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Background ozone variations at Mt. Cimone Station

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Abstract

In order to evaluate the background ozone concentration at Mt. Cimone (2165 m a.s.l.), the contribution of air masses characterised by different provenances is analysed in this paper. The analysis method is based on identification of background air masses which travelled above the 780 hPa pressure level for at least 48 h before arriving at Mt. Cimone. Not being recently mixed with boundary layer air, these air masses are characterised by a chemical age greater than 2 days. This analysis has shown that under background conditions the yearly principal maximum of ozone is recorded in spring and a secondary maximum is recorded in summer. In contrast, if we consider non-background conditions, the principal maximum is found in late summer and a secondary one in spring. In addition, the analysis indicates the presence of a smooth latitudinal gradient of background ozone concentrations in air masses arriving at Mt. Cimone, with higher concentrations coming from the north and lower ones from the south.

Keywords: Background ozone; Free troposphere; Trajectory analysis; Atmospheric transport; Background station

1. Introduction

In the last decades, the ozone concentration in the clean, background troposphere has doubled compared to the preindustrial years. Today its mixing ratio varies between 20 ppbv in winter and 60 ppbv in summer (Staehelin et al., 1994; Seinfeld and Pandis, 1998). This ozone increase took place throughout the 1970s and in the free troposphere of Northern mid-latitudes an increase of about 10% per decade is registered (London and Liu, 1992). An increase in anthropogenic activities leading to higher emissions of NO_x and hydrocarbons can be considered as the principal reason for this rise in tropospheric ozone concentrations. Ozone and photooxidants can be transported from the atmospheric boundary layer to the free troposphere and dispersed over large regions by long-range transport phenomena (Memmesheimer et al., 1997). In order to determine the background concentration of ozone at Mt. Cimone (MTC), we analysed the ozone concentration in an "unperturbed" free troposphere. In this paper "background conditions" are defined by a chemical age of air masses greater than 2–3 days (TOR-2, 1999). This prevents the surface ozone concentration measured at MTC from being directly affected by the transformation and transport of ozone and its precursors from polluted regions. This allowed us to determine the concentration of the background ozone present at MTC (2165 m a.s.l.) and in the Northern Mediterranean free troposphere. In fact, measurements at high mountain sites permit the investigation and assessment of the ozone concentration and other trace gases in the lower free troposphere. For this purpose, continuous measurements have been undertaken at four mountain peak stations during the EC project "Vertical Ozone Transports in the Alps"

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(VOTALP). This project studied the dynamics and chemistry processes of ozone and photooxidants connected to the different transport phenomena in the mountain regions. MTC is the only mountain station south of the Alps involved in the project.

2. Surface ozone behaviour

Mt. Cimone (44°12′N, 10°42′E, 2165 m a.s.l.), the highest peak of the Italian Northern Apennines, is characterised by a free horizon and is above the planetary boundary layer for most of the year. MTC overlooks the Mediterranean Basin to the south and southwest and the Po Basin to the north and northeast. The site is considered the most representative WMO–GAW (Global Atmosphere Watch) station in Italy, representative of the Northern Mediterranean free troposphere. Details of the site and measurements set-up have been reported in previous papers (Bonasoni et al., 1997, 2000).

At the MTC station the surface ozone concentration has a well-defined seasonal cycle (Fig. 1) with an yearly mean value of 53 ± 8 ppbv (1 standard deviation). As evidenced by the data measured during the period 1996–1998, the lowest monthly mean concentration of ozone, about 40 ppbv, occurred in the winter and increased to 68 ppbv in the summer (Fig. 1). The MTC surface ozone concentrations usually exhibit a secondary maximum in the spring, which is common among the other high mountain peak stations situated at mid-latitudes in the Northern Hemisphere.

