PERGAMON

Atmospheric Environment 34 (2000) 1355–1365

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Stratospheric ozone intrusion episodes recorded at Mt. Cimone during the VOTALP project: case studies

P. Bonasoni[a,*], F. Evangelisti[a], U. Bonafe[a], F. Ravegnani[a], F. Calzolari[a], A. Stohl[b], L. Tositti[c], O. Tubertini[c], T. Colombo[d]

[a]*Istituto per lo Studio dei Fenomeni Fisici e Chimici della Alta e Bassa Atmosfera, Consiglio Nazionale delle Ricerche, Via Gobetti 101, I-40129, Bologna, Italy*

[b]*Lehrstuhl fur Bioklimatologie und Immissionsforschung, Ludwig-Maximilians-Universität Munchen, Am Hochanger 13, D-85354 Freising- Weihenstephan, Germany*

[c]*Laboratorio di Radiochimica Ambientale, Dipartimento di Chimica, Università di Bologna, Via Selmi2, I-40126, Bologna, Italy*

[d]*Centro Aeronautico di Montagna, Servizio Meteorologico Aeronautica Militare, Via delle Ville 100, 41029 Sestola (Mo), Italy*

Received 25 January 1999; received in revised form 10 May 1999; accepted 28 May 1999

Abstract

Continuous measurements of ozone concentrations performed at baseline stations on high mountain summits allow stratosphere–troposphere exchange events to be monitored and their variability over small scales to be studied. In this paper we present two characteristic episodes related to lower stratosphere/upper troposphere vertical transport registered at Mt. Cimone during the VOTALP project and we highlight the use of carbon monoxide (CO) and carbon dioxide (CO_2) as non-conventional tracers of lower stratospheric air masses. In this way, stratosphere–troposphere exchange events transporting high ozone concentration into the troposphere have been identified by an accurate analysis of the CO and CO_2 behaviour. Moreover, three-dimensional ensemble trajectories, satellite maps (water vapour and total ozone), ground-based ozone measurements and ozone-soundings have been analysed together with conventional tracers as ^{7}Be and relative humidity as well as the normalised fraction $f(^{7}Be, ^{210}Pb)$ in order to fully characterise the examined events.

Keywords: Surface ozone; Carbon dioxide; Carbon monoxide; Tropopause folding; Cut-off low; Stratospheric tracers

1. Introduction

An increase in surface ozone at all altitudes between sea level and the free troposphere has been measured during the last decades in Europe. In particular, ozone concentrations have increased by almost a factor of two between the 1950s and the 1990s as reported by Low et al. (1990) and Staehelin et al. (1994). This rise is associated with increasing emissions of ozone precursors, which lead to photochemical ozone production in the boundary layer and in the free troposphere. Although only 0.1% of ozone produced in the stratosphere leaks into the troposphere (Crutzen, 1995), the contribution of vertical transport between the lower stratosphere and the troposphere cannot be entirely neglected (Follows and Austin, 1992). Consequently, the stratosphere–troposphere exchange (STE) is a significant process for the budget of ozone in the free troposphere. Nevertheless, STE is worth being investigated for a better knowledge of behaviour of the other trace gases that show different concentrations in the stratosphere and troposphere.

Observations at mountain top baseline stations, e.g. in the Alps or the Apennines, allow STE events to be better studied than by measurements in the flatlands. The STE short-time-scale variability can be studied by continuous measurements of surface ozone and other related atmospheric compounds, together with a systematic monitoring of stratospheric tracers. This approach, supported by climatological model studies (Stohl et al., 1999), allows

* Corresponding author.

1352-2310/00/$ - see front matter
PII: S1352-2310(99)00280-0

the contribution of stratospheric ozone that directly or indirectly reaches the lower troposphere to be revealed. This is one of the topics of the EC project "Vertical Ozone Transports in the Alps" (VOTALP), combining models of various complexities with baseline measurements undertaken at selected mountain peaks: Jungfraujoch, Sonnblick, Zugspitze and Mt. Cimone. In contrast to the other stations situated in the Alps, Mt. Cimone (MTC) lies in the Northern Apennines. It is involved in continuous baseline measurements of ozone, carbon monoxide, carbon dioxide (by the Italian Air Force Meteorological Service), radioactive cosmogenic and natural compounds. At this station, during the VOTALP project, we identified 26 events of high ozone levels associated with lower stratosphere/upper troposphere vertical transports within a period of 2 years. This value agrees with those reported by Reiter (1991) (1–2 days per month) and Elbern et al. (1997) (195 cases over a 10 year period) at the Zugspitze summit (2962 m a.s.l.) in the Northern Alps. Some of the episodes recorded at MTC have been revealed as tropopause foldings and cut-off lows, which are the most important STE processes, normally described through conventional meteorological (relative humidity), chemical (ozone), radiochemical (^{7}Be) and dynamical (potential vorticity) tracers. Less frequently the study of STE is based on the analysis of non-conventional tracers, as carbon monoxide and carbon dioxide, which can help to identify stratospheric intrusion events when some conventional tracers present ambiguous behaviour. Evidence for STE related to intense deformation of the tropopause (Ancellet et al., 1994) during cut-off low or tropopause folding events can also be obtained from satellite total ozone maps (TOMS, TOVS, SBUV-2, GOME), where a local ozone maximum can be observed, separated from the surroundings by very steep gradients in total ozone, typically 100 DU/500 km (WMO, 1985). Ground-based Dobson, Brewer and UV–Vis spectrometer measurements and ozone-soundings provide further information about the total ozone amount and its vertical profile during stratospheric ozone intrusion episodes.

In this paper we discuss two episodes of elevated surface ozone concentrations observed at Mt. Cimone in 1996, which were attributed to cut-off low and tropopause folding. In the first episode (cut-off low), characterised by unusual high relative humidity values, the analysis was accomplished by using the behaviour of the non-conventional tracer CO, as well as water vapour map, ozone profiles, total ozone maps and Dobson measurements. Dynamical and thermodynamical tracers, probably as a consequence of their low temporal resolution, have not yet supported this episode which, on the contrary, was unambiguously detected by the CO and O_3 chemical tracers. In the tropopause folding episode, well identified by conventional tracers (O_3, RH, ^{7}Be) we realised that CO_2 concentrations were useful to characterise an air mass coming from the stratosphere. In fact, during the warm season the registered steady concentration of this non-conventional tracer, higher than its normal tropospheric value, is typical of an air mass, which originated in the lower stratosphere where sources or sinks of carbon dioxide are not present.

2. Experimental

Mt. Cimone (44°12′ N, 10°42′ E) is the highest peak of the Northern Apennines (2165 m a.s.l.) that divide the north of Italy, including the Po Valley, from central Italy and the Mediterranean basin. Besides having a 360° free horizon, MTC has an elevation such that the measurement station lies above the planetary boundary layer during most of the year. Moreover, MTC can be affected by intense cyclogenetic activity often originating in the near Gulf of Genoa area (Buzzi et al., 1984; Davies and Schuepbach, 1994). The site is considered the most representative WMO-GAW weather station in Italy (WMO, 1994) and recently the ozone monitoring program actively contributes to the new World Data Centre for Surface Ozone (WDCSO3). Details of the site description were reported in a previous paper (Bonasoni et al., 1997).

