

We are grateful to the reviewers for the appropriate and constructive suggestions and for the proposed corrections to improve the paper. We have addressed all the issues raised and have modified the paper accordingly. We believe that, thanks to these inputs, the manuscript has definitely improved.

This is a summary of the changes we made and our responses to the reviewer #1's comments and recommendations.

Summary of the changes

(in black is the original comments of the reviewer, while our responses are highlighted in red)

Reviewer #1

General Remarks:

1. A basic analysis which demonstrates the relative importance of various processes (e.g. emission, transport, chemistry, and deposition) to the change of tracer mixing ratio in the studied region is highly recommended. Such analysis helps us know the importance of the target chemistry influence in the entire evolution. For example, the authors explained the influence of the exchange rate coefficient on Ox, NO_x, and OH based on their chemistry production and loss in section 3.1 and Figure 5. However, the changes of tracer mixing ratios come not only from chemistry, but also from other processes and sometimes the latter dominates a change (e.g. NO_x). I suggest adding a table or figure to depict the Ox, NO_x, and OH fields inside the box based on their information of mean mixing ratio (VM), the change of VM during the day (CVM), the fraction of CVM from each of the processes of emission, transport, chemistry, and deposition. Meanwhile, I suggest making the discussion more concise, specifically, by merging Fig5d and Fig6 and removing Fig 5 a-c. Qualitatively, the increase of O₃ and the decrease of NO_x in the box can be inferred directly from adopted tracer distributions because imported air brings high O₃ and low NO_x. In addition, the general contributions from the chemistry process shown in Fig 5 a-c are similar to those in Figure 7. OH change is special since it is attributed solely by atmospheric chemistry due to its very short lifetime.

As the reviewer suggested, additional budget analysis has been added, see the responses to the specific comments 8 and 9.

Considering the reviewer's suggestion, Figure 7 has been removed, Figure 6 and Figure 8(d) have been merged, and Figure 8(d) has been modified to show only gross rates in order to match Figure 5(d).