In the summertime a reverse diurnal variation of ozone, not found during the other periods of the year, is present at the site (Fig. 1). This variation is characterised by nighttime ozone values which are higher than those at mid-day by about 5 ppbv. These high nocturnal ozone values in the warm season are associated with the mountain wind regime, featuring downslope winds during the night. Normally, because of these downslope winds nighttime values at mountain stations are more representative of the regional background than the daytime values. Therefore, nighttime values are often used to study background conditions. However, in the case of MTC this is not always true. In summertime, mixing heights over the Po Basin can be very high and lead to the formation of nighttime reservoir layers at upper levels containing high ozone concentrations. Therefore, during the night, air from these reservoir layers may be brought down to MTC, causing the increase in ozone. Indeed, on calculating the seasonal cycle of ozone using the nighttime (00–05) data only (Fig. 2), a broad ozone peak is found in the warm season, while in the cold season the seasonal behaviour is similar to that exhibited when all the data are considered.

In this paper, we have estimated background ozone concentrations at MTC by considering only air masses which are unlikely to have undergone recent mixing with boundary layer or lower tropospheric air. For this reason three-dimensional backward trajectories were calculated with the FLEXTRA model (Stohl et al., 1995), with a maximum duration of 144 h calculated 8 times each day for the period 1996–1998. On average, these trajectories are accurate to within 15–20% of the travel distance (Stohl, 1998). However, individual trajectories may have much larger errors, especially since the model topography and the real topography do not match exactly and

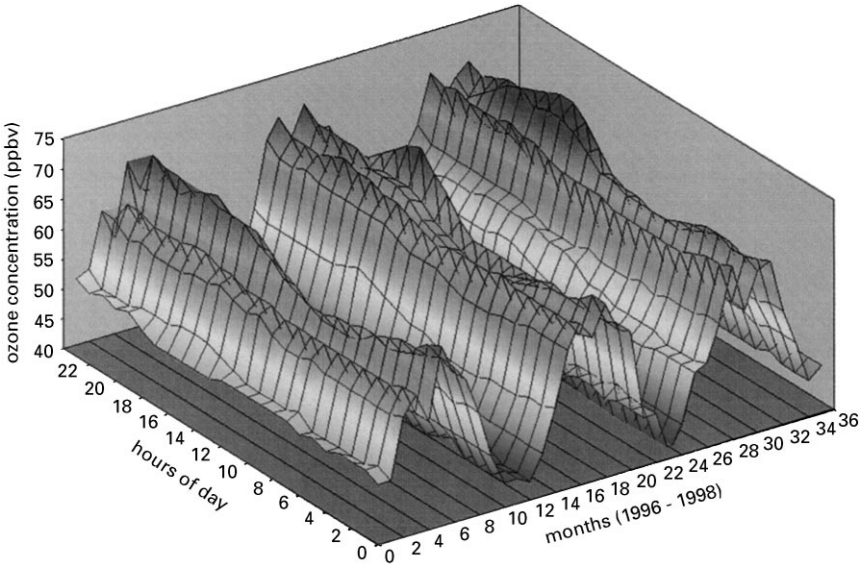

Fig. 1. Monthly ozone diurnal variation at Mt. Cimone from 1996 to 1998.

