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Comment on acp-2021-104

Anonymous Referee #2

Referee comment on "Winter $ClNO_2$ formation in the region of fresh anthropogenic emissions: seasonal variability and insights into daytime peaks in northern China" by Men Xia et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-104-RC2, 2021

Review of *Winter observations of ClNO2 in northern China: Spatiotemporal variability and insights into daytime peaks*

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General Comments:

This manuscript describes the measurements of ClNO2 and N2O5 at three different locations on the North China Plain (NCP) between 2017 and 2018 and assesses their resulting impact on the radical budget. The three locations are to be representative of an urban, a rural and a mountaintop location. The pollution levels at the rural location are more typical of what one might expect at semi-urban to urban locations so this could be better categorized (discussed further below). The authors show the novel finding of higher ClNO2 in the summer than winter seasons with daytime peaks. The authors demonstrate that the decreased wintertime ozone production coupled with increased loss of NO3 to fresh NO emissions as well as dry wintertime conditions result in lower ClNO2 mixing ratios in the wintertime vs the summertime. An assessment of N2O5 uptake coefficients supports this. This study illustrates that under certain conditions ClNO2 can be an important daytime source of Cl radicals. I feel the authors should be a little more forward in their abstract and conclusion in emphasizing the reasons for the lower wintertime ClNO2 than summer and not just wording it as the "observations". This is an important finding as these measurements were performed in more polluted conditions than many of the ClNO2 measurements in the literature. There are a few places (outlined below) where a little more detail would be helpful to give confidence in measurements without simply

citing other publications. Their analysis is well reasoned and consistent with the observations. Overall, the paper is well written and the content is suitable for publication in Atmospheric Chemistry and Physics after addressing the following points.

Specific Comments:

Table 1: A column showing the ranges of NOx and O3 observed at each of locations would be useful. Showing it summarized here would give the reader a simple indication of the ranges observed at each site. As mentioned before I do not really believe that the categorization of Wangdu site as rural is appropriate given the pollution levels described in the text. Perhaps polluted rural or remote polluted would work.

P5 L189: Were these multi-point calibrations or simply span checks? I believe from the SI they were multi-point but it would be helpful to clarify.

P5 L190: Were these backgrounds only conducted once daily? This seems rather infrequent as many CIMS groups zero their instruments on a significantly more frequent cycle to capture instrument background variability, which can be significant depending on the compound of interest. If they were only done once daily was it always at the same time of day? This should be stated.

P5 L192: How stable was the I(H2O)- signal during the campaign? It's unclear to me whether or not the authors (I couldn't seem to find it in the Xia et al 2019 paper either) added water vapour to the IMR or if the I(H2O)- peak was simply a result of ambient humidity. If it was added, it should be stated and how much. What were the typical count rates for this peak? I ask only because I know some versions of the THS CIMS have a preamp that can saturate around 200-250 kHz and thus some of the changes in ambient humidity may not be captured.

P5 L195: It is a little unclear to me which sensitivities are for which compounds. Did they both vary between 0.9-2.2 x 10^-5? For clarity these should be separated, i.e. N2O5 sensitivities varied between a and b, ClNO2 varied between c and d. Also the units of Hz/Hz/pptv should be expressed as pptv^-1. A better way for comparison with much of the CIMS literature would be to multiply by 1E6 normalized counts per second (ncps) removing the exponential and giving the units of ncps/pptv.

P6 L212: Were the ACSM and MARGA sampling from a common inlet? Was there any size selection (e.g. cyclone) on the front end? A line about this would help strengthen the argument that the missing chloride was simply refractory Chloride containing particles.

P6 L230: What VOC's were used in the calculation of kNO3? Was it simply the compounds listed in the table in the supplementary (S3)? Either way this table should likely be modified (or a separate table created) to give the actual compound names and formulas as opposed to simply showing their model parameter name. Depending on the completeness of the VOC species measured, kNO3 could very well be underestimated. A table summarizing the rate constants used (it could be in placed in the supplementary) would also be helpful or at a minimum a citation to the rate constants used.

