

Reply for Anonymous Referee #1

I agree with most of the comments and criticism that has been voiced already by the two other reviewers. This manuscript presents surface ozone data from a badly undersampled region on Earth. This makes me wish to eventually see this work published. However, the experimental description, and the data presentation and interpretation, as well as the writing of the manuscript need substantial additional work before it meets my expectation for peer-reviewed publication. Below are some specific comments in addition to the points already raised by the two other reviewers.

Total response: Thank you for your comments and suggestions on our article. 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 20: Clarify which data go with which station. Reduce significant figures of the averaged results here and in remainder of the text. Explain what the error margins are (e.g. 1-sigma variability of hourly data?).

Reply: The summary has been modified accordingly. The error range here refers to the standard deviation of the annual hourly average concentration.

“The annual mean values at the three stations (DA, SP and ZS) were 29.2 ± 7.5 ppb, 29.9 ± 5.0 ppb and 24.1 ± 5.8 ppb.”

Line 47: Define NO_x when it's mentioned for the first time.

Reply: Thanks for your suggestion. We have modified the original text and supplemented the definition of NO_x.

*“Ozone (O₃) photochemical production in the troposphere occurs by hydroxyl radical oxidation of carbon monoxide (CO), methane (CH₄) and non-methane hydrocarbons (generally referred to as NMHC) in the presence of **nitrogen oxides (NO_x)** (Monks et al., 2015)”*

Line 64: There are further publications that should be considered in the discussion of ozone chemistry in Antarctica: [Bauguitte et al., 2011; Davis et al., 2004; Davis et al.,

2008; Helmig et al., 2008a; Helmig et al., 2008b; Neff et al., 2008; Oltmans et al., 2008]

Reply: Thanks for your suggestion, this error has been corrected. We added references and reinterpreted the contents.

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; Bauguitte et al., 2011). Indeed, Helmig et al. (2008a,b) provide further insight into the vigorous photochemistry and ozone production that result from the highly elevated levels of nitrogen oxides (NO_x) in the Antarctic surface layer. During stable atmospheric conditions (which typically existed 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) provide the earlier results that shallow mixing layers associated with light winds and strong surface stability can be among the dominant factors leading to high NO levels were repeated. 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.

Line 111: The 2B ozone monitor does not quite reach the analytical accuracy and precision of regular benchtop ozone analyzers. It can also have quite some sensitivity drifts over time. The performance of the analyzers should be presented in more detail. Calibration results/graphs should be provided as Supplemental Material.

Reply: According to your suggestion, this part has been modified and replaced by new analysis and description. We found that there was drift in the instrument, but the data was available after cross concentration calibration. We make a detailed supplement to the performance characteristics of the instrument and the calibration chart.

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 made simultaneously. Combined with other improvements, this instrument is the fastest UV-based ozone monitor on the market, while have small size, weight, And power requirements characteristics. Fast measurements are particularly desirable for unattended station, 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). In order to better understand the monitoring accuracy and stability of model 205, we conducted a comparative test. During the experiment, the Thermo 49i produced by the Thermo Fisher Scientific company was used as a comparison with the Model 205 (Wang et al., 2017), and a UV-absorption ozone calibrator Thermo 49i-PS is used to generate the standard for Model 205 and Thermo 49i, During July 28,2016 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 was similar with Thermo 49i, so it can be concluded that Model 205 has a good applicability in practical work. Because of the extreme environment, we can't do quarterly

calibration like the Global Atmosphere Watch (GAW) stations. we could only calibrate the instrument during austral summer with a UV-absorption ozone calibrator Thermo 49i-PS. However, the appropriate correlation coefficients (r) were all greater than 0.99 in Jan 2017. The drift of the instrument is within the allowable range (Supplementary Material-Fig. S1).

