Reply for Anonymous Referee #3

This paper is within the scope of ACP and presents a potentially interesting observational record by investigating an interesting scientific topic. However, the used methodologies are not adequate (in some cases - see the use of PV - wrong) and, also for these reasons, the conclusions are far to be robust and mostly based on qualitative and arbitrary interpretation of data. Moreover, the manuscript suffers of strong deficiencies in the vocabulary and in the quality of figures. Finally, I did not see any acknowledgments to people or Institutions providing the ozone data from South Pole station: from which data repository has been this dataset obtained?

Thus, I'm sorry but I have to recommend rejection or a complete re-submission of a

new manuscript when the following shortcoming will be fixed. SPECIFICCOMMENTS:

Abstract: line 25: "To explain this unique finding, the occurrence of stratospheric intrusion (stratosphere-to-troposphere, STT) events was studied with the Stratosphere-to- Troposphere Exchange Flux (STEFLUX) tool". Here the author claimed STEFLUX was used in this work: unfortunately this is not the case (see also the related comment by one of the STEFLUX's authors). STEFLUX is a code developed by Putero et al (2016), see https://www.atmos-chem-phys.net/16/14203/2016/acp-16-14203-2016.pdf. No indication of the real use of STEFLUX can be found along the paper. At some point the authors claimed they selected back-trajectories coming from region with PV>2 pvu (by the way: in the southern polar stratosphere the PV is negative, so this is wrong!): this is a rather simple filtering of back-trajectories far to be the application (or a replication) of STELFLUX. Thus, this sentence should be removed from the abstract.

Total response: Thank you for your comments and suggestions on our article. We have made additional changes to this issue.

The Amundsen-Scott Station (89 ° 59'51.19 "S, 139 ° 16'22.41" E, altitude 2835 m) is located at the SP and operated by the United States. The near-surface ozone data were downloaded **from the Earth System Research Laboratory Global Monitoring Division under the NOAA (https://www.esrl.noaa.gov/gmd/dv/data).**

We revised and explained the errors and insufficient explanations in the article one by one according to the suggestions. The article has undergone great changes: (1) we have made great amendments to the contents and illustrations of section 3, adding references and deleting subjective judgments. (2) We have greatly revised the content of Section 4.2. We have re-analyzed this section by re-determining the weight of PSCF. (3) We made a major revision to section 4.3, contacted Dr. Putero, and cooperated in STEFLUX analysis. The conclusion of the article has been corrected accordingly.

Thank you for your constructive and insightful criticism and advice. We addressed all the

points raised by the reviewer as summarized below.

Line 58 -72 (page 4): this section is almost a "cut-and-paste" from a paper by other authors (Cristofanelli et al., Analysis of multi-year near-surface ozone observations at the WmO/GAW "Concordia" station).

Reply: According to your suggestion, we have re edited this paragraph.

Previous studies have shown that the near-surface O3 of Antarctica may be influenced by a number of climate related variables (Berman et al., 1999), i.e., the variation of UV flux caused by the variation of O3 column concentration over Antarctica (Jones and Wolff, 2003; Frey et al., 2015), accumulation and transport of long-distance, high concentration air masses (e.g., Legrand et al., 2016), and the depth of continental mixing layers. Many studies has observed summer episodes of "O3 enhancement events" (OEEs) in the Antarctic interior (e.g., Crawford et al., 2001; Legrand et al., 2009; Cristofanelli et al., 2018), and they attributed this phenomenon to the NOx emissions from snowpack and subsequent photochemical O3 production (for example, Jones et al., 2000). However, this may provide an input source for the entire Antarctic region (for example, Legrand et al., 2016; bauguitte et al., 2011). Indeed, Helmig et al. (2008a,b) provided further insight into the vigorous photochemistry and ozone production that result from the highly elevated levels of nitrogen oxides (NOx) in the Antarctic surface layer. During stable atmospheric conditions (which are typically observed during low wind and fair sky conditions) ozone accumulated in the surface layer to reach up to twice its background concentration. Neff et al. (2008a) show that shallow mixing layers associated with light winds and strong surface stability can be among the dominant factors leading to high NO levels. As shown in Cristofanelli et al. (2008) and Legrand et al. (2016), due to air mass transport, the photochemically-produced O3 in the PBL over the Antarctic Plateau can affect the O3 variability thousands of km away from the emission area.

