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Analysis of near-surface ozone variations in Terra Nova Bay, Antarctica

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Abstract: Ozone concentration measurements were made during December from 2001–2005 to quantify the contributions of different processes to near-surface ozone concentrations (O_3) in Terra Nova Bay, Antarctica. The average O_3 concentration was 20.3 ppbv. On days characterized by high solar radiation fluxes (HSR), significantly higher concentrations of O_3 (21.3 ppbv) were recorded compared to days with low solar radiation fluxes (LSR days, 16.8 ppbv). High O_3 concentrations could be related to strong winds from SW–NW. Three-dimensional back-trajectories show that air from the interior of the continent could affect O_3 at Terra Nova Bay. Moreover, during HSR days, high O_3 concentrations were also recorded in connection with weak circulation, suggesting that emissions from the Italian base (located 2 km north) could also represent a significant source of O_3. To clarify the role of local pollution in Terra Nova Bay, O_3 values were also calculated using the photochemical steady state (PSS) approximation under clear sky and cloudy conditions.

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Key words: katabatic wind, solar radiation fluxes, surface ozone, tropospheric ozone

Introduction

In the troposphere, ozone (O_3) is one of the most active gases involved in photochemical reactions. In fact, being the precursor of important oxidizing radicals (i.e. OH and NO_3), O_3 is one of the key agents influencing the oxidizing capacity of the troposphere. In Antarctica, several processes can influence tropospheric O_3 concentrations, e.g. photochemical processes involving reactive halogen atoms (Barrie *et al.* 1988, Roscoe *et al.* 2001, Tarasick & Bottenheim 2002) and NO_x (Crawford *et al.* 2001) as well as transport of air masses from lower latitudes (Murayama *et al.* 1992, Gruzdev & Stinov 1992) or vertical transport (Grudzev *et al.* 1993). During the summer season, the photochemical production of NO_x (Jones *et al.* 2001, Davis *et al.* 2001, Beine *et al.* 2002) due to the photolysis of NO^{3-} in snowpack interstitial air, as well as the photolysis of atmospheric HONO (Yang *et al.* 2002), can occur in the Polar Regions thus providing a surprisingly active photochemical environment.

Accurate knowledge of the latitudinal distribution of O_3 is needed to improve global modelling of O_3 and future levels of atmospheric greenhouse gases. That is why, within the framework of the Italian National Programme of Antarctic Researches (PNRA), continuous measurements of summer surface O_3 concentrations have been carried out at the Italian Antarctic research station at Terra Nova Bay (TNB) (Mario Zucchelli Station - 74.7°S, 164.1°E, 41 m a.s.l.) since 2001. In this paper, these near-surface ozone measurements will be presented and analysed for the first time.

Measurement site and method

The TNB M. Zucchelli summer station is located on the western edge of the Ross Sea (Fig. 1). During the period 2001–2005, five summer campaigns for the determination of surface O_3 concentrations were conducted at the clean-air facility of Icaro Camp (TNB-IC) located on the coast 2 km south from the main station. The O_3 measurements were undertaken in a purpose designed shelter with an air intake 5 m above the surface composed of a 2 m long Pyrex stack (67 mm diameter) enclosed in a steel cover. Air is forced through this by a blower with a flux velocity ranging from 1–3 m s^{-1}. Ozone measurements (at 1.8 l min^{-1}) were made every minute and with a precision and accuracy of ± 1 ppbv. Zero and span checks were automatically performed every 24 hours. Moreover, after each experimental campaign the O_3 analyser (DASIBI 1108 PC) was returned to the factory for ordinary maintenance and calibration. Standard meteorological parameters were continuously observed at 1 min intervals using an IRDAM WST7000 meteorological station at a height of 6 m above the ground. Surface measurements of shortwave incoming solar radiation (SW^{in}) were obtained using a CNR-1 Kipp & Zonen radiometer with a sensitivity of 10–35 μV Wm^{-2} in the spectral range from 305–2800 nm.

At TNB-IC, the seasonal behaviour of SW^{in} is characterized by a seasonal cycle with a relatively flat maximum in December (not shown here). Because of this characteristic pattern O_3 and meteorological parameters (on hourly basis) as well as SW^{in} (daily average values) have

