

Response to interactive comment on “Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China” by Hui Yun et al. from Anonymous Referee #3

The reviewers’ comments are italicized followed by our responses and changes in manuscript shown in blue and red, respectively. And the corrections are also marked as red color in the revised manuscript.

The manuscript “Nitrate formation from heterogeneous uptake of dinitrogen pentoxide during a severe winter haze in southern China” by Yun and Co-authors uses observations of aerosol and gases and model results to study the contribution of heterogeneous chemistry via N_2O_5 to nitrate formation in $PM_{2.5}$ during severe winter haze episodes.

The measurements were carried out in the rural site of Heshan, located near the Perl River Delta in Southern China. In addition to a comprehensive suite of measurements, Yun and co-authors present the results of a chemical box model to estimate daytime HNO_3 mixing ratios. The box model was constrained by observation and its results were used to assess the importance of nighttime N_2O_5 over daytime HNO_3 as source of secondary aerosol nitrate.

The paper is well written, well structured and conveys results of interest for the scientific community. However, the method section (as pointed out by Referees #1 and #2 as well) has to be improved and that some more discussion on 1)uncertainties, 2)sensitivity test of the model and 3)boundary layer dynamic needs to be added before publication.

Response: The description of the measurement method has been rewritten and some related references were added. A table presenting the detection limit and uncertainties for CIMS and other related instruments was added. Sensitivity tests were conducted by reducing 10% of the input concentrations of NMHCs to check the variation of the rate of $OH+NO_2$ during the daytime. We have added discussion on the role of boundary layer dynamics.

1) The description of the measurements should include the detection limits and the uncertainties, in particular for the species that were used to constrain the chemical box model.

Response: Table 1 with detection limits and measurement uncertainties was added in the revised manuscript.

Table 1. Technique, limit of detection, and uncertainty of measuring instruments for trace gases and aerosols.

Species	Measurement techniques	Uncertainty	Detection limits
$\text{ClNO}_2, \text{N}_2\text{O}_5$	CIMS	$\pm 25\%$	6 pptv
HONO	LOPAP	$\pm 20\%$	7 pptv
O_3	UV photometry	$\pm 5\%$	0.5 ppbv
NO	Chemiluminescence	$\pm 20\%$	0.06 ppbv
NO_2	Photolytical converter & Chemiluminescence	$\pm 20\%$	0.3 ppbv
NO_y	MoO catalytic converter & Chemiluminescence	$\pm 5\%$	<0.1 ppbv
SO_2	Pulsed-UV fluorescence	$\pm 5\%$	0.1 ppbv
CO	IR photometry	$\pm 5\%$	4 ppbv
NMHCs	GC-FID/MS	$\pm 15\text{--}20\%$	20-300 pptv
OVOCs	DNPH-HPLC	$\pm 1\text{--}15\%$	20-450 pptv
$\text{PM}_{2.5}$	MAAP	$\pm 10\%$	$<0.1 \mu\text{g m}^{-3}$
Aerosol Ions	GAC-IC	$\pm 10\%$	$0.01\text{--}0.16 \mu\text{g m}^{-3}$
OC/EC	RT-4 SUNSET	$\pm 4\text{--}6\%$	$0.2 \mu\text{g cm}^{-2}$

2) There should be a discussion in the main text or in the SI about the sensitivity of the box model to the uncertainties of the measurements (this, for example should be communicated with uncertainty bars in figure 7).

Response: Sensitivity tests were carried out by reducing the input concentrations by 10% to check the deviation of the average daytime (7:00-17:00) rate of $\text{OH}+\text{NO}_2$ reaction. The method of Relative Increment Reactivity (RIR) was applied here as the index of the sensitivity (see the following equation). R_1 means the original rate of $\text{OH}+\text{NO}_2$ reaction, while $R_{0.9}$ means the rate of $\text{OH}+\text{NO}_2$ reaction after the input concentrations were reduced to 90%.

$$\text{RIR} = \frac{(R_1 - R_{0.9})/R_1}{10\%}$$

NMHCs were categorized into four groups, including C4HC, LRHC, AROM and OLF, which

represent alkanes with ≥ 4 carbons, hydrocarbons with low reactivity (including ethane, propane and benzene), reactive aromatics (including all aromatics except for benzene), and reactive olefins (including all alkenes), respectively (Xue et al., 2014). From the following figure, the simulated rate of OH+NO₂ reaction was most sensitive to HONO (RIR of 0.6-0.8), followed by NO_x (RIR of 0.2-0.5) and OVOCs (RIR of 0-0.2).