Section 2.1: the experiments is not well described. As an instance no information are provided about the set-up of the measurement system as well as used materials. No information about the application of a Quality Assurance strategy and good/standard practices. No reference to the adoption of (international) calibration scale. No details about the execution of the intercomparison with the travelling standard Thermo 49iPS: the linear correlation coefficient is not sufficient to assess the overall quality of measurement (what about the total uncertainty)?

Reply: According to your suggestion, we have made a supplementary explanation for the experimental part and supplemented the alignment chart of calibration, and the relevant data will also be submitted as required.

The Kunlun Station (80°25'02"S, 77°06'59"E, altitude 4087 m) is located in the DA area, on the summit of the east Antarctic Ice Sheet (Figure 1). On the 1st of Jan 2016, we deployed

a Model 205 Dual Beam Ozone Monitor during the 33rd Chinese National Antarctic Research Expedition. The Model 205 Dual Beam Ozone Monitor makes use of two detection cells to improve precision, baseline stability, and response time. In the dual beam instrument, UV light intensity measurements I0 (ozone-scrubbed air) and I (unscrubbed air) are performed simultaneously. Combined with other improvements, this instrument is the fastest UV-based ozone monitor on the market, with such small size, weight, and power requirements characteristics. Fast measurements are particularly desirable for unattended stations, aircraft and balloon measurements, where high spatial resolution is desired. The Model 205 Dual Beam Ozone Monitor is an Environmental Protection Agency (EPA) federal equivalent method (FEM). To better understand the monitoring accuracy and stability of this device, we conducted a comparative test. During the experiment, the results of the Thermo 49i device produced by Thermo Fisher Scientific were compared to that of the Model 205 device(Wang et al., 2017), and a UV-absorption ozone calibrator Thermo 49i-PS was used to generate the standard for the Model 205 and Thermo 49i devices. From July 28 to July 29, natural air was continuously monitored by the two instruments at the same time. We found that the accuracy of the Model 205 device was similar with to that of the Thermo 49i device, so it can be concluded that Model 205 has a good applicability in practical work. Because of the extreme environment, we could not perform any quarterly calibrations, such as at Global Atmosphere Watch (GAW) stations. We could only calibrate the instrument during the austral summer with a UV-absorption ozone calibrator Thermo 49i-PS. However, the appropriate correlation coefficients (r) were all greater than 0.99 in January 2017, and the drift of the instrument was within the allowable range (Supplementary Material-Fig. S1).

Line 113: vocabulary issue: "Model-49iPS UV absorptive ozone calibrator" should be "UV-absorption ozone calibrator Thermo 49i-PS"

Reply: According to your suggestion, we have made replacement and modification .

Line 128: why data filtering? In general, I feel dangerous to automatically eliminate

data without motivation (i.e. error codes in the internal diagnostic, extremely inconsistent values,...).

Reply: The data filtering here is mainly for Zhongshan station and Kunlun station. The deleted data includes: (1) missing measured value. (2) Monitoring data during calibration. (3) Severe fluctuation data in case of obvious pollution.

Section 2.2 Meteorological simulations should be renamed as "Air mass back-trajectory calculations"

Reply: According to your suggestion, we have made replacement and modification. Please find in the Line161

Section 2.2: a very poor description of the methodology (and strategy) for back-trajectory calculation is provided (no indication about time resolution of back-trajectories and frequency of their calculation). A discussion about usability and limitation of the use of these kind of back-trajectories based on coarse meteorological data is missing (e..g. it seems that the authors did not perform any sensitivity study to evaluate the impact of selecting different altitude or geographical position of the trajectory arrival point, which is a rather common practice to evaluate associated uncertainty). The authors mentioned that a clustering has been performed but they not provide any information about the clustering methodology nor provided evidences for cluster calculation in the paper. Vocabulary issue: "and the back-up time was 120 h". What is the back-up time?

