

## **Referee #1:**

### **General comments:**

1. *Unfortunately, the paper remains a bit vague and less conclusive in some parts but refers to an accompanying paper that is still not yet available. As the present paper seems to lay the foundation for future analysis, the experimental section should be more elaborated on (see comments below) because a sound quality assurance of the data is key when looking at trends etc. Moreover, the findings should be more discussed in relation to other available time series at elevated Northern hemisphere measurement sites. This is already the case for the trends in Chapter 3.3 but could be extended to the sections where diurnal and seasonal cycles are presented.*

**Response:** Thank you for these valuable suggestions. We have added/corrected information in the site and measurements section (including the height of the measurement platform, the detailed processing procedure of the data, etc.), which hopefully will assure the reader of our sound data quality. The diurnal and seasonal cycle of ozone at WLG will be further discussed in relation to the other elevated northern hemispheric sites. However, this study mainly focuses on the long-term trends, which is why the added discussion was kept brief.

2. *The authors often refer to ozone concentrations but use ppb units. Concentrations cannot be given in ppb as numbers in ppb refer to mole fractions or mixing ratios.*

**Response:** We thank the referee for pointing it out. Indeed, by definition, mixing ratio and concentration is not the same, and the ppb values in the manuscript refer to the mixing ratio of ozone. According to the suggestion, we changed all the “concentration” to “mixing ratio”.

3. *The order of the Figures does not correspond with the appearance in the text. The references to Figs. 4 and 7 come earlier than the one to Fig. 3. Please reorder the Figures.*

**Response:** We thank the referee for the suggestion. Since the figures were ordered mainly according to the results and discussion section, we did not want to reorder

them, for better logicity and readability. However, we deleted the previous references of Fig 4 and 7 in the data and methodology section, since they were not indispensable.

**Specific comments:**

**1. Abstract:**

*The abstract is rather long; I suggest shortening it, e.g. by deleting “using a modified Mann–Kendall test and the Hilbert–Huang Transform analysis for the trend and periodicity analysis, respectively.” and “Analysis suggests that there is a season-diurnal cycle in the three-dimensional winds on top of Mt. Waliguan. Season dependent daytime and nighttime ranges of 6 h were determined based on the seasondiurnal cycle in the three-dimensional winds and were used to sort subsets of ozone data for trend analysis.”*

*Line 22: replace “increasing trend” by “positive trend”*

*Line 24: delete “relatively”*

*Lines 25-26: shorten the sentence to “Spectral analysis identified four episodes with different positive trends, with the largest increase ...”*

**Response:** Thanks for your advice, the abstract has accordingly been revised as:

“Tropospheric ozone is an important atmospheric oxidant, greenhouse gas and atmospheric pollutant at the same time. The level of tropospheric ozone, particularly in the surface layer, is impacted by emissions of precursors and is subjected to meteorological conditions. Due its importance, the long-term variation trend of baseline ozone is highly needed for environmental and climate change assessment. So far, studies about the long-term trends of ozone at representative sites are mainly available for European and North American sites. Similar studies are lacking for China, a country with rapid economic growth for recent decades, and many other developing countries. To uncover the long-term characteristics and trends of baseline surface ozone mixing ratio in western China, measurements at a global baseline Global Atmospheric Watch (GAW) station in the north-eastern Tibetan Plateau region (Mt. Waliguan) for the period of 1994 to 2013 were analysed in this

study. Results reveal higher surface ozone during the night and lower during the day at Waliguan, due to mountain-valley breezes. A seasonal maximum in summer was found, which was probably caused by enhanced stratosphere-to-troposphere exchange events and/or by tropospheric photochemistry. Significant positive trends in surface ozone were detected for both daytime (1.5-2.7 ppbv 10a<sup>-1</sup>) and nighttime (1.3-2.9 ppbv 10a<sup>-1</sup>). Autumn and spring revealed the largest increase rates, while summer and winter showed weaker increases. Spectral analysis identified four different episodes with different positive trends, with the largest increase occurring around May 2000 and Oct. 2010. A 2-4 year, 7 year and 11 year periodicity was found in the surface ozone mixing ratio. The results are highly valuable for related climate and environment change assessments of western China and surrounding areas, and for the validation of chemical-climate models.”

## 2. **Introduction:**

*Page 30990, line 14: reference to Lin, 2015 is missing*

**Response:** We appreciate your detailed inspection. There has been a mistake in creating a link to the reference, which has been corrected in the revised manuscript.

*Page 30991, lines 4-5: “there are a few representative sites ...”; does this statement refer to the situation in China? Which are the other stations? To my knowledge, the China Meteorological Administration also operates a remote measurement station at Shangri-La at nearly the same elevation than Mt. Waliguan. Are surface ozone observations available from the Shangri-La station?*

**Response:** Yes, this statement was referring to the situation in China, which we will make clear by rephrasing this sentence to “Continuous long-term observations of surface ozone are made only at a few representative sites in China, among which is the Mt. Waliguan (WLG) GAW station”. Continuous surface ozone measurements are also carried out at Shangri-La, Yunnan Province (since the end of 2007) and Akedala, Xinjiang Province (since 2009), which are both sites in western China. Waliguan is the site with the highest altitude and the longest (and most complete) surface ozone data record.

### 3. Section 2.1 Sites and measurements

*This part needs some elaboration. Duplicate ozone measurements seem to be available for most of the time. The authors state that data were used if the two analyzers agree within 5ppb. A quality control criterion of matching data within 5ppb is pretty lax and well above the data quality objectives for key GAW goals (see e.g. the GAW report #209 “Guidelines for Continuous Measurements of Ozone in the Troposphere”; available at <http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html>). How was the data flow implemented in detail? Was there one master and one backup instrument? How did they compare? Did you experience e.g. a steady bias, a perfect match, a difference as function of daytime, season, temperature, humidity ...? Or random differences? What happened when the master instrument didn't record data but data from the backup analyzer were available? Were the data from the backup instrument used to fill the gaps? Have the backup data been corrected based on a long-term master backup comparison? How many gaps were filled? Maybe an additional figure could help just showing a time series that illustrates which analyzer provided when data for the final data set used for the analysis. The authors mention that a TE49i model is used since 2011. Did this analyzer become the master instrument? How was it ensured that there is a smooth transition when changing the master instrument? Did the old and the new master run in parallel for a certain time? All these things are important information because the observed trends are small and could be also biased by some instrumental artefacts. When looking at Fig. 4a, there seems to be a discontinuity with slightly elevated ozone mole fractions for approximately the last two years. This step roughly coincides with the implementation of the TE49i analyzer. Can the authors comment on that?*

**Response:** We understand the referee's concern about the data quality and agree that it is fundamental for this and the upcoming study to assure the reader that our measurements are trustworthy. The GAW report #209 suggests for the case of two

instruments, to eliminate 1-minute averaged data showing a difference larger than 5 ppb. Since we had data records in 5-minute averages, we eliminated data with differences larger than 3 ppb (Apology for the wrong information in the previous manuscript). The data quality objectives in the GAW report #209 requires the measurement to have an uncertainty of  $\pm 1$  ppb or less. The following figure shows the occurrence frequency distribution with the difference of ozone mixing ratio between two instruments. As can be seen in figure 1, 95% of the data pairs show discrepancies within  $\pm 1$  ppb and the difference between two instruments shows nearly a random distribution around zero.

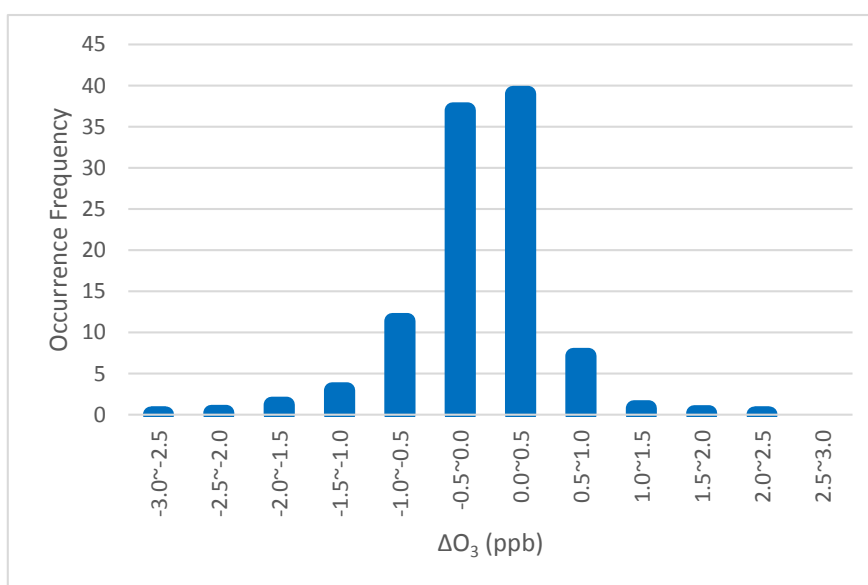


Figure 1 Occurrence count distribution with the difference of ozone mixing ratio between two instruments

The results of the audit reports from the World Calibration Centre for surface ozone should be further proof that our instruments were capable of fulfilling the data quality objectives.

The two instruments were run parallel to each other, with no particular differentiation of master or backup. Generally, they were in very good agreement with each other, and discrepancies larger than 3 ppb typically occurred, when one of the instruments was undergoing a change of particle filter or had a technical problem such as leaky valves. In that case, the data of the other instrument was used. There was only a small proportion of time, when one of the instruments did not

function well.

After the installation of the model TE49i ozone analyzer, our way of running the two instruments (parallel to each other) has not changed and the same criterion for data elimination has been applied. This, together with periodical calibrations using the ozone calibrator at the station, has ensured a smooth transition and no abrupt change in data quality due to the analyzer replacement. The slightly elevated ozone mixing ratio in the last two or three years was not due to the change of an analyzer rather due to other causes as will be discussed in part II.

*Page 30993, lines 10-11: "Surface ozone data are recorded every 5 minutes ...". I assume that this statement is misleading as the used ozone analyzers record data in 10 sec intervals. I suppose that the authors want to say that 5 min averages are recorded on the data acquisition. If this is the case, why not saying "Surface ozone data are recorded as 5-minute averages and corrected ..."*

**Response:** The correction suggested by the referee is adopted in the revised manuscript, thank you for the comment.

*What was the sampling height above ground for the ozone observations?*

**Response:** The sampling height is 7 m above ground. Thank you for pointing it out, we will add this information to the section on Site and Measurements.

*Page 30996, lines 4.5: rephrase the last sentence that it reads "The nighttime window also covers 6 h and is considered to be offset by 12 h to the daytime window."*

**Response:** The correction suggested by the referee has been accordingly made in the revised manuscript.

*Section 2.3: Did you use hourly averages for the analysis? Which software was used for the statistical analysis? Matlab? R? Did you use specific add-ons (packages)?*

**Response:** Thank you for the questions. As shown in Fig. 5, monthly average data were used in the seasonal Mann-Kendall analysis, which we will make clear in the

revised manuscript. A fortran program by USGS (Computer program for the Kendall Family of Trend Tests) was used, which we forgot to cite in the former manuscript. A proper citation will be added in the revised manuscript.

*Page 31000, line 22: replace “Past researches” by “Previous studies”*

**Response:** The correction suggested by the referee has been accordingly made in the revised manuscript.

*Page 31001, lines 10-11: How does the long-term time series of  $^{10}\text{Be}/^{7}\text{Be}$  look like. Is it possible to draw any conclusions on changes in STE strength?*

**Response:** Unfortunately, we do not have long-term measurements of  $^{10}\text{Be}/^{7}\text{Be}$ . We will have to look into other indicators of the STE strength and occurrence frequency.

*Page 31001, line 20: “total ozone column”, remove the “,”*

**Response:** Thank you for your careful reading, the correction is made in the revised manuscript.

*Page 31001, line 24: mention once more “based on zonal wind information”.*

**Response:** The correction suggested by the referee has been accordingly made in the revised manuscript. This indeed improved the readability of the manuscript.

*Page 31003, lines 6-8: this is mainly true for remote locations.*

*The seasonal ozone peak in the Northern Hemisphere typically occurs in spring, which is believed to be the result of enhanced photochemical production in spring (Monks, 2000; Vingarzan, 2004).*

**Response:** Thank you for pointing that out, we revised this sentence to: “The seasonal peak of the Northern Hemisphere background ozone typically occurs in spring, which is believed to be the result of enhanced photochemical production in spring (Monks, 2000; Vingarzan, 2004)”.

Page 31006: replace “Ds” by “DS” at various locations.

**Response:** The correction suggested by the referee has been accordingly made in the revised manuscript.

4. ***Summary:*** *the concluding chapter only summarizes the findings presented above. I would like to see some outlook beyond. What will be looked at next? What are the implications of the findings? What does it e.g. mean for efforts to reduce maximum ozone levels in urban agglomerations (e.g. if ozone input due to STE is getting stronger)? Can the results somehow be generalized? What does it mean for the Asian outflow towards the Western US? Is the observed trend in Western US maybe caused by changes in STE input rather than increasing ozone precursor emissions in Asia?*

**Response:** Thank you for the suggestion. We will add the following few sentences to summarize the implication of our findings and to give an outlook of what to expect in the second paper.

“As WLG is a high altitude mountain-top site in a remote region, measurements of surface ozone and other species can well represent a large scale situation. Previous air mass origin studies and modelling studies suggest that WLG is mostly under the influence of transport from the north-west direction, hence the upward trend in ozone might be a reflectance upon transport from Europe (Zhang et al., 2011; Li et al., 2014). Since Eastern China is in the downwind direction, our results imply that under rising background ozone conditions, even more effort needs to be put in reducing ozone precursors. In the second part of our study, the impact of different air-mass origins and the long-term variations of their occurrence frequencies on the surface ozone mixing ratio and its trend at WLG will be shown. The anthropogenic impact of the nearest major population centers on the ozone trend will be discussed. The long-term variation of STE and its link to surface ozone at WLG will be displayed. The possible connection of changes in atmospheric circulation oscillations and solar activities with the inner-annual and periodical variations of



ozone at WLG will be studied.”

The referee posed a question on the influence of rising ozone at WLG on western US air quality. WLG is located downwind of Europe and upwind of East Asia, one of the most polluted region of the world. If it should have any influence on Western US, it won't be as big of an influence as the outflow of East Asian ozone precursor emissions.