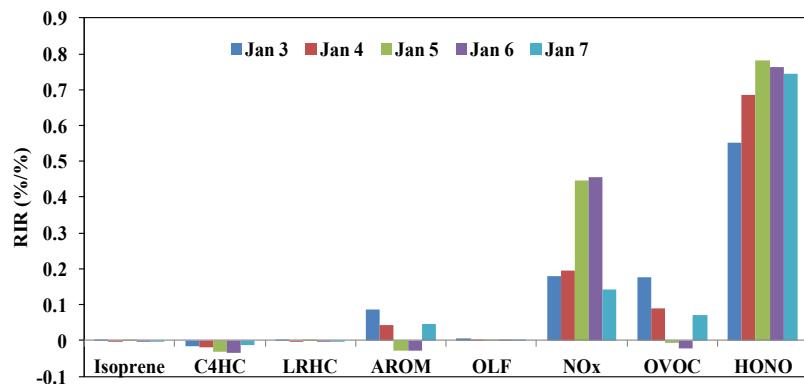


Figure 1. OBM-calculated RIRs to check the sensitivity of the average daytime (7:00-17:00) rate of OH+NO₂ reaction to the uncertainties of the measured input data.

Xue, L., Wang, T., Louie, P. K. K., Luk, C. W. Y., Blake, D. R., and Xu, Z.: Increasing external effects negate local efforts to control ozone air pollution: A case study of Hong Kong and implications for other Chinese cities, *Environmental Science and Technology*, 48, 10769-10775, 10.1021/es503278g, 2014.

Line 211-214: Sensitivity tests were carried out by reducing the input concentrations by 10% to check the deviation of the average daytime (7:00-17:00) rate of OH+NO₂ reaction. The simulated rate of OH+NO₂ reaction was most sensitive to HONO, followed by NO_x and OVOCs (see Text. S1 and Fig. S2).

3) In paragraph 2.2 a discussion about interference for species with the same nominal mass as I(N₂O₅)⁻ and I(ClNO₂)⁻ should be added. How much contribution from other species would Yun and Co-authors expect? If it was not negligible how would change the results from the box model/comparison?

Response: To the best of our knowledge, no interference was reported for I(N₂O₅)⁻ at 235 m/z in current publications. Besides, we compared ambient measurements of N₂O₅ using the

quadrupole CIMS and NOAA-CRDS in 2016 (Wang et al., 2016), and N_2O_5 measured by CIMS and CRDS matched well with each other (slope=0.99, $R^2=0.93$). Recent ambient measurement of ClNO_2 in Beijing with a Tof-CIMS showed that $\text{I}(\text{HNO}_3)(\text{H}_2\text{O})^-$ may cause $\sim 10\%$ interference of ClNO_2 at 208 m/z (Breton et al., 2018), but this kind of interference cannot be resolved by a quadrupole CIMS. For the quadrupole CIMS, we checked the correlation between the measured signal at 208 m/z ($\text{I}^{35}\text{ClNO}_2^-$) and at 210 m/z ($\text{I}^{37}\text{ClNO}_2^-$) during the present field campaign. The slope (0.317, $R^2 = 0.99$) was very close to the theoretical value of chlorine isotopic ratio of 0.32. Overall, we do not expect large ($>10\%$) interference to ClNO_2 and no known interference is known to the N_2O_5 signal.

Breton, M. L., Hallquist, Å. M., Pathak, R. K., Simpson, D., Wang, Y., Johansson, J., Zheng, J., Yang, Y., Shang, D., and Wang, H.: Chlorine oxidation of VOCs at a semi-rural site in Beijing: significant chlorine liberation from ClNO_2 and subsequent gas-and particle-phase Cl–VOC production, *Atmospheric Chemistry and Physics*, 18, 13013–13030, 2018.

Wang, T., Tham, Y. J., Xue, L., Li, Q., Zha, Q., Wang, Z., Poon, S. C., Dubé, W. P., Blake, D. R., and Louie, P. K.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, *J. Geophys. Res. Atmos.*, 121, 2476–2489, doi: 10.1002/2015JD024556, 2016.

4) *Relative humidity (RH) is known to affect measurements carried out with I-CIMS. Was the inlet used in this study humidified? Was the RH controlled/monitored during zero measurements? How could the zero affect the box model results (e.g., over/under estimation of $\text{N}_2\text{O}_5/\text{ClNO}_2$)? What are the biases that the 6 m sampling line could generate in their results?*

Response: Similar to our previous practice, the effect of RH on the sensitivity of N_2O_5 and ClNO_2 was measured by altering the RH in calibration during the present campaign (see below figure). The sensitivity of N_2O_5 and ClNO_2 in ambient measurement was corrected based on the RH monitored in real-time in the CIMS inlet.

