Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2022-386-RC1, 2022

Comment on acp-2022-386

Anonymous Referee #1

Referee comment on "Seasonal variation in nitryl chloride and its relation to gas-phase precursors during the JULIAC campaign in Germany" by Zhaofeng Tan et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-386-RC1, 2022

This manuscript presents observations of nitryl chloride (ClNO2), along with several precursor compounds, measured over several seasons at 50m above the surface at a rural site in western central Europe. ClNO2 is an important source of the powerful atmospheric oxidant atomic chlorine, and has been shown to demonstrate significant spatial variability due to its relatively complex production mechanism. Although many measurements have been made of ClNO2 at surface locations, the reduced concentrations close to nitric oxide (NO) emissions mean it is likely to be more efficiently produced in the nocturnal residual layer, from where subsequent mixing will allow it to influence surface photochemistry on the following day. The observations presented here are predominantly from within the nocturnal residual layer, and thus represent a significant contribution to the growing body of data on mid-continental ClNO2.

The authors present the ClNO2 data, and use co-located measurements of ClNO2 precursors to calculate a ClNO2 production efficiency to compare across the measurement period. This is a useful parameter on which to focus, as the complex nature of ClNO2 production results in significant variability, making it often difficult to constrain in models. The authors then use a chemical box-model to explore the effects of ozone (O3), nitrogen dioxide (NO2) and temperature on ClNO2 production across the experienced parameter space. This analysis is insightful; however, I feel the authors need to do more to demonstrate the sensitivity of their analysis and conclusions to other important parameters that control ClNO2 production. In particular, the sensitivity to the loss rate of the nitrate radical (NO3) to reaction with volatile organic compounds (VOC) warrants a more detailed sensitivity analysis than that presented in Fig. S9. The correlation between measured particulate chloride and calculated ClNO2 production efficiency should also be shown to support the argument made that this is not a limiting factor. Overall, the manuscript is well written and represents a valuable contribution to the field, and warrants publication in ACP once the following comments have been addressed.

- As particle surface area and chloride content are key factors in the production of ClNO2,

it would be useful for the reader if these data were presented somewhere in the paper or supplement and discussed in more detail. In section 3.4 the authors argue that ClNO2 production efficiency is not limited by particle chloride content, but I feel this statement would be better supported if the particle data were shown. Multiple factors can influence both the uptake of N2O5 to particles and the subsequent yield of ClNO2, such as chloride molarity and liquid water content. The authors acknowledge that they do not have sufficient data to fully characterise the particle phase, however, more could be done to demonstrate the sensitivity of the system to these parameters (e.g., McDuffie et al. 2018).

- As with comment 1, the conclusions of the work would be better supported if the sensitivity to the gas phase loss of NO3 to VOC reaction was demonstrated (beyond that shown in Fig. S9). In the modelling work presented in Sect. 3.5 the authors assume a constant NO3 reactive loss rate (kNO3) of 0.001 s-1. As this work is carried out across both summer and winter seasons, and due to the strong biogenic control of the k NO3, it seems unlikely that this constraint is valid. Observations of kNO3 at another site in Germany have shown kNO3 values approaching 0.3 s-1 (Liebmann et al. 2018). Although the authors do carry out a set of simulations with a value of kNO3 = 0.0005 s-1, a more thorough assessment of the model sensitivity to this parameter would better support the authors assumption that it plays a minor controlling role.
- It would be useful if the observations overlaid on the model isopleths in Fig. 6 (a) and (b) showed the observed ClNO2 mixing ratios to compare with the model values. Although the purpose of the modelling is not to recreate the observations, rather to investigate the chemical sensitivities of the system, it would provide confidence in the model's ability to accurately represent the chemistry if the general observational trends were recreated.

References

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