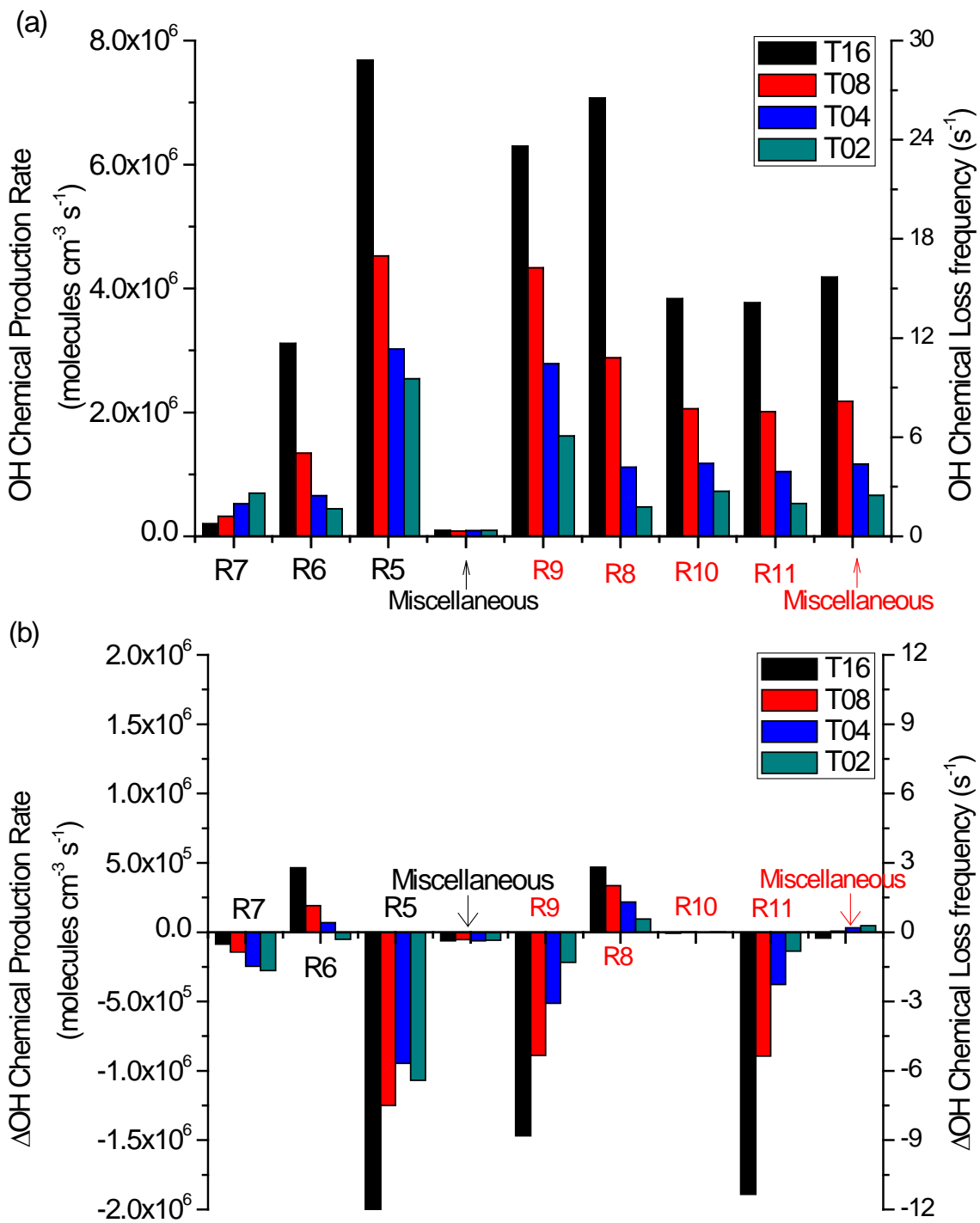


Fig. 6. (a) The daily average chemical production rates (labels in black) and chemical loss frequencies (labels in red) of OH for the NO_DUST simulation. (b) The differences between the DUST_H and NO_DUST simulations (DUST_H-NO_DUST). “Miscellaneous” represents the sum of all the other source or loss terms. The bar sequence is same as Fig. 5. The reactions are listed in Table 4.

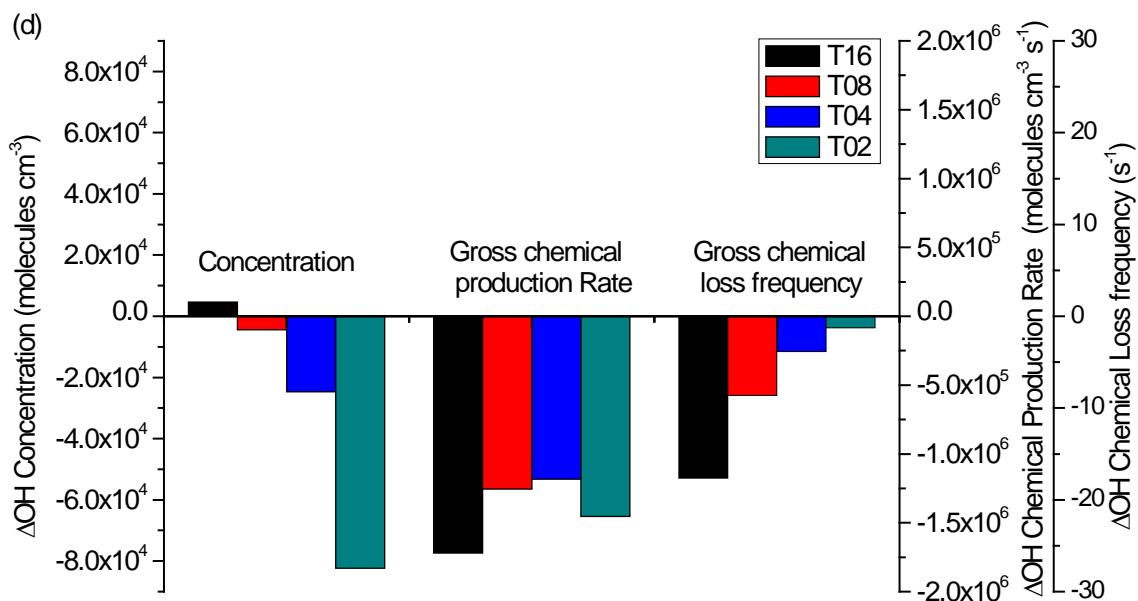


Fig. 8. Differences of the daily average mixing ratios and the gross chemical production rates B_{cp} and the gross chemical loss frequencies K_{cl} of (a) O_x , (b) NO and NO_2 (c) NO_x , and (d) OH, between the DUST_H and NO_DUST simulations (DUST_H-NO_DUST).

