Year-round record of surface ozone at coastal (Dumont d'Urville) and inland (Concordia) sites in East Antarctica

Michel Legrand, S. Preunkert, Benjamin Jourdain, H. Gallée, Florence Goutail, R. Weller, Joël E Savarino

Year-round record of surface ozone at coastal (Dumont d'Urville) and inland (Concordia) sites in East Antarctica

M. Legrand,[1] S. Preunkert,[1] B. Jourdain,[1] H. Gallée,[1] F. Goutail,[2] R. Weller,[3] and J. Savarino[1]

Received 23 December 2008; revised 17 July 2009; accepted 5 August 2009; published 30 October 2009.

[1] Surface ozone is measured since 2004 at the coastal East Antarctic station of Dumont d'Urville (DDU) and since 2007 at the Concordia station located on the high East Antarctic plateau. Ozone levels at Concordia reach a maximum of 35 ppbv in July and a minimum of 21 ppbv in February. From November to January, sudden increases of the ozone level, up to 15–20 ppbv above average, often take place. They are attributed to local photochemical ozone production as previously seen at the South Pole. The detailed examination of the diurnal ozone record in summer at Concordia suggests a local photochemical ozone production of around 0.2 ppbv h^{-1} during the morning. The ozone record at DDU exhibits a maximum of 35 ppbv in July and a minimum of 18 ppbv in January. Mixing ratios at DDU are always higher than those at Neumayer (NM), another coastal Antarctic station. A noticeable difference in the ozone records at the two coastal sites lies in the larger ozone depletion events occurring from July to September at NM compared to DDU, likely due to stronger BrO episodes in relation with a larger sea ice coverage offshore that site. A second difference is the large day-to-day fluctuations which are observed from November to January at DDU but not at NM. That is attributed to a stronger impact at DDU than at NM of air masses coming from the Antarctic plateau. The consequences of such a high oxidizing property of the atmosphere over East Antarctica are discussed with regard to the dimethylsulfide (DMS) chemistry.

Citation: Legrand, M., S. Preunkert, B. Jourdain, H. Gallée, F. Goutail, R. Weller, and J. Savarino (2009), Year-round record of surface ozone at coastal (Dumont d'Urville) and inland (Concordia) sites in East Antarctica, *J. Geophys. Res.*, *114*, D20306, doi:10.1029/2008JD011667.

1. Introduction

[2] At clean remote regions such as Antarctica, we would expect an accumulation of surface ozone in winter and a photochemical destruction in spring-summer. As discussed by *Crawford et al.* [2001], the seasonal cycle of surface ozone at the coastal sites of Neumayer and McMurdo over the 1997–1999 years consistently shows a maximum in July and a minimum in January. In contrast, at the South Pole the summer minimum is delayed in February and high values often occur from November to January, suggesting that the lower atmosphere of central Antarctica experiences a surprisingly high photochemical activity during summer months. As discussed by *Davis et al.* [2001], the photo-denitrification of surface snow is responsible for high NO_x levels at that site (a few hundreds of pptv) which leads to high levels of OH (24 h averaged concentration of 2×10^6 molecules cm^{-3} [*Mauldin et al.*, 2001]). Another consequence of these high NO_x summer levels at the South Pole is a significant photochemical production of ozone that is indeed detected in the ozone record [*Crawford et al.*, 2001].

[3] The high level of oxidants over the Antarctic plateau was first thought to be limited to a shallow mixed layer (20 to 100 m) [*Davis et al.*, 2004]. More recently, on the basis of NO_x data gained using aircraft samplings [*Davis et al.*, 2008], OH concentrations as high as 3×10^6 molecules cm^{-3} were simulated within a layer of 50 to 150 m thickness over the high Antarctic plateau [*Wang et al.*, 2008]. This very oxidizing canopy may affect the atmospheric behavior of some key atmospheric species. For instance, DMS emitted in summer by phytoplankton present in the surface Antarctic Ocean represents the major source of aerosol in these regions. Its oxidation into sulfur aerosol during its travel toward the Antarctic plateau will depend on the type and the level of oxidants.

[4] Conversely, the export of inland air masses may impact the atmospheric chemistry at coastal regions but the importance of this effect on the ozone budget of these regions remains unclear. As previously mentioned, the 1997–1999 ozone record at the coastal sites of Neumayer and McMurdo suggested that these two sites were not significantly impacted by ozone photochemically produced over the Antarctic plateau [*Crawford et al.*, 2001]. The more

[1] Laboratoire de Glaciologie et Géophysique de l'Environnement, Centre National de la Recherche Scientifique, Saint Martin d'Hères, France.
[2] Service d'Aéronomie, Institut Pierre-Simon Laplace, Paris, France.
[3] Alfred-Wegener-Institut für Polar- und Meeresforschung, Bremerhaven, Germany.

0148-0227/09/2008JD011667

extended study of surface ozone from *Helmig et al.* [2007] confirmed such an absence of impact of inland air masses at the coastal sites of Neumayer and Halley, but show that, at least in 2004, the McMurdo site experiences several times in November–December rapid increases of ozone by 5–10 ppbv above the seasonal background (not seen over the 1997–2000 years by *Crawford et al.* [2001]). Finally, such increases in November and December were also detected at the two other coastal sites of Sanae and Syowa.

[5] In order to generalize results gained at the South Pole, surface ozone measurements were initiated in February 2007 at the Concordia station located on the east part of the Antarctic plateau. One of the aims was here to scrutinize the ozone level at a continental site where diurnal sunlight variations take place in contrast to the unchanged 24 h sunlight conditions encountered at the South Pole. In addition, in order to complete information at coastal regions, in particular those more exposed to katabatic airflow than the previously investigated sites, surface ozone measurements were initiated in 2004 at the coastal station of Dumont d'Urville (DDU) located on the east flank of the Antarctic continent.

2. Sites and Methods

[6] Year-round surface ozone measurements were conducted in 2007 at the Concordia Station (central Antarctica, 75°06′S, 123°20′E, 3220 m above sea level) located 1100 km away from the nearest coast of East Antarctica. Measurements were made continuously with a UV absorption monitor (Thermo Electron Corporation model 49I, Franklin, Massachusetts). The instrument and the inlet of the sampling line are located at 17 m above the ground level. The data collected at 15 s intervals are reported here as 15 min or hourly averages. Measurements were occasionally disturbed for a few hours when the wind was blowing from the power supply building of the station (sector 20°W–50°W). In addition, under very low wind speed conditions (less than 2 m s^{-1}) measurements were disturbed for a few minutes when vehicles were leaving the station around 0800 and 1400 local time (LT) or back from work at 1200 and 1900 LT. Such events can be easily identified by fast changes of the ozone level in the 15 min record and were discarded from the data set. At the coastal site of DDU (66°40′S, 140°01′E, 40 m above the sea level) ozone measurements started in 2004. They will be compared to those made at the same time at other coastal sites such as Neumayer (70°37′S, 8°22′W). In very rare occasions, the wind was blowing from 35°E at DDU and the plume of the station power supply impacted the ozone line inlet.

[7] In order to assess the impact of atmospheric turbulence on the vertical mixing of chemical species such as ozone or NO_x, a simulation of the atmospheric circulation over the Antarctic ice sheet has been performed using the limited area model MAR (Modèle Atmosphérique Régional), for the period from 1 October 2007 until 29 February 2008. The horizontal resolution of MAR is 80 km. The model top level is situated at 1 hPa, and there are 60 levels in the vertical. The vertical resolution is roughly 3 m up to 40 m above the surface, and decreases upward. MAR has been developed at the Laboratoire de Glaciologie et Géophysique de l'Environnement for polar regions with a horizontal resolution of 80 km. It uses primitive equations with the hydrostatic assumption. A description of the model is given by *Gallée and Gorodetskaya* [2009] and reference therein. Briefly the turbulence scheme is based on an E-e scheme and on the Monin-Obukhov Similarity theory (MOS), respectively, outside and inside the lowest model layer, assumed to be the Surface Boundary Layer (SBL). A dependence of the Prandtl number on the Richardson number has been included in order to take into account the less efficient turbulent transport of heat under very stable conditions. MAR simulations have been recently validated with respect to observations from Automatic weather station at Concordia [*Gallée and Gorodetskaya*, 2009]. The boundary layer height was computed from MAR simulations by taking the height where the turbulent kinetic energy decreases below 5% of the value in the lowest layer of the model.

[8] Regular measurements of UV irradiances were done by using a 501 UV-Biometer from Solar Light. The instrument provides the biological effectiveness of the solar radiation accumulated every 5 min in the 290–315 nm wavelength range. The UV-Biometer was previously calibrated by the manufacturer before its set up at Concordia in January 2007.

