Multi-year variation of near-surface ozone at Zhongshan Station, Antarctica

Biao Tian1, Minghu Ding1,∗, Davide Putero2, Chuanjin Li3, Dongqi Zhang1, Jie Tang1, Xiangdong Zheng1, Lingen Bian1 and Cunde Xiao4

1 State Key Laboratory on Severe Weather, Chinese Academy of Meteorological Sciences, Beijing 100081, People’s Republic of China
2 CNR–ISAC, National Research Council of Italy, Institute of Atmospheric Sciences and Climate, corso Fiume 4, 10133 Turin, Italy
3 State Key Laboratory of Cryospheric Science, Northwest Institute of Eco-Environment and Resources, Chinese Academy of Sciences, Lanzhou 730000, People’s Republic of China
4 State Key Laboratory of Earth Surface Processes and Resource Ecology, Beijing Normal University, Beijing 100875, People’s Republic of China

∗ Author to whom any correspondence should be addressed.
E-mail: dingminghu@foxmail.com

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Abstract
With the support of the Chinese National Antarctic Research Expedition, near-surface ozone (O₃) was continuously monitored at Zhongshan Station (ZOS) (69°22′12″ S, 76°21′49″ E, 18.5 m above sea level) in East Antarctica from 2008 to 2020. The seasonal and diurnal variability of near-surface O₃ at ZOS were investigated. O₃ enhancement events (OEEs) were frequently observed in the warm season (OEEs in January accounted for 23.0% of all OEEs). The OEEs at ZOS were related to the photochemical reaction processes under the influences of O₃ and solar radiation in the stratosphere and synoptic-scale air mass transport from coastal areas (Princess Elizabeth Land, Wilkes Land, and Queen Mary Land), as evidenced by the recorded wind speed, solar shortwave irradiance, and total column ozone data and the computed potential source contribution function and concentration-weighted trajectory models. The results computed by the tool Stratosphere-to-Troposphere Exchange Flux indicated that stratosphere-to-troposphere transport had no direct impact on OEEs at ZOS. Therefore, synoptic-scale air mass transport is the main cause of OEEs in Antarctica, which is consistent with previous studies. Unlike OEEs at inland Antarctic stations, which are mainly affected by air mass transport from inland plateaus, OEEs at ZOS, a coastal station, are mainly affected by air mass transport from coastal land in East Antarctica.

1. Introduction
Tropospheric ozone (O₃) is an important short-lived greenhouse gas and a driver of atmospheric oxidation capacity (Schultz et al 2015). Within the influence of strong solar radiation (λ < 424 nm), volatile organic compounds and NOₓ (NO + NO₂), O₃ is produced photochemically and can accumulate to a hazardous level under favorable meteorological conditions (Wakamatsu et al 1996). In the case of NOₓ-rich air, NOₓ is accumulated because of reactions between NO and HO₂ or RO₂ (peroxy radicals), and then O₃ accumulates. While in the case of NOₓ-poor air, these peroxy radicals react with O₃, leading to loss (Lin et al 1988). Because of its high reactivity and short atmospheric residence time, the surface O₃ long-term trend is hard to evaluate (Cooper et al 2014, Monks et al 2015, Schultz et al 2015). This is especially true in Antarctica, a remote region from the human activities. Previous investigations suggested that O₃ production in the Antarctica planetary boundary layer (PBL) is affected by some global and regional climate-related variables, i.e. changes in UV fluxes due to total O₃ variability over Antarctica (e.g. Jones and Wolff 2003, Frey et al 2015), variability in long-range air mass transport patterns (e.g. Legrand et al 2016), and the
depth of the continental mixing layers. Sometimes, summer episodes of ‘O3 enhancement events’ (OEEs) could be observed in the Antarctica interior (e.g. Crawford et al 2001, Legrand et al 2009, Cristofanelli et al 2018) as well as at coastal sites influenced by air mass transport from the interior of the continent (e.g. Cristofanelli et al 2011). This phenomenon was attributed to the photodetritification of the summer snowpack, which can result in NOx emissions (Davis et al 2001) to the atmosphere and subsequent photochemical O3 production (e.g. NO2 + hv → NO + O; O + O2 + M → O3 + M; Jones et al 2000, Jones and Wolff 2003, David and Nair 2011). These processes are capable of driving the seasonality of near-surface O3 over the Antarctic Plateau (e.g. Crawford et al 2001, Legrand et al 2009), thus potentially providing a significant input of O3 to the whole Antarctic region (e.g. Legrand et al 2016). Indeed, as shown in Cristofanelli et al (2008) and Legrand et al (2016), due to air mass transport, photochemically produced O3 in the PBL over the Antarctic Plateau can affect the O3 variability thousands of km from the emission area.