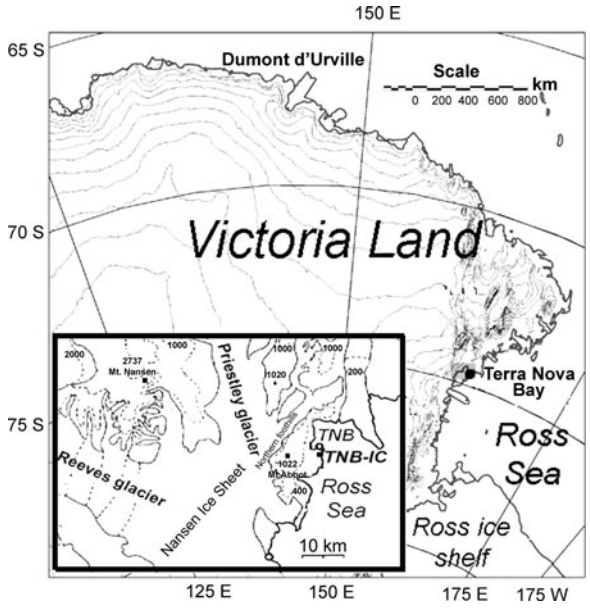

Fig. 1. Location of TNB and TNB-IC (map adapted by www.climantartide.it).

been analysed only for December from 2001–2005 (see next section).

The mean temperature during the selected period was -1°C and ranged from -10°C to 9°C at TNB-IC. More than the 30% of the hourly temperature values were above freezing. As a result, the area around the O_3 sampling site was not uniformly covered by snow during the summer season and rocky formations were often visible. As pointed out by Argentini & Mastrantonio (1994) and Argentini *et al.* (1995), the wind regime at TNB is influenced by a nearby mountain barrier (i.e. the Northern Foothills) which interacts with the katabatic circulation from two glaciers (i.e. Reeves and Priestley glaciers see Fig. 1), by barrier flows moving parallel to the Trans-Antarctic Mountains and finally by southerly winds related to meso- or synoptic scale lows in the western Ross Sea. This was also the case for TNB-IC where wind speeds higher than 6 m s^{-1} (a threshold value suggested by Argentini *et al.* (1995) to identify katabatic flows at TNB during summer) were mostly from the SW–NW sector and to a lesser extent from the south (not shown here).

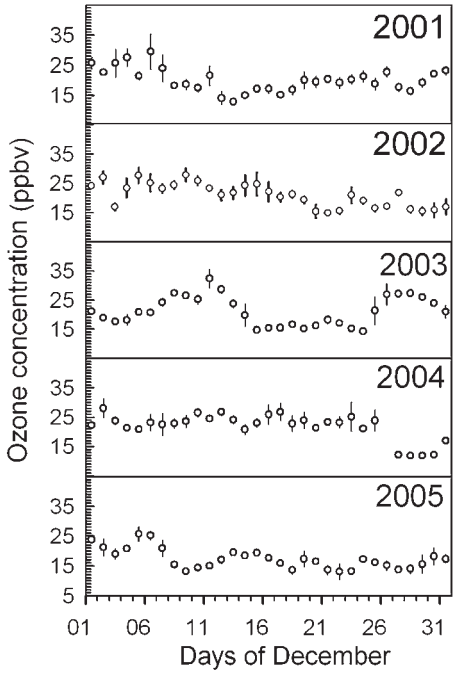

Fig. 2. Mean daily O_3 values at TNB-IC during December 2001–2005. The vertical lines mark the daily standard deviation values.

Table I. Basic statistical parameters (expressed as ppbv) for O_3 at TNB-IC as well as the number of "high solar radiation" (HSR) or "low solar radiation" (LSR) days selected during December from 2001–2005.

Year	Mean	SD	Min	Median	Max	HSR	LSR
2001	20.0	4.5	11.0	19.5	37.0	11	6
2002	21.0	4.4	11.8	21.2	37.5	3	8
2003	21.2	5.2	13.1	20.7	36.9	11	7
2004	21.9	4.9	11.0	22.5	35.7	7	3
2005	17.1	3.6	10.0	16.5	28.0	5	11
All data	20.3	4.9	10.0	20.0	375	37	35

Results and discussion

Environmental data analysis

The O_3 data recorded for December 2001–2005 are shown in Fig. 2, while a statistical overview is provided in Table I. We considered hourly O_3 deviations (O_3^{RES}) from a smoothed seasonal curve. This curve was obtained by computing, for each year, the average daily O_3 values. Then we averaged all the available years of data, thus obtaining the mean O_3 value for each given day (Fig. 3). Finally, we applied a three-time repeated 19-day moving average to obtain the seasonal fluctuation in the O_3 time series (Sebald *et al.*

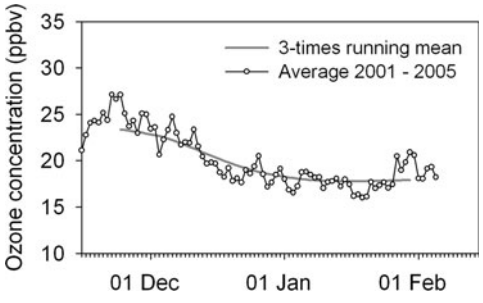

Fig. 3. Calculated average O_3 behaviour at TNB-IC for summer seasons 2001–2005 (open circles). The grey line represents the smoothed behaviour obtained by applying recursive (19-day) running mean.