2. The box model in the paper considered the processes of emission, horizontal transport, chemistry, and dry deposition. The results, therefore, reveal the tracer change in atmospheric boundary layer where is important in air quality studies. For climate change studies, we need to know the overall influence over column. It would be nice to see some discussion of the likely overall dust column impact.

A short note about the dust column impact has been added in the end of the paper (Page 20165, line 2): “For global atmospheric chemistry and climate change studies, the overall O_3 change in the column due to dust is important. In a 3-D model study, Bian and Zender (2003) reported that in the real atmosphere the sensitivity of O_3 to the vertical location of dust is complicated and can change signs depending on the presence of O_3 precursors. Given this complexity, the overall influence of dust over the column will be examined in a follow-up 3-D model study.”

Specific Comments:

1. Title: The word “Photochemistry” is not entirely appropriate since the study also included heterogeneous chemistry.

The title has been modified to “Impact of dust on tropospheric chemistry over polluted regions: a case study of the Beijing megacity”.

2. Page 4, line 18: Add table 1 after “12 heterogeneous removal reactions”.

“Table 1” has been added to Page 20149, line 14: “12 heterogeneous removal reactions on mineral dust (listed in Table 1)”.

3. Page 6, equation 4: What is the relationship between J_e in the equation and B_e in table 2?

Page 20151, line 18: “the increase in concentration C_i ” has been modified to “the increase in concentration C_i (which we call the source term, B_e)”.

Page 20151, line 20: Eq. 4 has been modified to “ $B_e = \frac{\partial C_i}{\partial t} = \frac{J_e}{Z_{pbl}}$ ”.

Page 20152, line 4: the sentence has been modified to “where v_d/Z_{pbl} is defined as the deposition coefficient K_d . Note that the parameters J_e (and thus B_e) and v_d (and thus K_d) differ for each species i ;”

4. Page 8, lines 5-7: Wind from different directions might bring quite a different inflow air mass. Did you check the tracers and dust imported from west and northwest separately? If the difference is significant, then separate treatment might be needed.

This is a nice suggestion, but unfortunately the data currently available is too sparse to allow such a refinement. We plan to follow up on this in 3D runs, and hope the current study will provide an additional incentive for such measurements in the future.

5. Page 8, line 21-24: I do not understand why you need to decrease dust surface areas from the faster advection to the slower one. Do you want to force equal deposition importance under various advection cases? The relative importance of deposition does become more important when the advection is weaker under the condition of the same dust surface area. Please clarify the sentence.

Page 20153, line 28: we will replace the sentence starting with “Since larger dust particles...” until the end of the paragraph with: “The T02 case provides the most rapid source of dust to the box model and thus the greatest dust concentrations (while the T16 run results in the lowest dust concentrations). However, as seen in Figure 2, the differences are only notable for large dust particles, which sediment rapidly and thus can be lost in appreciable amounts on the timescales of their transport through the box, especially for the T16 case. For smaller particles, the concentrations are essentially the same as in the upwind source region, since for these particles the transport timescale is much shorter than the deposition timescale.”

More details of the calculation of the dust surface area for different exchange rate cases are explained in the reply to the comment 16.

6. Page 8, last line to Page 9, line 5: What are the reactions referred here? The impact of dust photolysis alteration on reactions is pretty sensitive to the tracer’s photolytic spectrum. Any quantitative analysis based on the uniform rate (e.g. 50%) for all reactions and all considered conditions might be misled. I do not see useful information from the photolysis examined with this artificial perturbation rate.

Here we would like to assert that we do think that these sensitivity simulations are useful in showing that the order of magnitude of changes (e.g., > 50% change in OH) due to the influence of photolysis rates on dust is large, on the whole comparable to the direct influence via heterogeneous reactions. However, we agree with the referee about the very approximate nature of this approach, and thus add the following text (after the first sentence in line 26 on Page 20160): “It is important to note that the actual change in photolysis rates due to dust will vary from species to species, due to the wavelength-dependent effects of dust particles on the actinic flux; the approach here is only meant to establish an order-of-magnitude estimate of this effect, as an indicator of whether or not it is worth continued investigation for characterizing the effects of dust on chemistry in Beijing.”