3. Seasonal Cycle of Ozone at Concordia

[9] Hourly averaged ozone mixing ratios at Concordia from February 2007 to February 2008 are reported in Figure 1a. Large day-to-day fluctuations take place from early November to February. During that period, hourly averaged values often exceed the winter maximum of 35 ppbv. On a monthly basis (Figure 1b), mixing ratios reach a maximum close to 35 ppbv in July, decrease from August to February (~21 ppbv) but exhibit a secondary maximum of 31 ppbv in November. As seen in Figure 1b the seasonal ozone cycle at Concordia is very similar to the one observed at the South Pole. As first discussed by *Crawford et al.* [2001] for the South Pole, the occurrence of a secondary maximum in November is surprising since such very remote regions would experience winter accumulation of ozone transported from other regions followed by photochemical destruction in spring and summer. The authors concluded that these relatively high ozone levels are related to a photochemical production induced by the high NO_x levels generated by the photodenitrification of the Antarctic snowpack. The Concordia ozone record thus confirms that this process is not confined to the South Pole region but takes place over a large area of the Antarctic plateau as recently stated by *Davis et al.* [2008].

[10] The hourly variability of surface ozone levels at Concordia in summer is detailed in Figure 2. It shows sometimes very fast increases of the ozone level (up to 15 ppbv within 12 h), for instance the events from 7 December, 2000 LT, to 8 December, 0800 LT, 12 December, 2000 LT, to 13 December 0800 LT, and 25 December, 2000 LT, to 26 December, 0800 LT. If attributed to a local photochemistry these rapid changes would suggest a local ozone production rate of 30 ppbv per day. This value is some 5 times higher than model calculations suggesting an upper limit of ozone production rate for South Pole conditions of 3.6/6.0 ppbv per day [*Crawford et al.*, 2001]

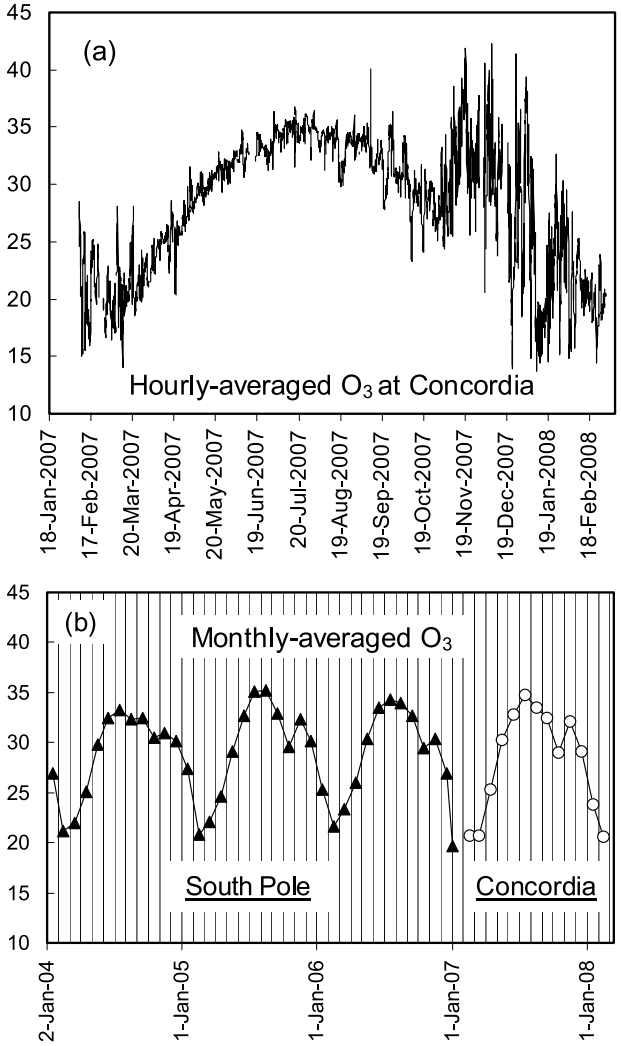

Figure 1. (a) Hourly averaged surface ozone mixing ratio (in ppbv) at Concordia from February 2007 to February 2008. (b) Monthly averaged surface ozone mixing ratio (in ppbv) at the South Pole (2004–2006) (http://gaw.kishou.go.jp/cgi-bin/wdcgg/catalogue.cgi) and Concordia (2007).

and 4.8/6.5 ppbv per day [*Chen et al.*, 2004]. Note also that these fast ozone increases at Concordia occurred at night when the mean UVb (290–315 nm) irradiance was relatively low (~0.1 W m^{-2} from 2000 to 0600 LT) against a constant value 0.3 W m^{-2} over 24 h at the South Pole or 0.9 W m^{-2} from 0800 to 1600 LT at Concordia. We can thus conclude that these fast changes of ozone at Concordia likely result from transport. In the following we examine the effect of the air origin on the ozone level by analyzing their trajectory.

[11] To characterize air masses arriving at Concordia 5 day backward trajectories were computed with the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (R. R. Draxler and G. D. Rolph, NOAA Air Resources Laboratory, Silver Spring, Maryland, 2003, available at http://www.arl.noaa.gov/ready/hysplit4.html) twice per day (at 0000 and 1200 UTC, i.e., at 0800 and 2000 LT) for November–December 2007 and January 2008. Two atmospheric levels were considered above Concordia as starting point to compute the back trajectories: 3250 and 3500 m above sea level (i.e., 20 and 270 m above the Concordia ground, respectively). An isentropic vertical motion calculation method was applied to reanalyze the data set. Back trajectories remain very similar at the two levels and we only show those at 3250 m above sea level. Ozone levels can be related to three different categories of situation based on air mass back trajectories. The synoptic-scale origins of air masses were attributed to be marine, coastal, and continental origin. Marine origin is attributed when during the 5 days air masses have traveled at least 1 day over the ocean. Coastal and continental origins refer to air masses having traveled only over the Antarctic continent in regions of altitudes lower and higher than 2500 m asl, respectively. This limit was chosen on the basis of the study from *Frey et al.* [2005] showing that enhanced surface ozone levels were not seen in Antarctic regions located below 2500 m asl. For continental origin we separate those coming from East and West Antarctica.

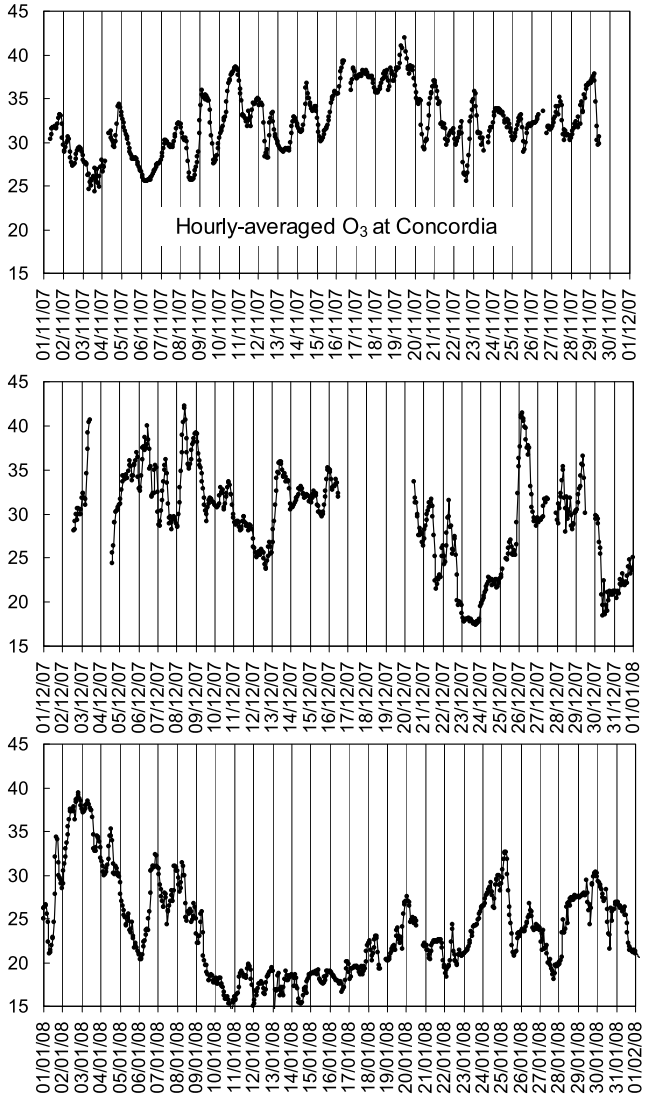

Figure 2. Hourly averaged surface ozone mixing ratio (in ppbv) at Concordia in summer (November 2007 to January 2008). The vertical lines refer to local midnight time.

