Responses to the Interactive comment from Referee #1 on "Summer ozone variation in North China based on satellite and site observations" by Lihua Zhou et al.

Anonymous Referee #1

To reviewer:

Thank you very much for your great efforts on our manuscript. We also appreciate the referees for the valuable suggestions and questions.

This manuscript aims to analyze the variation and the influential factors in summertime ozone over North China using multi-satellite and ground-based observations. While topic is of importance to the field, I don't think the authors have presented and interpreted the data in a convincing way. There are a number of issues:

1.

(1) comments from Referees

I don't think satellite-observed tropospheric ozone can be used as an indicator of surface ozone pollution for several reasons. First, satellite retrieval of tropospheric ozone is very uncertain, as the abundance from stratospheric ozone is so dominated that separating tropospheric ozone from stratospheric ozone is very difficult. There is no discussion on the uncertainties of OMI ozone throughout the paper. Second, tropospheric ozone is not the same as the near-surface ozone. Upper tropospheric ozone is more often considered as a greenhouse gas, while near-surface ozone is considered as a pollutant. Throughout the manuscript, the authors fail to distinguish tropospheric ozone with near-surface ozone. The authors mention that they use ground-observed ozone, but there are almost no discussions on this. How does the trend in ground-level ozone agree with satellite-observed tropospheric ozone?

(2) author's response

Thank you for your comments. Considering the above reasons，We intend to use ground-level ozone observation data to verify tropospheric ozone changes. At the same time, we have added an introduction to satellite tropospheric ozone.
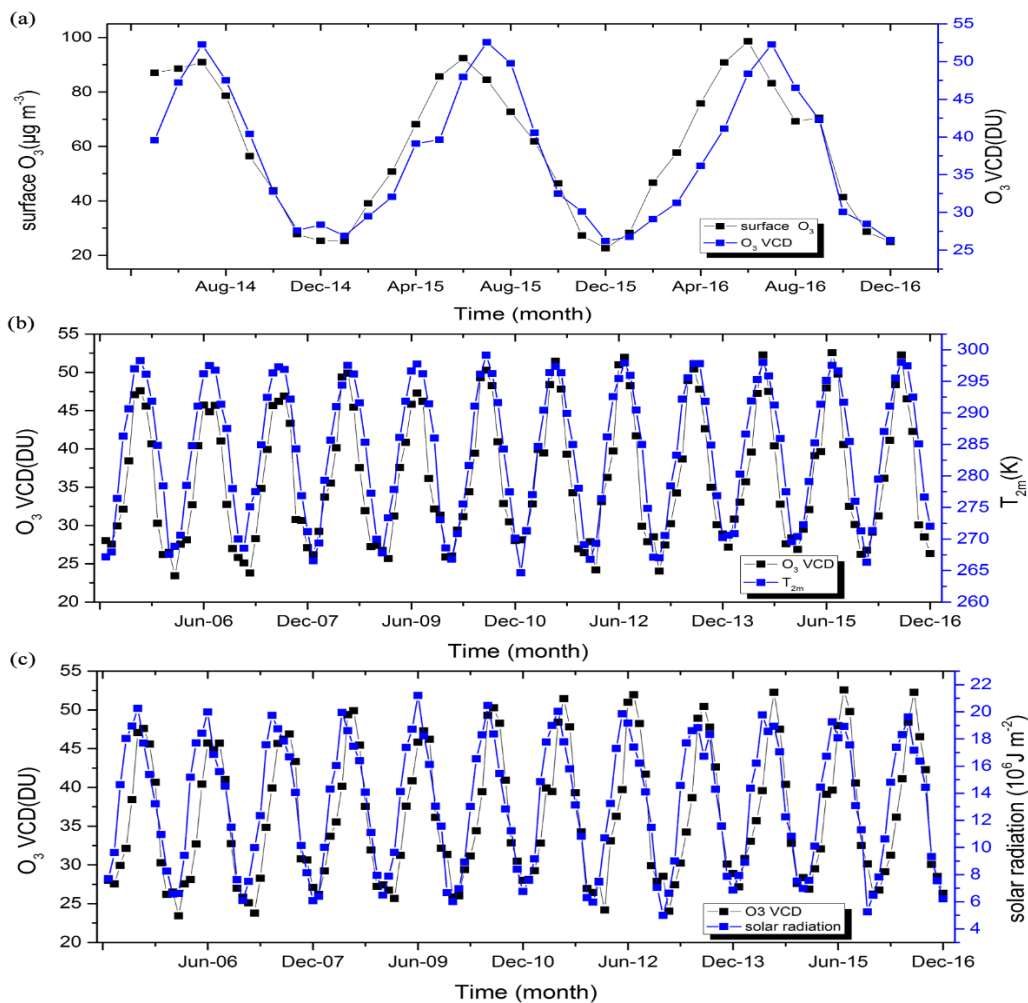
(3) author's changes in manuscript