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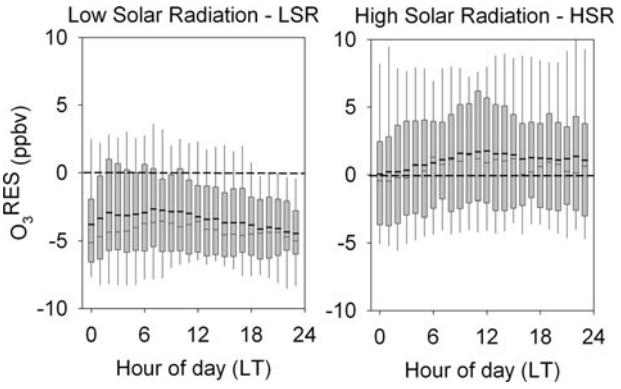

Fig. 4. Diurnal variation of O_3^{RES} at TNB-IC during LSR and HSR days (December 2001–05). The lowest box boundary indicates the 25th percentile, the thin (dashed) line within the box marks the median (mean value), and the highest box boundary indicates the 75th percentile. Whiskers (error bars) above and below the box indicate the 90th and 10th percentiles.

2000, Tarasova & Karpetchko 2003). The resulting seasonal O_3 cycle is characterized by a declining trend from November–January, in agreement with data from other coastal sites in Antarctica (Helmig *et al.* 2007).

We identified days characterized by high solar radiation fluxes (HSR days) when the daily SW^{in} was greater than the 75th percentile over the period 2001–2005 (i.e. 406.6 W m^{-2}). In the same way, we identified low solar radiation days (LSR days) when the daily SW^{in} was lesser than the 25th percentile over the period 2001–2005 (i.e. 299.3 W m^{-2}). This allowed us to select 37 HSR days and 35 LSR days at TNB-IC (see Table I). On average, hourly O_3 concentrations recorded during HSR days were 4.5 ppbv (+ 27%) higher than for LSR days. This difference is significant at the 95% confidence level, using a Student *t*-test. During LSR days on average no diurnal variation was present, while for the HSR days an O_3 increase was detected around noon (Fig. 4). This diurnal variation with an amplitude of 1.7 ppbv (6.5 ppbv, considering the 75th percentile of hourly O_3 values), suggests that photochemical O_3 production processes are active in this Antarctic environment.

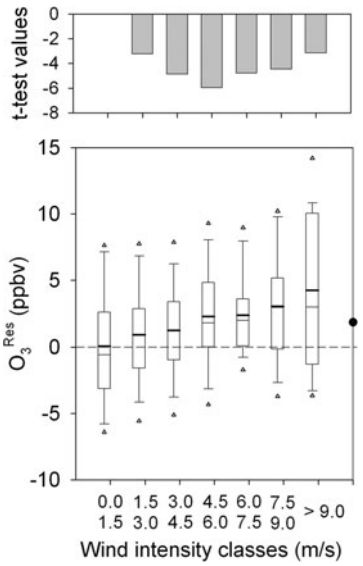

Fig. 5. O_3^{RES} for HSR days as function of wind intensity classes. Box-and-whiskers are defined as Fig. 4, but the 5th and 95th percentiles are also reported (triangles). On the upper plate, the *t*-test values for the significance of the difference between the average of O_3^{RES} for when sorted according to a separation value of wind intensity are reported.

Ozone data analysis

To identify the processes leading to the high O_3 values recorded at TNB-IC during HSR days, O_3^{RES} data were firstly related to local wind intensity using a box-and-whiskers plot. The boxes and whiskers denote the 10, 25, 50, 75 and 90 percentiles, and the bold lines the mean values of the O_3^{RES} distributions for different classes of wind intensity (Fig. 5). The results show that O_3^{RES} values shift towards higher values with increasing wind intensity, thus suggesting that the observed O_3 concentrations could be affected by non-local sources. Observations carried out at other Polar sites (Crawford *et al.* 2001, Davis *et al.* 2001, Beine *et al.* 2002) suggested that, under strong wind conditions, the O_3 production efficiency related to local NO_x emission from snow is low. Moreover, the low snow cover around TNB-IC rules out the possibility that local emissions of NO_x from surface snow represent a significant contribution to the O_3 increases during HSR days. To investigate what type of transport processes could affect the O_3 concentrations, the O_3^{RES} data were successively sorted in two classes according to a hypothetical separation value of wind intensity ranging from 1.5–9 m s^{-1}. Following Gerasopoulos *et al.* (2001), we compared the overall mean of O_3^{RES} calculated above and below each wind intensity threshold value reported in the x-axis of Fig. 5. The results indicate a transition class at about 4.5–6 m s^{-1}, where the difference between the two means is maximized in absolute terms. In fact, it is for this wind speed that the *t*-test parameter achieved the greatest absolute value (Fig. 5. upper section). A separation value of 4.5–6 m s^{-1} is comparable with the threshold identified by Argentini *et al.* (1995) to determine the onset of katabatic flows at TNB. Moreover, 92% of wind speeds higher than 6 m s^{-1} (which account for 15% of the HSR days) were from the SW–NW, confirming the influence of katabatic flows (Argentini *et al.* 1995). During summer, katabatic winds are less frequent than during winter. In summer, downslope flows are usually related to synoptic forcing (Bromwich *et al.* 1993) or nocturnal katabatic breezes (Cava *et al.*

