

Response to the interactive comment on “Gaseous pollutants in Beijing urban area during the heating period 2007–2008: variability, sources, meteorological and chemical impacts” by W. Lin et al.

W. Lin et al.

We thank both referees for reviewing our paper and providing very constructive comments and suggestions. We have revised our manuscript according to their comments and suggestions.

Response to comments by referee #1

Anonymous Referee #1

Received and published: 25 April 2011

This article presents the measurements of gaseous pollutants in Beijing during the winter of 2007. The variations in the ambient levels of air pollutants were attributed to the changes of synoptic weather systems. The sources of NO_y were resolved using regression analysis, and the ozone production efficiency of NO_x was inferred. The topic of this article is consistent with the scope of ACP. Considering that published data for characterizing the megacity air pollution in the East Asia, particularly in China, are rather limited so far, this paper is valuable to further studies upon the air quality and atmospheric chemistry in that region. However, there are indeed some issues need to be clarified or discussed in more details before the final publication in ACP.

1. It was inferred that the air pollutants were mostly emitted from local sources according to the high NO_x/NO_y ratio. Please note that the oxidation of NO_x should have been declined in wintertime. The NO_x/NO_y ratio could not be decreasing along the transport of air mass like in summertime. I suggest making a comparison of NO_x/NO_y between a stagnant and a long range transport air mass to see if the inference is warranted.

Response: The NO_x/NO_y ratio in this paper (section 3.5) is used as an indicator of the photochemical age of air mass. We found the NO_x/NO_y varying in the range of 0.7-1 and believe that the conversion of NO_x is fairly slow. The most direct explanation to the high NO_x/NO_y ratio is the high contribution of local emission to observed NO_x. But, you are right; due to declined oxidation of NO_x in winter, air masses transported from far away may have higher NO_x/NO_y, too. To make our inference more robust, some more clues are needed. We calculated the NO_x/NO_y and NO/NO_y ratios for higher and lower wind speeds. For wind speeds lower than 2 m/s, the NO_x/NO_y and NO/NO_y ratios are 0.87 and 0.44, respectively; for wind speed higher than 4 m/s, the ratios are 0.81 and 0.16, respectively. According to Table 4 and Fig. 9, NO_x/NO_y (NO/NO_y) is 0.90 (0.21) for the longest trajectory cluster (clu 4), and 0.85 (0.44) and 0.84 (0.42) for the two shortest trajectory clusters (clu2 and clu7). It seems that for the urban site in Beijing, the NO_x/NO_y ratio of long-range transported air is not much lower than that of local air. This may reflect the fact that the photochemical conversion of NO_x in winter is at minimum in Beijing and its surrounding areas. However, long-range transport or stronger wind speed promotes the vertical mixing of O₃ and enhances the O₃ level (as shown in Table 4), which helps the conversion of surface NO to NO₂. This leads to much lower NO/NO_y (≤ 0.21) for long-rang transported air compared to local air. For the whole dataset, the average NO/NO_y is 0.40, which is close to the value for lower wind condition and nearly twice of that for long-range transport condition. In addition, long-range transported airmasses in winter Beijing are mainly from the northwest sector and contain much lower NO_x as shown in Table 4, hence can dilute the

NO_x concentration in local air of Beijing. Therefore, local sources contribute most of the ambient NO_x in urban Beijing in winter. We will include these points in the revised manuscript.

2. The sources of NO_y were resolved using CO and SO₂ as indicators of mobile and stationary sources, respectively. This approach assumes that the CO in Beijing is exclusively from mobile sources, and SO₂ is exclusively from stationary sources. Does this assumption be supported by the emission inventories? For instance, there could be substantial emissions of CO from biomass burning in North China. Thus, what are the uncertainties associated with the assumption?