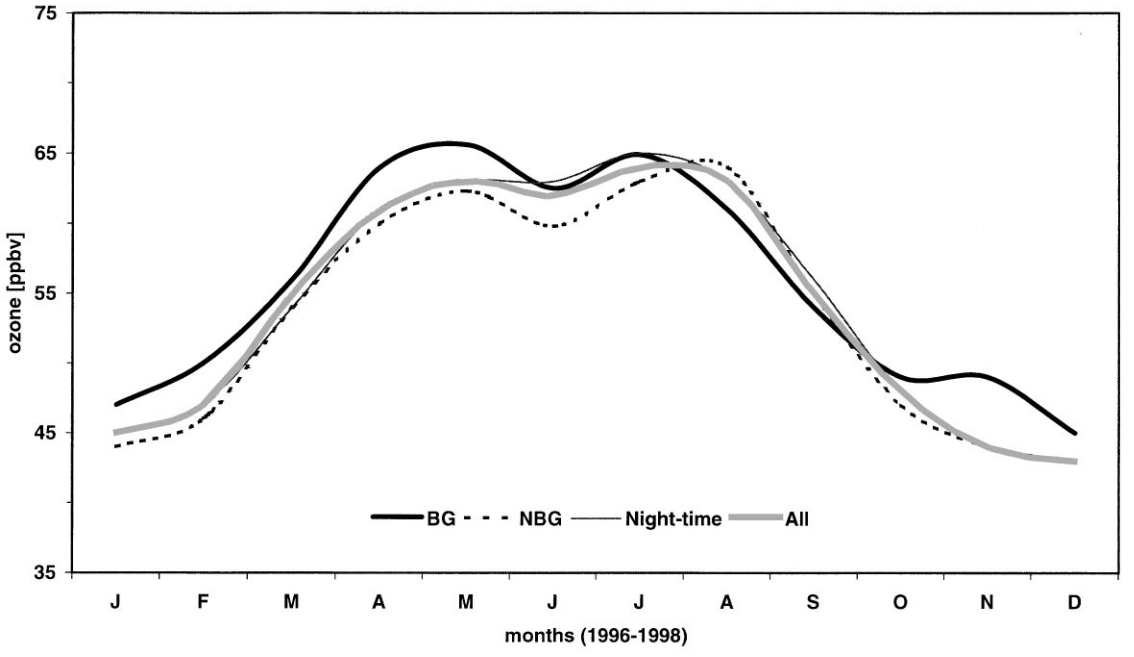

Fig. 2. Average seasonal cycle of ozone at Mt. Cimone, 1996–1998: background: continuous thick black line; non-background: dotted line; nighttime (00–05): continuous thin black line; all data: continuous thick grey line.

thus the arrival height of the trajectories is to some degree arbitrarily chosen to be at 2165 m a.s.l., i.e. the height of the real topography at the measurement station.

In order to ensure a sufficiently long period of clean-air conditions, we have considered only the back-trajectories that travelled above the 780 hPa level (MTC is typically at 790 hPa) for at least the last 48 h before reaching the station. This approach neglects possible contamination with boundary layer air by convection, because the trajectory calculations do not resolve individual convective cells that may contaminate an otherwise clean air mass with pollutants from the boundary layer. In some cases, this may lead to an erroneous classification as background conditions. However, convection on the smaller scales is usually associated with slower ascent on the larger scales also. Since we excluded practically all ascending trajectories, this should be a very efficient filter to remove contaminated data.

The orography of the nearby Po Basin can favour the stagnation of air masses, even for a few days, under particular weather conditions. Therefore, a travel time of 24 h taken by air masses above 780 hPa would not have been sufficient to describe MTC background conditions. Consequently, we rejected all ozone data associated with air masses which during the last two days reached a level below 780 hPa. On applying this method an yearly concentration of 55 ± 7 ppbv was obtained for the background ozone values, higher than the yearly mean value for non-background conditions (53 ± 8 ppbv). Unlike the non-background conditions, the seasonal cycle for the background ozone concentrations presents a principal maximum in spring and a secondary maximum in summer, as shown in Fig. 2. These high spring values constitute the ozone spring maximum in the Northern Hemisphere (Logan, 1985; Penkett and Brice, 1986), which is mainly thought to be owing to the contribution of air masses transported from the stratosphere (Oltmans et al., 1996) and to photochemical in situ production in the free troposphere (Beekmann et al., 1994; Liu et al., 1987; Yienger et al., 1999). The summer–winter peak-to-peak amplitude of 19 ppbv between the 44 ppbv winter minimum and the 63 ppbv summer maximum (Fig. 2) agrees with the investigations and analysis for measurements carried out at other European high mountain stations in clean-air conditions (Scheel et al., 1997). This background ozone peak-to-peak amplitude is lower than that registered at MTC under non-background conditions (22 ppbv).

