Point-by-point responses to reviewers

We thank the reviewer for the detailed and thoughtful review of our manuscript entitled "Improving the representation of HONO chemistry in CMAQ and examining its impact on haze over China". Those comments are all valuable and very helpful for revising and improving our paper. We think the incorporation of the reviewers' suggestion has led to a much improved manuscript. Detailed below is our response to the issues raised by the reviewers. We also detail the specific changes incorporated in the revised manuscript in response to the reviewers' comments.

Reviewer #1:

Zhang et al. implemented new (heterogeneous) HONO formation mechanisms into the CMAQ model to evaluate HONO formation and impacts in China, especially their Beijing site. The new parameterization shows much better agreement with ground observations in Beijing and the vertical profiles in another field campaign, compared to the original one. In China, in order to get a better prediction of air quality, it is important to have a good HONO parameterization in the model. Some revision should be made before accepting the manuscript.

It is critical for the HONO modeling study to clarify why specific parameterization is used. The authors have tried to conduct sensitivity runs and presented results in the SI. However, it is still not convincing why some HONO uptake coefficients were used in the model. Were they based on laboratory experiments, empirical parameters obtained from the field, or simply obtained from other models? These should be clarified.

[General Comment]: 1.1 For example, at Lines 192-195, are these uptake coefficients based on experimental data? Please clarify here how uncertain they are.

[Response]:

The selection of uptake coefficients on ground surface and aerosol surface are mainly based on the empirical data derived from either experiments or observations. As the reviewer suggested, we have summarized the variation range of the parameters and several sensitivity results to clarify the associated uncertainties. We referred to some experimental data measured in our laboratory. Experimental data measured on MgO surface fall in the range of 1.6×10^{-6} as reported by Ma et al. (2017) and on the hematite surface in the range of 1.9×10^{-7} - 1.6×10^{-6} as reported by Liu et al. (2015). The derived empirical data obtained by VandenBoer et al.(2013) from the field observation fall in the range of 2×10^{-6} - 1.6×10^{-5} . The empirical uptake coefficient used in models varied widely ranging from 10^{-7} to 10^{-3} (Table S2). The majority γ_{NO2} value employed in literature is about 10^{-6} . When the uptake coefficient changes by 10 times, the HONO concentration from the heterogeneous reaction on ground surface changes by a factor of two.

Table S2: The uptake coefficient of NO₂ used in other studies.

γ no2	Reference	γ NO2	Reference
1×10 ⁻⁶	(Li et al., 2018a)	8×10 ⁻⁶	(Liu et al., 2019b)
1×10 ⁻⁵	(Fu et al., 2019)	1×10 ⁻⁶	(Liu et al., 2014)
1×10 ⁻⁶	(Ndour et al., 2008)	2~7×10 ⁻⁴	(Lu et al., 2018)
1×10 ⁻⁷	(Stemmler et al., 2007)	5×10 ⁻⁶	(Meng et al., 2020)
10 ⁻³ ~10 ⁻⁴	(Li et al., 2018b)	1~6×10 ⁻⁷	(Monge et al., 2010)
1×10 ⁻⁶	(Liu et al., 2019a)	3×10 ⁻⁵	(Spataro et al., 2013)
1×10 ⁻⁶	(Liu et al., 2021)		

The detailed revises refer to:

Page 5, Line 170:

The selection criteria and possible ranges of the uptake coefficient are discussed in SI. Supplemental Information Page 2, Line 47-55:

The selection of uptake coefficients on ground surface and aerosol surface are mainly based on the empirical data derived from either experiments or observations. Experimental data measured on MgO surface fall in the range of 1.6×10^{-6} as reported by Ma et al. (2017) and on hematite surface in the range of 1.9×10^{-7} - 1.6×10^{-6} as reported by Liu et al. (2015). The derived empirical data obtained by VandenBoer et al. (2013) from the field observation fall in the range of 2×10^{-6} - 1.6×10^{-5} . The empirical uptake coefficient used in models varied widely ranging from 10^{-7} to 10^{-3} (Table S2). The majority γ_{NO2} value employed in literature is about 10^{-6} .

[General Comment]: 1.2 Lines 203-205: Please explain why 1.7/H is used in this study and in previous studies, and how uncertain it is.