Response: According to the INTEX-B_v1.2 data in Table S1 (<http://mic.greenresource.cn/intex-b2006>; Zhang, Q., D. G. Streets, G. R. Carmichael, K. B. He, H. Huo, A. Kannari, Z. Klimont, I. S. Park, S. Reddy, J. S. Fu, D. Chen, L. Duan, Y. Lei, L. T. Wang, and Z. L. Yao: Asian emissions in 2006 for the NASA INTEX-B mission, *Atmos. Chem. Phys.*, 9, 5131-5153, 2009.), transportation contributes 52% to CO for the entire area of Beijing and 60% to CO for the grid (Center at 40°N,116.5°E with 0.5° × 0.5°) where the CMA site locates. Emissions from stationary sources (industry, power plant and residential) make a contribution of 38% to CO for the entire city and 40% for the CMA grid. About 73% of SO₂ are emitted from power plant and industry sources both for the entire Beijing and for the CMA grid, and transportation contributes only less 4% to SO₂. Emissions of CO from biomass burning in North China (outside Beijing, mainly from south of Beijing because Beijing locates in the north edge of the North China plain) seems not significant in winter because the prevailing winds in winter are from north (Fig.2), the clean sector. Therefore, the major uncertainties associated with the assumption may be from the co-emission of CO and SO₂ by industry and power plant sources, which should be less than 40%. We will provide above information in the revised manuscript.

Table S1. The emission inventories (Unit: Gg, Year: 2006) in Beijing

	Power	Industry	Residential	Transportation	Total
CO	23.3	868.6	363.8	1334.8	2590.6
SO ₂	118.0	62.0	62.7	4.9	247.6
NO _x	101.5	64.5	30.4	130.2	326.7
CO*	2.6	103.5	58.6	247.9	412.6
SO ₂ *	13.6	4.8	5.7	0.9	25.1
NO _x *	11.4	6.2	2.7	2.3	43.3

*grid data at 40°N, 116.5°E where the CMA locates

3. It was shown that the co-linearity between CO and SO₂ was not significant. However, the correlation analysis gave a high correlation coefficient of 0.8. Thus, the correlation was rather obvious. Please clarify this contradiction.

Response: According to the emission inventories shown in Table S1, more than 50% of CO are from mobile sources and about 96% of SO₂ from stationary sources. The great difference in emission sources is consistent with the insignificant co-linearity between CO and SO₂, which is suggested by the low VIF value. As CO and SO₂ are mainly from the local sources in winter in urban Beijing, the meteorological factors may exert similar influences on the concentrations of both gases, with wind direction, wind speed, and mixing layer height being the key factors. Table 1 indicates that both CO and SO₂ are significantly

anti-correlated with WS. Figure 7 (Note: this will be “Figure 6” after removing the original Figure 6, see the response to the 5th comment by the second referee) shows that strong north wind causes extremely low concentrations of both gases. Therefore, the significant correlation between CO and SO₂ may more be caused by similar meteorological impacts than by co-linearity between them. We will clarify this in the revised manuscript.

4. The contributions from mobile and point sources to NO_y were estimated as 66+/-30% and 40+/-16%, respectively, and gave a total contribution > 100%. Please make clarification.

Response: The background levels of CO and SO₂ could be neglected when comparing with the urban level of CO and SO₂ in winter Beijing urban. So, in the regression analysis, the background levels of CO and SO₂ are not excluded. This, together with statistical uncertainties, may have introduced bias to the final results, causing a total contribution > 100%.

5. An averaged OPE_x of 0.76 was estimated by the regression of O_x vs. NO_z. It seems that the analysis was based on the whole dataset of the study. The relationship between ozone production rate and the level of NO_x is known being nonlinear, and is sensitive to the concentration and reactivity of the VOCs. The O_x-NO_z regression is usually applied to a period of several hours. Given that the meteorological conditions, VOCs concentration/composition, and the radicals production and loss could be varied from day to day, the results of the analysis could be very unreliable, as shown in the figure 11 of the manuscript. I'd like to suggest making analysis for daily data and giving the range of the daily OPE_x for the study period.