If we compare the seasonal ozone cycle obtained from background conditions with that obtained from nocturnal data (Fig. 2) the differences are evident. This is principally due to the different data filtering methods used. In fact, although the wind data used in the trajectory method has a too coarse geographical resolution to resolve the local wind system, the trajectory method still describes the background ozone conditions in the free

troposphere better than using nighttime data. The nighttime ozone concentration measured at MTC should be considered as a representative of only the "local free troposphere".

3. Trajectory analysis and background ozone concentration

In order to estimate the contribution of different air mass origins to the MTC area, we evaluated their frequency as a function of trajectory starting positions within the domain 80°N, 50°W and 20°N, 50°E. We divided this domain into six different regions: Arctic, Atlantic Ocean, Continental Europe, Eastern Europe, Mediterranean Basin and Saharan–African region (Fig. 3). This analysis was carried out both for warm (April–September) and cold (October–March) season periods and for background and non-background conditions, as reported in the tables in Fig. 3. As shown, about 70% of background air masses (60% of non-background) that reached MTC in the period 1996–1998 came from Atlantic and Arctic areas. The smallest contribution came from Mediterranean Basin and the Eastern area (Fig. 3).

To study the relation of ozone concentrations to air mass path, we have applied the trajectory statistics method of Seibert et al. (1994). A description and comparison of this technique with other advanced trajectory analysis methods can be found in Stohl (1998). Basically, it attributes a measured ozone value to every point along the trajectory arriving at the time of measurement. Applying this method for all measurement data, average concentrations can be obtained on a three-dimensional grid superimposed on the domain with available trajectory data. The concentration fields obtained in this way can be interpreted as the "source regions" of ozone measured at MTC, that the regions from where ozone concentrations are transported to MTC. With this method, we cannot say whether the ozone is actually formed in these regions or whether it is produced on transit from precursors emitted in these regions. Also, the concentration fields are valid only for the receptor site MTC and not in a more general sense, because the meteorological conditions are specific to the individual pathways towards MTC. We made the analysis for two height levels: above (background conditions) and below (non-background conditions) 780 hPa. For the analysis of the background conditions, we additionally required