Reply: According to your suggestion, we have made replacement and modificatio. Please find in the Line177~183.

The integral error part of the trajectory calculation error can be estimated by simulating the backward trajectory at the end of the forward trajectory and comparing the differences of the tracks. The starting point of the backward integration is set as (77.12 ° E, 80.42 ° S, 20m AGL), the backward integration is 120h. And then the point reached at this time is taken as the starting point. At this moment as the initial time, the forward simulation is 120h. In this simulation experiment, the contribution of integration error to trajectory calculation error is very small Within 72 hours. With the extension of integration time, the integration error slightly increases.

Line 170: the assigned weights look arbitrary. No explanation or motivation provided.

Reply：To expound the uncertainty due to the low values of nij, the PSCF values were scaled by a weighting function Wij (Polissar et al., 1999). We recalculated the weights of NOEE and OEE.

$$W_{ij(NOEE)} = \begin{cases} 1.00 & nij > 12Nave \\ 0.70 & 12Nave > nij > 3Nave \\ 0.42 & 3Nave > nij > 1.5Nave \\ 0.05 & Nave > nij \end{cases}$$

$$W_{ij(OEE)} = \begin{cases} 1.00 & nij > 8Nave \\ 0.70 & 8Nave > nij > 2Nave \\ 0.42 & 2Nave > nij > 1Nave \\ 0.05 & Nave > nij \end{cases}$$
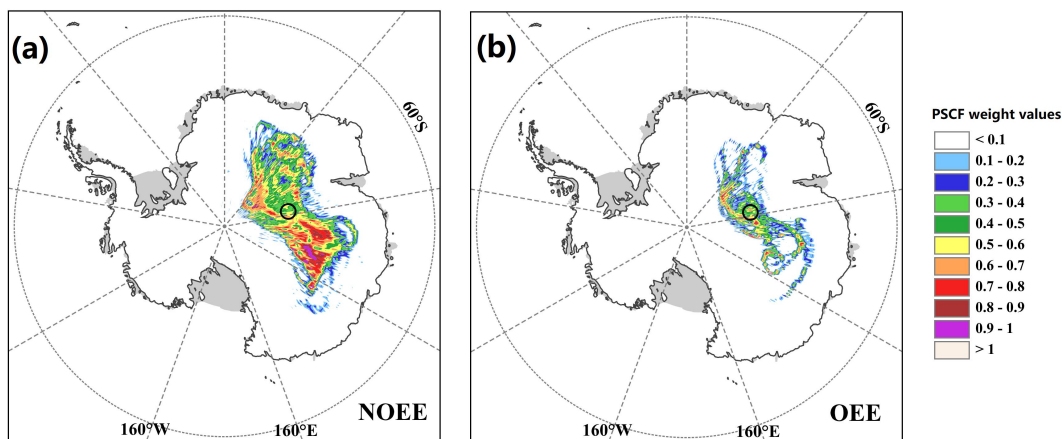
Figure 7. Likely source areas of surface ozone at Kunlun Station during the NOEEs (a) and OEEs (b) identified using PSCF (Potential Source Contribution Function).

Line 185: this sentence is not clear at all

Reply：The sentence has been modified..Please find in the Line 225~227.

Interestingly, the SP had the highest near-surface ozone concentration during non-polar night, whereas at DA presented the highest concentration occurred during polar night and the largest variation occurred at this site.

Line 194: "In Antarctica, the emissions of ozone precursors are generally less than those at mid and low latitudes". Which precursors are emitted in Antarctica? By which process? What do you mean with "generic less"? Please try to be quantitative.

Reply: According to your suggestion, to explain the seasonal variation characteristics of the three sites more clearly, Section 3.2 has changed a lot.

In this part, we define Oct-Mar as the warm season and Apr-Sept as the cold season, which is similarly to the definition of polar day and night.