2.1 Satellite data

Tropospheric ozone data is obtained from combined observations of two satellite instruments, Ozone Monitoring Instrument (OMI) and Microwave Limb Sounder (MLS). Daily OMI/MLS tropospheric ozone data were determined by subtracting MLS stratospheric column ozone from OMI total column ozone. Stratospheric column ozone from MLS was spatially interpolated (2D Gaussian/linear latitude-longitude interpolation) each day to fill in between the actual along-track measurements. The monthly means were then determined by averaging all available daily data within each month. The formatting of the data files is 1 degree latitude by 1.25 degree longitude resolution. OMI total column ozone was filtered for near clear-sky conditions by including only measurements when coincident OMI reflectivity was less than 0.3 (https://acd ext.gsfc.nasa.gov/Data_services/cloud_slice/new_data.html).

The correlation coefficient R between OMI/MLS tropospheric O_3 and WOUDC ozonesonde tropospheric O_3 is 0.92, RMS is 6.0ppbv from April to October. And the deviation is smaller in the location with lower latitude. It indicates closely similar signatures for seasonal cycles and spatial variability from the comparisons of OMI/MLS tropospheric ozone between the climatology and other data products (Ziemke et al., 2006, 2011).

Daily sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), monthly formaldehyde (HCHO) data are from the OMI aboard the EOS Aura spacecraft, launched on July 15, 2004. The spatial resolution is $0.25°\times0.25°$. Detailed data descriptions are provided in the OMI Data User's Guide and references there in (Zhou et al., 2017; Huang et al., 2015; Zhu et al., 2014; Gray et al., 2011). The daily retrieved total column carbon monoxide (CO) is from Measurement of Pollution in the Troposphere (MOPITT), available at https://terra.nasa.gov/about/terra-instruments/mopitt(Heald et al., 2003). And its resolution is $1° \times 1°$. In our analysis, the missing values are eliminated. Individual satellite observations have large errors, but averaging over long periods of time and large spatial extent can reduce them. And systematic errors affect all data, so the impact on the trend is not obvious.

Fig.2(a) shows the tropospheric ozone from OMI/MLS satellite and the ground observations in North China. The correlation coefficient between them is 0.89. And the statistical results are significant at 0.05. But it seems that the tropospheric ozone peak is one month later than the ground peak. The correlation coefficient between the ground value and the troposphere value in next month is greater, which is 0.93 and significant at 0.05.Thusthere is a high correlation between the tropospheric ozone and the ground ozone concentration.

Figure 2: The tropospheric ozone vertical column density (VCD), near - surface ozone, monthly temperature at 2 metre (T$_{2m}$) and surface net solar radiation (SSR) in North China.

2

(1) comments from Referees

The trend analysis and the attribution is not convincing to me for a number of reasons. First, the trend analysis is mostly qualitative. The authors suggest an overall increasing trend of ozone from 2005 to 2016, but there is no information on the trend and the statistical significance of the trend. Same is true for other components. Second, the authors try to attribute the trend to other factors by analyzing if the trend in ozone coincides with NO2 or CO or SO2 or HCHO, but I couldn't see how they are correlated just by reading the manuscript. I'd suggest the authors at least **provide R2 for the correlation.** Even if they are statistically correlated, correlation doesn't mean causality. Third, the authors conclude that VOC, temperature and radiation are the most important factors for increasing ozone, but Figure 6 shows the inter-annual variability of ozone does not follow any of them. I'd suggest the authors provide more quantitative evidence.

(2) author's response

More data analysis, correlation analysis and significance testing are added. We distinguished interannual and seasonal variation of tropospheric ozone and calculate the correlation coefficient separately.

