinguishes between eight typical flow patterns over the Alps. Four episodes with 34 days have been selected to cover the clusters:

Name	Period	remarks
SB1	12. - 20. August 1996	2nd IOP VOTALP Valley campaign
SB2	8. - 15. May 1998	VOTALP/LOOP PIPAPO campaign
SB3	1. - 9. June 1998	VOTALP/LOOP PIPAPO campaign
SB4	6. - 15. August 1998	ozone alert in some German states

The episodes cover the 7 most frequent clusters (98.5% of all days). The model domains are designed in a way, that the innermost domain (nest2) covers the complete Alps. The grid sizes are somewhat coarser than in the other simulations (coarse grid 90km, nest1 30km, nest2 10km).

Base case simulations and a sensitivity study have been calculated. The sensitivity experiment had a flat topography to demonstrate the effect of the Alps on the vertical mixing.

The 700hPa level (~3km) is used to analyse the concentrations of ozone and other trace gases (NOx, PAN) as well as the process tendencies (for instance chemical production).

Cluster	**Description**	**Frequency**	**Ozone Alps ppb**	**Ozone Europe ppb**	**NOx Alps ppt**	**NOx Europe ppt**	**PAN Alps ppt**	**PAN Europe ppt**
1	frontal passage	11.5%	62.3	54.0	109.	38.	701.	262.
2	anticyclonic NW flow	35.6%	61.9	53.9	87.	39.	459.	171.
3	Persistent high pressure	6.3%	68.5	54.6	94.	36.	621.	171.
4	disturbance from SW	21.6%	49.4	50.9	102.	53.	181.	139.

5	frontal passage after high pressure	5.3%	64.3	53.9	102.	48.	435.	214.
6	trough crossing the Alps	15.5%	60.0	53.2	142.	43.	538.	207.
7	foehn situation	2.8%	67.5	51.1	107.	37.	736.	189.
8	Mediterranean cyclogenesis	1.5%	-	-	-	-	-	-
	weighted Average		59.6	53.1	103.	43.	455.	183.

Table 1: Cluster analysis: daily average concentrations of ozone, NOx and PAN as average over the Alps (nest2) and Europe (coarse grid) at 700hPa derived from the EURAD simulation. Within column 3 the frequency of occurrence of each cluster during the period 1995-1998 is shown. All clusters are at least covered by two days, except cluster 8, which is not covered.

The concentrations of ozone and typical anthropogenic pollutants like NOx and PAN are significantly higher in the free troposphere at 700hPa over the Alps than over total Europe. Ozone by about 12%, the other species mentioned by a factor greater than two. Due to the availability of precursors there is also a significant chemical production of ozone over the Alps (see figure 2). The greatest differences in ozone over the two regions can be found when the concentrations are highest over the Alps. The flow conditions belonging to these clusters (3, 5 and 7) favour high boundary layer ozone concentrations and thermal advection towards the Alps.

Cluster	**Ozone**	**ppb**	**NOx**	**Ppt**	**PAN**	**ppt**	**O3 chem.**	**prod.**
	base case	**flat**	**base case**	**flat**	**base case**	**flat**	**ppb/day base case**	**flat**
1	62.3	59.6	109.	37.	701.	368.	1.9	-3.7
2	61.9	58.2	87.	29.	459.	96.	0.7	-1.4
3	68.5	58.1	94.	17.	621.	30.	-1.0	-2.8
4	49.4	49.3	102.	44.	181.	100.	1.9	-0.3
5	64.3	61.0	102.	30.	435.	144.	0.7	-1.0
6	60.0	61.2	142.	40.	538.	297.	2.6	-1.4
7	67.5	64.3	107.	17.	736.	71.	1.0	-1.5
9	-	-	-	-	-	-	-	-
Average	59.6	57.2	103.	34.	455.	158.	1.3	-1.5

Table 2: Cluster analysis. Comparison base case and sensitivity study without topography. Ozone, NOx, PAN and chemical net ozone production as an average over the Alpine domain (nest2) and over all days for each cluster.

The comparison of the base case simulation with the sensitivity study with flat topography shows (figure 2, upper part), that without the mountains there would be much lower precursor concentrations in the lower free troposphere. There would even be a chemical net ozone destruction. Again, the differences were the largest under fair weather conditions. On the other hand, the ozone concentrations did not differ very much for cluster where frontal passages, clouds and precipitation are likely to occur in the Alpine region.

3. Deviations from technical annex and reasons

There are no deviations from the workplan

4. Conclusions

II: Climatology of ozone influx from the stratosphere

The model calculations helped to distinguish between the different processes that potentially could control the observed ozone concentrations at the measurement sites. They highlighted the very complex transport and transformation pattern of stratospheric intrusions for specific events. The findings based on the EURAD model calculations support the reliability of FLEXPART calculations. Gas phase chemistry and cloud effects had no significant influence on the concentration of ozone in the intrusion zone over time scales of a few days during the selected episodes.

IV: Advection of urban plumes into the Alps

The Alps are surrounded by heavy polluted regions where VOC control strategies would be efficient. The Alps however tend to be NOx limited. The episodes simulated in VOTALP I and VOTALP II often showed advection of urban plumes towards the Alps, especially under fair weather conditions. In such situations these air masses may reach the free troposphere and lead to a significant increase of air pollutants at these heights.

V: The Alpine effect on the European ozone concentrations

Within this work package the aim was to give a more general estimate on what is the effect of the Alps on the European ozone concentrations. It could be shown, that the Alps indeed are a special region with enhanced vertical transport (see also Seibert et al., 2000). The pollutant concentrations on average are much higher in the lower free troposphere over the Alps than over Europe. They would be significantly lower in this region without the topography related processes. Among these processes vertical transport is the most important, but local anthropogenic emissions at high altitudes do also play a role.

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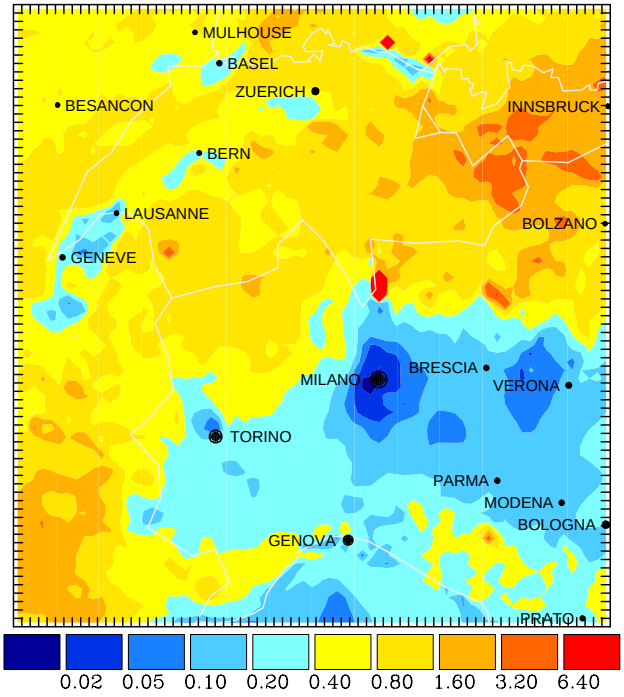

Figure 1: Simulation of the VOTALP/LOOP Milano campaign - 13 May 1998, 14UTC.
"Indicator species" H_2O_2/HNO_3 low values show VOC-limited regions, high values NO_x-limited areas.

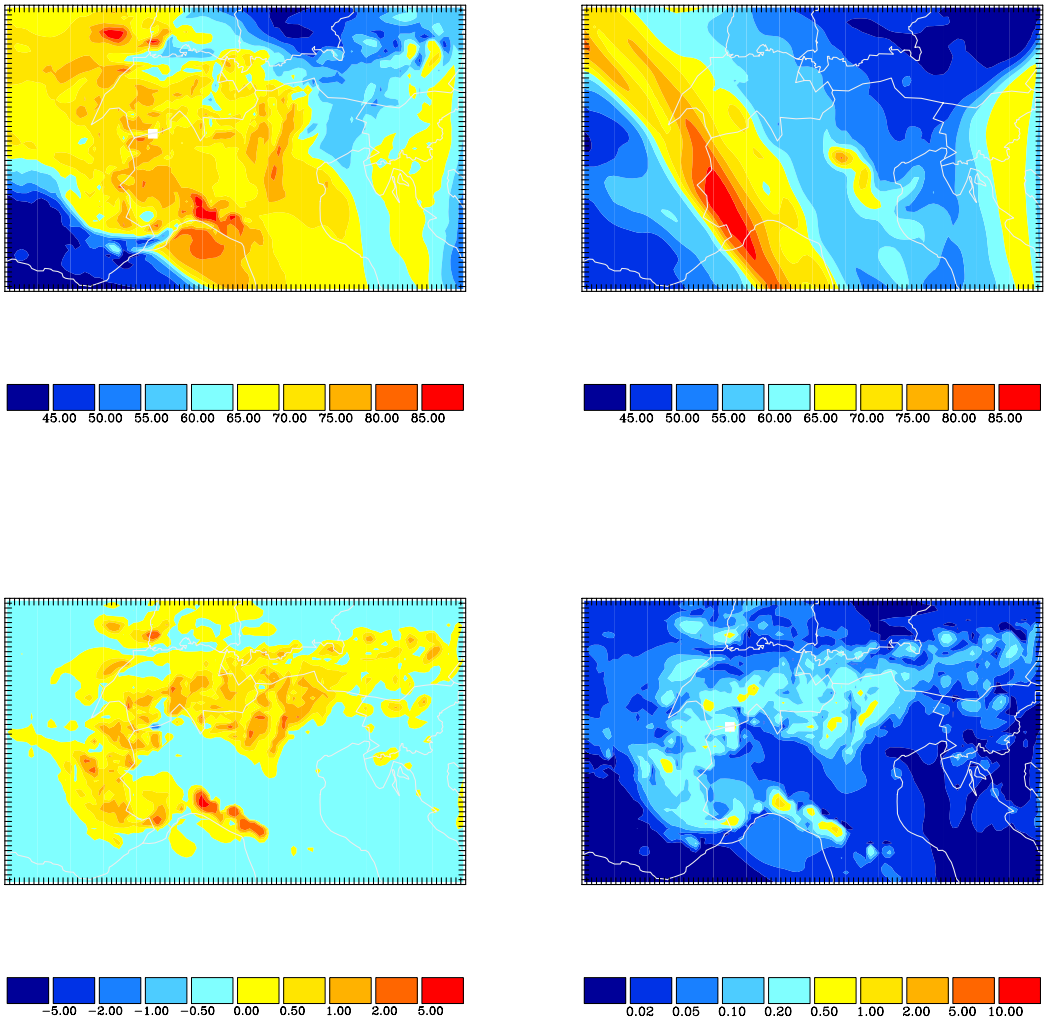

Figure 2: Summertime ozone budget study - 13 May 1998 12UTC. All fields EURAD-CTM nest2 (10km) at the 700hPa level (~3km height). Upper left: Base case, ozone [ppb], upper right: Sensitivity study with flat topography, ozone [ppb], lower left: Base case, net ozone production [ppb/h] by gas phase chemistry, lower right: Base case, NO_x [ppb]. The upper figures show how the alpine topography modifies the ozone fields in the lower free troposphere. The lower part shows the significant ozone production over the orography. The highest production rates can be found were the availability of NO_x as a precursor is the highest.

Final Report of IFU

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1. Objectives for the reporting period

In mountainous regions, the vertical exchange of trace gases between the boundary layer and the lower free troposphere is enhanced due to increased turbulence, orographically induced secondary circulations, and discontinuities at the top of the boundary layer. Thus, the Alps are assumed to play an important role in European trace gas budgets, notably the ozone budget. IFU participated in several work packages of VOTALP II in order to clarify different aspects of the ozone budget in the Alpine region.

A numerical simulation with a mesoscale Eulerian model was planned to investigate the role of local ozone production and ozone advection in Alpine valleys, lidar measurements were to be made to detect stratospheric ozone intrusions, mountain peak measurements of O_3, ^7Be, CO, and meteorological parameters should be evaluated statistically to determine the frequency of occurrence of different air masses and to quantify the fraction of stratospheric intrusions, and field measurements in the Alpine foothills were to be designed to trace the advection of urban plumes into the Alps and to investigate the vertical exchange between the boundary layer and the free troposphere.

2. Main results

Numerical modelling of the local ozone budgets in steep Alpine valleys (WP I and IV)

Because of the field study in the Mesolcina valley during VOTALP I we selected this area and its extensions to the Po basin for numerical simulations of the ozone budget. At the beginning of this project no coupled Eulerian model was available which could have done a simulation for suc a steep valley immediately. Thus, extensive model development took place based on the MCCM model. As MCCM (the coupled Meteorology Chemistry Climate Model of IFU based on MM5 and RADM2 chemistry (Grell et al., 2000)) has never before been used systematically for a study in such an orographically complex area, significantly more work than anticipated had to be spent to make the model run satisfactorily for the selected region.

The work in this project has led to substantial improvements in the model. Especially the advection scheme for temperature was changed from the advection of actual temperature to advection of potential temperature.

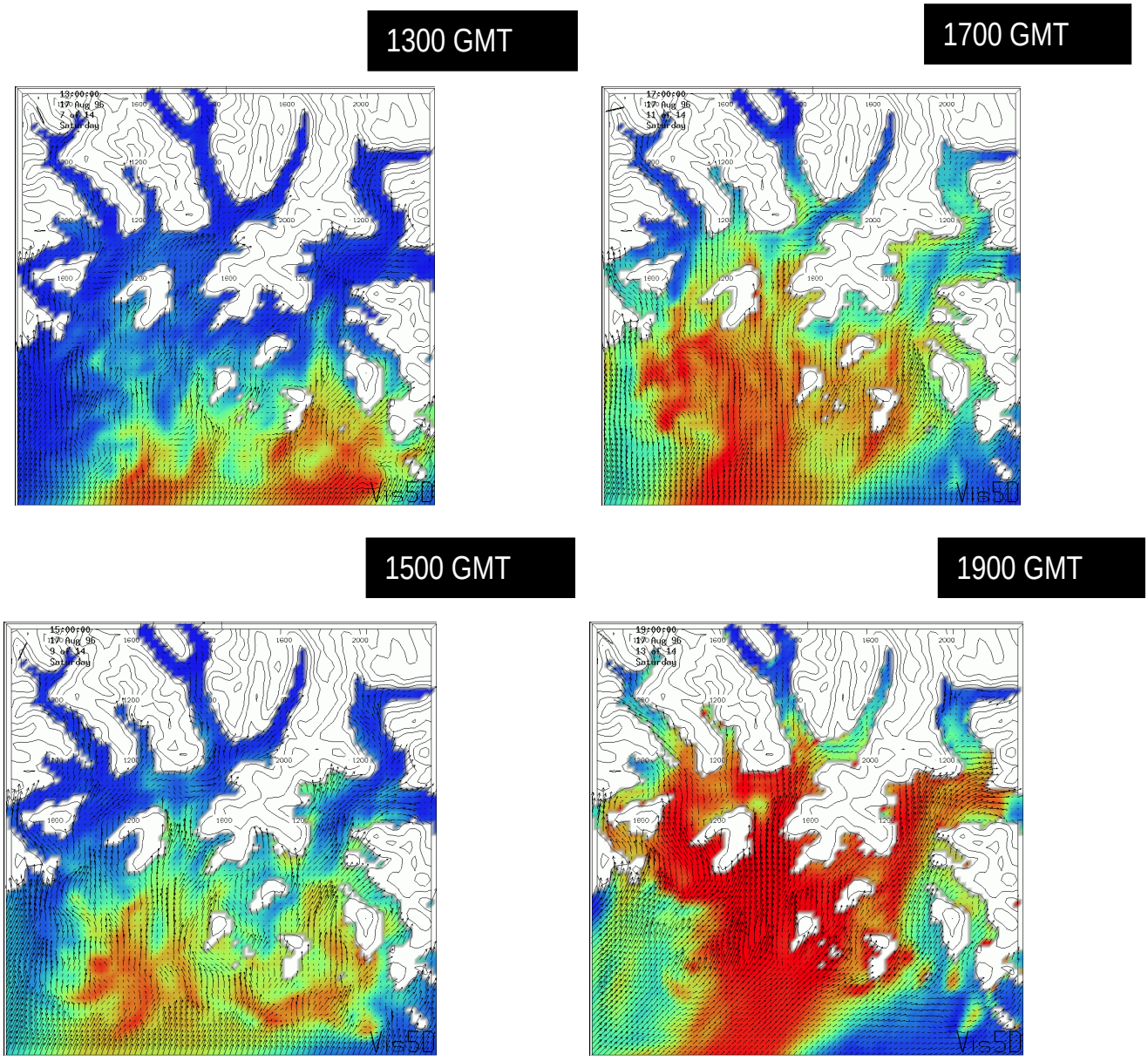

Figure 1: Advection of NO_2 into Alpine valleys during the afternoon of August 17, 1996. MCCM simulation with 1 km grid resolution. The data are shown for a horizontal layer 1300 m a.s.l. White areas indicate mountains higher than 1300 m. Horizontal wind is plotted as arrows, NO_2-concentration in colours (blue: below 2 ppb, red: above 6 ppb).

The second SOP of the VOTALP I valley campaign in August 1996 has been simulated with MCCM. A nesting strategy was chosen, the outermost domain having a grid resolution of 54 km (D1) and the innermost nest having a grid resolution of 1 km (D3). In the vertical were 27 levels, the lowest level was 15 m above ground. Simulations have been made for domain D1 from August 13, 00Z to August 19, 00Z with NCEP (National Center for Environmental Prediction) analysis fields as a first guess. For domain D3, simulations were performed for the two most interesting days August 16 and August 17, 1996. The emission inventory for chemical constituents was based on CORINE (Co-ordination de l'information de

l'environnement, European Environmental Agency) data, but for Switzerland a special inventory with 5 km resolution was provided.

The simulation results are analysed here in order to see how far pollutants from the Po basin are advected into Alpine valleys, and how they influence the ozone concentration there. Figure 1 shows the advection of NO_2 from the foreland into the Alpine valleys during the afternoon by the well-developed system of valley winds. The upper parts of the interior valleys were not reached by this advection during one day. The diurnal evolution of the ozone concentrations gives similar patterns.

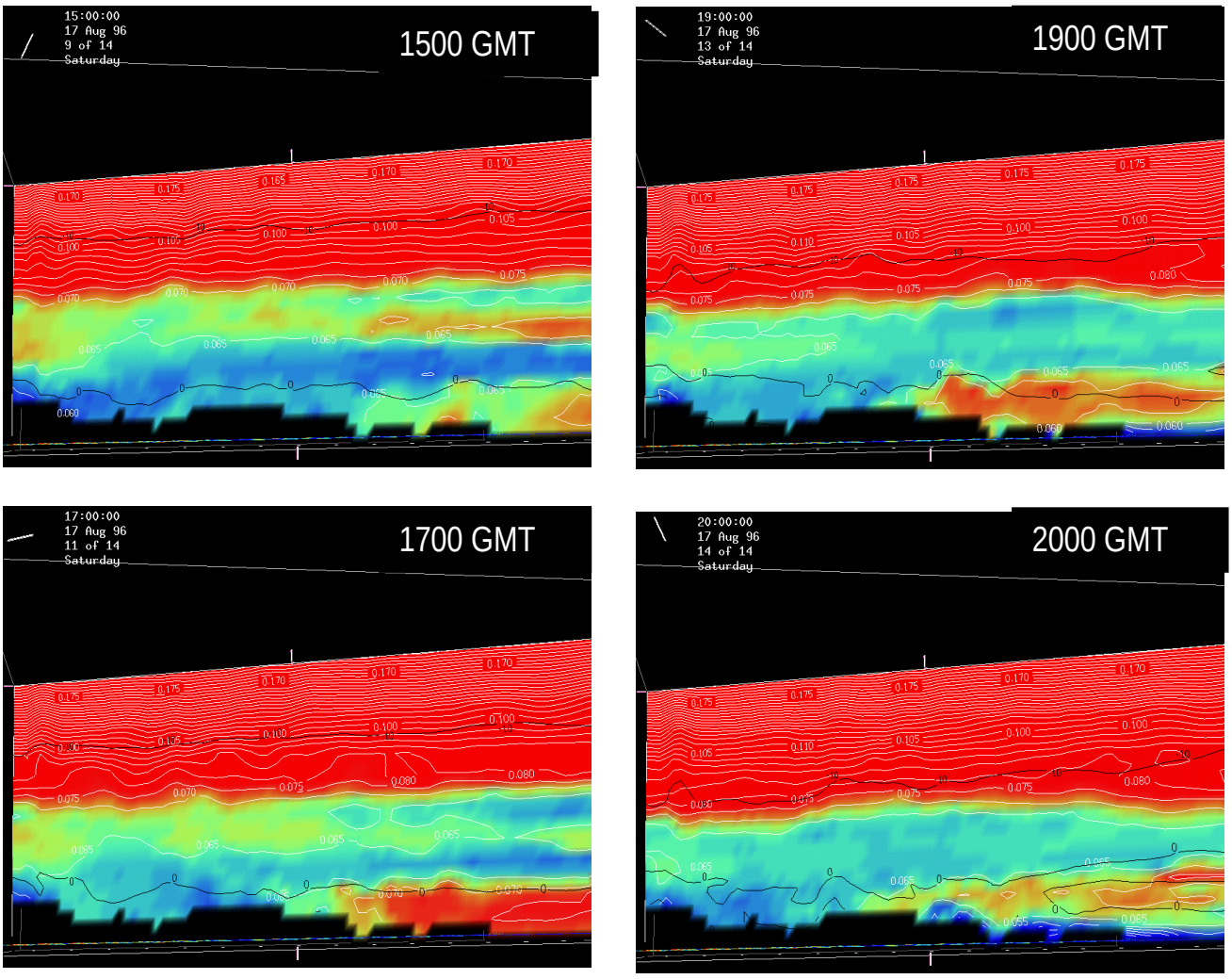

Figure 2: Latitude-height cross-sections of the ozone concentration. North is to the left. The highest mountains (black shades) to the left are between 2500 m and 3000 m high. Red: above 70 ppb ozone, blue: below 60 ppb. The large red part in the upper half of the frames depicts high ozone values in the upper troposphere and stratosphere. North-South wind component is indicated by black isolines with 10 m/s interval. Positive values (winds towards North) can be found in the near-surface layer.