Response: We appreciate the reviewer's suggestion and have calculated daily OPE_x using the NO_z and O_x data between 7:00-11:00. The obtained OPE_x values are in the range of 0-8.9 (ppb/ppb) with the mean($\pm 1\sigma$) and median values being 1.1(± 1.6) and 0.5 (ppb/ppb), respectively. 73% of daily OPE_x are greater than 0.

The corresponding text in the manuscript will be changed to:

“Figure 11 (Note: this will be “Figure 10” after removing the original Figure 6, see the response to the 5th comment by the second referee) shows the time series of daily OPE_x during the observation period. Daily OPE_x values are calculated using the NO_z and O_x data between 7:00-11:00. The OPE_x values are in the range of 0-8.9 (ppb/ppb) with the mean($\pm 1\sigma$) and median values being 1.1(± 1.6) and 0.5 (ppb/ppb), respectively. To date, most of the reported OPE values are obtained for the warm seasons (Xu et al., 2009), winter OPE values are only available for the Harvard Forest site (Hirsch et al., 1996) and the Alps site (Zanis et al., 2007). The mean value of 1.1 can be considered as the average OPE_x in winter for an urban site in the megacity Beijing. This winter OPE_x value is much smaller than the reported OPE_x values of 3.9-9.7 in summer (Chou et al., 2009) and 1.5-6.0 in fall (An, 2006) for Beijing. The smaller winter OPE value in Beijing could be due to the weaker photochemistry and higher NO_x concentration. At high NO_x concentrations, OPE tends to decrease with the increase of the NO_x concentration (Kleinman et al., 2002; Ge et al., 2010). In the megacities like Beijing, the NO_x level is usually much higher than needed for photochemical O₃ production. Excessive NO_x causes net O₃ loss rather than accumulation. About 27% of daily OPE_x are negative, implying consumption of O₃ by excessive NO_x. Such O₃ loss due to high NO_x was also observed at the rural site Gucheng in the North China Plain (Lin et al., 2009). Taking the average OPE of 1.1 and the average daytime enhancement of NO_z (about 5 ppb), one can obtain an average photochemical O₃ production of about 5 ppb. This is a small but significant source for surface O₃ in winter

in Beijing.”

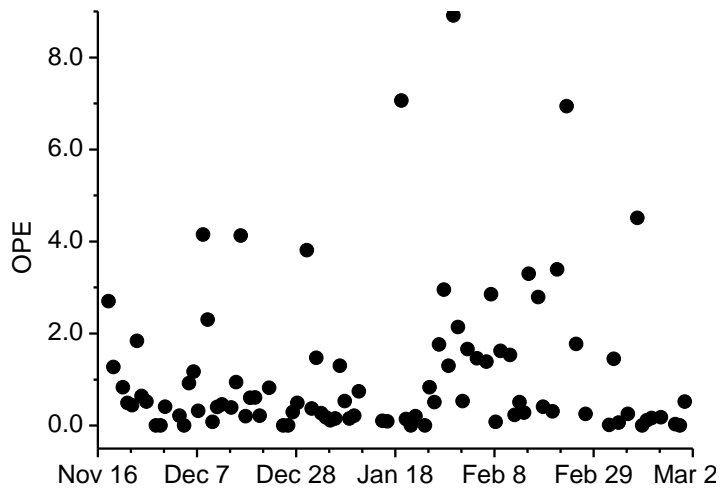


Fig. 11. Time series of daily OPEx during the observation period for the CMA site

(Note: this will be “Figure 10” after removing the original Figure 6, see the response to the 5th comment by the second referre.)

Response to comments by referee #2

Anonymous Referee #2

Received and published: 26 April 2011

General Comments: It is an interesting and well structured article and I suggest publication of the article after taking into account the comments listed below.