**5. References:** *Add urls to the Zellweger et al. audit reports, if online available.*

**Response:** URLs have been added for the audit reports, thank you for the suggestion.

**6. Figures:**

*Figs. 2 and 3: is it confusing to have two different sets of white dots and dashed lines in Figs. 2 and 3. Since the differences in the seasonal-diurnal variations are discussed in Section 3.1, I suggest to add the daytime range based on the zonal wind (white dots from Fig. 2) in Fig. 3 and to draw the white dots in Fig. 3 based on minimum ozone in a different color. This makes it easier for the reader to compare the different features. The +/- 3h band is maybe even not needed here.*

**Response:** We thank the referee for the good advice, the correction suggested above has been accordingly made and the discussion on Fig. 3 will be adjusted to the following new figure:

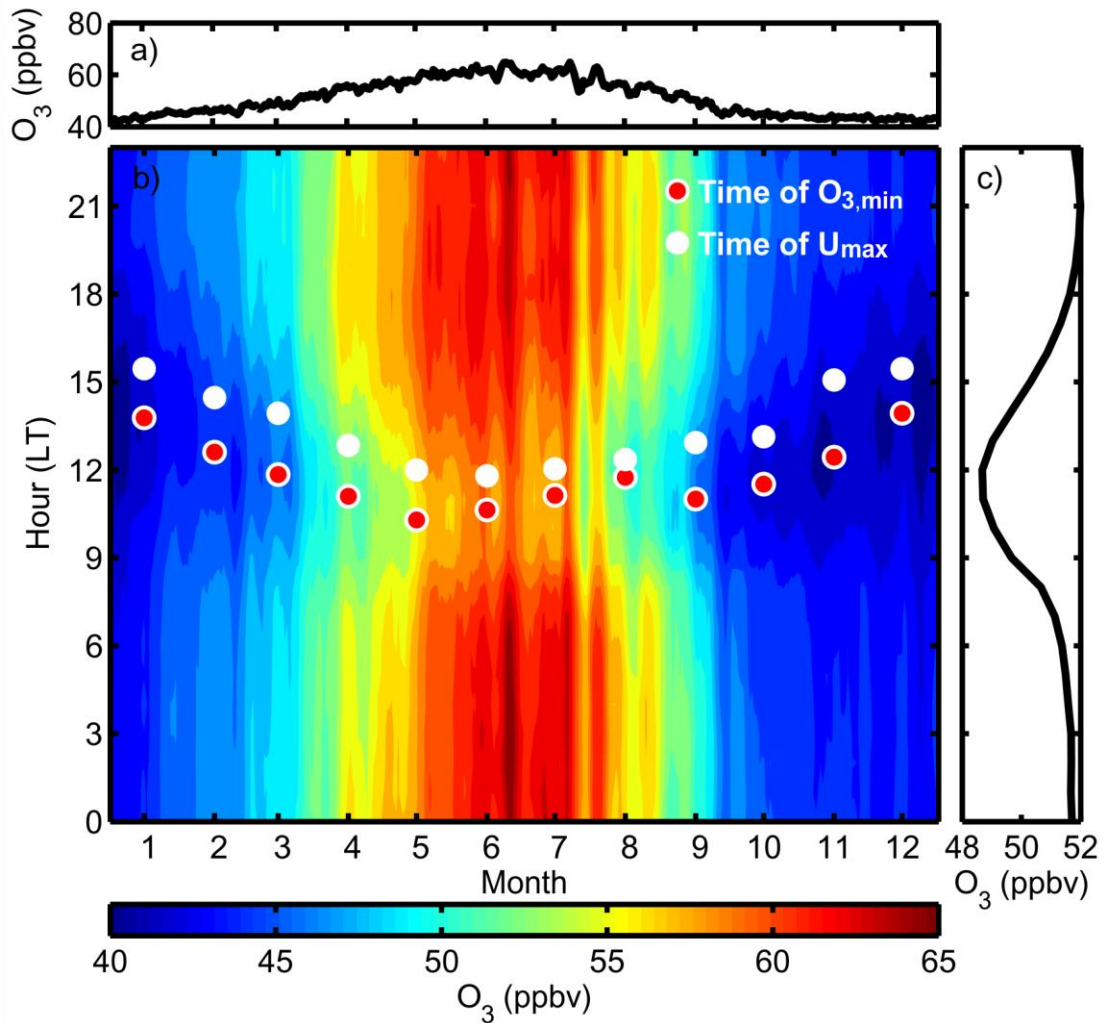


Figure 3 The average seasonal variation (a), season-diurnal variation (b) and diurnal variation (c) of ozone during 1995 to 2013. White and red dots stand for the monthly average local time associated with the diurnal maximum zonal wind and minimum ozone, respectively.

*Fig. 5: add on the right hand side of panels a5 to b5 "all", "daytime", "nighttime"; add below the x-axis of the c-row "all", "spring", "summer", ...*

**Response:** The correction suggested by the referee has been accordingly made in the revised manuscript. The new Fig. 5 is shown below:

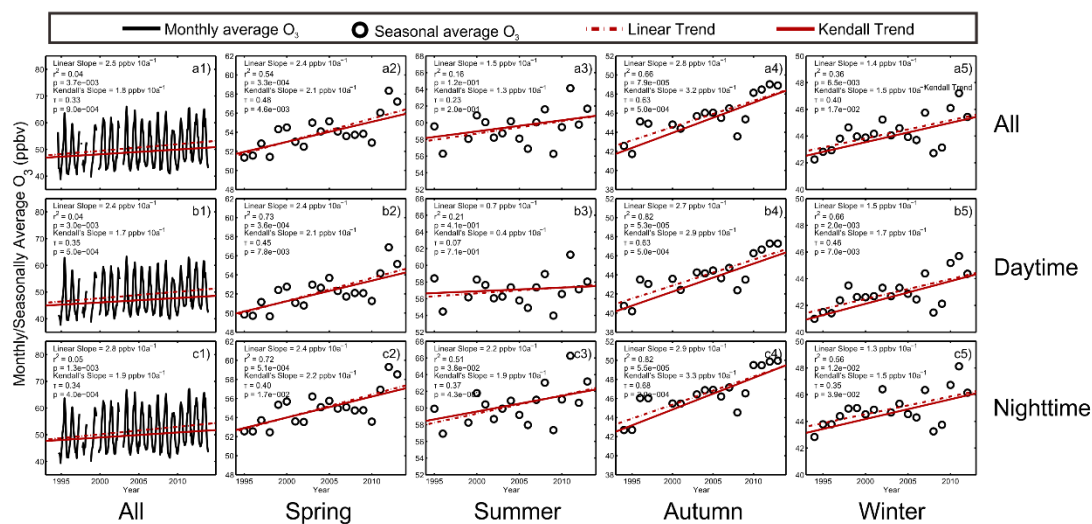


Figure 5. 1) Monthly, 2) spring (MAM), 3) summer (JJA), 4) autumn (SON) and 5) winter time average all day (a), daytime (b) and nighttime (c) surface ozone mixing ratio during 1994 to 2013 (black solid line or black circles) and its variation trend (red lines: dotted line stands for the linear variation and solid line stands for the Kendall's variation slope).

## Referee #2:

### General comments:

*The manuscript presents long-term changes of surface ozone measured at Mount Waliguan in western China. The authors conducted a spearman's linear trend analysis and the Man-Kendall's trend test to determine the slopes of the time series and their 95% confidence intervals (Table 1 and Figure 5). Diurnal and seasonal variations of the slopes are discussed. Spectral analysis is used to determine the time scales of ozone variations (Figures 6 to 8). The scientific approach and applied methods in the manuscript are overall valid. High-quality ozone measurements are sparse in China, and thus the long-term ozone data at Mount Waliguan are highly valuable. However, some discussions presented in the current manuscript are vague or sometimes inaccurate.*

*The present manuscript does not provide conclusive evidence on the causes of seasonal ozone trends measured at Mt. Waliguan. The record clearly shows large interannual*

*variability (e.g., the 2011-2012 high-ozone anomalies in spring), which can substantially influence the slope of the linear regression (Fig.7b), but there are no thorough discussions on what are going on. For instance, are there any changes in largescale circulation patterns during 2011-2012: shifts in the location of the jet stream, anomalies in 500 hPa geopotential height, variability of STE or regional pollution transport?*

**Response:** There is indeed a large inter-annual variability, which is part of the reason why we performed the Hilbert Huang Transform (HHT) spectral analysis. The HHT analysis can dissect the ozone signal into signals of various variation time scales and the overall trend clearly displays an upward trend, confirming the results of the linear regression. The cause of the inter-annual variation is too complicated to be put into one paper. There are changes in atmospheric circulation, STE, solar activities and anthropogenic emissions, which vary at different time scales and impact surface ozone at the same time. The impact of STE has been studied using the deep stratosphere to troposphere transfer (STT) mass flux that reaches the PBL(Škerlak et al., 2014). The monthly and seasonal average STT mass flux is shown in Figure 2. Overall, there is no significant correlation between the ozone mixing ratio and the STT mass flux, except for autumn, where there is a significant positive correlation of  $r=0.65$  ( $p<0.01$ ). The STT mass flux shows a peak in early 2011 and 2013, during the end of winter to the beginning of the spring period. The STT peaks in spring during 2011 and 2013 are not as pronounced as those in 2004 or 2006, which does not explain the increase in ozone during 2011 to 2013 (Fig. 1b). Summertime STT mass flux was low during 2011 to 2013, unable to explain the peak in summertime ozone (Fig. 1c). Autumn and winter show better correlations, both displaying elevated STT mass flux and ozone mixing ratios during 2011 to 2013. However, the continuous rise in autumn ozone mixing ratio was not solely caused by STE, since the STT mass flux in 2011 was low. The ozone peak during wintertime occurred in 2012, while the major STT mass flux peaks are found in 2011 and 2013. The linear variation trend of STT mass flux is listed in Table 1. The only significant upward trend is found in autumn. Spring and winter also show upward trends, while summer shows a weak negative trend. These results agree well

with the ozone variation trends found in our study, suggesting that the overall variation trends of STT mass flux and ozone might be linked each other, however, since STT is not the only influencing factor, its inter-annual variation is not able to explain that of surface ozone. Therefore, the interannual and long-term variations were also resulted from other causes, which will be discussed in the Part II paper.

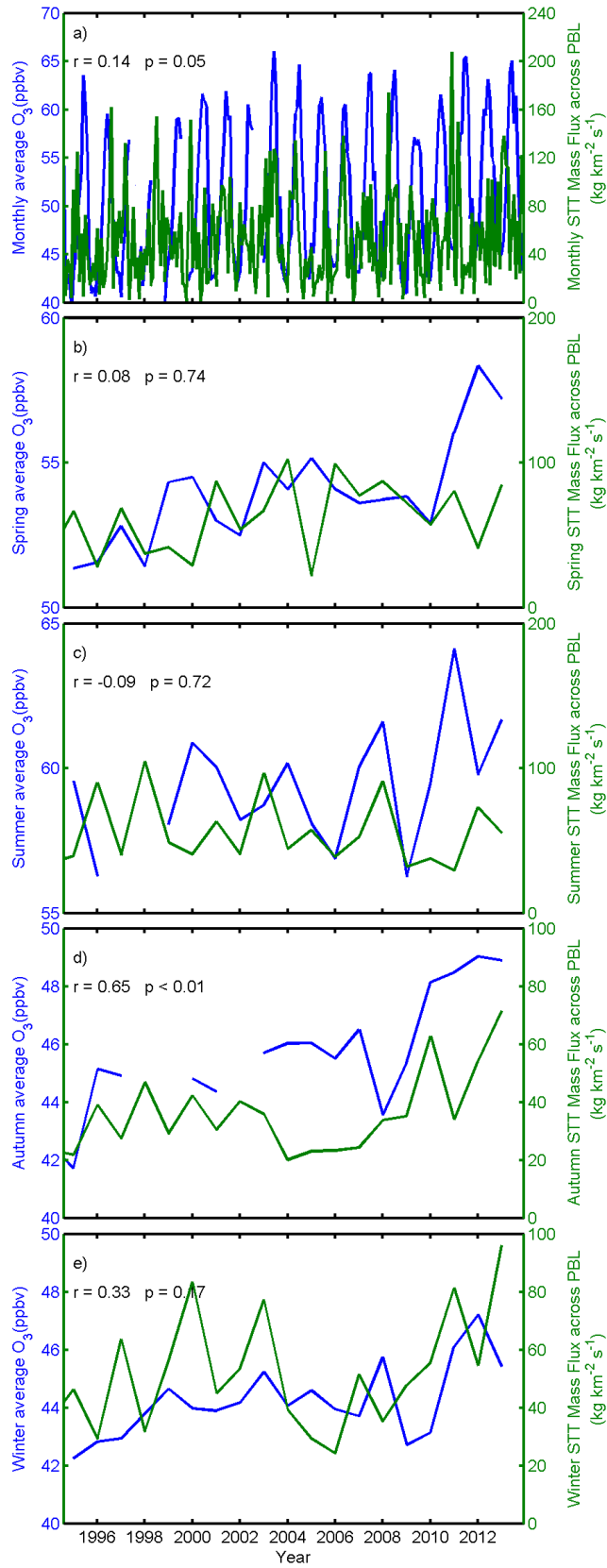


Figure 2 a) Monthly, b) spring, c) autumn and d) winter time average ozone mixing ratio and STT mass flux across PBL during 1994 to 2013

Table 1 Monthly, spring, autumn and winter time average STT mass flux across PBL linear variation trend during 1994 to 2013

	Slope (kg km <sup>-2</sup> s <sup>-1</sup> decade <sup>-1</sup> )	p-value
All	8.2±8.9	0.07
Spring	15.3±21.0	0.14
Summer	-3.2±19.5	0.74
Autumn	11.5±10.2	0.03
Winter	10.5±17.6	0.23

*There is a citation to the Part II paper in prep on the influencing factors. The referee suggests that the authors try to condense the discussions and combine the two manuscripts into one concise, thorough, and well-structured paper, which is better than two incomplete papers and will result in better citations in the future.*

**Response:** The second paper is already under preparation. Since the influencing factors of ozone at Waliguan are rather complicated and the major factors deserve to be more thoroughly investigated. We understand the referee's concern. However, from what we have now, the content regarding the causes of long-term and interannual variations of ozone at Waliguan would be too much to be added to the current paper without influencing its conciseness. Therefore, we would like to keep it a companion paper, but we will try our best to improve the current one and leave the reader with the following few sentences in the summary, as an outlook into the next one, as to what to expect in part II:

“In the second part of our study, the impact of different air-mass origins and the long-term variations of their occurrence frequencies on the surface ozone mixing ratio and its trend at WLG will be shown. The anthropogenic impact of the nearest major population centers on the ozone trend will be discussed. The long-term variation of STE and its link to surface ozone at WLG will be displayed. The possible connection of changes in atmospheric circulation oscillations and solar activities with the inner-annual and periodical variations of ozone at WLG will be studied.”

*The manuscript also needs be carefully proofread for the correct use of English Language. There are quite a few errors.*

**Response:** We apologize for the linguistic mistakes, we will proofread the manuscript carefully and make according corrections.

**Specific comments:**

1. *Abstract, Line 16-18: Since this manuscript is NOT about the seasonal cycle of ozone at Waliguan, I don't think you need to get into what causes the summertime ozone maximum in the abstract. The seasonal cycle has been extensively discussed in the literature (e.g. Zhu et al., Ma et al., Ding et al.) as the authors noted in the main text.*

**Response:** We accept the referee's suggestion and deleted the cause of the seasonal cycle in the abstract.

2. *Abstract, Line 19-20: "Seasonal-dependent daytime and nighttime ranges of 6h ..." Awkward wording.*

**Response:** The abstract in the previous manuscript was too long, hence the following two sentences have been deleted, solving the problem with the awkward wording:

*"Analysis suggests that there is a season-diurnal cycle in the three-dimensional winds on top of Mt. Waliguan. Season dependent daytime and nighttime ranges of 6 h were determined based on the season-diurnal cycle in the three-dimensional winds and were used to sort subsets of ozone data for trend analysis."*

3. *Abstract, Line 22-23 and Figures 6-8: What does the range of the slope represent? It is more appropriate to report the trends with its 95% confidence intervals in the format of  $x \pm x$  ppbv yr<sup>-1</sup>. The daytime trend for JJA is statistically insignificant at the 95% confidence level (Table 1 and Figure 5b3). I would suggest in the abstract reporting the nighttime trends in  $x \pm x$  ppbv yr<sup>-1</sup> for annual mean and for each season, which is the most useful information for the future readers of the paper. Observed conditions during nighttime at the 3.8 km altitude of Mount Waliguan*



*represent downslope influence of free tropospheric air. Thus nighttime measurements are more representative of baseline conditions compared to daytime measurements. Related to this comment, I would suggest restricting the spectral analysis in Figures 6-8 to nighttime data that are representative of large-scale conditions. Daytime data are influenced by local boundary layer air, particularly during summer, as evidenced by the large differences in daytime and nighttime trend for JJA (Table 1).*

**Response:** Thank you for the advice, we have revised this part of the abstract and included the 95% confidence level as well as the nighttime trends for each season. We would like to keep Figures 6-8 as they are, because we want to keep the information in the data complete and not just show the nighttime result. We also performed daytime and nighttime spectral analysis, which will be probably used in the second paper.