The MTC laboratory operates automatically, the measured parameters being averaged on a 1-min basis and transmitted daily to the FISBAT-CNR Institute in Bologna. The intake line of sample air is 2 m above the roof and 10 m above the ground and consists of a glass tube through which the sampled air is passed at a constant flow rate. Those parts of the system that are outside the building are heated to prevent ice formation during the cold season. Inside the building the analysers draw their sample air via a manifold pipe fitted to a glass tube. An overvoltage and lightning protection system is used to prevent damage to the instrumentation and to ensure the continuity of the measurements.

Surface ozone concentration measurements are carried out by using two UV-photometric analysers (Dasibi 1108 W/GEN and Dasibi 1003) operating simultaneously, which are calibrated six times a year by an ozone calibrator (Dasibi 1108 PC). Zero and span checks are automatically performed every 24 h, while the accuracy and precision are ± 2 ppb. The CO analyser is made up of an assembled gas chromatographic system coupled to a reduction gas detector and is automated through a computer controlling the whole system by means of two interfaces. Its accuracy and precision is approximately ± 2 ppb. The air intake is 1 m above the roof and 10 m above the ground. CO data have a bi-hourly frequency following previous practice (Corazza and Tesi, 1995), while details of the CO experimental set-up are reported in Bonasoni et al. (1997). The CO_2 measurement system has been operating continuously since March 1979 (Colombo et al., 1994) and the accuracy and precision are

$\pm$0.1 ppm. The air sample intake is 15 m above the ground and carbon dioxide values are determined in a dry air by a NDIR-analyser, calibrated every 6 h and controlled by a computer in which the data are stored every 10 min.

^{7}Be and ^{210}Pb are determined at 477.6 and 46.7 keV, respectively, by direct γ-spectrometry of aerosol samples, collected by a PM-10 High Volume Sampler (Thermo Environmental Instruments Inc. – Flow rate = 1.13 m^3 min^{-1}) on glass fibre filters, using a *n*-type intrinsic Hyper Pure Ge detector (relative efficiency = 38%; full-width at half-maximum = 2.03 at 1332 keV). Spectra are processed with a specific software package (Silgamma – EMCA II). The time resolution of each sample is 48 h and the sampled volume amounts to approximately 3250 m^3. The samples are conditioned at a constant temperature (20°C) and relative humidity (30%) in order to determine the aerosol mass loading.

3. Ozone and vertical exchange

The MTC surface ozone concentrations usually exhibit a minimum in the winter, a principal maximum in the summer and a secondary maximum in the spring as often observed at background monitoring sites (Beekmann et al., 1994; Scheel et al., 1997). During most part of the year no evident diurnal variation in surface ozone is present at MTC, except during the warm season when a reverse diurnal variation of ozone occurs. This reverse diurnal variation, as reported from other baseline mountain stations (Oltmans, 1981; Aneja et al., 1991), is characterised by ozone values around midday being lower than nighttime values (Colombo et al., 1992) and are associated with a mountain wind regime (anabatic wind during the day, katabatic wind during the night). The statistical analysis of ozone hourly mean values performed on the 1996–1997 summer data shows that the difference between the night and day values is about 5 ppbv.

Stratospheric ozone intrusion events at Mt. Cimone have been identified both by meteorological analyses, measurements of chemical (O_3, CO and CO_2), meteorological (relative humidity) and cosmogenic (^{7}Be) parameters and by studying Three Dimensional Back Trajectory (3DBT) and potential vorticity. In particular, high concentrations of ^{7}Be are indicative for stratospheric intrusions. For instance, Reiter et al. (1983) suggested a threshold value of 8 mBq/m^3, above which an air mass probably has stratospheric characteristics. It is important to note that the effective lifetime of the ^{7}Be in the troposphere is determined by the physical lifetime of the carrier aerosol versus its radioactive lifetime. This has the implication that wet scavenging can affect the role of ^{7}Be as a stratospheric tracer under certain weather conditions. For this reason, in an attempt to obtain clearer information about the stratospheric origin of the air mass, we considered the normalised fraction f (^{7}Be, ^{210}Pb) = (^{7}Be)/(^{7}Be + n^{210}Pb), where n is approximated by the ratio of the standard deviation of (^{7}Be) to the standard deviation of (^{210}Pb) in the sample set, as suggested by Graustein and Turekian (1996). This expression, based on the use of independent radionuclides with the same fate in the atmosphere, represents the relative variation of cosmogenic ^{7}Be to crustal ^{210}Pb. Thus, the normalised fraction f (^{7}Be, ^{210}Pb) is not affected by wet scavenging, assuming that both ^{7}Be and ^{210}Pb are scavenged at a similar rate. High values of f (^{7}Be, ^{210}Pb), in the 0–1 range, are associated with upper atmosphere air masses, low values with boundary layer air masses (Graustein and Turekian, 1996).

Cosmogenic ^{7}Be ($t_{0.5}$ = 53.3 d) is produced throughout the atmosphere by spallation reactions of cosmic rays with maximum production rate in the stratosphere at about 15–18 km (Lal and Peters, 1967). From this level its equilibrium concentration decreases steadily towards earth's surface. ^{210}Pb ($t_{0.5}$ = 22.3 yr) is a relatively long-lived descendant of the noble gas ^{222}Rn ($t_{0.5}$ = 3.8 d) emitted by all the crustal materials. Therefore, ^{7}Be is considered the most representative aerosol radioactive stratospheric tracer and ^{210}Pb is an excellent boundary layer aerosol tracer (Koch et al., 1996). Since 1996, 112 ^{7}Be and ^{210}Pb measurements have been carried out at Mt. Cimone. Among these, 28 values of ^{7}Be exceeded the threshold value of 8 mBq m^{-3}: the maximum ^{7}Be value of 23.6 mBq m^{-3}, ^{210}Pb = 0.3 mBq m^{-3}, f (^{7}Be, ^{210}Pb) = 0.98 were recorded on 8 July 1997.

The intrusion events recorded at a mountain peak as Mt. Cimone are sometimes difficult to detect, because air masses of stratospheric origin can reach the measurement site after experiencing dilution, dispersion or removal processes, which could have modified their physical–chemical characteristics while travelling through the troposphere. In these cases ozone concentrations may exhibit significant variations. With the aim of identifying whether high ozone levels recorded indicate a high-altitude origin of the air mass, correlation analyses of MTC ozone concentrations with stratospheric and boundary layer tracers were carried out (Bonasoni et al., 1998).