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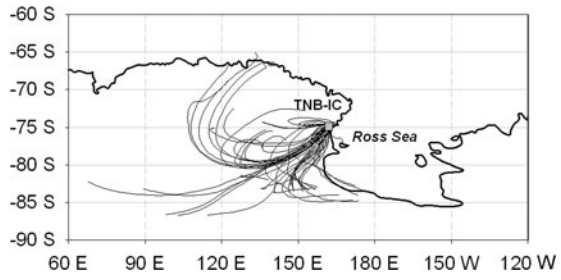

Fig. 6. 72 hour back trajectories ending at TNB-IC and calculated during HSR days for local wind intensities greater than 6 m s^{-1}.

2004). Summer katabatic events can also be triggered by synoptic disturbances. For instance, Carrasco & Bromwich (1995) observed a cyclonic circulation supporting a katabatic event (with north-westerly wind direction) at the Reeves Glacier. Nevertheless, once established, these summer katabatic flows transport negatively buoyant air from the Antarctic plateau through narrow glaciated valleys (e.g. Priestly and Reeves glaciers) and finally over the steep coastal slopes. Here, these katabatic outflows favour the presence of clear sky conditions (Bromwich *et al.* 2003) and consequently high solar radiation fluxes at the surface.

To support this hypothesis, for each of the HSR days, 72-hour back-trajectories have been calculated with a time step of three hours using the Hybrid Single Particle Lagrangian Integrated Trajectory model - HYSPLIT (Draxler & Rolph 2003). It should be noted that both due to the coarse FNL meteorological data resolution and the complex topography around TNB areas, caution should be take in interpreting back-trajectory results. Nevertheless, these trajectories should identify the synoptic-scale circulation of air masses. The results show that for wind speeds greater than 6 m s^{-1} (Fig. 6), the air masses were mostly of continental origin. As observed by Crawford *et al.* (2001) and Davis *et al.* (2001), during summer the surface layer of the Antarctic plateau represents a net source of O_3 and its precursors (i.e. NO_x emitted by the snow surface). Moreover, Weller *et al.* (2002) suggested that for coastal sites with pronounced katabatic winds, a significant summertime contribution to the NO_y chemistry might be due to air transport from the Antarctic plateau. The increase of O_3 levels at TNB-IC recorded in connection with strong winds blowing from continental areas (from SW–NW), could thus also be a result of air mass transport from the Antarctic plateau. However, as the O_3 mixing ratio in the Antarctic troposphere increases with altitude (Grudzev & Stinov 1992, Tarasick & Bottenheim 2002), contributions related to vertical transport cannot be excluded. Although it is well established that ozone increases systematically with altitude in the troposphere (Staehelin *et al.* 1994), Murayama *et al.* (1992) found that during the period from late spring to summer O_3 increases only gradually with height in the lower troposphere and only at altitudes higher than 4 km steeply increases, based on O_3 concentrations reported from ozone soundings from Syowa station (69.0°S, 39.5°E).

To investigate the possibility that air transport from the upper troposphere/lower stratosphere could affect TNB-IC during the HSR days we considered the vertical displacement of the HYSPLIT 72-hour back-trajectories before reaching the measurement site. Only 15% of the trajectories start at altitudes above 4 km a.s.l. Moreover, about 75% (50%) of the trajectories remained at an altitude below 400 m above ground level during the last 180 km (350 km) before reaching TNB-IC. This supports the theory that O_3 increases recorded at TNB-IC are caused by air masses originating from low altitudes above the Antarctic continent.

