Review

Surface ozone at Nam Co (4730 m a.s.l.) in the inland Tibetan Plateau: variation, synthesis comparison and regional representativeness

Authors: Xiufeng Yin, Shichang Kang, Benjamin de Foy, Zhiyuan Cong, Jiali Luo, Lang Zhang, Yaoming Ma, Guoshuai Zhang, Dipesh Rupakheti, Qianggong Zhang

Summary of paper

The Tibetan Plateau is considered as an ideal region for studying processes of the background atmosphere. Sites in the southern, northern, and central regions of the Tibetan Plateau exhibit different patterns of variation in surface ozone. Measurements for the period January 2011 to October 2015 of surface ozone concentrations at Nam Co Station are summarized using mostly monthly averaged values. A large annual cycle was observed with maximum ozone mixing ratios occurring in the spring with minimum ratios occurring during the winter. The authors indicate that Nam Co Station represents a background region, where surface ozone receives negligible local anthropogenic emissions. The authors state that surface ozone at Nam Co Station is mainly dominated by natural processes involving photochemical reactions and potential local vertical mixing. Model results indicate that the study site is affected by the surrounding areas in different seasons and that air masses from the northern Tibetan Plateau lead to increased ozone levels in the summer. The authors believe that in contrast to the surface ozone levels measured at the edges of the Tibetan Plateau, those at Nam Co Station appear to be less affected by stratospheric intrusions and human activities, which makes Nam Co Station representative of vast background areas in the central Tibetan Plateau. By comparing measurements at Nam Co Station with those from other sites in the Tibetan Plateau and beyond, the authors' goal is to expand the understanding of ozone cycles and transport processes over the Tibetan Plateau.

General Comments

I would like to see another version of this manuscript after the authors have made their modifications.

A key question I have is to what extent do the authors believe that stratospheric intrusions (not necessarily originating directly above the site) influence the Nam Co station? The reason I am asking this question is that the authors state "In contrast to the surface ozone levels at the edges of the Tibetan Plateau, those at Nam Co Station are less affected by stratospheric intrusions and human activities which makes Nam Co Station representative of vast background areas in the central Tibetan Plateau." I am not sure what the authors are intending to say in this sentence. Does the sentence mean that stratospheric intrusions play an unimportant role at the site in influencing the surface ozone concentrations or do the authors mean that the Nam Co site is influenced by "aged" stratospheric intrusions but to a lesser extent than those intrusions that occur at the southern and northern portions of the Tibetan Plateau? Based on the detailed focus on stratospheric intrusions in the manuscript, I suspect that the authors believe that STE plays an important role at the Nam Co Station in enhancing surface concentrations during specific seasons

but that STE plays ***less*** of a role when compared to stations located at the southern and northern portions of the Tibetan Plateau. I would appreciate it if the authors would clarify this.

The authors devote a considerable amount of the manuscript to discussing the contribution from stratospheric intrusions during specific periods of the year. Using mostly monthly and annual average surface ozone mixing ratios, the authors report a large annual cycle with maximum ozone mixing ratios occurring in the spring, with minimum ratios occurring during the winter. As noted by the authors, during the spring, Nam Co was affected by aged stratospheric originating over the Himalayas rather than being influenced by transport from fresh stratospheric air masses directly above the station. In spring, the air masses that arrived at Nam Co Station were predominantly from the west and from the south, and the 3-D clusters indicated that the air masses traveled through the Himalayas before reaching Nam Co Station. The authors note that Cristofanelli et al. (2010), Putero et al. (2016) and Chen et al. (2011) found that the frequency of stratospheric intrusions in the Himalayas was high in spring, and slightly lower than during the winter. Škerlak et al. (2014) showed that the seasonal average ozone flux from the stratosphere to the troposphere in the Himalayas was the highest in spring. The authors noted that air masses transported in the spring from the Himalayas led to higher concentrations of surface ozone at Nam Co Station.

For the summer months, the authors note that were more backward trajectories coming from the northern Tibetan Plateau than in other seasons. HYSPLIT backward trajectories arriving at Nam Co Station in the summer were classified into 6 clusters. Clusters which came from the northern Tibetan Plateau had higher mean surface ozone levels than clusters which came from the southern Tibetan Plateau. The authors indicate that the air masses that arrived at Nam Co Station from the northern Tibetan Plateau and northwestern China by horizontal wind transport likely resulted in the higher ozone concentrations at Nam Co Station during the summer. However, Trajectories 2 and 3 during the summertime also contain high ozone concentrations (Fig. 11).

