

## **Responses to referee #1:**

The manuscript 'Surface gas pollutants in Lhasa, a highland city of Tibet: current levels and pollution implications' by L. Ran et al. presents measurements of CO, NO/NO<sub>2</sub>/NO<sub>x</sub>, SO<sub>2</sub> and O<sub>3</sub> made within the city of Lhasa. Data is interpreted in terms of meteorological influence, and comparison with available data from 1998 is shown. Especially the recent data seems to be of good quality, although information on measurement uncertainties is lacking. Since the data has been acquired at a location with very little available data sets, it is a valuable contribution which deserves to be published in ACP after addressing a few mainly minor issues. The manuscript is well structured and of appropriate length. However, the analysis made is very descriptive, and a few interesting aspects could be discussed in more depth.

**We highly appreciate the referee's instructive suggestions. We have addressed each comment as below and corresponding revisions have been made in the manuscript.**

Specific comments:

1. P11789 L12: '...the content of oxygen in Lhasa is about 68% of that at the sea level': In absolute terms this is true, but the relative O<sub>2</sub> content is still the same. Altitude dependent emissions of vehicles is an interesting aspect, but I doubt if this effect is really contributing much compared to the general increase in vehicle numbers.

**According to the referee's suggestion, we added the term of 'absolute' in the revised manuscript. We made a great effort trying to obtain data regarding altitude dependent emissions of vehicles, but those above 3000 m could not be found. Distinct black smoke of vehicular exhausts can often be seen in Lhasa. However, we can exactly not tell how much incomplete combustion and an increase in vehicle numbers contribute to the increased emissions of vehicles, respectively. Thus, we revised corresponding sentence as:**

**At a high altitude above 3650 m, the absolute content of oxygen in Lhasa is about 68% of that at the sea level. Incomplete fuel combustion in the low oxygen-containing atmosphere (Chaffin and Ullman, 1994; Bishop et al., 2001; Nagpure et al., 2011), as well as the rapidly increasing vehicles undoubtedly enhances atmospheric pollutants of vehicular origin.**

2. P11789 L12: 'The atmosphere in Lhasa was found to be photochemically active (Lin et al., 2008)': I am not sure if this sentence is needed or makes sense. If you decide to keep it, a few more words of the results of Lin et al. are needed. The atmosphere is probably everywhere photochemically active, but due to the altitude, photochemistry might even play a more important role.

**Thank you. Lin et al. (2008) calculated the OH production potential over the Tibetan plateau and found the air there is photochemically active due to the strong solar**

**radiation and relatively high ozone background. We have revised this sentence as:**

**With a high production potential of OH radicals over the Tibetan Plateau, where the solar radiation is strong due to the high altitude as well as the low latitude and the background concentration of ozone is high, the atmosphere in Lhasa was found to be very photochemically active (Lin et al., 2008).**

3. P11790 L4: ‘...air quality in Lhasa was quite fine’: A more quantitative statement or a brief comparison with data from other cities would be helpful.

**Thank you for this helpful suggestion. A more quantitative comparison has been given in the revised manuscript as:**

**In comparison with many other cities in China (He et al., 2002 and the references therein), air quality in Lhasa was quite fine. The level of air pollutants in Lhasa has never exceeded the national air quality standards according to the reports of the local environment protection bureau.**

4. P11790 L12: Delete ‘Finally is the summary.’

**We have deleted this sentence.**

5. P11791 L6: Are the measurements ongoing, or is the presented data part of a campaign?

**The observational data presented here was obtained from a one-year campaign. In view of the importance of the data, we have been trying to continue the measurements.**

6. P11791 L20: Does the TE 49CPS have traceability to an ozone reference instrument?

**Yes, the TE 49CPS is traceable to the NIST standard, the Standard Reference Photometer (SRP) in WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane, Empa Dübendorf, Switzerland.**

7. P11791 L23 and throughout the whole manuscript: Concentration in this context is the wrong terminology. It should be ‘mole fraction’ instead of concentration (see e.g. <http://gaw.empa.ch/glossary/glossary.html>). Please carefully revise terminology throughout the whole paper. The unit should also be nmol/mol (ppb might be acceptable) but not ppbv. All ppbv need to be replaced by ppb.