For wind speeds below 6 m s^{-1} an average O_3^{RES} of 1.0 ppbv was recorded, but the O_3^{RES} diurnal cycle amplitude increased to 2.3 ppbv suggesting the existence of local processes affecting O_3 concentrations. Winds weaker than 6 m s^{-1} came from the following sectors: north (31%), north-east and south (both 21%). Highly significant enhanced O_3 concentration was associated with winds from N ($O_3^{RES} = 2.1$ ppbv), which included the TNB main station facility, where diesel generators were operating. With no NO_x or particle measurements at TNB-IC during the considered periods, we suspected that these enhanced O_3 concentrations could be due to the emission of "local pollution" from the exhaust of the TNB main station facility. In fact, during previous measurements carried out during the summers 1997 and 1998, high levels of NO_2 and NO_y were identified and related with local pollution from the Italian station main facilities (Allegrini *et al.* 2000). During HSR days, significantly enhanced O_3 concentrations were also observed with winds from the east and south-east ($O_3^{RES} = 1.0$ ppbv). As these observations were mostly recorded under very low wind intensities (< 2 m s^{-1}), they were also attributed to emissions from the main Italian station. Finally, O_3 concentrations representative of the TNB-IC average conditions (i.e. $O_3^{RES} = -0.1$ ppbv) were recorded in connection with winds from the south. Usually, air masses from this direction have had no trajectory over the Antarctic continent, but were rather advected to TNB-IC by cyclonic areas situated over the western Ross Sea. This pathway provides photochemical processes little opportunity to add or remove O_3 to/from the air masses before reaching the measurement site.

On LSR days, lower than average O_3 concentrations (O_3^{RES}: -3.4 ppbv) were recorded at TNB-IC (Fig. 4). Probably, these low O_3 values were related both to the origin of air masses reaching the measurement site and the weather conditions. In fact, LSR days were often related (about 40% of time) with humid air masses (average RH value: 79%) coming from sectors ranging from east to south, which includes the Ross Sea. Moreover, the METAR (METeorological Aerodrome Report; WMO 1995) available for the years 2001–2004 at the TNB

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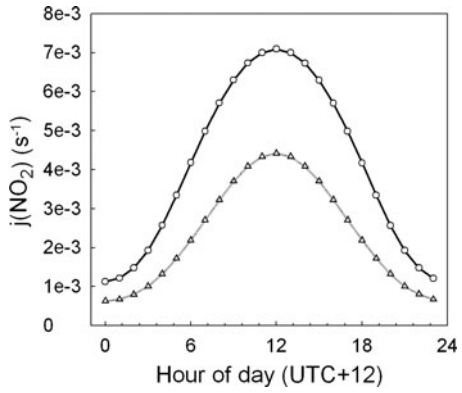

Fig. 7. 16 December 2004: diurnal cycles of $j(NO_2)$ simulated for TNB-IC by using the TUV model and assuming the following Cloud Optical Depth (COD): COD = 0 (open circles), COD = 10 (solid triangles).

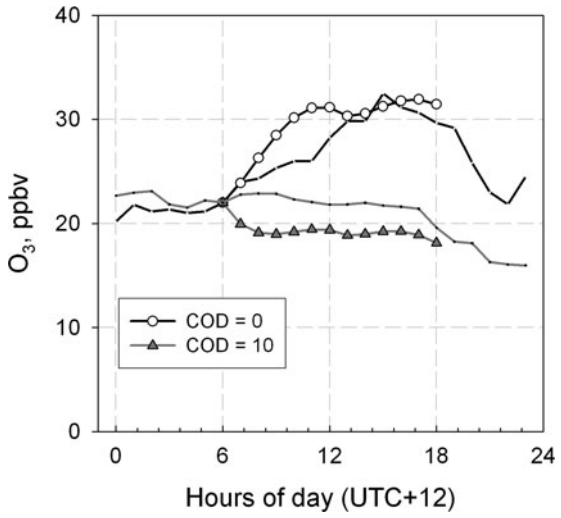

Fig. 8. O_3 concentrations recorded on the HSR days 16 December 2004 (black line) with O_3 concentrations calculated assuming a PSS approximation for polluted NO_X levels (Allegrini *et al.* 2000) as well as for different Cloud Optical Depth (COD): COD = 0 (open circles), COD = 10 (solid triangles). For comparison, O_3 concentrations recorded on a representative LSR day (31 December 2003) were also reported (solid lighter line).

aviation field (about 2 km away from our sampling site), indicated snow events or drifting snow for most of the LSR days (about the 85%). During LSR days, significantly lower than average O_3 concentrations were recorded also in connection with northerly winds (averaged O_3^{RES} = -2.3 ppbv), suggesting a possible influence due to O_3 titration by NO_x from the main Italian station and/or lower photochemical O_3 production under low SW^{in}.