During the summer, according to Škerlak et al. (2014), the northern Tibetan Plateau is the hot spot of stratosphere-to-troposphere ozone flux. Do other trajectories (e.g., 2 and 3) during the summertime also exhibit possible contributions from STE? A further reading of Škerlak et al. (2014) indicates that the hotspot region of the Tibetan Plateau is most likely affected by stratospheric intrusions during the months of DJF, MAM, and JJA (page 926 of Škerlak et al., 2014). Škerlak et al. (2014) indicate that there are **intense** deep STT ozone fluxes over the Tibetan Plateau during MAM and JJA. Škerlak et al. (2014) indicate that the global hotspots, where surface ozone concentrations are most likely influenced by STE, is the Tibetan Plateau in all seasons except for SON (page 934).

As indicated above, the authors mostly used monthly and annual average surface ozone mixing ratios to characterize the ozone concentrations at the Nam Co Station. The use of monthly or annual average concentrations "smoothes" the variability associated with hourly average concentrations. Thus, if one were interested in assessing the magnitude of the ozone concentration enhancements that may be associated with STT events, he or she might wish to focus on the frequency and time of year when high hourly average concentrations occur. Although I am not suggesting that the authors have to perform an additional assessment, I think the authors, using ***hourly*** average concentrations, have an opportunity to include in their current

manuscript an expanded discussion on the potential importance of aged stratospheric air originating at other locations that is transported to the site. Fig. S1 provides potentially important information about the day-to-day variability of the hourly concentrations. I have reproduced Fig. S1 below. The figure illustrates the variability of the hourly average concentrations for the period from January 2011 until October 2015. As anticipated, the frequency of the highest hourly average concentrations (e.g., 70 ppb to > 90 ppb) occurs during the springtime and early summertime (Fig. S1). This agrees with the authors' observations based on the monthly average concentrations. However, unlike the pattern described based on the monthly averages, high hourly average concentrations are also occurring during the winter and summertime for some of the years. During the months of SON, the frequency of high hourly average concentrations is much lower than those values exhibited during the DJF, MAM, and JJA seasons. Thus, there appears to be different patterns observed when using the monthly average concentration results with those using the hourly average concentration results.

Investigating the pattern for when the highest hourly average concentrations occur, it appears that this pattern is similar to the one described by Škerlak et al. (2014), which indicated stratospheric intrusion hotspots in the Tibetan Plateau during the months of DJF, MAM, and JJA. If the authors wish to, they have the opportunity to expand their discussion in their manuscript to comment on the degree to which the observed enhanced hourly average ozone concentrations may be associated at the Nam Co Station with STE.

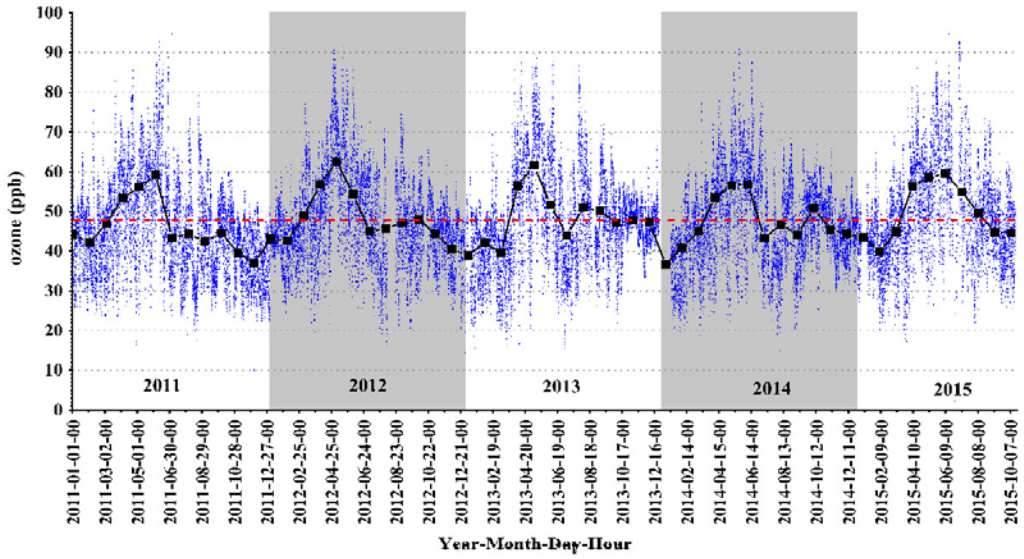

Fig. S1. Variation of surface ozone at Nam Co Station from January 2011 to October 2015. Hourly mean mixing ratios of surface ozone are in blue dots; monthly mean mixing ratios of surface ozone are in black dots; average mixing ratio of surface ozone during whole measurement period in red dash line.

Specific Line-by-Line Comments

1. Title: I would suggest that the title be slightly modified as follows: Surface ozone at Nam Co in the inland Tibetan Plateau: variation, synthesis comparison and regional representativeness.