Figure 2 shows in a latitude-height cross section from the Po basin to the upper end of the Mesolcina valley how the advection with the diurnal wind system happened. The top of the boundary layer in which the diurnal wind reversal and the main pollutant transport took place is marked well by the zero-isoline of the North-South component of the wind. During this day there was a northerly flow in the free troposphere and a southerly flow in the boundary layer

during daytime. The maximum ozone concentrations in the boundary layer were found at 17:00 GMT (19:00 local daylight saving time). Later on, the ozone concentrations in the boundary layer generally decreased again. At 20:00 GMT already low ozone concentrations were seen in a shallow surface layer in the southern (right) half of the frame due to titration with fresh NO emissions. Also from this Figure it becomes obvious that the advection by the valley winds was not sufficient to transport photo-oxidants within one single day from the industrial region around Milano to the innermost tips of the Alpine valleys. Thus, the ozone concentration in inneralpine valleys was mainly dominated by turbulent vertical exchange between the boundary layer and the reservoir layer above.

Stratospheric intrusions (WP II)

Climatology of ozone influx from the stratosphere

During the entire time of the project, the measurements at Zugspitze were performed as foreseen, comprising O_3, ^{7}Be, meteorological parameters as well as natural radioactivity as a tracer of air from the ground, and carbon monoxide (CO), which is, in addition to its role in air-chemistry, a tracer of anthropogenic pollution. The data sets obtained at Zugspitze have been used for climatological studies. Moreover, part of them contributed to the results of measurement campaigns.

For the statistical climatological studies it was necessary to develop appropriate criteria in order to select specific atmospheric conditions. The filters applied are meteorological conditions/parameters, tracers, such as ^{7}Be, levels of other trace species (e.g. CO, NO_y) as well as general weather patterns. In order to visualise the effect of data selection on an annual basis (1/2-h data points) and in an interactive way, a set of special spreadsheets was developed. Among others, it automatically yields all 12 monthly means of the selected O_3 values, the related data coverage (in %), and the monthly means for the complementary (non-selected) data. The latter is of importance for estimating the relevance of a specific selection for the overall ozone level. Visual inspection of the annual data sets, although somewhat subjective, provides a valuable tool for identifying details of atmospheric variations that would not be noticed from automated data processing alone.

The problem of detecting stratospheric signatures in the ozone records by way of appropriate data filtering was pointed out in VOTALP I. Here data selection according to specific criteria was considered in detail. Different methods were compared for the records spanning the time 1990-1998. In particular, sensitivity studies were performed by systematic variation of threshold values. However, since not all parameters were available for all of the nine years, the long-term climatology had to be based on parameters having nearly uninterrupted records.

As shown in VOTALP I, the combined criteria "^{7}Be > 8 mBq m^{-3} AND rel. humidity (RH) < 40%" was fulfilled at Zugspitze for about 5% of the time during 1996-1997. In order to account for the long-term behaviour of ^{7}Be at Zugspitze, with a significant decrease of the monthly means at the beginning of the 90s, a variable, statistically determined threshold value was preferred. The 85th percentiles (P85) of the annual ^{7}Be data were finally chosen, keeping in mind the drawback that this means a predetermination of the number of cases. However, for most of the years the 85th percentiles were close to 8 mBq m^{-3}.

While in VOTALP I the focus was on the identification of stratospheric events and on the determination of their frequency, the work in VOTALP II was more directly aiming at an estimate of the actual ozone contribution to the overall budget. Therefore, the analyses were extended to longer time series (1990-1998). Moreover, different filtering criteria were tested

with the aim of weakening the requirements. In particular the threshold for RH was increased to 60%. This seemed to be suggested by some events, which showed a clear stratospheric signature (also confirmed by trajectories), but still rather high RH values (e.g. Zugspitze, August 20, 1996). Generally, values above 20 - 30% RH during the stratospheric events detected at Zugspitze indicated that considerable mixing in the troposphere had taken place prior to arrival of the air parcel at the site. Such a dilution of the stratospheric air was also indicated by the generally small variations of CO, with the decrease being too small to be used in automatic detection algorithms. Among the other criteria tested for the detection of stratospheric events was the following combination of four parameters: "O_3 > 1 (or 1.1)*5-day moving average (to exclude low values a priori) AND ^{7}Be > 85th percentile (on avg. 8 mBq m^{-3}) AND RH < 80% (or even 90 % if indicated by distinct cases) AND NRad < 4 Bq m^{-3} " (with NRad ="natural radioactivity" as a surrogate for ^{222}Rn as tracer for air from the ground). In summary, accepting higher RH values for the filter criteria means including more situations during which ozone at Zugspitze is only partly influenced by direct stratospheric events, while the air is mainly representing O_3 concentrations of the upper and free troposphere.

Since not all data sets were available for the entire 9-year period, more complex combinations of criteria have been applied to individual years only. For these cases the performance of the complex filters was compared to the simpler data filtering procedures. Actually, the overall performance of the complex combinations was not really superior to the simpler criteria, the latter were therefore preferred for the climatological analyses.

For one combined criterion (" ^{7}Be > 85th P. AND RH<60%"), which seemed to be well suited for the 1990-1998 ozone record, a detailed climatological estimate was performed, which was based on daily values averaged over the period 1990-1998 as well as on the respective monthly statistics. Using this criterion, the contribution of detected stratospheric events to the ozone concentration at Zugspitze was calculated from the mixing ratios (selected vs. unselected data points) and their respective frequency of observation. On an annual average, the calculation based on daily ozone mixing ratios yielded a contribution of 8.2%. The annual ozone input related to distinct stratospheric events detected at 3000 m can be assumed to be about 4 ppb of O_3. With a value of 11.8% the contribution for the winter half-year was significantly higher than for the summer half-year (5.5%).

Since further results on data filtering (see section on WP III and IV "Analysis of existing data") were based on calculations using monthly averaged values, the respective stratospheric results are also given in Table 1, which compares the ozone contributions of several atmospheric conditions for two different altitudes (Wank: 1780 m, Zugspitze: 3962 m). The seasonal cycle (in ppb) constructed from the data filtered with respect to stratospheric influence is shown in Fig. 3 (top right). On average, the O_3 mixing ratios from the filtered data are 5.6 ppb above the all-data average, with a minimum deviation of 4 ppb in April and a maximum of 9 ppb in November. Note that these ppb-values ignore the frequency of stratospheric events, and therefore do not reflect the actual stratospheric contribution.

Lidar measurements

The lidar measurements at Garmisch-Partenkirchen were continued during VOTALP II. However, due to two longer periods of system damage the activities were reduced to about 100 measurements per year. A comparison of the O_3 lidar results with the in-situ measurements at Zugspitze has shown good agreement with respect to the mixing ratios determined for 3 km and the number of stratospheric cases concurrently detected.

Table 1: Ozone climatology for the sites Zugspitze (ZUG) and Wank (WNK). The numbers represent the ozone contributions of characteristic atmospheric conditions as obtained from filtered data. The related monthly O_3 mixing ratios are displayed in Fig. 3. For details on the data filters see text. Note that for each of the filters listed below the sum of the O_3 contributions from selected (filtered) and excluded data is equal to 100%. The signs "+" and "-" in the table indicate that the annual average mixing ratio for the selected data is above or below the all-data average (cf. Fig. 3).

Atmospheric Condition	**Data Filter**	**O_3 Contribution of the Filtered Data [%]**			
		Annual		**Summer**	**Winter**
ZUG					
Stratospheric influence	^{7}Be > P85 & RH<60%	8.8	+	5.7	12.1
Dry air (subsidence)	RH < 60%	22.8	+	11.7	34.5
Excluding humid / cloudy conditions	RH < 90%	48.6	+	39.3	58.0
Fine weather (subsidence)	Visibility > 60 km	36.0	+	23.1	49.5
High humidity	RH ≥ 90 %	51.4	-	60.7	42.0
Unpolluted air	CO low	13.6	-	10.4	17.2
Polluted air	CO high	12.1	-	11.7	12.2
WNK					
Dry air (subsidence)	RH < 60%	31.6	+	21.1	42.2
Unpolluted air	NOy low	26.3	-	14.2	39.9
Polluted air	NOy high	12.4	-	13.1	11.2
Polluted air (mainly NE direction)	SO_2 > 1 ppb	7.4	-	6.5	7.6

The ongoing analysis of older data yielded an important by-product: The first detection of the North-American ozone plume over Central Europe. During several of the stratospheric episodes high ozone values were observed in the upper troposphere which could not be ascribed to stratospheric air. The transport pathway was unambiguously identified by calculations with the FLEXTRA and FLEXPART models, carried out by A. Stohl (Stohl and Trickl, 1999, and unpublished material). Polluted air from the boundary layer of the eastern United States is exported off-shore, lifted to heights near 10 km in a warm conveyor belt and subsequently rapidly transported to Europe in the vicinity of the jet stream. Such episodes have been observed for periods as long as four days. Since, in addition, the ozone mixing ratios consistently ranged between 80 and 100 ppb a significant contribution of the intercontinental transport to the European background ozone concentration must be expected (see also the results of the Garmisch Experiment in the following section).

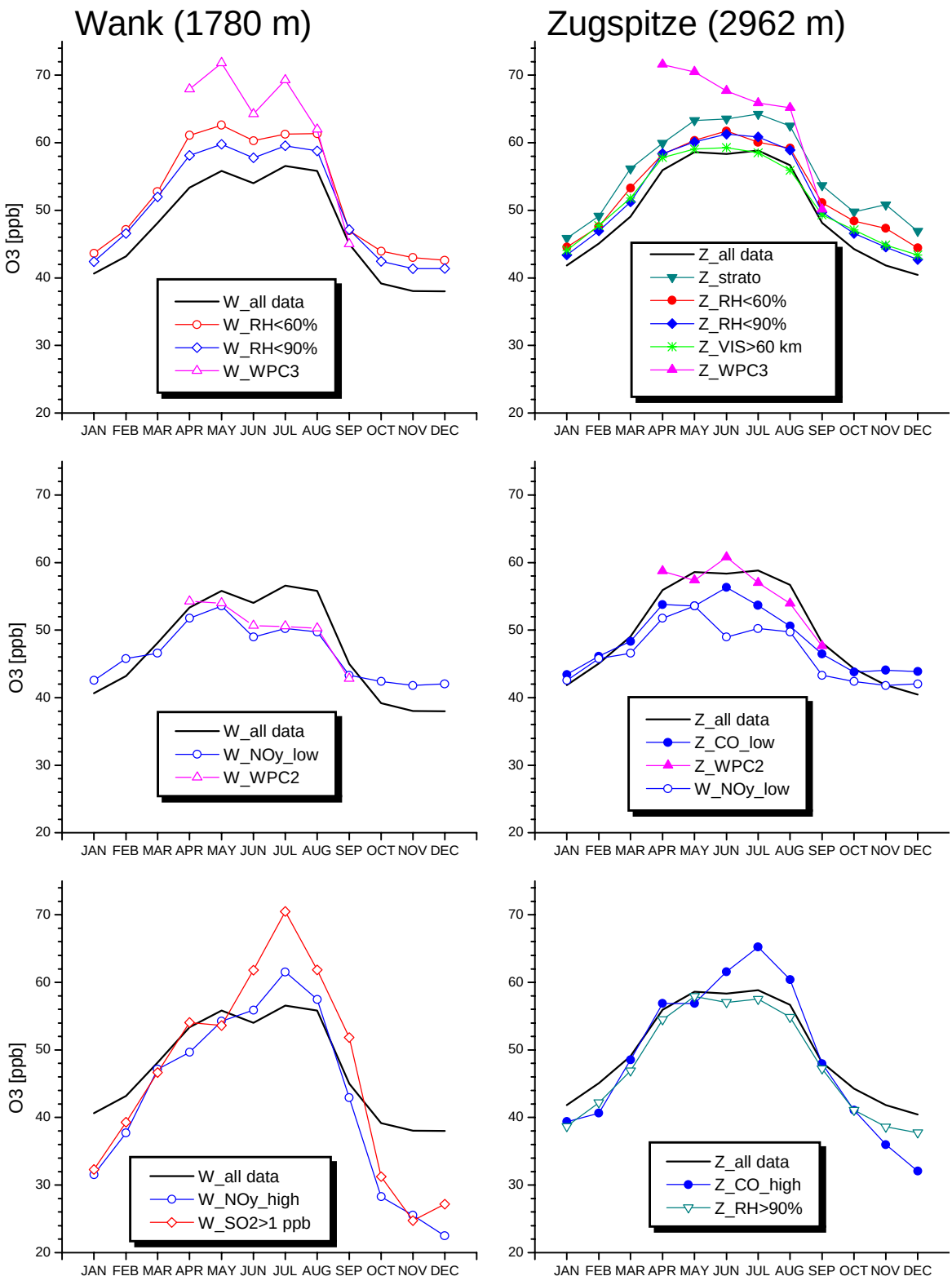

Figure 3: Monthly mean ozone values (1990-1998) obtained for different data filtering. In each plot the "all-data" case is shown for comparison. Weather pattern classifications were only applied for 1995-1998 (Apr. - Sep.). Note that the different ozone levels obtained from filtered data do not indicate the frequency of occurrence of the respective atmospheric conditions. For the resulting individual contributions (in %) see Table 1.

Vertical exchange and advection of urban plumes (WP III and IV)

Analysis of existing data

The question of the effect of urban plumes on the ozone concentration at Wank and Garmisch was addressed statistically by filtering ozone data from the sites Wank (mountain top, 1780 m a.s.l.) and Garmisch (valley floor, 740 m a.s.l.) with respect to the north-east (NE) wind sector. Based on previous studies, air from the NE sector was known to be particularly polluted at times, and would most likely, under certain conditions, also contain a contribution from the pollution of Munich. Since wind measurements at both sites are strongly biased by the local orography, the wind direction measured at the Hohenpeißenberg observatory (MOHP) was used instead. The data filter finally applied requested wind directions at MOHP between 0 and 45 °, being stable during two hours in sequence. Moreover, the different travel times to MOHP and Wank/Garmisch were accounted for by a time lag of two hours. The O_3 concentrations at Garmisch are strongly reduced during the night by local effects, such as inversion. Therefore, only day-time measurements between 9 and 18 h (CET) were considered for both stations.

Based on averaged daily values (1990-1998), the contribution of the north-east sector was calculated from the different mixing ratios (selected vs. unselected data points) and their respective frequency of observation. Air from the NE sector was found to contribute by 11.3% and 10.9% to the ozone at Garmisch (G) and Wank (W), respectively, during the summer half-year (April – Sepember). During this part of the year there is a net surplus of ozone due to photochemical production fuelled by elevated precursor concentrations in air masses advected within the north-east sector. The average summer mixing ratios for data selected according to NE wind filter condition amounted to 49.1 ppb (G) and 56.6 ppb (W), which is significantly above the values obtained for the complementary data set, excluding the NE sector (43.5 (G) and 51.8 ppb (W)). During the winter half-year, the north-easterly advection yielded a contribution of 4.2% for Garmisch and 4.0% for the Wank site. Due to the pollution frequently encountered in the north-easterly air masses, there is a small net loss of ozone. The average mixing ratios obtained for the NE sector were 23.2 ppb (G) and 38.4 ppb (W), both slightly lower than the values calculated for other atmospheric conditions (23.4 (G) and 41.1 ppb (W)).

Another major issue within WP IV was the analysis of long-term records from the mountain sites Wank and Zugspitze with respect to different atmospheric conditions, such as polluted or unpolluted air. The studies discussed below were based directly on monthly mean values obtained from the selected data. These means, in turn, were averaged over the years 1990-1998, unless otherwise stated. The results thus obtained are shown as seasonal cycles in Fig. 3. The contribution of the selected conditions to the overall ozone level is summarised in Table 1.

Data selection by relative humidity (RH) or visibility (e.g. VIS > 60 km) alone is appropriate to simply exclude the influence of moist air/cloudy conditions, which can often be associated with less clean air. The disadvantage of both parameters is that they are unspecific filters, i.e. the thus selected data still comprise different atmospheric conditions, such as increased O_3 due to subsidence and regional photochemical production. Fig. 3 (top) shows examples of results from the RH and VIS filtering. At least during winter, both data filters seem to yield a reasonable proxy for unpolluted air, i.e. background concentrations. We use the term 'background concentrations' to denote O_3 levels that are least biased by regional influence. As seen from the respective plots in Fig. 3, the criterion RH < 60% yields significantly higher O_3

values for Wank compared to Zugspitze for the months April, May and August, which may reflect an increased contribution from photochemistry at the lower site. It was found that variations of the RH cut-off levels in the range between 60 – 80%, or even 90%, had only a small effect on the resulting ozone means. In the annual profile, the average O_3 levels determined by way of RH criteria in this range agreed well for most of the months (Fig. 3, top).

Possible candidates for data filtering with respect to polluted/unpolluted air are the trace gases CO, NO_y, and with some limitations also SO_2. As to SO_2, its atmospheric concentrations have considerably decreased in recent years due to reduced emissions. Even in moderately polluted air, SO_2 may be at the instrumental detection limit, but in case of high concentrations it is definitely indicative of pollution. Appropriate cut-off levels for NO_y and CO were determined empirically by visual inspection of the respective effects on the data of different years. Finally, the following filter settings were used for establishing a climatology: Unpolluted air: CO < 0.85*7-day moving average; NO_y < 30th percentile of annual data (for Wank (1990-1998), these percentiles ranged between 0.7 and 1.1 ppb). Polluted air: CO > 1.15*7-day mov. avg.; NO_y > 85th percentile (with a range of these percentiles from 2.4 to 3.2 ppb between 1990 and 1998).

For Zugspitze, CO was preferred for the 9-year climatology, since its record was nearly complete, in contrast to NO_y. On the other hand, that trace gas was uninterruptedly measured at Wank, where no CO measurements took place. The thus obtained ozone results are shown in Fig 3. For some selected years, data filtering by NO_y levels at Zugspitze was compared to CO-based filtering, and generally showed reasonable agreement. Filtering with respect to clean air by using low CO levels is well suited for excluding conditions of enhanced O_3 loss or production in polluted air in winter and summer, respectively. As found in previous studies, unpolluted air tends to yield an increase of the winter minimum and a decrease of the summer maximum of the seasonal cycle of O_3 (Fig. 3). In contrast, the selection of polluted air using a data filter with a high CO (or NO_y) cut-off shows peak-to-peak amplitudes above the average due to elevated O_3 maxima in summer and reduced minimum levels in winter (Fig. 3. bottom).

Another type of data filter used here consisted of weather pattern classifications (WPC). Since a number of different weather conditions are related to specific advection patterns, O_3 mixing ratios sorted according to WPC can differ significantly and provide insight in the underlying processes. Eight WPC types (summer half-years 1995-1998) based on cluster analysis of wind fields were provided by IMP (G. Wotawa). Three of them were considered for all four years; the following two ones seemed to be of particular interest, combined with sufficient frequency of occurrence. WPC = 2 represents anti-cyclonic north-westerly flow (low temperature, low precipitation). The related O_3 mixing ratios are close to clean air levels as seen particularly from the agreement with the NO_y filter result (Fig. 3). The difference between Wank and Zugspitze for the WPC = 2 selection points to the possibility that the two sites at different altitudes are frequently within different air masses. A stronger influence of the upper/free troposphere at Zugspitze due to subsidence seems a probable explanation. WPC = 3 stands for persistent high pressure over Central Europe (daily increasing temperatures). Under these conditions the highest ozone concentrations are recorded at the mountain sites Wank and Zugspitze, which can even surpass the stratospheric peaks. The 4-year averages are presented in Fig. 3 (top). In spite of the large scatter seen in the Wank results, there is a remarkable agreement between the extremely high O_3 levels at both stations.

Some noteworthy, but infrequently occurring types of air composition could be identified in the records, particularly for Zugspitze. Clean air from the central Atlantic yielded low CO and low O_3 values, which ranged between 25 and 35 ppb. These compare well with O_3 levels in marine air reported in the literature. Air originating from the Sahara region was associated with low humidity and elevated temperatures. Since such events were infrequent (less than once per month), no climatology was established for such conditions.

An interesting feature of the ozone records at Garmisch, Wank and Zugspitze is their pronounced short-term variability on a time scale of synoptic processes. This is related to the geographical and meteorological conditions in the centre of the European continent, where the advection patterns tend to vary rapidly. In spite of the predominantly westerly airflow, no really dominant air-chemical conditions can be assigned. The high variability of the O_3 concentrations at the three locations became particularly evident from time series plots showing all 1/2-h data from an individual year together. Very frequently, processes having opposite effects on the ozone level follow each other within a few days or at even shorter times. When averaging over longer periods, such as a month, many of the variations (plus/minus) cancel each other, yielding mean values representative of the overall regional ozone levels. These agree well with averages obtained from a central band of concentrations as, e.g., defined by the range of ± 10% around 11-day moving averages. As was seen from the annual plots, such a band of O_3 concentrations comes close to what one would visually imagine as the most representative ozone levels.

Field experiments

Two experimental activities to investigate the vertical exchange mechanisms between ABL and LFT (lower free troposphere) took place. One experiment (Sormano Experiment) at the southern foothills of the Alps north of Milano has been performed in spring 1998 in a joint campaign with the EUROTRAC 2 project LOOP ("**L**imitation **o**f **o**xidant **p**roduction"). A second experiment (Garmisch Experiment) was planned for August/September 1998 at the northern foothills between Munich and Garmisch-Partenkirchen. Due to the lack of sufficient radiation caused by a thin high-lying cloud layer it had to be interrupted and was resumed in May 1999. Both experiments comprised surface and aircraft measurements. In both experiments IFU provided its mobile remote-sensing instrumentation comprising a SODAR for the continuous acoustic sounding of wind and turbulence up to about 1 km above the ground, FTIR and DOAS for the continuous determination of path-integrated concentrations of trace gases such as CO, N_2O, CO_2, CH_4 (FTIR), and ozone, NO, NO_2, SO_2 (DOAS) next to the ground and an ozone lidar for the optical remote sensing of vertical profiles of the ozone concentration up to about 3 km above ground. During the Garmisch experiment additional equipment was operated, such as the stationary ozone and aerosol lidars and the in-situ instrumentation at the three monitoring stations IFU (740 m a.s.l.), Wank (1780 m a.s.l.) and Zugspitze (2962 m a.s.l.).