**We thank the referee for this very helpful comment. We have revised this sentence as “Ambient mixing ratios of trace gases were recorded as 1-minute averages (ppb).” We have also corrected the unit from ppbv to ppb.**

8. P11793 L19: ‘are displayed’ instead of ‘were displayed’. This should be changed

throughout the manuscript.

**Thank you. We have revised the manuscript accordingly.**

9. P11797 L11: Unit (USD?) is missing.

**Thanks. The missing unit is RMB. We have added it to the manuscript.**

10. P11797/8 and Figure 6: It is quite astonishing that CO remained almost constant between 1998 and 2012, whereas NO<sub>2</sub> became a factor of almost 40 higher. Both species are indicators for relatively fresh emissions, and high CO levels in combination with very low NO<sub>2</sub> as observed in 1998 seem to be unlikely. How can you exclude measurement artifacts? What were/are the measurement uncertainties? It would be helpful to provide measurement uncertainties together with the data. The analytical techniques were different in 1998 and 2012, and I would expect a very large measurement uncertainty for the NO<sub>2</sub> data in 1998. The fact that CO and NO<sub>2</sub> do not show any significant correlation in 1998 potentially indicates that data quality of the 1998 NO<sub>2</sub> measurements was not sufficient. Or do you have other explanations? Please address this in more detail.

**The GFC/NDIR technique was used in the measurement of CO in both 1998 and 2012. The quality control procedures in 1998 were similar to that in 2012. Due to the very low concentrations of NO<sub>2</sub> and SO<sub>2</sub> in Lhasa, no commercial on-line analyzers could meet the requirements of such measurements in 1998. The absorbent technique with a relatively long sampling time was thereby used at that time. The recorded data were finally corrected by reference standards in the laboratory. The measurement uncertainties are believed not to be the explanations for a high CO level together with a very low NO<sub>2</sub> level in 1998. The more possible reason might be the difference in the emission sources at the two sites in different years. Biomass burning was dominant in 1998, while fossil fuel burning is dominant now.**

11. P11801 L12: CO has not significantly increased (again: why?). Should it be O<sub>3</sub> instead?

**Thank you very much. It's O<sub>3</sub> instead of CO. We have corrected this sentence.**

## **Responses to referee #2:**

This paper presents data analysis for the air quality in Lhasa, Tibet. The manuscript is well organized and the data set is highly valuable to our understandings of the atmospheric chemistry in that region. However, there are some issues need to be discussed in further details. Thus I'd like to recommend a major revision to this article. The followings are some specific comments that should be considered carefully in the revision.

**We highly appreciate the referee's instructive suggestions. We have addressed each concern as below and corresponding revisions have been made in the manuscript.**

Specific comments:

1. The ambient levels of trace gases measured in this study (2012) are compared with those measured in 1998. This comparison is very interesting and provides direct evidences for the environmental changes occurred during the 15 years. However, as different methods were used in the two investigations, results from the comparative study seem ambiguous. I suggest address the differences in instrumentation clearly in the revision, particularly in terms of measurement uncertainty.