Also note that additional simulations have been added according to the suggestions from the reviewer #2 (please see the reply to the second comment of the reviewer #2).

7. Page 9, line 6: Could you elaborate why 96 hours is long enough to establish an equilibrium even for CO, whose lifetime is about 50 days in Beijing during spring season?

For the tracers relatively long chemical lifetimes (like CO here), their local concentration (like in the “box” here) are determined almost entirely by the transport and emission processes, and thus by the transport timescale, rather than the chemical lifetimes. For the transport timescale of 16

hours (T16), a 96-hour spinup should be sufficient for the tracers to be within a few percent of equilibrium.

8. Page 11, lines 4-5: Again, what fraction of the increase of O₃ daily average mixing ratio is attributed to chemistry, and what fraction is attributed to transport and other processes?

9. Page 11, lines 7-9: The budget analysis would also help the explanation here.

As the viewer suggested in comments 8 and 9, additional budget analysis has been added. Page 20156, line 3: “Since the model is nearly in steady state, the change in O₃ mixing ratio during the day (calculated as the mixing ratios at the end of day five minus the beginning of the fifth day) is very small and the balance between its net production term (i.e. the transport process) and its net loss terms (i.e. the deposition process and the chemistry process) is reached, as listed in Table 4. The emission budget is zero because no emission of O₃ is considered. The transport process is the only production term of O₃ and the corresponding major competitive process is the net chemical loss. It is qualitatively similar for O_x. The relationship between O_x mixing ratio and these four processes in steady state is described in Eq. (8).” has been added to the beginning of this paragraph.

Page 20156, line 15: “Similar to O₃, the change in NO_x mixing ratio during the day is very small and the balance between its production term (i.e. the emission process) and its loss terms (i.e. the transport process, the deposition process and the chemistry process) is reached, as listed in Table 4. However, different from O₃, the emission process is the only production term of NO_x and the corresponding major competitive process is the transport process. In Eq. (8),” has been added in the beginning of this paragraph.

Table 4. Changes in O₃ and NO_x mixing ratios (y) during the course of the 5th day of NO_DUST simulation, and factors contributing to the budget of each. (unit: ppbv)

Tracer Rate Process Contribution	O ₃				NO _x			
	T16	T08	T04	T02	T16	T08	T04	T02
Change in y	1.6E-15	3.9E-16	-2.5E-16	2.5E-10	0.2	0.1	0.2	-0.01
Transport	80.6	150.1	231.7	230.9	-341.4	-350.7	-356.4	-355.5
Emission	0	0	0	0	365.1	365.1	365.1	365.1
Deposition	-1.1	-1.9	-4.3	-8.3	-15.5	-11.2	-7.9	-4.3
Chemistry	-79.5	-148.2	-227.4	-222.6	-7.9	-3.2	-0.7	-5.4

10. Page 12, line 7: Should be “decreasing slightly from the T16 case to the T08”, not “to the T04”.

Page 20157, line 16: “to the T04” has been modified to “to the T08”.

11. Page 12, line 15: Please define the relative change. Please also indicate the “changes” as increase or decrease.

Page 20157, line 24: “(in percentage, calculated as $100 \times (\text{DUST}_H - \text{NO_DUST}) / \text{NO_DUST}$)” has been inserted after “relative change”, and “which changes slightly with increasing values of K_i ” has been modified to “which increases in amount slightly from the T16 case to the T04 case, then decreases in amount slightly to the T02 case”.

Page 20158, line 17: “(in percentage, calculated as $(\text{DUST}_H - \text{NO_DUST}) / \text{NO_DUST}$)” has been deleted.

12. Page 13, line 15: It would be helpful if the authors explain clearly why T04, not T02, has the largest change.

Page 20158, line 25: “Because the relative increase of NO is largest in the T04 case, it is thus the T04 case, instead of the T02 case, which has the largest relative increase in the K_{cl} of O_x ,” has been inserted after “Fig. 8b.”.