Results from the Sormano Experiment

The measurement sites used by IFU were on a pass close to Sormano at 1124 m a.s.l. (Colma di Sormano) and on a valley floor close to Barni about 10 km further north in the mountains from June 1 to June 8, 1998. The pass is on the first mountain range rising from the Po basin about 40 km north of Milano. A major amount of air coming from the Po basin and entering the mountains in this area is channelled through this pass. On the pass we deployed the FTIR and DOAS spectrometer with open 270-m absorption paths close to the surface, a meteorology station, and the SODAR. As the SODAR can receive backscattered signals from

the atmosphere from heights up to about 1000 m above ground, we were able to retrieve vertical wind and turbulence profiles up to about 2100 m a.s.l. at this site. We expected to find the upper boundary of the atmospheric boundary layer within this range. Barni at 630 m a.s.l. was the location of the ozone lidar. For the lidar the lower site in a valley was chosen because meaningful results from the lidar cannot be obtained for the first 200 m above the ground During that campaign the vertical operating range of the lidar was limited to 2 to 3 km above the ground, depending on the ozone concentration. This was still sufficient to cover more than the atmospheric boundary layer under all conditions.

The synoptic situation during the experiment was dominated by a trough over Western Europe which induced warm weather and southerly synoptic winds over the experiment area. Embedded in this synoptic flow were smaller disturbances which caused thunderstorms, especially in the morning of June 5. On the pass, during the daylight hours the winds came from south-easterly directions, during the nights they came from the north-west. Except thunderstorm gusts, the wind speed is between 1 and 2 m/s during the day, and below 1 m/s during most nights. These surface measurements indicate a diurnal wind system with flow from the plane to the mountains during the day and the opposite flow during the night.

Figure 4 shows the results of the DOAS for ozone for the entire period from June 1 to 7, 1997. After recalibration, mostly excellent agreement with the mixing ratios measured by PSI not far from the pass was obtained. The most striking feature is the pronounced diurnal cycle. During nighttime the O_3 mixing ratio consistently dropped to values between 30 and 60 ppb, caused either by the orographic wind system or the occasional showers. The drop in concentration may be seen as ideal for the desired observation of the concentration increase due to the advection from the Milano area. The source area outside the mountains was obviously not much affected by the ozone depletion. In this way, a day-by-day increase of the ozone values could be seen, at least until June 4 when the mixing ratio reached about 120 ppb.

The CO concentrations measured with FTIR showed similar maxima in the late afternoon and early evening when southerly surface winds prevailed. After the change to northerly surface winds in the evening, CO concentrations declined immediately, much quicker than the ozone concentrations. The DOAS and FTIR paths were oriented perpendicularly to the flow across the pass at a height of a few meters above the ground. The difference in speed with which the species concentrations decreased after the turn of the surface wind indicates that the spatial distribution of ozone is more large-scale than the one of CO. Maximum temperatures were continuously rising from day to day during the measurement period and so did the ozone concentrations. This is typical of an early summer ozone smog episode.

The lidar ozone data obtained at Barni for 1100 m a.s.l. almost perfectly reproduced the DOAS measurements. The polluted layer always ended above the local crest height (1200 to 1600 m). As an example Figs. 5a and 5b give the diurnal series of June 4, the most spectacular day. After noon the gradual advection-induced increase of the ozone mixing ratio in the boundary layer to 120 ppb is seen. The lidar backscatter profiles also yielded information on the aerosol layering. In general the air around Barni was rather clear during that week with slightly increasing aerosol concentrations several hundred metres above the valley. This indicates a response to the first mountain step north of Erba. The upper boundary of the aerosol agreed with that of elevated ozone in the afternoon. Very interestingly, there was not much vertical motion of the aerosol layer during the day and no indication of orographically induced local upward transport.

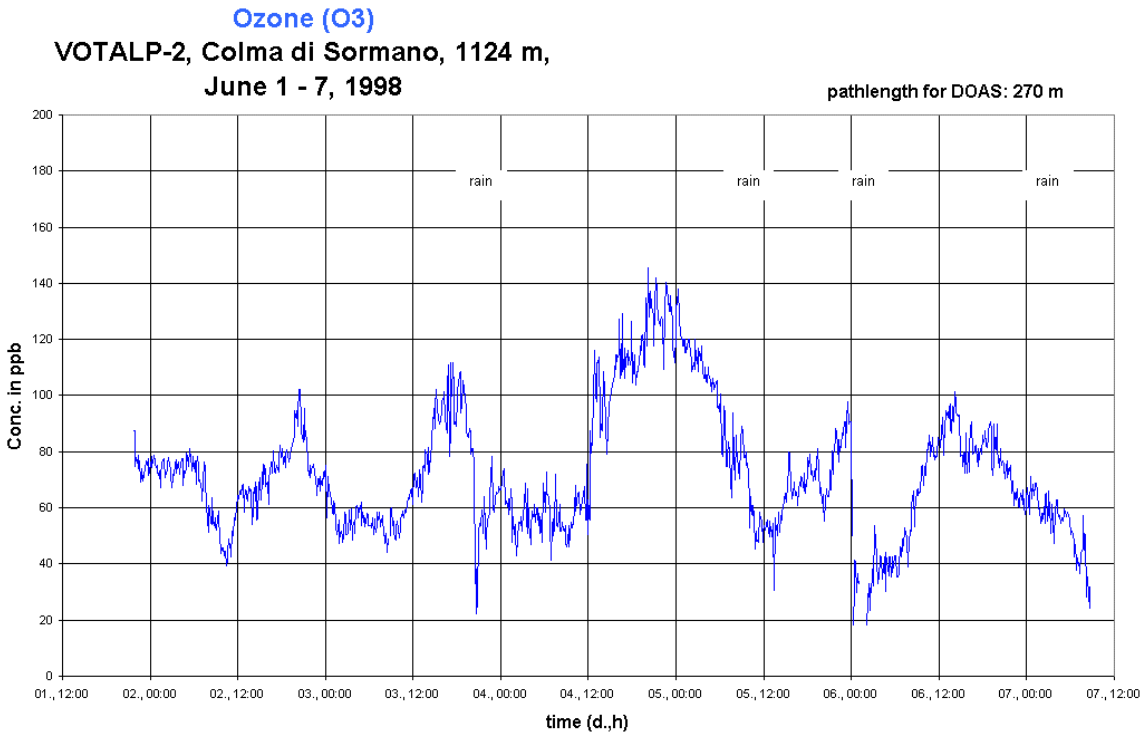

Figure 4: Ozone measurements of the IFU DOAS at Colma di Sormano (1124 m a.s.l.) from June 1 to June 7, 1998

A comparison with ozone-sonde ascents of the mobile sonde station operated by PSI started at Seregno (outside the mountains) at 12:57 CET and at Barni (10 m away from the lidar) yielded quite different upper pollution boundaries. The Seregno ozone boundary was 1700 m (corresponds to half value of the concentration drop), the lidar yielded 1900 m (ozone and aerosol) and the sonde at the lidar location 2100 m. This discrepancy between lidar and sonde is tentatively ascribed to a drift of the balloon during its ascent. Considering the daytime up-valley wind direction and assuming an up-valley drift of the slowly rising balloon this could indicate a terrain-following change of the boundary-layer height from Seregno into the Alps.

The SODAR was operated with a vertical resolution of 40 m and a temporal resolution of 30 min in this experiment. Up to 1 km over the pass south-easterly winds prevailed during that period. This flow was triggered by the large-scale pressure gradient. Only in the early morning hours of June 2 northerly winds could be found in the lower layers. Thus, we can conclude from a synopsis of surface and SODAR data that the nocturnal northwesterly flow towards the plane over the pass of Colma di Sormano is a very shallow flow which was not deeper than about 40 m. The enhancement of the southerly daytime wind components on the other hand reached up to about 200 m on June 2 and up to about 600 m above the pass on the other days.

From the variance of the vertical velocity component (Fig. 6) the intensity of atmospheric turbulence and, thus, the intensity of the vertical turbulent exchange of trace substances can be estimated. The mean wind data showed enhanced southerly winds every noon and afternoon which advected air from the Milano region and which explained the diurnal course of the air pollutant concentrations measured with FTIR and DOAS. Over the pass the layer with southerly winds typically was 500 to 600 m thick (upper lid of this layer at about 1700 m a.s.l.). This advection explained most of the ozone increase in the ozone profiles over Barni.

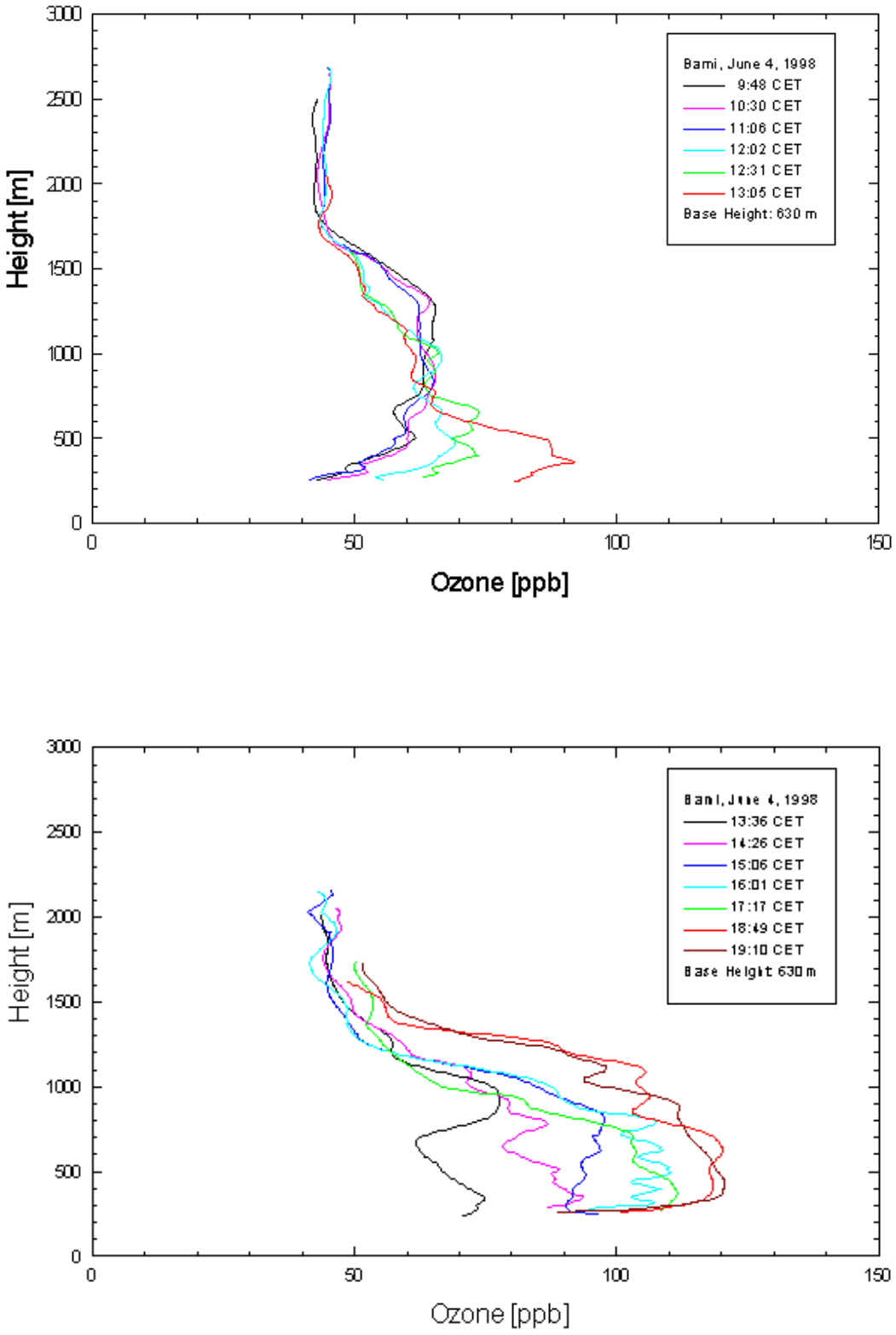

Figure 5: Ozone profiles obtained with the mobile ozone lidar at Barni (630 m a.s.l.) on June 4, 1998. a) (top) morning, b) (bottom) afternoon.

Additionally, increased levels of atmospheric turbulence could be observed up to about 800 m above ground (up to 1900 m a.s.l.) over the pass around noon and in the afternoon (Fig. 6). This means that pollutants which were advected from the south were mixed into the next higher atmospheric layer by turbulent motions over the pass. These heights up to which turbulent mixture took place over the pass coincided very well with the vertical ozone profiles from the lidar measurements in Barni (see above).

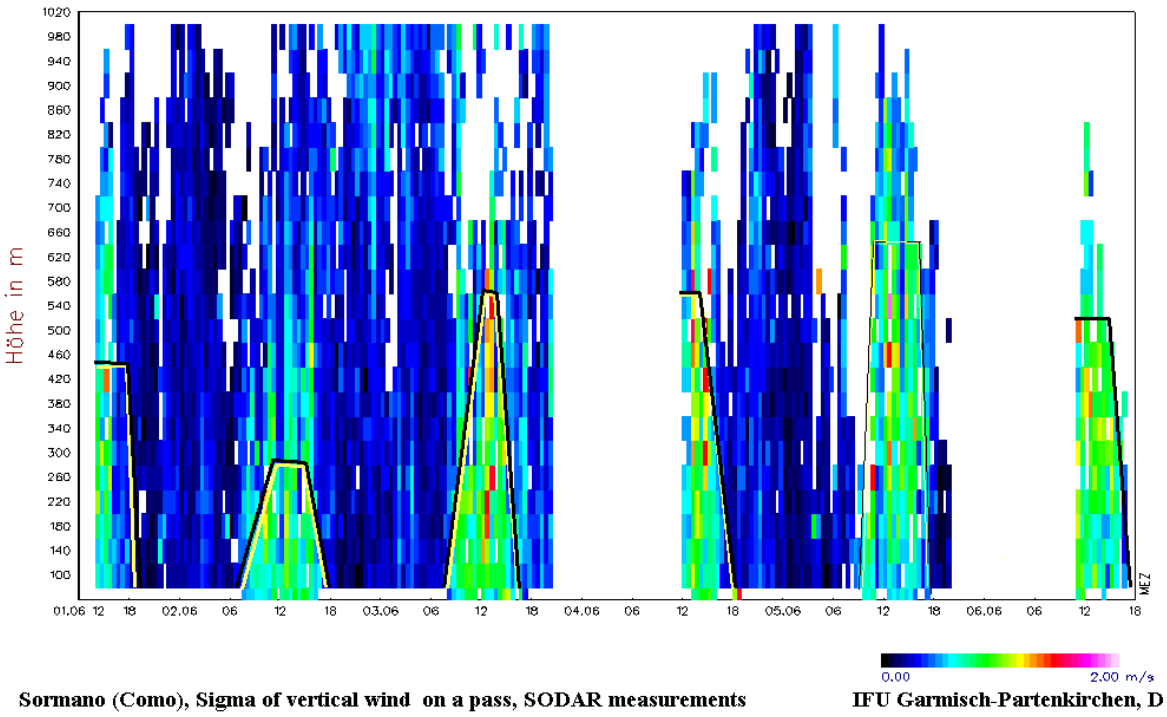

Figure 6: The variation of the vertical wind speed (σ_w) for June 1 to June 6, 1998 over the pass Colma di Sormano (1124 m a.s.l.) 40 km north of Milano, measured by SODAR. The black line indicates the height of the daytime boundary layer in which the wind blew from the Po basin towards the Alps.

Results from the Garmisch Experiment

The purpose of this second field campaign between Munich and the Alps was to detect experimentally the urban plume from Munich and to investigate how the advected pollutants are transported upward in the boundary layer over the Alpine foreland and inside the Alps. In order to trace the plume from outside the mountains on its way to the Wetterstein mountain range south of Garmisch-Partenkirchen both ozone lidars of IFU were simultaneously operated at IFU and outside the mountains, together with the mountain stations. Mobile instrumentation (ozone lidar, SODAR, DOAS, FTIR) was placed at a site north of the Loisach valley in the Murnauer Moos, but could only be used during the August-1998 period of the campaign. The flood preceding part two of the event (May 26 to 30, 1999) destroyed most of the equipment. Only SODAR measurements could take place at that site. Auxiliary chemical instrumentation was built up at a new, dryer site. There, meteorology, ozone, and nitric oxides were measured. As this new site was situated between the motorway A95 and the national highway no. 2, the measurements showed a very locally influenced chemistry dominated by the car exhausts from the two nearby roads (distance was a few hundred meters each). Therefore, the results are not shown here.

The ozone lidar measurements at IFU could be performed without major problems. In addition, the big aerosol lidar of IFU was operated to observe the arrival of the in-valley flow and to determine the boundary-layer height at Garmisch-Partenkirchen. The mountain stations continuously yielded data on ozone, nitric oxides and other relevant parameters.

Additionally, IFU collected ozone data from various other measurement positions in the area. They are shown for May 27 in Figure 7. The wind in the Alpine foreland turned towards Northeast at about 14:00 CET. This turn was initiated by the presence of the Alps over which the air had become warmer than over the foreland. This wind turn can be observed frequently in summer when there are no or only a few clouds over the Alps. About two hours after this turn of the wind direction air from Munich arrived at three of the measurement positions in the experiment area. This time interval can be understood as the time which the wind system needed to extend towards the area of Munich and the subsequent travel time of the urban air towards the measurement positions.

At first the plume was detected at Weilheim (station operated by the Bavarian Environmental Agency) at 16:00 CET, then at Hohenpeißenberg (observatory of the German Weather Service) and Bromberg (temporal station of the project partner University of Ljubljana/Slowenia) at 16:30 CET. Weilheim is about 10 km closer to Munich than the other two stations. The plume could not be detected in the surroundings of Garmisch (Wank (IFU station), Garmisch (IFU station), and Zugspitze (station operated by the German Federal Environmental Agency)) which is about 40 to 50 km south of Weilheim. Thus, it can be concluded that the urban plume from Munich was attracted towards the Alps by the diurnal wind turn due to the presence of the Alps. It moved southwestwards from Munich and hit the stations Weilheim, Hohenpeißenberg, and Bromberg. The presence and orientation of the plume was confirmed from aircraft data recorded by METAIR, Switzerland, also participating in this experiment. The plume reached the Alpine foreland too late too be completely sucked into the Loisach valley and to Garmisch-Partenkirchen.

In the plume the ozone concentration was about 10 ppb higher than in the surrounding air. CO measurements at Hohenpeißenberg confirmed the urban origin of the air masses within the plume. The peak at Weilheim is somewhat lower and narrower than at Hohenpeißenberg and at Bromberg because this station is much more affected by car traffic than the other two stations.

The lidar and station measurements at Garmisch-Partenkirchen showed enhanced ozone mixing ratios between 60 and 80 ppb throughout the observation period. The highest values were observed on May 27. Very interestingly, the ozone mixing ratio above 5 km reached values between 100 and 150 ppb for the entire four days. Trajectory calculations by one of the VOTALP partners (A. Stohl) revealed an origin of a major part of this air in the boundary layer of the United States (see WP II). This is the most spectacular event of intercontinental transport ever observed with our lidar. The ozone-rich layers also contained traces of aerosol which confirms the origin in the boundary layer.

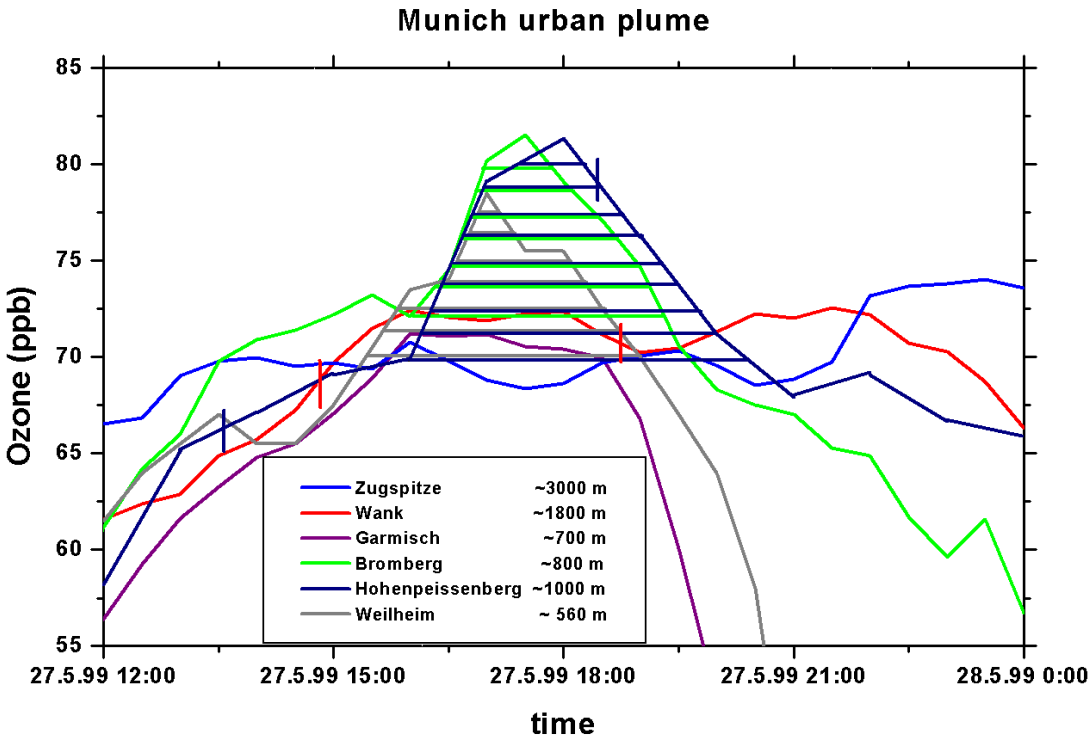

Figure 7: Urban plume of Munich on the afternoon of May 27, 1999 (Central European Time). Ozone concentrations at various stations between Munich and the Zugspitze. Enhancement of ozone concentration due to the advection of the Munich plume is indicated by the hatched area for Weilheim, Hohenpeißenberg and Bromberg.

3. Deviations from technical annex and reasons

Nearly all tasks were performed as planned. Only the planned preliminary sensitivity studies with the numerical model were not completed during the term of VOTALP II because the adaptation of the model to the steep orography turned out to be much more time-consuming than expected. Additionally, two of the staff members (Georg Grell and Oliver Reitebuch) left IFU before the end of the project. The stationary ozone lidar measurements at IFU had to be interrupted twice due to system damage.