(3) author's changes in manuscript

3.1 Interannual variation of tropospheric ozone

Due to lack of data, ground observation data was only obtained after 2014 in North China. Monthly mean tropospheric ozone, temperature at a height of 2 meters, surface solar radiation are available for the period of 2005 to 2016. Fig.2(a) shows the tropospheric ozone from OMI/MLS satellite and the ground observations in North China. The correlation coefficient between them is 0.89. And the statistical results are significant at 0.05. But it seems that the tropospheric ozone peak is one month later than the ground peak. The correlation coefficient between the ground value and the troposphere value in next month is greater, which is 0.93 and significant at 0.05.Thusthere is a high correlation between the tropospheric ozone and the ground ozone concentration.

Previous studies have shown that changes in ozone are the result of a common image of meteorological factors and precursors. Therefore, we first analyze the impacts of two important meteorological factors, temperature and solar radiation on ozone. Fig. 2(b) shows the correspondence between near-surface temperature and tropospheric ozone. The trends for them are very consistent, with a significant statistical correlation coefficient of 0.93. And their annual peaks also appeared at the same time (summer).More details about ozone changes in the summer will be discussed later. The effect of solar radiation on ozone can be seen in Fig. 2(c). The correlation coefficient between the two time series is0.82.Tropospheric ozone peak generally appears 1-2 months later than the solar radiation. But the solar radiation is highly correlated with the ground-level ozone, with a significant statistical correlation coefficient of 0.98.

Surface concentrations of trace gases NO_2, SO_2, CO are collected for all sites in NCP for the period 2014 -2016.We eliminated the missing values and averaged the data for all sites. The correlation coefficients and significance of the gases with ozone are shown in Table 1. The statistical analysis shows these gases are negatively correlated with the tropospheric and ground-level ozone, and the results are significant (at level of 0.05).This suggests that the ozone pollution and the trace gas pollution might not be concurrent.

The above results are based on monthly averages. To examine the interannual variations of ozone and trace gases, we use the case of Beijing, since more historical data for Beijing is available compared with the surrounding provinces or cities (Hebei, Tianjin, Shandong, Shanxi and Henan).

Figure 3 shows the interannual variations of tropospheric ozone and ground-level trace gases as well as 2 m temperature and solar radiation from 2005 to 2016. Interannual variations in solar radiation and temperature presented nonobvious pattern. There was a rising trend in tropospheric ozone (0.14 DU/a). After 2013, the concentration of CO increased and maintained a stable value. After 2008, the level of NO_2 has dropped. Since 2006, SO_2 has been declining continuously. Table 2 shows the correlation coefficient between annual tropospheric ozone and ground observations of NO_2, SO_2, CO, temperature (T), surface solar radiation downwards (R) in Beijing. There is a significant negative correlation between tropospheric ozone and SO_2.The same is true for NO_2.This indicates that the interannual variation of ozone is opposite to that of NO_2 and SO_2.The reduction of these two trace gases did not reduce ozone, and even increased the production of ozone. The positive relationship between ozone and CO is weak, and the results are not significant. The annual ozone has a weak negative correlation with annual temperature and solar radiation, and the results are not significant either. Therefore, once the monthly value change is removed, the relationship between ozone and meteorological factors might probably be smoothed and hidden. Therefore, the study of ozone needs to be divided into seasons. And this part is introduced below in Sect. 3.2.

Although temperature and solar radiation are also important factors in photochemical production of O_3 (Tang et al., 2006), from the statistical relationship, the positive correlation is weak and not significant between tropospheric O_3 and temperature/solar radiation (Table 3). VOCs and NOx are the major ozone precursors. As shown in Table 3, the relationship between O_3 and NO_2 is not so significant, and the correlation coefficient is 0.05. Another significant factor is formaldehyde with a correlation coefficient of 0.3 with O_3. Sulfur dioxide and carbon monoxide are not important ozone precursors.

Studies have shown that the variation trend of tropospheric O_3 is rising, with an average growth rate 0.2DU/year. The tropospheric ozone column in North China has been at a high level for the past 3 years. The trend of tropospheric O_3 and ground-level O_3 is relatively consistent on seasonal changes. If all seasons considered, temperature and solar radiation are the dominant factors affecting ozone. In the summer, there is a significant positive relationship of O_3 with satellite observations of HCHO. However, O_3 variation trends are opposite to SO_2 and NO_2 over 2012 - 2016. Since HCHO increases by 0.048×10^{15} molec cm^{-2} per year during 2005 to 2016, and NO_2 is reduced by 0.90×10^{15} molec cm^{-2} per year in summer since 2012. This indicates that the increase in ozone in North China was probably caused by the increase of non-methane volatile organic compounds (NMVOC), rather than by nitrogen oxides. For all seasons, the effects of SO_2 and CO on ozone are not significant.