In agreement with previous studies (Oltmans et al., 1976; Gruzdev et al., 1993; Ghude et al., 2005), the concentrations of near-surface ozone at the three stations were high and less variable during the cold season and low and more variable during the warm season (Figure 4). In Antarctica, the emissions of ozone precursors are generally less than those at mid and low latitudes, whereas ultraviolet radiation is relatively strong; thus, when solar radiation occurs, the depletion effect is much greater than the effects from photochemical reactions during the warm season (Schnell et al., 1991). As explained by previous studies, during the polar night, due to the lack of light, the photochemical reactions stoped. Moreover, due to the lack of loss effect, the ozone concentration gradually increased and the fluctuations became smaller. During the polar night, the monthly variation of surface ozone at ZS was lower than that at the DA but higher than that at the SP. However, due to strong UV radiation in the low

latitude areas and the presence of bromine controlled ozone depletion events in coastal areas, the ZS shows a large seasonal variations during the non-polar night (Wang et al., 2011; Prados-Roman et al., 2017). However, at the SP Station, the largest standard deviation was observed in December, similarly to the characteristics at Dome-C station (DC) from November to December (Legrand et al., 2009; Cristofanelli et al., 2018). Figures 3 and 4 show that the near-surface ozone showed obviously larger variations at the DA than the SP during the polar night, since, due to the different of geographical location, the meteorological conditions of DA and SP are different. The abnormal fluctuation of ozone concentration over the DA during the polar night may be related to its special geographical environment.

As mentioned in the introduction section, mountainous topography/mountain waves may disturb advection transport in the stratosphere and lead to downward transportation to the troposphere (Robinson et al., 1983). DA is on the summit of the east Antarctic Ice Sheet, and the tropospheric depth is only ~4.6 km (Liang et al., 2015), which favours exchange between the stratosphere and troposphere. However, the topography in this area is very flat and creates a disadvantage for mountain waves. Does ozone transport occur? We will analyse and discuss this question in section 4.

Line 207: "Specifically, the largest standard deviation was observed in October at DA because of multiple influences, including photochemical reactions by ozone precursors and ultraviolet radiation, photolysis reactions by strengthened ultraviolet radiation, and external air masses from the coast." These are only assumptions: not proofs are provided by the authors

Reply: According to your suggestion, we have deleted this paragraph. In the last paragraph, we added references and explanations. Please find in the Line 231-248.

Line 216: vocabulary issue: "Is there ozone exchange happening?" Ozone is transported not "exchanged".

Reply: exchange -> transport

Section 3: Overall, I think that the analysis of diurnal variation is not well executed in Section 3. What "normal days" are? If the authors' goal was to investigate the diurnal variability of ozone some relative measure should be used instead of actual mixing ratio (see for instance the earlier work by Helmig et al., 2007: "A review of surface ozone in the polar regions").

Reply: Thanks for your advice. We recalculated the average daily variation of each month. The standard deviation of the diurnal variation of each month is calculated to express the characteristics of its diurnal fluctuation. There is no diurnal radiation or temperature cycle at three stations. The section 3.3 has changed a lot.
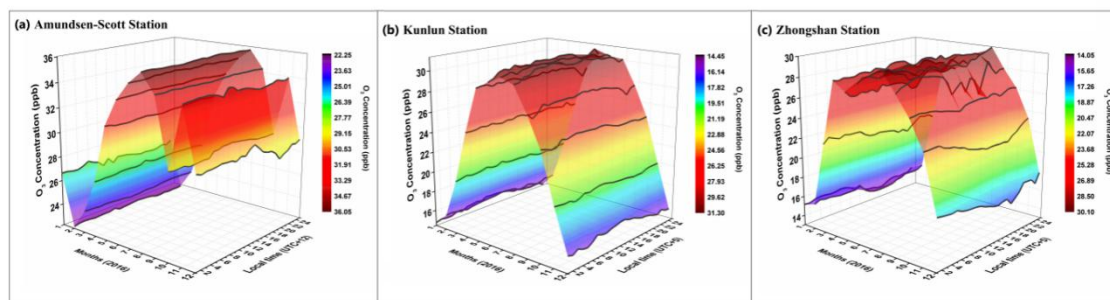
To characterize the typical monthly O3 diurnal variations at these three stations, we analysed the mean diurnal variations of O3 at the three stations (Figure 4) and the standard deviation of the mean diurnal variations (Figure 5). At the DA site, the mean diurnal concentrations of each month were relatively steady, and with the standard deviation of the mean diurnal concentration of each month was lower than 0.4 ppb. At the SP, the mean diurnal concentrations were less variable as well. Except for December, the standard deviation of the mean diurnal concentration was lower than 0.3 ppb. At the ZS, except for October, the standard deviation of the mean diurnal concentration is greater than that in the other two stations. In particular, the standard deviation of the mean diurnal concentration of the ZS in September, November and December exceeded 0.5 ppb. The mean diurnal variations in different time periods were not obvious, and the mean diurnal concentrations of the three stations fluctuated within a range of less than 1 ppb, indicating that daily photochemistry reactions did not have the main impacts on the overall characteristics of near-surface ozone at the three stations. The magnitude of the diurnal variation was low, which is similar to the variations found at other Antarctic stations (Gruzdev et al., 1993; Ghude et al., 2005; Oltmans et al., 2008).