P8 L268: Is the assumption of a constant 2 ppm CH4 mixing ratio reasonable for both the high and low coal burning seasons? I don't have a feeling for what the difference would be and I'm little surprised it wasn't measured as part of the list of VOC's.

P7 L484: I feel like a plot showing the NOx (or even just NO) data would be of value. Perhaps Figure 1 could be modified to add this as a trace. While it is well described in the text it would be of value to the reader to see the trends overlaid with the other time traces.

Figure 2: It would be easier to visualize the winter/summer comparison contrast with the plots overlaid on each other. If the axis could also be consistent across the measurement locations, it would make it easier for the reader to discern the differences between the measurement locations.

P9 L321: The presence of elevated ClNO2 with high NO levels suppressing N2O5 formation is a really important observation from this work and should probably be highlighted more than it is. The authors should consider including a figure so that the reader can better visualize this. Perhaps one with a couple of panels showing two or 3 different elevated ClNO2/NO events.

Figure 3: I really like this figure but there are perhaps a couple of references missing. I know of at least 1

(McDuffie, E. E., Womack, C. C., Fibiger, D. L., Dube, W. P., Franchin, A., Middlebrook, A. M., Goldberger, L., Lee, B. H., Thornton, J. A., Moravek, A., Murphy, J. G., Baasandorj, M., and Brown, S. S.: On the contribution of nocturnal heterogeneous reactive nitrogen chemistry to particulate matter formation during wintertime pollution events in Northern Utah, Atmos. Chem. Phys., 19, 9287–9308, https://doi.org/10.5194/acp-19-9287-2019, 2019.)

I encourage the authors to go back through the literature to make sure that no other measurements have been missed.

P15 L527: Any idea where the source of BrCl might be? Was Br2 observed during any of the campaigns?

Supplementary S1.1

It is not true that there is no known interference for N2O5 at m/z 235. Veres et al (2020) have shown that in the marine boundary layer that hydroperoxymethyl thioformate (a DMS oxidation product) does overlap with N2O5 in the I- CIMS spectrum at m/z 235. While this interference is not likely to be present in this case, some discussion of it is warranted. Was DMS one of the VOC's measured? It would also be useful to include a table showing the masses measured with their corresponding integration times to demonstrate the instruments duty cycle.

Citation: *Veres, P. R., Neuman, J. A., Bertram, T. H., Assaf, E., Wolfe, G. M., Williamson, C. J., Weinzierl, B., Tilmes, S., Thompson, C. R., Thames, A. B., Schroder, J. C., Saiz-Lopez, A., Rollins, A. W., Roberts, J. M., Price, D., Peischl, J., Nault, B. A., Møller, K. H., Miller, D. O., Meinardi, S., Li, Q., Lamarque, J.-F., Kupc, A., Kjaergaard, H. G., Kinnison, D., Jimenez, J. L., Jernigan, C. M., Hornbrook, R. S., Hills, A., Dollner, M., Day, D. A., Cuevas, C. A., Campuzano-Jost, P., Burkholder, J., Bui, T. P., Brune, W. H., Brown, S. S., Brock, C. A., Bourgeois, I., Blake, D. R., Apel, E. C., and Ryerson, T. B.: Global airborne sampling reveals a previously unobserved dimethyl sulfide oxidation mechanism in the marine atmosphere, Proceedings of the National Academy of Sciences, 117, 4505-4510, 10.1073/pnas.1919344117, 2020.*

Figure S6: I find the number of colours used on this plots a little overwhelming. Perhaps you could recycle the same two colours per stacked plot as there is only one trace per axis?

Figure S7: I think these panels would be more informative/useful if the plots were binned

by RH as opposed to simply being coloured by RH. It would more strongly demonstrate the higher corrrelations at high RH values. If this resulted in too many plots the results could be summarized in a table with a single exemplar plot.

Technical Corrections:

P4 L142: I assume this should read "*during the heating period"*?

P10 L363-364: The wording appears reversed; I'm assuming it's a simple translation issue. The decrease in SO2 should be due to the reduced effect of coal-fired power.