2. Lines 24-25: The authors state "Model results indicate that the study site is affected by the surrounding areas in different seasons and that air masses from the northern Tibetan Plateau lead to increased ozone levels in the summer." I think the authors are not necessarily indicating that there is an increase during the summer at Nam Co due to air masses from the northern Tibetan Plateau but that the air masses from the northern Tibetan Plateau ***contribute*** to the enhancement of ozone levels measured at the site. The word "increase" gives the impression that relative to the spring, the summer monthly averages are higher. The monthly average levels at the site are lower than those observed during the spring and therefore, I am suggesting a slight change in the wording.
3. Lines 34-35: I would suggest references that represent comprehensive summaries of human health and vegetation effects, such as LRTAP Convention (2015), REVIHAAP (2013), and US EPA (2013).
4. Line 45-46: The sentence: "In this situation, background sites can represent areas with surface ozone concentrations that are under the control of largely uniform synoptic systems and are minimally affected by local anthropogenic sources." What does "in this situation" refer to?
5. Lines 141-143: The sentence "In cells with high PSCF values are associated with the arrival of air parcels at the receptor site that have pollutant mixing ratios that exceed the criterion value" does not appear to be complete. Should the sentence start with "Cells with high PSCF…"?
6. Line 155: The sentence states "The mean surface ozone mixing ratio at Nam Co Station during the entire observational period was 47.6 ± 11.6 ppb…." I am not suggesting any change in this sentence but I do want to point out that the authors on Lines 33 and 34 state that "High levels of surface ozone are currently a major environmental concern because of the harm ozone poses to health and vegetation." This is a correct statement. However, researchers who assess human health and vegetation effects focus on the occurrence of high, as well as mid-level hourly average concentrations, and normally do not focus on high annual average concentrations. Annual, seasonal, or monthly average ozone concentrations are not necessarily the best metrics to use when assessing either human health or vegetation effects. While monthly and annual average concentrations are used for assessing the performance of global modeling results, these metrics are not necessarily relevant for assessing human health and vegetation effects.
7. Page 156: Table 1 indicates that the data capture was as follows: 2011 (75.25%), 2012 (90.30%), 2013 (75.90%), 2014 (70.05%), and 2015 (66.21%). Was the 66.21% data capture observed in 2015 related to the entire 12 months or was this value the data capture for the period January – October 2015?
8. Lines 182-183: The authors state "The transition between high levels during the daytime and low levels during the nighttime was fast." I would appreciate it if the authors could please explain why the transition was fast.
9. Lines 186-187: The authors state "Relatively large diurnal amplitudes were observed in spring, with much smaller diurnal amplitudes observed during summer, autumn and winter." Can the authors offer an explanation for this observation? Could this observation be associated with STE making it to the ground during the spring more frequently than during the other seasons?
10. Lines 194-196: The authors state "^{35}S results (Lin et al., 2016) also support this result by showing that in the spring; Nam Co was affected by aged stratospheric air originating

over the Himalayas rather than being affected by transport from fresh stratospheric air masses directly above Nam Co Station." Should the ";" be placed with a "," to make a complete sentence?

11. Lines 188-200: The authors state "A multiple linear regression model was used to quantify the contributions of various factors (including temperature, clear sky solar radiation, potential vorticity, wind speed, humidity, annual cycle, interannual variation and WRF-FLEXPART trajectory clusters) to the measured maximum daily 8-hour average surface ozone." If in the authors' multiple linear regression model the variables (i.e., temperature, clear sky solar radiation, potential vorticity, wind speed, humidity, annual cycle, interannual variation and WRF-FLEXPART trajectory clusters) were not independent, what would be the effect on the outcome of the results using the model?
12. Lines 209-211: The authors state" Specific humidity was the second largest contributor (20%; Table 2) with a negative coefficient indicating that higher surface ozone was associated with drier conditions possibly due to transport of continental air masses; or impacts from air masses aloft." If the Nam Co Station were influenced by "aged" stratospheric intrusions, would the lower humidity still be associated with the "aged" transported air from the stratosphere originating over the Himalayas after several days? Perhaps a short comment in the manuscript might be in order.
13. Lines 212-214: The authors state "The negative coefficient indicates that air masses transported from the south to Nam Co were associated with lower surface ozone. For the whole measurements period, it seems that transport of surface ozone is not the main influencing factor to the daily surface ozone variations in the multiple linear regression model." However, in Lines 287-290, the authors indicate that "Backward trajectories and PSCF were utilized to identify the source of surface ozone at Nam Co Station and to assess the regional representativity of surface ozone at Nam Co. In spring, the air masses that arrived at Nam Co Station were predominantly from the west and from the south, and the 3-D clusters indicated that the air masses traveled through the Himalayas before reaching Nam Co Station (Fig. 10)." If the air masses traveled through the Himalayas during the spring before reaching the Nam Co Station, at times would not the air masses represent "aged" stratospheric intrusions and wouldn't these air masses influence the daily surface ozone variation? Is there a difference in the conclusions reached using the multiple linear regression model versus the back trajectory and the PSCF analyses? Perhaps I am missing something here.
14. Lines 256-258: The authors state "This type has a plateau of high surface ozone in spring and summer and a minimum in winter. Sites of this type occur in regions with strong ozone precursor emissions in the summer (such as the central European continent) or in regions where stratospheric intrusion occurs frequently in summer." Could the authors please provide examples for specific regions of the world where stratospheric intrusions frequently occur during the summer. Perhaps the results from Škerlak et al. (2014) might be a good source.
15. Lines 271-273: The authors state "Sites in the central Tibetan Plateau including Nam Co Station showed maximum ozone during late spring-early summer and relatively low levels in the remainder of year (Fig. 9B), corresponding to the Spring-maximum type. Compared with the surface ozone levels at Nam Co Station, those at Lhasa and Dangxiong were much lower." This conclusion is based upon the use of monthly average