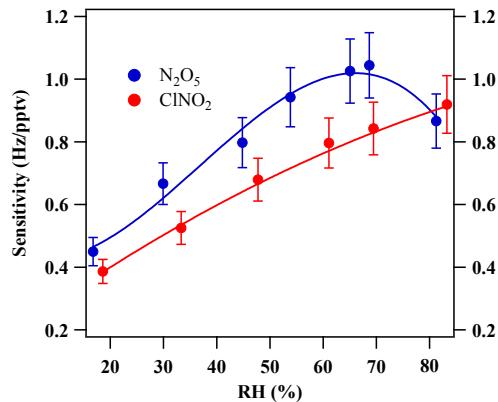


Figure 2. The sensitivity of CIMS as a function of RH for (a) N_2O_5 at 235 m/z and (b) ClNO_2 at 208 m/z at Heshan site.

The inlet in this study was not humidified. Since the sampling period in this study was humid enough ($\text{RH} > 40\%$) to form the reagent $\text{I}(\text{H}_2\text{O})^-$, a humidified inlet was not necessary.

The RH was not controlled but monitored during zero (and ambient) measurements.

The zero signals were subtracted from the total signals during data processing, thus they do not affect final data and thus modeling results.

The 6 m sampling tubing was replaced every day in late afternoon. The wall loss of N_2O_5 was measured by injecting synthetic N_2O_5 each time before and after replacing the sampling tubing. The measured wall loss of N_2O_5 was $\sim 10\%$ for the clean tubing and increased to $\sim 40\%$ after one day's sampling. Because our analysis mainly focused on data in the first few hours of evening, the loss was insignificant and thus was not corrected in our final data. However, this bias can be important at later period before tube replacement.

In the revised manuscript, we have added description on dependence of sensitivity on RH and how to correct it and also the above figure as Fig. S1. We also added the following sentences.

Line 134-137: The average sensitivity of N_2O_5 and ClNO_2 was 0.9 ± 0.3 and 0.7 ± 0.2 Hz pptv⁻¹, respectively. The dependence of the sensitivity on the relative humidity was measured during the field study (see Fig. S1) which was used to correct for the RH effect based on the measured ambient RH values.

Line 145-150: The loss of N_2O_5 on the tubing wall was checked on site by injecting N_2O_5 into

the ambient air before and after the tubing replacement, and the loss was around 10% in the “clean” tubing and increased to nearly 40% in the next afternoon. Because our analysis mainly focused on data in the first few hours of evening, the loss was insignificant and thus was not corrected in our final data. However, this bias can be important at later period before tube replacement.

5) *The boundary layer plays a significant role in the time evolution of the concentrations of nitrate in the particle. Yun and Co-authors make little to no mention of its role. For example, one might expect that particulate nitrate would increase also in the early morning hours due to the contribution of the residual layer during the mixing. This doesn't seem to happen in the observations presented in this work. May the Authors discuss why that would be the case?*

Response: This point was also raised by other referees. The description of boundary layer dynamics has been added in the revised version. The absence of nitrate increase in the early morning in our study is consistent with previous observations at the site (Yue et al., 2015). It may be explained by enhanced evaporation of NH_4NO_3 to HNO_3 and NH_3 due to increased temperature.

Yue, D., Zhong, L., Zhang, T., Shen, J., Zhou, Y., Zeng, L., Dong, H., and Ye, S.: Pollution properties of water-soluble secondary inorganic ions in atmospheric $\text{PM}_{2.5}$ in the Pearl River Delta region, *Aerosol Air Qual. Res.*, 15, 1737-1747, 2015.

6) *An increase in particulate nitrate concentrations (as well as $\text{PM}_{2.5}$) could also be due to a dilution effect (same magnitude of aerosol sources but reduced volume in which the aerosols are mixed). I recommend adding a few sentences explaining how the mixing of the residual layer in the morning hours could affect the results presented here.*

Response: The following discussion was added in the manuscript.

Line 242-250: Apart from chemical reactions, the evolution of the Planetary Boundary Layer (PBL) also affects the concentrations of trace gas and aerosols. The height of PBL generally decreases after sunset with the faster drop in temperature of land, which could lead to the accumulation of primary pollutants (and secondary pollutants) at surface if significant local sources are present. For example, on the night Jan 4-5 (see Fig 5), the CO and NO_y levels

increased between 18:00-19:00 with enhancement of ClNO_2 and nitrate, indicative of accumulation of primary emissions, but afterward the primary pollutants decreased for three hours while the latter two continued to increase due to the nighttime chemical process.