

### **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 1. 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.

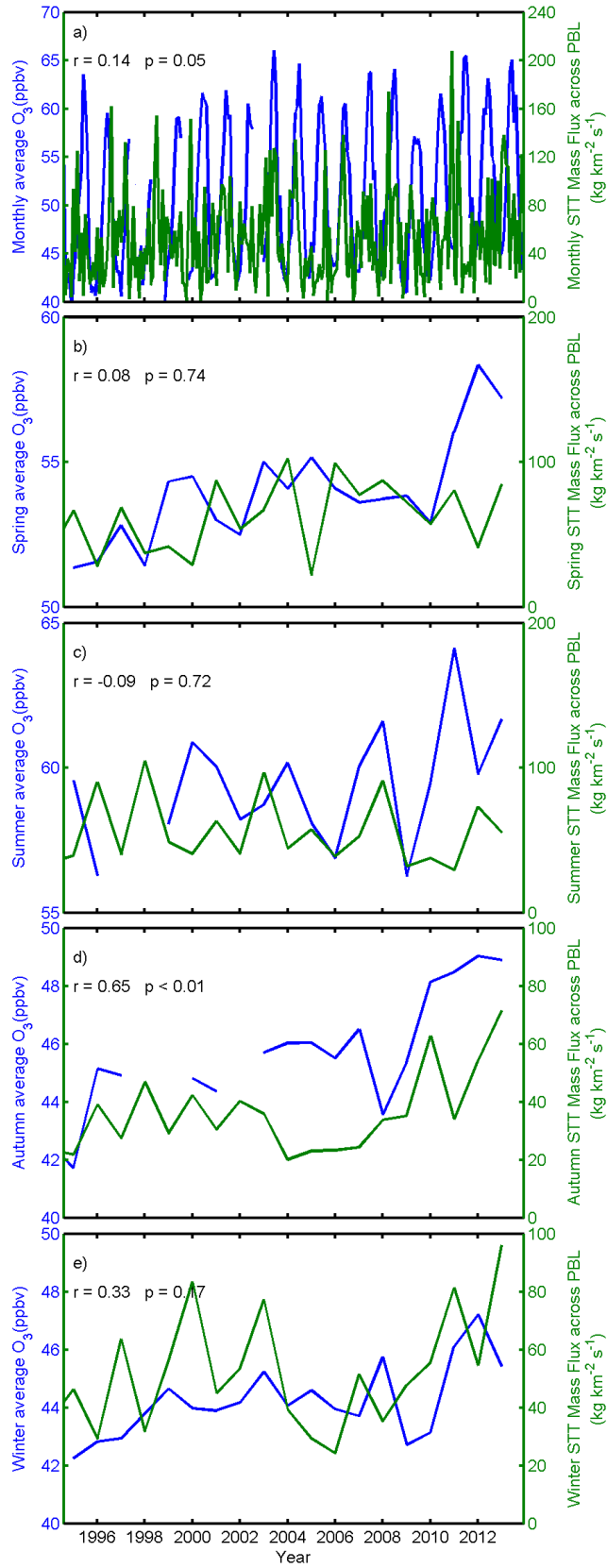


Figure 1 a) Monthly, b) spring, c) autumn and d) winter time average ozone mixing ratio and STT mass flux across PBL during 1994 to 2013

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-1. 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-1 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

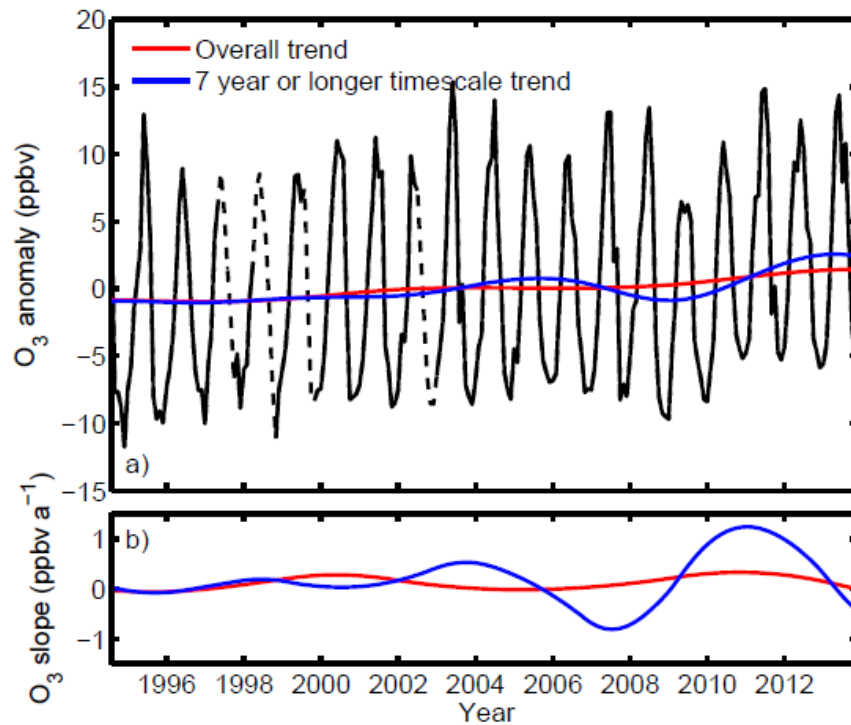
U.S. revealed significant decrease due to the implementation of NO<sub>x</sub> emission control measures, while ozone mixing ratios at the other sites in the northern mid-latitudes have entered a steady stage with either slow or no growth (Tarasova et al., 2009;Oltmans et al., 2013).”

**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.