Moreover, middle and low latitude near-surface O3 concentrations at high-elevation sites can also be increased by the downward transport of O3-rich air from upper troposphere and lower stratosphere (e.g. Bonasoni et al 2000, Stohl and Sodemann 2010, Yin et al 2017). The earliest study, carried out by aircraft flight NSFC-130 over the Ellsworth Mountains of Antarctica in 1978, found that mountainous terrain can induce atmospheric waves that propagate across the tropopause. The tropospheric and stratospheric air may mix, leading to an increase in tropospheric O3 (e.g. Robinson et al 1983). O3 sounding at the Resolute and Amundsen-Scott Stations (South Pole, SOP) also found the transportation from the stratosphere to the troposphere, the flux of which could reach 5 × 1016 mol cm−2 s−1 (e.g. Gruzdev and Sitnov 1993). Recently, Traversi et al (2017) suggested that the variability of air mass transport from the stratosphere to the Antarctic Plateau can affect nitrate content in the low troposphere and the snowpack, leading to O3 variation.

In summary, the near-surface O3 could be affected by many processes, especially the in-situ production, synoptic-scale air mass transport, ‘deep’ Stratosphere-to-Troposphere Transport (STT) events. In 2008, as part of International Polar Year project, Chinese National Antarctic Research Expedition established an on line observation system of atmospheric composition at Zhongshan Station (ZOS), the edge of Lambert glacier basin, east Antarctica (figure 1). Based on the data, only general characteristics of near-surface O3 have been introduced (e.g. Wang et al 2011, Bian et al 2018). Thus in this paper, the detailed source and sink mechanism was analyzed combined with meteorology, solar shortwave irradiance, and total column O3 (TCO) experiments.

2. Description of sites and methods

2.1. Sites and instruments

The online observation system of atmospheric composition were installed at the Swan Ridge (69°22′12″ S, 76°21′49″ E, 18.5 m a.s.l.), northwest of the Nella fjord. Strong E orENE winds (45°–135°) dominate here, occupying 92% of time (Wang et al 2011). It implies human pollution from ZOS is weak.

In January 2008, an EC9810A ultraviolet photometric absorption O3 analyzer was deployed to monitoring near-surface O3, with an EC9811 as calibrator. Unfortunately, the instrument encountered a failure in January 2014, and the data was not credible till January 2016 when a TE491 ultraviolet photometric absorption O3 analyzer and a TE491ps ultraviolet photometric absorption O3 calibrator (Thermo Company) replaced. The measurement frequency was 1 min. Data are available at https://doi.org/10.11856/SNS.D.2021.001.v0. The meteorological monitoring including solar shortwave irradiance, wind speed was started in 1989 according to the World Meteorological Organization requirements. The Brewer monitoring including TCO was started in 1993 according to the World Ozone and Ultraviolet Radiation Data Centre.

2.2. Calibration process and results

In general, the zero-point, range and operating parameters of the O3 analyzer should be checked regularly and before each operation. The calibration procedure followed the China’s environmental protection standard ‘ambient air—determination of O3—ultraviolet method’ (HJ590-2010) (www.mee.gov.cn/gkml/sthjbgw/sthjbgg/201808/120180815_451411.htm), which is stricter than the standards of the U.S. Environmental Protection Agency (www.epa.gov/ttn/amtic/files/ambient/pm25/qa/QAHandbook-Vol-II.pdf): the slope of the calibration curve ranged between 0.95 and 1.05, and the intercept ranged between −5 and 5 ppb. Every 3 months in ZOS, five standard concentrations of O3 gas were generated for each calibration. From 2008 to 2020, 44 calibrations were made (e.g. excluding 2014 and 2015 data due to instrumental failure and it can be seen in supplement 1 available online at stacks.iop.org/ERL/17/044003/mmedia for the detailed results), and the correlation coefficient r was greater than 0.999 for the calibration quality of the observed data.