**According to the referee's suggestion, we made more description of the measurements in section 2.2 to address the differences in instruments. The most different measurement methods were for NO<sub>2</sub> and SO<sub>2</sub>. As for O<sub>3</sub> and CO, the same measurement principles and similar quality control procedures were used in both 1998 and 2012. Linear uncertainty of O<sub>3</sub> and CO analyzers were about 2%. Due to the extremely low mixing ratios of NO<sub>2</sub> and SO<sub>2</sub> in 1998, the absorbent technique with a relatively long sampling time was used (the lowest detect limits are 0.03 ppb and 0.02 ppb, respectively for SO<sub>2</sub> and NO<sub>2</sub>). The recorded data were finally corrected by reference standards in the laboratory. The measurement uncertainties should not be responsible for the differences in observed mixing ratios of the trace gases.**

2. The scientific argument for comparing the air quality measurements made in Lhasa with those from Beijing and NCP is very weak. The two cities (areas) are so different in many ways. I'd like to suggest a comparison with another high altitude urban area, such as Mexico City, in the world. Many papers in the ACP special issue for the Mexico Study can serve as your reference.

**The NCP region, as one of the most polluted areas in the world, has raised widespread concerns in the recent years. We compared the air quality in Lhasa with that in the polluted NCP, just in order to indicate that the air pollution is already quite noticeable in Lhasa. Lhasa is not comparable with the Mexico City in the population, geographic area, energy consumption, etc., except in the altitude to some degree (Lhasa: 3650m; the Mexico City: 2240m). This is why we did not make a comparison between air quality in Lhasa and the Mexico City in the old version. According to the referee's suggestion, we**

have made an additional comparison for each trace gas in section 3.2:

**The highest hourly O<sub>3</sub> mixing ratio of 90.6 ppb in Lhasa was also observed in May, while in another more industrialized high altitude urban area, the Mexico City, hourly ozone mixing ratios could easily exceeded 120 ppbv (Molina and Molina, 2004; Lei et al., 2008).**

**The air in Lhasa was mostly polluted from November to January with respect to the levels of SO<sub>2</sub> ( $2.72 \pm 2.05$  ppb) and O<sub>3</sub> precursors NO<sub>x</sub> ( $29.58 \pm 16.16$  ppb) and CO ( $570 \pm 300$  ppb), possibly as a result of slowed removal processes, increased emissions and accumulation within the boundary layer. The mixing ratios of SO<sub>2</sub> and O<sub>3</sub> precursors during the most polluted season in Lhasa were at least less than half of those in urban Mexico City based on yearly averages (Molina and Molina, 2004; Stephens et al., 2008), since Lhasa is less populated and industrialized than the Mexico City.**

**Lei, W., Zavala, M., de Foy, B., Volkamer, R., and Molina, L. T.: Characterizing ozone production and response under different meteorological conditions in Mexico City, Atmos. Chem. Phys., 8, 7571-7581, 2008.**

**Molina, M. J., and Molina, L. T.: Megacities and Atmospheric Pollution, 1. Air & Waste Manage. Assoc., 54, 644-680, 2004.**

**Stephens, S., Madronich, S., Wu, F., Olson, J. B., Ramos, R., Retama, A., and Munoz, R.: Weekly patterns of Mexico City's surface concentrations of CO, NO<sub>x</sub>, PM<sub>10</sub> and O<sub>3</sub> during 1986-2007, Atmos. Chem. Phys., 8, 5313-5325, 2008.**

3. The seasonal differences in nighttime ozone levels were attributed to emission of NO in cold seasons [Sec 3.2]. I disagree with this argument. As shown in Figure 5, it is obvious that, in line with O<sub>3</sub>, high Ox levels were also observed in spring and summer. Thus, the NO-O<sub>3</sub> titration was unlikely responsible for the observed phenomena.

**The nighttime O<sub>3</sub> in winter is relatively lower than that in other seasons, but the mixing ratio of NO is higher than that in other seasons. We believe that the NO-O<sub>3</sub> titration contributed more to the low O<sub>3</sub> level in winter night, not only because of the higher NO level but also because of the more stable surface layer under relatively lower wind speed in winter (see Figure 3).**

4. It was indicated that the mixing ratio of ozone peaked in spring (Sec 3.2), and local photochemical production of ozone was suggested as the main cause responsible for the seasonal features (Sec 3.3). The two arguments are not exactly consistent with each other because the photochemical production of ozone should be higher in summer than in spring. The formation of spring ozone maxima could be much more complicated than the simple attribution discussed in this paper, and merits an in-depth analysis in the revision.