Some of the foreseen equipment of IFU which was already set up for the VOTALP II field experiment near Garmisch could not be used because an unexpected flood at Whitsuntide 1999 destroyed the instruments. Additional instrumentation, such as the aerosol lidar and some in situ instruments were used instead.

4. Conclusions

For the first time coupled simulations with a numerical model for meteorology and air chemistry have been performed for very steep orography. The height range was between around 500 m and 3000 m within a few kilometers. The model results from MCCM showed that the diurnal wind system of the Alps as a whole causes advection of polluted air from the surrounding plains into the Alpine valleys. The polluted air travels about 100 km a day. Thus, it does not reach the central regions of the Alps within one day. The model simulations confirmed results found in the field experiments during VOTALP I and VOTALP II.

The four years of vertical sounding with the wide-range ozone lidar at IFU during VOTALP I and II have impressively demonstrated the capabilities of high-density ground-based sounding for atmospheric transport investigations. A lot of information on stratospheric air intrusions has been accumulated never seen before in lidar measurements with similar detail. The close co-operation of lidar, stations and modelling groups has been unique. The simultaneous observation of intercontinental transport during major stratospheric episodes has been a great surprise. The high ozone values reaching Europe in the upper troposphere during such events strongly suggest to reconsider the issue of the background ozone concentration in the free troposphere over our continent.

In addition, we have analysed here two examples of enhanced horizontal and vertical exchange of ozone over the Alpine foothills. Two processes worked together: a diurnal wind system advected ozone from the Po basin and Munich respectively towards the Alps and thermally induced atmospheric turbulence then mixed the ozone even higher up into the LFT. The fate of the ozone in the LFT was not monitored during this experiment.

This experiment has demonstrated that the combination of in-situ sensors and remote-sensing instrumentation is an ideal means to observe not only the diurnal course of atmospheric parameters like wind and species concentrations at the surface, but it also allows to infer horizontal and vertical transports of atmospheric pollutants. Several features in the diurnal course of surface concentrations can only be understood if vertical and horizontal transport is known. Furthermore, the understanding of these transport processes is an important prerequisite for the design of atmospheric pollution mitigation strategies.

Vertical wind and turbulence profiles from SODAR measurements have proved to be valuable especially in orographically structured terrain where simple vertical profile functions cannot be used. These profiles are used nowadays in dispersion studies and in wind energy conversion assessment studies. Vertically pointing lidar and SODAR measurements together provide valuable information on the diurnal development and structure of the atmospheric boundary layer.

Apart from concentration measurement as shown above, path-integrated DOAS and FTIR measurements can also be used together with inverse numerical simulation techniques to determine the emission strength of diffuse or inaccessible emission sources. These sources include agricultural plants and petrol industry.

The data records from Garmisch, Wank and Zugspitze have provided valuable input data for campaigns and, more importantly, for climatological estimates concerning the contributions of a number of different atmospheric processes to the actual ozone concentrations. Based on measurements at Zugspitze between 1990 and 1998 and the data filtering criteria set up during the project, the ozone influx at 3000 m via directly detected stratospheric events was estimated to be 4 ppb on an annual average. The relative ozone contributions of this type of process were found to be about 5 – 6 % during the summer half-year and about 12 % during winter.

With a similar climatological approach the contribution of air from the north-east sector, including the Munich plume, was estimated for Garmisch and Wank. For both locations this sector can be assumed to yield a relative ozone contribution of about 4 % during winter and about 11 % during summer.

By several climatological estimates the contributions of a variety of atmospheric conditions could be quantified. This was predominantly made for the mountain sites Wank and Zugspitze, since the conditions at their altitudes are much more representative than at a valley

site. The occurrence of conditions such as "stratospheric intrusion", "dry air", or "subsidence" tends to increase the observed ozone level throughout the year. In contrast, pollution-related processes, notably O_3 removal or O_3 production, generally have opposite (+ / -) effects on the ozone levels observed during winter and summer. The degree of pollution results in modifications of the shape of the seasonal cycle. On an annual scale the respective contributions can cancel each other, either to some extent only or nearly completely, depending on processes considered and location. The generally high variability in the ozone records of the three sites is pointed out explicitely.

Acknowledgements

Thanks are due to the German Weather Service (DWD) for kindly providing series of meteorological and air quality data from the Meteorological Observatory at Hohenpeißenberg. We also thank the Bavarian Agency for the Protection of the Environment (LfU) for the air quality data from Weilheim.

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Final Report of PSI

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1. Objectives for the reporting period

The main objectives of the PSI subcontractor can be summarized in the following points:

- Study of vertical pollutant exchange over Alpine foothills by budget analysis of aircraft measurements, including ozone soundings.
- Investigation of advection of the urban plumes of Milano and Munich into the Alpine area by aircraft measurements
- Statistical investigation of the effect of urban plumes on the Alpine foothills, using aircraft measurements of former campaigns.
- Evaluation of the effect of emission reductions in the Milano area and the Po valley on the pollutant concentrations in the Mesolcina valley, using a lagrangian photochemical model.

2. Main results obtained (methodology, results and discussion)

Vertical pollutant exchange over Alpine foothills by budget analysis of aircraft measurements (Figure 1)

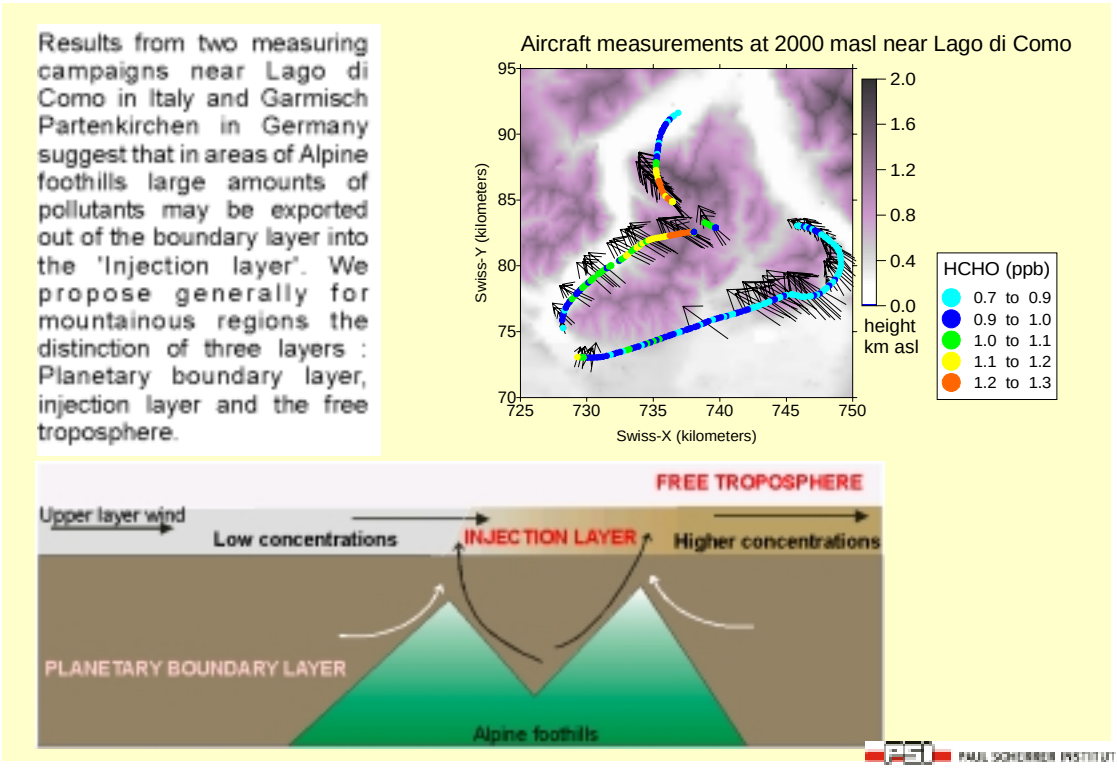
Experiment

Two field studies were performed, the first campaign near Lago di Como in Italy from June 1 - June 14, 1998, the second campaign near Garmisch-Partenkirchen in Germany from May 26 - May 30, 1999. The measurements were successfully performed, including aircraft observations and ozone soundings. The Garmisch campaign was originally started in late August 1998, but the campaign was stopped because of unfavorable weather and the campaign was postponed to late spring of 1999.

Concept

The main hypothesis behind these field campaigns is described in the lower picture of Figure 1. The pollutant levels (especially primary pollutants) in an airmass at altitudes above the planetary boundary layer will increase, going from up-wind to down-wind conditions. This increase would be interpreted as pollutant injections from below, induced by the Alpine foothills.

Figure 1:



Results

As can be seen in Figure 1, the hypothesized concentration increase can be observed for formaldehyde with considerably higher concentrations down-wind of the hilly area compared to the air up-wind of the hills. This was also found for aerosols, water vapor and NOx. The increases were in the order of 30-40%. In general, increases are found if the concentration of the compound is higher in the boundary layer than above. This is not necessarily the case for ozone. Flux budget calculations were performed but the quality was not very high because the GPS-signal and thus the wind measurements were highly disturbed by strong radio-emitters in the foothill area.

- Very similar results were found for a foothill area near Garmisch. Large concentration increases of primary pollutants were found down-wind of the mountainous area above the planetary boundary layer. In contrast to the Como region, reliable flux budget measurements were possible. In stationary cases, convergent flow could be observed in the planetary boundary layer and substantial divergent flow above the foothills. Around 1500-2000 meters, only small divergent or convergent flows were found. The divergent flow resulted in an increase of average wind speed of up to 1 m/s, comparing down-wind with up-wind average wind speeds within 20 km distance.
- The divergent flow yields a net average vertical wind speed of 0.03 - 0.1 m/s into the layer with substantial concentration increases. A similar net vertical flow of around 0.1 m/s was found over the deep Alpine Mesolcina valley (VOTALP I). In box model approaches, exchange velocities between the free troposphere and the planetary boundary layer are typically about 0.002 m/s, i.e. 10 to 50 times lower than the net velocities of 'organized' thermally induced vertical transport.

- Substantial concentration increases are only found at altitudes of around 500-800 meters above the hill crests, typically up to 2200 m MSL in the Como region, 2400 m MSL in the Garmisch area. In one case in the Garmisch campaign, localized minor concentration increases were found at 3400 m MSL. This can be induced by high reaching thermals, possibly induced by higher reaching cumulus clouds.
- The Alpine foothills do not directly contribute as much to the concentration increases at very high altitudes (3000 m MSL to 4000 m MSL) as found in the case of the deep Alpine Mesolcina valley during VOTALP I.
- Combining results from VOTALP II and VOTALP I, we believe that the foothill findings can serve as a model for the processes over the whole Alps. Convergent flow is expected in the boundary layer, divergent flow at high altitudes with considerably higher concentration down-wind of the Alps. Within an airmass moving with the mean wind over the Alps, we expect the concentrations to gradually increase due to injections below. The airmass acts as a 'tape recorder' accumulating the vertical pollutant injections from below.
- Over flat terrain, the free troposphere lies above the planetary boundary layer. In the Alpine area, there is another layer between the boundary layer and the free troposphere that we would like to call the mountain injection layer. This layer is not as well vertically mixed as the planetary boundary layer, but this layer is influenced by air injections out of the boundary layer that will be incorporated with the injection layer. Typical altitudes of these layers over the core of the Alps in summer are: planetary boundary layer: 2000 m MSL, injection layer : 2000-4000 m MSL, free troposphere: 4000 m MSL up to the tropopause.

Investigation of advection of the urban plumes of Milano and Munich into the Alpine area by aircraft and other measurements

Experiments

The Milano campaign was combined with a field campaign of LOOP (Limitation Of Ozone Production) EUROTRAC project. In combination with the VOTALP flights, aircraft measurements were performed on more than 10 days. The main focus of the Garmisch flight pattern were the budgets over the foothills. Nevertheless, also the Munich plume moving into the Alpine foothills was studied.

Results

- Up to 100 ppb of ozone can be produced in the Milano plume on one afternoon, yielding concentration of up to 200 ppb ozone. This could be observed by aircraft measurements but also statistically by comparing the ozone concentrations 20 km north of Milano (down-wind) at 1700 h with the ozone concentrations at 1300 h 20 km south of Milano (up-wind). Down-wind of the plume, the concentrations were about 30-40 ppb higher than generally in the northern part of the Po Basin.
- The very high concentrations reach the Alpine foothills but do usually not get into the core of the Alpine area as already shown in VOTALP I.
- Statistical intercomparison of the wind profiler data in Seregno and the Swiss model outputs showed that the Swiss model does not predict the winds in the Po Basin very well. On average, the vector difference between the modeled wind and the measured wind is as

large as the wind vector itself without a dependence on time of day and altitude. It is thus not safe to use SM-model data for accurately describing the wind field in the Po Basin.

- Together with other groups in the project, including ground based measurements, the Munich plume with 'excess' ozone concentrations of around 10-20 ppb was observed on May 27, 1999. The Munich plume was transported towards the Alps on that day.

Statistical investigation of the effect of urban plumes on the Alpine foothills, using aircraft measurements of former campaigns.

Concept

Aircraft measurements of many years exist in the region of the Po Basin north of Milano, in Vienna and Munich. The aircraft data shall be used to derive general patterns for the influence of these plumes on the Alpine foothills. This analysis was widely extended by the analysis of 10-year ozone data at fixed stations in the Alpine foothills. The aircraft data was also used to characterize the VOC patterns in the different areas around the Alps.

Results

- The best data coverage by aircraft data was in the Po Basin. It turned out that we have just for this area enough data to provide some statistical insight into the occurrence and strength of the Milano plume and its influence on the Alpine foothills. By scaling the ozone distribution by the average concentration of the individual flight, ozone concentrations were 0.77 - 0.9 times the average south of Milano and in the northern part of the canton Ticino and over the Lago Maggiore. North of Milano reaching into the Alpine foothill area, the concentrations were 1.04 - 1.1 times the average ozone concentration of the individual flight. These differences could be much larger for very high ozone events but reflect the average pattern in the area.
- Statistical evaluation of the measurements in Mendrisio (southern part of Switzerland in the Alpine foothills (Figure 2)) shows that the mean ozone concentrations in summer have considerably decreased in the 90ies. The number of days with O3_max>90 ppb have decreased from around 15-20 in 1990 to around 5 days in the year 2000. The meteorological conditions reflected by the temperature modulated the ozone signal but did not show a significant trend.
- The advection of the plume Milano was detected at Mendrisio by strong increases of ozone in the late afternoon as shown in examples in Figure 3. Statistically, we calculated the number of days when the O3 maximum was higher than 40 ppb compared to the ozone concentration at noon. During these days, the winds come from the south, the ozone concentrations were on average much higher than on other days with equal afternoon average temperature. During the 1990ies, such days were found on 17.4 % of the days in July, 8.9% of the days in June, and 6.2% of the days in August. During the other months, only very few such events occurred.

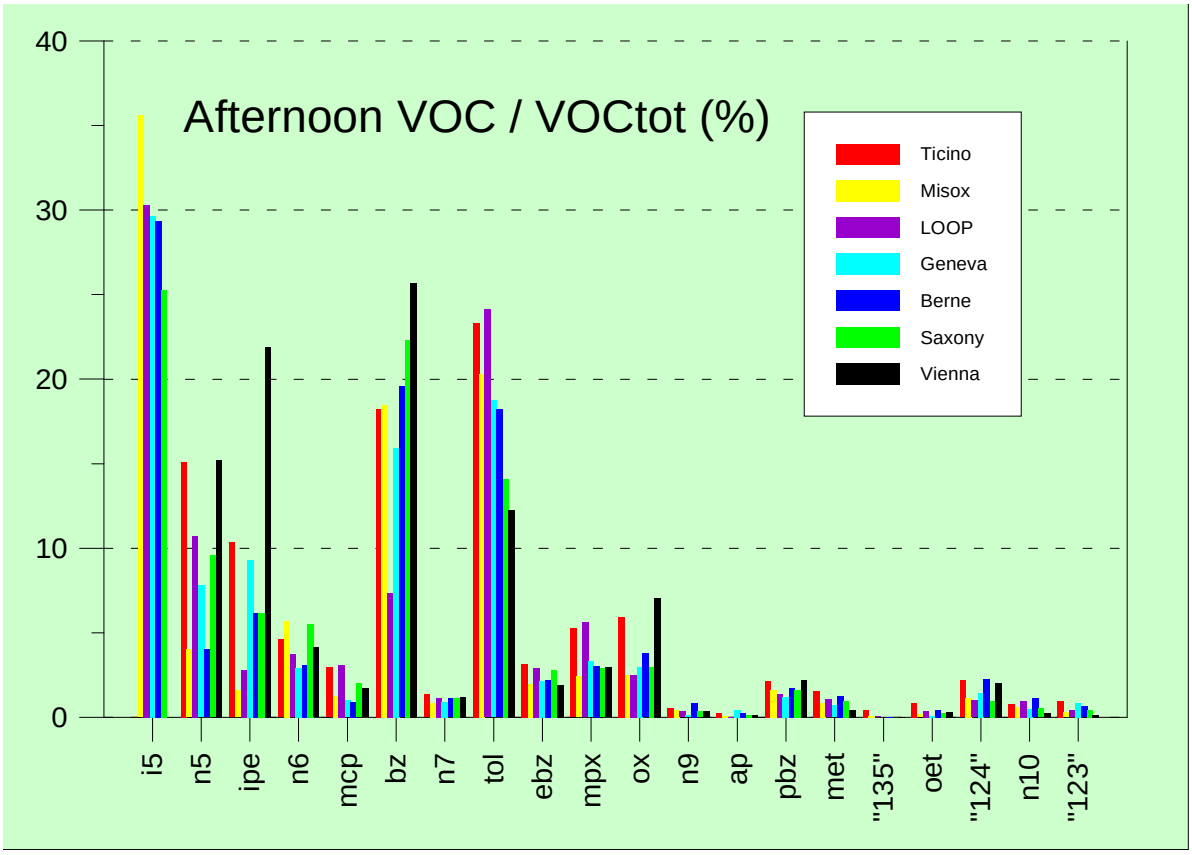


Figure 2

- If the wind path is coming from the north in southern Switzerland, the ozone concentrations are lowest for the summer months, around 50-60 ppb and highest during winter, around 40 ppb (Figure 4). On these days, the relative humidity was very low. This led to the hypothesis that northerly foehn bring down background concentrations into the Alpine foothill area. This was confirmed by looking at differences in potential temperature between Jungfraujoch (3500 mMSL) in the core of the Alps and at Stabio, a meteorological station in the Alpine foothills. In the cases of these northerly winds, the difference in potential temperature was very low, indicating that in fact the airmasses at high altitudes over the Alps were brought down to the Alpine foothills. The concentration at Mendrisio in these northerly wind cases as a function of temperature and season correspond very well to the seasonal cycle observed at Jungfraujoch. The northerly wind cases occur at around 6% of the days in Mendrisio in all seasons.
- During May and June 1999, statistical analysis of measurements at Verzago (20 kilometers north of Milan) shows that the highest concentrations in the foothills are found when the winds are low in the morning (the plume is not dispersed too much) and when the air is originating from the Milano city area. Compared to days with other origins, the ozone concentrations are 30- 50 ppb higher in these conditions, ideal for high ozone concentrations north of Milano.
- The VOC patterns (individual VOC / VOCtot) are rather similar in the different regions around the Alps where aircraft measurements have been performed in the last 6 years (Figure 5). This might reflect that during summer, the dominant anthropogenic VOC source is the traffic.
- Exceptionally high ortho-xylene concentrations were found in the Vienna region.

- Low benzene concentrations (compared to the sum of VOCs) were found in the Po Basin in 1998. According to measurements in the gasoline and trends in surface concentrations this is caused by lower benzene content in Italy than in other European regions because benzene concentrations of less than 1% was enforced much earlier in Italy than elsewhere. Toluene/benzene ratios often exceed 5 in the Po Basin compared to 2 in other regions of Europe. Even within one flight, one can observe the higher ratios of toluene/benzene in the Po Basin compared to the northern part of Canton Ticino in Switzerland where the aircraft was starting and landing. This shows that lowering the benzene content in gasoline will improve the situation regarding cancerogenic benzene concentrations in the air.
- The absolute concentration differences in the different regions are reflected by the VOC emission inventories, e.g. the Po Basin area exhibiting the highest VOC concentrations.
- Taking VOCs from C4-C10 into account, isoprene contributes 30-60% of the total reactivity towards OH in the afternoon in the different regions. Most important anthropogenic contributors to the OH-reactivity are n-butane, iso-pentane, toluene, m- and p-xylene, ortho-xylene, 1,2,4 trimethylbenzene. Isoprene is in all regions by far the most important individual contributor to OH-reactivity.