Furthermore, a variance test was applied to remove abnormal data based on the Laida criterion method, which assumes that the records obey a normal distribution. The formula is |x − x̄| > 3σ, where xi is the measured value, x̄ is the time series mean and σ is the standard deviation. After processing, 99.2% of the hourly mean data were retained from ZOS time series (excluding 2014 and 2015).
2.3. Air mass back-trajectory calculation

The HYSPLIT back trajectory analysis is a common application to determine the origin of air masses and establish source-receptor relationships (Stein et al. 2015). It has been proven credible in previous Antarctica researches (e.g. Legrand et al. 2009, Hara et al. 2011). The TrajStat tools (MeteoInfoMap plugin for air mass trajectory statistic; Wang 2014) were used to derive the model results in this study. Because O$_3$ usually has a half-life of several days in troposphere (Seinfeld et al. 1998), the backward trajectory starting height was set at 100 m above the surface, and the total run time was 120 h for each trajectory. Each run was performed at time intervals of 24 h (00:00). In order to explore the major pathways of air mass arriving at the study area, the clustering analysis was carried out based on Euclidean distance. The final cluster number was 4, which was determined by the point of inflexion on a curve of total spatial variance vs. number of clusters.

2.3.1. The PSCF model

The potential source contribution function (PSCF) model has often been applied to locate air masses associated with high levels of near-surface O$_3$ at different sites (Dimitriou and Kassomenos 2015, Sharma et al. 2017, Yin et al. 2017). In the summer over the Antarctic Plateau, higher PSCF values may point to sources of NO$_X$ released from the snow that support O$_3$ production (Cristofanelli et al. 2018). The PSCF values for the grid cells in the study domain were calculated by counting the trajectory segment endpoints that terminated within each cell (Ashbaugh et al. 1985). If the total number of end points that fall in a cell is $n_{ij}$ and there are $m_{ij}$ points for which the measured O$_3$ parameter exceeds a criterion value selected for this parameter, then the PSCF, can be determined as

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}}. \quad (1)$$

The cells with high PSCF values are associated with the arrival of air parcels at the receptor site, which has near-surface O$_3$ concentrations higher than the criterion value (i.e. the criterion threshold is the average concentration of non-OEEs (NOEEs) and OEEs). These cells are indicative of areas with ‘high potential’ contributions of the constituent. However, the identical PSCF $n_{ij}$ values can be obtained from cells with very different counts of back-trajectory points. To explain the uncertainty due to the low values of $n_{ij}$, the PSCF values were scaled by a weighting function $W_{ij}$ (Polissar et al. 1999). The weighted PSCF (WPSCF) values when the total number of endpoints in a cell was less than approximately three times the average number of endpoints per cell. In this case, $W_{ij}$ was set as follows:

$$W_{ij(OEE)} = \begin{cases} 1.00 & n_{ij} > 80 \text{Nave} \\ 0.70 & 80 \text{Nave} > n_{ij} > 20 \text{Nave} \\ 0.42 & 20 \text{Nave} > n_{ij} > 10 \text{Nave} \\ 0.05 & \text{Nave} > n_{ij} \end{cases} \quad (2)$$

where Nave represents the mean $n_{ij}$ of all grid cells. The WPSCF values were obtained by multiplying the original PSCF values by the weighting factor.