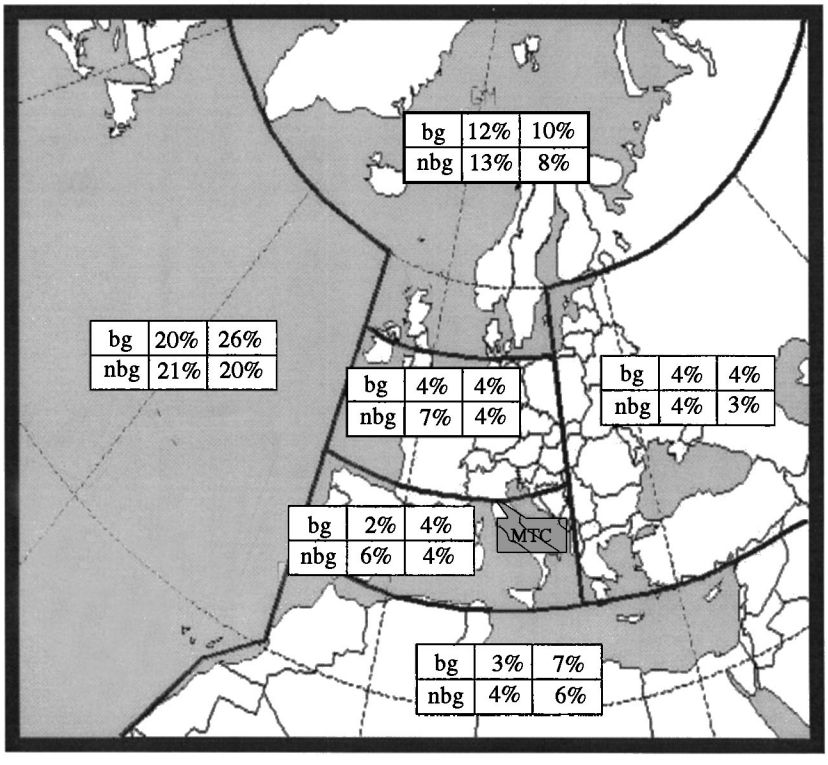

Fig. 3. Areas of air mass origin associated with the MTC backward trajectories. In the boxes the "background" (bg) and "non-background" (nbg) mean values of air mass contributions (%) are reported for warm (second column) and cold (third column) season.

that no other trajectory position within the last 48 h before arrival was located below 780 hPa in order to exclude influence from the boundary layer. Again, the analysis was done for the warm season and cold season separately.

The typical meteorological conditions during the warm season, in presence of sufficient precursor emissions, can favour regional-scale ozone formation in the boundary layer. During this period, high values of non-background ozone (Fig. 2) were measured at MTC. In fact, the densely industrialised and inhabited area of the Po Basin is the dominant ozone source identified by the trajectory statistics (Fig. 4a). Concentrations in the cleaner air masses arriving from the Atlantic Ocean are lower by some 10 ppbv. In contrast, the influence of the Po Basin is clearly absent for the background ozone concentrations, as shown in Fig. 4b. In general, there is a rather smooth spatial concentration gradient, with the lowest concentrations coming from the southwest and the highest from the north (Fig. 4b).

During the cold season, the background ozone values in air masses of different provenances are quite uniform, with slightly higher concentrations associated with air masses coming from the north (Fig. 4d). In fact, in late winter and in spring high background ozone concentration in the Northern Hemisphere is related to photochemistry and to the transport of air masses of stratospheric origin. This last contribution is probably