		surface O_3	T_{2m}	R	surface CO	surface NO_2	surface SO_2
O_3 VCD	R*	8.92E-01	9.28E-01	8.23E-01	-8.13E-01	-8.86E-01	-8.15E-01
	P	7.25E-12	1.67E-62	2.94E-36	1.53E-08	1.55E-11	2.38E-08
surface O_3	R*		8.84E-01	9.76E-01	-8.13E-01	-8.69E-01	-7.89E-01
	P		1.90E-11	2.09E-21	1.85E-10	1.15E-10	1.32E-07

*$p<0.05$.

Table 2: Correlation coefficient between annual tropospheric ozone and ground observation NO₂, SO₂, CO, temperature (T), surface solar radiation downwards (R) in Beijing.

		SO$_2$ （mg m^{-3})	NO$_2$ （mg m^{-3})	CO （mg m^{-3})	T(K)	R(J m^{-2})
O_3(DU)	R*	-0.8747	-0.7395	0.3041	-0.2458	-0.3009
	P	0.0002	0.0060	0.3366	0.2458	0.3419

*$p<0.05$.

Table 3. Correlation coefficient value from satellite observations in summer during 2005 – 2016 in NCP.

		NO$_2$	SO$_2$	HCHO	CO	Radiation	T
O_3 VCD	R*	0.05	-0.33	0.37	-0.13	0.17	0.28
	P	0.76	0.05	0.02	0.44	0.33	0.10

*$p<0.05$.

3

(1) comments from Referees

While the idea of combining satellite and in-situ observations is interesting, I don't see any connection between them. The authors simply analyze them separately. I think ground-based observations could be useful for validating the variation seen from satellite observations.
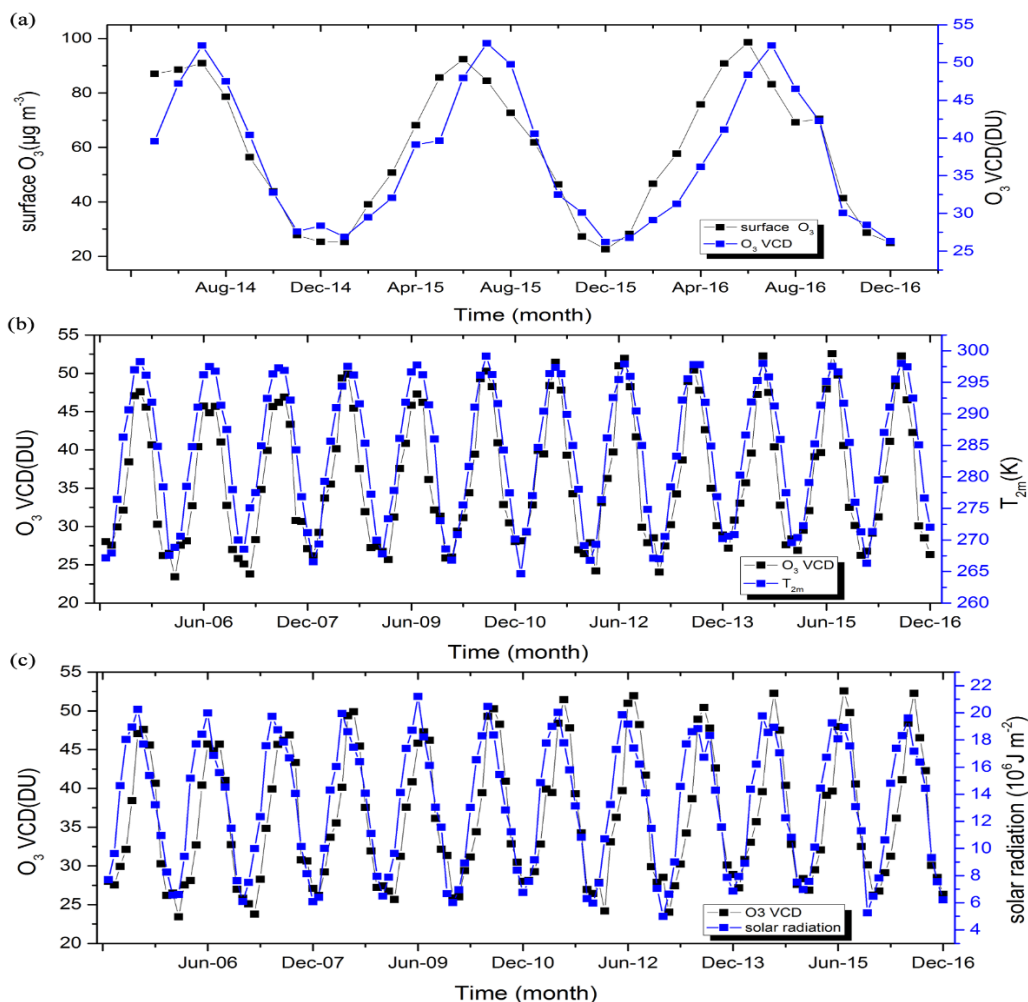
(2) author's response