Major comments:

1. The authors state that high wind speed concurs usually with lower humidity and hence this is a possible reason for the positive correlation of RH with all pollutants except ozone. However, they should also consider that RH is negatively correlated with temperature (as warmer air can hold more humid air). It may be that the negative correlation of ozone with RH is linked with the positive correlation between ozone and temperature as a consequence of the temperature versus RH anti-correlation.

Response: Yes, it's true that RH is negatively correlated with temperature. As shown in Fig. S1, the average diurnal cycles of O₃, T, RH, and wind speed look similar or dissimilar. These similarity or dissimilarity in the diurnal patterns puzzle the interpretation of the correlations. However, wind speed is the more important factor causing the positive RH-O₃ correlation. As shown in Table 1, the absolute value of the correlation coefficient (R) of the WS-RH correlation is much larger than that of the WS-T correlation; and the absolute R values of the WS-O₃ correlation and the RH-O₃ correlation are much larger than that of the T-O₃ correlation. These suggest that RH is more closely linked with WS than with T, and there are closer relationships among WS, RH and O₃. Furthermore, we can use daily mean data instead of hourly mean data to make the correlations between O₃, T, RH, and WS. This can avoid the influence of the diurnal variations on the correlations. As shown in Table S2, T is not significant correlated with O₃, RH, and WS anymore. Therefore, in winter Beijing, wind speed is the main factor indirectly causing the negative correlation of RH with O₃ and the positive correlation of RH with other pollutants. The major points mentioned here will be included in the revised version.

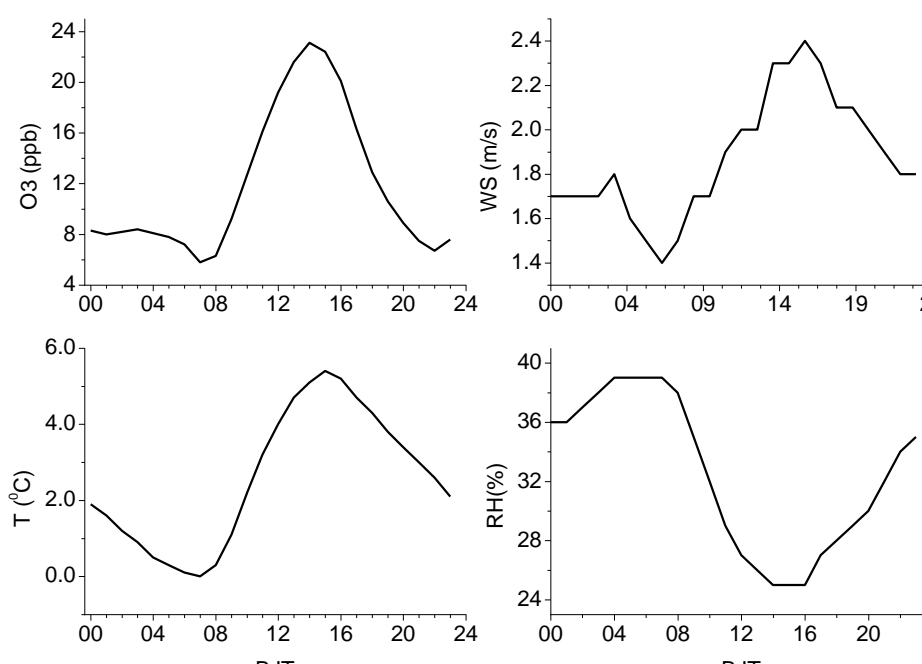


Fig. S1. The average diurnal variations of O₃, T, RH, and WS

Table S2. The correlations between O₃, T, RH, and WS

	O ₃	WS	T	RH
O ₃	1.00			
WS	0.79*	1.00		
T	0.09	0.03	1.00	
RH	-0.61*	-0.59*	-0.13	1.00

*P<0.01

2. Are the slopes of daytime regression lines in Table 2 significantly different from the nighttime slopes? I would suggest that the authors should also consider the errors of the slopes in order to give an answer for my above mentioned question.