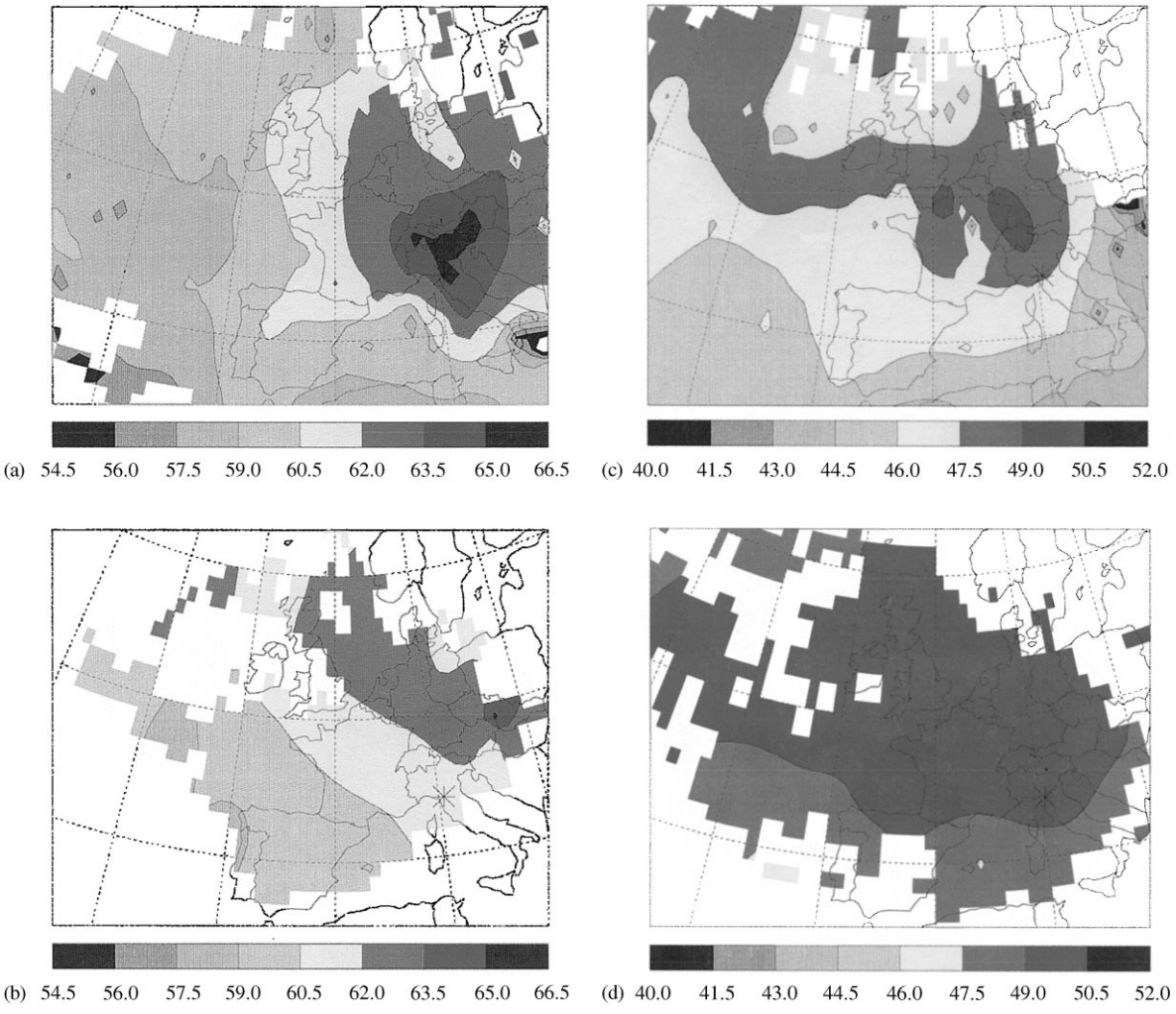

Fig. 4. Concentration fields of ozone (ppbv) obtained with trajectory statistics for the years 1996–1998. Grid cells that were crossed by less than 10 trajectories are left blank. The statistics were calculated for the warm season (a and b) and the cold season (c and d) and for background conditions, i.e. trajectory points above 780 hPa and excluding all trajectories that penetrated below 780 hPa during the last 48 h of transport (b and d), and for non-background conditions, i.e. trajectory points below 780 hPa (a and c). Warm season is the April–September period, cold season is the October–March period.

due to the strong impact of individual events rather than their frequency (Oltmans et al., 1996), as also confirmed by MTC stratospheric ozone intrusion analyses carried out during the VOTALP project (Stohl et al., 2000; Bonasoni et al., 2000).

Tropospheric photochemistry can also contribute strongly to the Northern Hemisphere spring ozone maximum. In fact, a winter build up of carbon monoxide and non-methane hydrocarbons in the remote troposphere provides the dominant fuels for the photochemical ozone production (Wang et al., 1998). The spring build up of photochemical ozone on a large hemispheric scale is confirmed by the maximum of PAN (considered an unambiguous marker for tropospheric chemistry) and by its strong correlation with ozone (Singh et al., 1992, Solberg et al., 1997).

The comparison of background with non-background ozone concentration for cold season evidenced a quite different picture (Figs. 4c and d), confirming the decoupling between free tropospheric and boundary layer air masses. The much lower ozone values at lower levels, shown in Fig. 4c, compared to the background conditions are explained by a slower ozone production due to different causes: a reduced solar radiation, the longer chemical lifetime of most atmospheric compounds, a local-regional titration of ozone by NO during this cold period and ozone depletion by dry deposition. Nevertheless, transport pathways over polluted regions in Central Europe still indicate the possibility of ozone formation in the cold season also. However, the local maximum in the Po Basin found in the warm season is missing. Obviously, transport times from this region to MTC are too short to allow significant ozone formation in the cold season. In non-background conditions (Figs. 4a and c), the lowest ozone values are found in air masses that reached MTC from latitudes lower than 35°N and in particular from African desert areas, as reported recently in other studies (Scheel et al., 1997, Bonasoni et al., 1998).