2.3.2. The CWT model

In the PSCF model, grid cells can have identical PSCF values when sample concentrations are slightly higher or much higher than the criterion value, making it difficult for the PSCF model to distinguish between strong pollution sources and weak pollution sources. In contrast, the concentration-weighted trajectory (CWT) model can well distinguish between strong and weak pollution sources. In the CWT model, each
grid cell is assigned a weighted concentration by averaging the sample concentrations with associated trajectories crossing the grid cell, as shown below:

$$W_{\text{CWT}}_{ij} = \frac{\sum_{b=1}^{M} c_{b} T_{ijb}}{\sum_{b=1}^{M} T_{ijb}} \times W_{ij},$$  

(3)

where $W_{\text{CWT}}_{ij}$ is the average weighted concentration in the $ij$th cell, $b$ is the index of the trajectory, $M$ is the total number of trajectories, $c_{b}$ is the concentration observed on arrival of trajectory $b$, and $T_{ijb}$ is the time spent in the $ij$th cell by trajectory $l$. A high value for $W_{\text{CWT}}_{ij}$ implies that air parcels traveling over the $ij$th cell would be, on average, associated with high concentrations at the receptor. Besides, the using of $W_{ij}$ in weighted concentration weighted trajectory (WCWT) same as that in WPSCE.

### 3. Results and discussion

#### 3.1. Near-surface $O_3$ variability

Figure 2 shows the time series of the monthly mean $O_3$ concentrations at ZOS from January 2008 to December 2020. $O_3$ was high in winter and low in summer. The lowest $O_3$ concentrations (12.2–19.9 ppb) were observed in January (2009, 2010, 2011, 2012, 2016, 2017, 2019, and 2020) and December (2008, 2013, and 2018). The highest $O_3$ concentrations (30.9–35.2 ppb) were observed in June (2013 and 2020), July (2008, 2009, 2010, 2011, 2012, 2016, and 2017), and August (2018 and 2019), which reflect the net $O_3$ accumulation effect during the Antarctic polar night. As the solar altitude rises and UV irradiation increases during early spring, near-surface $O_3$ starts to photolyze. Moreover, the NO$_x$, OH$^-$ ion (hydroxide), and HO$_2$ concentrations remain extremely low due to the low solar radiation, and photolysis of $O_3$ still dominates, leading to a considerable decrease in $O_3$ concentration (Monks 2000).

During the warm season (September–January), the $O_3$ concentration at ZOS exhibited large monthly fluctuations. This phenomenon has been observed at many other coastal stations, such as the Syowa, Neumayer, Halley, and Arrival Heights stations (Ghude et al. 2006, Helmig et al. 2008, Wang et al. 2011, Bian et al. 2018). Surprisingly, abnormally high $O_3$ concentrations also occurred in September and October, sometimes exceeding the $O_3$ concentrations during the Antarctic polar night (as shown in figure 4). This phenomenon has been observed at other Antarctic inland stations, such as the SOP and Dome C (DMC) (Helmig et al. 2008, Oltmans et al. 2008).

To analyze the diurnal variability characteristics of $O_3$ at ZOS, the $\Delta O_3$ (hourly growth rate of $O_3$) and diurnal variability of $O_3$ were calculated (figure 3(b)). The $O_3$ concentration at ZOS showed a clear diurnal cycle, with a maximum value at approximately 23:00 coordinated universal time (UTC) (4:00 local time (LT)) and a minimum value at approximately 9:00 UTC (14:00 LT). At ZOS, the monthly $\Delta O_3$ varied little, ranging from −0.8 to 0.8 ppb h$^{-1}$, much smaller than the mean monthly $\Delta O_3$ of 0.16 ppb h$^{-1}$ at DMC (Cristofanelli et al. 2018). During the polar night, the daily mean wind speed remained stable, ranging from 6 to 8 m s$^{-1}$, but the $\Delta O_3$ varied greatly at times (especially from 14:00 to 22:00 LT). This could only be attributed to the strong vertical exchange between the free atmosphere and PBL.

Wind can promote mixing and transport between the PBL and the upper free atmosphere so that trace pollutants are continuously diffused in the horizontal and vertical directions. The diurnal variability of the wind speed may directly affect the reaction and transfer processes of near-surface $O_3$ (e.g. Argentini et al. 2000). The $O_3$ concentrations continuously increase in spring and fall mornings with low wind speeds mainly because low wind speeds promote the accumulation of $O_3$ precursors near the surface (Haman et al. 2014). At the DMC, strong winds contribute to the dilution of snowpack surface-emitted $O_3$ precursors, which reduces the source contribution to the local photochemical process of $O_3$ formation (Legrand et al. 2016). However, the wind speed at ZOS showed a notable diurnal cycle (figure 3(a)), which was positively correlated with the diurnal variability of $O_3$ ($r^2 = 0.983$, $P < 0.01$). This diurnal variability of $O_3$ at ZOS increased with wind speed, making it different from the diurnal variability of $O_3$ observed at DMC station. This difference may be attributed to the differences in geographical location and underlying surface between these two stations. Considering the diurnal variation characteristics of wind speed, the diurnal variability of $O_3$ at ZOS should be related to synoptic-scale air mass transport and the environmental background. In other words, the diurnal
variability of $O_3$ at ZOS can represent the background characteristics of a large area.