4. *Abstract, Line 27: “with the largest increase occurring around May 2000”. Where do you see this? In Figure 6f? But it does not show up in the 7-year trend (Figure 6e and Figure 7b). Aren't the changes in the ozone increasing rates (slope) just the manifestation of the interannual variability?*

**Response:** This sentence was referring to the overall trend in Fig. 7a. Inter-annual variability is a mixed result caused by changes in atmospheric circulation, changes in ozone concentration from upwind directions and changes in local precursor or ozone mixing ratios. Local surface ozone mixing ratio at WLG shows underlying signals with different periodicities, which suggests that it may be under the influence of more than one atmospheric oscillation process. This is why we need to do the spectral analysis. The separated signals can and will be compared with different atmospheric circulation oscillation processes in the second paper. Here in Fig. 7a, the 7-year trend is based on the sum of the residual and the last two IMFs, while the overall trend is based on the sum of the residual and the last IMF. That is why the 7-year trend shows fluctuations on a relatively smaller time scale than the overall trend and shows distinct variation slopes. However, both signals should not

be largely influenced much by year-to-year variations, since these signals are already in the third IMF.

5. *Somewhere in the abstract, please denote the altitude of Mt Waliguan.*

**Response:** The location and altitude of the Mt. Waliguan station have been added to the abstract.

6. *Page 30989, Line 15-28, awkward wording*

**Response:** Thank you for pointing it out, we take it you mean the sentence in Line 15-18. This sentence was rephrased as: “Since ozone is a secondary gas pollutant, observed surface mixing ratios are influenced both by local photochemistry and by transport processes of ozone or its precursors from nearby locations (Wang et al., 2006a; Lal et al., 2014).”

7. *Page 30989, Line 20: It is important to clarify that the STE influence on surface ozone is most relevant at alpine sites. Thus, please change “local surface ozone concentrations” to “surface ozone concentrations at high-elevation sites”.*

**Response:** We agree with the referee and have made the according change.

8. *P30990, Line 1-3: Also cite Parrish et al. (2012, ACP) and Logan et al. (2012, JGR, D09301).*

**Response:** Thank you for providing these two relevant references, citations have been added.

9. *P30990, Line 9-10: → “... in causing high-ozone events at western U.S. alpine sites during spring (e.g. Langford et al., 2009; Ambrose et al., 2011; Lin et al., 2012a; Lin et al., 2015)”.*

**Response:** The suggested change has been adopted, thank you for the advice.

10. *P30990, Line 10-15: The discussions of the results from Lin et al. (2015b) are not*

*quite accurate. They found statistically insignificant ozone trend for the short record of 1995-2008 but the trend is significant for the longer time period of 1995-2014. Consider revising the text as follows: “A recent study by Lin et al. (2015b) found that although rising Asian emissions contribute to increasing springtime baseline ozone over the western U.S. from the 1980s to the 2000s, the observed western US ozone trend over the short period of 1995-2008 previously reported by Cooper et al. (2010) has been strongly biased by meteorological variability and measurement sampling artifacts. Nevertheless, the impact of Asian pollution outflow events on western US surface ozone is evident (e.g., Lin et al., 2012b).”*

**Response:** We agree with the referee and the suggested change has been adopted, thanks for the advice.

- 11.** *The last sentence in P30990: Revise “NCP, YRD and PRD. Observed ozone ...” to “NCP, YRD and PRD, where observed ozone ...”*

**Response:** The suggested change has been made.

- 12.** *P30992, Line 2: “a larger scale” compared to what? You can just say “on a large scale”.*

**Response:** The suggested correction has been made.

- 13.** *P30991, Line 19-30: It is not clear why you bring up the discussions on ENSO and its influence on western ozone. I think the connection is that both WLG and western US are high-elevation regions prone to the STE influence, which can be modulated by climate variability such as ENSO events. Also, Voulgarakis et al. (2011) did not say that changes in dynamics after el nino events hardly leads to changes in stratospheric ozone. In fact, the influence of el nino events on lower stratospheric ozone at midlatitudes are well known (see introduction and changes in mean ozone aloft sections in Lin et al. [2015a] and references therein). Please consider revising the text as follows: QBO (...) and ENSO (...) have been shown to influence total ozone burdens over the Tibet (Ji et al., 2001; Zou et al., 2001). This influence could*

*extend to the lower troposphere via STE and thus affect ozone variability measured at the 3.8 km altitude of WLG. A few studies suggested that the change in dynamics after El Niño events can promote the cross-tropopause ozone exchange and lead to a rise in global mean tropospheric ozone concentration (e.g., Voulgarakis et al., 2011). Over western U.S. high elevation regions prone to deep stratospheric intrusions, however, Lin et al. (2015b) found that the increased frequency of deep tropopause folds that form in upper-level frontal zones following strong La Niña winters exerts a stronger influence on springtime ozone levels at the surface than the El Niño-related increase in lower stratospheric ozone burden. The Tibetan Plateau has also been identified as a preferred region for deep stratospheric intrusions (Skerlak et al., 2014, ACP). To extent to which ENSO events, jet characteristics, and STE modulate interannual variability of lower tropospheric ozone at WLG requires further investigation.*

**Response:** The results of Voulgarakis et al. (2011) was indeed misinterpreted. Their results suggest that inter-annual variability in stratospheric ozone has little influence on the STE ozone amount. We thank the referee for the kind suggestion and have made according changes.

- 14.** *P30992, Line 3-5: Need to clarify that the debates are on the causes of the ozone season cycle at WLG.*

**Response:** We agree with this comment and have revised the text into:

“Previous studies of ozone at WLG were all based on short-term measurements and were mostly model-based mechanism studies on the causes of the ozone seasonal cycle, which did not lead to consensus and brought upon debates (Ma et al., 2002a;Ma et al., 2005;Zhu et al., 2004), while ...”

- 15.** *P31001, Line 15-20: again here discussions on interannual variability and the influence of QBO is vague (see Major comments and Comment 13 above).*

**Response:** Thank you for the suggestion, we rephrased this part to: “The long-term variation of the annual average ozone exhibits a clear increasing trend (Fig. 4a). A

2-4 year cycle seems to exist within the long-term variation of surface ozone. Previous study has shown that there is a quasi-biannual oscillation (QBO) within the total ozone column density over the Tibetan Plateau, which is in antiphase with the QBO of the tropical stratospheric winds, exhibiting a 29 month cycle (Ji et al., 2001). The influence of the QBO could extend to WLG station at the 3.8 km altitude via STE. Thus, the surface ozone at WLG might also have a QBO with a similar periodicity, which is related to that of the total ozone column.”

**16.** *P31003, Line 1-5: The daytime and nighttime trends during JJA have overlapping confidence limits (second column in Table 1); do you conduct statistical testing if they are significantly different at the 95% confidence level? If not, try to avoid using wording like “significantly distinct ...”. To me, “significant” implies statistical results. During JJA when boundary layer mixing peaks seasonally, daytime measurements at the 3.8 altitude of WLG are influenced by boundary layer air via an upslope flow. Thus daytime measurements at WLG during JJA are NOT representative of baseline conditions on a large scale, which could possibly explain the lack of significant daytime ozone trend at WLG during JJA. For the other seasons there is little difference between daytime and nighttime trends because boundary layer mixing is shallower compared to JJA and WLG is always located in the free troposphere. You can discuss these features without expanding to another paper.*

**Response:** We agree with the referee on the first part of this comment and have therefore changed “significantly distinct” to “distinct”. However, on the second half of this comment, we cannot fully agree. Although it is true that the PBL height must be shallower during the seasons other than JJA, we do not believe that during daytime WLG is entirely in the free troposphere. WLG is a site on top of mountain on a high plateau, unlike Mauna Loa and some other mountain sites. The valley southeast to Waliguan has an altitude of 2.4~2.8 km a.s.l., the water reservoir (Longyangxia Gorge Reservoir) to the southwest keeps a water level of ~2.5 km a.s.l., the Qinghai lake to the northwest has a water level of ~3.2 km a.s.l., and the

valley to the northeast has an altitude of ~3.3 km a.s.l. So the height difference between WLG and surrounding valleys is no larger than 1.5 km. For high alpine sites with strong radiation, it is very easy for the PBL to develop to a height of 1.5 km, even outside the summer season. The upslope flow during the day caused by the mountain valley breeze exists in all seasons, as can be seen from Figure 2c. The duration of the upslope flow is longest during spring time, rather than summer time. Hence, this should not be the main cause for the difference in daytime and nighttime trends. We believe the main cause is that only during summertime, the daytime ozone is often influenced by easterly and south-easterly boundary layer air-masses, which are typically associated with anthropogenic emissions from nearby cities.

This part of the discussion is added to the revised manuscript.

**17.** *P31003, Line 8-10: But the differences in spring and autumn trends at WLG are very small. I think you point is “the largest increase in ozone concentration was found in spring and autumn when seasonal mean ozone concentrations are lower than summer”?*

**Response:** Our point is that the season with the largest increase in ozone doesn't coincide with the season with the largest mixing ratio in ozone. For better understanding, we will rephrase this part as the following:

“The seasonal ozone peak in the Northern Hemisphere typically occurs in spring, which is believed to be the result of enhanced photochemical production in spring (Monks, 2000;Vingarzan, 2004). Unlike other sites in the Northern Hemisphere, the seasonal ozone peak at WLG occurs during summer. However, the largest increase in ozone mixing ratio was found in autumn rather than in summer.”

**18.** *P31003 to P31004: Again, the description of the results from Lin et al. (2015b) is not quite accurate. Please make sure that you carefully read all papers cited in the manuscript and portray past literature accurately. Given limited time, the referee only checked a few papers.*

**Response:** We apologize for the inaccurate description. We should not have said that the increasing trend of  $0.31 \pm 0.21$  ppbv a<sup>-1</sup> over western North America during 1995-2014 was insignificant, what we meant was that it was relatively not as significant as the background ozone increasing trend, that was associated with Asian influence. To be more accurate, we rephrased this part of the text into the following:

“Lin et al. (2015b) reported that springtime free-tropospheric ozone displays an increasing trend of  $0.31 \pm 0.21$  ppbv a<sup>-1</sup> over western North America during 1995-2014, however, by shutting of North American emissions in the model and focusing on the subset of ozone associated with Asian influence (also possibly mixed with stratospheric intrusions), the background ozone revealed a more significant increasing rate of  $0.55 \pm 0.14$  ppbv a<sup>-1</sup> during 1992-2012.”

19. P31004, Line 8-10, *“From past literature we can discern that, both strong increasing and decreasing trends were mostly caused by the variation in ozone concentrations in the 1990s”. This statement is not necessarily true for any region in the world. For instance, the largest ozone decreases over the eastern United States occur in the 2000s when U.S. NO<sub>x</sub> emission controls were implemented.*

**Response:** Thank you for pointing that out. This statement was only to summarize results from Jungfraujoch and Kislovodsk, we will make it clear in the revised manuscript. This section has been revised as:

“Tarasova et al. (2009) attributed the strong decrease in ozone in Kislovodsk to control measures of Europe and the breakdown of the former USSR. Both the strong increasing and decreasing trends at Jungfraujoch and Kislovodsk were mostly caused by the variation in ozone mixing ratios in the 1990s. The positive trend at Jungfraujoch during the 1990s was strongest in spring and weakest in summer and autumn, while the reduction at Kislovodsk was strongest in summer and weaker in autumn and winter (Tarasova et al., 2009 ). After 2000, the eastern U.S. revealed significant decrease due to the implementation of NO<sub>x</sub> emission control measures, while ozone mixing ratios at the other sites in the northern mid-latitudes have

entered a steady stage with either slow or no growth (Tarasova et al., 2009;Oltmans et al., 2013).”

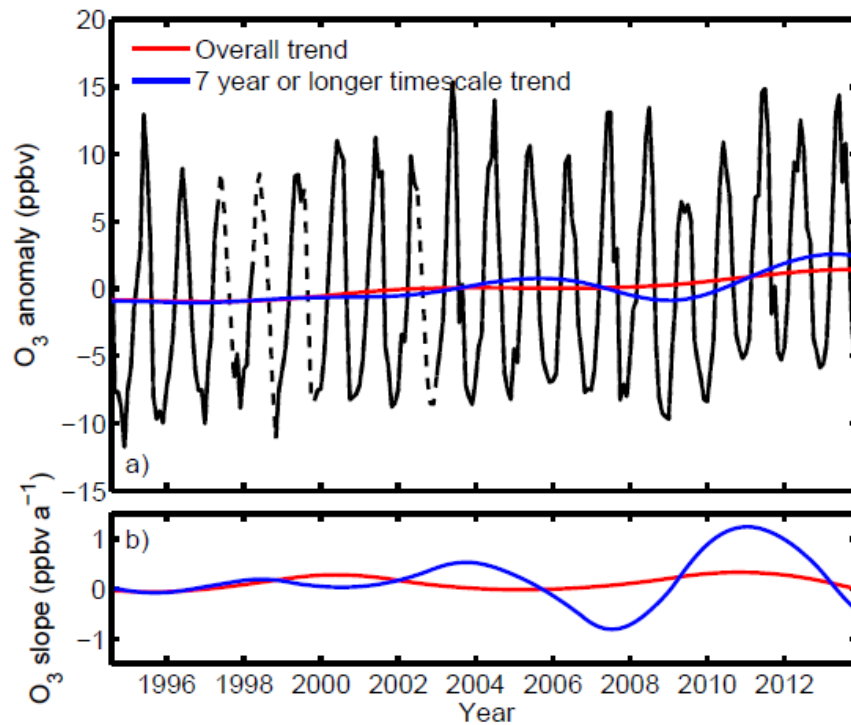
**20.** *P31004, about Line 25-30: Please also add the description of c1 to c5 time scales in the caption of Figure 6.*

**Response:** Thank you for this suggestion, the caption of Figure 6 has been modified as: “The interpolated monthly average ozone mixing ratio at WLG from 1994 to 2013 (the interpolated data given in dashed lines, a) and its intrinsic mode functions c1-c5 (b-f, from the lowest order IMF to the highest order IMF) and its residue, r (g). The time segments in (a) were determined by the slope of the c5. The red slashed lines are the Kendall’s trends and the numbers are the Kendall’s slope (in ppbv 10a<sup>-1</sup>).”

**21.** *P31006, about Line 5-8: But the highest ozone values are found in 2011-2012 (per the time series shown in Figure 5), not 2008 and 2013. I don’t find the analysis shown in Figure 8 useful at all.*

**Response:** The instantaneous energy is a measure to evaluate the variation of the spectral energy at a given frequency span. We think it did quite a good job identifying the peaks in the data. As you can see probably clearer in Figure 7, there is indeed a peak in 2008. And although the following high peak indeed occurs in 2011, the maximum value in 2013 is higher than that in 2012 and very close to that of 2011. The annual mean values of 2011-2013 (53.7, 53.5 and 53.2 ppbv, respectively) are very close to each other and the median value for 2013 (52.5 ppbv) even exceeded that of 2011 (52.0 ppbv). Thus, it is hard to say whether on a climatic time scale the peak occurs in 2011 or 2013. This part of the discussion should mainly proof that the method we used here is robust and that we can base our following studies upon these results.