Response: the errors are now included in Table 2. The differences between the daytime and nighttime slopes are larger than a few times of the errors, suggesting that the slopes of daytime regression lines are significantly different from the nighttime ones.

Table 2. The slopes, intercepts, with their errors, and correlation coefficients (R²) values in the regression lines of CO-NO_x, SO₂-NO_x, CO-NO_y, and SO₂-NO_y

	Slope (ppb/ppb)	Intercept (ppb)	R ²	Slope (ppb/ppb)	Intercept (ppb)	R ²
	CO-NO _y			SO ₂ -NO _y		
All data	26.6±0.2	49±22	0.817	0.372±0.004	4.6±0.4	0.734
Daytime	24.1±0.3	117±23	0.844	0.342±0.005	4.4±0.5	0.758
Nighttime	28.9±0.4	-18±35	0.813	0.399±0.006	4.8±0.6	0.731
	CO-NO _x			SO ₂ -NO _x		
All data	29.3±0.3	147±23	0.785	0.413±0.005	5.7±0.4	0.717
Daytime	27.3±0.3	196±26	0.824	0.388±0.006	5.5±0.5	0.739
Nighttime	30.9±0.5	105±39	0.764	0.432±0.007	6.1±0.6	0.706

3. I think that the fact that wind speed correlates positively with ozone and negatively with all other pollutants is not adequately emphasized. There is some discussion that physical processes such as transport of ozone from above or the clean sector is the reason for the different behaviour for ozone versus wind speed correlation but more elaboration is needed and possibly relevant references for this effect.

Response: The similar phenomenon can also be found in the references in this paper, such as An et al., 2007, 2008; Li et al., 2007; Lin et al., 2009; etc. In winter, pollutants are constrained in the shallower boundary layer. As a consequence, surface O₃ is removed due to the titration of NO. Stronger wind promotes the dilution of primary pollutants and the downwards mixing of O₃-richer air, as shown in Fig. 7. We have shown in Fig. 8 that higher O₃ levels are distributed in the clean (in terms of primary pollutants) sector W-N, in which the wind speed is the highest (Fig. 2). We also have shown that the rapid-moving trajectories (concurring with high wind speed) are from the clean sector (Fig. 9) and associated with

highest O₃ and lowest primary pollutants (Table 4). In the text on pages 6932-6934 (lines 19-22 on page 6932; lines 1-10 on page 6933; lines 1-9 on page 6934), we have tried to analyze and explain the physical processes. Since high wind speed often concurs with downwards transport of air masses from the clean sector, it is hardly possible to separate the impacts of different processes on O₃ and primary pollutants.

4. In page 6930 the authors claim that collinearity between CO and SO₂ is not significant. However this statement sounds strange since Table 1 indicates a correlation of 0.808 between these two pollutants. Please clarify and explain the statistical measures VIF and condition index.

Response: see response to the 3rd comment by the first anonymous referee.

4. In page 6931 the authors state that the coefficients a and b were applied to the calculation of relative contribution of mobile and points sources. Please clarify which are these calculations.

Response: For each hourly data, $(a*[CO])$ and $(b*[SO_2])$ are calculated and then the values are divided by $[NO_y]$ to represent the relative contributions of mobile and points sources, respectively.

5. Furthermore it is found that the relative contribution from mobile sources has a maximum at 13:00. Is that sensible? Shouldn't be the maximum of mobile sources at early morning with the highest traffic? Please clarify this issue.