4. Vertical transport: case studies

4.1. 12 March 1996

During 11–12 March 1996, a cut-off low event developed over central Europe. The meteorological situation was characterised by a Russian–Siberian anticyclone located northeast of Scandinavia, developing on 11 March and strengthening on 12 March, that favoured the development of a blocking system with a low-pressure area over central Europe, northeast of Italy. The

low-pressure system was present on 12 March at all the isobaric levels from the surface up to 100 hPa. Particularly, at 300 hPa (Fig. 1) the wind intensity reached 210 km h^{-1} on the southwestern side of the closed configuration, where the maximum values of vorticity were present. Under these conditions, a slanting stratospheric air mass can penetrate into the troposphere (Davies and Schuepbach, 1994; Holton et al., 1995) and may be revealed by a dry band in the satellite water vapour map. Such a dry dark slot extending from Northern Europe to north-central Italy is visible in the Meteosat-5 water vapour image on 12 March (Fig. 2). On the same day, low humidity values between 450 and 750 hPa were recorded by the 12:00 UTC radiosonde started at Milano-Linate (45.6 N, 9.2 E, 103 m a.s.l.) and, more strongly, by the Udine radiosonde (46.0 N, 13.1 E, 94 m a.s.l.), indicating the descent of air masses with stratospheric characteristics. The presence of a dry layer was also detected in the ozone-sounding performed at midnight on 12 March (Fig. 3) at S. Pietro Capofiume (WODC station n.297 in the Po valley), following the MTC ozone alert. The relative humidity profile features a very dry layer between 700 and 300 hPa, while the temperature is considerably lower than on 13 March, when a second ozone sounding was carried out at noon (Fig. 3).

In a deep trough the tropopause may descend to very low levels, leading to an increase of the ozone vertical column amount (Vaughan and Price, 1989). This is shown by WMO daily ozone maps, Dobson–Brewer station measurements and SBUV-2 satellite data, as reported in Fig. 4, showing the large change in ozone amount between 11–12 March and the previous and following days. This has been confirmed also by the values of the daily ground-based vertical ozone column at Sestola (44.2 N, 10.8 E, 1030 m. a.s.l., near Mt. Cimone), Hohenpeissenberg (47.8 N, 11.0 E, 975 m a.s.l.) and Sonnblick (47.05 N, 12.96 E, 3106 m a.s.l.) stations. In comparison with the ozone values measured on the previous and following days (345–370 DU), up to 90–100 DU more total ozone was recorded on 11 March (444 DU at Sestola, 446 DU at Hohenpeissenberg, 441 DU at Sonnblick) and on 12 March (466 DU at

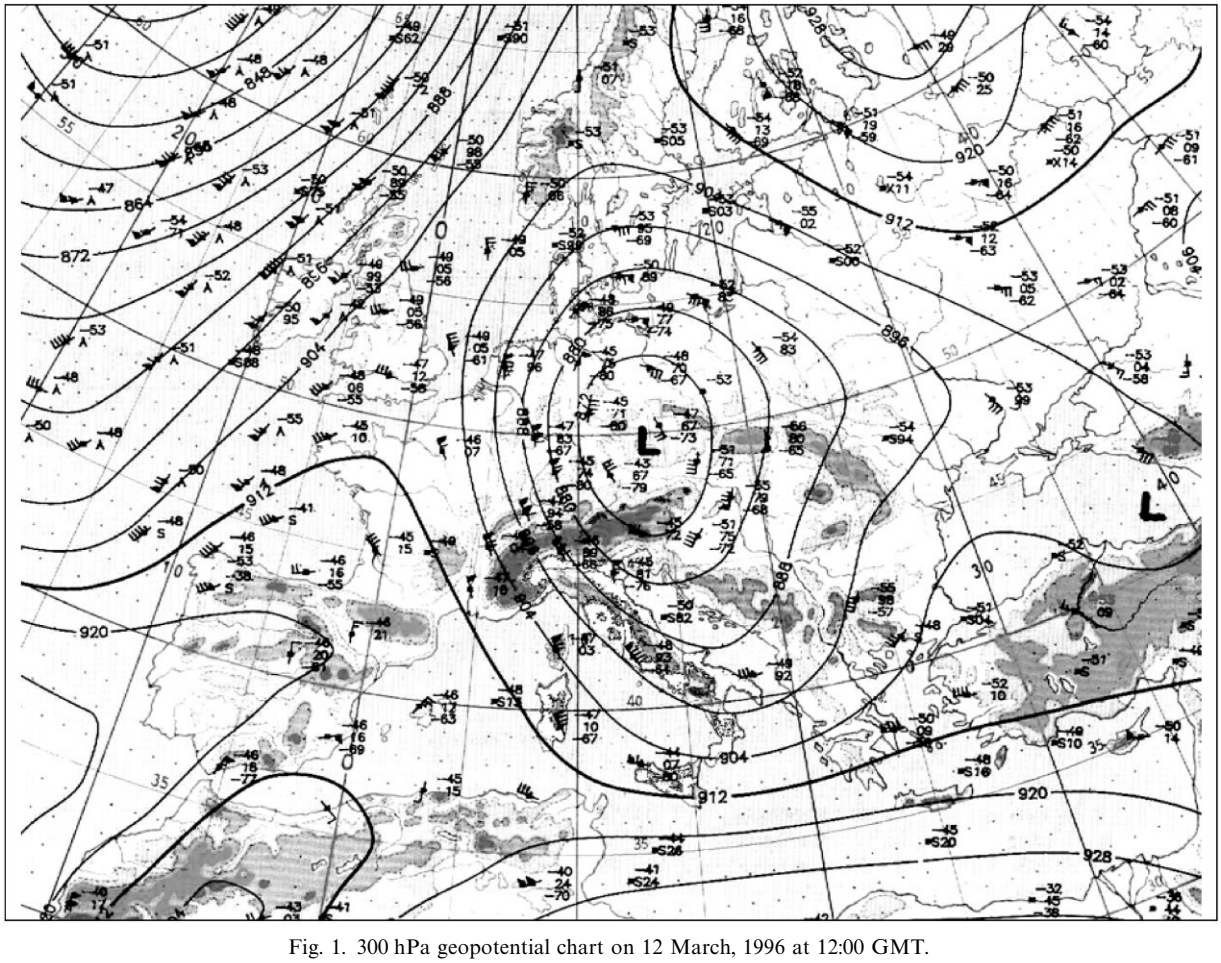

Fig. 1. 300 hPa geopotential chart on 12 March, 1996 at 12:00 GMT.

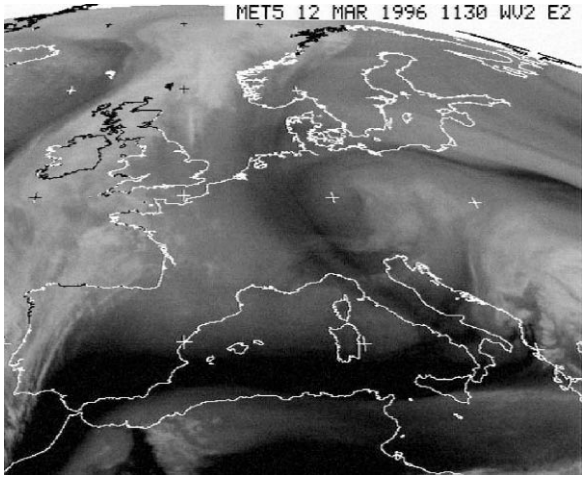

Fig. 2. METEOSAT water vapour map on 12 March, 1996 at 11:30 GMT.