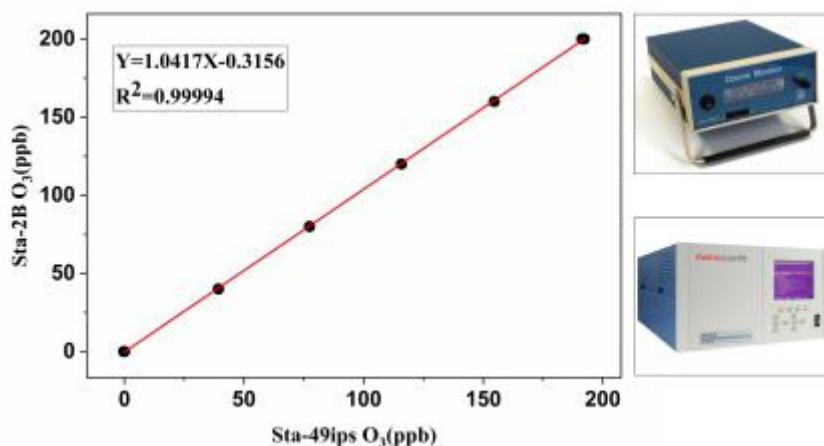


Figure S1. Dynamic calibration of the linear equation about Model 205

Line 117: Please provide more information on the reference ozone monitor. This is not a commonly recognized instrument.

Reply: According to your suggestion, this part has been modified and replaced by new analysis and description. We make a detailed supplement to the performance characteristics of the instrument.

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 I_0 (ozone-scrubbed air) and I (unscrubbed air) are made simultaneously. Combined with other improvements, this instrument is the fastest UV-based ozone monitor on the market, while have small size, weight, And power requirements characteristics. Fast measurements are particularly desirable for unattended station, 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). In order to better understand the monitoring accuracy and stability of model 205, we conducted a comparative test. During the experiment, the Thermo 49i produced by the Thermo Fisher Scientific company was used as a comparison with the Model 205 (Wang et al., 2017), and a UV-absorption ozone calibrator Thermo 49i-PS is used to generate the standard for Model 205 and Thermo 49i, During July 28,2016 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 was similar with Thermo 49i, so it can be concluded that Model 205 has a good applicability in practical work. Because of the extreme environment, we can't do quarterly calibration like the Global Atmosphere Watch (GAW) stations. we could only calibrate the instrument during austral summer with a UV-absorption ozone calibrator Thermo 49i-PS.

However, the appropriate correlation coefficients (r) were all greater than 0.99 in Jan 2017. The drift of the instrument is within the allowable range (Supplementary Material-Fig. S1).

Line 125: Give credit, possibly offer co-authorship to the P.I.s and agencies that produced the data from South Pole.

Reply: According to your suggestion, 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>).

Line 131: What caused the loss of data coverage at Kunlun Station?

Reply: Due to the time when the Chinese Antarctic scientific expedition arrived at Dome A, the instrument made normal observation from January 20, 2016. As a result, January's data is missing a lot.

Line 155: Define 'PM'.

Reply: The words used here are not accurate. The original text is changed here to: "If the total number of end points that fall in the cell is n_{ij} and there are m_{ij} points for which the measured ozone parameter exceeds a criterion value selected for this parameter, then the conditional probability, the PSCF, can then be defined as:"

Line 176: 'Concentration' is the wrong term as ozone data are presented as molar ratio, not as concentration.

Reply: The error has been changed. Concentration -> molar ratio

Line 179: Specify if you mean average, median, or ? higher mole fractions.

Reply: According to your suggestion, this part has been modified and replaced by new analysis and description.

*The annual mean molar ratios of near-surface ozone at DA, the SP, and the ZS were 29.2 ± 7.5 ppb, 29.9 ± 5.0 ppb and 24.1 ± 5.8 ppb, respectively. **The maximum annual mean molar ratio reached 42.5 ppb, 46.4 ppb and 32.8 ppb, and the minimum annual mean molar ratios were 14.0 ppb, 10.9 ppb and 9.9 ppb, respectively. The inland stations are characterized by higher annual mean molar ratios than the coastal station.***

Line 182: Define the polar day and night windows by day of year margins.