Line 225: "Because of the limited number of normal days, the diurnal concentration fluctuated". If the dashed area represents a confidence interval (not explained in the figure), the diel (not "diurnal": vocabulary issue) cycle looks well consistent and not "erratic", instead. On the contrary, it is the green series that looks more "noisy". Please avoid using this kind of background colors in the Figure 4 plots. Is time expressed as UTC or what else in Figure 4? The diel variability of ozone (even when evident, see green line in plot 4a or black line in plot 4c) is not explained or motivated enough by the authors.

Reply: Thanks for your advice. We recalculated the average daily variation of each month. The standard deviation of the diurnal variation of each month is calculated to express the characteristics of its diurnal fluctuation.There is no diurnal radiation or temperature cycle at three stations. The section 3.3 has changed a lot. The error has been changed.

To characterize the typical monthly O3 diurnal variations at these three stations, we analysed the mean diurnal variations of O3 at the three stations (Figure 4) and the standard deviation of the mean diurnal variations (Figure 5). At the DA site, the mean diurnal concentrations of each month were relatively steady, and with the standard deviation of the mean diurnal concentration of each month was lower than 0.4 ppb. At the SP, the mean diurnal concentrations were less variable as well. Except for December, the standard deviation of the mean diurnal concentration was lower than 0.3 ppb. At the ZS, except for October, the standard deviation of the mean diurnal concentration is greater than that in the other two stations. In particular, the standard deviation of the mean diurnal concentration of the ZS in September, November and December exceeded 0.5 ppb. The mean diurnal variations in different time periods were not obvious, and the mean diurnal concentrations of the three stations fluctuated within a range of less than 1 ppb, indicating that daily photochemistry reactions did not have the main impacts on the overall characteristics of near-surface ozone

at the three stations. The magnitude of the diurnal variation was low, which is similar to the variations found at other Antarctic stations (Gruzdev et al., 1993; Ghude et al., 2005; Oltmans et al., 2008).

Figure 4. Mean diurnal variations in near-surface ozone concentrations at the Amundsen-Scott Station (a), Kunlun Station (b) and Zhongshan Station (c) during 2016
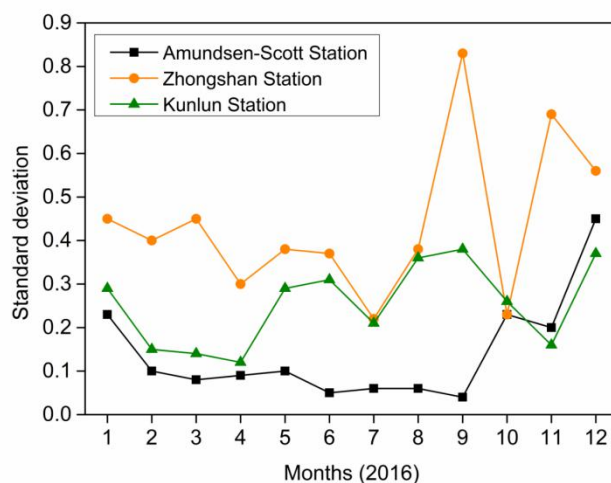
Figure 5. The Standard deviation of mean diurnal variations in near-surface ozone concentrations at the Amundsen-Scott Station, Kunlun Station and Zhongshan Station during 2016

Line 230: I do not agree. This can suggest that local photochemistry cannot have a role. But probably, if you consider the transport time, the integrated contribution of photochemistry related with snowpack NOx emissions can be relevant. This should be better assessed in the paper.