[Response]:

1.7/H represents the ground surface area density (S/Vg) in the model. Effective surface area of ground can be higher than the geometric surface area due to the presence of trees, buildings, and other surface areas. A factor of 1.4-2.2 for the ratio of effective surface area to geometric surface area was measured by Voogt and Oke (1997). Hence, S/Vg =2.2S'/HS'= 2.2/H, S' represents the geometric surface area of the first layer. Previous HONO simulation studies (Vogel et al., 2003; Li et al., 2019; Liu et al., 2019b) used a value of 1.7/H for their modeling studies; we used a value of 1.7 by following these studies. We also perform a sensitivity case by setting S/Vg to 2.2/H. Predicted results are shown in Figure S3. The average HONO increased by 17.2% (from 2.5 ppb with 1.7/H (REV) to 2.9 ppb with 2.2/H).

We have clarified this point in the revised manuscript as follows.

Page 5, Line 179-186:

Following the suggestions of Vogel et al. (2003), Li et al., (2019) and Liu et al., (2019), we use a value of 1.7/H (S/Vg =1.7S'/HS'=1.7/H, S' represents the geometric surface area of the first layer. 1.7 is the effective surface factor per ground surface in first layer. H is the model's first-layer height.) for surface area-to-volume ratio of ground (S/Vg) to calculate the rate constant for the reaction on ground surfaces. We also conducted sensitivity analysis by using the value of 2.2/H which is suggested from Voogt and Oke

(1997). The result suggests slightly higher concentrations but with similar model performance (details in Figure S4 in Supplemental Information).

Supplemental Information Page 2, Line 103-104:

S/Vg was set to 2.2/H in another sensitivity case. The average HONO increased by 17.2% (from 2.5 ppb with 1.7/H (HONO_REV) to 2.9 ppb with 2.2/H).



Figure S4 A comparison of observed and simulated HONO concentrations in Beijing. HONO observation is denoted as OBS, final simulated HONO concentration with ground surface density of 1.7/H is denoted as REV, and HONO with ground surface density of 2.2/H is denoted as 2.2/H.

[General Comment]: 1.3 Lines 233-236: HNO3 and HCI deposition velocities could be highly uncertain. Please see Jaegle et al. 2018. Please give more details on how HNO3 and HCI deposition velocities were parameterized in the model and how uncertain they are.

[Response]:

The contribution of HONO from acid displacement (5.5% for HNO₃ and 0.7% for HCI) is far less than the heterogeneous reaction on the ground surface (86.2%). The dry deposition velocities of HNO₃ and HCI in CMAQ is calculated using a big-leaf resistance model (Wesely, 1989; Wesely, 2007). The total resistance to dry deposition (which is the inverse of v) is calculated as the sum of the bulk surface resistance, R_{surf}, the aerodynamic resistance, R_a, the quasi-laminar boundary layer resistance, R_{bc}. Rsurf includes the influence of vegetation, canopy, ground, etc. Considering the average temperature in our study is around 1.6 °C which is above the threshold value for low temperatures as suggested in Jaegle's method (-2°C) (Jaeglé et al., 2018), we used the default mechanism of the surface resistance in CMAQ without modification. However, our model calculated deposition velocities fall within the reported ranges of values (Jaeglé et al., 2018). For example, the modeling value of v(HNO₃) falls within the range of 3×10^{-4} cm s⁻¹ to 4.1cm s⁻¹ with an average velocity of 0.5 cm s⁻¹. The

simulated value of v(HCl) falls in 1×10^{-4} cm s⁻¹ to 0.1 cm s⁻¹ with an average velocity of 0.02 cm s⁻¹.

$$v = (R_{surf} + Ra + R_{bc})^{-1}$$

 $R_{bc} = \frac{5}{v(\frac{k}{d})^{\frac{2}{3}}}$

v is the cell friction velocity (m/s); k is kinematic viscosity(cm²/s); d is molecular diffusivity (cm²/s);

We clarified this point in the revised manuscript as follows.

Page 6 Line 211-214:

The dry deposition velocities of HNO₃ and HCl in CMAQ is calculated using a big-leaf resistance model (Wesely, 1989; Wesely, 2007). Calculated deposition velocities fall in the reported ranges of values by Jaeglé et al. (2018) (details in Supplemental Information).

[General Comment]: 1.4 Please double check the reference lists. Change it to ACP format. Cite the final ACP papers, not ACPD, e.g. Line 853, Line 977.

[Response]:

We have updated all references and changed ACPD to the final ACP format.

Other comments

[Other Comment]: 1.5 Table 2, 8a and 8b: Please change S/Vg to 1.7/H.