Hohenpeissenberg, 461 DU at Sonnblick, no data for Sestola). Furthermore, a steep ozone gradient of 93 DU/230 km between Sestola and Roma University and of 65 DU/150 km between Sestola and Ispra J.R.C. were recorded on 11 March, confirming that the Sestola-Mt. Cimone area was localised on the southwest boundary of the low.

On 12 March we registered very high levels of O_3 concentration on the MTC summit during a short period as reported in Fig. 5. The hourly mean ozone peak of about 110 ppbv, compared to an ozone monthly mean value of 57 ppbv, occurred around midday simultaneously with a large distinct decrease of the CO concentrations down to values of about 76 ppbv compared to a CO monthly mean of 173 ppbv. Relative humidity values lower than 20% were recorded until 6 h before the event, while during this event relative humidity stayed around 85%. In fact, the weather conditions observed at Mt. Cimone by the Italian Meteorological Service (station id. LIVC) on 12 March reported no hour of insolation, fog and light snow from the morning. On the contrary, the day before a clear and sunny sky was observed. The 3DBT, calculated with the FLEXTRA model (Stohl et al., 1995) at 12:00 on 12 March, shows that the origin of the air mass is situated at 600 hPa over central Europe, while 36 h before the air mass was travelling at quite low levels over the northwest of Italy and was likely to transport air mixed in the lower troposphere over Mt. Cimone. Nevertheless, the concentration of ozone precursors and the ozone concentration values

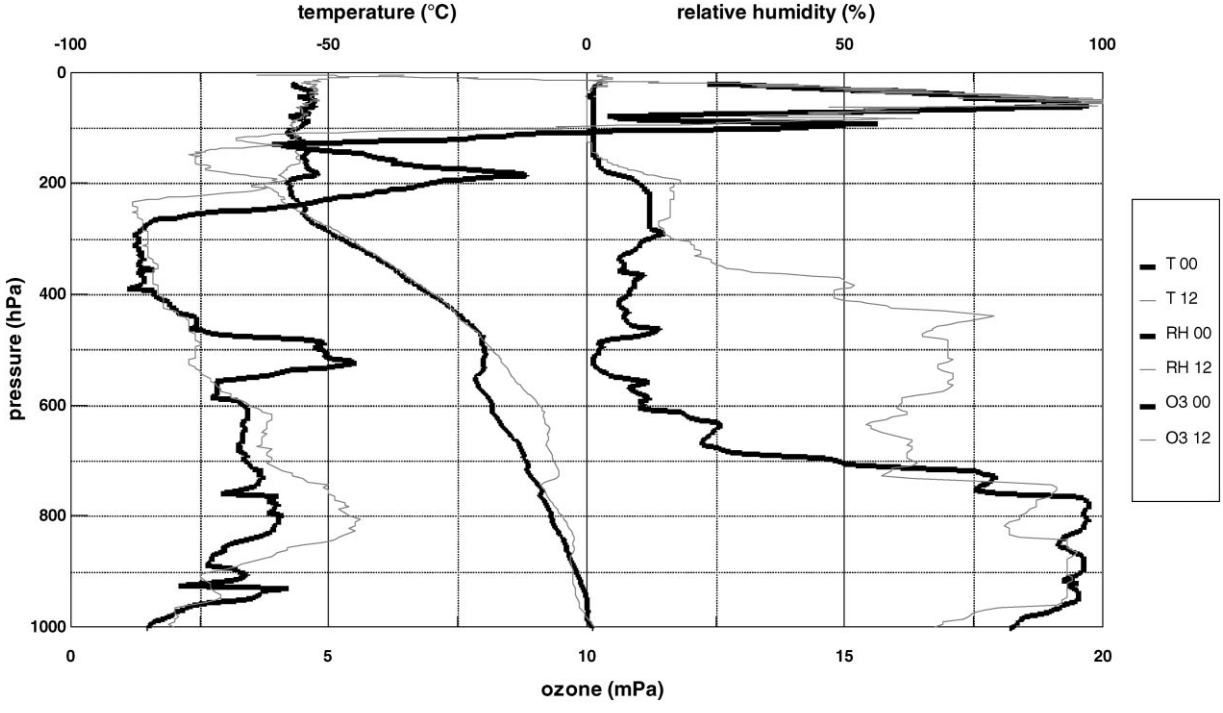

Fig. 3. Ozone-soundings at S. Pietro Capofiume on 12 March, 1996 at midnight (dark thick line) and on 13 March, 1996 at noon (grey thin line). Ozone, temperature and relative humidity profiles are shown: ozone concentration (mPa) on the bottom x-axis, temperature (°C) on the top-left x-axis, relative humidity (%) on the top-right x-axis.