3.2. Identification of OEEs

Similar with the procedure in Cristofanelli et al. (2018), the OEE day was selected based on a two-step method. First, the annual cycle of $O_3$ mean daily values was fitted with a sinusoidal curve. This represents an 'undisturbed' $O_3$ annual cycle, not affected by OEEs. In the second step, the probability density function (PDF) of the deviations from the sinusoidal fit was calculated, then a Gaussian fit was applied to the obtained PDF. It is proved that the deviations from the Gaussian distribution (calculated by using the Origin® 9 statistical tool) can be used to identify observations affected by non-background variability (e.g. Giostra et al. 2011). In order to obtain a threshold value for selecting non-background $O_3$ daily values possibly affected by 'anomalous' $O_3$ enhancements, we computed the further Gaussian fitting of PDF points falling above 1σ (standard deviation) of the Gaussian PDF. The intersection of the two fitting curves is taken as our screening threshold (table 1).

The OEE and NOEE days at ZOS were selected (figure 4). A total of 178 d over the 11 years period were affected by OEEs: 41 d in January (23.0%), 40 d in November (22.5%), 39 d in December (21.9%), 26 d in October (14.6%) and 11 d in September (6.2%). The frequency of OEE was less than 4% during other months (figure 5). Most of the OEEs at ZOS occurred in the warm season (September–January) and its intensity was much stronger than in the cold season. And we only found three OEEs during the polar night of 2018 (2%). Besides, we did not find obvious interannual variation characteristics of OEEs during 2008–2020.

Indeed, as suggested by Chevalier et al. (2007), the comparison between hourly and daily $O_3$’s standard deviations were allowed to discriminate the relative contribution to the overall $O_3$ variability due to the diurnal variation process (PBL photochemistry and other processes) and the synoptic-scale variation process, i.e. weather change, synoptic-scale air mass transport, etc. The standard deviations based on hourly $O_3$ data during OEEs was minimal in January (2.9 ppb) and maximum in December (4.8 ppb). This indicated that the diurnal-scale process (i.e. PBL photochemistry and dynamics) played a role in enhancing $O_3$ variability during summer. However, even in December, the ratio between daily and hourly standard deviations suggested that 88.2% of $O_3$ variability at ZOS was associated with longer temporal scale processes.

Indeed, as suggested by Chevalier et al. (2007), comparison of the hourly and daily $O_3$ standard deviations allows us to distinguish between the relative contributions of the diurnal variation processes (photochemical and other processes in the PBL) and the synoptic-scale variation processes (e.g. weather change, synoptic-scale air mass transport, etc) to the overall $O_3$ variability. Through calculation, we found that the annual mean contribution rate of the synoptic-scale variation processes at ZOS was 74%. In particular, the mean contribution rate of the synoptic-scale variation processes in the warm season (September–January) reached 81%. This indicates that the OEEs at ZOS are little affected by the diurnal variation processes and are mainly affected by the synoptic-scale variation processes.

Figure 3. Monthly wind speed (a) and $O_3$ (b) diurnal cycles from 2008 to 2020 at ZOS. The $\Delta O_3$ is the hourly growth rate of $O_3$. The point-line in the figure represents the average diurnal cycles of wind speed and $O_3$ from 2008 to 2020. The hot spot map shows the average daily variation characteristics of wind speed and $\Delta O_3$ in the different months from 2008 to 2020.
Table 1. The screening threshold values for 2008–2020 at ZOS.

| Year | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2016 | 2017 | 2018 | 2019 | 2020 |
|------|------|------|------|------|------|------|------|------|------|------|------|
| Threshold (ppb) | 3.6  | 3.9  | 2.7  | 3.8  | 3.6  | 4.3  | 5.0  | 3.4  | 3.3  | 2.6  | 3.9  |

Figure 4. Daily average $O_3$ values during 2008–2020 at ZOS. Red and black dots represent OEE days and NOEE days, respectively.