[Response]:

We have changed the S/V_g to 1.7/H in Table 2 in accordance with the reviewer's comments.

[Other Comment]: 1.6 Line 267: What is "existing heterogeneous hydrolysis of NO2"?

[Response]:

We have removed "existing" and clarified "heterogeneous hydrolysis of NO2" as follows:

Page 7, Line 242-249:

We performed two different simulations using CMAQv5.3 for December 7-22, 2015. One simulation denoted by "ORI" used the gas-phase HONO chemistry in CB6r3 along with the heterogeneous hydrolysis of NO₂ in CMAQv5.3. The implementation of the heterogeneous hydrolysis of NO₂ in CMAQ has previously been described by Sarwar et al. (2008). They accounted for aerosol surface area as well as the ground surface area provided by leaves and building and other structures. Leaf area was estimated using 2 \times LAI/H (LAI is the leaf area index and H is the surface layer height in the model) while building and other structure surface areas were estimated using 0.002 \times PURB (PURB = percent urban area of a grid-cell in the model).

[Other Comment]: 1.7: Please show how NMB is calculated here.

[Response]:

We have added the following text to show how we calculate NMB.

Page 7, Line257-259:

Normalized Mean Bias (NMB)= $100 \times \sum (M_i - O_i) / \sum O_i$, O_i is observed HONO concentration, and M_i is the simulated HONO concentration in model (Jaeglé et al., 2018).

[Other Comment]: 1.8 Line 336: What additional sources could that be?

[Response]:

Aerosol indirect effect (Xing et al., 2017), soil emission (Oswald et al., 2013b), the photolysis of nitrate (Romer et al., 2018) and other unknown sources may cause the underestimation of the daily HONO concentration. We have mentioned these sources separately inL223, L327, L348, L496, SI (L110-L132). In order to avoid repetitive discussion, only the cited sources are added as follows:

Page 8, Line 306-308:

It also increases day-time concentrations, however, predicted values are substantially lower than the observed data, which suggests that additional processes (Oswald et al., 2013a; Xing et al., 2017; Romer et al., 2018) are needed to close the gap between observed and predicted day-time HONO concentrations.

[Other Comment]: 1.9 Fig.1: Please explain what the error bars are.

[Response]: We have added the following text in line 300 to explain error bars: Page 9, Line 313: Error bars represent 5%-95% values of all HONO concentrations.

[Other Comment]: 1.10 Line 365: Please provide values for vehicle exhausts.

[Response]: We have added the reported values (0.001-0.008) for vehicle exhausts as follows: Page 10, Line 332: The observed HONO/NO₂ ratios ranging between 0.003 and 0.15 are much higher than reported values in the vehicle exhausts (0.001-0.008) which suggests that HONO formation is governed mainly by the secondary production (Kirchstetter et al., 1996; Kurtenbach et al., 2001).

[Other Comment]: 1.11 Line 464: As shown in Fig. 1, daytime HONO was significantly underestimated in the model. Please discuss how this affects OH concentrations.

[Response]:

OH concentration is affected not only by the daytime HONO concentration but also by the photolysis rate of HONO. In REV case, we only considered the HONO heterogeneous sources which increase OH concentration as we discussed in section 3.3. Daytime OH concentrations can potentially be higher than the predicted values since daytime HONO concentrations are lower than observed data. However, the aerosol indirect effect may reduce OH concentration as it may slow the HO_x formation rate from HONO. A future study incorporating aerosol indirect effect is needed to improve the representation of HONO chemistry in CMAQ and examining its impact on OH concentration. We revised the text as follows:

Page 14 Line 462-465:

The daytime underestimation of HONO in Fig.1 can potentially lead to the underestimation of OH concentration; however, the aerosol indirect effect may lower the OH concentration by reducing the rates of HO_x formation. Therefore, more accurate HONO simulation needs to consider more complex and significant atmospheric chemical processes.

[Other Comment]: 1.12 Fig. 6: It should show the REV case instead of ORI case, as the REV cases are with HONO updates, the main focus of this study.



[Response]:

As the reviewer suggested, we have replaced figures in ORI cases to REV cases in the revised manuscript as follows.





Fig. 6 Spatial distributions of monthly averaged (a) HONO, (b) sulfate, (c) nitrate, (d) ammonium, (e) anthro-VOC-derived SOA, (f) and bio-VOC-derived SOA concentrations simulated with **REV** and the differences (**REV-ORI**) between the two simulations in December 2015.