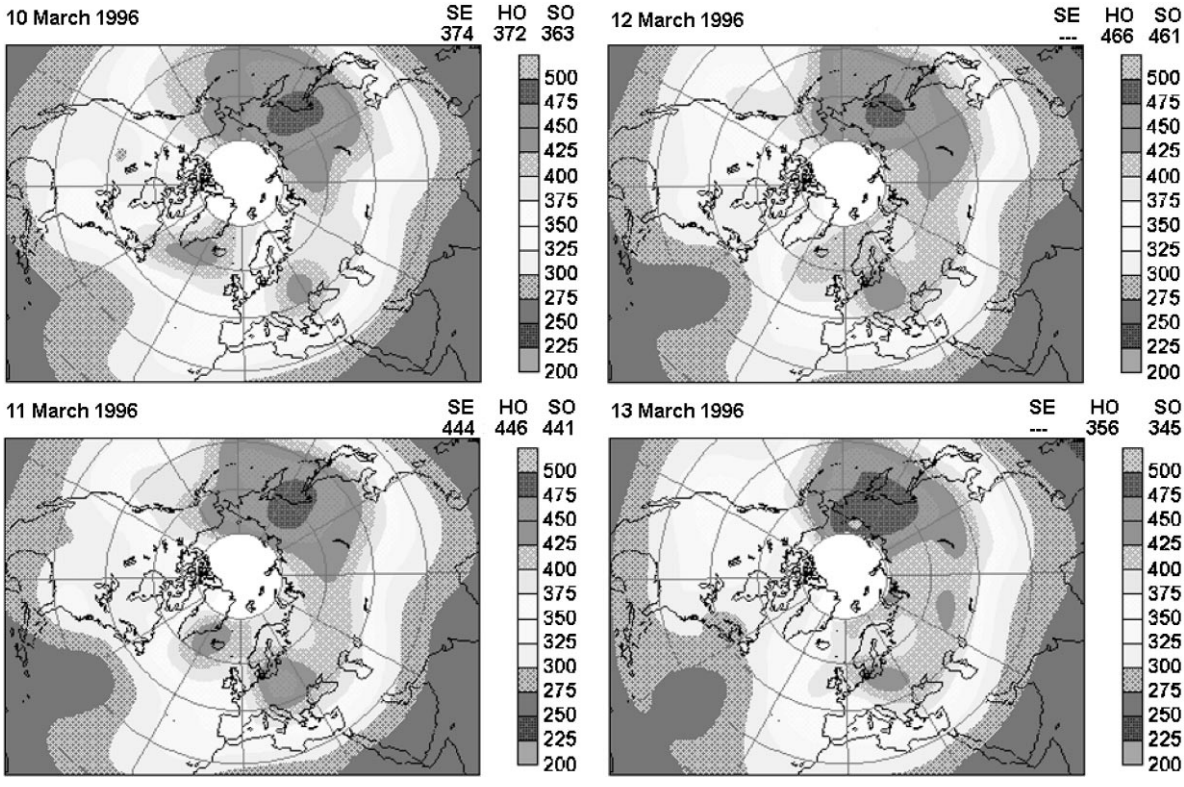

Fig. 4. WMO Daily Total Ozone Maps (10 March–13 March, 1996). The label grey scale bar at the right indicates the total column ozone values in Dobson Units (DU). On the top-right corner the values measured at Sestola (SE), Hohenpeissenberg (HO) and Sonnblick (SO) are shown in DU. The maps are obtained from WMO Northern Hemisphere Daily Ozone Mapping Centre operated by the Laboratory of Atmospheric Physics at the University of Thessaloniki (Greece).

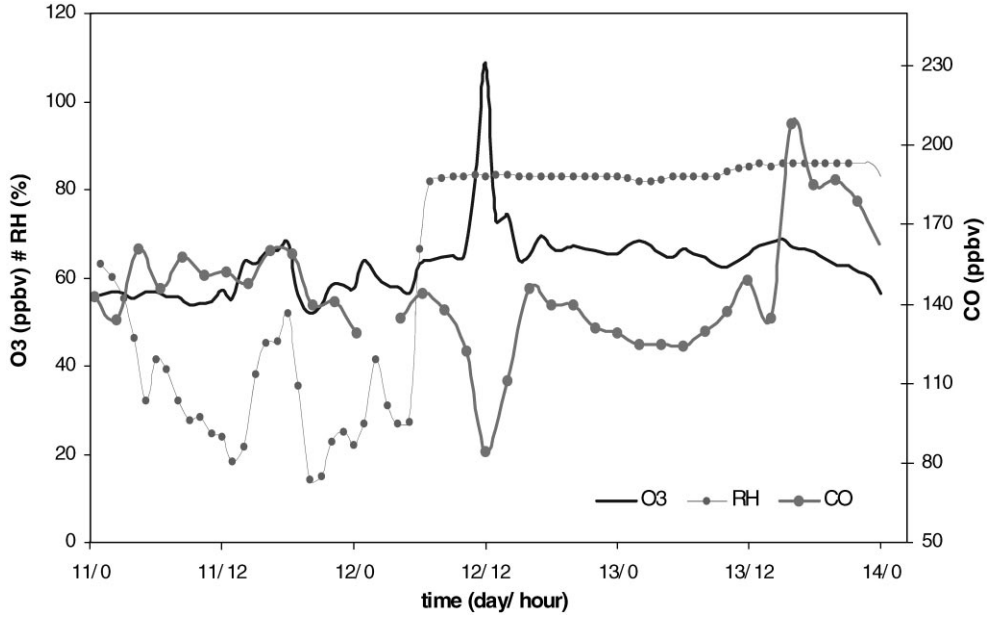

Fig. 5. Ozone (O_3), carbon monoxide (CO) and relative humidity (RH) behaviour on 11–13 March 1996 at Mt. Cimone.

recorded in the surface layer in Northern Italy during the considered period were very low, as shown by the mean values of surface ozone (20 ppbv) measured in the Po valley. This prevents the association of the high ozone level recorded at Mt. Cimone with anthropogenic origin of ozone transported from the Po valley up to the measurement site. Moreover, both high ozone and low CO values seem to indicate that the air mass was characterised by an upper atmospheric component.

In the ozone vertical profile at S. Pietro Capofiume at midnight on 12 March (Fig. 3) three distinct layers with high ozone concentration can be seen: the first at about 55 hPa, the second, above the tropopause, at 180 hPa, and the third, the lowest, at about 500 hPa. In this last layer, an ozone bulge with ozone partial pressure of 5.5 mPa was found between 490 and 550 hPa. In the second vertical ozone profile, 12 h later, such a clear and marked stratification was almost totally absent, though a wide bulge of high ozone concentration with the same partial pressure is still present in the lower troposphere characterised by moist air masses. These ozone soundings show that 12 h after the recording of the event at