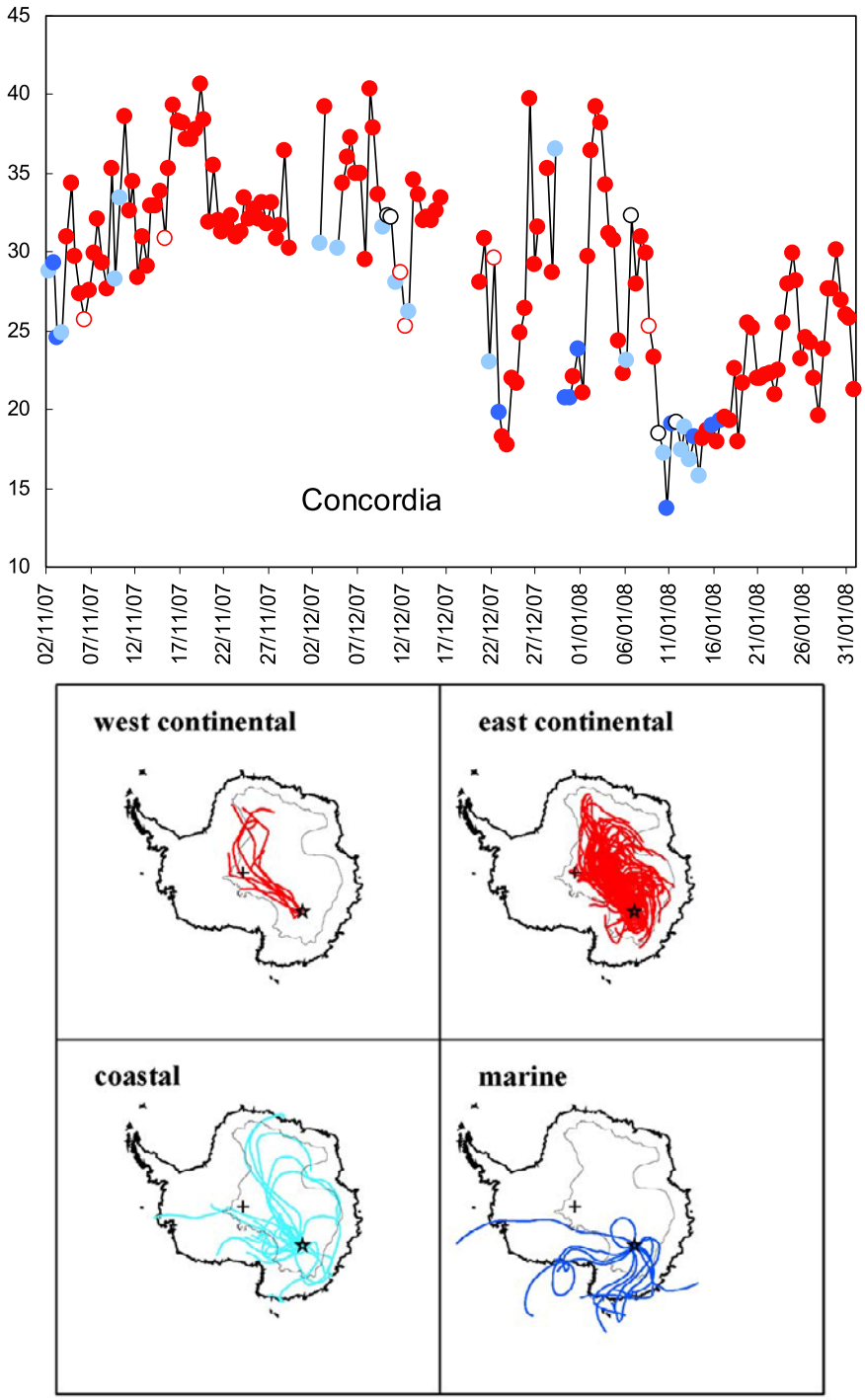

Figure 3. (top) Ozone mixing ratios (in ppbv) at Concordia from November 2007 to January 2008 at 0800 and 2000 local time (LT). Blue points refer to air mass transport from the ocean (dark blue) or from coastal Antarctica (light blue) (see text). Red circles refer to air mass transport from inland East (solid circles) or West (open circles) Antarctica. Open black circles correspond to mixed conditions. (bottom) Corresponding 5 day backward trajectories.

[12] Ozone mixing ratios at Concordia in November (Figure 3) always exceeded the mean value of around 22 ppbv observed at Neumayer, a site not significantly impacted by photochemical ozone production related to the presence of the Antarctic snowpack (see discussions in section 5). The beginning of November was characterized at Concordia by a rather low ozone value (27.6 ppbv from 2 November in the evening to 3 November in the morning) coinciding with the single occurrence of marine air input during that month (Figure 3). For the rest of November, back trajectories indicate most of the time a continental origin except late 9 November when air arrived from coastal regions and the ozone level was temporary decreased. Note that, when continental air masses were occasionally coming

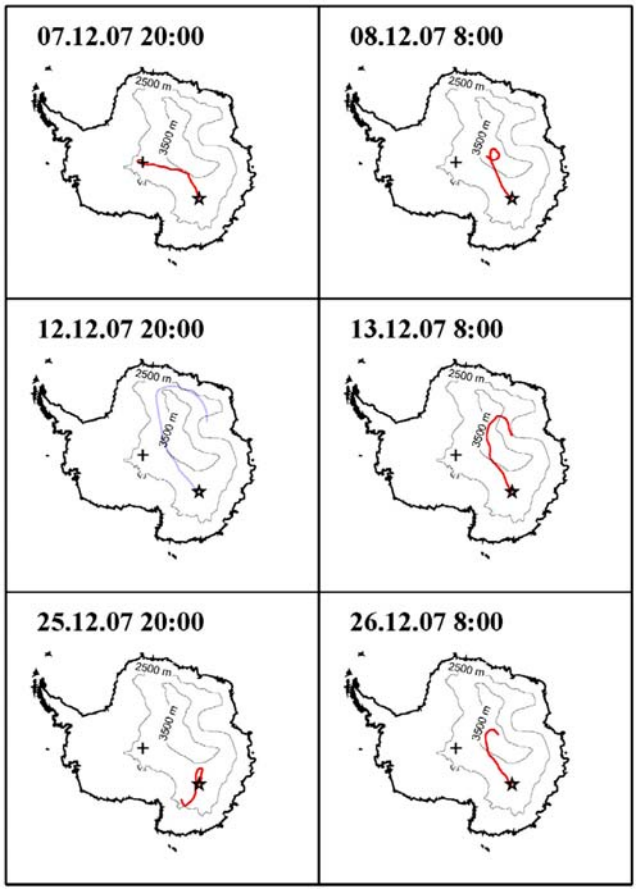

Figure 4. Change of 5 day backward trajectories at Concordia from 7 December, 2000 LT, to 8 December, 0800 LT, from 12 December, 2000 LT, to 13 December, 0800 LT, and from 25 December, 2000 LT, to 26 December, 0800 LT, that were accompanied by a sudden increase of ozone levels (section 3).

from West Antarctica (open red circles in Figure 3) the ozone level tended to slightly decrease. More variable conditions took place in December and January (Figure 3). Advection of marine air masses reached Concordia in two occasions (22 December and 30/31 December) coinciding with the lowest ozone value for that months (20–25 ppbv, Figure 3). More frequently than in November air masses coming from coastal regions reached the site and were generally accompanied by a moderate decrease of the ozone level. Even when continental conditions with air arriving from East Antarctica were maintained sudden changes from day to day took place (from 7 December, 2000 LT, to 8 December, 0800 LT, and from 25 December, 2000 LT, to 26 December, 0800 LT). As seen in Figure 4, these two sudden increases of the ozone level coincided with a change of the airflow bringing air from the highest part of the East Antarctic plateau. January was characterized by a long period of continental transport interrupted for several days by successive marine inputs (from 10 to 17 January, Figure 3). Over this mid-January time period the ozone level was maintained at the lowest level of the summer season. At that time ozone mixing ratio remained below 20 ppbv (down to 16 ppbv from 10 January in the evening to 11 January in the morning). These values are closed to the mean value of 15.5 ppbv observed at the coastal site of Neumayer in January. From this discussion it appears that the synoptic origin of air masses reaching Concordia influences the ozone level, with the lowest values observed when the air masses spent at least one day above the ocean during the previous 5 days and the highest values when the air masses have always traveled over the highest part of the Antarctic plateau.