Reply: Due to the lack of measured NOx data, we can only illustrate the average daily characteristics of ground ozone concentration at three stations according to the chart. However, the general characteristics show that the daily photochemistry reactions did not have the main impacts on the overall characteristics of near-surface ozone at the three stations.

For the difference of diurnal variation of three stations in different months, more

measured data should be used for accurate analysis in the future.

Line 241 一 245: This part is confuse and the description of cycle leading to ozone production is not correct. Sorry but I cannot really understand why the cold environment can motivate the daytime variability at NA.

Reply: In the absence of measured evidence, I think your criticism is right. I deleted my subjective guesses, hoping to bring them to the next experiment.

Line 254 一 264: again, this is mostly a cut-and-past from an already published paper.

Reply: The sentence has been modified.

Our method to select the days characterized by OEEs is based on the two-steps procedure shown in Cristofanelli et al. (2018). The first step consists in calculating the O3 annual cycle not affected by the OEEs (by using a sinusoidal fit), while the second one concerns the calculation of a probability density function (PDF) of the deviations from the sinusoidal fit, plus the application of a Gaussian fit to the obtained PDF. As reported in Giostra et al. (2011), the deviations from the Gaussian distribution (calculated by using the Origin 9© statistical tool) indicate observations affected by non-background variability.

Figure 6: The analysis and interpretation of back-trajectory analysis presented in Figure 6 is not robust at all. Firstly the conditional probability should be calculated for winter and summer, if you want to demonstrate a prominent role of STT versus other processes in winter. From Figure 6, it looks that only a small number of TRJ are used for this analysis (how much?): unfortunately this strongly limits the statistical robustness of results (that, in any case, do not support STT occurrence). Moreover, I'm not able to see any difference between back-trajectories in polar night/day that you used for motivate the role of STT during the winter.

Reply: The fourth section has changed a lot. The original error no longer exists.

Line 339: "Here, we use STEFLUX to 340 identify STT events and define the height of tropospheric potential vorticity PVU = 2." You did not use STEFLUX, actually. Moreover, in the Southern Hemisphere medium-high latitude, stratospheric air-masses can be traced setting PV < - 2 pvu and not PV > 2 pvu!

Reply: The fourth section has changed a lot. The original error no longer exists.

Line 370: "To quantitatively analyse the influence of STT events on OEEs, we examined 370 the appearance of STT events above DA and found that STT events (550 hPa PV>2 PVU) accounted for 55% of the polar night in 2016." This is wrong: firstly, to trace stratospheric air-masses, you should detect PV values lower than 一 2 pvu. Secondly, as clearly see by Figure 7 at 550 hPa the PV variability is affected by non-adiabatic process occurring near the surface and thus it cannot be used to trace STE.

Reply: The fourth section has changed a lot. The original error no longer exists.

From Figure 7 is not possible to see any obvious correlation between ozone at DA and the downward transport of stratospheric air masses: the supposed link between high near-surface O3 at DA and occurrence of STE is not supported by a quantitative analysis (only a qualitative comment to Figure 7 is provided). Moreover, the wrong detection methodology used to identify the STE events brings an evident overestimation of STT occurrence: all the winter period (except August) appeared to be affected by STT (even without effect on near-surface O3, see e.g. the period from 6/20 to 7/15 which not support your hypothesis).

Reply: The fourth section has changed a lot. The original error no longer exists.

Finally, Figure 8 does not provide any reasonable support to the hypothesis that STE are driving O3 variability during winter. I do not see any evident differences between OEE and NOEE. It is not clear why using the rate of change of the hourly O3 m.r. instead of the actual O3 m.r.

Reply: The fourth section has changed a lot. The original error no longer exists.