Calculation of PSS-derived O_3 concentrations

To investigate the possibility that local emissions from the TNB main facilities can lead to photochemical O_3 production during HSR days, a simple steady-state kinetic scheme was applied to a representative HSR day (16 December 2004) during which O_3 showed an evident diurnal cycle in conjunction with a weak northerly wind from the Italian station. The amount of visible and UV solar irradiance as well as the $j(NO_2)$ values were calculated using the Tropospheric Ultraviolet Visible (TUV) radiative transfer model (Madronich & Flocke 1998). To evaluate the effect on solar irradiance as well as on the photolysis rate constant produced by realistic Cloud Optical Depth (COD) values (Barnard and Long 2004), TUV was run both assuming clear sky (COD = 0, Fig. 7) and cloudy conditions (COD = 10, Fig. 7).

Hourly O_3 concentrations were calculated basing on the photochemical steady state (PSS) approximation for NO_x and O_3, which is assumed to be determined by the following reaction (Seinfeld & Pandis 1998, Volz-Thomas *et al.* 2003):

$$NO_2 + h\nu \rightarrow NO + O \qquad \lambda < 420\,nm \qquad (R1)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (R2)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (R3)$$

Under this assumption, the O_3 temporal evolution can be calculated by the following equation (Chudzyński *et al.* 2001):

$$\frac{dO_3}{dt} = j(NO_2) \cdot [NO_2] - k_3 \cdot [O_3] \cdot ([NO]_0 + [NO_2]_0 - [NO_2]) \qquad (1)$$

$[NO]_0$ and $[NO_2]_0$ denote the initial values for the considered species, and for the rate constant k_3 the formula recommended by the NASA panel was applied ($k = 3 \times 10^{-12}$ exp(-1500/T) cm^{-3} s^{-1}), as indicated by Sander *et al.* (2000). Because no $[NO]_x$ data were available from TNB-IC for this period, we used a value of 100 pptv for $[NO_2]_0$, as measured by Allegrini *et al.* (2000) in conjunction with local pollution episodes at TNB. $[NO]_0$ was found using the best fit between the O_3 calculation and the experimental data. Note that early morning and late afternoon O_3 values were not calculated because solar intensity was too low and varied rapidly, preventing the PSS reaching equilibrium (Carpenter *et al.* 1998). Figure 8 compares measured O_3 data and PSS-derived O_3 values for the different COD values. For clear sky conditions (COD = 0), a quite good agreement between measured and calculated O_3 was found assuming a $[NO]_0$ of 25 pptv, while for COD = 10 the O_3 concentration inferred from the PSS equations strongly underestimated the experimental data. On the other hand, the results obtained for COD = 10 trace quite well the temporal evolution of O_3 recorded during a representative LSR day (31 December 2003) characterized by air masses coming from the Italian station. In fact, during this LSR day the O_3 concentrations systematically decreased at TNB-IC as is well reproduced

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by the PSS calculation (Fig. 8). The above results suggest that relatively high NO_x values can be transported from the Italian station to the measurement site leading to O_3 production in presence of sufficient solar radiation.

Conclusions

Analysis of hourly O_3 concentrations recorded for December over the five years 2001–2005, shows that for HSR days significantly higher O_3 values (21.3 ppbv) were recorded compared to LSR days (16.8 ppbv). Transport processes during strong wind events from the Antarctic continental area (SW–NW) could explain part of the high O_3 values recorded during HSR days. Three-dimensional back-trajectories confirm that air mass transport from the interior of the continent can significantly affect surface O_3 at the measurement site. If we assume that TNB-IC is affected by katabatic flows when local wind speed exceeds 6 m s^{-1} from SW–NW directions, this contribution amounts to 17% (3.4 ppbv) of the December mean O_3 concentration. Even if contributions from higher tropospheric levels cannot be ruled out, for coastal regions frequently affected by katabatic flows (i.e. TNB-IC) the contribution from the Antarctic plateau is probably more important, as these air masses can be enriched in photochemical O_3 produced by the precursors emitted by the snow pack during summer (Crawford *et al.* 2001, Oltmans *et al.* 2007).

The data also suggest that under high solar radiation fluxes, the main facilities of the Italian station are a source for surface O_3 at TNB-IC. In fact, during HSR days a significant (at the 95% confidence level) O_3 increase (+7%, 1.5 ppbv) has been recorded in conjunction with air masses originating from the main Italian station. A simple O_3 calculation based on NO_x–O_3 chemistry using the PSS approximation and driven by solar radiation fluxes provided by a TUV model was performed. During two representative HSR and LSR days, the daily evolution of the calculated O_3 concentrations compares favourably with observed data, assuming NO_x levels that are representative for local pollution. This further suggests that the emissions from the Italian station could affect O_3 levels at TNB-IC, which should be carefully considered when estimating background O_3 conditions at this measurement site.