[13] The comparison of ozone levels observed at Concordia during the different marine events is interesting. For instance, whereas on 10 January the ozone level of 16.3 ppbv was only slightly higher than the one observed at Neumayer at that time of the year (15.4 ppbv), a larger difference took place on 2 November (27.6 ppbv at Concordia against 23 ppbv at Neumayer). The 5 day backward trajectories for 10 January indicate that the marine air mass had traveled less than 1 day over the Antarctic continent in regions of altitudes higher than

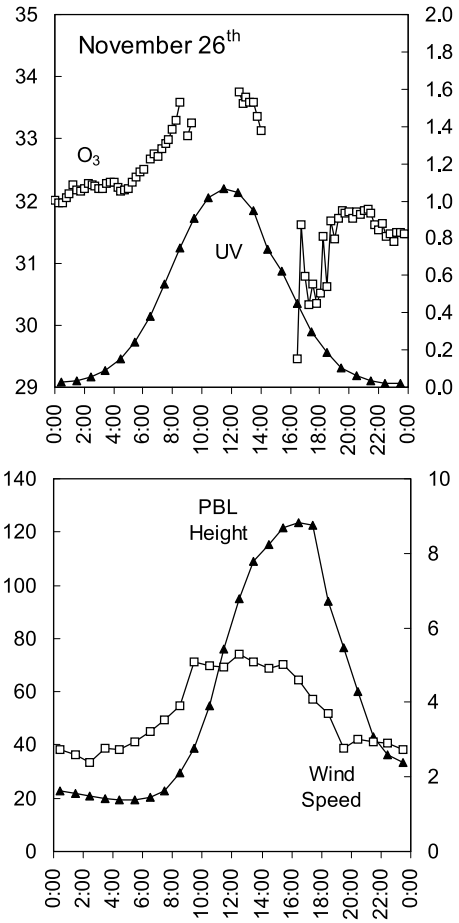

Figure 5. (top) The 26 November diurnal change of ozone mixing ratio at Concordia (open square, left scale in ppbv) and UV irradiance (triangles, right scale in W m^{-2}). (bottom) Simulated PBL height (triangles, left scale in meters) (see section 2) and wind speed (squares, right scale in m s^{-1}) as observed from the Concordia Automatic Weather Station (AWS 8989) of University of Wisconsin-Madison (available at ftp://amrc.ssec.wisc.edu/pub/aws/).

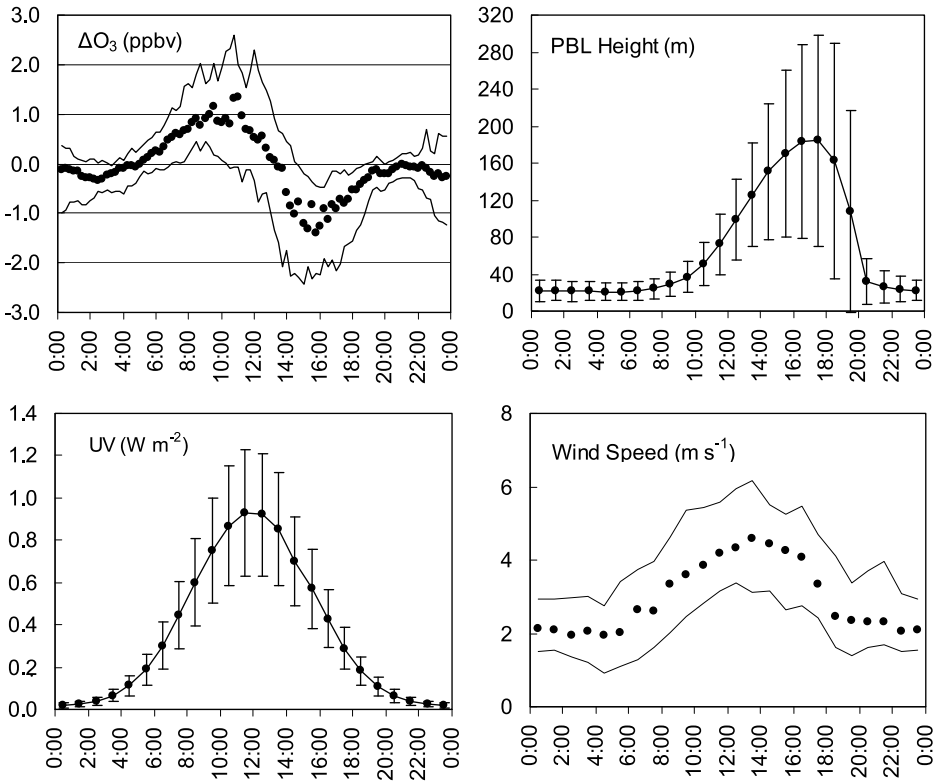

Figure 6. (top left) Residual change of ozone (ΔO_3) with respect to the general change from early morning to late evening observed over 40 days characterized by stable continental conditions (see section 4). Circles refer to the median value and the two solid lines to the 25th and 75th quartiles. (top right) Mean ($\pm 1\sigma$) simulated PBL height over the 40 days. (bottom left) Mean ($\pm 1\sigma$) of UV irradiance over the 40 days. (bottom right) Wind speed as observed from the Concordia Automatic Weather Station (circles refer to the median value, and the two solid lines refer to the 25th and 75th quartiles) over the 40 days.

2500 m asl, strongly limiting its filling with ozone photo chemically produced from the NO_x snowpack emissions. It was not the case on 2 November for which the 5 day backward trajectories indicate a longer time contact of the air mass (2.5 days) with the high Antarctic plateau. If we assume that the air mass reaching Concordia on 2 November initially contained 23 ppbv of ozone, the ozone level of 27.6 ppbv at its arrival corresponds to a mean increasing rate of 1.7 ppbv per day. Since during transport exchange between boundary layer and free troposphere may dilute the amount of ozone that had been produced within the boundary layer, this value represents a lower limit of the ozone production within the boundary layer.

[14] From 12 to 29 November, backward trajectories indicate a permanent air mass transport from the East Antarctic plateau to Concordia (Figure 3). Over that period the UV irradiance at noon at Concordia remained high (1.0–1.3 W m^{-2}) from 12 to 19 November and was then reduced (0.65 W m^{-2} at noon on 22 and 23 November). From 12 to 19 November the surface wind speed at Concordia remained close to 3 m s^{-1}. The ozone level gradually increased from ~30 ppbv on 13 November to ~40 ppbv on 19 November corresponding to a mean increasing rate of 1.4 ppbv per day. Under these sustained sunny conditions and air masses reaching Concordia having continuously traveled over East Antarctica and neglecting possible change of the vertical exchange between boundary layer and free troposphere, this change of ozone may correspond to a mean daily photochemical production of ozone having taken place in the air mass during its travel over the East Antarctic plateau. If is correct, that is twice lower than the one (5–7 ppbv per day or even more) derived under sustained stable boundary and sunny conditions at the South Pole by *Helmig et al.* [2008]. Even thought air masses at the South Pole and Concordia experience different exposure to UV radiations (~0.3 W m^{-2} over 24 h at South Pole, from 0.01 W m^{-2} at midnight to ~1 W m^{-2} at noon at Concordia), it seems that the ozone production is at least 2 times lower in the Concordia region than in the vicinity of the South Pole. The ozone production rate in the region of Concordia is further discussed in section 4.

4. Diurnal Cycle of Ozone in Summer at Concordia

[15] Though the Concordia and the South Pole sites experience different photochemical conditions (see further discussions below), the calculated photochemical ozone production at the South Pole can be as high as 3.6–6.5 ppbv per day (i.e., 0.15–0.30 ppbv per hour over the entire