4. Conclusion

Surface ozone variations at Mt. Cimone, a site representative of Northern Mediterranean free troposphere, during the period 1996–1998 have been studied in order to assess the behaviour of background ozone concentrations. This work presents and discusses three years of ozone measurements by analysing its concentration as a function of air mass origin and path using six-day backward trajectories. We defined background ozone as the ozone in air masses that do not penetrate below 780 hPa for at least 48 h before reaching MTC. In addition, we compared this ozone behaviour with that calculated using only the nighttime (00–05) values connected to downslope winds and considered representative of the "local free troposphere".

The analysis revealed that background ozone concentrations recorded at MTC present an yearly mean of 55 ppbv, 53 ppbv for non-background, and 54 ppbv for nighttime values. The background ozone behaviour exhibits a principal maximum in spring and a secondary maximum in summer. This background spring ozone maximum can be considered characteristic of the seasonal ozone cycles in the clean Northern hemispheric atmosphere. On the contrary, the ozone cycle for nighttime values has a broad maximum which rises from spring to summer. Because nighttime downslope winds can bring down polluted reservoir layers from the Po Basin to the station, nighttime values should be considered representative only of the "local free troposphere". An annual peak-to-peak amplitude of 19 ppbv, which is lower than that for non-background and nighttime data, characterises the ozone seasonal cycle for background conditions.

When analysing the Mt. Cimone ozone concentration using trajectory statistics, a quite different picture emerged for background and non-background conditions. These differences are particularly pronounced in the warm season when the highest background ozone concentrations were related to air masses coming from northerly and easterly latitudes. In contrast, the highest ozone values for non-background conditions originated in Northern Italy and central Europe. This confirms that during the warm period, polluted air masses in these areas are the main contributors to high non-background ozone values at the Mt. Cimone Station. On the contrary, the lowest ozone values were related to air masses flowing from low latitudes, in particular from the Saharan desert. In this way, a smooth background ozone latitudinal gradient was found in the MTC data.

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References

Beekmann, M., Ancellet, G., Megie, G., 1994. Climatology of tropospheric ozone in southern Europe and its relation to potential vorticity. Journal of Geophysical Research 99, 12841–12853.

Bonasoni, P., Calzolari, F., Colombo, T., Corazza, E., Santaguida, R., Tesi, G., 1997. Continuous CO and H_2 measurements at Mt. Cimone (Italy): preliminary results. Atmospheric Environment 31, 959–967.

Bonasoni, P., Bonafè, U., Colombo, T., Santaguida, R., Lenaz, R., Tesi, G., 1998. Effects of Saharan dust transport on trace gases concentration. In: Bojkov, Visconti (Eds.), XVIII Quadr. Ozone Symp., l'Aquila, Italy, 12–21 September 1996, pp. 323–326.

Bonasoni, P., Evangelisti, F., Bonafè, U., Ravegnani, F., Calzolari, F., Stohl, A., Tositti, L., Tubertini, O., Colombo, T., 2000. Stratospheric ozone intrusion episodes recorded at Mt. Cimone during the VOTALP project: case studies. Atmospheric Environment 34, 1355–1365.

Liu, S.C., Trainer, M., Fehsenfeld, F.C., Parrish, D.D., Williams, E.J., Fahey, D.W., Hubler, G., Marphy, P.C., 1987. Ozone production in the rural troposphere and the implications for regional and global ozone distributions. Journal of Geophysical Research 92, 191–207.

Logan, J.A., 1985. Tropospheric ozone: seasonal behaviour, trends and anthropogenic influence. Journal of Geophysical Research 90, 10463–10482.