**Figure 7.** (a) The anomaly of the interpolated monthly average ozone (black line) the sum of last IMF and the residual ( $c_5 + r$ , red line) and the sum of the last two IMFs and the residual ( $c_4 + c_5 + r$ , blue line); (b) the slope of the sum of last IMF and the residual ( $c_5 + r$ , red line) and the sum of the last two IMFs and the residual ( $c_4 + c_5 + r$ , blue line).

### Reference:

Škerlak, B., Sprenger, M., and Wernli, H.: A global climatology of stratosphere–troposphere exchange using the ERA-Interim data set from 1979 to 2011, *Atmos. Chem. Phys.*, 14, 913–937, 10.5194/acp-14-913-2014, 2014.

1 **Long-term trends of surface ozone and its influencing factors at the**  
2 **Mt. Waliguan GAW station, China, Part 1: Overall trends and**  
3 **characteristics.**

4 **W. Y. Xu<sup>1</sup>, W. L. Lin<sup>2</sup>, X. B. Xu<sup>1,\*</sup>, J. Tang<sup>2</sup>, J.Q. Huang<sup>3</sup>, H. Wu<sup>3</sup>, X.C.Zhang<sup>2</sup>**

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11

12 **Abstract**

13 Tropospheric ozone is an important atmospheric oxidant, greenhouse gas and atmospheric  
14 pollutant at the same time. The level of tropospheric ozone, particularly in the surface layer, is  
15 impacted by emissions of precursors and is subjected to meteorological conditions. Due its  
16 importance, the long-term variation trend of baseline ozone is highly needed for environmental  
17 and climate change assessment. So far, studies about the long-term trends of ozone at  
18 representative sites are mainly available for European and North American sites. Similar studies  
19 are lacking for China, a country with rapid economic growth for recent decades, and many other  
20 developing countries. To uncover the long-term characteristics and trends of baseline surface  
21 ozone ~~concentration~~ mixing ratio in western China, measurements at a global baseline Global  
22 Atmospheric Watch (GAW) station in the north-eastern Tibetan Plateau region (Mt. Waliguan),  
23 36°17' N, 100°54' E, 3816m a.s.l.) for the period of 1994 to 2013 were analysed in this study,  
24 using a modified Mann-Kendall test and the Hilbert-Huang Transform analysis for the trend  
25 and periodicity analysis, respectively. Results reveal higher surface ozone during the night and  
26 lower during the day at Waliguan, ~~due to~~ caused by mountain-valley breezes. ~~A and a~~ seasonal  
27 maximum in summer ~~was found, which was probably caused by enhanced stratosphere to~~  
28 ~~troposphere exchange events and/or by tropospheric photochemistry. Analysis suggests that~~  
29 ~~there is a season diurnal cycle in the three-dimensional winds on top of Mt. Waliguan. Season-~~

1 ~~dependent daytime and nighttime ranges of 6 hours were determined based on the season-~~  
2 ~~diurnal cycle in the three dimensional winds and were used to sort subsets of ozone data for~~  
3 ~~trend analysis.~~ Significant ~~increasing~~positive trends in surface ozone were detected for both  
4 daytime (~~2.4±1.5-2.76~~ ppbv 10a<sup>-1</sup>) and nighttime (~~2.8±1.3-2.9-7~~ ppbv 10a<sup>-1</sup>).  
5 ~~Autumn~~Nighttime ozone mixing ratios are more representative of the free tropospheric  
6 condition, with autumn (~~2.9±1.1~~ ppbv 10a<sup>-1</sup>) and spring ~~revealed~~(~~2.4±1.2~~ ppbv 10a<sup>-1</sup>)  
7 ~~revealing~~ the largest increase rates, while summer (~~2.2±2.0~~ ppbv 10a<sup>-1</sup>) and winter ~~showed~~  
8 ~~relatively~~(~~1.3±1.0~~ ppbv 10a<sup>-1</sup>) ~~show~~ weaker increases. ~~The HHT spectral analysis confirmed~~  
9 ~~the increasing trends in surface ozone concentration and could further identify~~Spectral analysis  
10 ~~identified~~ four different ~~stages~~episodes with different ~~increasing rates~~positive trends, with the  
11 largest increase occurring around May 2000 and Oct. 2010. A 2-4 year, 7 year and 11 year  
12 periodicity was found in the surface ozone ~~concentration~~mixing ratio. The results are highly  
13 valuable for related climate and environment change assessments of western China and  
14 surrounding areas, and for the validation of chemical-climate models.

## 16 1 Introduction

17 Ozone (O<sub>3</sub>) is one of the key atmospheric species and is closely related to climate change and  
18 environmental issues (IPCC, 2013). The stratospheric ozone layer protects living organisms at  
19 the Earth's surface against the harmful solar UV radiation, while tropospheric ozone is an  
20 important greenhouse gas and governs oxidation processes in the Earth's atmosphere through  
21 formation of OH radical (Stachelin et al., 2001;Lelieveld and Dentener, 2000). In the surface  
22 layer, ozone is also one of the toxic gases for human beings and vegetation.

23 Since stratospheric ozone is much higher in ~~concentration~~mixing ratio than tropospheric ozone,  
24 it can be well monitored by satellites with retrieved column density. However, ozone in the  
25 troposphere, particularly surface ozone is highly variable in space and time. ~~Since #ozone is a~~  
26 ~~secondary gas pollutant, observed surface ozone is not only~~concentrations are influenced both  
27 ~~by local photochemistry, but also and by nearby photochemical production-transport processes~~  
28 ~~of ozone or anthropogenic emissions of ozoneits precursors, which could reach the~~  
29 ~~measurement site via transport processes from nearby locations~~ (Wang et al., 2006a;Lal et al.,  
30 2014). Deep convection and stratosphere-to-troposphere exchange (STE) events can also bring  
31 down ozone-rich air from above and influence ~~local~~surface ozone ~~concentrations~~mixing ratios  
32 ~~at high-elevation sites~~ (Bonasoni et al., 2000;Ding and Wang, 2006;Stohl et al., 2000;Tang et

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1 al., 2011;Lefohn et al., 2012;Jia et al., 2015;Ma et al., 2014;Langford et al., 2009;Langford et  
2 al., 2015;Lin et al., 2012a;Lin et al., 2015a). All these influencing factors make it very hard to  
3 obtain the background ozone ~~concentration~~mixing ratio and to understand the causes of  
4 observed ozone trends.

5 Many Global Atmosphere Watch (GAW) stations of the World Meteorological Organization  
6 (WMO) and environmental monitoring sites have been setup to monitor surface ozone due to  
7 its importance and due to the urgent need to evaluate the trends of background ozone. Past  
8 trends in surface background ozone have been reported for Europe and North America (Cooper  
9 et al., 2010;Cui et al., 2011;Gilge et al., 2010;Oltmans et al., 2013;Vingarzan, 2004;Parrish et  
10 al., 2012;Logan et al., 2012), which mostly revealed strong increases in ozone before 2000 and  
11 slow or even no growth afterwards. Data from some important regions, e.g., East Asia and  
12 South America, are very scarce. China, as one of the rapidly developing countries, is  
13 contributing increasing ozone precursor ~~concentrations~~mixing ratios to the atmosphere and was  
14 thought to be most responsible for the increase in ozone in the western United States (Cooper  
15 et al., 2010), though other studies would suggest that STE events had an equivalent important  
16 role in causing high-ozone ~~concentration~~events at ~~the US west coast~~western U.S. alpine sites  
17 during spring (e.g., Langford et al., 2009; Ambrose et al., 2011; Lin et al., 2012a; Lin et al.,  
18 2015a). A ~~most-recent studies~~study by Lin et al. (2015b) ~~reported insignificant increasing trends~~  
19 ~~for western US during 1995-2014 and by revisiting the work of~~ found that although rising Asian  
20 emissions contribute to increasing springtime baseline ozone over the western U.S. from the  
21 1980s to the 2000s, the observed western US ozone trend over the short period of 1995-2008  
22 previously reported by Cooper et al. (2010) ~~they found overestimated trends during 1995-2008~~  
23 ~~due to sampling biases. Nevertheless, the impact of Asian outflow on western US ozone~~  
24 ~~concentrations is highly evident~~ has been strongly biased by meteorological variability and  
25 measurement sampling artefacts. Nevertheless, the impact of Asian pollution outflow events on  
26 western US surface ozone is evident (Lin et al., 2012b;Lin et al., 2015a).

27 Long-term trends in ozone in China, however, were seldom reported. Ding et al. (2008) studied  
28 the tropospheric ozone climatology over Beijing based on aircraft data and found a 2% increase  
29 of boundary layer ozone from the period of 1995-1999 to 2000-2005 in Beijing in the North  
30 China Plain (NCP) region, which was mostly driven by the increasing anthropogenic emissions  
31 in the surrounding regions. Upper tropospheric ozone displayed weaker increasing trends.  
32 Wang et al. (2012) reported a similar increasing trend of lower tropospheric ozone and a larger

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1 upper tropospheric ozone increase for the period of 2002 to 2010 based on ozonesonde  
2 measurements in Beijing. Xu et al. (2008) observed positive trends and increased variability in  
3 ozone at Lin'an, a background site in the Yangtze River Delta (YRD) region. Wang et al. (2009)  
4 found a significant increasing trend of 0.58 ppbv yr<sup>-1</sup> during 1994 to 2007 at a coastal site of  
5 Hong Kong in the Pearl River Delta (PRD) region, which were caused by rapid increases in  
6 ozone precursor emissions in the upwind source regions. The above studies were all carried out  
7 in the eastern part of China, in the three most polluted regions NCP, YRD and PRD. ~~Observed,~~  
8 ~~where observed~~ ozone ~~concentrations~~ ~~mixing ratios~~ were mainly under the influence of regional  
9 air pollution and are not representative of the background ozone level on a larger scale. The  
10 trends of ozone over other parts of China remain to be studied based on long-term observations.

11 Continuous long-term observations of surface ozone are made only at a few representative sites,  
12 among which is the Mt. Waliguan (WLG) GAW station. The WLG station, established in 1994,  
13 is situated in the northeastern edge of the Tibetan Plateau, where population is scarce and  
14 industries hardly exist. A few studies have already been performed on short-term measurements  
15 of ozone at WLG. Past research already revealed that surface ozone at the site is highly  
16 representative of free-tropospheric ozone (Ma et al., 2002b) and is often influenced by  
17 stratosphere-to-troposphere exchange (STE) events (Ding and Wang, 2006; Zhu et al., 2004).  
18 Air masses from the west are dominant at WLG and were associated with the highest ozone  
19 ~~concentrations~~ ~~mixing ratios~~ (Wang et al., 2006b). Only in summer a substantial part of the  
20 airflows come from the eastern sector and exposes the surface ozone ~~concentration~~ ~~mixing ratio~~  
21 to some regional anthropogenic influences (Wang et al., 2006b; Xue et al., 2011). Other than  
22 STE, meteorological factors with very short timescales such as the diurnal cycle in topographic  
23 wind or with very long timescales such as the solar cycle also have significant impacts on  
24 tropospheric ozone at WLG (Huang et al., 2009; Wang et al., 2006b; Zhang et al., 2009). QBO  
25 (Quasi Bi-annual Oscillation) and ENSO (El Niño and Southern Oscillation) have been  
26 ~~proved~~ ~~shown~~ to be significant influencing factors on the ~~influence~~ total ozone ~~at WLG~~ ~~burdens~~  
27 ~~over the Tibet~~ (Ji et al., 2001; Zou et al., 2001), ~~which~~. This influence could ~~potentially~~ ~~extend~~  
28 ~~to the lower troposphere via STE and thus~~ affect ~~tropospheric ozone as well~~. ~~suggest~~ ~~ozone~~  
29 ~~variability measured at the 3.8 km altitude of WLG. A few studies suggested~~ that the change in  
30 dynamics after El Niño events ~~hardly leads to changes in stratospheric ozone, but~~ can promote  
31 the cross-tropopause ozone exchange and lead to ~~the~~ rise in global ~~mean~~ tropospheric ozone  
32 ~~centration~~ (e.g. Voulgarakis et al., 2011) ~~concentration~~. Over western U.S. high elevation  
33 ~~regions prone to deep stratospheric intrusions, however~~, Lin et al. (2015a) found that ~~El Niño~~

1 ~~events only enhanced the increased frequency of deep tropopause folds that form in upper~~  
2 ~~tropospheric ozone, which could not reach the surface. Springs-level frontal zones~~ following  
3 strong La Niña winters, ~~however, displayed increasing frequencies in~~ ~~exerts a stronger~~  
4 ~~influence on springtime ozone levels at the surface than the El Niño-related increase in lower~~  
5 ~~stratospheric ozone burden. The Tibetan Plateau has also been identified as a preferred region~~  
6 ~~for deep~~ stratospheric intrusions (Škerlak et al., 2014). ~~The extent to which ENSO events, jet~~  
7 ~~characteristics and increased surface ozone concentrations. Their model results show that this~~  
8 ~~is the mechanism that contributes the most to the~~STE modulate inter-annual variability of ozone  
9 ~~in the western US during spring, while Asian pollution and wildfires had very little impact~~lower  
10 ~~tropospheric ozone at WLG requires further investigation.~~

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11 ~~Past~~Previous studies of ozone at WLG were all based on short-term measurements and were  
12 ~~most~~mostly model-based mechanism studies ~~on the causes of the ozone seasonal cycle, which~~  
13 ~~often reached controversial results~~did not lead to consensus and brought upon debates (Ma et  
14 al., 2002a; Ma et al., 2005; Zhu et al., 2004), while the overall variation characteristics and long-  
15 term trend of ozone at WLG remain unclear. In this study, we present an analysis of 20 year  
16 surface ozone ~~concentration~~mixing ratio at WLG. Besides unravelling the characteristics of  
17 ozone variations and the overall variation trend of ozone, a precise and adaptive spectral  
18 analysis method will be applied to investigate the trend during different periods and the  
19 underlying periodicities within the data.

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## 21 2 Data and Methodology

### 22 2.1 Site and Measurements

23 The Mt. Waliguan site (WLG, 36°17' N, 100°54' E, 3816 m asl) is located in Qinghai Province,  
24 China. It is one of the global baseline stations of the WMO/GAW network and the only one in  
25 the hinterland of Eurasia continent. ~~Mt. Waliguan~~WLG is situated at the northeast edge of the  
26 Qinghai-Tibetan Plateau and surrounded by highland steppes, tundra, desserts, salt lakes, etc  
27 (Figure 1). With very few population (about 6 persons km<sup>-2</sup>) and nearly no industry within 30  
28 km, the WLG site is far from major anthropogenic sources. However, some impact of long-  
29 range transport of anthropogenic pollutants from the NE-SE sector cannot be excluded,  
30 particularly from the major cities Xining (about 90 km northeast of WLG, population ~2.13  
31 millions) and Lanzhou (about 260 km east of WLG, population ~3.1 millions). Such impact, if

1 any, may be significant only during the warmer period (May-September), as suggested by past  
2 air mass trajectory studies (Zhang et al., 2011).