13. Page 13, line 10: Does this line have the same font size as the other lines?

The font sizes do not appear different to us; in any case, this should be corrected during the final formatting if accepted to ACP.

14. Page 18, last 4 lines: Please clarify the rates stated in this line. To which species do they refer? How do you come up with these numbers?

Page 20164, line 6: “we estimate that the relative contributions of the heterogeneous removal on dust and the decrease in photolytic rates are 87% and 13%, respectively.” has been modified to “we estimate that the relative contributions of the overall heterogeneous removals on dust and the decrease in photolytic rates to the decrease of O_x are approximately 87% (calculated by $(C_{(DUST_H)} - C_{(NO_DUST)}) / (C_{(DUST_H+J)} - C_{(NO_DUST)})$) and 28% (calculated by $(C_{(DUST_J)} - C_{(NO_DUST)}) / (C_{(DUST_H+J)} - C_{(NO_DUST)})$), respectively (note that combining the two processes in the DUST_H+J run might lead to non-linear effects, so that this is only an approximate relative apportionment).”

15. Table 2: What is the initial and upwind dust concentration? Why is it necessary to cite both deposition velocities and deposition coefficients here? Why is it lower for all NO_x and VOC and higher for O₃ in upwind airmass?

The upwind dust concentration is shown in Figure 2.

It is not necessary to cite both deposition velocities and deposition coefficients here; we thought it would be easier for the reader to have both values and save needing to convert, but since the referee suggests this could lead to confusion, the deposition coefficients have been removed from Table 2.

Due to the strong emission of NO_x in the Beijing area, the ozone production efficiency is lower in the “box” than in the upwind area where there is less NO_x. As a result, we have lower ozone precursors and higher ozone in the upwind area than in the “box” (note that this phenomenon has commonly been observed in and around North American and European cities). We will add a note on this in the revised version (Page 20152, line 23, after “in Table 2”): “One may note that it is lower for all NO_x and VOC and higher for O₃ in the upwind airmass than in the “box”. This is caused by the strong emission of NO_x in the Beijing area, that results in lower ozone production efficiency in the “box” than in the upwind area, where there is less NO_x. This phenomenon has commonly been observed in and around North American and European cities (e.g. Kleinman et al., 1994; Kleinman, 2000).”.

16. Figure 2: How do you derive these different dust distributions?

Page 20153, line 28 to Page 20154, line 3 have been modified to “The dust number concentration dN of size bin i at time step t is calculated in two steps, first:

$$dN_{t,i} = dN_{t-1,i} + (dN_{0,i} - dN_{t-1,i}) \cdot \Delta t \cdot f \quad (7)$$

where $dN_{0,i}$ is the “upwind dust concentration” derived from our observation data; Δt is the time step interval length; f is the exchange rate coefficient. This is followed by:

$$dN_{t,i} = dN_{t,i} \cdot (1 - \Delta t \cdot v_{di} / Z_{pbl}) \quad (8)$$

where v_{di} is the deposition velocity of size bin i ; Z_{pbl} is the planet boundary layer height. Then the dust surface area concentration $dS_{t,i}$ is estimated by:

$$dS_{t,i} = dN_{t,i} \cdot 4 \cdot \pi \cdot r_i^2 \quad (9)$$

where r_i is the radius of the dust particle of size bin i . The combination of the increase in the exchange rate coefficient f from the T16 case to the T02 case, and the larger v_{di} for the larger dust particles results in the dust distributions shown in Figure 2.”

17. Figure 8: I like this figure because it depicts the influence due to dust heterogeneous influence directly and clearly.

We appreciate this.

Additional modifications:

Page 20158, line 12: “the relative change in C ” has been modified to “the change in C ”.

Page 20159, line 3: “ Δc ” has been modified to “ ΔK_{cl} ”.

The symbol “ y ” has been used for mixing ratios and the symbol “ C ” has been used for concentrations through the paper.

References

Kleinman, L. I., et al. Ozone formation at a rural site in the southeastern United States. *J. Geophys. Res.*, 1994, 99, 3469– 3482.

Kleinman, L. I. Ozone process insights from field experiments, II, Observation-based analysis for ozone production. *Atmos. Environ.* 2000, 34, 2023~2033.