Ground observations do help to verify satellite observations, so we intend to add this comparison.

(3) author's changes in manuscript

Fig.2(a) shows the tropospheric ozone from OMI/MLS satellite and the ground observations in North

China. The correlation coefficient between them is 0.89. And the statistical results are significant at 0.05. But it seems that the tropospheric ozone peak is one month later than the ground peak. The correlation coefficient between the ground value and the troposphere value in next month is greater, which is 0.93 and significant at 0.05. Thus there is a high correlation between the tropospheric ozone and the ground ozone concentration.

Figure 2: The tropospheric ozone vertical column density (VCD), near - surface ozone, monthly temperature at 2 metre (T_{2m}) and surface net solar radiation (SSR) in North China.

4

(1) comments from Referees

The authors tend to use satellite data without considering the potential issues (e.g. missing values, detection limit) and uncertainties of satellite retrieval. I think the authors should at least discuss how the uncertainties of satellite retrieval would affect the results.

(2) author's response

The authors appreciate your constructive comments. We will provide uncertainty analysis of satellite data, such as missing values, factors that affect the inversion results. In the calculation process, we eliminate the missing values, which may have a certain impact on the observations.

(3) author's changes in manuscript

Tropospheric ozone data is obtained from combined observations of two satellite instruments, Ozone Monitoring Instrument (OMI) and Microwave Limb Sounder (MLS). Daily OMI/MLS tropospheric

ozone data were determined by subtracting MLS stratospheric column ozone from OMI total column ozone. Stratospheric column ozone from MLS was spatially interpolated (2D Gaussian/linear latitude-longitude interpolation) each day to fill in between the actual along-track measurements. The monthly means were then determined by averaging all available daily data within each month. The formatting of the data files is 1 degree latitude by 1.25 degree longitude resolution. OMI total column ozone was filtered for near clear-sky conditions by including only measurements when coincident OMI reflectivity was less than 0.3 (https://acd ext.gsfc.nasa.gov/Data_services/cloud_slice/new_data.html).The correlation coefficient R between OMI/MLS tropospheric $O_3$and WOUDC ozonesonde tropospheric $O_3$is 0.92, RMS is 6.0ppbv from April to October. And the deviation is smaller in the location with lower latitude. It indicates closely similar signatures for seasonal cycles and spatial variability from the comparisons of OMI/MLS tropospheric ozone between the climatology and other data products (Ziemke et al., 2006, 2011).

5

(1) comments from Referees

The Introduction should be expanded to include the large body of literature behind this topic. For example, how severe is the ozone pollution in China? How have ozone and its precursors changed over the past decades? How have satellite data been used for studying air pollution (especially ozone) in China?

(2) author's response

We reorganized the introduction and added the corresponding references.

(3) author's changes in manuscript

O_3 pollution in China is serious. Yangtze River Delta (YRD) is one of the regions experienced serious O_3 pollution, with the highest frequency occurring in late spring and early summer (Cheung and Wang, 2001). Pearl River Delta (PRD) is another region with serious ozone pollution (Zhang et al., 2011).North China Plain (NCP) has been not only suffering from severe hazy weather but also one of the regions with serious O_3 pollution in summer. It was reported that the high level O_3 concentration reached 286 ppbv in the rural region of Beijing (Wang et al., 2006). Most of the research on ozone in NCP was based on model simulations and site observations (Duan et al., 2008;Xie et al., 2008;Shao et al., 2009; An et al., 2012), and lacks long-term sequence presentation. This is the focus of this paper.