Response: This is also for us a puzzle. According to Fig. 5, the lowest concentration of NO_y appears at 13:00. During 13-16:00, the ratio CO/NO_y equals to its average. In morning rush hours, CO/NO_y is the lowest of the day. This might be one of the reasons that the highest relative contribution from mobile source is at 13:00 instead of at early morning. Another possibility might be that pollutants emitted by near surface mobile sources can more easily reach the monitoring site (38 m above ground) during early afternoon with good atmospheric mixing than other time of day. Since the relative contribution from mobile source depends not only on the strength of mobile source but also on the strength of stationary sources, it cannot be simply linked to the traffic intensity. Moreover, our estimate may contain large uncertainties, as discussed in the response to the 2nd comment by the first reviewer. Therefore, the diurnal variations of the relative contributions from mobile and stationary sources do not provide sound result. Fig. 6 will not be included in revised version.

6. In page 6932 it is anticipated that the period with the highest ozone (24.2 ppbv) is linked with cold and dry air rapidly descending to the site. The RH of the air masses is as low as 20%. Such dry air masses are often linked to stratospheric air descending to lower troposphere. Have the authors explored this possibility. Deep stratosphere to troposphere transport events down to the surface are rare but may happen. There are a number of such cases explored in the literature (Stohl et al., Atmospheric Environment, 34:1323–1354, 2000; Gerasopoulos et al., Atmospheric Environment, 35:6347–6360, 2006; Akritidis et al, Meteorology and Atmospheric Physics, 109:9-18 , 2010).

Response: In winter, dry and cold air masses from northwest or north, e.g., from Siberia, often invade Beijing, bringing very clean and dry air with very low RH and relatively higher O₃ level. When this happens, the diurnal patterns of O₃ look not as normal as the typical pattern with O₃ maximum in the afternoon

and minimum before morning. During the event from Dec. 28, 2007-Jan. 1, 2008, strong vertical air transport occurred as shown in cluster 4 in Fig. 4. To understand whether or not this event was linked with deep stratosphere to troposphere transport, 120-h backward trajectories (0,6,12, 18 UT from Dec. 12, 2007 to Jan. 3, 2008) are calculated and plotted in Fig. S2. The trajectories are grouped in two distinct clusters, with the one being associated with descending events and the other 2 days before and after the events. The heights of the endpoints are 10 m above ground level (a.g.l) in Fig.S2a (all trajectories) and Fig. S2b (mean trajectories) and 1500 m a.g.l. in Fig.S2c (all trajectories) and Fig.S2d (mean trajectories). During the high O₃ events, air mass from 1000-3500 m a.g.l. over East Europe was transported to the surface layer of Beijing and air mass from 1500-4500 m a.g.l. over Northeast Europe was transported to 1500m a.g.l. over Beijing. However, there is no evidence showing air mass directly from stratosphere. Most air masses arriving the surface were mainly transported from the free troposphere to the site. We will include the major results of this analysis at the end of Section 3.4.