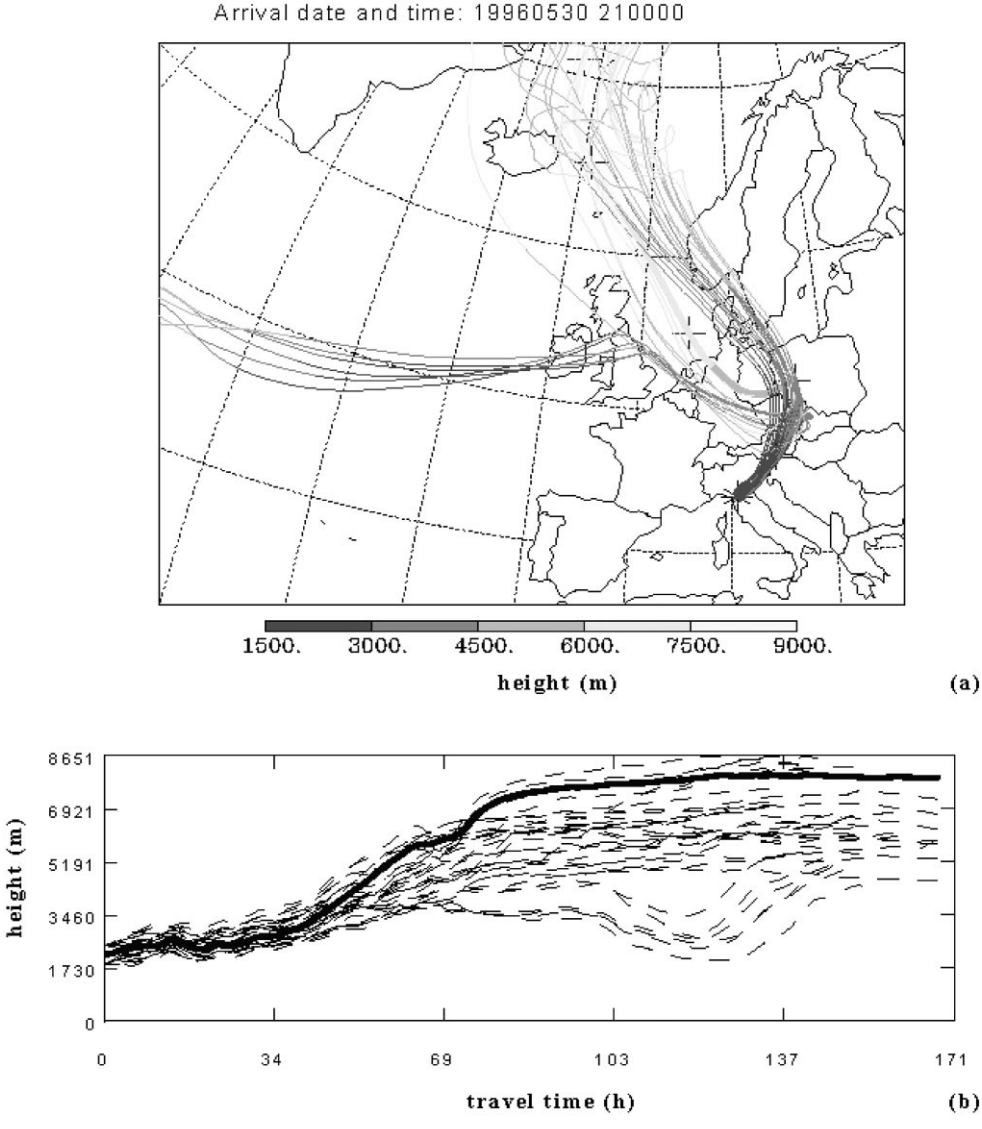

Fig. 6. (a) Three-dimensional back trajectory ensemble arriving at Mt. Cimone on 30 May, 1996 at 21:00 GMT. The highest trajectory originated from North above 7500 m a.s.l. The 3DBT ensemble consists of 33 trajectories, starting at the altitude of Mt. Cimone and at 300 m below and above, and in a circle of approximately 50 km around Mt. Cimone. (b) Vertical displacement of air parcels arriving at Mt. Cimone on 30 May, 1996, at 21:00 GMT. The reference trajectory starting exactly at the location of Mt. Cimone is drawn in bold.

Mt. Cimone, the air masses in the free troposphere still had characteristics typical of the lower stratosphere, confirming that dry air masses with high ozone concentrations slanted down from high layers and reached relatively low altitudes.

From the data analysis we can state that a modification of the tropopause over the Northern Apennines occurred on 11 March, when the ozone total column increased by 70 DU compared to the day before at Sestola, and stratospheric air reached the mid-troposphere. The following day (12 March) this air, instead of descending directly to the ground, penetrated towards lower altitudes and reached the MTC summit after mixing with lower tropospheric moist air. In spite of this moisture condition, the distinct ozone concentration spike and low CO recorded values are a clear indication that a vertical transport of stratospheric air masses occurred at the mountain site.

4.2. 30–31 May 1996

The episode of tropopause folding, which occurred in Central Europe at the end of May 1996 has been thoroughly studied within the VOTALP project and is discussed in detail by Stohl et al. (1999). Our presentation of this episode provides a further contribution to this discussion. In fact, not only the behaviour of conventional stratospheric tracers (O_3, ^{7}Be and RH) will be considered, but also in particular the atmospheric CO_2 response will be introduced as a tracer of upper tropospheric/lower stratospheric origin of the air masses. CO_2 is usually monitored because of its greenhouse effect upon the earth's climate. However, in the analysis of this event we present CO_2 as an interesting tracer of atmospheric vertical exchange, owing to the differences between the stratospheric and tropospheric CO_2 concentrations at northern mid latitudes (Strahan et al., 1998; Huntrieser et al., 1998).

The tropopause folding event detected at the end of May 1996 extended from Scandinavia over the Balkan region to Crete and reached a minimum height of about 600 hPa. The anticyclonic subsidence in the western part of the folding transported ozone-rich air downwards, which intruded into the middle troposphere, spreading over the Alps and the Northern Apennines. The air masses which reached Mt. Cimone on 30 May and 31 had crossed the tropopause folding area over central Europe on 29 May and passed over the north-east of Italy at an altitude of about 3000 m, as confirmed by the three-dimensional back trajectory ensemble analysis (Fig. 6a and b).

At Mt. Cimone, during the morning of 30 May, the CO_2 concentration, instead of showing a decrease due to the onset of photosynthetic activity of the vegetation when a mountain breeze regime is present, typical for this time of day during this season, shows an anomalous increase of about 7 ppmv beginning at 6:00 (Fig. 7a), associated with a simultaneous ozone increase of about 10 ppbv (Fig. 7b). Remarkably, during this event carbon dioxide concentrations remained at a constant high level for 4 h (Fig. 7a). This was caused by the air masses coming from high altitudes with concentration values typical of the upper troposphere, which are similar to those of a non-vegetated and unpolluted area. However, during the daylight hours the air coming from the forested valley below with the up-slope winds is normally poor in CO_2 concentration. The CO_2 increase is concomitant with an increase of temperature, pressure (Fig. 7c) and ozone (Fig. 7b), with a strong reduction of relative humidity (Fig. 7a) and is proceeded by a strong (up to 25 m s^{-1}) easterly wind speed (Fig. 7d). Subsequently, a reduction in wind speed restored the up-slope wind system and CO_2-poor air masses from the valley below reached the measurement site. Starting from the evening of 30 May, when the up-slope wind system collapsed, very dry air masses were transported from the N–NE direction to Mt. Cimone for a period of more than 12 h. They were characterised by ozone concentrations of up to 100 ppbv in the morning of 31 May (Fig. 7b). During this period, the relative humidity strongly decreased to around 0% and almost constant values of CO concentration were recorded. Moreover, the air masses were characterised by unusually constant and high CO_2 concentration, 367.0 ppmv, in comparison with the monthly mean of 364.6 ppmv (Fig. 7a). This emphasises that the transport from the upper troposphere/lower stratosphere, where neither a CO_2 source nor a CO_2 sink is present, is similar to that from a barren area.

During this event, ^{7}Be values of 14.8 (on 30 May) and of 12.7 mBq m^{-3} (31 May) were detected, both indicating a stratospheric source on the basis of the 8 mBq m^{-3} threshold suggested by Reiter et al. (1983). The analysis of the normalised fraction f (^{7}Be, ^{210}Pb) values, calculated for 30 May (0.77) and 31 May (0.61), underlines the major stratospheric character of the air mass reaching MTC on 30 May, compared to that of the following day, when a major contribution of mixing with lower tropospheric air is already present.