Research on long – term changes of ozone pollution is very limited due to the lack of data. In the PRD, the increasing rate of $O_3$was 0.86 ppbv/year from 2006 to 2011(Li et al., 2014). In the NCP, aircraft data indicated boundary-layer ozone with a large increase of 2%/year in the summer time during 1995–2005; the surface daily 1-hour maximum ozone in urban Beijing increased 1.3%/year during 2001–2006 (Tang et al., 2009) and the daily 8-hourmaximum O_3 at rural Shangdianzi rose at a rate of 1.1 ppbv/year during 2003–2015 (Maet al., 2016). However, due to the environmental protection regulations in China, the emissions of precursors decreased since 2011 and 2012. For 2010 and 2014, NO-emissions were 1.6 and 1.5 Gg/d in PRD respectively, 3.9 and 3.0 Gg/d in the YRD, and 15.6 and 14.3 Gg/d in NCP. OMI HCHO data shows upward trends in East Asia resulting from anthropogenic effects; however, the trends are negative in the PRD. Areas around the Bohai Sea have become more NO-saturated (Souri et al., 2017).

A large range in spatial distribution and long-term temporal changes of O_3 are observed in satellite data. Typically, O_3 pollution is closely related to other air pollutants, such as NO_x and volatile organic compounds (VOCs) (Sillman et al., 2003), as well as temperature and humidity. A lot of work has been done on case studies of the O_3–VOC–NOx system sensitivity. However, the ozone long term trend is

less noticed and studied (Carrillo-Torres et al., 2017).

In recent years, satellite data have been used to study air pollutants (Safieddine et al., 2016;Jin and Holloway, 2015).Atmospheric environmental satellite loads have nadir and limb scan modes. Limb mode instruments provide vertical column density and vertical profile data. Microwave Limb Sounder (MLS), Tropospheric Emission Spectrometer (TES), Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) are all limb instruments and provide trace gas profiles (NO_2, SO_2, O_3, CO, H_2O, NO, HCHO etc.). Ozone Monitoring Instrument (OMI), Measurement of Pollution in the Troposphere (MOPITT) and Total Ozone Monitoring Spectrometer (TOMS) are nadir instruments and provide total vertical column(O_3, SO_2, NO_2, HCHO, CO, CH_4).These data had be used to study air pollution (Irie et al.,2008), greenhouse gas emissions (Zhang et al.,2013) in China. Satellite data of column density for SO_2, NO_2 and CO are often used to study air pollution directly. However, due to the particular characteristics of the vertical distribution of ozone (the peak in the stratosphere), it is not appropriate to use the total amount of the nadir column data alone. It is necessary to combine the vertical profile data observed by the limb instrument to study the ozone change in the troposphere.

6

(1) comments from Referees

Overall, I think the language of the manuscript should be further polished. There are several grammatical errors, which should be edited carefully.

(2) author's response

Thank for your comments. We have modified and polished the article.

(3) author's changes in manuscript

We almost checked the grammar and presentation errors of each sentence in the article. so please read the manuscript.

Specific comments:

Thank you for your comments. We really appreciate your precious comments. We have response the specific comments point to point.

1

(1) comments from Referees

Page 1 Line 29: How could you not consider the transport of ozone? Since it's an observation-based study. The spatial patterns you see reflect combining effects of horizontal/vertical transport, chemistry, deposition.

(2) author's response

Yes, it is a statement error. Delete it.

2

(1) comments from Referees

Page 2 Line 5: The references do not use OMI observations to characterize ozone variability. They are focused on NO_2, not ozone.

(2) author's response

The statement does not match the reference

(3) author's changes in manuscript

Numerous studies have shown that Ozone Monitoring Instrument (OMI) observations are reliable for assessment of sources, as well as regional and global characterization of spatiotemporal variability of NO_2 and SO_2 (Krotkov et al., 2016; Boersma et al., 2009; Boersma et al., 2008).

3

(1) comments from Referees

Page 2 Line 15: The description of the satellite data is not clear to me. For example, did you use Level-2 or Level-3 data? Are they daily or monthly products? Which satellite retrieval did you use? I'd suggest the authors refer the relevant papers of the product developers and include more details on the retrieval.

(2) author's response

We will add more detailed data description.