London, J., Liu, S., 1992. Long-term tropospheric and lower stratospheric ozone variations from ozonosondes observations. Journal of Atmospheric and Terrestrial Physics 5, 599–625.

Memmesheimer, M., Ebel, A., Roemer, M., 1997. Budget calculations for ozone and its precursors: seasonal and episodic features based on model simulations. Journal of Atmospheric Chemistry 28, 283–317.

Oltmans, S.J., Levy II, H., Harris, J.M., Merrill, J.T., Moody, J.L., Lathrop, J.S., Cuevas, E., Trainer, M., O'Neil, M.S., Prospero, J.M., Vomel, H., Johnsonn, B.J., 1996. Summer and spring ozone profiles over the North Atlantic from ozonesonde measurements. Journal of Geophysical Research 101, 29179–29200.

Penkett, S.A., Brice, K.A., 1986. The spring maximum in photooxidants in the Northern Hemisphere troposphere. Nature 319, 655–657.

Scheel, H.E., Areskoung, H., Geiss, H., Gomischel, B., Granby, K., Haszpra, L., Klasink, L., Kley, D., Laurila, T., Lindskog, T., Roemer, M., Schmitt, R., Simmonds, P., Solberg, S., Toupance, G., 1997. On the spatial distribution and seasonal variation of lower-troposphere ozone over Europe. Journal of Atmospheric Chemistry 28, 11–28.

Seibert, P., Kromp-Kolb, H., Baltensperger, U., Jost, D.T., Schwikowski, M., Kasper, A., Puxbaum, H., 1994. Trajectory analysis of aerosol measurements at high alpine sites. In: Borrell, P.M., Borrell, P., Cvitas, T., Seiler, W. (Eds.), Transport and Transformation of Pollutants in the Troposphere. Academic Publishing, Den Haag, pp. 689–693.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric Chemistry and Physics from Air Pollution to Climate Change. Wiley, New York.

Singh, H.B., Herlth, D., O'Hara, D., Zahnle, K., Bradshaw, J.D., Sandholm, S.T., Talbot, R.W., Crutzen, P.J., Kanakidou, M.A., 1992. Relationship of peroxyacetyl nitrate to active and total odd nitrogen at Northern high latitudes: Influence of reservoir species on NO_x and O_3. Journal of Geophysical Research 97 (D15), 16523–16530.

Solberg, S., Krognes, T., Stordal, F., Hov, O., Beine, H.J., Jaffe, D.A., Klemisthav, K.C., Penkett, S.A., 1997. Reactive nitrogen compounds at Spitsbergen in the Norvegian Arctic. Journal of Atmospheric Chemistry 28, 113–123.

Staehelin, J., Thudium, J., Buehler, R., Volz-Thomas, A., Graber, W., 1994. Trends in surface zone 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., 1998. Computation, accuracy and applications of trajectories – a review and bibliography. Atmospheric Environment 32, 947–966.

Stohl, A., Spichtinger-Rakowsky, N., Bonasoni, P., Feldmann, H., Memmesheimer, M., Scheel, H.E., Trickl, T., Hübener, S.H., 2000. The influence of stratospheric intrusions on alpine ozone concentrations. Atmospheric Environment 34, 1323–1364.

TOR-2 Tropospheric Ozone Research, 1999. Annual report 1998. International Scientific Secretariat GSF. Munchen.

Yienger, J.J., Klonecki, Levy, H., Moxin, W.J., Carmichael, G.R., 1999. An evaluation of chemistry's role in the winter–spring ozone maximum found in the Northern midlatitude free troposphere. Journal of Geophysical Research 104, 3655–3667.

Wang, Y., Jacob, D.J., Logan, J.A., 1998. Global simulation of tropospheric O_3–NO_x-hydrocarbon chemistry; 3. Origin of tropospheric ozone and effects of nonmethane hydrocarbons. Journal of Geophysical Research 103, 10757–19767.