5. Conclusions

The different chemical composition of tropospheric and stratospheric air parcels often permits the identification of air masses with a different origin. A stratospheric air mass can reach a location in the lower troposphere either via direct descent or, alternatively, by descent followed by horizontal transport. In this second case, due to the longer time periods involved, considerable mixing with tropospheric air may occur. Stratospheric air mass intrusions rarely reach the ground without experiencing significant dilution with tropospheric air, which usually

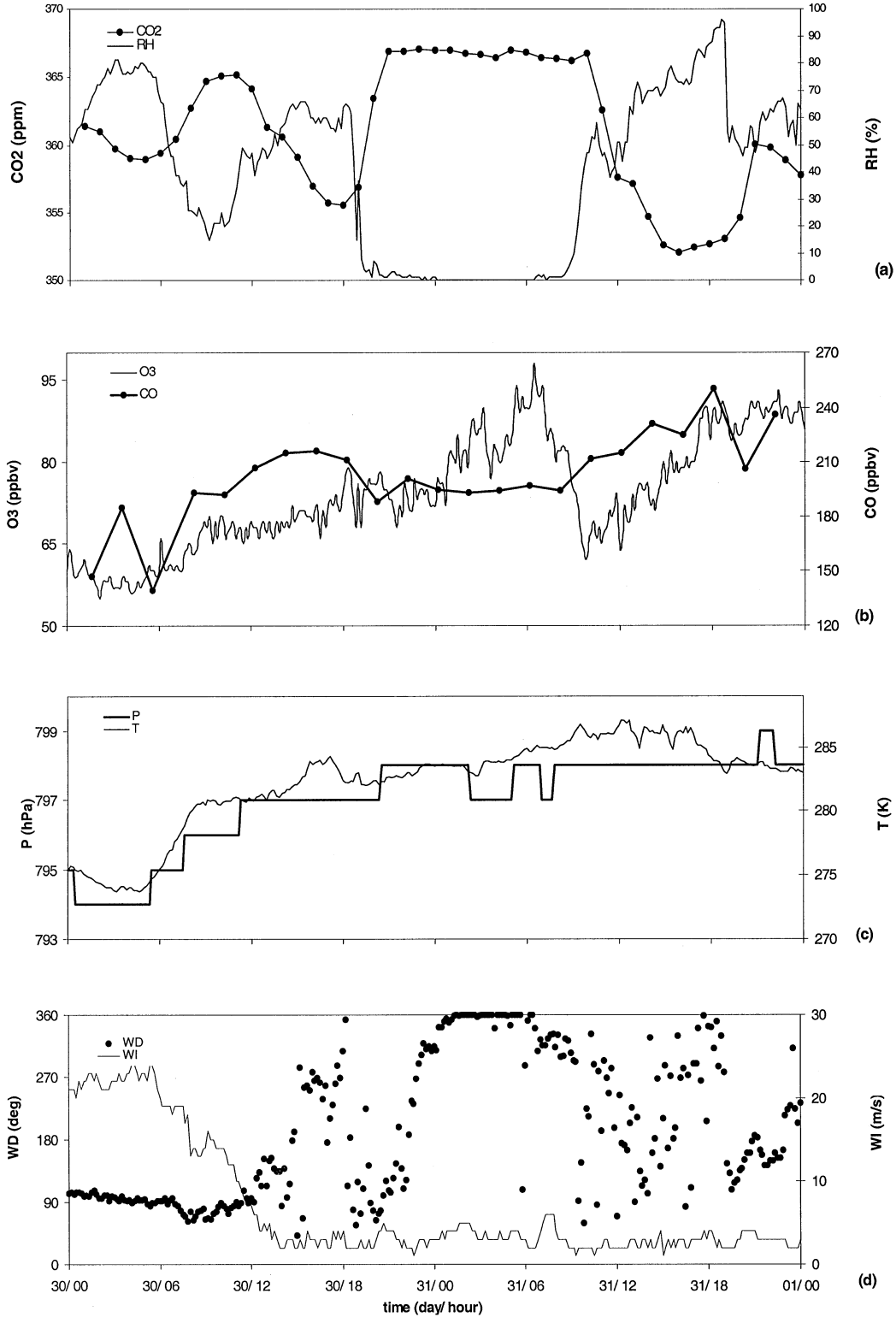

Fig. 7. Mt. Cimone measurements from 30 May to 1 June, 1996: a – Carbon dioxide (CO_2) and relative humidity (RH); b – Ozone (O_3) and carbon monoxide (CO), c – Pressure (P) and temperature (T), d – Wind direction (WD) and wind speed (WI). Time is expressed on the *x*-axis as day/hour.

prevents the stratospheric air mass to be detected with confidence. Thus, only continuous measurements of meteorological, chemical and radiochemical stratospheric compounds performed at high mountain peak stations permit to suitably study stratosphere–troposphere exchange events.

The stratospheric chemical compounds considered as tracers of air mass intrusion are characterised by high stratospheric–tropospheric gradient in their concentration or composition. In this way, ozone, ^{7}Be and relative humidity are considered conventional tracers of stratospheric intrusions. However, in some cases, when the origin of the stratospheric air mass is not clearly traced by these conventional parameters, this approach may be inadequate to identify and study vertical transport of air masses from upper levels. In these cases carbon dioxide and carbon monoxide non-conventional tracers can provide an important contribution to reveal the origin of the air mass. In fact, as the CO concentration decreases with altitude, the very low values registered during the first episode presented in this paper clearly indicated the origin of a stratospheric air mass, which reached Mt. Cimone. During the second episodes the CO_2 seasonal concentration and its typical daily tropospheric variation were modified by an air mass with high concentration and steady behaviour of CO_2 characteristic of a stratospheric origin. These stratospheric intrusion processes depend on the degree of dilution of the air mass and its lower troposphere mixing. In order to highlight the stratospheric character of this air mass the normalised fraction $f(^{7}Be, ^{210}PB)$ has also been taken into consideration.

In this paper we have presented two episodes of stratospheric intrusions that occurred at Mt. Cimone during the VOTALP project and revealed using CO and CO_2 as non-conventional tracers together with conventional tracers (O_3, RH, ^{7}Be), water vapour satellite maps and three-dimensional backward trajectory analysis. Ozone satellite observations and ground-based ozone vertical column measurements have been also useful tools to emphasise the localised ozone maximum trapped in the intense deformation of the tropopause during stratospheric intrusion events.

Acknowledgements

Authors thank WMO Northern Hemisphere Daily Ozone Mapping Centre operated by the Laboratory of Atmospheric Physics at the University of Thessaloniki (Greece) for the ozone maps; ECMWF for the meteorological synoptic map, Atmospheric Environment Service – World Ozone Data Centre and all those who operated the Dobson–Brewer WMO ozone stations mentioned in this paper. Authors are also grateful to two anonymous reviewers for constructive comments and useful suggestions on this manuscript.

This study was part of VOTALP, funded by the European Commission under Framework Programme IV, Environment and Climate, Contract No. ENV4-CT95-0025, and by the government of Switzerland.

References

Ancellet, G., Beekmann, M., Papayannis, A., 1994. Impact of a cutoff low development on downward transport of ozone in the troposphere. Journal of Geophysical Research 93 (D2), 3451–3468.

Aneja, V.P., Businger, S., Zheng, Li, Claiborn, C.S., Murthy, A., 1991. Ozone climatology at high elevations in the southern Appalachians. Journal of Geophysical Research 96(D1), 1007–1021.