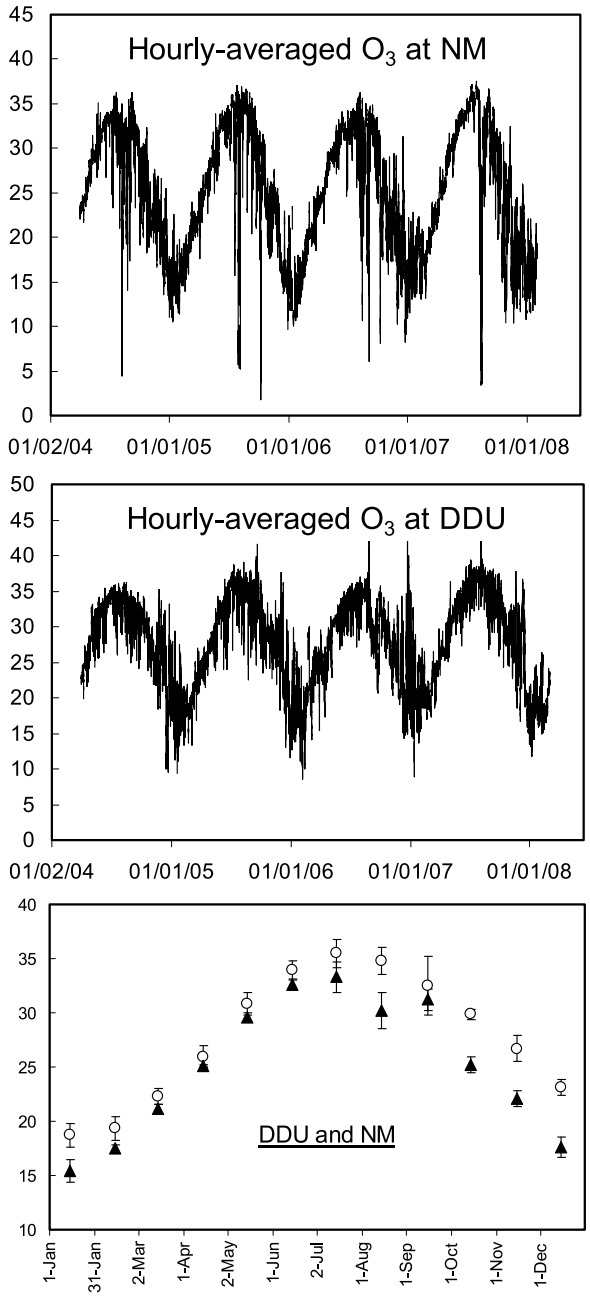

Figure 7. Hourly averaged surface ozone mixing ratio (in ppbv) at (top) Neumayer and (middle) Dumont d'Urville from early 2004 to early 2008. (bottom) Monthly averaged ozone mixing ratio ($\pm 1\sigma$) at Neumayer (triangles) and Dumont d'Urville (circles).

course of the day). If similar at Concordia, the local ozone production would be detectable by examining the diurnal ozone change following the diurnal change of solar radiations there.

[16] Since as discussed in section 3, the day-to-day change of air mass origin sometimes strongly modulates the ozone levels, in order to identify a possible photochemical ozone production we examine the diurnal cycle over the days for which (1) the 5 days backward trajectories indicate transport from inland East Antarctic and (2) no significant change of the surface wind direction at Concordia had occurred over the course of the day. On the 80 days of ozone measurements (from 1 November to 31 January), 40 days fit with the two preceding criteria, the 40 others corresponding to west Antarctica, coastal or marine origins of the air mass and/or changes of the surface wind direction during the day. At least at the first order, this approach would minimize the influence of changing synoptic transport of air masses from different source regions on the diurnal ozone change. Very rare were the days over which the change of ozone from early morning to evening was less than 1 ppbv. An example of such a case is reported in Figure 5, showing an increase of ozone levels above average in the morning followed by a decrease during the afternoon. Apart from this singular case and to account for the change of ozone over the course of the day resulting from a possible in homogeneity of ozone level over the East Antarctic plateau, for each of the considered 40 days the raw data were corrected by subtracting, when exist, the change between early morning and late evening (sometimes an increasing or a decreasing trend). The residual values calculated each 15 min (ΔO_3) are reported in Figure 6. The ΔO_3 values remain close to zero early morning (from 0000 to 0500 LT) and evening (from 1900 to 2400 LT). The diurnal cycle of ΔO_3 is characterized by a regular increase of values from 0500 to 1100 LT (from 0 to 1.2 ppbv), a decrease down to -1 ppbv at 1500–1600 LT and a reincrease toward zero at 19:00.

[17] As seen in Figure 6, such a diurnal change of residual ozone levels with respect to the general diurnal trend seems to be related to the diurnal change of sunlight radiations. Indeed, in contrast to the South Pole where no daily variations of sunlight takes place, solar radiations at Concordia are strongly reduced during the night hours compared to the day hours. A consequence of this diurnal radiation cycle is a change of the sensible heat flux during the course of the day, leading to an increase of the PBL height during the afternoon. This phenomenon is well simulated by the MAR simulations (Figures 5 and 6) and may explain the observed drop of ozone levels in the afternoon at Concordia with respect to the rest of the day. Another consequence of the increase of solar radiations at Concordia from night to day hours would be an enhancement of the photochemical cycles of NO_x emitted from the snow surface, and hence an increase of the local ozone production rate. Figure 6 shows a mean ozone increase of 0.2 ppbv per hour from 0500 to 1100 LT that can be reasonably attributed to a local photochemical production taking place during the morning when there are enough solar radiations and the ozone production remains confined within a thin stable PBL. This value at Concordia lies in the upper range (0.15–0.30 ppbv per hour) of the local photochemical ozone production estimated for the South Pole conditions but a comparison between the two sites remains difficult. Indeed, the UV irradiance at Concordia is higher in the morning at Concordia (0.3 W m^{-2} at 0700 LT and 0.9 W m^{-2} at 1200 LT) than the one experienced over the entire day at the South Pole (0.3 W m^{-2}). That would strengthen the hourly ozone production during the morning at Concordia with respect to the one at the South Pole. The ozone production rate also depends of the NO_x level. Under the constant solar radiations at the South Pole, *Chen et al.* [2004] showed that up to 150 pptv of NO the ozone production increases toward

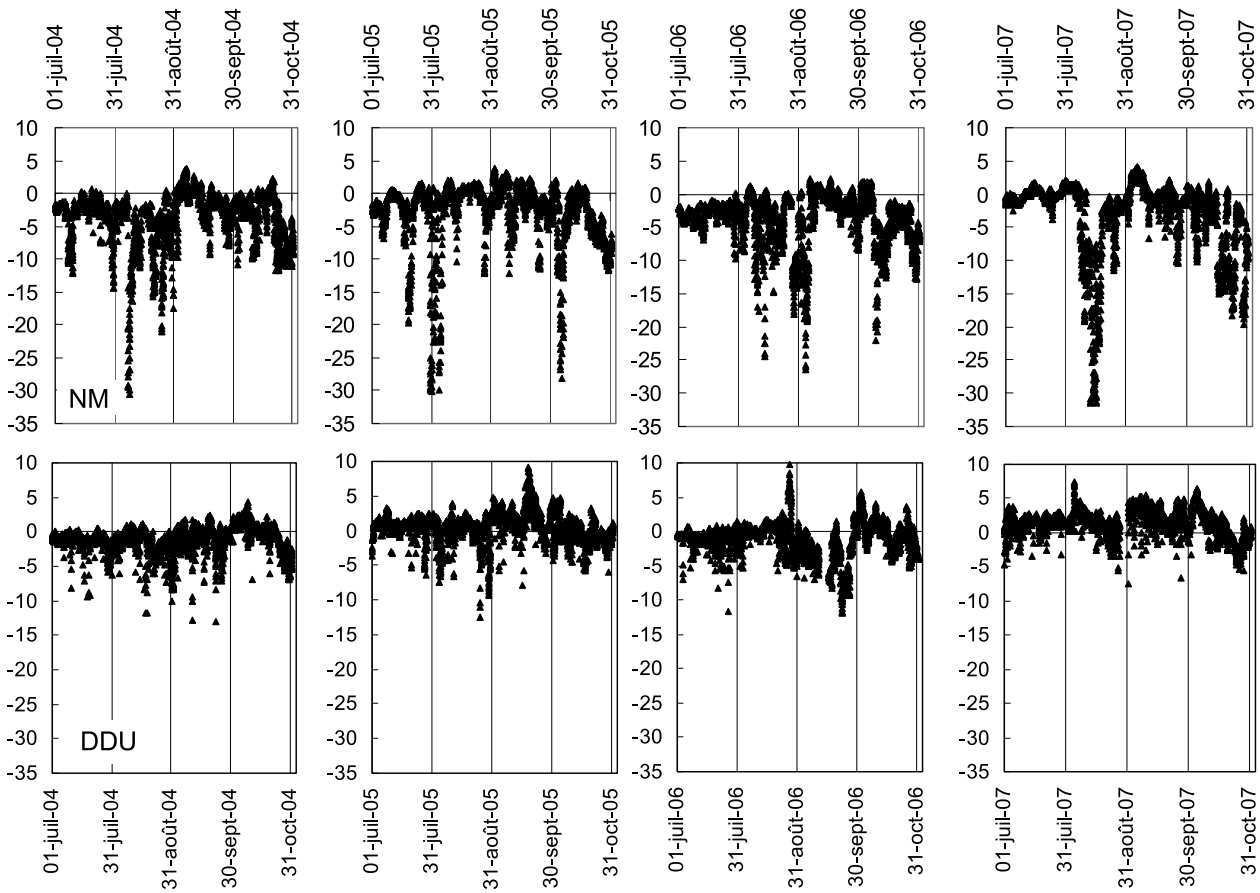

Figure 8. Drop of hourly ozone mixing ratio (in ppbv) with respect to background values from July to September (see section 5) at (top) NM and (bottom) DDU over the 2004–2007 years. Background values of 35.5, 35.0, 32.5, and 32.0 ppbv were assumed for July, August, September, and October, respectively.

