Responses to the Interactive comment from Referee #2 on **"Summer ozone variation in North China based on satellite and site observations" by Lihua Zhou et al.**

Anonymous Referee #2

Received and published: 27 July 2018

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 paper investigated summer ozone variation in North China based on satellite and site observations. The conclusion is the production rate of ozone is most sensitive to temperature change, instead of emissions changes. I have concerns about the conclusion of the paper and would like to recommend substantial improvements of the analysis.

General comments:

1.

(1) comments from Referees

I recommend the authors to polish the manuscript with the help with native speakers. For instance, in the abstract, the 1st sentence is very lengthy; the term of "organic gas content" is not widely used. I guess the authors may want to use NMVOC instead. In introduction, the 2nd sentence is very hard to understand. It is very easy to be lost when reading the manuscript.

(2) author's response

Thank you for your constructive comments. We have followed your advice and polished the article. Every sentence was checked

(3) author's changes in manuscript

In the abstract, the 1st sentence was reorganized as" Air pollution in North China is relatively serious compared with other regions in China. Fine particle pollution has been studied in-depth, but there is less research about long- term troposphere ozone (O_3) variation." "organic gas content" is changed as" Non-Methane Volatile Organic Compounds (NMVOC)". In introduction, the 2nd sentence is changed as" Ozone (O_3) in the atmosphere is mostly distributed within the stratosphere, and tropospheric O_3 is about one-tenth of stratospheric O_3.”.

2.

(1) comments from Referees

Introduction. The introduction needs substantial improvements. It is difficult to follow the story line of the introduction. What are the existed findings? What new findings will be expected in this study? How would you like to organize your manuscript?

(2) author's response

Thank for your advice. Upon the reviewer’s comments, we rewrote the introduction and improved the background of this research.

(3) author's changes in manuscript

Ozone (O_3) in the atmosphere is mostly distributed within the stratosphere, and tropospheric O_3 is about one-tenth of stratospheric O_3. However, tropospheric O_3 has direct and detrimental impacts on human health and ecosystems. The production of tropospheric O_3 is chemically controlled by the nonlinear relationship of its precursors, volatile organic compounds (VOC) as well as nitrogen dioxide (NOx) (Seinfeld and Pandis, 2012), implying the complexity to fully understand the O_3 pollution.

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. 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 SO_2 and NO_2 (Krotkov et al., 2016; Boersma et al., 2009; Boersma et al., 2008). 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.

In this study, O_3 long-term variations are investigated based on atmospheric compositions obtained from satellite observations. Therefore, we introduce tropospheric ozone from OMI/MLS satellite and the ground observations in North China in Sect. 3.1; Sect. 3.2 discusses seasonal variation of tropospheric ozone and temporal and spatial distributions of other components; while Sect. 3.3

describes relationships between O_3 and other factors based on ground observations.

3.

(1) comments from Referees

Page 2, line 26. The motivation of selecting summer as the study period is not convincing. I expect seasonal variations in O_3 and its precursors. The dominated driver for O_3 variations could change over seasons.

(2) author's response

The authors appreciate your comments. Depending on your requirements, we add increase variations in O_3 and driver for O_3 variations throughout the year. Statistical relationship is as follows.

Table 1: Correlation coefficient among monthly tropospheric ozone, ground-level ozone, NO_2, SO_2, CO, T, R in NCP.

		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 O3	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.

(3) author's changes in manuscript

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 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.

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.

4.

(1) comments from Referees

Section 3.2.4. "We conclude that although the concentration of nitrogen oxides decreased over this period, the concentration of O3 did not decrease because VOCs have continued to increase (Duncan et al., 2010)." It loos risky for me to make the conclusion merely based on the upward trend of HCHO and downward trend of NOx.

The authors followed to state that "Clearly, temperature and solar radiation are also important factors (Tang et al., 2006).", without any further details. I'm not sure about what is "clearly" here.

(2) author's response

The authors appreciate you constructive comments. The previous statement may not be rigorous and is a conjecture. The previous conclusions lacked the support of data, so we performed regression statistics and significance tests on the factors involved, and revised and explained the conclusions through tests and calculations.

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) author's changes in manuscript

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.

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 between tropospheric O_3 and temperature/solar radiation is weak and not significant (Table 3).

5.

(1) comments from Referees

The total columns of O3 are used as indicators of surface O3, which looks improper for me.

(2) author's response

Thank you so much for your comments. Indeed, the total columns of O_3 not equal to surface O_3. But their seasonal changes are closely related. For example, they all reach annual peaks in the summer and reach the annual valley in the winter. Further, high concentrations of the total column are often accompanied with high surface O_3. The correlation coefficient (R^2) between them is reached 0.8, and the results are significant.

(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.Thusthere is a high correlation between the tropospheric ozone and the ground ozone concentration.

Table 1: Correlation coefficient among monthly tropospheric ozone, ground-level ozone, NO_2, SO_2, CO, T, R in NCP.

		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 O3	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

*$p<0.05$.

6.

(1) comments from Referees

Overall, I feel an in-depth analysis is missing. The manuscript only listed the trends of a few pollutants, which has been documented by existing literatures. The author may want to perform sensitivity analysis using CTMs to validate whether the conclusion is solid.

(2) author's response

Thank you so much for your comments. This article does lack mechanism analysis. The model CTMs is necessary for in-depth analysis. We are going to do this work in the future. This article uses observational data to characterize phenomenon and make simple analysis temporarily.

Specific comments:

We appreciate your precious comments. We have modified the paper followed your comments point ot point.

1

(1) comments from Referees

Page 1, line 28, I don't get the meaning of the sentence.

(2) author's response

It is changed as "There are a lot of research on a case study of the O3–VOC–NOx system sensitivity. However, the ozone research for long term trend changes are less".

(3) author's changes in manuscript

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

2

(1) comments from Referees

Page 2, line 3, what do you mean by "macro changes"?

(2) author's response

This change refers to the overall change of the region, not a change in a site.

(3) author's changes in manuscript

We rewrote the introduction and removed the sentence.

3

(1) comments from Referees

Page 2, line 13. The grammar seems not proper for "launched 15 July 2004".

(2) author's response

This is a syntax error

(3) author's changes in manuscript

It is changed as "launched on July 15, 2004".

4

(1) comments from Referees

Page 2, line 16. It looks not right for me to say "The resolution of these data is 360° ×180°".

(2) author's response

This is a false representation

(3) author's changes in manuscript

It is changed as "1° × 1°".

5

(1) comments from Referees

Page 2, line 17. The data source for daily SO_2, NO_2 and 8-h O_3 data is missing.

(2) author's response

From China National Environment Monitoring Centre: http://www.cnemc.cn/

(3) author's changes in manuscript

Ground measurements for daily SO_2, NO_2, 8-h O_3 data and other near-ground gas data were obtained by averaging hourly data recorded at China National Environment Monitoring Centre (available at http://www.cnemc.cn/).

6

(1) comments from Referees

Page 3, line 23. The statement of "Therefore, over long periods, the amount of NO2 and the total amount of nitrogen oxides are basically the same. " is not correct.

(2) author's response

This sentence is expressed properly, so deleting.

(3) author's changes in manuscript

Therefore, the nitrogen oxides in the atmosphere are mainly these two species, having a final form of NO_2.

The reviewer's comments helped us to consider the issue more comprehensively and improved the paper greatly. We express our deep gratitude.