The spring maximum of O<sub>3</sub> in Lhasa is consistent with the observations at background sites elsewhere in the Northern Hemisphere (Monks et al., 2000) and also with a nearby high altitude site in the southeast of Tibetan plateau (Ma et al., 2014). This suggests that the large-scale background of O<sub>3</sub> in spring also plays a role in the observed surface O<sub>3</sub> in Lhasa. Under the influence of the Asian summer monsoon, more precipitation occurs (Figure 2) and inhibits the formation and accumulation of O<sub>3</sub>, since precipitation can remove O<sub>3</sub> and its precursors from the troposphere and reduce UV radiation. Therefore, the average O<sub>3</sub> mixing ratio is lower in summer than in spring although the photochemical production of O<sub>3</sub> should be higher. This seasonal pattern is similar to that reported by Ma et al. (2014). According to the diurnal pattern of O<sub>3</sub> behavior, distinct local ozone photochemical production is also expected. We thank the referee for this suggestion and have added in section 3.3:

Although ozone photochemical production should be higher in summer than in spring, the average O<sub>3</sub> mixing ratio was lower in summer than in spring as mentioned in section 3.2. This suggests that the large-scale background of O<sub>3</sub> in spring (Monks, 2000) also plays a role in the observed surface O<sub>3</sub> in Lhasa. Under the influence of the Asian summer monsoon, more precipitation occurs and inhibits the formation and accumulation of O<sub>3</sub>, since precipitation could efficiently remove O<sub>3</sub> and its precursors from the troposphere (Ma et al., 2014).

Monks, P. S.: A review of the observations and origins of the spring ozone maximum, *Atmos. Environ.*, **34**, 3545-3561, 2000.

Ma, J., Lin, W. L., Zheng, X. D., Xu, X. B., Li, Z., and Yang, L. L.: Influence of air mass downward transport on the variability of surface ozone at Xianggelila Regional Atmosphere Background Station, southwest China, *Atmos. Chem. Phys.*, **14**, 5311-5325, doi:10.5194/acp-14-5311-2014, 2014.

5. I think that readers will not appreciate the content of Table 1 where you compared your measurement with a “self-defined” air quality standard. Are you trying to propose a new national air quality standard? Any Epi or toxicological data available to support this “new standard”? What implications are given from a case against this new standard? Please note that the national air quality standard is not merely a set of “numbers”.

**We appreciate the referee’s helpful comments. We have revised Table 1 according to the referee’s instructive suggestion in comment 6.**

6. As a scientific paper, you can setup your criteria for data screen and define some pollution events in your study. Then, I strongly suggest make a table of descriptive statistics straightforward to the “measurements”, i.e. the mixing ratios of respective trace gases, for selected cases or periods.

**We set up our own ‘criteria’ to show the relative polluted conditions, since the air**

quality in Lhasa is generally fine and the level of pollutants has never exceeded the national air quality standards according to the reports of the local environment protection bureau.

According to the referee's suggestion, we revised Table 1 to give descriptive statistics and revised the interpretation in the text accordingly.