0.15–0.30 ppbv per hour with the NO levels but higher NO levels slow down the ozone production (0.08 ppbv per hour with NO level of 600 pptv). Therefore, the absence of NO_x data at Concordia renders difficult to compare the two sites in terms of local ozone production. Even an estimate of the NOx level at Concordia in the light of the South Pole data is not easy since the NO_x flux emitted by the snowpack is dependent on the UV irradiance [*Jones et al.*, 2001] and would be higher at Concordia during late morning than at the South Pole, this latter acting however at all time of the day. Furthermore the atmospheric lifetime of NO_x within the PBL at Concordia would change over the course of the day. To date, during a flight carried out under high sunlight conditions at Mid point, a site similar to Concordia with respect to solar zenithal angles, D. L. Slusher et al. (Results from the ANTCI 2005 Antarctic Plateau Airborne Study, submitted to *Journal of Geophysical Research*, 2009) reported NO mixing ratios in the range of 50 pptv below 50 m above the snow surface. Such a NO level clearly permits a significant ozone production (0.12 ppbv per hour under the South Pole conditions [*Chen et al.*, 2004]).

[18] In conclusion, the diurnal cycle of the UV irradiance at Concordia significantly modulates the ozone levels with a significant local ozone production during the morning when a thin PBL (<50 m) is maintained. Later in the afternoon, the high solar radiations leads to a strong increase of the PBL height, and the less confined ozone production cannot be detected.

5. Seasonal Cycle of Ozone at Coastal Sites

[19] Figure 7 compares the hourly averaged surface ozone mixing ratios at DDU and NM over the last 4 years. Noticeable differences between the two sites appear both in winter and summer. In winter, the very large ozone depletion events (ODE) that occur from July to October at NM, if exist at DDU, remain far less pronounced (Figure 8). For instance, drops of the ozone level as large as 15 ppbv that occurred 3% of the time at NM are never detected at DDU. Moderate drops of 5 ppbv are commonly observed at NM (22% of the time) at NM but remain rare at DDU (3% of the time). This difference between the two sites is likely the result of the larger and more frequent BrO events in the region of NM compared to DDU as suggested by the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) satellite data. The 2004–2007 ozone record at NM indicates the lowest August ozone level in 2004 (28.9 ppbv instead of 32.5 ppbv in August 2005) consistently with the SCIAMACHY data (http://www.iup.uni-bremen.de/doas/scia_data_browser.htm) that show tropospheric BrO vertical column densities over a large area (up to latitudes as low as 58°S) of the Atlantic Ocean larger in August 2004 ($>8.5 \times 10^{13}$ molecules cm^{-2})

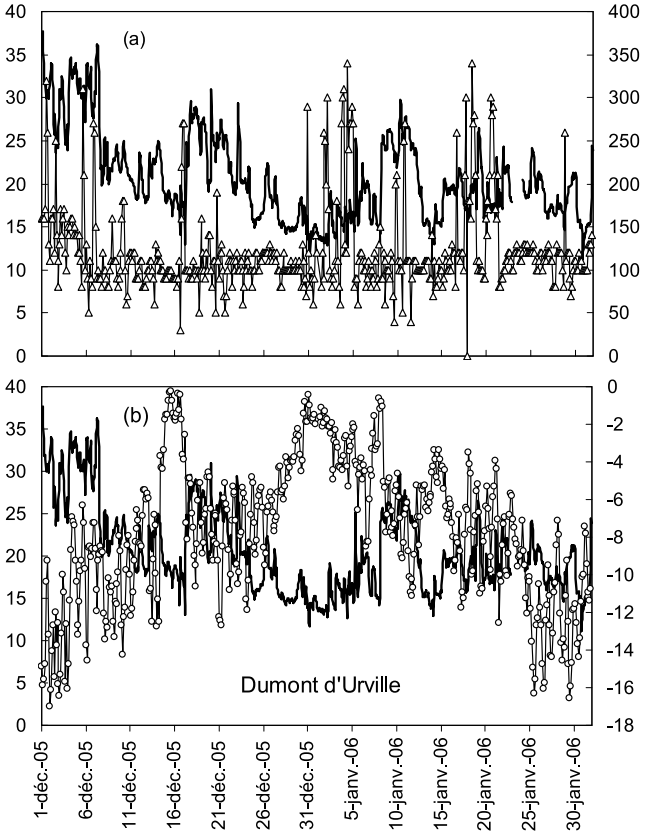

Figure 9. Hourly averaged ozone mixing ratio at DDU in December 2005 and January 2006 (solid lines, in ppbv left scale) versus (a) the local wind direction (triangles, in °E right scale) and (b) the dew point (circles, in °C right scale).

than in August 2005 (7.5×10^{13} molecules cm^{-2}). In August 2004, the vertical column densities over the Indian Ocean only reach 7.0×10^{13} molecules cm^{-2} over a very narrow latitude belt. This regional difference in the occurrence of the BrO events is probably related to a larger area of 1 year old sea ice cover at the end of winter in the Atlantic Ocean that faces NM (2500 km) than in the Indian Ocean that faces DDU (600 km). In addition, it has to be emphasized that NM is most of the time exposed to easterly flow bringing air masses from the Atlantic Ocean whereas DDU is more exposed to inland than oceanic air masses [*König-Langlo et al.*, 1998].

[20] From November to January the ozone record at DDU exhibits numerous sudden increases up to values close to the midwinter maximum (Figure 7). Such a pattern of the ozone summer record at a coastal Antarctic site differ from the Neumayer one where, as previously noted by *Crawford et al.* [2001] for 1997–1999 years and *Helmig et al.* [2007] for 2004, no large enhancements of ozone level are not detected during spring-summer. As a consequence, the monthly mean ozone levels at DDU exceed those at NM by a few ppbv, the difference reaching a maximum of 5.5 ppbv in December (Figure 7) for over the 2004–2007 years. The case of the McMurdo site appears to be intermediate, from no increase in spring-summer like at Neumayer and large and frequent increases like at DDU. For instance, the monthly mean level of ozone in December 2004 was 16.3, 19.3, and 22.2 ppbv at NM, McMurdo, and DDU, respectively.

[21] The summer ozone record at DDU has been examined in the light of the surface wind direction. In general this exercise was not very conclusive as shown for the summer 2005/2006 in Figure 9. This summer was characterized by three periods over which the ozone level was relatively high: 31 ppbv from 1 to 7 December, 25 ppbv from 18 to 21 December and from 8 to 12 January. These values are well above the 15 ppbv record at NM at that time of the year. Over this summer the expected value of 15 ppbv was only reached from 27 December to 5 January and 13–15 January. Over the high ozone level period in early December, the wind direction suggests that indeed air masses came from the Antarctic plateau (wind direction well above 100°E). More unclear is the situation from 18 to 21 December and from 8 to 12 January with wind direction remaining rather close to 100°E. This wind direction corresponds to wind blowing along the coast but does not indicate if the air mass was previously traveling over the ocean or came from the Antarctic plateau. Examination of ozone levels versus backward trajectories (Figure 10) is more fruitful. The three periods of high ozone levels correspond to days during which air masses came from the Antarctic plateau (above 2500 m asl). Conversely low ozone levels (close to 15 ppbv) are observed when air masses came from the ocean. Note also that the change from marine to continental flow is, as expected, accompanied by a large increase of the dew point (Figure 9). This discussion suggests that the high levels of ozone often recorded at DDU in summer are related to air masses coming from the high Antarctic plateau. The absence of significant impact of inland air masses at NM compared to DDU is due to a large difference in the regional topography at the two sites [*König-Langlo et al.*, 1998].

[22] The high ozone levels that are sometimes observed at DDU are almost as high as those observed over the high plateau at Concordia or South Pole. For instance, beginning of December 2005 the high values observed at DDU (31 ± 3 ppbv, Figure 10) were caused by air masses arriving from the Antarctic plateau. At the same time the ozone level at the South Pole was 35 ± 3.6 ppbv. The difference in the ozone levels between the two sites over this period is expected to be larger if one simply considers the dilution during the transport to the coast of an ozone rich air mass parcel of PBL originated from the high East Antarctic plateau. In fact, simulated NO_x emissions over the entire Antarctic continent predicts the highest NO_x mixing ratios over the central part of the East Antarctic plateau [*Wang et al.*, 2008], and due to the nonlinearity of the HO_x chemistry the highest OH levels and ozone photochemical production are predicted in downslope drainage area of East Antarctica. As an example, along 140°E the maximum OH concentration (4×10^6 molecules cm^{-3}) is simulated at 68°S (i.e., 200 km from DDU) with OH values exceeding 3×10^6 molecules cm^{-3} in a layer of 100 m thickness. The proximity from DDU of this very oxidizing canopy may explain the observed high ozone levels under continental flow conditions.