(3) author's changes in manuscript

Tropospheric ozone data is obtained from combined observations of two satellite instruments, Ozone Monitoring Instrument (OMI) and Microwave Limb Sounder (MLS). Daily OMI/MLS tropospheric ozone data were determined by subtracting MLS stratospheric column ozone from OMI total column ozone. Stratospheric column ozone from MLS was spatially interpolated (2D Gaussian/linear latitude-longitude interpolation) each day to fill in between the actual along-track measurements. The monthly means were then determined by averaging all available daily data within each month. The formatting of the data files is 1 degree latitude by 1.25 degree longitude resolution. OMI total column ozone was filtered for near clear-sky conditions by including only measurements when coincident OMI reflectivity was less than 0.3 (https://acd ext.gsfc.nasa.gov/Data_services/cloud_slice/new_data.html).Thecorrelation coefficient R between OMI/MLS tropospheric $O_3$and WOUDC ozonesonde tropospheric $O_3$is 0.92, RMS is 6.0ppbv from April to October. And the deviation is smaller in the location with lower latitude. It indicates closely similar signatures for seasonal cycles and spatial variability from the comparisons of OMI/MLS tropospheric ozone between the climatology and other data products (Ziemke et al., 2006, 2011).

Daily sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), monthly formaldehyde (HCHO) data are from the OMI aboard the EOS Aura spacecraft, launched on July 15, 2004. The spatial resolution is 0.25°×0.25°. Detailed data descriptions are provided in the OMI Data User's Guide and references there in (Zhou et al., 2017; Huang et al., 2015; Zhu et al., 2014; Gray et al., 2011). The daily retrieved total column carbon monoxide (CO) is from Measurement of Pollution in the Troposphere (MOPITT), available at https://terra.nasa.gov/about/terra-instruments/mopitt(Heald et al., 2003). And its resolution is $1° \times 1°$. In our analysis, the missing values are eliminated. Individual satellite observations have large errors, but averaging over long periods of time and large spatial extent can reduce them. And systematic errors affect all data, so the impact on the trend is not obvious.

4

(1) comments from Referees

Page 2 Line 16: How could the resolution be 360 x 180 degree?

(2) author's response

This is a statement error.

(3) author's changes in manuscript

And its resolution is $1° \times 1°$.

5

(1) comments from Referees

Table 1: What's the meaning of reporting the percentage of the concentration of Ozone?

(2) author's response

Percentage $=(O_{3(montnly)}/O_{3(total\ year)})*100\%$.

(3) author's changes in manuscript

The table 1 was deleted and briefly described.

6

(1) comments from Referees

Page 3 Line 1: What do you mean by concentrations here? Concentration of ozone? I don't see any correlation between ozone and NO_2 in June and August.

(2) author's response

In summer, the relationship between ozone and nitrogen dioxide has a correlation analysis.

(3) author's changes in manuscript

Table 3. Correlation coefficient value from satellite observations in summer during 2005 – 2016 in NCP.

		NO_2	SO_2	HCHO	CO	Radiation	T
O_3 VCD	R*	0.05	-0.33	0.37	-0.13	0.17	0.28
	P	0.76	0.05	0.02	0.44	0.33	0.10

*$p<0.05$.

VOCs and NOx are the major ozone precursors. As shown in Table 3, the relationship between O_3 and NO_2 is not so significant, and the correlation coefficient is 0.05. Another significant factor is formaldehyde with a correlation coefficient of 0.3 with O_3.

7

(1) comments from Referees

Page 5 Line 3: What's the basis of the conclusion?

(2) author's response

According to supplementary data, monthly solar radiation and temperature are positively correlated with ozone concentration. For summer analysis alone, the correlation is not significant.

(3) author's changes in manuscript

We first analyze the impacts of two important meteorological factors, temperature and solar radiation on ozone. Fig. 2(b) shows the correspondence between near-surface temperature and tropospheric ozone. The trends for them are very consistent, with a significant statistical correlation coefficient of 0.93.And their annual peaks also appeared at the same time (summer).More details about ozone changes in the summer will be discussed later. The effect of solar radiation on ozone can be seen in Fig. 2(c).The correlation coefficient between the two time series is 0.82.Tropospheric ozone peak generally appears 1-2 months later than the solar radiation. But the solar radiation is highly correlated with the ground-level ozone, with a significant statistical correlation coefficient of 0.98.

Although temperature and solar radiation are also important factors in photochemical production of O_3 (Tang et al., 2006), from the statistical relationship, the positive correlation is weak and not significant between tropospheric O_3 and temperature/solar radiation (Table 3).

The reviewer's comments helped us improve the article content greatly, and we thank you again. We express our deep gratitude.