3 The WLG baseline station was established in 1994. Long-term monitoring program for surface  
4 ozone began in August 1994. The ~~concentration~~mixing ratio of surface ozone has been  
5 measured using two ozone analysers (Model 49, Thermal Environmental Instruments; one of  
6 the analyzers was replaced with a Model 49i ozone analyzer in 2011~~)-~~ at a sampling height of  
7 7 meters. The analysers have been automatically zeroed alternatively every second day by  
8 introducing ozone-free air for 45 min. Seasonal multipoint calibrations have been done using  
9 an ozone calibrator (Model 49PS, Thermal Environmental Instruments). In the years 1994, 1995,  
10 2000, 2004, and 2009, the ozone calibrator and analysers at WLG were compared with the  
11 transfer standard from the WMO World Calibration Centre for Surface Ozone and Carbon  
12 Monoxide, EMPA Dübendorf, Switzerland. Intercomparison results show excellent or good  
13 agreement between the WLG instruments and the transfer standard (Zellweger et al.,  
14 2000; Zellweger et al., 2004; Zellweger et al., 2009). Surface ozone data are recorded ~~every~~as 5  
15 ~~min~~-minute averages and corrected annually based on the zero-checks and multipoint  
16 calibrations. If the observed ozone values from the two analysers agree within ~~53~~ ppb, average  
17 values are calculated and included in the final dataset. Otherwise, causes for the differences are  
18 searched by the principal investigator and only data from the well-performing analyser are  
19 included in the dataset. ~~Ozone concentrations in 5 min resolution~~averaged ozone mixing ratios  
20 from Aug. 1994 to Dec. 2013 were then averaged into hourly data and used in this study. In the  
21 trend analysis, monthly average ozone ~~concentrations~~mixing ratios were acquired by first  
22 calculating the daily average ozone values and then performing a monthly averaging. A data  
23 completeness of 75% was required for each averaging step.

24 Meteorological observations have been made at the site using automatic weather stations (AWS)  
25 installed on the ground level and on an 80 m tower at 2, 10, 20, 40 and 80 m. These observations  
26 provide meteorological parameters such as temperature, pressure, precipitation, and wind  
27 speed/direction in 5 min resolution. Additionally, the vertical velocity is measured at the 80 m  
28 platform. The 10 m horizontal wind and 80 m vertical wind data from Aug. 1994 to Dec. 2013  
29 are used in this study and have been accordingly averaged into hourly data, which meet a data  
30 completeness requirement of 75%.

31

## 1 2.2 Determination of daytime and nighttime

2 Past research has already revealed that the surface ozone at WLG is governed by different air  
3 masses during daytime and nighttime (Ma et al., 2002b). The WLG station experiences upslope  
4 winds during the day and is controlled by boundary layer (BL) air, while during the night, winds  
5 go downslope and the site is controlled by free tropospheric (FT) air. The boundary layer air is  
6 largely influenced by local photochemistry and contains pollutants transported from nearby  
7 areas, while the free-tropospheric air represents the background ozone and may sometimes  
8 contain signals of long-range transport or STE events. Hence, it is of necessity to differentiate  
9 daytime and nighttime ozone ~~concentration~~mixing ratio in order to study the trend signals  
10 brought by different air masses.

11 In the previous study (Xu et al., 2011), daytime and the nighttime were defined as a fixed time  
12 ranges (e.g. 11:00-16:00 LT for daytime and 23:00-4:00 LT for nighttime). However, the actual  
13 well-developed day and night time range varies with season. So does the local wind. Figures  
14 2a-c respectively show the season-diurnal variation characteristics of 10 m zonal ( $u$ ) and  
15 meridional ( $v$ ) wind velocity and the 80 m vertical ( $w$ ) wind velocity. Due to the local  
16 topography, the WLG station is under the influence of mountain-valley breezes and all three  
17 wind vectors exhibit distinct diurnal variation characteristics. The height difference to the west  
18 of Mt. WLG is much larger than that to the east, hence valley breezes during daytime come  
19 from the west accompanied by upward drafts, resulting in a diurnal maximum  $u$  and  $w$  vector  
20 between noontime and middle afternoon depending on season. The  $v$  vector changes from  
21 southern winds to northern winds around noontime. Mountain breezes during the night come  
22 from the east-south sector accompanied by subsiding air flows, resulting in low  $u$  and  $w$  and  
23 high  $v$  during the night. The dominant air flow at WLG is westerly during the cold seasons,  
24 which enhances the westerly valley breeze during the day and cancels out the easterly mountain  
25 breeze during the night. During the warm seasons, easterly winds gain in frequency, which  
26 sometimes cancels out the daytime valley breeze and enhances the nighttime mountain breeze.  
27 The distinct diurnal variation of the wind can be used to define a daytime and nighttime range  
28 that varies with season. The white dots in Figure 2 represent the monthly average occurrence  
29 hour of the diurnal maximum  $u$ . In this study, a 6 hour time range that is centred around the  
30 white dots is used as the daytime range (white dashed lines in Figure 2). The nighttime  
31 range window also covers 6 hours and leaves a 6-hour transition stage after the end and before  
32 the start of is considered to be offset by 12 h to the daytime range window.

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### 2 2.3 Trend analysis

3 The trend analysis was performed using a both spearman's linear trend analysis and the  
 4 modified Mann-Kendall's trend test. The Mann-Kendall test is performed using a Fortran  
 5 program developed by Helsel et al. (2006). Here, a brief description on the modified Mann-  
 6 Kendall test will be given. The Mann-Kendall test is a non-parametric test commonly used to  
 7 detect trends. Hamed and Ramachandra Rao (1998) modified the test, so that it can be used on  
 8 data with seasonality.

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9 For two sets of observations  $X = x_1, x_2, \dots, x_n$  and  $Y = y_1, y_2, \dots, y_n$ , the rank correlation test as  
 10 proposed by (Kendall, 1955) is performed as the following:

11 
$$S = \sum_{i < j} a_{ij} b_{ij} \tag{1}$$

12 Where  $a_{ij} = \text{sign}(x_j - x_i) = \begin{cases} 1 & x_i < x_j \\ 0 & x_i = x_j \text{ and } b_{ij} \text{ is the equivalent for } Y. \\ -1 & x_i > x_j \end{cases} \tag{2}$

13 If Y is replaced with the time order  $T = 1, 2, \dots, n$ , the test becomes a trend test and  $S = \sum_{i < j} a_{ij}$ .  
 14 The significance of the trend is tested by comparing the standardized test statistic  $Z =$   
 15  $S / \sqrt{\text{var}(S)}$  to the standard normal variate at a given significance level ( $Z_\alpha$ ). Here, a modified  
 16  $\text{var}(S)$  is given by:

17 
$$\text{var}(S) = \frac{n(n-1)(2n+5)}{18} \frac{n}{n_s^*}, \tag{3}$$

18 where  $\frac{n}{n_s^*}$  represents a correction for the autocorrelation that exists in the data and can be  
 19 obtained by an approximation to the theoretical values.

20 
$$\frac{n}{n_s^*} = 1 + \frac{2}{n(n-1)(n-2)} \sum_{i=1}^n (n-i)(n-i-1)(n-i-2) \rho_s(i) \tag{4}$$

21 Here  $\rho_s(i)$  is the autocorrelation function of the ranks of the observations.

22 If  $|Z| > Z_{1-\alpha/2}$ , then the data is non-stationary, a positive Z would indicate a positive trend and a  
 23 negative Z would suggest a declining trend. If  $|Z| \leq Z_{1-\alpha/2}$ , then the data is stationary. Here we  
 24 use  $\alpha = 0.05$ , hence the corresponding critical  $Z_{1-\alpha/2} = 1.96$ . A non-parametric method is then used  
 25 to estimate the slope of the trend, details can be found in Sen (1968).

26

## 1 2.4 The Hilbert-Huang Transform analysis

2 The Hilbert-Huang Transform (HHT) analysis is a combination of the Empirical Mode  
3 Decomposition (EMD) and the Hilbert Spectral analysis proposed by (Huang et al., 1998). It is  
4 often used to analyse the time-frequency variation of non-linear and non-stationary processes.  
5 The EMD acts as a time-frequency filter, it decomposes the data into several oscillation modes  
6 with different characteristic time scales. The HHT method has proved to be an efficient and  
7 precise method in investigating the periodicity, long-term oscillations and trends that are  
8 embedded within the data (Huang and Wu, 2008). So far, it has been widely applied in  
9 atmospheric and climatic studies including wind field, temperature and rainfall analysis (Rao  
10 and Hsu, 2008;Lundquist, 2003;El-Askary et al., 2004), but it has not been used on atmospheric  
11 composition data yet. Here we give a brief description of the HHT method.

12 First, the EMD is performed on the data, to decompose the data into  $n$  intrinsic mode functions  
13 (IMF),  $c_1, c_2, \dots, c_n$ , and one residual  $r_n$ , which are ordered from the smallest to the largest  
14 variational time scale (Huang et al., 2003).

$$15 \quad x(t) = \sum_{j=1}^n c_j + r_n \quad (5)$$

16 Then the Hilbert transform is applied to each IMF using Eq. 6,

$$17 \quad y(t) = \frac{1}{\pi} P \int_{-\infty}^{\infty} \frac{x(t')}{t-t'} dt' \quad (6)$$

18 Where P is the Cauchy principal value. An analytical signal is then obtained with Eq.7,

$$19 \quad z(t) = x(t) + iy(t) = a(t)e^{i\theta(t)}, \quad (7)$$

$$20 \quad \text{where, } a(t) = [x^2(t) + y^2(t)]^{1/2} \text{ and } \theta(t) = \arctan\left(\frac{y(t)}{x(t)}\right). \quad (8)$$

21 The instantaneous frequency  $\omega$  can be calculated as the following:

$$22 \quad \omega(t) = \frac{d\theta(t)}{dt}. \quad (9)$$

23 Thus, Eq.5 can be transformed into the following expression:

$$24 \quad x(t) = \Re \sum_{j=1}^n a_j(t) \exp\left(i \int \omega_j(\tau) d\tau\right), \quad (10)$$

25 where  $\Re$  is the real part of the complex number.

26 To obtain the Hilbert amplitude spectrum  $H(\omega, t)$ , we assign for each time  $t$ , the calculated  
27 amplitude  $a_j(t)$  to the according  $\omega_j(t)$ . An integration of  $H(\omega, t)$  over the frequency span would

1 yield the instantaneous energy (IE), which represents the time variation of the energy. An  
 2 integration along the time span would yield the marginal Hilbert spectrum  $h(\omega)$ , which provides  
 3 information on how the frequency is distributed over the entire span.

4 The degree of stationarity  $DS(\omega)$  is often used to investigate the stationarity and periodicity of  
 5 the data, it is defined as:

$$6 \quad DS(\omega) = \frac{1}{T} \int_0^T \left(1 - \frac{H(\omega, t)}{h(\omega)/T}\right)^2 dt, \quad (11)$$

7 where T is the entire time span.

8 The volatility which is defined as the ratio of the sum of certain IMF components  $S_h(t)$  to the  
 9 original signal  $S(t)$ , here we use the summation of residual and all the IMFs but the first one as  
 10  $S_h(t)$ :

$$11 \quad V(t, T) = \frac{S_h(t)}{S(t)} = \frac{\sum_{j=2}^n c_j(t) + r(t)}{S(t)}, \quad (12)$$

12 where  $n$  is the number of IMFs.

### 13 **2.5 The gap-filling of the monthly average ozone data**

14 To perform the HHT analysis, a complete, even-spaced dataset is required. Hence we need to  
 15 fill the gaps in the monthly average surface ozone ~~concentration~~ ~~mixing ratio~~ data. The location  
 16 of the gaps can be seen in Figure 4b. It can be noted that gaps could be found in 1997, 1998,  
 17 1999 and 2002. If the gap is small and occurs in between the ozone seasonal low and peak value,  
 18 then a spline interpolation would suffice. However, this is not the case for some gaps. In 1997  
 19 and 1998, the gaps occur during summertime, when ozone ~~concentration~~ ~~mixing ratio~~ should be  
 20 highest. In 2002, the gap continues on to winter, when ozone ~~concentration~~ ~~mixing ratio~~ should  
 21 be lowest. A simple spline interpolation would underestimate the seasonal peak value and  
 22 overestimate the seasonal low. Hence, we applied the following method to fill the gaps.

23 First, the monthly mean ozone timeseries during 1994 to 2013, as is shown in Figure 4b, is  
 24 shaped into an array  $O_3(i, j)$  of the size [20 years  $\times$  12 months], where  $i=1994, \dots, 2013$  and  
 25  $j=1, \dots, 12$ .

26 The gaps in  $O_3(i, j)$  are filled by applying a spline interpolation on each row of the array:

$$27 \quad O_{3, spline}(1994, \dots, 2013, j) = spline(O_3(1994, \dots, 2013, j)), j = 1, \dots, 12 \quad (13)$$

1 In this way, both the average value of ozone ~~concentration~~mixing ratio at a certain month and  
2 the overall ozone variation trend will be considered. A complete dataset of average monthly  
3 ozone ~~concentration~~mixing ratio can then be recreated by using interpolated data only on  
4 months of missing observation data:

$$5 \quad O_{3,complete} = \begin{cases} O_{3,spline}, & \text{missing } O_3 \\ O_3, & \text{existing } O_3 \end{cases} \quad (14)$$

6 The result is displayed in Figure 7a, with the original data in solid lines and interpolated data  
7 in dashed lines. Our method could yield a reasonable interpolated timeseries with both seasonal  
8 low and peak values occurring at the right time of year.

### 9 **3 Results and Discussion**

#### 10 **3.1 Season-diurnal variation characteristics of ozone**

11 The average season-diurnal variation of surface ozone during 1994 to 2013 is displayed in  
12 Figure 3. The seasonal maximum ozone occurs during summer, with an average peak in June-  
13 July, while the minimum is found in winter (Figure 3a), which will be discussed in detail in  
14 Section 3.2.

15 Daily maximum ozone usually occurs during nighttime, while the daily minimum ozone is  
16 found around noontime, on average at 12 am, Beijing Local Time (Figure 3c). Ma et al. (2002b)  
17 suggest that the WLG station is mostly influenced by boundary layer (BL) air that is brought  
18 up through an upslope flow during the day, while a downslope flow brings down free  
19 tropospheric (FT) air during the night. The BL air masses are typically characterised by lower  
20 ozone ~~concentrations~~mixing ratios in comparison with FT air masses, hence the occurrence of  
21 the daily ozone minimum value indicates the time when the BL is fully developed and the air  
22 within is well mixed.

23 From Figure 3b) it can be denoted that, the occurrence time of the daily minimum ozone  
24 ~~concentration~~ ~~(white~~mixing ratio (red dots) shows a significant seasonal variation similar to  
25 that of the maximum zonal ~~and vertical~~-wind velocity ~~(-)~~(white dots), with the former occurring  
26 1-2 hours earlier than the later. Due to the seasonal variation of the development of the boundary  
27 layer, the daily minimum ozone should occur earlier in the day during warm seasons and later  
28 in the day during cold seasons. This phenomenon can indeed be confirmed by Figure 3b),  
29 however, the ozone minimum of June-August seems to occur later than expected. This  
30 phenomenon could not be found in the season-diurnal variation of horizontal or vertical wind

1 speeds, thus it is not caused by boundary layer development. A possible explanation might be  
2 that the photochemical production of ozone was enhanced at early noon during summertime,  
3 leading to a delayed noontime minimum. The in-situ ozone production/destruction in different  
4 seasons is not well quantified at the moment. ~~Past researches~~ Previous studies focused on  
5 modelling the photochemical net production in spring and summer and reached to controversial  
6 conclusions (Ma et al., 2002b; Wang et al., 2015). Hence there is a need for more investigation  
7 into the cause for such a phenomenon.