concentrations. Is there any indication that the use of the frequency of high hourly average concentrations might provide a different pattern?

16. Lines 313-314: The authors state "The atmospheric environment of the Tibetan Plateau and its relationship to regional and global change are of universal concern due to the rapid responses and feedbacks specific to the “Third Pole”. I would appreciate it if the authors would please expand on this sentence to explain what they mean.
17. Line 324-327: The authors state "Waliguan, in the northern Tibetan Plateau, is occasionally influenced by regional polluted air masses (Zhu et al., 2004; Xue et al., 2011; Zhang et al., 2011). Its mountainous landform facilitates mountain-valley breezes and may sometimes pump up local anthropogenic emissions especially during the winter (Xue et al., 2011)." I was under the impression that local anthropogenic sources are small near Mt. Waliguan. Mt. Waliguan is far from major cities, such as Xining (90 km) and Lanzhou (260 km) in the eastern sector. I would appreciate it if the authors would further elaborate concerning the enhancement at Mt. Waliguan from local anthropogenic emissions.
18. Lines 332-335: The authors state "During the summer, surface ozone concentrations at Nam Co Station are higher than the northern hemisphere average, which suggests that there are impacts of long-range transport. Nam Co is less influenced by stratospheric intrusions than NCOP on the slopes of Mount Everest, and it is minimally influenced by local anthropogenic emission as evidenced by the constant long-term variation of surface ozone and consistent diurnal variation regardless of season, as discussed above." What is the influence of stratospheric intrusions on Nam Co during the summer? Škerlak et al. (2014) appear to indicate that it is important during the summer. If the surface ozone concentrations during the summer at Nam Co Station are higher than the northern hemisphere average, could the suggested long-range transport be associated with "aged" air masses from the stratosphere that are being transported to the site? I think it would help the reader to clarify what the authors mean by " there are impacts of long-range transport."
19. Line 340: The summary needs to be expanded. It is very minimal at this time.
20. Lines 348-349: The authors state " Synthesis comparison indicated that Nam Co is less influenced by stratospheric intrusions and anthropogenic disturbances than sites along the rim of the Tibetan Plateau." I would appreciate it if the authors could please clarify this sentence. Should the sentence read "While the Nam Co Station is less influenced by stratospheric intrusions and anthropogenic disturbances than sites along the rim of the Tibetan Plateau, the site does exhibit during specific months large contributions associated with transported "aged" air masses associated with stratospheric intrusions." I do not wish to impose this interpretation on the authors, but rather elicit from them if this is what they are attempting to say. If not, could they please provide a concise sentence that clearly describes their conclusion on the importance of stratospheric intrusions associated with long-range transport in enhancing the surface ozone concentrations at Nam Co. I think this would help the reader.
21. Supplement: Fig. S1. I would suggest improving the readability of the title of the x-axis (Year-Month-Day-Hour). It seems to not be clear on my copy. Does the first symbol in the time series identified as 2011-01-01 in Fig. S1 represent the January average or just the 2011-01-01 point? I am not sure what the first dot represents. The meaning of the first dot is confusing.

References

LRTAP Convention, 2015. Chapter III: Mapping Critical levels for Vegetation, of the Manual on Methodologies and Criteria for Modelling and Mapping Critical Loads and Levels and Air Pollution Effects, Risks and Trends. Available at: http://icpvegetation.ceh.ac.uk/publications/documents/Ch3-MapMan-2016-05-03_vf.pdf.

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