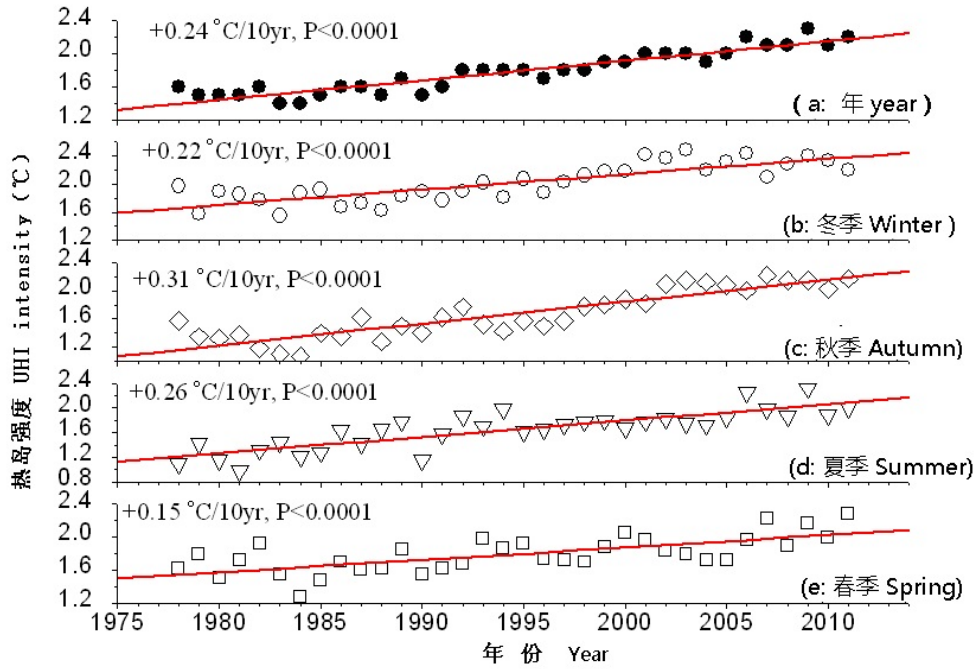
A pollution event is defined here as the hourly average mixing ratio exceeding 80 ppb for O<sub>3</sub>, 50 ppb for NO<sub>x</sub>, 1000 ppb for CO and 10 ppb for SO<sub>2</sub>. The average mixing ratios of the traces gases under thus defined polluted conditions and non-polluted conditions are accordingly given in Table 1. The exceedance frequency (%) based on hourly averages is given in the brackets.

**Table 1. Hourly average mixing ratios of the traces gases under polluted conditions (defined in this paper) and non-polluted conditions. The exceedance frequency (%) based on hourly averages is given in the brackets.**

	O <sub>3</sub> (ppb)		NO <sub>x</sub> (ppb)		CO (ppb)		SO <sub>2</sub> (ppb)	
	Polluted	Non-P	Polluted	Non-P	Polluted	Non-P	Polluted	Non-P
Spring	83.8(1.6)	48.3	67.42(2.0)	12.43	1187(0.8)	322	-	0.61
Summer	85.5(0.1)	37.8	62.72(1.7)	14.43	1273(1.3)	407	-	0.46
Autumn	-	31.6	99.38(10.9)	14.85	1567(6.5)	332	15.34(1.9)	1.19
Winter	-	27.6	101.21(10.8)	13.76	1968(10.4)	345	18.31(3.9)	1.53

7. How did you define “urban heat island intensity” (Sec 3.4)? Some data analysis or references are needed to support your simple statement.

We used the routine meteorological observational data in urban and rural areas of Lhasa to calculate the temperature difference and the urban heat island intensity. A figure from an in-publishing manuscript [Tsering et al., 2014: Analysis of urban heat island effect in Lhasa city, accepted by Plateau and Mountain Meteorology Research] is shown below, displaying the urban heat island intensity in Lhasa in different years. We directly gave the conclusion in the manuscript.



8. Again, information of measurement precision is needed to facilitate the comparison between two datasets (shown in Figure 6). This is particularly important to the discussion on the differences in the changes of CO and NO<sub>2</sub>.

We have added the related information in section 2.2 according to the first comment. It is believed that the measurement uncertainties are not the explanations for the differences in the changes of CO and NO<sub>2</sub> mixing ratios. The more possible reason might be the difference in the emission sources at the two sites in different years. Biomass burning was dominant in 1998, while fossil fuel burning is dominant now. We have revised the manuscript accordingly.