### 9 **3.2 Season-annual variation characteristics of ozone**

10 Figure 4 displays the season-annual variation of surface ozone during 1994 to 2013. Again, the  
11 ozone ~~concentration~~ mixing ratio peaks in summer and is lowest during winter (Fig. 4b), with  
12 an average seasonal peak occurring in June during 1994 to 2013 (Fig. 4c). Previous studies  
13 reported the same seasonal ozone pattern, but attributed the summertime peak to different  
14 causes, e.g., more frequent STE events (Ding and Wang, 2006; Tang et al., 2011), enhanced  
15 vertical convection (Ma et al., 2005), long-range transport from eastern-central China, central-  
16 southern Asia or even Europe during summer (Zhu et al., 2004) and stronger cross boundary  
17 transport and vertical convection during the East Asian summer monsoon season (Yang et al.,  
18 2014). From Fig. 2c it can be noted that nighttime subsiding wind is indeed strongest in summer,  
19 which supports the hypothesis of downward transport of ozone. Zheng et al. (2011) argue that  
20 STE reaches maximum strength in spring and shows a decline in late spring based on  $^{10}\text{Be}/^{7}\text{Be}$   
21 measurements, indicating that the continuous ozone increase in summer is caused by the  
22 photochemical production.

23 The long-term variation of the annual average ozone exhibits a clear increasing trend (Fig. 4a).  
24 A 2-4 year cycle seems to exist within the long-term variation of surface ozone. ~~Past~~  
25 ~~research~~ Previous study has shown that there is a quasi-biannual oscillation (QBO) within the  
26 total ozone column density over the Tibetan Plateau, which is in antiphase with the QBO of the  
27 tropical stratospheric winds, exhibiting a 29 month cycle (Ji et al., 2001). The influence of the  
28 QBO could extend to WLG station, ~~with its high at the 3.8 km altitude, is very representative~~  
29 ~~of the tropospheric background and also highly influenced by via~~ STE. Thus, the surface ozone  
30 at WLG might also have a QBO ~~that~~ with a similar periodicity, which is related to that of the  
31 total ozone column.

### 1 3.3 Long-term variation trends of ozone

2 The trends of monthly average all-day, daytime and nighttime ozone during 1994 to 2013 are  
3 displayed in Figs. 5a1-c1, respectively. Ozone data in Figs. 5b1 and 5c1 are the subsets of data  
4 from the daytime and nighttime ranges determined in Section 2.2- [based on zonal wind](#)  
5 [information](#). The increase in surface ozone in the past two decades is evident in all three data  
6 subsets, with a slightly stronger increase in the nighttime data. The linear trends for all-day,  
7 daytime and nighttime ozone [concentrations-mixing ratios](#) reached 2.5, 2.4 and 2.8 ppbv  $10a^{-1}$ ,  
8 respectively, while the Kendall slopes reached 1.8, 1.7, 1.9 ppbv  $10a^{-1}$ , respectively. The  
9 Kendall slope is smaller than the linear regression slope, mainly because the linear regression  
10 method does not consider the seasonality within the data. However, both methods yielded  
11 statistically significant increasing trends.

12 To further investigate the trend in ozone in different seasons, the trend of seasonal average  
13 ozone during 1994 to 2013 was calculated and are shown in Figs. 5a-c (2-5). After eliminating  
14 the seasonality in the data, the linear least squares fitting slopes and Kendall's slope yielded  
15 very similar results, thus we only listed the linear slopes and p-values in Table 1. The strongest  
16 increase in surface ozone was found in autumn (SON), followed by spring (MAM), respectively  
17 reaching 2.8 and 2.4 ppbv  $10a^{-1}$  in the seasonal average of all-day ozone [concentrations-mixing](#)  
18 [ratios](#). In comparison, summer (JJA) and winter (DJF) both showed much weaker increasing  
19 trends, with rates of 1.5 and 1.4 ppbv  $10a^{-1}$ , respectively, amongst which the summertime trend  
20 could not even reach a confidence level of 95%. In summer the daytime increasing rate is  
21 significantly lower than the nighttime one, respectively reaching 0.7 and 2.2 ppbv  $10a^{-1}$ . The  
22 nighttime slope reached the confidence level of 95%, while the daytime slope is statistically  
23 insignificant.

24 Past investigations on the air-mass origin of WLG have shown that WLG is mostly governed  
25 by western and northwestern air-masses, air-masses coming from the eastern sector takes up  
26 only 2%, 5% and 8% in winter, spring and autumn, respectively (Zhang et al., 2011). However,  
27 in summer there is a significant percentage (30%) of air-masses coming from the eastern  
28 direction. Since the two major cities in the vicinity of WLG are both in the east, summertime is  
29 believed to be the season in which WLG is most influenced by nearby anthropogenic activities.  
30 From the diurnal variation of the horizontal wind speeds (Figs. 2a-b) it can be discerned that  
31 daytime winds are weak northern winds, while nighttime winds are rather strong north-easterly  
32 winds, which are more in favour of transporting anthropogenic pollution to WLG.

1 As already mentioned before in Section 3.2, some research believe that STE is also most  
2 frequent in summer at WLG (Ding and Wang, 2006). During the night the WLG site is governed  
3 by downwards winds, which may bring down air with high ozone ~~concentrations~~mixing ratios  
4 from above. Hence, an increase in the frequency of STE events would also result in increasing  
5 nighttime ozone ~~concentrations~~mixing ratios in summer. Whether it is anthropogenic activities  
6 or rather meteorological factors, that has led to ~~significantly~~the distinct daytime and nighttime  
7 ozone variation slopes in summer, still needs further investigations and will be discussed in Part  
8 2 of our study.

9 ~~The seasonal ozone peak in of the Northern Hemisphere background ozone~~ typically occurs in  
10 spring, which is believed to be the result of enhanced photochemical production in spring  
11 (Monks, 2000;Vingarzan, 2004). ~~The~~Unlike other sites in the Northern Hemisphere, the  
12 seasonal ozone peak at WLG occurs ~~in~~during summer, ~~however~~. However, the largest increase  
13 in ozone ~~concentration~~mixing ratio was found in autumn rather than ~~spring or in~~ summer. Lin  
14 et al. (2014) also reported significant increasing ozone trends in autumn rather than spring at  
15 the Mauna Loa Observatory in Hawaii in the past 4 decades and attributed this phenomenon to  
16 strengthened ozone-rich air flows from Eurasia. The reason why we observed the largest  
17 increase in ozone levels during autumn also needs further exploration and will be handled in  
18 Part 2.

19 Here we present a comparison between the seasonal ozone variation trends of all the high  
20 altitude (>1200 m asl) sites in the northern hemisphere (Table 2). The stations have been sorted  
21 by latitude. The low latitude sites, Mauna Loa and Izaña, both show increasing trends ( $3.1 \pm 0.7$   
22 and  $1.4 \pm 0.5$  ppbv  $10a^{-1}$ ) during 1991 to 2010 (Oltmans et al., 2013). Lin et al. (2014) suggested  
23 that, in the period of 1995 to 2011 in comparison with the period of 1980 to 1995, the Mauna  
24 Loa site in Hawaii displays strong increasing ozone ~~concentrations~~mixing ratios during summer  
25 and autumn. The mid-latitude stations exhibit inconsistent trends. Significantly positive trends  
26 were detected in the Rocky Mountains, USA ( $3.3 \pm 0.5$  ppbv  $10a^{-1}$ , Oltmans et al., 2013) and at  
27 Jungfraujoch, Switzerland ( $3.2 \pm 1.8$  ppbv  $10a^{-1}$ , Cui et al., 2011). Tarasova et al. (2009) found  
28 evidence for increased stratospheric contribution to surface ozone at Jungfraujoch. The  
29 strongest increase at Jungfraujoch was detected in winter, the weakest in summer. Gilge et al.  
30 (2010) also reported increased wintertime ozone at other two alpine sites in central Europe  
31 during 1995-2007. Lin et al. (2015b) reported that springtime free-tropospheric ozone displays  
32 an ~~insignificant~~ increasing trend of  $0.31 \pm 0.21$  ppbv  $a^{-1}$  over western North America during

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1 1995-2014, however, by shutting of North American emissions in the model, and focusing on  
2 the subset of ozone associated with Asian influence ~~and~~ (also possibly mixed with stratospheric  
3 intrusions), the background ozone revealed a more significant increasing rate of  
4 0.55±0.14 ppbv a<sup>-1</sup> during 1992-2012. No significant trends were found at Pinadale, USA and  
5 Zugspitze, Germany. Negative trends were revealed at Kislovodsk, Russia ( $-3.7\pm 1.4$  ppbv  $10a^{-1}$   
6 <sup>1</sup>, Tarasova et al., 2009) and Whiteface, USA ( $-2.2\pm 0.6$  ppbv  $10a^{-1}$ , Oltmans, 2013). Tarasova  
7 et al. (2009) attributed the strong decrease in ozone in Kislovodsk to control measures of Europe  
8 and the breakdown of the former USSR. ~~From past literature we can discern that, both~~ Both the  
9 strong increasing and decreasing trends at Jungfraujoch and Kislovodsk were mostly caused by  
10 the variation in ozone ~~concentrations~~ mixing ratios in the 1990s. The positive trend at  
11 Jungfraujoch during the 1990s was strongest in spring and weakest in summer and autumn,  
12 while the reduction at Kislovodsk was strongest in summer and weaker in autumn and winter  
13 (Tarasova et al., 2009). ~~After 2000, ozone concentrations.~~ After 2000, the eastern U.S. revealed  
14 significant decrease due to the implementation of NO<sub>x</sub> emission control measures, while ozone  
15 mixing ratios at the other sites in the northern mid-latitudes have entered a steady stage with  
16 either slow or no growth (Tarasova et al., 2009; Oltmans et al., 2013).

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17 In comparison ~~with other sites,~~ Mt. Waliguan, WLG shows a continuous rise of ozone  
18 ~~concentration~~ mixing ratio throughout the past 2 decades and the most significant positive trends  
19 appear in autumn and spring, unlike the other mid-latitude stations. The cause of this  
20 phenomenon still needs further exploration.

### 21 3.4 Hilbert-Huang Spectral Analysis of surface ozone at WLG

22 The long-term variation of surface ozone may be the result from changes in emissions of ozone  
23 precursors, but may also be caused by year-to-year fluctuations or multiyear oscillations of  
24 climate conditions. All the related factors have different periodicities, which is why the  
25 variation of ozone is highly non-linear. To unravel the potential oscillations on different time  
26 scales in the ozone timeseries, we performed an HHT analysis on the ozone data from WLG  
27 using the method given in Section 2.4. The result of the EMD is shown in Fig. 6. The monthly  
28 average ozone signal could be decomposed into 5 IMFs with different characteristic time scales.  
29 The lowest order IMF (c1) shows an oscillation with the highest frequency. The second IMF  
30 (c2) shows the seasonal variation in the ozone signal. C3 reveals 3-4 year oscillations, c4 shows  
31 7 year oscillations and the highest order IMF (c5 in Fig. 6f) shows the longest oscillations  
32 pattern, with a quasi-10-year periodicity.



1 Segmentations is performed by finding the local extrema of  $c_5$ . The total time span could be  
2 separated into 4 segments, as indicated by the dotted lines in Fig. 6a. The slope of the segments  
3 of  $c_5$  can indicate whether the value is increasing or declining. To determine the significance  
4 of the trend, the modified Mann-Kendall trend test is performed on each segment and the results  
5 are given in Table 3. The first segment lasts 3 years (from Aug. 1994 to Jun. 1997) and reveals  
6 no significant trend ( $z=1.42$ ), with an increasing slope of  $2.7 \text{ ppbv } 10\text{a}^{-1}$ . The second segment  
7 lasts for 5 years (from Jul. 1997 to May 2002) and displays a significant upward trend ( $z=3.66$ ).  
8 The increasing slope reaches  $4.2 \text{ ppbv } 10\text{a}^{-1}$ . Afterwards the increasing speed of ozone  
9 concentrationmixing ratios at WLG slows down in segment 3, lasting 6 years (from Jun. 2002  
10 to Apr. 2008), with a variation slope of  $3.0 \text{ ppbv } 10\text{a}^{-1}$ , however, the increasing trend remains  
11 significant ( $z=3.57$ ). In the last segment, which starts in May 2008 and ends in Jul. 2013, the  
12 significant upward trend continues ( $z=3.65$ ) with a larger increasing slope ( $3.6 \text{ ppbv } 10\text{a}^{-1}$ ) than  
13 that in segment 3.

14 Overall, surface ozone concentrationmixing ratio at WLG has been rising continuously since  
15 1997. Figure 7a shows the anomaly of the interpolated monthly average ozone during 1994 to  
16 2013, its overall variation trend (represented by  $c_5+r$  in Fig. 6) and its variation on a scale of 7-  
17 year or longer (represented by  $c_4+c_5+r$  in Fig. 6). The corresponding variation slopes of the  
18 overall variation trend and the 7-year or longer variation is depicted in Fig. 7b. The overall  
19 variation trend confirms the continuous increase since Jan. 1997. The two largest slopes are  
20 respectively detected in May 2000 and Oct. 2010. The 7-year or longer trend line displays a rise  
21 in ozone after Aug. 1996, which reaches a maximum increasing speed in Sep. 2003. Afterwards,  
22 the increase slows down and turns into a decreasing trend in Sep. 2005. After Jan. 2009, ozone  
23 concentrationmixing ratios went up again, reaching a maximum increasing speed in Dec. 2010.

24 The Hilbert Energy Spectrum is depicted in Fig. 8d, along with the volatility, instantaneous  
25 energy (IE) and the degree of stationarity ( $\Phi_{\text{DS}}$ ) (Figs. 8b, c, e). Both the volatility and the IE  
26 reflect the variation of energy with time. Compared to the mean IE, which represents the  
27 temporal variation of the frequency averaged energy, volatility rather focuses on the ratio of the  
28 variation of certain signals to the total signal. Peaks in the mean IE could be found in 1994-  
29 1995, 2000-2001, 2003, 2008 and 2013, which corresponds to the high ozone  
30 concentrationmixing ratio values in the data. High values of volatility were found around 2003,  
31 2008 and 2012, which mostly agree with those of the IE. The cause for these high anomalies  
32 still needs to be investigated upon.

1 The  $D_sDS$  corresponding to each frequency, as displayed in Fig. 8e, can provide information  
2 on the underlying periodicity within the original signal. The smaller  $D_sDS$  is, the more  
3 stationary the data is at this frequency. The lower  $D_sDS$  values are observed in the low  
4 frequency part. A dip-down at the frequencies between 0.08 and 0.12 could be found, which  
5 corresponds to the annual cycle of ozone. Other dip-downs are found at even lower frequencies,  
6 corresponding to 2.5a, 3.5a, 7a and 11a cycles. Among all the known atmospheric factors that  
7 have an impact on the ozone concentration mixing ratio at WLG, QBO has a quasi-2-year cycle,  
8 ENSO bears a 2 to 7 year cycle and solar activities vary with a 11 year cycle. The combined  
9 effect of QBO and ENSO could be responsible for the 2.5a or 3.5a periodicity as suggested by  
10 the  $D_sDS$ . Further investigations of these periodicities will be carried out in Part 2.