6. Implications for the Sulfur Chemistry at Coastal Antarctic Regions

[23] We here discuss the impact of our findings on the atmospheric chemistry of DMS at coastal Antarctic sites in

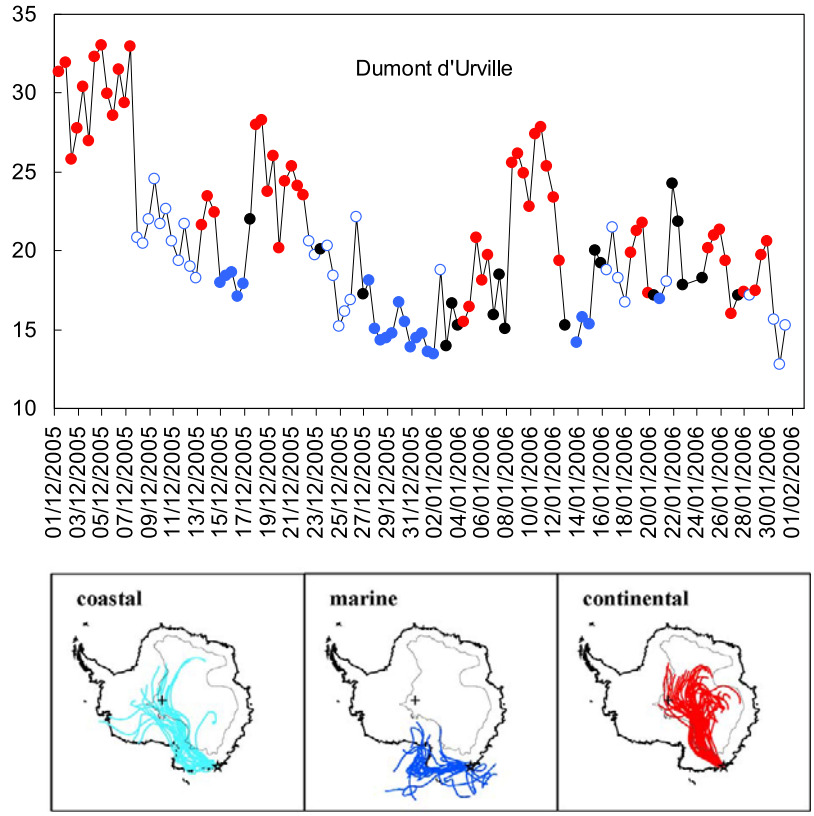

Figure 10. (top) Ozone mixing ratio (in ppbv) at Dumont d'Urville from December 2005 to January 2006 at 1000 and 2200 LT. Blue points refer to air mass transport from the ocean (solid blue circles) or coastal Antarctica (open blue circles) (see section 5). Red points refer to air mass transport from inland Antarctica (above 2500 m asl). Black circles correspond to mixed conditions. (bottom) Corresponding 5 day backward trajectories.

summer when high DMS amount is emitted from the Antarctic ocean. The most efficient atmospheric oxidants of DMS are OH, BrO, and NO_3 whereas others like Cl, IO, and O_3 are less efficient (see *Barnes et al.* [2006] for a review). In summer only OH and BrO may efficiently compete in oxidizing the DMS.

[24] Previous studies dealing with atmospheric DMS and its oxidation products in summer at coastal Antarctic sites had first considered only the OH chemistry (see *Davis et al.* [1998] for Palmer, *Legrand et al.* [2001] and *Jourdain and Legrand* [2001] for DDU). At the coastal Antarctic site of Palmer, diurnal averaged OH concentrations ranging from 1×10^5 to 2×10^5 radicals cm^{-3} were observed in February [*Jefferson et al.*, 1998]. Model simulations reproduce fairly well observations and indicate that the primary source of OH at Palmer is related to the reaction $O(^1D) + H_2O \rightarrow 2OH$ where $O(^1D)$ is produced by the ozone photolysis. More recently, measurements of BrO made over 1 year at Halley by *Saiz-Lopez et al.* [2007] indicate a mean level of 3 pptv during January–March. Such high BrO levels in summer make the BrO reaction on DMS producing DMSO four times faster that the one with OH (addition pathway) [*Read et al.*, 2008] whose levels reach 4×10^5 radicals cm^{-3} at that site [*Bloss et al.*, 2007].

[25] For DDU where no OH measurements are available, the IMAGE model simulated diurnal averaged OH concentrations for January close to 2×10^5 radicals cm^{-3} [*Pham et al.*, 1995]. These simulations which did not consider the NO_x emissions from the snow over the Antarctic continent predict 17–18 ppbv of ozone at DDU in January. Since we found that ozone-rich inland Antarctic air masses often reach DDU we may expect larger OH concentrations than those predicted by models. 3D model simulations of the photochemical impact of snow NO_x emissions [*Wang et al.*, 2008] suggested that the site of DDU would indeed experience mean daily OH levels as high as $1–2 \times 10^6$ molecule cm^{-3}. Note that these simulations were made by considering only the emissions of NO_x and neglected the H_2O_2 and HCHO ones that were also found to significantly contribute to the HO_x budget [*Chen et al.*, 2004]. Referring to Halley where no ozone-rich inland Antarctic air masses have been detected, we may expect 24 h average OH concentrations at DDU at least as high as 4×10^5 radicals cm^{-3}.

[26] Conversely, as suggested by *Preunkert et al.* [2008], BrO concentrations at DDU would be far lower than at Halley. Indeed *Wagner et al.* [2007] showed that the level of BrO which has a lifetime of a few hours in the marine boundary layer is strongly dependent on the time contact spent by the air mass with sea ice. Since in summer the sea ice is quasi absent in the oceanic sector facing DDU whereas the distance between the sea ice edge and the Halley site is still as high as 600 km in January, far lower BrO levels are expected in the marine boundary layer of the Indian sector compared to the Atlantic sector at that season.

Further evidence for low BrO levels in the vicinity of DDU came from the oxygen and nitrogen isotope analysis of airborne nitrate showing no direct implication of the BrO radical in the formation of nitric acid at this site [*Savarino et al.*, 2007] as opposed to what was recently observed in the Arctic where high levels of BrO are commonly observed at polar sunrise [*Morin et al.*, 2008].

[27] Thus it is likely that the DMS chemistry acting in the boundary layer at coastal Antarctic sites in summer is quite different from West to East Antarctica, with BrO chemistry been promoted by the larger sea ice coverage in West part of Antarctica while OH chemistry been promoted by NO_x emissions from the East Antarctic plateau and export toward the coast. As above mentioned with 4×10^5 OH radicals cm^{-3} and 3 pptv of BrO at Halley the reaction of BrO on DMS is four times faster than the OH addition reaction [*Read et al.*, 2008]. On the other hand, a reasonable assumption of 1 pptv of BrO and 8×10^5 OH radicals cm^{-3} make the OH addition reaction on DMS producing DMSO faster that the one with BrO at DDU. As discussed by *Read et al.* [2008], the high level of BrO at Halley also strengthen the production of MSA and impact the MSA to non-sea-salt sulfate ratio in aerosol there. It can therefore be concluded that further studies dedicated to DMS and their oxidation by products, in particular discussing the ratio of DMSO to DMS or the one of MSA to non-sea-salt sulfate, at coastal Antarctic sites would take into account both the halogen chemistry associated with the presence of sea ice as well as the OH chemistry associated with the snowpack emissions.

7. Summary

[28] This first study dealing with the seasonal cycle of surface ozone levels in East Antarctica, at the coastal DDU site and Concordia, located on the high East Antarctic plateau, has highlighted some specificities of East Antarctica with respect to Central and West Antarctica. Ozone levels are similarly high in summer (up to 40 ppbv) at Concordia and South Pole. The detailed examination of the diurnal ozone cycle at Concordia in summer suggests a local photochemical production in the range of 0.2 ppbv h^{-1} during the morning within the relatively thin planetary boundary layer. Further field studies extended to NO_x and OH radicals are required to better understand the impact of the diurnal change of UV irradiance on the build up of the very oxidizing canopy there. Compared to other coastal Antarctic sites, the site of DDU appears unique with high ozone levels in summer in relation with the proximity from DDU of a very oxidizing canopy that impacts this site under continental flow conditions which occur quite often. As a consequence the DMS chemistry acting in the boundary layer at the East Antarctic coast in summer, is mainly initiated by the OH chemistry promoted by NO_x emissions from the East Antarctic plateau. In contrast the BrO chemistry dominates the OH chemistry in the western part of Antarctica due to the larger sea ice coverage in this area.