Figure 5. The OEE occurrence probability from 2008 to 2018 at ZOS.

3.3. Possible influence of the in-situ production
In Antarctica, a decrease in TCO can enhance the incident UV radiation, leading to stronger photolysis of nitrates in snowpacks and thus the release of more $NO_X$. This could affect in situ photochemical production of $O_3$ in the long term (e.g. Jones and Wolff 2003). Figure 6 shows the monthly mean variability of OEE frequency, TCO, and solar shortwave irradiance at ZOS. The correlation coefficient ($r$) between the OEE frequency and solar shortwave irradiance reached 0.91 ($P < 0.05$). This indicates that as the solar shortwave irradiance increases during early summer, the photolysis of nitrates becomes stronger, thus increasing $NO_X$ emission (Warneck and Wurzinger 1989, Honrath et al 2000). The corresponding chemical reaction process is as follows: $NO_3^- + hv \rightarrow NO_2 + O^-, O^- + H \rightarrow OH^-$. Then, NO$_2$ will produce $O_3$ through further photochemical reactions, resulting in favorable conditions for OEEs.

As shown in figure 6, the correlation coefficient between the OEE frequency and TCO and the correlation coefficient between the OEE frequency and solar shortwave irradiance reached −0.93 and 0.99 ($P < 0.05$), respectively, during the period from July to October, providing strong evidence for the important role of stratospheric $O_3$ in modulating the near-surface atmospheric photochemical reaction processes by controlling UV radiation. The occurrence of
an O₃ hole has gradually increased the incident UV radiation (the effect of the O₃ hole on solar shortwave irradiance can be determined by calculating the difference in the slope between the solar shortwave irradiance–time curve for the period from February to May (−0.25) and that for the period from July to October (0.29)), which is also beneficial to the formation of OEEs (Jones et al 2000, Jones and Wolff 2003).

3.4. Role of synoptic-scale air mass transport
To better study the effect of synoptic-scale processes in triggering OEEs, we calculated the total time that air masses spent over the plateau and coastal land areas (i.e. the area within the boundaries of 90°−66.5° S and 40°−160° E) before arrival at ZOS. The time spent by air masses over all land trajectories of OEEs was approximately 3.73% of the time spent by air masses over all trajectories and was approximately 78% of the time spent by air masses over all OEE trajectories (figure 7(a)). Clearly, the total time spent by air masses over the plateau and coastal land areas significantly impacted the OEEs at ZOS (figure 7(b)). The correlation between the two reached r = 0.82 and passed the 99% confidence level. The finding is in agreement with Legrand et al (2016) and Cristofanelli et al (2018). Just like the conclusion drawn in section 3.2, synoptic-scale air mass transport plays a pivotal role in triggering OEEs at ZOS.

By clustering of OEE trajectories, we found that all air mass trajectories during OEEs originated from the coastal land areas of East Antarctica (the red, blue, yellow, and green lines in figure 8(a)). The O₃ concentrations of the four clusters were similar, all of them being between 20 and 31 ppb, with mean values from 25 to 27 ppb (figure 8(d)). In all months, the coastal cluster dominated during OEEs at ZOS (figure 8(c)). Furthermore, the pressures associated with the four clusters were higher than 550 hPa (figure 8(b)). These results indicate that most air masses were transported to ZOS through the troposphere over the Queen Mary Land, Wilkes Land, and Princess Elizabeth Land.

The PSCF and CWT models were applied to find the potential pollution sources of O₃ during OEEs. The WPSCF values were high (>0.4) in the coastal area east of ZOS (from 76° to 150° E) (figure 9(a)). The WCWT values were greater than 20 ppb in the areas east of ZOS (figure 9(b)), which also indicated that the area east of ZOS was the O₃ source region that had the greatest impact on the O₃ at ZOS. The model results further confirmed that OEEs at ZOS were mainly caused by the transport of O₃-rich air masses from the atmosphere over the coastal land areas of the Princess Elizabeth Land, Wilkes Land, and Queen Mary Land.