3. Deviations from technical annex and reasons

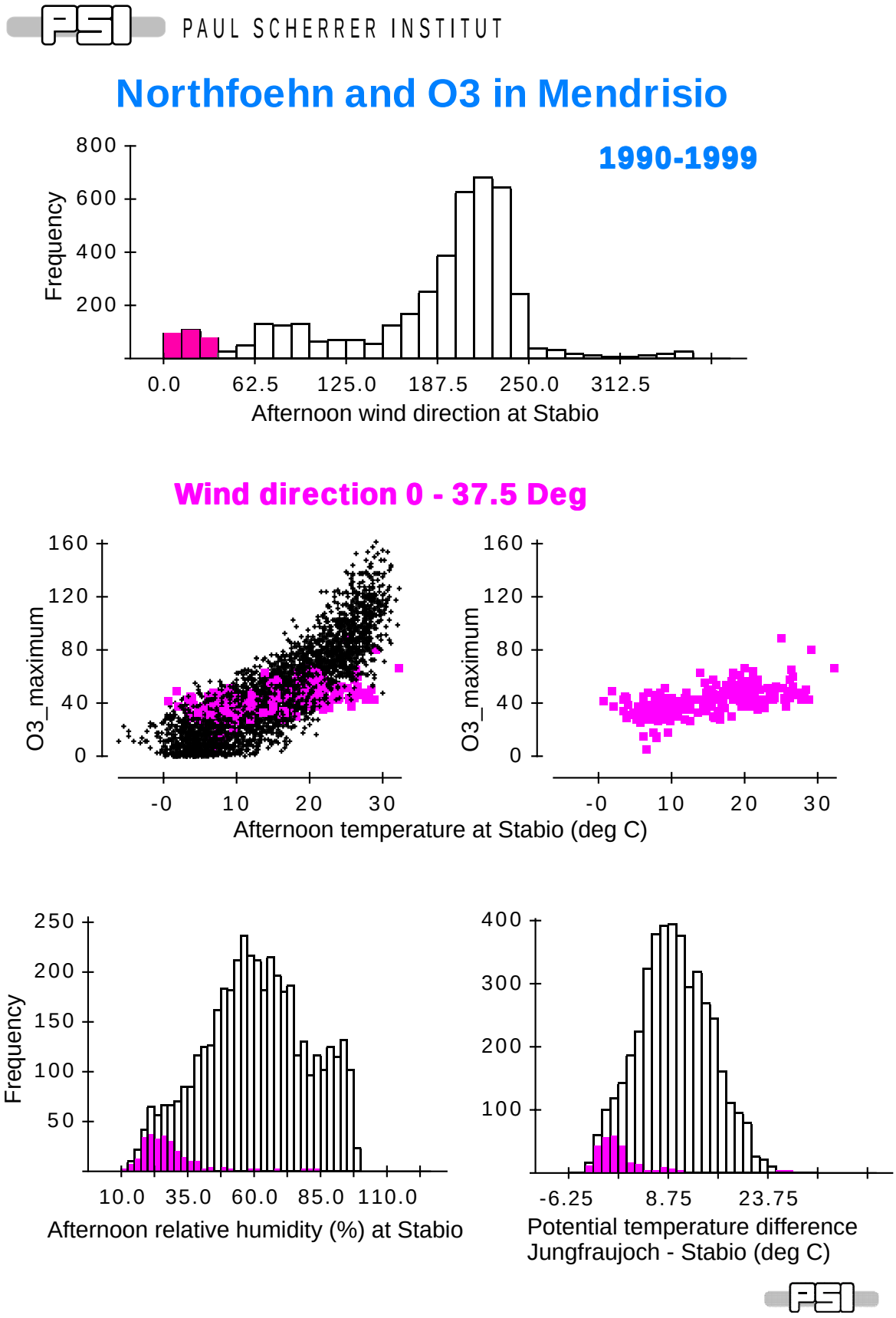
- The number of flights considering the budget analysis and the plume study were far higher than the minimum of two days south and north of the Alps. The delay in the measurement campaign in Munich due to unfavorable weather has caused a delay in the data analysis.
- No boundary layer model has been used to study the height of the boundary layer. The main results could be derived without model from the data obtained.
- Boundary layer top entrainment was not calculated from the buoyancy flux. The study was focusing on the budget analysis and thus on the net vertical exchange flows.
- The analysis of existing data was extended from analysis of aircraft measurements to the analysis of 10-year data of ozone measurements in the Alpine foothills. The aircraft data was also used to characterize VOC concentration distributions in different regions around the Alps, which was not intended in the working plan.
- PSI did not use a lagrangian model for the advection of pollution to the Alpine foothills. During VOTALP I, we figured that a lagrangian model cannot adequately describe the vertical exchange processes in the Alpine foothills. Our statistical analysis of the Swiss Model forecast and wind profiler data showed that the Swiss Model is not predicting the flow towards the Alps with good accuracy. The lagrangian approach was used by the Vienna group in the project. PSI decided to focus and extend their work on the statistical analysis of the measured data.

4. Conclusions

The PSI has contributed to several new findings regarding ozone transports in the Alps, using novel approaches:

- Considerable concentration increases above Alpine foothills can be observed. Alpine foothills cannot be neglected regarding vertical pollutant transport. These budget studies were the first studies ever to characterize vertical net transport of pollutants over foothills.

- Compared to deep Alpine valleys, pollutants are not injected to very high altitudes like 3000-4000 m MSL above the Mesolcina valley as found in VOTALP I.
- Vertical net wind speed can be up to 0.1 m/s
- Milano is a strong pollutant source. The pollutants of this area often hit the Alpine foothills in summer months.
- In northerly Foehn situations, free tropospheric air is brought down to the boundary layer of the Alpine foothills. The concentrations are low in summer, high in winter during these cases.
- Ozone levels have decreased in the 90ies in the Alpine foothills
- Benzene concentration levels are relatively low in comparison to the total VOC load in the Po Basin due to regulations in Italy that the benzene content in the gasoline is lower than 1 %.
- Results from the PSI group suggest a new distinction of 3 vertical air layers in the Alpine area: planetary boundary layer, new: injection layer, and free troposphere.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Northfoehn and O3 in Mendrisio
1990-1999
Frequency
800
600
400
200
0.0
62.5
125.0
187.5
250.0
312.5
Afternoon wind direction at Stabio
Wind direction 0 - 37.5 Deg
O3_maximum
160
120
80
40
0
-0
10
20
30
Afternoon temperature at Stabio (deg C)
Frequency
250
200
150
100
50
10.0
35.0
60.0
85.0
110.0
Afternoon relative humidity (%) at Stabio
400
300
200
100
-6.25
8.75
23.75
Potential temperature difference
Jungfraujoch - Stabio (deg C)

Figure 3

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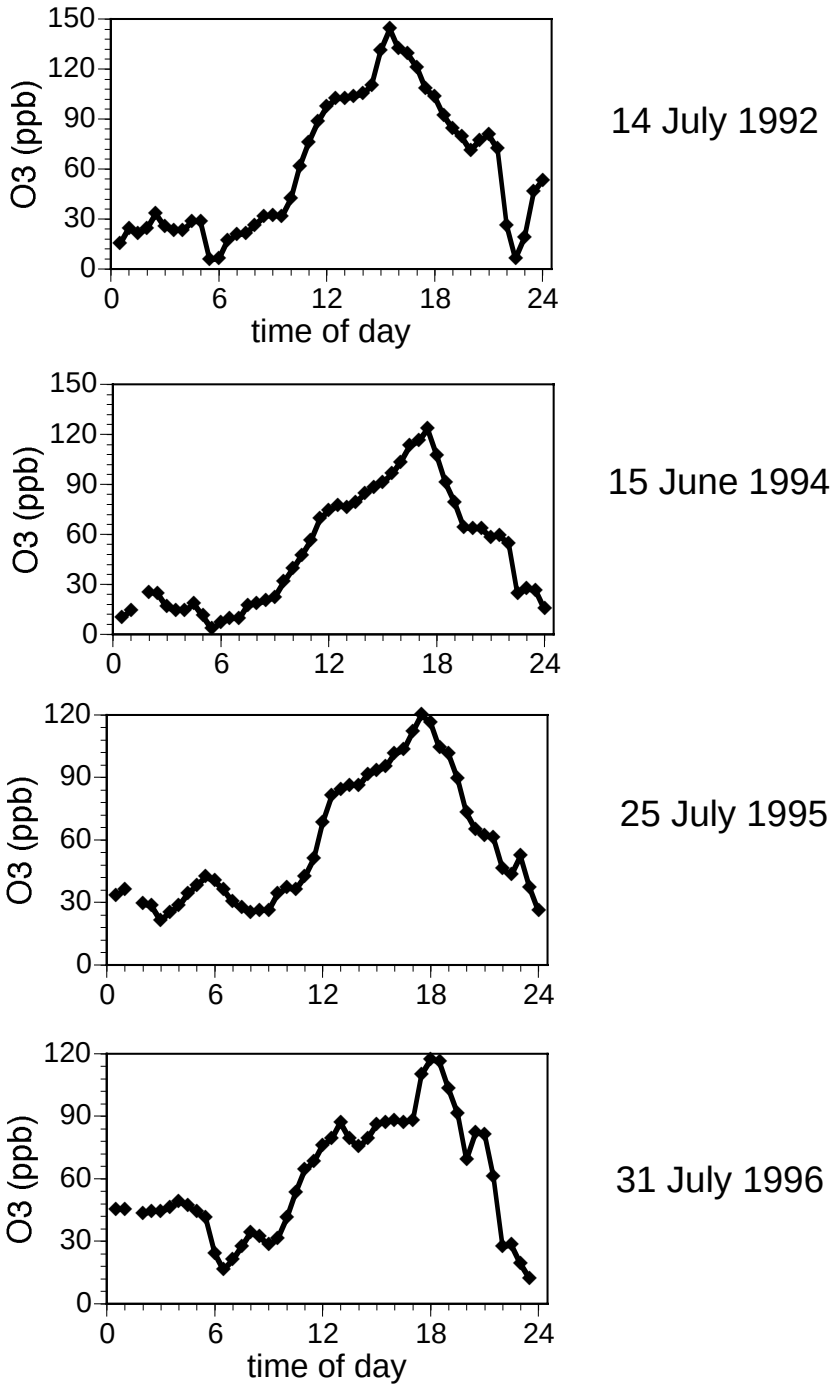

Figure 4

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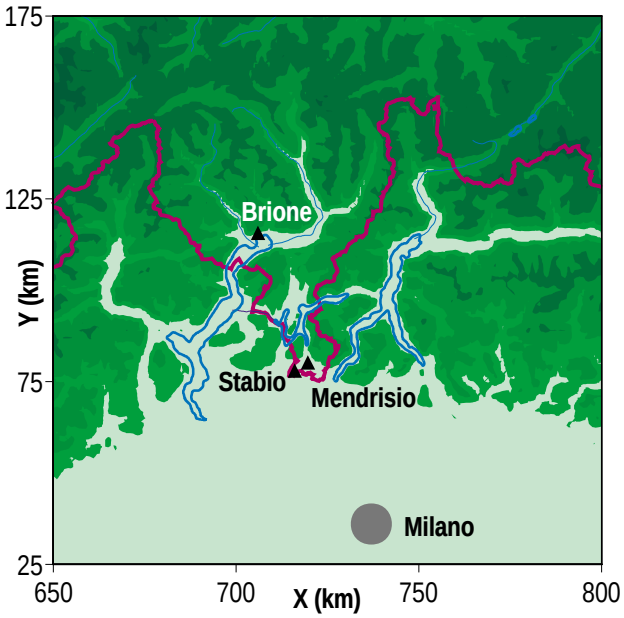
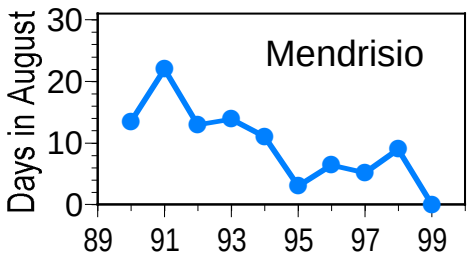
Ozone trends in Southern Switzerland in the 1990'ies



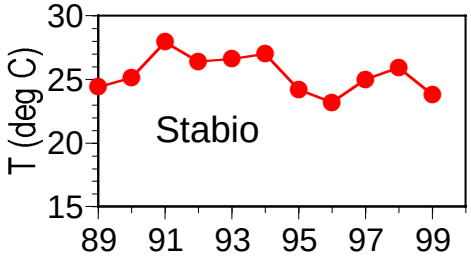
August:

- Number of days with max. ozone > 90 ppb significantly decreases in Mendrisio.
- Mean monthly ozone conc. decreases at Mendrisio and Brione.
- Afternoon-temperature at Stabio shows no trend. However, temperature modulates the ozone signal.

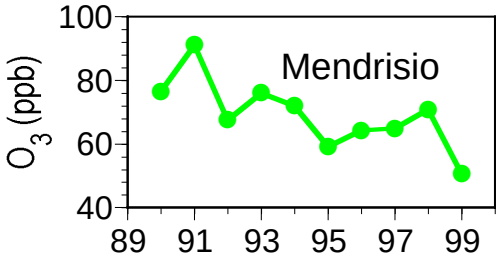
Days with O_3_max > 90 ppb



August afternoon temperature



August mean ozone concentrations



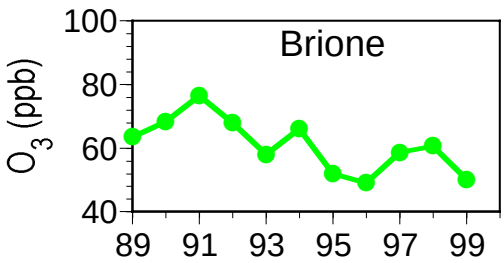


Figure 5

Final Report of LRU

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P. Zanis

1. Objectives for the reporting period

- Establish set-ups and methods for a continuous measurement of aerosol surface area concentrations, ^{210}Pb, and ^{220}Rn decay products in air at Jungfraujoch.
- Carry out continuous measurements of ^{7}Be, ^{220}Rn and ^{222}Rn decay products, and aerosol surface area concentrations at Jungfraujoch.
- Carry out ^{210}Pb measurements in previously defined samples.
- Explore possibilities to also detect ^{10}Be.
- Explore possibilities to measure ^{7}Be at Jungfraujoch with a time resolution of 24 h.
- Performing an intercomparison exercise of sampling and measurement of ^{7}Be at the four stations Jungfraujoch, Mte. Cimone, Sonnblick, and Zugspitze.

2. Main results

Methodology

Be-7 measurements

To measure ^{7}Be activity concentrations at Jungfraujoch particle bound ^{7}Be is collected on glass fibre filters (Binzer 227/1/60; diameter 15 cm) using a HIVOL air sampler (Digitel). After a sampling time of 48 h the filters are changed automatically. One air filter represents a total air volume of 2131 m^3 at local conditions (average temperature 265 K, average pressure 653 hPa). Within about 60 days after end of sampling halves of these filters are available for non-destructive gamma-ray measurements.*

Each filter sample is measured in a calibrated geometry with a PGT well-detector for about 24 h. ^{7}Be is determined with gamma spectrometry via its 478 keV decay line (10.34 %). The detector efficiency for the given sample geometry is 19.0 % at 478 keV. A modified Nuclear Data program (PEAK V16.5 code) is used to deduce absolute activities from the measured count-rates.

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* We thank EMPA Dübendorf (Switzerland) for providing these filter samples. EMPA Dübendorf operates the HIVOL sampler at the Jungfraujoch Sphinx observatory (elevation 3580 m a.s.l.) to measure bi-dayly averages of total suspended particulate matter (TSP) within the Swiss National Monitoring Network for Air Polution (NABEL) program.

To explore the possibilities of measuring ^{7}Be at Jungfraujoch with a time resolution of 24 h, a second HIVOL air sampler with a modified air inlet was installed temporary at Jungfraujoch. The filters were changed after sampling times of 6 h and 24 h, respectively. The other measuring procedures were the same as for the routine measurements.

In order to assess the quality of the ^{7}Be measurements, four filters were loaded simultaneously at Linz and used as control samples for intercomparison. As these samples differ in geometry and material from the filters routinely applied the PGT well-detector was recalibrated using blank filters loaded with a ^{7}Be standard reference solution. The other measuring procedures were the same as for the routine measurements. Aliqouts of the ^{7}Be standard reference solution were delivered to the other laboratories too.

Pb-210 measurements

To measure ^{210}Pb activity concentrations at Jungfraujoch the same air filter samples as used to measure ^{7}Be are measured with a high-purity germanium well-detector for at least 24 h. The measuring time is chosen in dependence on the ^{210}Pb activity to assure that the uncertainty due to counting statistics is less than 10 %. ^{210}Pb is determined with gamma spectrometry via its 46.5 keV decay line (relative intensity 4.25 %).The detector system was calibrated indirectly by measuring the ^{210}Pb activity concentration of several samples in the Labor für Umwelt- und Radioanalytik of the VKTA Rossendorf. The detector efficiency of the LRU germanium well-detector for the given sample geometry was determined to be 82 %.

Rn-222 decay product measurements

For the measurement of the ^{222}Rn decay products the calibrated set-up “turbo-epiphaniometer” at Jungfraujoch is used. All details concerning the calibration of this device are described in [1]. As explained in this reference, continuous alpha spectrometry is used to determine the aerosol-borne activity of ^{214}Po via its 100 % 7.6869 MeV decay line. For that, air is pumped through a filter station (4 l/min, monitored by a thermal mass flow meter). Here the aerosol particles are deposited on a Nuclepore filter. The alpha-activity of the deposited aerosol particles is measured with a Passivated Implanted Planar Silicon (PIPS) detector facing the Nuclepore filter. Every four hours the spectrum is analysed and the peak area of the 7.6869 MeV alpha line determined.

Rn-220 decay product measurements

^{220}Rn decay products are measured simultaneously with the ^{222}Rn decay products. The ^{220}Rn decay product ^{212}Pb is determined by continuous alpha spectrometric measurements of the 8.78 MeV α-decay events of ^{212}Po in analogy to the measurement of the ^{222}Rn decay products as described above.

Measurement of aerosol surface area concentrations

Continuous aerosol measurements have been performed at Jungfraujoch since 1988 with a time resolution of 1 h by means of an epiphaniometer as described in detail in [2,3]. The epiphaniometer signal corresponds to a surface area concentration (Fuchs surface).

Results, Discussion

Be-7 measurements

The routine measurements of ^{7}Be at Jungfraujoch as established during VOTALP I has been continued without serious failures. During the reporting period only seven samples had to be dropped due to technical failures of the HIVOL sampler. All ^{7}Be data up to the end of 1999 have been transferred to the VOTALP data base up to the end of March 2000.

The second HIVOL sampler which would be necessary for ^{7}Be measurements with a time resolution of 24 h was tested between July and September 1998. During this period about 50 % of the samples had to be dropped due to the variable meteorological conditions which caused technical failures of the HIVOL sampler. The routinely used HIVOL sampler which is operated by EMPA Dübendorf works stable even at extreme meteorological conditions because of its high sophisticated air inlet. This in mind we did not see any solution to measure ^{7}Be at Jungfraujoch routinely with a time resolution of 24 h with the moderate funding of VOTALP II.

The intercomparison exercise showed that all ^{7}Be results of the four participating laboratories were within twice the standard deviation of the mean. This result confirms that the ^{7}Be measurement procedures at all laboratories are under control and hence that the differences in the ^{7}Be concentrations as observed at the peak stations do not originate from the ^{7}Be measurement procedures applied. A further statistical analysis of the intercomparison results should allow to address minor systematic errors as a precondition to minimize them and to increase the quality of measurement further.

Pb-210 measurements

^{210}Pb activity concentrations at Jungfraujoch have been measured in about 30 air filter samples taken in September and October 1997. ^{210}Pb activity concentrations varying between 0.2 and 1.2 mBq/m^3 are determined with average statistical errors of single measurements of about 20 %. The data may be provided to the VOTALP community. The limited capacity of the detection system did not allow to measure ^{210}Pb activity concentrations at Jungfraujoch routinely.

Rn-222 decay product measurements

^{222}Rn activity concentration data are available in Bq/m^3 with a time resolution of 4 h. Due to partly poor counting statistics, average statistical errors of single measurements are about 20 %.

In contrast to the VOTALP I time period the turbo epiphaniometer worked very stable (to be updated). Data up to December 31, 1999 will be transferred to the VOTALP data base up to the end of April 2000.

Rn-220 decay product measurements

^{220}Rn decay product data have been analyzed up to December 1999 and will be provided upon request.

Measurement of aerosol surface area concentrations

Epiphaniometer data for the reporting period cannot be supplied due to technical failures.

Detection of Be-10

Possibilities to detect ^{10}Be have been explored. A chemical method to separate Be from glass fibre filters prior to the ^{10}Be determination by accelerator mass spectrometry has been evaluated. The detection limit for ^{10}Be amounts to 10^5 ^{10}Be atoms or a ^{10}Be/^{9}Be ratio of 10^{-14}.

3. Deviations from technical annex and reasons

There are no deviations from the workplan

4. Conclusions

As seen from **Figure 1** the average monthly arithmetic mean values of the atmospheric concentration of ^{7}Be at Jungfraujoch for the time period April 1996 to December 1999 show a weak seasonal variation with slightly enhanced values in summer and lower values in early winter. A similar weak seasonal dependence was also found for the nearby low altitude site Muehleberg at the Swiss Plateau. The summer maximum obviously results from the enhanced vertical tropospheric exchange during the summer time but is less pronounced compared to those of ^{210}Pb, ^{212}Pb, ^{214}Pb, or the Epiphaniometer aerosol surface signal [2] due to different source areas and transport processes. This is in contrast to the climatology of stratospheric intrusions for Jungfraujoch which was derived from measured data on the basis of relative humidity, ozone, and ^{7}Be showing no clear seasonal variation and in contrast to observations at Zugspitze and Sonnblick showing a clear seasonal variation with a summer minimum [4]. Further work is necessary to investigate the origin of these differences.

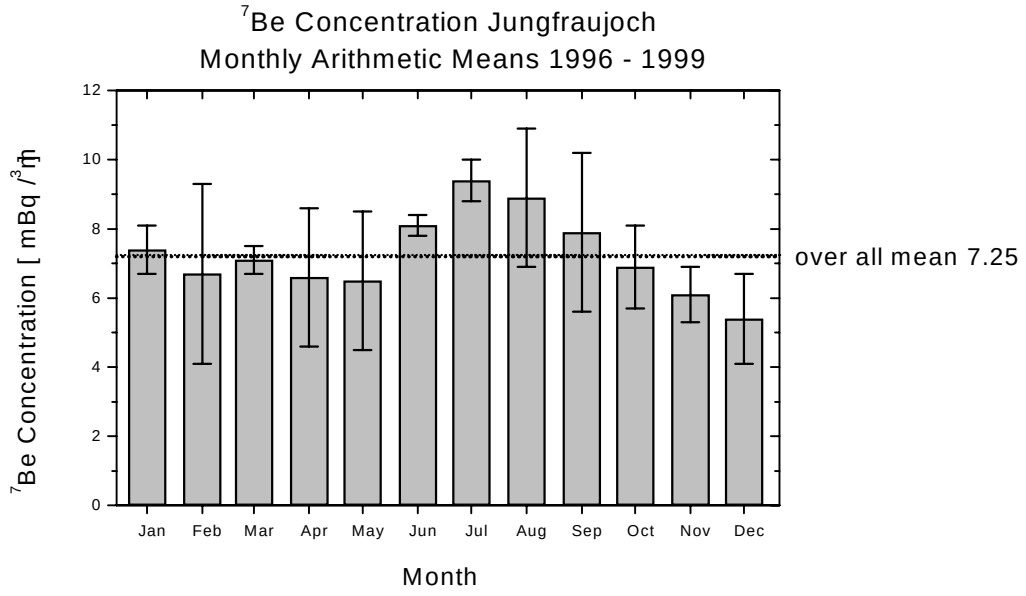

Figure 1: Monthly arithmetic means of ^{7}Be activity concentrations at Jungfraujoch for the time period April 1996 to december 1999.