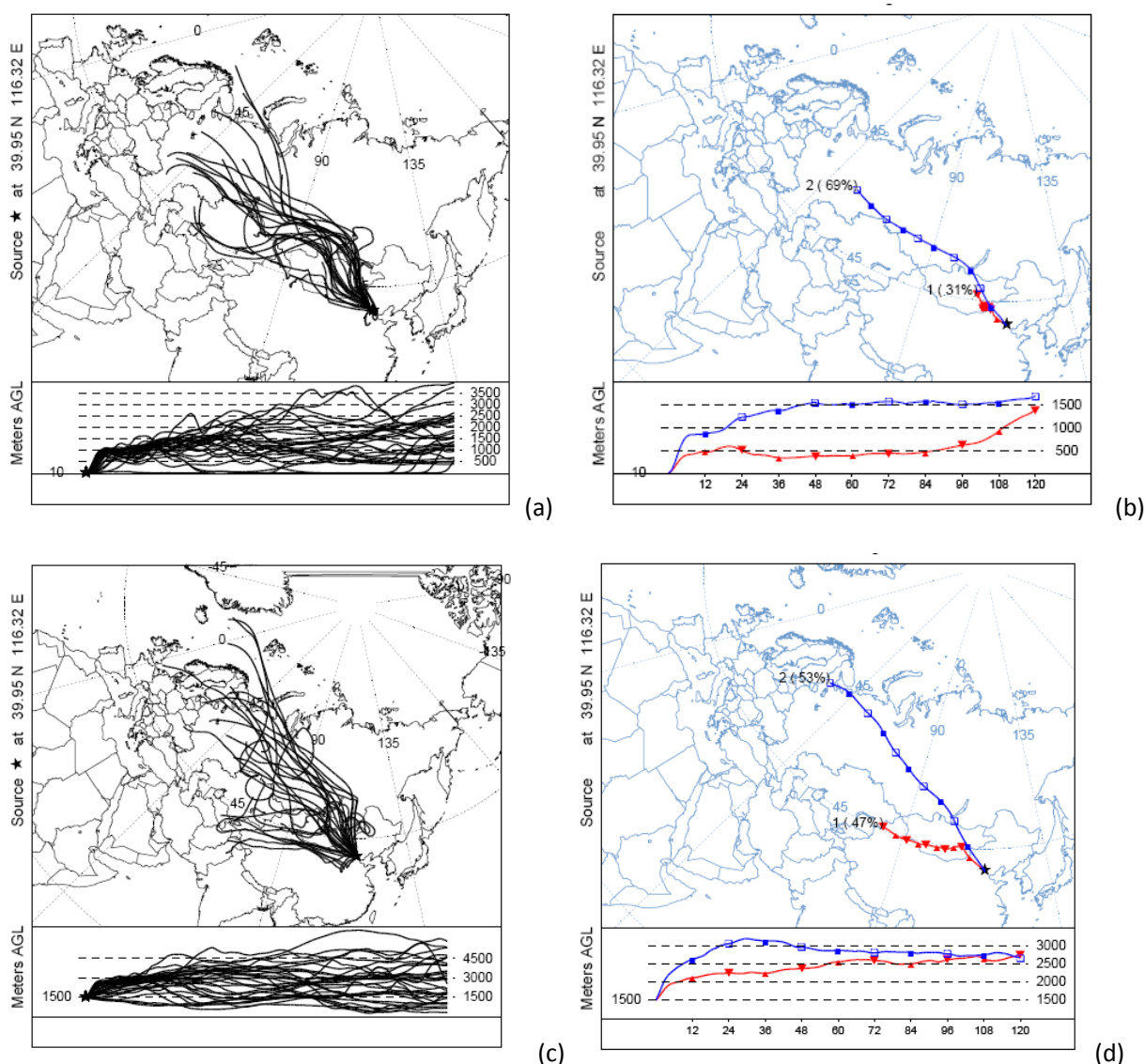


Fig. S2 The 120-h backward trajectories and mean trajectories to 10 m and 1500 m a.g.l. over the CMA site

7. A common index to estimate the ozone production in polluted areas as well as the clean free troposphere, is the OPE. It seems that the OPE calculation in Figure 11 is based on daily means which is not scientifically

meaningful. By definition OPE is meaningful if you follow an air mass and see the number of O₃ molecules chemically produced per molecule of NO_x oxidized to NO_z within this air mass. Considering that you are in a station that receives for a few hours air masses of similar origin you may assume that OPE calculation is also meaningful from a scatter of $\hat{\delta}^3$ versus NO_z within a few hours. Hence this means that OPE should be based on hourly data of a specific day. Then someone can explore for many different days the range of OPE calculations.

Response: see the response to the 5th comment of the first referee.

8. Minor comments: “dynamic” in line 3 of page 6928 should rather read “dynamical” or “physical”. The word “valleys” in line 26 of page 6929 does not sound as the most appropriate word.

Response: “dynamic” will be changed to “dynamical” and “particularly the synchronous peaks and valleys” is changed to “particularly the similar patterns”.