#### 11 **4 Summary**

12 In this paper we present the characteristics, trends and periodicity of surface ozone  
13 concentration mixing ratio at a global baseline GAW station in the eastern Tibetan Plateau  
14 region (Mt. Waliguan) during the past two decades. The trends and periodicity of ozone were  
15 investigated using a modified Mann-Kendall test and an adaptive method (Hilbert Huang  
16 Transform) that is suited for analysing non-stationary and non-linear natural processes.

17 Results reveal that surface ozone at Waliguan WLG is higher during the night and lower during  
18 the day, because the station is under the control of ozone-rich free-tropospheric air during the  
19 night and boundary layer air during the day due to mountain-valley breeze. Ozone displays a  
20 seasonal maximum in summer and minimum in winter, which is probably caused by enhanced  
21 stratosphere-to-troposphere exchange events and/or by tropospheric photochemistry. Analysis  
22 suggests that there is a season-diurnal cycle in the three-dimensional winds on top of Mt.  
23 Waliguan. This allows for defining well-development daytime and nighttime ranges that change  
24 from month to month. Trends of surface ozone were calculated for the data subsets of the  
25 defined daytime and nighttime as well as for all-day in different seasons. Both daytime and  
26 nighttime surface ozone has been significantly increasing at Waliguan WLG. Autumn and  
27 spring revealed the largest increase rates, while summer and winter showed relatively weaker  
28 increases. A significant daytime and nighttime difference in trend could only be found in  
29 summer, where nighttime ozone was significantly increasing and daytime ozone bears no  
30 significant trend. Summer is the season during which Waliguan WLG is mostly influenced by  
31 airmasses from the eastern sector. Whether anthropogenic activities in the two nearest major

1 cities in the eastern sector have impacts on the trend of summertime ozone still needs further  
2 exploration.

3 Results of the HHT spectral analysis confirm the increasing trends in surface ozone  
4 ~~concentration~~mixing ratio and could further identify four different stages with different  
5 increasing rates. The overall trend indicates that the largest increase occurred around May 2000  
6 and Oct. 2010. The ozone signal was also decomposed into five intrinsic mode functions with  
7 different time scales. A 2-4 year, 7 year and 11 year periodicity was found within the data, the  
8 cause of which still needs further investigation.

9 The results obtained in this work are very valuable for related climate and environment change  
10 assessments of western China and surrounding areas, and for the validation of chemical-climate  
11 models. As WLG is a high altitude mountain-top site in a remote region, measurements of  
12 surface ozone and other species can well represent a large scale situation. Previous t air mass  
13 origin studies and modelling studies suggest that WLG is mostly under the influence of  
14 transport from the north-west direction, hence the upward trend in ozone might be a reflectance  
15 upon transport from Europe (Zhang et al., 2011;Li et al., 2014). Since Eastern China is in the  
16 downwind direction, our results imply that under rising background ozone conditions, even  
17 more effort needs to be put in reducing ozone precursors. In the second part of our study, the  
18 impact of different air-mass origins and the long-term variations of their occurrence frequencies  
19 on the surface ozone mixing ratio and its trend at WLG will be shown. The anthropogenic  
20 impact of the nearest major population centers on the ozone trend will be discussed. The long-  
21 term variation of STE and its link to surface ozone at WLG will be displayed. The possible  
22 connection of changes in atmospheric circulation oscillations and solar activities with the inner-  
23 annual and periodical variations of ozone at WLG will be studied.

24

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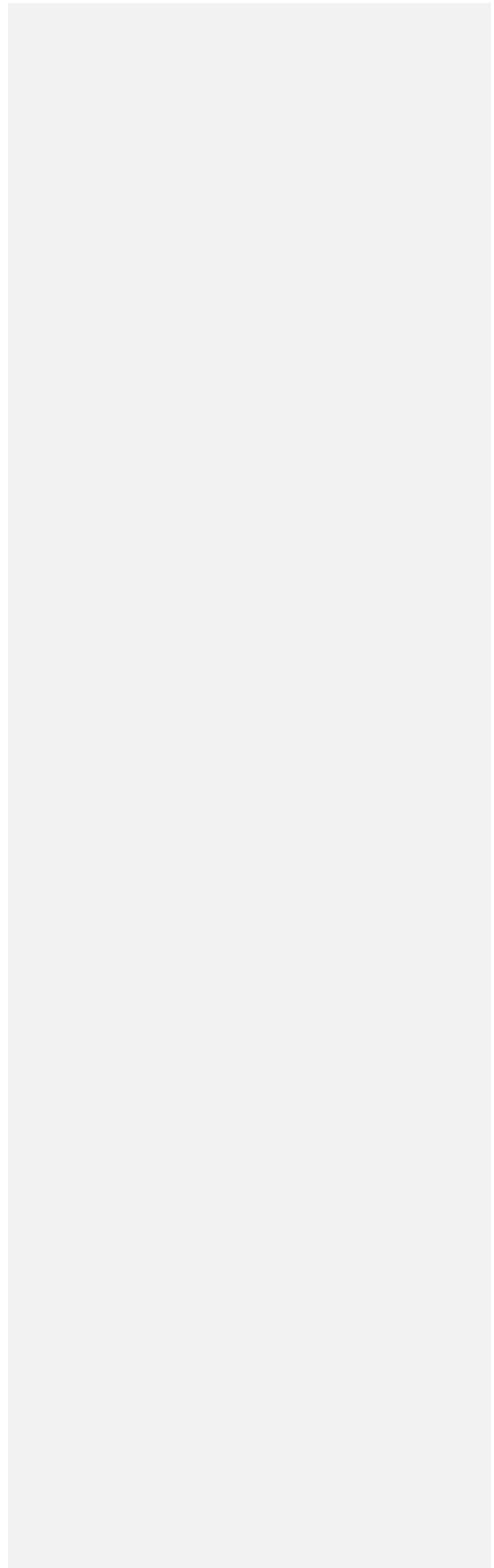
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1 Table 1 The linear slope, 95% confidence interval (in ppbv 10a<sup>-1</sup>) and the p-values (in  
 2 parenthesis) of seasonal average surface ozone ~~concentration~~mixing ratio during 1994 to 2013

Data subset	MAM	JJA	SON	DJF
All Day	2.4±1.1 (<0.01)	1.5±1.9 (0.12)	2.8±1.1 (<0.01)	1.4±0.9 (<0.01)
Day	2.4±1.1 (<0.01)	0.7±1.8 (0.41)	2.7±1.0 (<0.01)	1.5±0.9 (<0.01)
Night	2.4±1.2 (<0.01)	2.2±2.0 (0.04)	2.9±1.1 (<0.01)	1.3±1.0 (0.01)

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2 Table 2 The linear slope (in ppbv  $10a^{-1}$ ) and the 95% confidence interval of all-year and  
 3 seasonal average surface ozone ~~e~~concentrationmixing\_ratio during 1994 to 2013 at north  
 4 hemispheric high altitude GAW sites.

Station (Location)	Time Span	All Year	MAM	JJA	SON	DJF	Reference
Mauna Loa, USA (19.5N, 155.6W, 3397 m asl)	1991-2010	3.1±0.7					(Oltmans et al., 2013)
Izaña, Spain (28.3N, 16.5W, 2367 m asl)	1991-2010	1.4±0.5					(Oltmans et al., 2013)
Waliguan, China (36.3N, 100.9E, 3816 m asl)	1994-2013	2.5±1.7	2.4±1.1	1.5±1.9	2.8±1.1	1.4 ±0.9	This work
Rocky, USA (40.3N, 105.6W, 2743 m asl)	1991-2010	3.3±0.5					(Oltmans et al., 2013)
Pinadale, USA (42.9N, 109.8W, 2743 m asl)	1991-2010	-0.5±0.4					(Oltmans et al., 2013)
Kislovodsk, Russia (43.70N, 42.70E, 2070 m asl)	1991-2006	-3.7±1.4	-2.0±2.0	-1.4±2.4	-6.0±2.1	-3.0±2.5	(Tarasova et al., 2009)
Whiteface, USA (44.4N, 73.9W, 1484 m asl)	1991-2010	-2.2±0.6					(Oltmans et al., 2013)
Jungfrauoch, Switzerland (46.5N, 8.0E, 3580 m asl)	1990-2008	3.2±1.8	3.3±2.2	2.2±2.8	3.3±1.6	4.9±1.7	(Cui et al., 2011)
Zugspitze, Germany (47.4N, 11.0E, 2960 m asl)	1991-2010	0.5±0.4					(Oltmans et al., 2013)

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2 Table 3 Modified Mann-Kendall trend test on segments based on the last IMF.

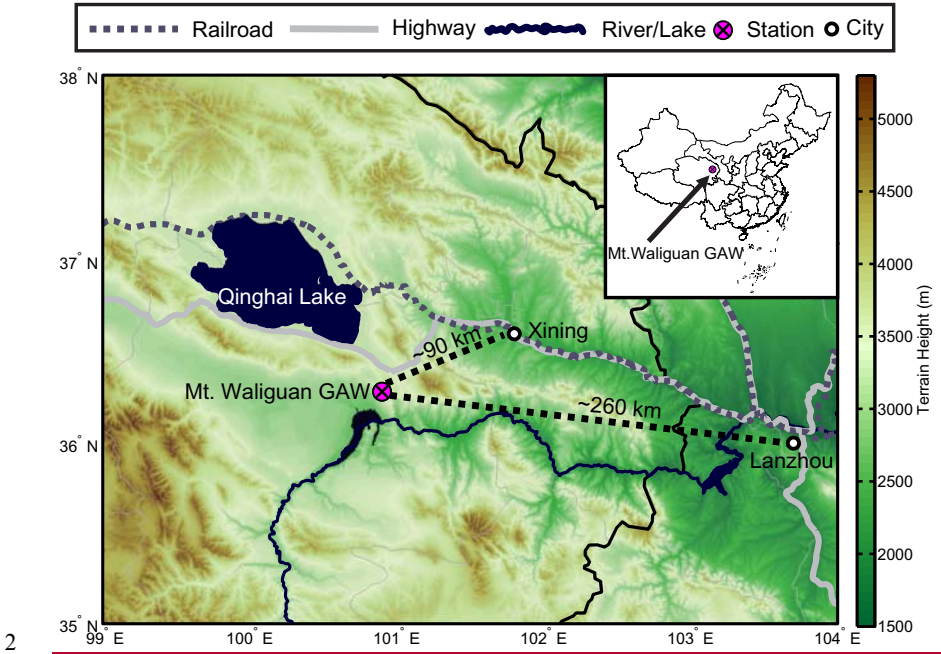
Segment	Time Range	Slope of c5	Modified Mann-Kendall test (z)	Slope of O <sub>3</sub> (ppbv 10a <sup>-1</sup> )
1	Aug1994- Jun1997	-	No significant trend (z =1.42)	2.7
2	Jul1997-May2002	+	Significant upward trend (z =3.66)	4.2
3	Jun2002-Apr2008	-	Significant upward trend (z =3.57)	3.0
4	May2008-Jul2013	+	Significant upward trend (z = 3.42)	3.6

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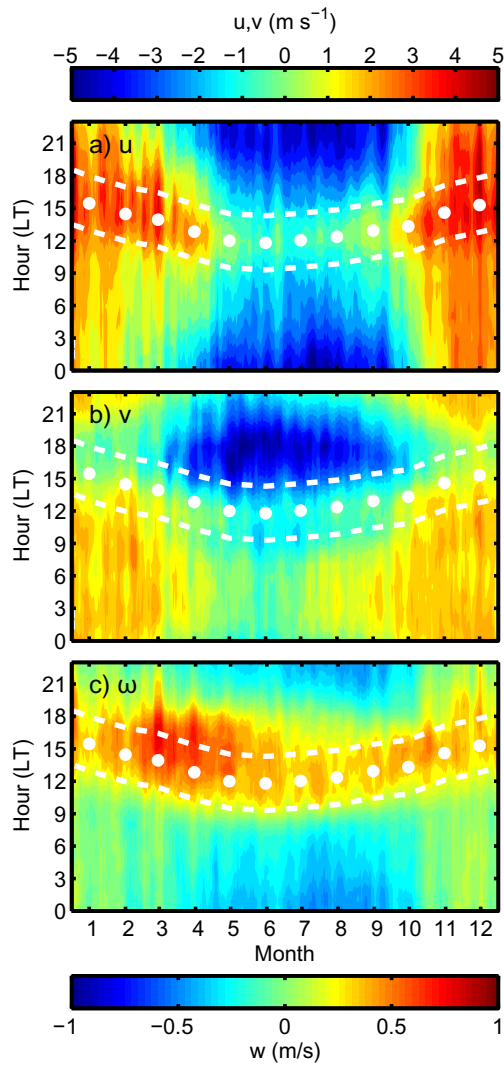


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3 Figure 1 The location of the Mt. Waliguan GAW site and the two major cities in its vicinity.

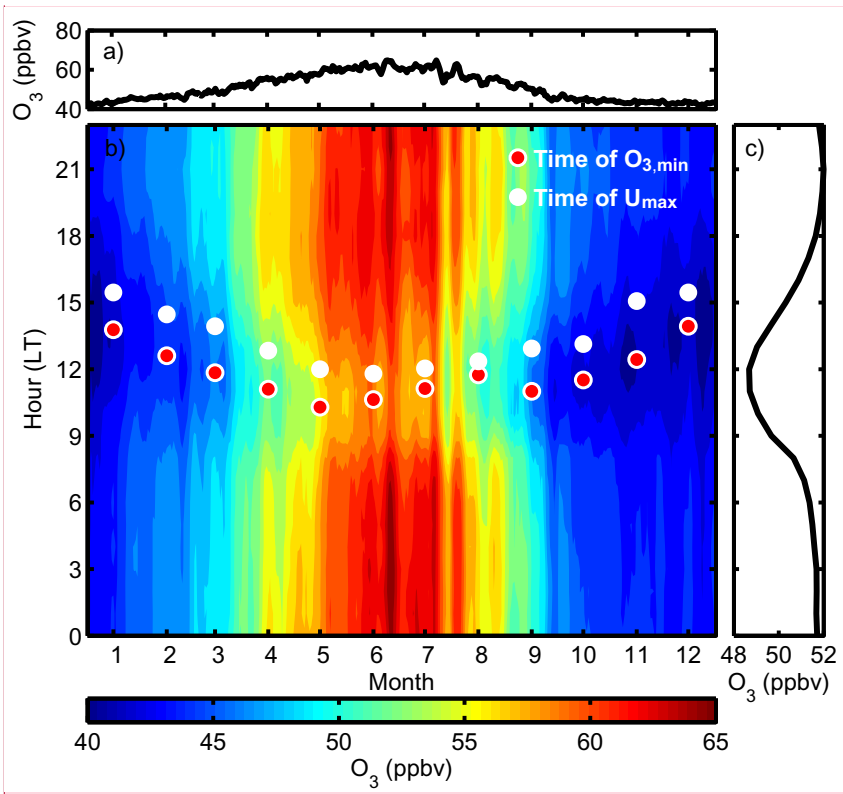
4 The shading stands for the topographic height.