5. Publications

During the reporting period results of VOTALP I and VOTALP II were presented at three international conferences [5, 6, 7] and in the PSI annual reports 1998 and 1999 [8, 10]. Two papers have been accepted for publication [4, 9].

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Final Report of FKKT

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mag. Alenka Levart, dipl. ing.

1. Objectives for the reporting period:

A. To participate in the joint measurement campaigns in the Milan and Garmisch-Partenkirchen area where ozone, nitrogen oxides, photolysis frequency of NO_2 (J_{NO2}) and meteorological parameters were measured at one site as well as volatile organic compounds (VOCs) at two sites;

B. To evaluate and interpret the data from the field campaigns;

C. To contribute to the VOTALP - data base, the intermediate and the final report;

D. To participate at the project workshops and PPC meetings.

2. Main results obtained (methodology, results, discussion):

Methodology

During the campaign in the Milan area continuous measurements of NO and NO_2 concentration, J_{NO2} and net solar radiation were performed at the site Colma del Piano (1236 m a.s.l.) between May 22 and June 10, 1998. Additionally, sampling of NMVOCs (C_2 - C_{10}) was done at the stations Alpe del Vicere (903 m a.s.l.) and Monte Boletto (1278 m a.s.l.) on several days between June 1 and 10, 1998. During the sampling intervals air temperature, relative humidity and photosynthetic active radiation (PAR) were measured at the site Alpe del Vicere as well.

During the campaign in the Garmisch-Partenkirchen area (May 26 – 29, 1999) measurements of ozone, nitrogen oxides, J_{NO2}, meteorological parameters, photosynthetic active radiation (PAR) and sampling of VOCs were done at the Bromberg site (810 m a.s.l.). Additionally VOCs samples were taken at the Wank elevated monitoring station at 1776 m a.s.l.

VOC sampling was, generally, performed every two hours between 6:00 and 22:00 as well as at 2:00 during the night-time. Stainless steel tubes filled with three different adsorbents (160 mg of Tenax TA, 80 mg of Carbotrap and 290 mg of Carbosieve) were used. Two VOC samples of a volume of 2 - 3 l were taken simultaneously. One served for the analysis of light VOCs (C_2-C_7) and the second one for the determination of higher VOCs (above C_5). The light VOCs were analysed on a GC/FID system; the analysis of higher VOC was performed with a GC system with two parallel detectors (MSD and FID).

At the end of the “Milano” campaign several parallel VOC samples were taken at the Verzago site in order to make an intercomparison of the sampling and analytical systems with the ETH

Zürich for the VOCs as well as an intercomparison of the J_{NO2} photometers. A calibration of the NO_x analyser was done just after each campaign as well.

A comparison of VOC concentrations between the results obtained with the IFU model and the measurements performed during the Mesolcina campaign of the VOTALP I project should be done. This comparison between the model results and the measured data was done in two stages. During the first stage the measured VOCs were grouped into the classes which are defined within the photochemical model. Afterwards the model's results should be compared with the field measurements in order to evaluate the performance of the photochemical model.

Results and Discussion

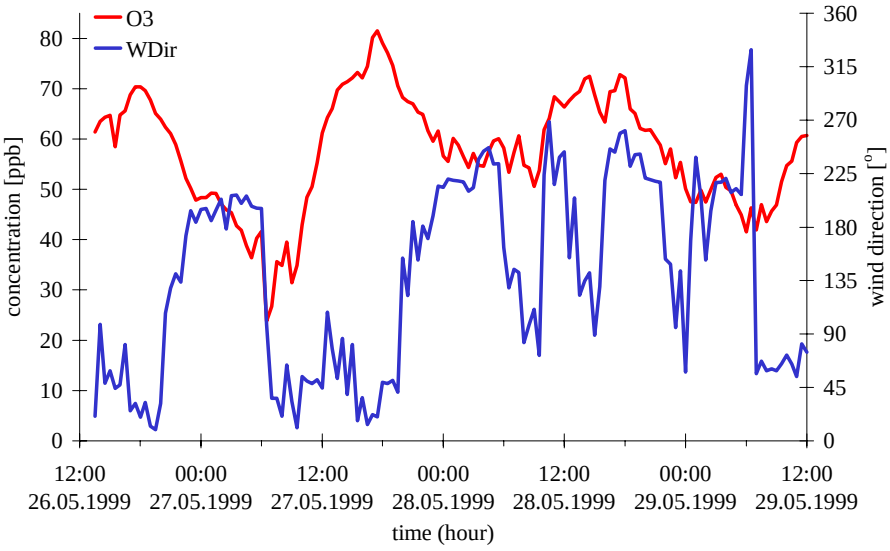

Figure 1: Ozone concentration and wind direction during the campaign at the Bromberg site

The meteorological circumstances influence strongly the diurnal variation of chemical compounds, especially in a complex terrain. Depending on the day-time period our measurement sites were generally influenced by the up- and down-slope flows. As a consequence the trace gases from different air layers and different pollution source areas could be traced during the 24 hour cycle of the wind system as it can be seen in the figure 1, where ozone concentration and wind direction at the Bromberg site are presented. During the day-time the site was influenced by the up-slope flow from N – E wind sector and during the night-time by the down-slope flow between 180^o and 240^o. The ozone concentration decreased during the night-time, reached minimum value after the dissipation of the night-time inversion layer, when polluted air mass reached the site. With the begin of the N - E flow air masses from the polluted area of Munich were transported toward the site, the photochemical ozone production was favoured by clear sky weather conditions on May 26, 27 and 29 what caused an increasing ozone concentration. The maximum values were recorded during late afternoons of these days what coincided with the arrival time of the Munich plum. The plum of the city of Munich influenced strongly the ozone concentration levels at the Bromberg station placed at the foothills of the Alps.

While the highest NO_2 concentration at the Bromberg site reached up to 7 ppb, were the highest concentrations in the Milano area with over 15 ppb much higher, in spite of the fact that the Colma del Piano was placed even at a higher elevation. However, the relation between the wind direction, trajectories and the diurnal variation of the NO_2 concentration was not so

straight as in the case for ozone at Bromberg. The diurnal variations of the NO_2 concentration showed at both sites during the majority of the days the maxima during the late evening hours (between 19:00 and 22:00) under down-slope flow conditions (Fig. 2). At the Colma del Piano site on only 4 days the daily maximum of the NO_2 concentration was recorded during the afternoon hours - between 14:00 and 17:00 - as it has been anticipated due to the expected transport of polluted air masses from the Po basin with the up-slope flow toward the monitoring station during the day-time. This phenomenon can be related to the regional and meso-scale transport processes of the highly polluted reservoir layer which reached the sites while the photolytical NO_2 destruction and subsequent conversion is not any more present.

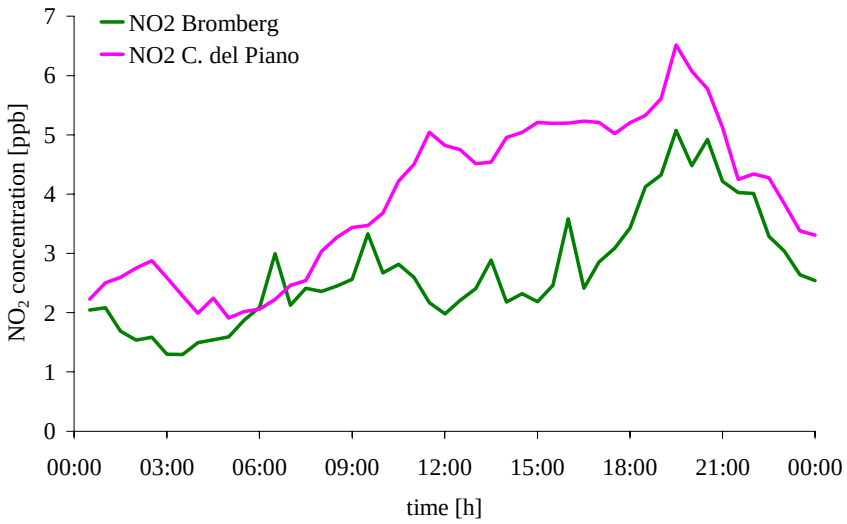

Figure 2: Diurnal variation of the NO_2 concentration at the sites Colma del Piano and Bromberg

Classification of VOC

Volatile organic compounds emitted into the troposphere are removed by reaction with a number of reactive species like different radicals and ozone, and by photolysis and wet and dry deposition (Finlayson-Pitts, 1986). Several chemical models are available for modelling of photochemical processes in the atmosphere. Since these processes are not yet fully understood or they are very complex some simplifications are usually included in the models; organic compounds are grouped into the classes that show similar chemical behaviour in the atmosphere. In order to group individual VOCs into these prescribed classes a detailed knowledge of the kinetic parameters for the reactions with reactive species is required. The dominant gas phase chemical degradation processes of VOCs are the reactions with OH radicals and ozone during the day and with NO_3 radicals at night. Despite extensive experimental work carried out during the last several years, measured reaction rate constants are available for only around 500 organic compounds (Atkinson, 1986, 1989, 1994). Thus it is important to develop a theoretical prediction model, which can be used to obtain estimates of the necessary kinetic parameters.

In quantitative structure property relationship (QSPR) studies a correlation between chemical structure and chosen property was investigated. Such studies include, generally, two main stages. First the chemical compounds must be translated into a computer readable form, and afterwards the quantitative correlation between chemical structure and its property can be obtained using different statistical and learning procedures, e.g. multiple linear regression

model (MLR), several types of artificial neural networks, partial least-square (PLS) method, etc.

A new approach for the calculation of reaction rate constants for the reaction of O_3 with different organic compounds was developed during the project. The same method can be also used for the calculation of reaction rate constants for the reaction of VOCs with other reactive species present in the atmosphere. Predicted kinetic parameters were used for the grouping of the organic compounds measured during the Mesolcina campaign into the VOC classes which were defined within the photochemical model.

The data set contains acyclic and cyclic alkanes, alkenes, halocarbons, N and O containing compounds, aromatics and terpenoid compounds. This leads to a final number of 116 compounds which were used for the creation of the model. Experimental rate constants for the reaction of O_3 with different organic compounds were obtained at 25^{o}C and 101.3 kPa.

In order to obtain molecular descriptors needed for the creation of the models the optimised structural co-ordinates and net atomic charges were calculated by MOPAC software package (Stewart, 1990). More than 500 different topological, geometric, informational, electrostatic, electrotopological and quantum-chemical descriptors were calculated from the MOPAC output files using CODESSA software (Katritzky, 1995, 1996). The descriptors employed in the study contained the information about the connections between atoms, symmetry, shape, branching, distribution of charge, and quantum-chemical properties of the molecule.

CODESSA software was also used for the selection of the best subset of structural descriptors for MLR model by minimising an error in the prediction. The information rich descriptors used for the modelling were chosen by stepwise selection procedure described by Katritzky (1995 and 1996).

All compounds were transformed to a computer-readable form, that is, into a set of different molecular descriptors. Afterwards a multiple linear regression model (MLR) was used as a modelling technique. The selection of the optimal number of structural descriptors was based on the best prediction capabilities of the MLR model. The influence of the dimension of the MLR model on its prediction capabilities was tested by leave-one-out cross validation procedure (Figure 3).

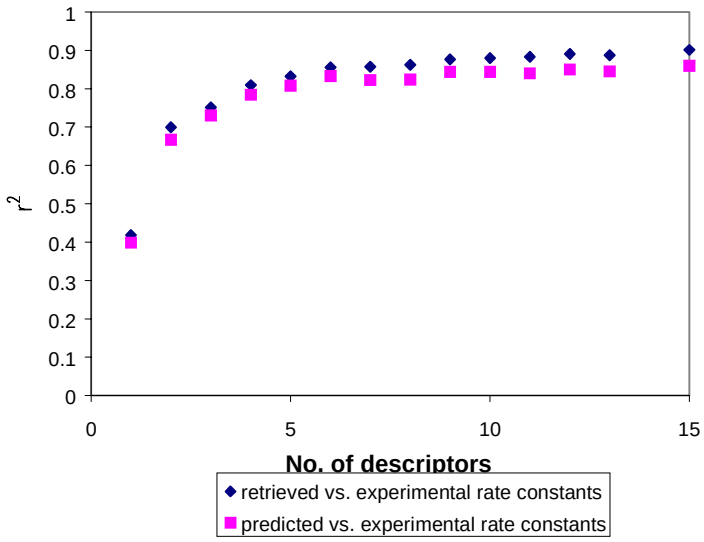

Figure 3: The squared correlation coefficient (r^2) for the linear regressions: retrieved rate constants vs experimental and predicted rate constants vs. experimental values obtained with MLR model.

10-parameter MLR model was used for the prediction of log(k_{O3}) values from the chemical structure. Results are shown in figure 4. An average root mean squared error (RMS) was around 0.876. Therefore it was shown that the developed model is a good tool for the estimation of rate constants where experimental parameter are not available. A detailed description of modelling technique was described by Pompe and Veber (2000).

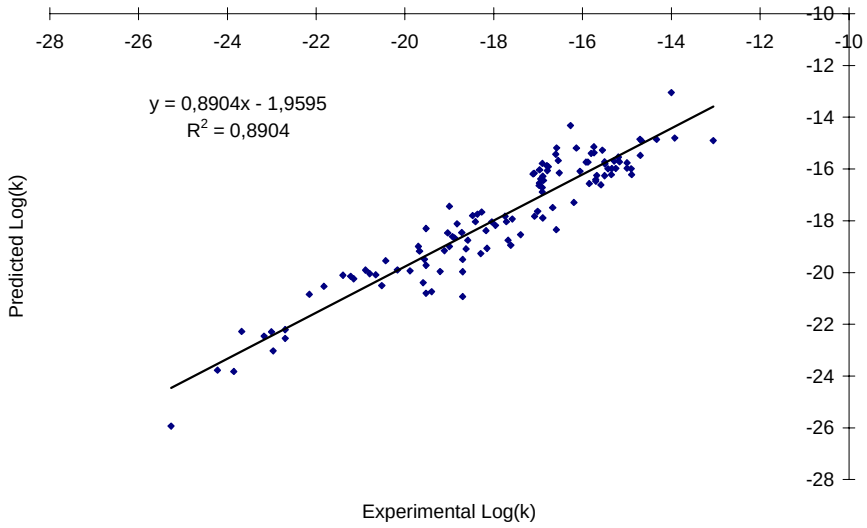

Figure 4: Predicted vs. experimental log(k) values.

The developed technique can be used for the prediction of log (k_x) values which are required for the classification of VOCs into the model classes.

VOC field measurements

Results of an exercise determining the precision of the analytical procedure showed that the precision of the analytical method was between 5 and 12% (Table 1).

Table 1: Precision of the analytical procedure for four samples taken simultaneously 3 times.

	Average concentration (µg/m^3)	standard deviation	RSD (%)
1st set			
Benzene	5.30	0.31	6
Toluene	9.60	0.44	5
Ethylbenzene	1.50	0.09	6
m/p-Xylene	4.91	0.31	6
o-Xylene	1.91	0.20	11
2nd set			
Benzene	5.82	0.54	9
Toluene	12.13	0.39	3
Ethylbenzene	2.02	0.17	8
m/p-Xylene	6.27	0.14	2
o-Xylene	2.41	0.10	4
3rd set			
Benzene	5.42	0.63	12
Toluene	12.28	0.30	2
Ethylbenzene	2.00	0.09	4
m/p-Xylene	6.27	0.19	3
o-Xylene	2.40	0.20	8

The accuracy of the measurements was determined as well. At the end of the first VOTALP II field campaign our analytical procedure for the determination of VOCs was compared with the analytical procedure of ETH from Zurich. The ETH used similar purge and trap procedure with the AIRMOTECH gas chromatograph. Eight samples were taken simultaneously. The intercomparison showed excellent agreement between both measurement techniques.

More than 20 different VOCs were determined during both VOTALP campaigns. The average concentrations of the selected VOCs during both campaigns are shown in Figure 5.

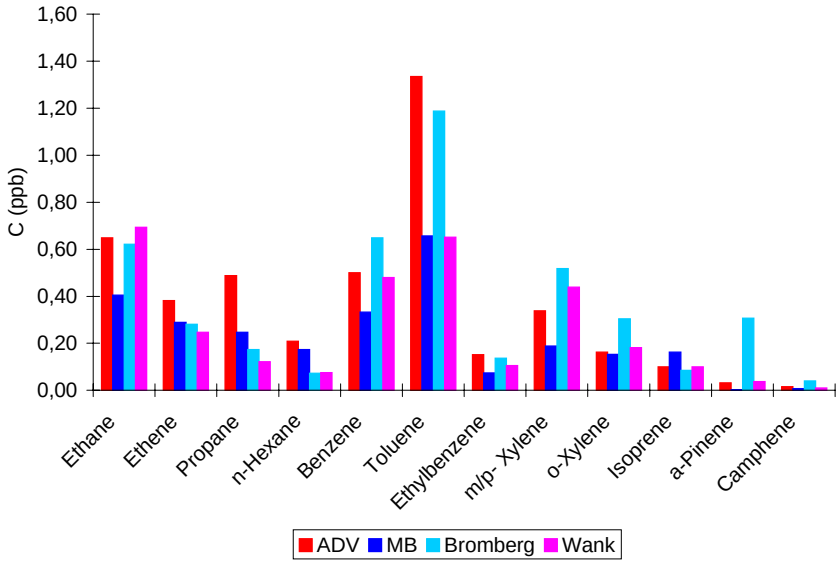

Figure 5: Average concentrations of selected VOCs during both VOTALP II campaigns

During each of the campaigns the VOC samples were taken at two measuring sites. One of them was chosen closer to anthropogenic pollution sources and the second one at mountain peaks in order to obtain background VOC concentrations. In both cases the concentrations of VOCs were higher at lower situated stations (Alpe del Vicere and Bromberg) than at background stations (Monte Boletto and Wank). The background levels of different VOCs measured at Monte Boletto (MB) and Wank were similar. The lower levels of anthropogenic VOCs at Monte Boletto and Wank can be explained by the distance from the sources of pollution. On the other hand the lower levels of the biogenic VOCs can be explained by lower local emissions due to lower temperatures at higher elevations and less vegetation.

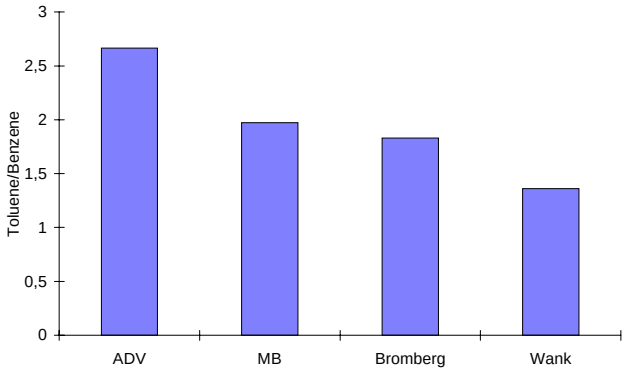

Figure 6: Toluene/benzene ratio at all sampling sites

Beside lower levels of almost all VOCs at both background station compared to the polluted ones it was found that the age of air at Monte Boletto and Wank was slightly higher than at Alpe del Vicere (ADV) and Bromberg, respectively (Figure 6). An estimation of the age of air masses can be obtained from the toluene/benzene ratios. Lower ratios represent older air masses.

Finally, correlations between individual VOCs at the same sampling site were determined. If VOCs show high pairwise correlation it means that they probably have the same source. High correlations between benzene derivatives like toluene, ethylbenzene and o,m,p-xylenes (Fig. 7, 8, 9) for all measuring sites except Bromberg were calculated (Fig. 10). The literature data show that the main source of these VOCs is traffic. We did not find significant correlations between benzene and above mentioned compounds. The reason can be that the majority of benzene has been already removed from the gasoline due to its toxicity. Therefore it seems that the traffic is no longer the predominant source of atmospheric benzene.