[29] **Acknowledgments.** National financial support and field logistic supplies for over winter and summer campaigns were provided by Institut Paul Emile Victor (IPEV) at Concordia and Dumont d'Urville within the French programs 903/904 and 414, respectively. This work was also partly funded by the Centre National de la Recherche Scientifique (CNRS-INSU) within the program LEFE-CHAT. The authors gratefully acknowledge the Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model on READY website (http://www.arl.noaa.gov/ready.html) used in this publication and the Automatic Weather Station Project run by Charles R. Stearns at the University of Wisconsin-Madison which is funded by the National Science Foundation of the United States of America for meteorological parameters for Concordia. We also thank Météo-France, which provided us with meteorological data for Dumont d'Urville. Finally, the authors would like to thank the three anonymous reviewers and an associate editor of the journal for their helpful comments on the manuscript.

References

Barnes, I., J. Hjorth, and N. Mihalopoulos (2006), Dimethyl sulphide and dimethyl sulfoxide and their oxidation in the atmosphere, *Chem. Rev.*, *106*, 940–975, doi:10.1021/cr020529+.

Bloss, W. J., J. D. Lee, D. E. Heard, R. A. Salmon, S.-J.-B. Bauguitte, H. K. Roscoe, and A. E. Jones (2007), Observations of OH and HO_2 radicals in coastal Antarctica, *Atmos. Chem. Phys.*, *7*, 4171–4185.

Chen, G., et al. (2004), A reassessment of HO_x South Pole chemistry based on observations recorded during ISCAT, *Atmos. Environ.*, *38*, 5451–5461, doi:10.1016/j.atmosenv.2003.07.018.

Crawford, J. H., et al. (2001), Evidence for photochemical production of ozone at the South Pole surface, *Geophys. Res. Lett.*, *28*(19), 3641–3644, doi:10.1029/2001GL013055.

Davis, D. D., G. Chen, P. Kasibhatla, A. Jefferson, D. Tanner, F. Eisele, D. Lenschow, W. Neff, and H. Berresheim (1998), DMS oxidation in the Antarctic marine boundary layer: Comparison of model simulations and field observations of DMS, DMSO, $DMSO_2$, H_2SO_4(g), MSA(g), and MSA(p), *J. Geophys. Res.*, *103*, 1657–1678, doi:10.1029/97JD03452.

Davis, D. D., et al. (2001), Unexpected high levels of NO observed at South Pole, *Geophys. Res. Lett.*, *28*(19), 3625–3628, doi:10.1029/2000GL012584.

Davis, D. D., et al. (2004), An overview of ISCAT 2000, *Atmos. Environ.*, *38*, 5363–5373, doi:10.1016/j.atmosenv.2004.05.037.

Davis, D. D., et al. (2008), A reassessment of Antarctic plateau reactive nitrogen based on ANTCI 2003 airborne and ground based measurements, *Atmos. Environ.*, *42*, 2831–2848, doi:10.1016/j.atmosenv.2007.07.039.

Frey, M. M., R. W. Steward, J. R. McConnell, and R. C. Bales (2005), Atmospheric hydroperoxides in West Antarctica: Links to stratospheric ozone atmospheric oxidation capacity, *J. Geophys. Res.*, *110*, D23301, doi:10.1029/2005JD006110.

Gallée, H., and I. Gorodetskaya (2009), Validation of a limited area model over Dome C, Antarctic Plateau, during winter, *Clim. Dyn.*, doi:10.1007/s00382-008-0499-y, in press.

Helmig, D., S. J. Oltmans, D. Carlson, J.-F. Lamarque, A. Jones, C. Labuschagne, K. Anlauf, and K. Hayden (2007), A review of surface ozone in the polar regions, *Atmos. Environ.*, *41*, 5138–5161, doi:10.1016/j.atmosenv.2006.09.053.

Helmig, D., B. Johnson, M. Warshawsky, T. Morse, W. Neff, F. Eisele, and D. D. Davis (2008), Elevated ozone in the boundary-layer at South Pole during the Antarctic tropospheric chemistry investigation (ANTCI), *Atmos. Environ.*, *42*, 2788–2803.

Jefferson, A., D. J. Taner, F. L. Eisele, D. D. Davis, G. Chen, J. Crawford, J. W. Huey, A. L. Torres, and H. Berresheim (1998), OH photochemistry and methane sulfonic acid formation in the coastal Antarctic boundary layer, *J. Geophys. Res.*, *103*, 1647–1656, doi:10.1029/97JD02376.

Jones, A. E., R. Weller, P. S. Anderson, H.-W. Jacobi, E. W. Wolff, O. Schrems, and H. Miller (2001), Measurements of NO_x emissions from the Antarctic snowpack, *Geophys. Res. Lett.*, *28*(8), 1499–1502, doi:10.1029/2000GL011956.

Jourdain, B., and M. Legrand (2001), Seasonal variations of dimethyl sulfide, dimethyl sulfoxide, sulfur dioxide, methanesulfonate, and non-sea-salt sulfate aerosols at Dumont d'Urville (December 1998 to July 1999), *J. Geophys. Res.*, *106*, 14,391–14,408, doi:10.1029/2000JD900841.

König-Langlo, G., J. C. King, and P. Pettré (1998), Climatology of the three coastal Antarctic stations Dumont d'Urville, Neumayer, and Halley, *J. Geophys. Res.*, *103*, 10,935–10,946, doi:10.1029/97JD00527.

Legrand, M., J. Sciare, B. Jourdain, and C. Genthon (2001), Daily variations of dimethyl sulfide, dimethyl sulfoxide, methanesulfonate, and non-sea-salt sulfate aerosols at Dumont d'Urville (December 1998 to March 1999), *J. Geophys. Res.*, *106*, 14,409–14,422, doi:10.1029/2000JD900840.

Mauldin, R. L., III, et al. (2001), Measurements of OH, H_2SO_4, and MSA at the South Pole during ISCAT, *Atmos. Environ.*, *28*, 3629–3632.

Morin, S., J. Savarino, M. M. Frey, N. Yan, S. Bekki, J. Bottenheim, and J. Martins (2008), Tracing the origin and fate of NO_x in the Arctic atmosphere using stable isotopes, *Science*, *322*, doi:10.1126/science.1161910.

Pham, M., J. F. Muller, G. Brasseur, C. Granier, and G. Mégie (1995), A three-dimensional study of tropospheric sulfur cycle, *J. Geophys. Res.*, *100*, 26,061–26,092, doi:10.1029/95JD02095.

Preunkert, S., B. Jourdain, M. Legrand, R. Udisti, S. Becagli, and O. Cerri (2008), Seasonality of sulfur species (sulfate, methanesulfonate and dimethyl sulfur) in Antarctica: Inland versus coastal regions, *J. Geophys. Res.*, *113*, D15302, doi:10.1029/2008JD009937.

Read, K. A., et al. (2008), DMS and MSA measurements in the Antarctic boundary layer: Impact of BrO on MSA production, *Atmos. Chem. Phys.*, *8*, 2657–2694.

Saiz-Lopez, A., A. S. Mahajan, R. A. Salmon, S.-J.-B. Bauguitte, A. E. Jones, H. K. Roscoe, and J. M. C. Plane (2007), Boundary layer halogens in coastal Antarctica, *Science*, *317*, 348–351, doi:10.1126/science.1141408.

Savarino, J., J. Kaiser, S. Morin, D. M. Sigman, and M. H. Thiemens (2007), Nitrogen and oxygen isotopic constraints on the origin of atmospheric nitrate in coastal Antarctica, *Atmos. Chem. Phys.*, *7*, 1925–1945.

Wagner, T., O. Ibrahim, R. Sinreich, U. Frieß, R. von Glasow, and U. Platt (2007), Enhanced tropospheric BrO over Antarctic sea ice in mid winter observed by MAX-DOAS on board the research vessel Polarstern, *Atmos. Chem. Phys.*, *7*, 3129–3142.

Wang, Y., Y. Choi, T. Zeng, D. D. Davis, M. Buhr, L. G. Huey, and W. Neff (2008), Assessing the photochemical impact of snow NO_x emissions over Antarctica during ANTCI 2003, *Atmos. Environ.*, *42*, 2849–2863, doi:10.1016/j.atmosenv.2007.07.062.

H. Gallée, B. Jourdain, M. Legrand, S. Preunkert, and J. Savarino, Laboratoire de Glaciologie et Géophysique de l'Environnement, Centre National de la Recherche Scientifique, 54 Rue Molieres, BP 96, F-38402 Saint Martin d'Hères, France. (michel.legrand@lgge.obs.ujf-grenoble.fr)

F. Goutail, Service d'Aéronomie, Institut Pierre-Simon Laplace, F-75252 Paris, France.

R. Weller, Alfred-Wegener-Institut für Polar- und Meeresforschung, D-27515 Bremerhaven, Germany.