Reply: We have followed your suggestion and made some supplementary changes to this sentence.

In Figure 3, we define the polar day and night windows by day of year margins and used different shading colours to signify the polar day and polar night.

Line 189: I found this whole section hard to read and comprehend.

Reply: In order to explain the seasonal variation characteristics of the three sites more clearly. The section 3.2 has changed a lot.

In this part, we determine Oct-Mar as the warm season and Apr-Sept as the cold season, similar to the definition of polar day and night.

In agreement with previous studies (Oltmans et al., 1976; Gruzdev et al., 1993; Ghude S D et al., 2005), the concentrations of near-surface ozone at the three stations were high and less changeable during the cold season and low and more changeable 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 there is solar radiation, the depletion effect is much greater than the effects from photochemical reactions during the warm season (Schnell et al., 1991). As previous studies have explained, during the polar night, due to the lack of light, photochemical reaction stopped. And Due to the lack of loss effect, the ozone concentration gradually increases and the fluctuation becomes smaller. During the polar night, the monthly variation of surface ozone in ZS is smaller, higher than SP, but lower than DA. However, due to strong UV radiation in low latitude areas and the presence of bromine controlled ozone depletion events in coastal areas, the station shows a large seasonal variation during the non polar night (Wang et al., 2011; Prados-Roman et al., 2017). However, at the Amundsen-Scott Station, the largest standard deviation was observed in December, similar to the characteristics at 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 DA than at the SP during the polar night. Due to the difference of geographical location, the meteorological conditions of DA and SP are different. The abnormal fluctuation of ozone concentration over 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 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. Is there ozone transport happening? We will analyse and discuss this question in section 4.

Line 219: Same here. What do you actually mean by 'diurnal variability'?

Reply: It is the change characteristics of the diurnal variation of each month.

Line 224: How can you state that the diurnal concentration fluctuated greatly if the standard deviation is just 0.7 ppb?

Reply: Yes, the expression here is ambiguous. We have reinterpreted and charted Section 3.3. We found that the diurnal variation fluctuation of three stations was less than 1 ppb.

Line 244: There is a rich body of more recent ozone snow photochemistry literature that should be considered in this discussion as well.

Reply: Due to the lack of measured NO_x 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 422: The Neff et al., 2008, paper is about South Pole.

Reply: We have revised it in the article.

Line 430-432: I have been wondering about this all along reading this manuscript. Is this SST discussion even worth the effort given these pretty obvious limitations?

Reply: The section 4.2 has changed a lot. Indeed, STEFLUX was applied, state here the importance of investigating STT events in Antarctica, which is a region poorly studied in this respect, and where large differences between the estimates of STT frequencies exist.

Line 436-437: Absolutely not acceptable. Quality-controlled final data should be made available in a well-recognized public data archive.

Reply: We will make available in a well-recognized public data archive.

Line 636: I would prefer defining the time windows by day of year. There is no diurnal radiation or temperature cycle at South Pole. How do the authors explain the diurnal behavior seen in the ozone 'on a normal day'?

Reply: According to your suggestion, this part has been modified and replaced by new analysis and description. I agree with you. 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 analyzed the mean diurnal variations of three stations (Figure 4) and the standard deviation of mean diurnal variations (Figure 5). At DA, the mean diurnal concentrations of each month were relatively steady, with the standard deviation of the mean diurnal concentration of each month is lower than 0.4ppb. At the SP, the mean diurnal concentrations of each month were less changeable too. Except for December, the standard deviation of mean diurnal concentration was lower than 0.3ppb. At the ZS, except for October, the standard deviation of mean diurnal concentration in other months is greater than that in other two stations. In particular, the standard deviation of the mean diurnal concentration of ZS in September, November and December exceeded 0.5ppb. 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 S D et al., 2005; Oltmans et al., 2008).