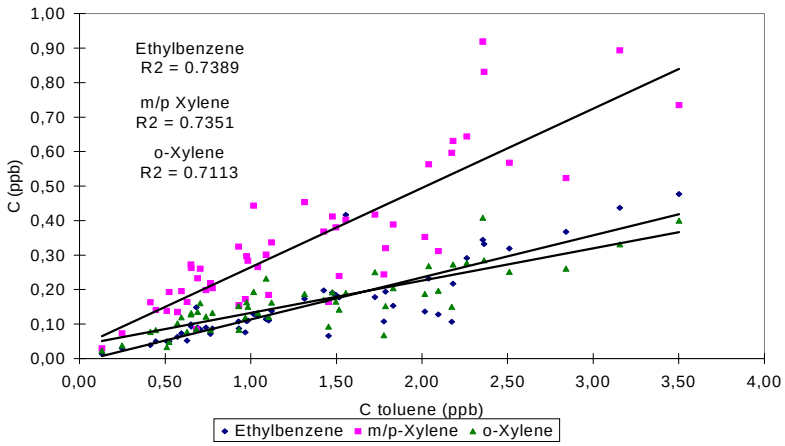

Figure 7: Correlation between concentrations of substituted benzenes and toluene at Alpe del Vicere

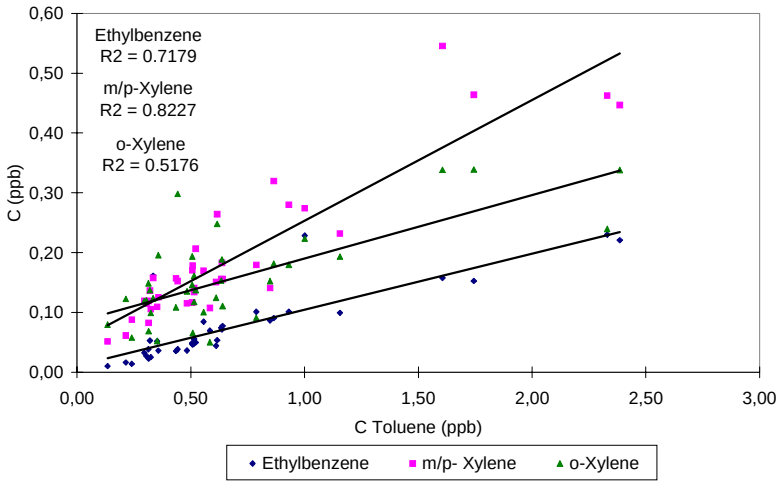

Figure 8: Correlation between concentrations of substituted benzenes and toluene at Monte Boletto

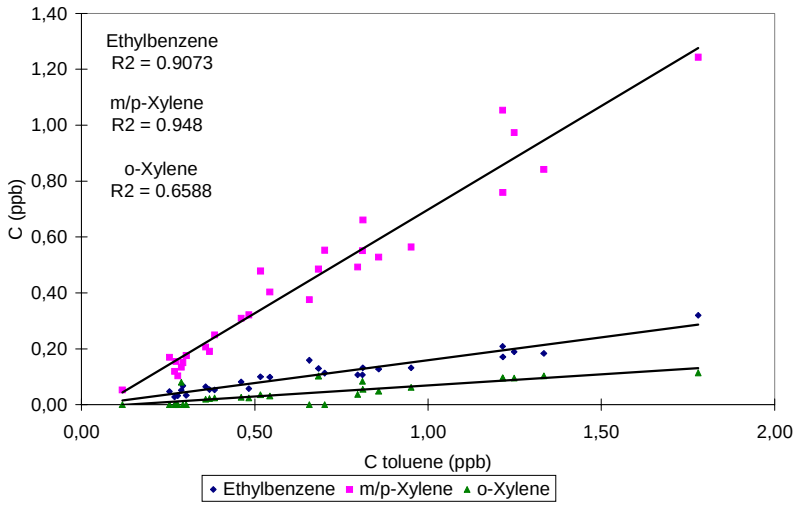

Figure 9: Correlation between concentrations of substituted benzenes and toluene at Wank

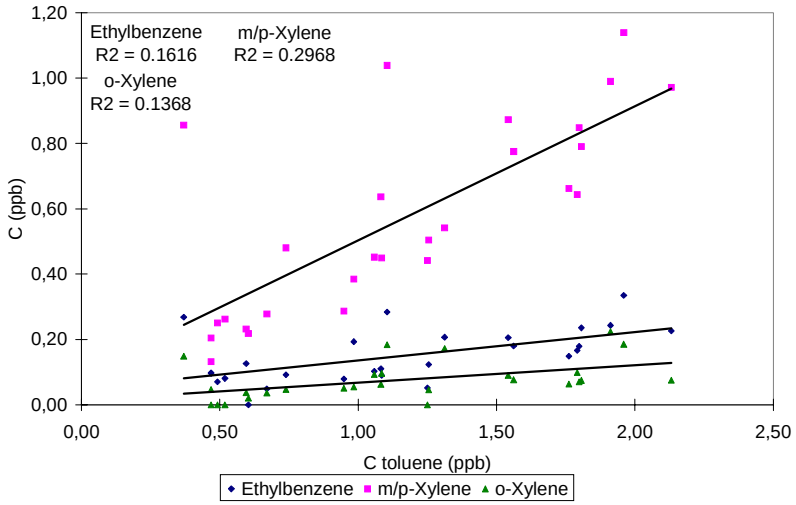

Figure 10: Correlation between concentrations of substituted benzenes and toluene at Bromberg

3. Deviations from the technical annex and reasons

The validation of the photochemical model (work package I) by comparison of the modelled data and performed measurements was not accomplished since it was not possible to satisfactorily model the biogenic emissions in the Mesolcina Valley experiment.

4. Conclusions

During the joint measurement campaigns in the Milan area and in the Garmisch-Partenkirchen area measurements of ozone, nitrogen oxides, volatile organic compounds (VOCs), J_{NO2}, PAR and meteorological parameters were performed.

During the days when photochemical ozone production in the plume of the city of Munich was favoured, increasing ozone concentrations with highest ozone values during late afternoons were observed at the Bromberg site, placed at the foothills of the Alps.

The diurnal variations of the NO_2 concentration showed maxima between evening hours under down-slope flow conditions what could be related to the regional and meso-scale transport processes of the highly polluted reservoir layer while the photolytical NO_2 destruction and subsequent conversion was not any more present.

A calculation procedure for prediction of reaction rate constants of O_3 with different organic compounds was developed during the project. It could be shown that the developed model is a good tool for the estimation of rate constants where experimental parameter are not available.

Anthropogenic VOCs were generally more abundant than biogenic ones. Observed diurnal cycles of biogenic VOC can be explained by the emission pattern of the plants.

The site Alpe del Vicere and Bromberg, located at lower elevation were exposed to higher VOCs concentrations of anthropogenic as well as biogenic origin than the elevated sites Monte Boletto and Wank.

High correlations between benzene derivatives at all measuring sites (except Bromberg) were found, what points out traffic as the most important emission source. However, some results show that benzene concentration has changed during the last few years.

Final Report of CNR-ISAO

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1. Objectives for the reporting period

- Participation in the work packages II and V.
- Continuous measurements at Mt. Cimone station of: ozone, carbon monoxide, Be-7, Pb-210, UVA, UVB; routine acquisition of meteorological data (i.e. temperature, relative humidity, pressure, wind direction and wind intensity). Since 1996, surface ozone has been continuously monitored according to the WMO guidelines for ozone measurements at a free tropospheric station.
- Identification of stratospheric intrusions of air masses rich in ozone concentration in order to quantify its amount at the surface level. Case study of stratospheric intrusions**.**
- State of knowledge of background ozone in Apennines – Mt. Cimone areas; study of the Mt. Cimone ozone concentration registered in background conditions.

2. Main results obtained

Surface ozone analysis

The surface ozone concentration recorded at Mt. Cimone (2165 m a.s.l.) during the period 1996-1999 shows a well-defined seasonal cycle (Figure 1) with a yearly mean value of 55 ± 8 ppb. The behaviour of ozone concentration shows a maximum in the spring and summer and a minimum in winter.

In order to evaluate the provenience of air masses arriving at Mt. Cimone, correlation between ozone concentrations and three-dimensional backward trajectories has been carried out for the period 1996-1998. This analysis showed that the main provenience of the air masses came from the Atlantic Ocean area and that the yearly mean ozone concentration associated with these air masses was 54 ppb. The highest yearly ozone mean values are related to continental European air masses, where the ozone precursors and the elevated photochemical activity can influence the ozone concentration particularly during the summer season. The lowest values of

ozone concentration are referred to air masses coming from latitude lower than 35° N: marked contributions to the lowest ozone concentrations have been registered as the same time as dust transport events from the Saharan desert.

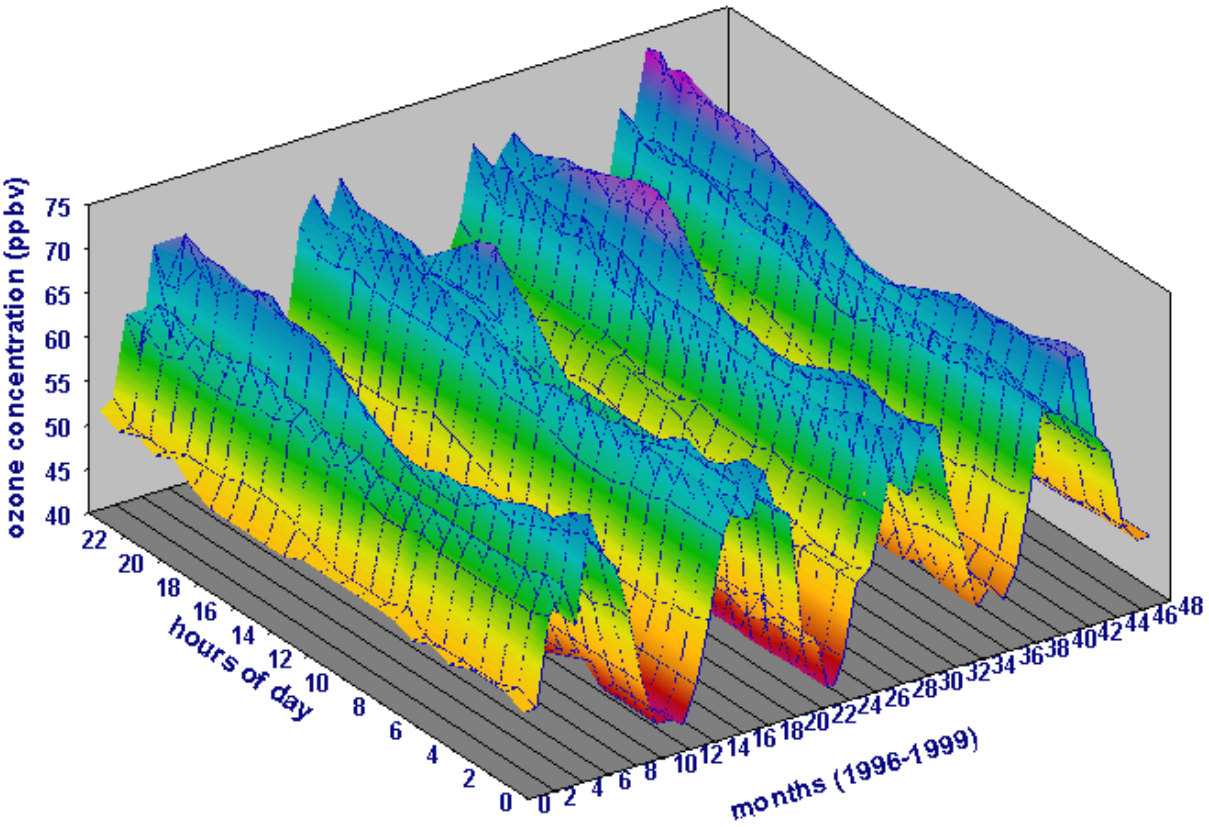

Figure 1: Monthly surface ozone diurnal variation at the Mt. Cimone station during 1996-1999.

As shown in Figure 1, a principal ozone maximum was recorded during the summer seasons, when the air mass circulation in the northern side of the Northern Apennines was affected by the presence of the Po Basin. Under particular meteorological conditions the pollutants can be spread out from polluted areas and transported up to the mountains to high vertical levels and redistributed over long ranges. During summer, boundary layer ozone plume events coming from the Po Basin were registered at Mt. Cimone. To better establish the provenience of these polluted air masses, investigation on ozone, meteorological parameters and biological particles (i.e. pollen grains and fungal spores) have been carried out. In this way the origin area of polluted air masses thanks to biological tracers was discovered.

Beryllium-7 as tracer for stratospheric intrusions and Lead-210 analysis

Continuous radionuclide measurements started in 1998 through a PC-controlled PM10 high volume sampler that permitted a sampling of 48 hours for each sample. 277 samples were taken out in the years 1998-1999, 129 in the first and 148 in the second year. The mean value of ^{7}Be was 6.0 ± 2.6 mBq/m^{3} and 5.2 ± 2.1 mBq/m^{3} respectively in 1998 and 1999 (Figure 2). The monthly mean concentration of ^{7}Be (Figure 3) presents an evident maximum during summer season, probably due to enhanced vertical exchange.

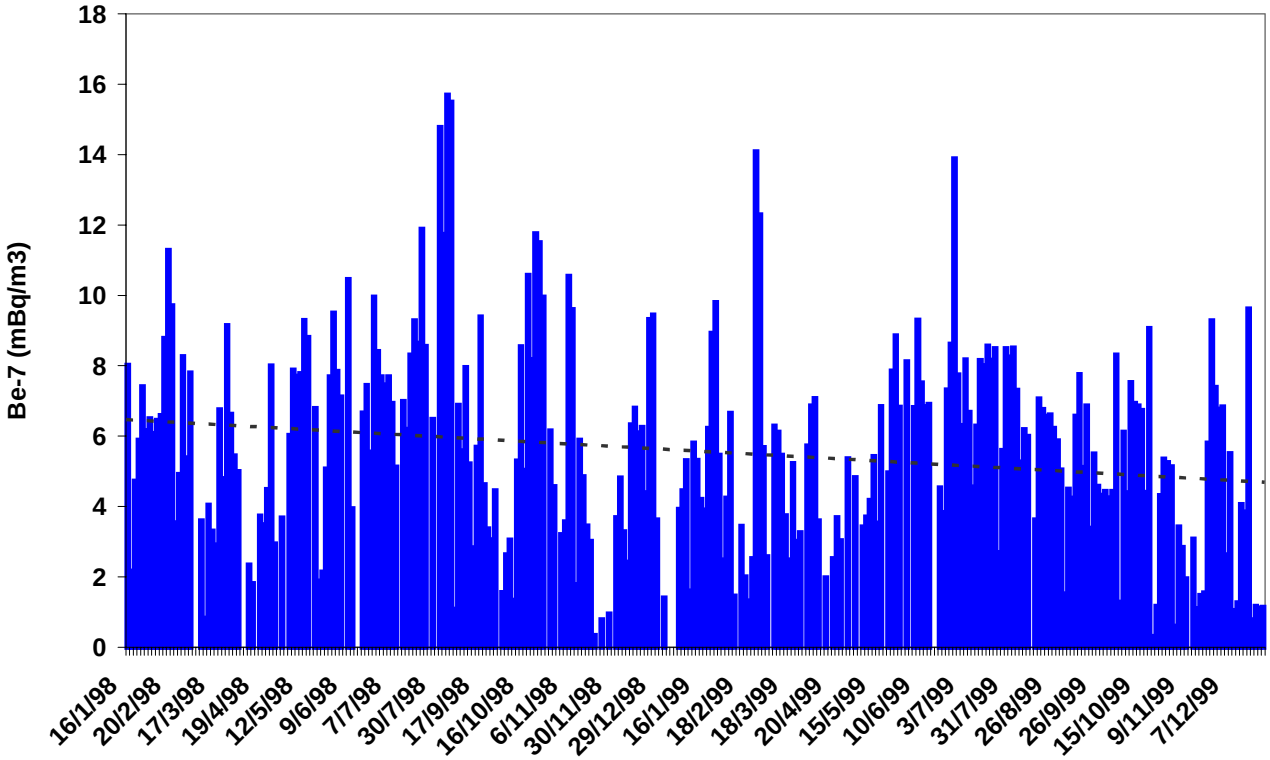

Figure 2: Be-7 monthly behaviour at the Mt. Cimone station during 1998 and 1999.

The threshold value of 8 mBq/m^3 for detecting stratospheric intrusions was exceeded in the 25% and 15% of cases respectively in 1998 and 1999, whereas the ^{7}Be concentration exceeded the values of 10 mBq/m^3 respectively in 9% and 2% of the cases. In 1998 a yearly maximum of 15.7 mBq/m^3 was registered on 9-10 of August, while in 1999 a yearly maximum of 14.1 mBq/m^3 was registered at the end of February.

Two years Beryllium-7 data show a slightly decreasing trend from 1998 through 1999 (Figure 2). The same behaviour is observed for the same period also at a ground level station south of Alps (Ispra) and sited a few hundred kilometres north from Mt. Cimone. This suggests an influence from an increase in solar activity, for which the maximum is forecasted in 2000. In fact, it is known that 11-year solar cycle is anticorrelated with cosmogenic radionuclide production as a consequence of cosmic ray deflection during solar activity maxima.

Since ^{7}Be ($t_{0.5}$ = 53.3 d) is a representative aerosol radioactive stratospheric tracer and ^{210}Pb ($t_{0.5}$ = 22.3 yr) is an excellent boundary layer aerosol tracer, their relative abundance in aerosols can be considered a useful indicator of air masses coming from upper altitudes.

In spite of maximum ^{7}Be concentration recorded during 1998 and 1999 summer seasons, Mt. Cimone measurements of ^{7}Be and ^{210}Pb show an interesting seasonal cycle of the ratio ^{7}Be /^{210}Pb (Figure 4). This behaviour presents larger variation in the cold season, when particularly strong stratospheric intrusion events are present at Mt. Cimone while phenomena of strong tropospheric mixing are nearly absent.

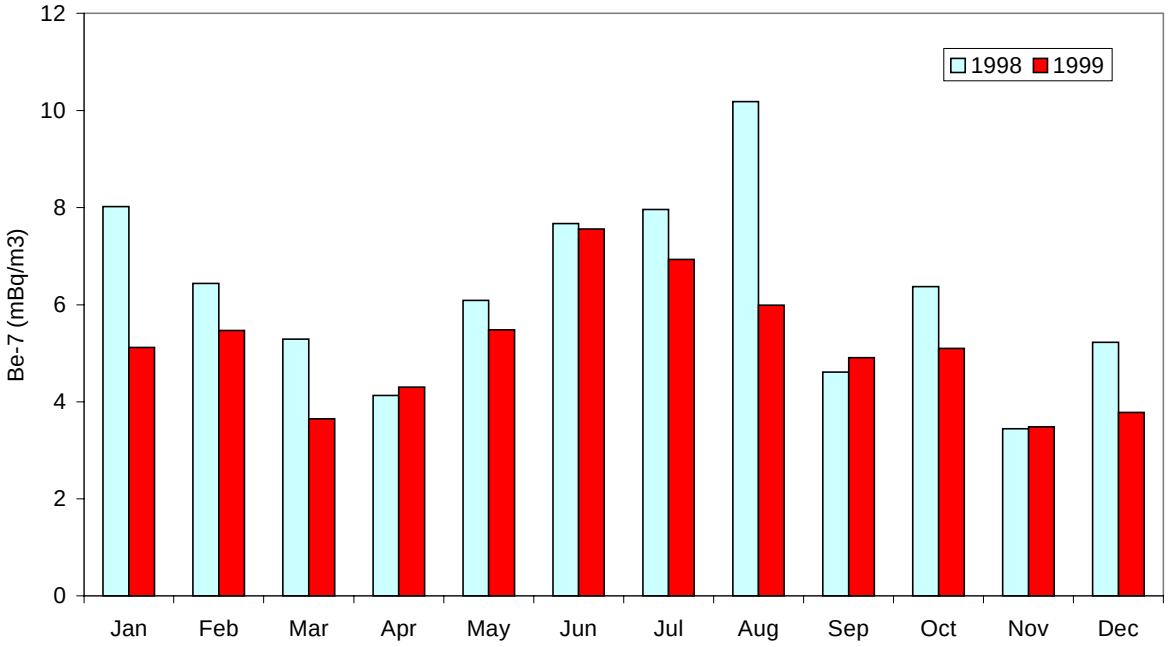

Figure 3: Be-7 monthly behaviour at the Mt. Cimone station during 1998 and 1999.

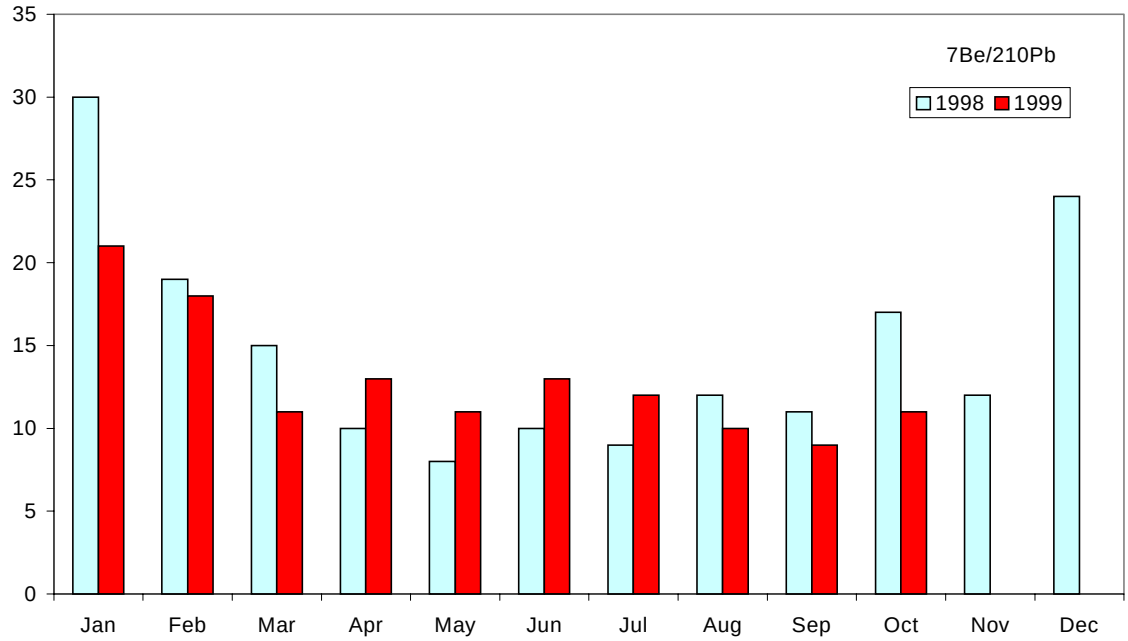

Figure 4: Mt. Cimone seasonal Be-7/Pb-210 ratio recorded in the 1998 and 1999.

WP II: Climatology of ozone flux from the stratosphere.

Identification of yearly frequency and intensity of stratospheric intrusions

To define the relationship between stratospheric intrusions (SI) and ozone concentration at Mt. Cimone, two years of ozone, beryllium-7 and relative humidity measurements have been analysed. Three-dimensional backward trajectories, potential vorticity and potential temperature were also useful to identify the SI episodes. The years 1998 and 1999 were the first years of continuous ^{7}Be sampling carried out at an Italian mountain station, helpful to study and quantify the stratospheric intrusions that occurred south of the Alps.

Considering the two years of observation we can summarise that about 28 stratospheric intrusion episodes, in several cases lasting a few days, were registered. Twenty of these episodes were characterised by values of $^{7}Be>8$ mBq/m^3 and RH<40% and the mean maximum increase in O_3 concentration, as compared to monthly mean value, was about 18%. If we consider only events with $^{7}Be>8$ mBq/m^3 and RH<10%, the mean maximum ozone concentration increased up to about 40%.

This analysis confirms that the yearly frequency of stratospheric intrusions recorded at MTC can be evaluated in about 12-14 events/year (similar results were obtained in 1996 and 1997 during VOTALP I project). The most intense episodes of stratospheric intrusions were registered in late winter and early spring.

To estimate the contribution of these events to the surface ozone concentration, regardless of the season, the ratio R_{O3}, between the ozone maximum recorded during each event and the monthly ozone concentration, was calculated. In this way the maximum percentage of stratospheric O_3 intruded in troposphere during specific episodes was assessed.