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References

Allegrini, I., Ianniello, A., Vazzana, C., Montagnoli, M. & Valentini, F. 2000. Measurements for the determination of nitrogen containing species (NO_2 and NO_y) on Antarctica troposphere. *In* Colacino, M. & Giovanelli, G., *eds. Italian Research on Antarctic Atmosphere*. Bologna: Società Italiana di Fisica, 357–361.

Argentini, S. & Mastrantonio, G. 1994. Barrier winds recorded during two summer campaigns and their interaction with the katabatic floes as observed by a tri-axial Doppler Sodar. *International Journal of Remote Sensing*, **15**, 455–466.

Argentini, S., Del Buono, P., Della Vedova, A.M. & Mastrantonio, G. 1995. A statistical analysis of wind in Terra Nova Bay, Antarctica, for the austral summers 1988 and 1999. *Atmospheric Research*, **39**, 145–256.

Barrie, L.A., Bottenheim, J.W., Schnell, R.C., Crutzen, P.J. & Rasmussen, R.A. 1988. Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere. *Nature*, **334**, 138–141.

Barnard, J.C. & Long, C.N. 2004. A simple empirical equation to calculate cloud optical thickness using shortwave broadband measurements. *Journal of Applied Meteorology*, **43**, 1057–1066.

Beine, H.J., Honrath, R.E., Dominè, F., Simpson, W.R. & Fuentes, J.D. 2002. NO_x during background and ozone depletion periods at Alert: fluxes above the snow surface. *Journal of Geophysical Research*, **107**, 10.1029/2002JD002082.

Bromwich, H.D., Parish, T.R., Pellegrini, A., Stearns, C.R. & Weidner, G.A. 1993. Spatial and temporal characteristics of the intense katabatic winds at Terra Nova Bay, Antarctica. *Antarctic Research Series*, **61**, 47–68.

Bromwich, H.D., Monaghan, A.J., Powers, J.G., Cassano, J.J., He-Lin, W., Ying-Hwa, K. & Pellegrini, A. 2003. Antarctic Mesoscale Prediction System (AMPS): a case study from the 2000–01 field season. *Monthly Weather Review*, **131**, 412–434.

Carrasco, J.F. & Bromwich, D.H. 1995. A midtropospheric subsynoptic-scale vortex that developed over the Ross Sea and Ross Ice Shelf of Antarctica. *Antarctic Science*, **7**, 199–210.

Carpenter, L.J., Clemitshaw, K.C., Burgess, R.A., Penkett, S.A., Cape, J.N. & McFadyen, G.G. 1998. Investigation and evaluation of the NO_x/O_3 photochemical steady state. *Atmospheric Environment*, **32**, 3353–3365.

Cava, D., Schipa, S., Tagliazucca, M. & Giostra, U. 2004. Some characteristics of atmospheric boundary layer in an Antarctic coastal region. *In* Colacino, M., *ed. Italian Research on Antarctic Atmosphere and SCAR Workshop on Oceanography*. Bologna: Società Italiana di Fisica, 185–198.

Chudzynski, S., Czyzewski, A., Ernst, K., Pietruczuk, A., Skubiszak, W., Stacewicz, T., Stelmaszczyk, K., Szymanski, A., Sowka, I., Zwozdziak, A. & Zwozdziak, J. 2001. Observation of ozone concentration during the solar eclipse. *Atmospheric Research*, **57**, 43–49.

Crawford, J.H., Davis, D.D., Chen, G., Buhr, M., Oltmans, S., Weller, R., Mauldin, L., Eisele, F., Shetter, R., Lefer, B., Arimoto, R. & Hogan, A. 2001. Evidence for photochemical production of ozone at the South Pole surface. *Geophysical Research Letters*, **28**, 3641–3644.

Davis, D., Nowak, J.B., Chen, G., Buhr, M., Arimoto, R., Hogan, A., Eisele, F., Mauldin, L., Tanner, D., Shetter, R., Lefer, B. & McMurry, P. 2001. Unexpected high levels of NO observed at South Pole. *Geophysical Research Letters*, **28**, 3625–3628.

Draxler, R.R. & Rolph, G.D. 2003. *HYSPLIT* (*HYbrid Single-Particle Lagrangian Integrated Trajectory*) *Model access via NOAA ARL READY Website* (*http://www.arl.noaa.gov/ready/hysplit4.html*). Silver Spring, MD: NOAA Air Resources Laboratory.

Gerasopoulos, E., Zanis, P., Stohl, A., Papastefanou, C., Ringer, W., Tobler, L., Hubener, S., Gaggler, H.W., Kanter, H.J., Tositti, L. & Sandrini, S. 2001. A climatology of 7Be at four high-altitude stations at the Alps and the Northern Apennines. *Atmospheric Environment*, **35**, 6347–6360.