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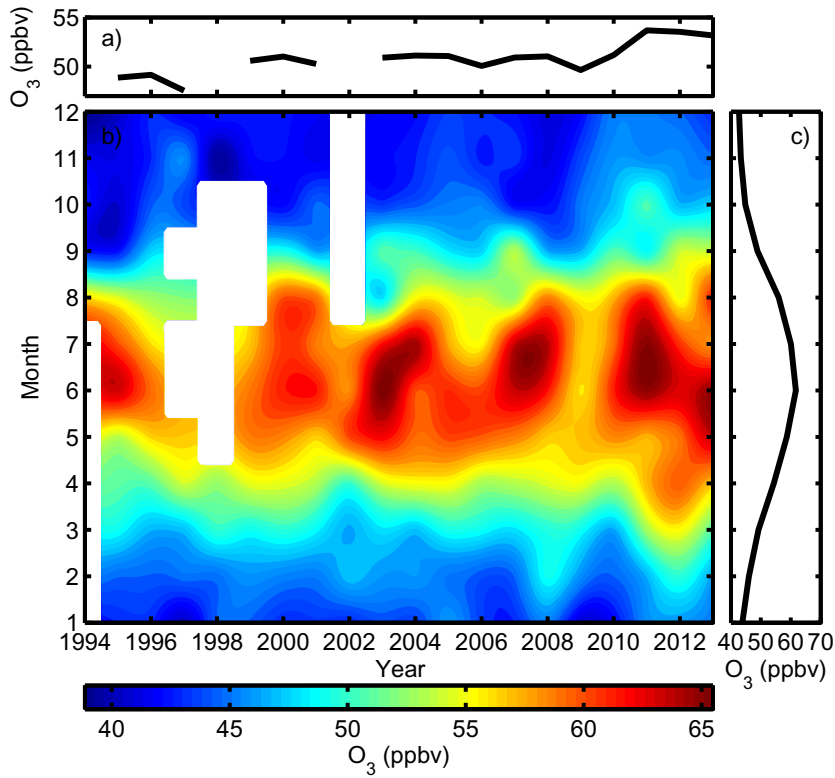
1  
 2 Figure 2 The average season-diurnal variation of surface zonal (a), meridional (b) and vertical  
 3 (c) wind velocity on top of Mt. Waliguan during 1995-2013. The monthly average hour  
 4 associated with the diurnal maximum zonal wind speed is given by the white dots, the daytime  
 5 range is provided by the white dashed lines, which covers 6 hours centered around the white  
 6 dots.  
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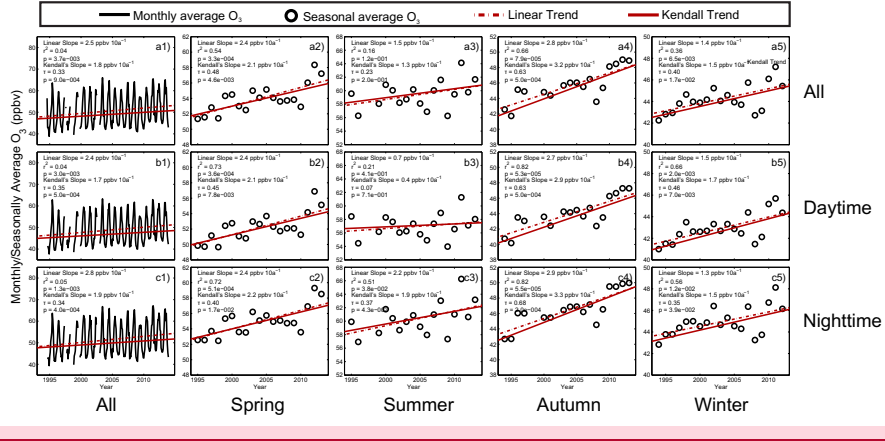
批注 [u1]: Added red dots and removed white slashed lines

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 2 Figure 3 The average seasonal variation (a), season-diurnal variation (b) and diurnal variation  
 3 (c) of ozone during 1995 to 2013. White dots stands for the monthly average local time  
 4 associated with the diurnal minimum ozone, the white dashed line stands for a 6 hours range  
 5 centered around the white dots.  
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 2 Figure 4 The average inter-annual variation (a), season-annual variation (b) and seasonal  
 3 variation (c) of ozone during 1994 to 2013.  
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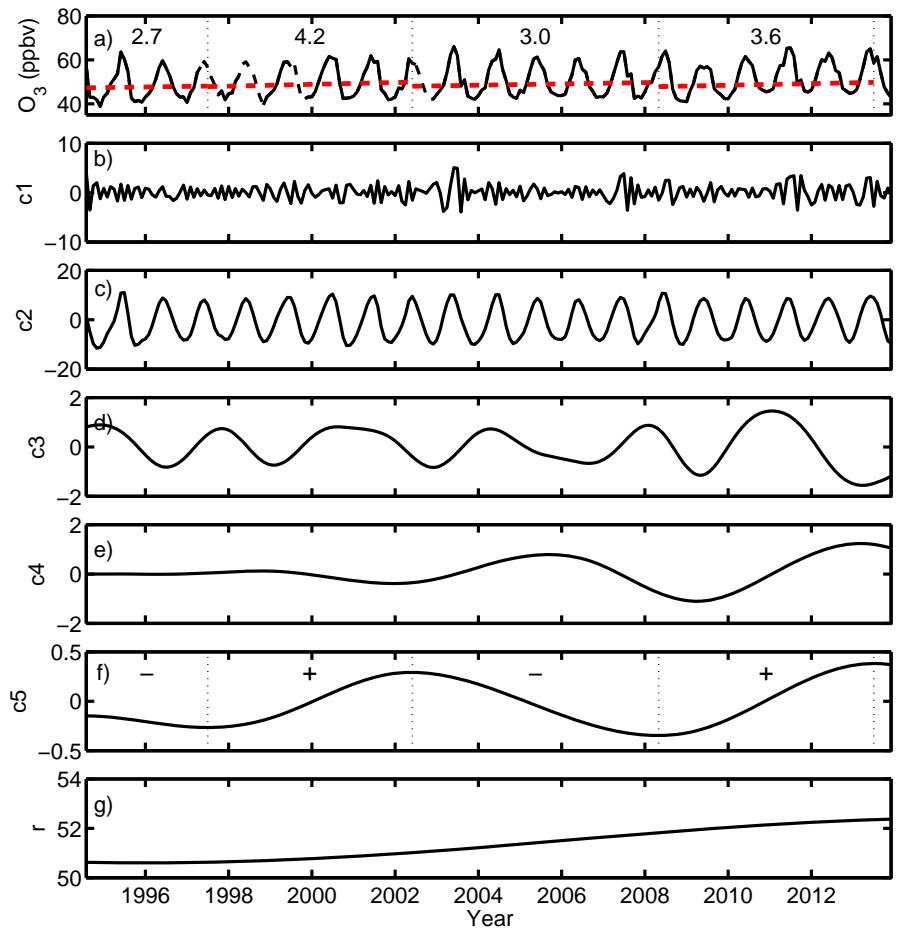


批注 [u2]: Added "All, Daytime, Nighttime" and "All, Spring, Summer, Autumn, Winter" labels

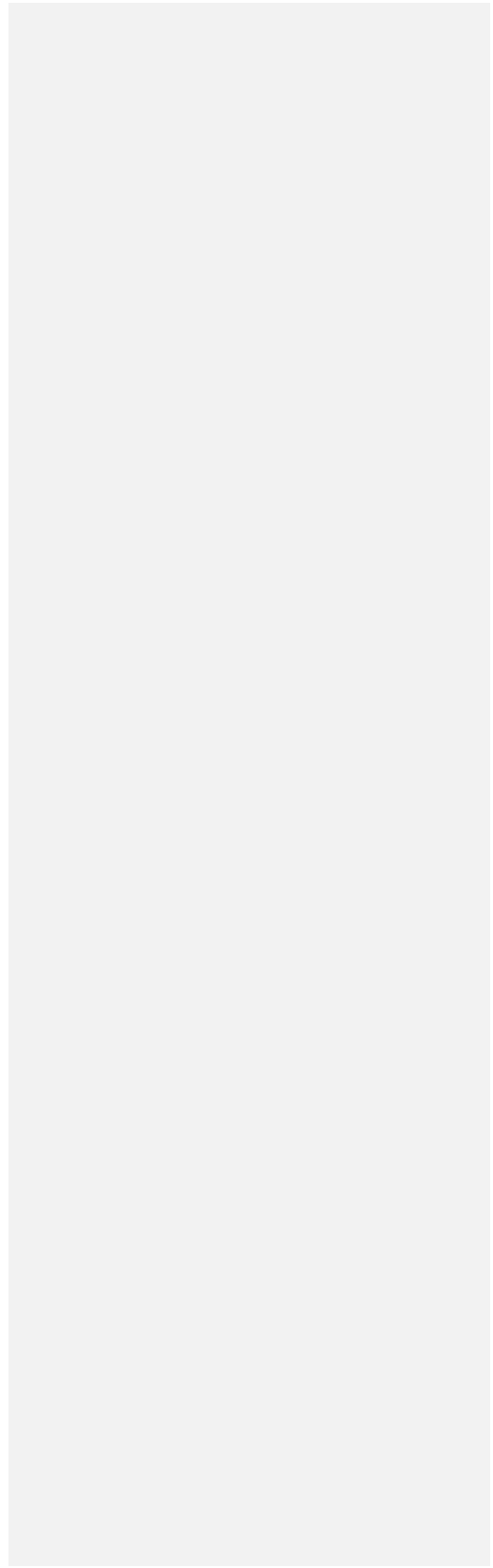
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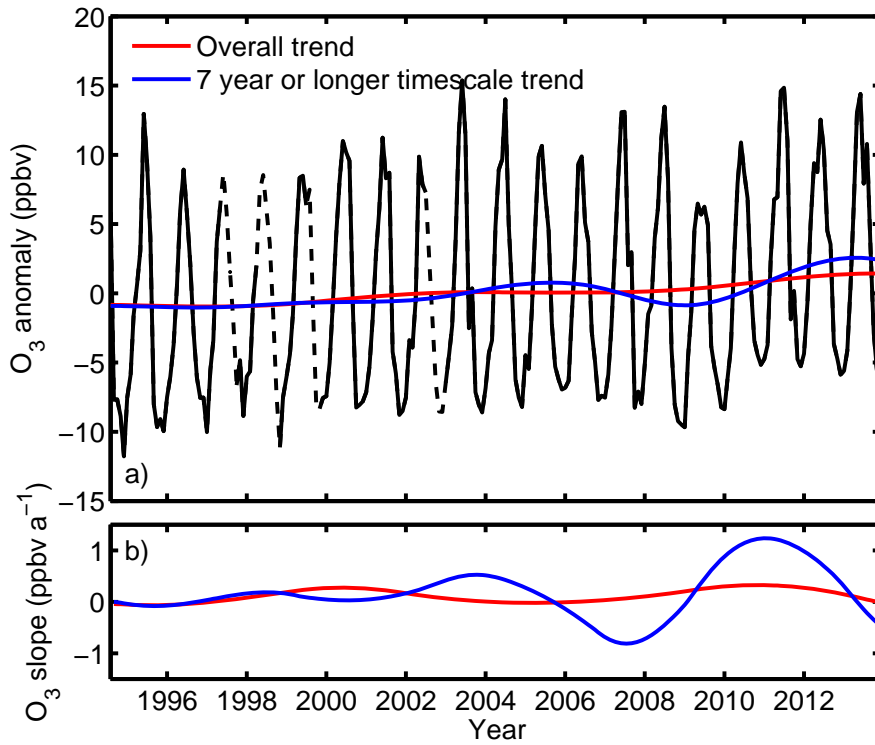
3 Figure 5 1) Monthly, 2) spring (MAM), 3) summer (JJA), 4) autumn (SON) and 5)  
 4 ~~winter~~winter time average all day (a), daytime (b) and nighttime (c) surface ozone  
 5 ~~concentration~~mixing ratio during 1994 to 2013 (black solid line or black circles) and its  
 6 variation trend (red lines: dotted line stands for the linear variation and solid line stands for the  
 7 Kendall's variation slope).

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 2 Figure 6 The interpolated monthly average ozone ~~concentration~~ mixing ratio at WLG from 1994  
 3 to 2013 (the interpolated data given in dashed lines, a) and its intrinsic mode functions c1-c5  
 4 (b-f, from the lowest order IMF to the highest order IMF) and its residue, r (g). The time  
 5 segments in (a) were determined by the slope of the c5. The red slashed lines are the Kendall's  
 6 trends and the numbers are the Kendall's slope (in ppbv  $\cdot 10a^{-1}$ ).  
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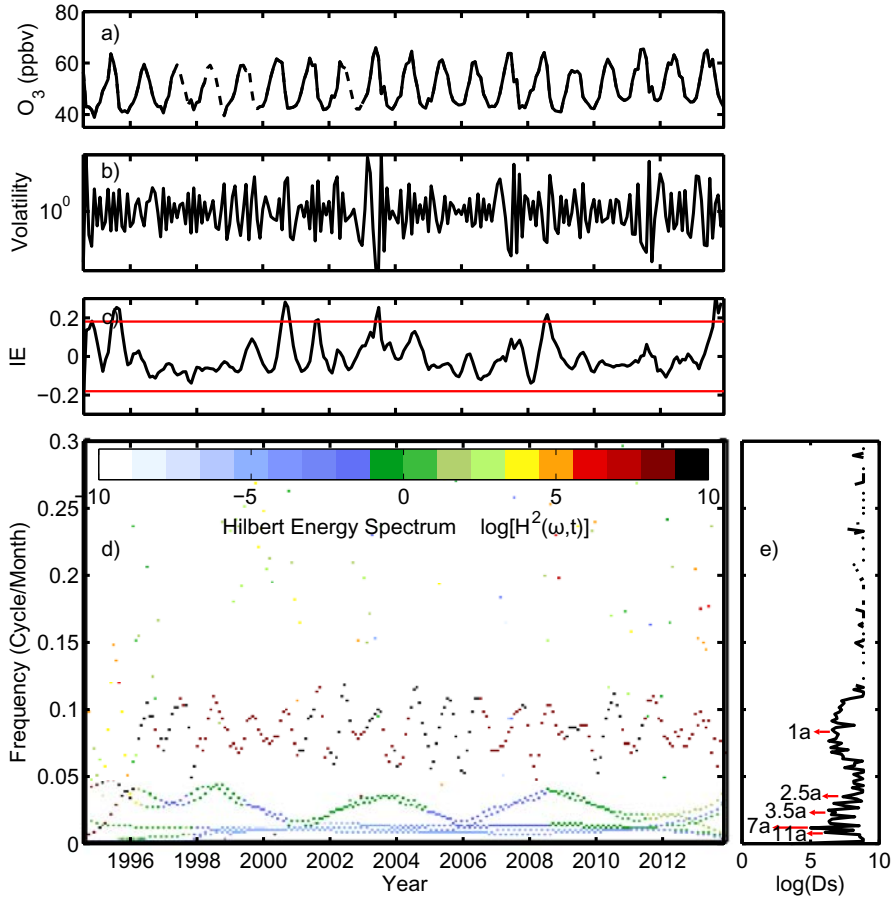




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 2 Figure 7 a) The anomaly of the interpolated monthly average ozone (black line) the sum of last  
 3 IMF and the residual (c5+r, red line) and the sum of the last two IMFs and the residual (c4+c5+r,  
 4 blue line); b) the slope of the sum of last IMF and the residual (c5+r, red line) and the sum of  
 5 the last two IMFs and the residual (c4+c5+r, blue line).

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3 Figure 8 The interpolated monthly average ozone ~~concentration~~mixing ratio signal at Mt. WLG  
 4 during 1994 to 2013 (a), the volatility (b), the normalized mean value of the instantaneous  
 5 energy (red lines:  $\pm 2\sigma$ )(c), Hilbert Energy Spectrum (d) and the degree of stationarity (e).

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