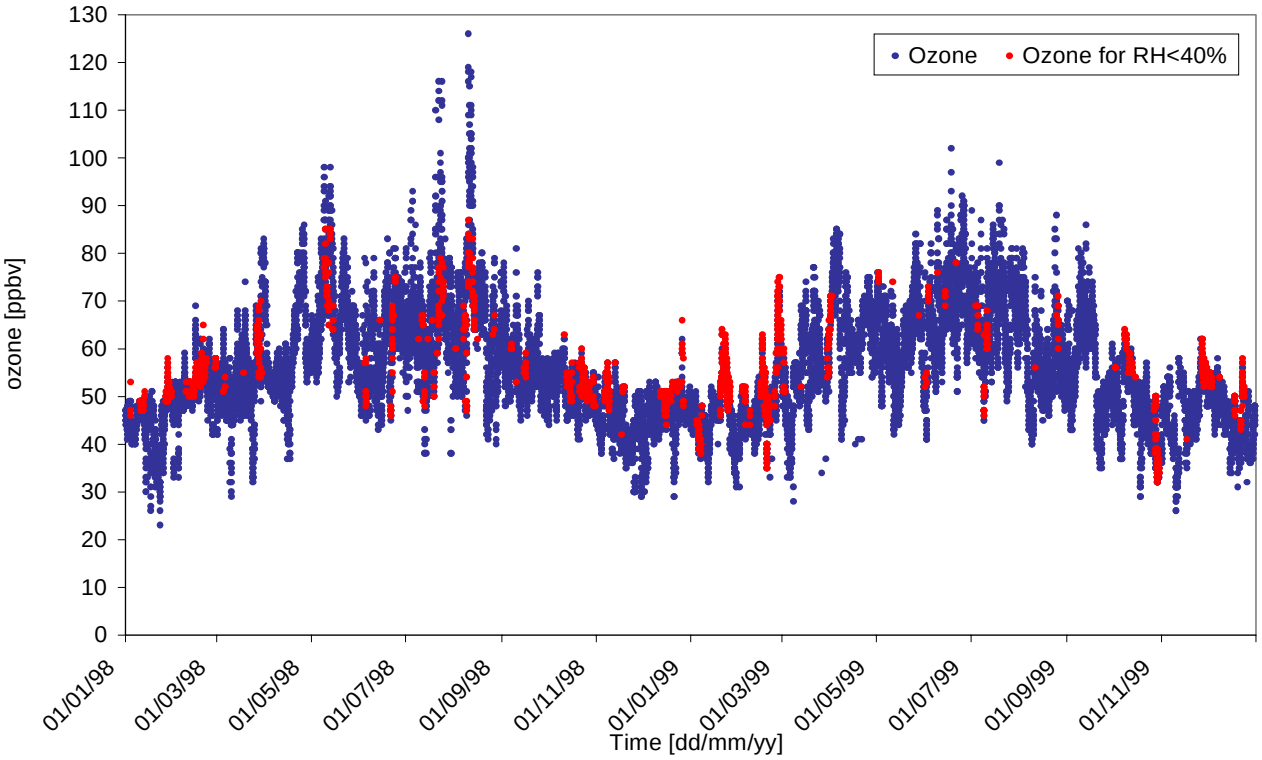

Figure 5: Surface ozone concentration from Jan, 1 1998 to Dec 31 1999 at Mt. Cimone. In red the values of ozone for relative humidity lesser than 40% are reported.

In the period 1998-1999 about 28 episodes recorded at Mt. Cimone related to SI, with RH lower than 40%, ^{7}Be higher than 8 mBq/m^{3} and R_{O3} value more than 1.10, were individuated.

About 60% of these episodes were registered in 1998. We evaluated the mean R_{O3} value considering five different filters as: 1) RH<40%, 2) RH<40% and ^{7}Be>8 mBq/m^{3}, 3) RH<40% and ^{7}Be>8 mBq/m^{3} and excluding summer season, 4) RH<20% and ^{7}Be>8 mBq/m^{3}, 5) RH<10% and ^{7}Be>8 mBq/m^{3}.

As can be seen in the Figure 6, the more selective the criterion, applied to reveal the contribution of stratospheric air masses to local ozone, the more the R_{O3} value increases. This indicates that highest stratospheric ozone concentrations recorded at Mt. Cimone occurred in air masses characterised by high concentrations of ^{7}Be and very low relative humidity values.

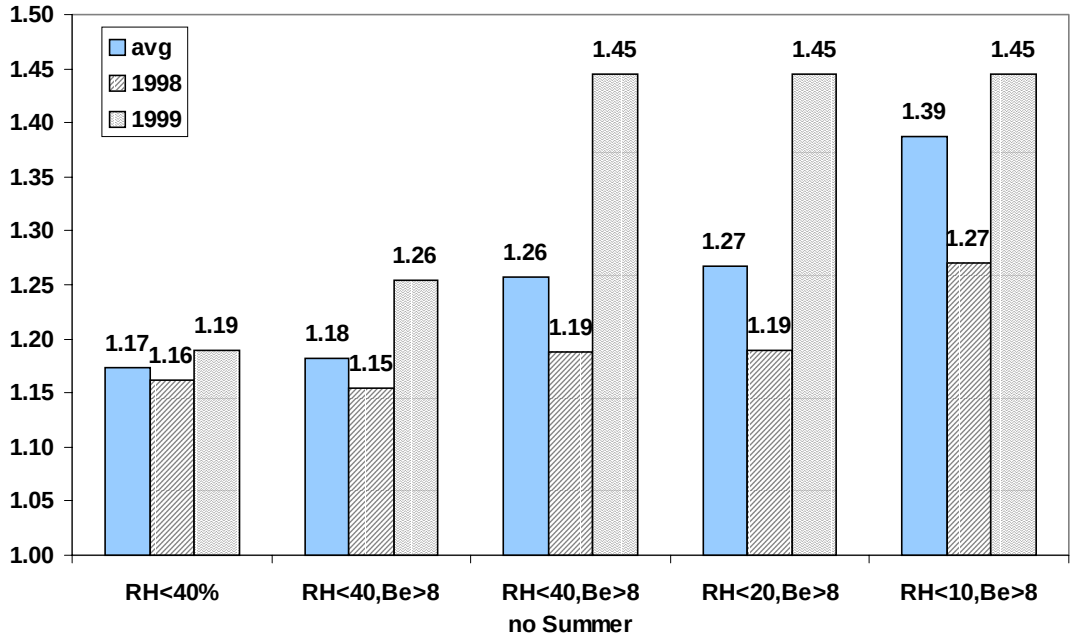

Figure 6: R_{O3} mean values (1998, 1999, average) during stratospheric intrusion episodes as a function of five different criteria.

It is interesting to note that if we consider the filter 3) RH<40, Be>8 and no summer data, (so that the analysis did not take into consideration the June, July and August data), an increase in R_{O3} value is evident, although very high values of ^{7}Be were sampled in the summers 1998 and 1999. This fact could be explained considering that during these periods the ozone concentration of stratospheric origin (aged?) air masses that reached the measurement site had values comparable with those present at MTC level. High concentration of stratospheric ozone could be easily mixed with the tropospheric ozone as a result of strong mixing processes, as the elevated ^{7}Be and ^{210}Pb concentrations would prove. The high ^{7}Be concentration values recorded during these frequent summer events suggest that the threshold of 8 mBq/m^{3} for ^{7}Be is too low to indicate stratospheric intrusions during summer season at the MTC station.

Four cases of stratospheric intrusion episodes at MTC have been studied in detail. These events were characterised by ^{7}Be values more than 9 mBq/m^{3}, relative humidity lesser than 10% and R_{O3} between 1.26 and 1.56. The air masses that reached the MTC station came from an altitude above 8-9 km and with elevated potential vorticity values. These events occurred in November 1998 and in 1999 on January, February and December and are shown in the Figures 7, 8, 9, 10 where the ozone, relative humidity and ^{7}Be behaviours are red, blue and green lines

respectively. During these episodes the mean maximum ozone concentration recorded at Mt. Cimone was 39% higher than the monthly mean values.

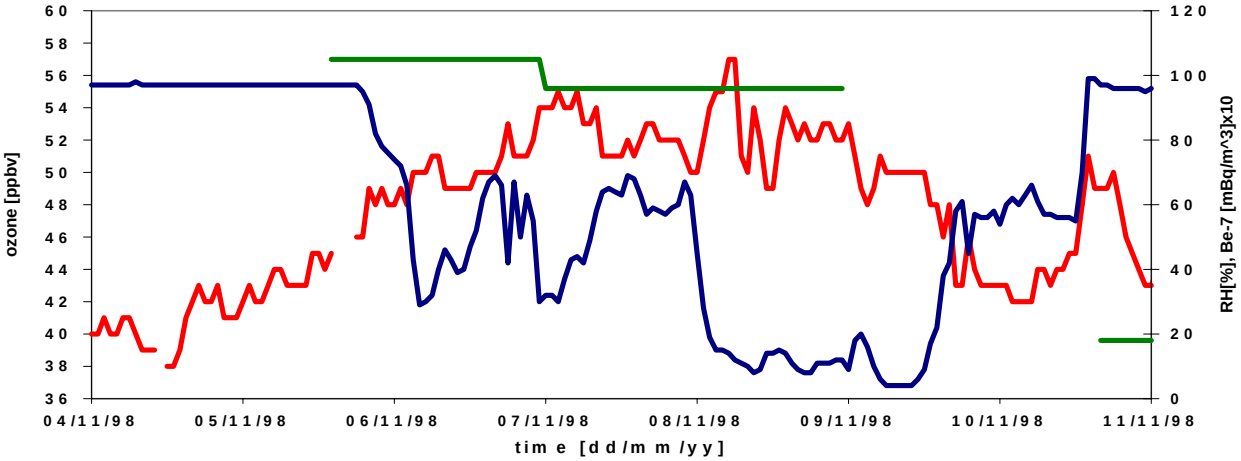

Figure 7: November 1998

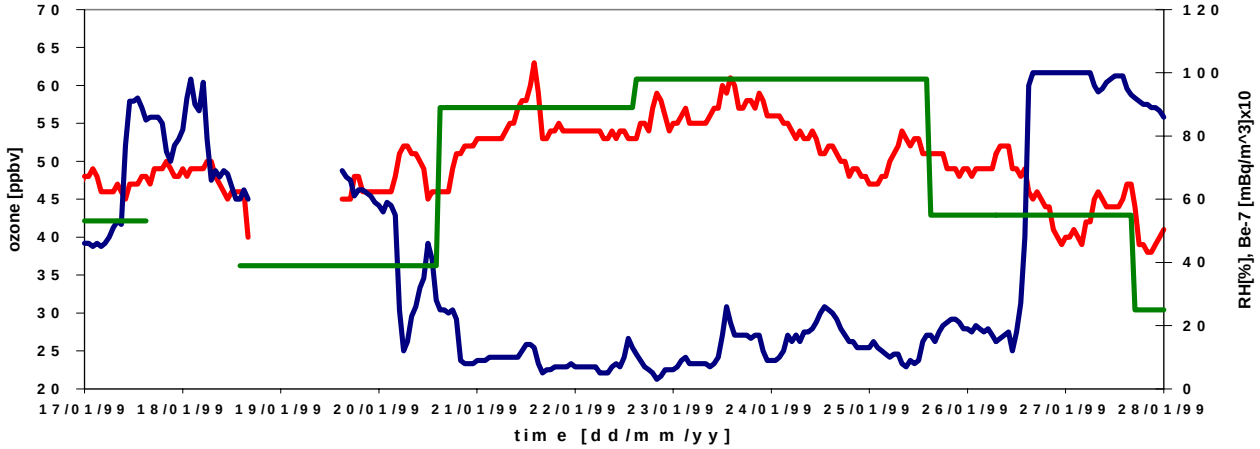

Figure 8: January 1999

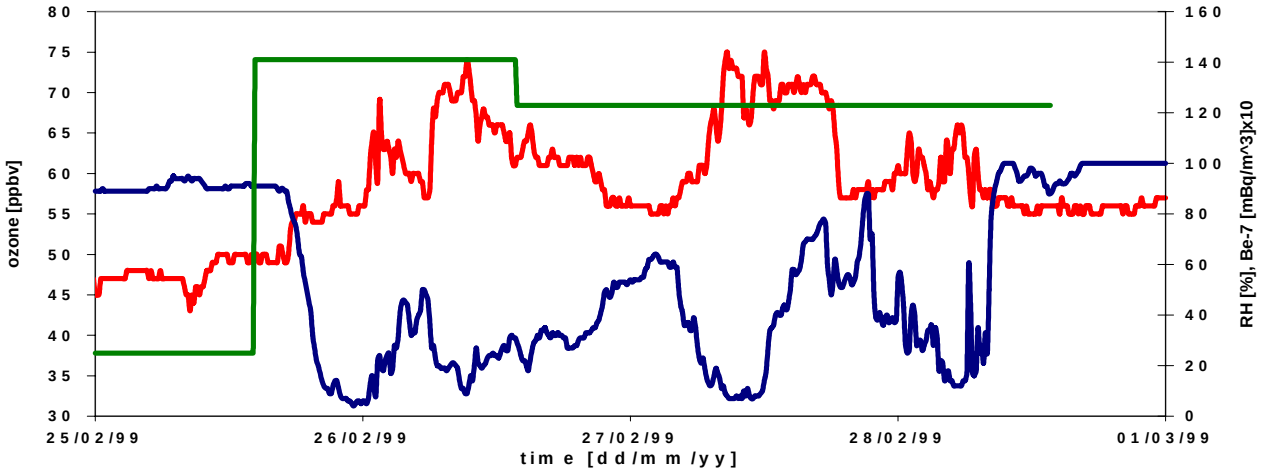

Figure 9: February 1999

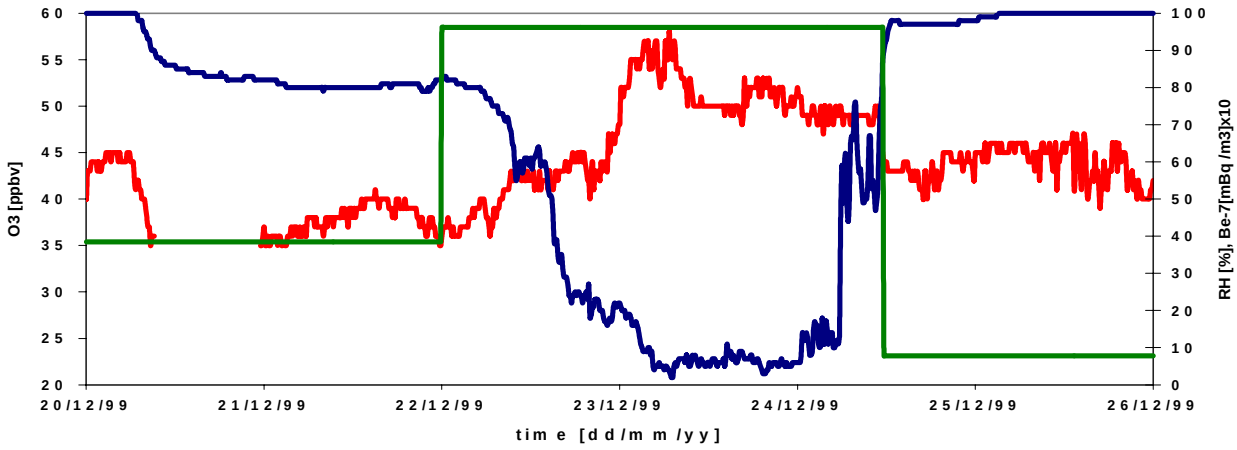

Figure 10: December 1999

Evidence for STE related to intense deformation of the tropopause during cut-off low or tropopause folding events can also be obtained from satellite total ozone maps. During a deep trough the tropopause may descend to very low levels, leading to an increase of the ozone vertical column and a consequent local maximum of total ozone amount can be observed, separated from the surroundings by very steep gradients in total ozone, typically 100 DU / 500 km. Dobson ground-based ozone measurements performed near Mt. Cimone (Sestola) evidenced similar phenomena during episodes of stratospheric ozone intrusion registered at MTC. In particular, stratospheric intrusion episodes in March 1996, in February and December 1999 traced by MTC surface data, promoted large changes in ozone amount between the day of SI and the previous and following days as reported in the daily ozone satellite maps. Up to 80-100 DU more total ozone was recorded during the period of SI (1996) from Dobson at Sestola. This episode is described in detail in a scientific paper on Atmospheric Environment (Bonasoni et. al., 2000).

WP V: Background ozone concentration and summer ozone

In order to describe Mt. Cimone background conditions and to estimate the values of background ozone concentration during the period 1996-1998, an analysis between ozone and three-dimensional backward trajectories (with a maximum duration of 144 hours calculated 8 times each day with the FLEXTRA model), was carried out.

As Mt. Cimone is typically at 790 hPa, to guarantee a sufficiently long period of background conditions, only the back-trajectories that travelled above the 780 hPa level for at least the last two days before reaching the station have been considered. The seasonal cycle of ozone concentration, registered in background conditions and concerning the period 1996 – 1998, is represented in Figure 11. In this way a yearly concentration of 55 ± 7 ppb was obtained. An ozone summer-winter peak-to-peak amplitude of 19 ppb between the 44 ppb winter minimum and the 63 ppb summer maximum was measured. Therefore, the seasonal cycle for the background ozone concentrations presents a well-defined principal maximum in spring and a secondary maximum in summer.

The high values of ozone recorded at Mt. Cimone in spring are related to the Northern-Hemisphere ozone spring maximum. This maximum seems to be due to chemical processes taking place in the upper and middle troposphere with in-situ photochemical production and to stratospheric intrusions that can reach the lower free troposphere. In fact, although the seasonal maximum concentration of ^{7}Be was registered in summer, probably due to strong vertical atmospheric mixing, the more intense stratospheric intrusion episodes appeared at Mt. Cimone in late winter or spring.

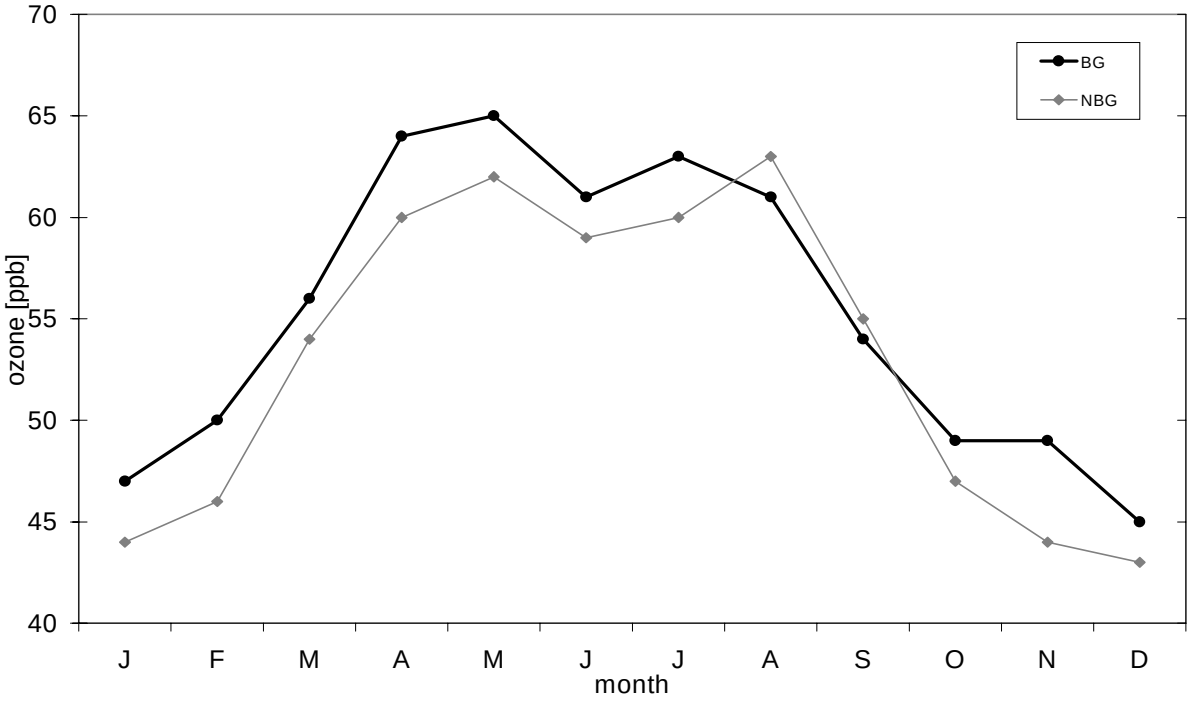

Figure 11: Background (BG) and non-background (NBG) ozone seasonal cycle at the Mt. Cimone station during 1996-1998.

During summer, the characteristic meteorological conditions, in presence of sufficient precursor emissions, can favour regional-scale ozone formation in the boundary layer of northern Italy. During this period, high values of non-background ozone were measured at MTC, as shown in the Figure 11, and their origins are connected with the densely industrialised and inhabited area of the Po Basin, considered the dominant anthropogenic ozone source. In particular, during August and September the ozone concentration in non background conditions exceeded the background ozone concentration, influenced by cleaner air masses coming from the Atlantic Ocean.

3. Deviations from technical annex and reasons

- During short time period, due to particularly adverse weather conditions, the ozone analysers and meteorological sensors suffered from damage that prevented them from operating correctly.
- Due to analyser failure, no carbon monoxide measurements have been available in the period December 1998 to July 1999.

4. Conclusions

The Mt. Cimone measurements planned for the VOTALP II Project regularly started from March 1998 and finished at the end of February 2000. Measurements of ozone, carbon monoxide, Be-7, UVA, UVB and meteorological parameters are available in the VOTALP server's database.

Studies related to these measurements during the Project permitted high levels of ozone concentration recorded at Mt. Cimone to be associated with different mechanisms. Episodes of stratospheric intrusions, mixing of aged stratospheric air masses in troposphere and subsequent transport to the ground level, vertical exchanges between boundary layer and free troposphere have been registered and studied.

In order to quantify the contribution of stratospheric intrusions to Mt. Cimone background ozone concentration, investigation of stratospheric intrusion and its correlation with surface ozone, relative humidity, ^{7}Be and three dimensional backward trajectories has been conducted.

The measurements of trace gases carried out at Mt. Cimone station permitted to determine the seasonal cycle of atmospheric ozone in background conditions. The ozone concentration in the "unperturbed" free troposphere presents an evident maximum in spring and one reduced in summer.

Background ozone latitudinal gradient was present in the Mt. Cimone data. In fact, analysis of ozone and back-trajectories showed that the highest ozone concentrations were related to air masses coming from higher latitudes, while low values were related to air masses coming from the Saharan desert.