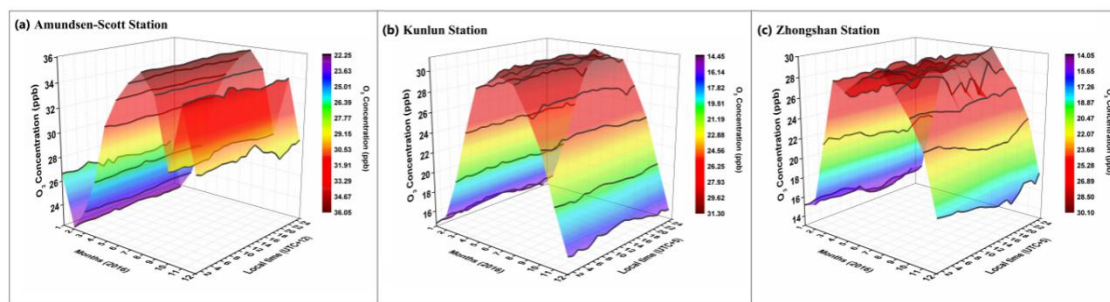


Figure 4. Mean diurnal variations in near-surface ozone concentrations at the Amundsen-Scott Station (a), Kunlun Station (b) and Zhongshan Station (c) during 2016

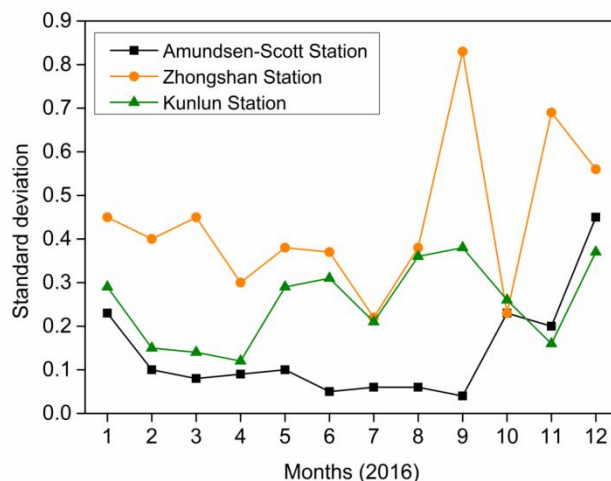


Figure 5. The Standard deviation of mean diurnal variations in near-surface ozone concentrations at the Amundsen-Scott Station, Kunlun Station and Zhongshan Station during 2016

Line 639: Explain abbreviations in the graphs in the figure legend.

Reply: The error has been changed.

Line 640: I would expect the annual frequency results to be much smaller than the monthly results. How can they be this similar?

Reply: The Reviewer is right, but this is related to the error in the formula within the caption.

$$\textit{Monthly frequency} = \frac{\text{number of OEE days for each month}}{\text{number of days in the month}}$$

$$\textit{Annual frequency} = \frac{\text{number of OEE days for each month}}{\text{total number of OEE days}}.$$

Line 643: Trajectory colors are hard to differentiate.

Reply: The error has been changed.

Line 649: Harmonize time stamps between figures.

Reply: The error has been changed.

Line 656: What are you trying to show with this figure? I don't really see a convincing dependency?

Reply: According to the content of the article, the figure has been modified and corrected.

References

Bauguitte, S. J. B., N. Brough, M. M. Frey, A. E. Jones, D. J. Maxfield, H. K. Roscoe, M. C. Rose, and E. W. Wolff (2011), A network of autonomous surface ozone monitors in Antarctica: technical description and first results, *Atmospheric Measurement Techniques*, 4(4), 645-658, doi:10.5194/amt-4-645-2011.

Davis, D., G. Chen, M. Buhr, J. Crawford, D. Lenschow, B. Lefer, R. Shetter, F. Eisele, L. Mauldin, and A. Hogan (2004), South Pole NO_x chemistry: an assessment of fac-