GRUZDEV, A.N. & STINOV, S.A. 1992. Tropospheric ozone annual variation and possible troposphere-stratosphere coupling in the Artic and Antarctic as derived from ozone sounding at Resolute and Amundsen-Scott stations. *Tellus*, **45B**, 89–98.

GRUZDEV, A.N., ELOKOV, A.S., MAKAROV, O.V. & MOKHOV, I.I. 1993. Some recent results of Russian measurements of surface ozone in Antarctica. a meteorological interpretation. *Tellus*, **45B**, 99–105.

HELMIG, D., OLTMANS, S.J., CARLSON, D., LAMARQUE, J.-F., JONES, A., LABUSCHAGNE, C., ANLAUF, K. & HAYDEN, K. 2007. A review of surface ozone in the polar region. *Atmospheric Environment*, 10.1016/j.atmosenv.2006.09.253.

JONES, A.E., WELLER, R., ANDERSON, P.S., JACOBI, H.-W., WOLFF, E.W., SCHREMS, O. & MILLER, H. 2001. Measurements of NOx emissions from the Antarctic snowpack. *Geophysical Research Letters*, **28**, 1499–1502.

OLTMANS, S.J., JOHNSON, B.J. & HELMIG, D. 2007. Episodes of high ozone amounts at South Pole during summer and their impact on the long-term surface ozone variation. *Atmospheric Environment*, 10.1016/j.atmosenv.2007.10.020.

MADRONICH, S. & FLOCKE, F. 1998. The role of solar radiation in atmospheric chemistry. *In* BOULE, P., *ed. Handbook of environmental chemistry*. Heidelberg: Springer, 1–26.

MURAYAMA, S., NAKAZAWA, T., TANAKA, M., AOKI, S. & KAWAGUCHI, S. 1992. Variations of tropospheric ozone concentration over Syowa Station, Antarctica. *Tellus*, **44B**, 262–272.

ROSCOE, H.K., KREHER, K. & FRIESS, U. 2001. Ozone loss episodes in the free Antarctic troposphere, suggesting a possible climate feedback. *Geophysical Research Letters*, **28**, 2911–2914.

SANDER, S.P. 2000. *Chemical kinetics and photochemical data for use in stratospheric modelling*. Evaluation no 14. JPL Publication 02–25. Pasadena, CA: NASA. http://jpldataeval.jpl.nasa.gov/

SEBALD, L., TREFFEISEN, R., REIMER, E. & HIES, T. 2000. Spectral analysis of air pollutants. Part 2: Ozone time series. *Atmospheric Environment*, **34**, 3503–3509.

SEINFELD, J.H. & PANDIS, S.N. 1998. *Atmospheric chemistry and physics: from air pollution to climate change*. New York: Wiley, 1326 pp.

STAEHELIN, J., THUDIUM, J., BUELHER, R., VOLZ-THOMAS, A. & GRABER, W. 1994. Trends in surface ozone concentrations at Arosa (Switzerland). *Atmospheric Environment*, **28**, 75–87.

TARASICK, D.W. & BOTTENHEIM, J.W. 2002. Surface ozone depletion episodes in the Arctic and Antarctic from historical ozonesonde records. *Atmospheric Chemistry and Physics*, **2**, 197–205.

TARASOVA, O.A. & KARPETCHKO, A.Y. 2003. Accounting for local meteorological effects in the ozone time-series of Lovozero (Kola Peninsula). *Atmospheric Chemistry and Physics*, **3**, 941–949.

VOLZ-THOMAS, A., PAETZ, H.-W., HOUBEN, N., KONRAD, S., MIHELCIC, D., KLUEPFEL, T. & PERNER, D. 2003. Inorganic trace gases and peroxy radicals during BERLIOZ at Pabstthum: an investigation of the photostationary state of NO_x and O_3. *Journal of Geophysical Research*, **108**, 10.1029/2001JD001255.

YANG, J., HONRATH, R.E., PETERSON, M.C., DIBB, J.E., SUMNER, A.L., SHEPSON, P.B., FREY, M., JACOBI, H.-W., SWANSON, A. & BLAKE, N. 2002. Impacts of snowpack emissions on deduced levels of OH and peroxy radicals at Summit, Greenland. *Atmospheric Environment*, **36**, 2523–2534.

WELLER, R., JONES, A.E., WILLE, A., JACOBI, H.-W., MCINTYRE, H.P., STURGES, W.T., HUKE, M. & WAGENBACH, D. 2002. Seasonality of reactive nitrogen oxides (NO_y) at Neumayer Station, Antarctica. *Journal of Geophysical Research*, **107**, 1687–1697.

WMO. 1995. *International Codes - vol. I.1* (*Annex II to WMO Technical Regulations*). *WMO–No. 306*. Geneva: World Meteorological Organization.