3.5. Role of STT events
We applied the Stratosphere-to-Troposphere Exchange Flux (STELFUX) tool to assess the possible contribution of STT to near-surface O₃ variability of ZOS, and to determine the measurement periods...
possibly affected by STT events (i.e. stratospheric air masses transferred down to the lower troposphere). We set the top lid of the target box at 300 hPa, and the following geographical boundaries: 68°–71° S and 75°–78° E. If at least 1 stratospheric trajectory crossed the 3D target box, then a ‘deep’ STT event at ZOS was detected (i.e. the STEFLUX ‘target box’; for further details on the methodology, see Putero et al 2016).

Figure 10 showed the annual (figure 10(a)) and monthly (figure 10(b)) distributions of STT events occurring at ZOS during the 2008–2018 (i.e. Since the STEFLUX tool are based on ERA-Interim data, the calculations were performed until 31 August 2018). The seasonal variation was not obvious, because of the low frequency of STT events. For example, the highest monthly frequency of STT events was only 0.9% (July). It was almost an order of magnitude lower than that of the OEEs. Therefore, it can be inferred that there was no direct link between the

STT and OEE. This pattern was also reported in some previous studies (e.g. Stohl and Sodemann 2010, Cristofanelli et al 2018).

However, some previous studies had considered the STT process is complex on Antarctica (Roscoe 2004, Mihalikova and Kirkwood 2013). The STEFLUX is only able to consider relatively ‘young’ events (i.e. 4 d old). This can lead to an underestimation of the real influence of STT at ZOS. In addition, STT events can play a role by transporting nitric acid, from stratosphere to the Antarctic atmosphere, thus indirectly affecting near-surface O₃ concentration and facilitating the occurrence of OEEs (Traversi et al 2014, 2017). For stations on the Antarctic coast, e.g. Neumayer, stratospheric air mass intrusions in late summer/early autumn have been proven by long-term measurements of ³⁰Be/³⁰Be in surface aerosol particles (Elsässer et al 2011). At ZOS, through an observational analysis of the Δ¹⁴CO₂, it was also confirmed that the OEE of 6 January 2011 was affected by
Figure 10. Annual (a) and monthly (b) distributions of ‘deep’ STT events at ZOS from 2008 to 2018, obtained by STEFLUX.

the STT (Zheng et al 2020). Therefore, it is important to carry out further studies to better assess this process.

4. Conclusion

Using observations from 2008 to 2020, the background characteristics of near-surface O$_3$ at ZOS in Antarctica were studied. The results suggest that synoptic-scale air mass transport controls the occurrence of OEEs, which is consistent with the findings of studies at the SOP and DMC (Neff et al 2008, Cristofanelli et al 2018). The variations in solar shortwave irradiance and TCO and their relationships with O$_3$ from July to October confirm that the decrease in TCO could enhance the incident UV radiation, leading to more intense photolysis of nitrates on snowpack surfaces and thus affecting the near-surface photochemical production of O$_3$ in the long term. In addition, this study found that STT events rarely occur at ZOS and are not directly related to the occurrence of OEEs. Unlike the OEEs at the Antarctic inland stations, the OEEs at ZOS are mainly related to the transport of air masses with high O$_3$ concentrations over coastal land. In summary, the synoptic-scale transport of air masses with high O$_3$ concentrations is the main cause of OEEs at both low-latitude coastal stations and high-latitude inland stations in Antarctica.

The mechanism by which near-surface O$_3$ changes at ZOS revealed in this paper is of great significance to research on atmospheric chemistry in the Antarctic region. In Antarctica, only a few observation stations have conducted long-term continuous observations of near-surface O$_3$. There is an urgent need for more research in this field, especially assessments of the overall regional status of near-surface O$_3$ based on relevant atmospheric chemistry models, which will be the focus of our future research.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.11856/SNS.D.2021.001.v0. Data will be available from 19 December 2023 (Ding et al 2021).

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