Beekmann, M., Ancellet, G., Mancier, C., 1994. Tropospheric ozone monitoring at the Observatoire de Haute Provence. In: Borrell, P.M., Borrel, P., Cvitas, T., Seiler, W. (Eds.), Proceedings of EUROTRAC Symposium. pp. 367–372.

Bonasoni, P., Calzolari, F., Colombo, T., Corazza, E., Santaguida, R., Tesi, G., 1997. Continuous CO and H2 measurements at Mt. Cimone (Italy): preliminary results. Atmospheric Environment 31, 959–967.

Bonasoni, P., Tositti, L., Evangelisti F., Sthol, A., Bonafè, U., Calzolari, F., Colombo, T., Kromp-Kolb, H., Tubertini, O., 1998. Influence of horizontal and vertical transport of air masses on the background ozone concentration at Mt.Cimone station. 25th International Conference on Alpine Meteorology, Torino 14–19 September. Booklet of Proceedings, pp. 240–245.

Buzzi, A., Giovannelli, G., Nanni, T., Tagliazucca, M., 1984. Study of high ozone concentrations in the troposphere associated with lee cyclogenesis during ALPEX. Beiträge zur Physik der Atmosphäre 57, 380–392.

Colombo, T., Cundari, V., Bonasoni, P., Cervino, M., Evangelisti, F., Georgiadis, T., Giovanelli, G., 1992. Episodes of vertical and horizontal ozone transport monitored at Italy's Mt. Cimone Observatory. Proceedings of Quadriennial Ozone Symposium Charlottesville, VA, USA, NASA Conference Publication 3266.

Colombo, T., Santaguida, R., 1994. Atmospheric CO_2 record from in situ measurement at Mt.Cimone. In: Boden, T.A., Kaiser, D.P., Sepanski, R.J., Stoss, F.W. (Eds.), Trends '93: A Compendium of Data on Global Change. ORNL/CDIAC-65. Carbon Dioxide Information Analysis Center. Oak Ridge National Laboratory, Oak Ridge, TE, USA, pp. 169–172.

Corazza, E., Tesi, G., 1995. Tropospheric hydrogen and carbon monoxide in Antarctica and in Greenland. Science of the Total Environment 160/161, 803–809.

Crutzen, P.J., 1995. Ozone in the troposphere. Composition, Chemistry and Climate of the Atmosphere. In: Singh, H.B. (Ed.), Van Nostrand Reinhold, New York, pp. 349–393.

Davies, T.D., Schuepbach, E., 1994. Episodes of high ozone concentrations at the earth's surface resulting from transport down from the upper troposphere/lower stratosphere: a review and case studies. Atmospheric Environment 28, 53–68.

Elbern, H., Kowol, R., Sladkovic, R., Ebel, A., 1997. Deep stratospheric intrusions: a statistical assessment with model guided analyses. Atmospheric Environment 31, 3207–3226.

Follows, M.J., Austin, J.F., 1992. A zonal average model of the stratospheric contributions to the tropospheric ozone budget. Journal of Geophysical Research 97 (D16), 18047–18060.

Graustein, W.C., Turekian, K.K., 1996. ^{7}Be and ^{210}Pb indicate an upper troposphere source for elevated ozone in the summertime subtropical free troposphere of the eastern North Atlantic. Geophysical Research Letters 23 (5), 539–542.

Holton, J.R., Haynes, P.H., McIntyre, M.E., Douglass, A.R., Rood, R.B., Pfister, L., 1995. Stratosphere–troposphere exchange. Reviews of Geophysics 33, 403–439.

Huntrieser, H., Schlager, H., Feigl, Holler, H., 1998. Transport and production of NO_x in electrified thunderstorms: survey of previous studies and new observatios at midlatitudes. Journal of Geophysical Research 103, 28247–28264.

Koch, D.M., Jacob, D.J., Graustein, W.C., 1996. Vertical transport of tropospheric aerosol as indicated by ^{7}Be and ^{210}Pb in a chemical tracer model. Journal of Geophysical Research 101 (D13), 18651–18666.

Lal, D., Peters, B., 1967. Cosmic rays produced radioactivity on the earth. Encyclopaedia of Physics. Springer, New York.

Low, P.S., Davies, T.D., Kelly, P.M., Farmer, G., 1990. Trends in surface ozone at Hohenpeissenberg and Arkona. Journal of Geophysical Research 95 (D13), 22441–22453.

Oltmans, S.J., 1981. Surface ozone measurements in clean air. Journal of Geophysical Research 86 (C2), 1174–1180.

Reiter, R., 1991. On the mean daily and seasonal variations of the vertical ozone profiles in the lower troposphere. Atmospheric Environment 25A, 1751–1757.

Reiter, R., Munzert, K., Kanter, H.J., Poetzl, K., 1983. Cosmogenic radionuclides and ozone at a mountain station at 3.0 km a.s.l. Archive Meteriology Geophysik and Bioclamatologic 32B, 131–160.

Scheel, H.E., Ancellet, G., Areskoung, H. Beck, J. et al., 1997. Spatial and temporal variability of tropospheric ozone over Europe. In: Ø ystein Hov (Ed)., Tropospheric Ozone Research – Transport and Chemical Transformation of Pollutants in the Troposphere, Vol. 6. pp. 49–56. EUROTRAC. (Chapter 2).

Staehelin, J., Thudium, J., Buehler, R., Volz-Thomas, A., Graber, W., 1994. Trends in surface ozone concentrations at Arosa (Switzerland). Atmospheric Environment 28, 75–87.

Stohl, A., Wotawa, G., Seibert, P., Kromp-Kolb, H., 1995. Interpolation errors in wind fields as a function of spatial and temporal resolution and their impact on different types of kinematic trajectories. Journal of Applied Meteorology 34, 2149–2165.

Stohl, A., Spichtinger-Rakowsky, N., Bonasoni, P., Feldman, H., Memmesheimer, M., Scheel, H.E., Trickl, T., Hübener, S., Ringer, W., Mandl, M., 1999. The influence of stratospheric intrusions on alpine ozone concentrations. Atmospheric Environment 34, 1323–1354.

Strahan, S.E., Douglass, A.R., Nielsen, J.E., Boering, K.A., 1998. The CO_2 seasonal cycle as a tracer of transport. Journal of Geophysical Research 103(D12), pp 13729–13741.

Vaughan, G., Price, J.D., 1989. Ozone transport into the troposphere in a cut-off low event. In: Bojkov, R.D., Fabian, P., Ozone in the Atmosphere. Deepak Pub., Hampton (USA), pp. 415–418.

World Meteorological Organization, 1985. Atmospheric Ozone 1985: assessment of our understanding of the processes controlling its present distribution and change – Report N.16 – Vol. 1. Strat-Trop Exchange, 151–240.

World Meteorological Organization – Global Atmospheric Watch, 1994. Report on the measurements of atmospheric turbidity in BAPMoN. Report N 94, 1–73.