

## Comment on acp-2022-386

Anonymous Referee #2

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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-RC2>, 2022

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Tan et al. report the measurements of ClNO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and related parameters for three seasons in 2019, obtained during the Jülich Atmospheric Chemistry Project (JULIAC) campaign in Germany. An important result of this study is the variations of ClNO<sub>2</sub> production efficiency in different seasons, which are most sensitive to the availability of NO<sub>2</sub> and increase with the decreasing temperature. This finding is valuable as it enhances our understanding on the dependence of ClNO<sub>2</sub> formation on the availability of NO<sub>2</sub> and O<sub>3</sub> in Europe. Overall, the manuscript is well presented, however, I feel that the importance of the study and discussion of results can be further strengthened and improved. My comments are as below.

- Line 19: Delete the word 'ion' (same for line 52)
- Line 22: Please specify the date instead of using 'one night in September'
- Line 58: The yield for ClNO<sub>2</sub> ( $\delta_{\text{ClNO}_2}$ ) can be equal to 0 or 1, therefore, it should be  $\leq$
- Line 62–63: 'The forward and back reactions constitute a fast thermal equilibrium between NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> that is established within a minute at room temperature.' Revise this sentence by justifying how the equilibrium can be established within a minute. Is this based on the authors' calculation or from the literature? The concentration of NO<sub>2</sub> can also influence the equilibrium of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub>
- Line 75: ClNO<sub>2</sub> usually present at night but not always is the case. Suggest to delete the word 'only'
- Line 123: The authors should highlight in the introduction or conclusion why investigation on the seasonal variation of ClNO<sub>2</sub> concentrations and its formation are scientifically important
- Line 168: The concentration of Cl<sub>2</sub> in the cylinder used for calibration is 5 ppmv ( $\pm 5\%$ ). As we know Cl<sub>2</sub> is a very reactive gas that can be lost on surfaces. Is this  $\pm 5\%$  a reliable value? The authors should provide details on whether they have quantified the output concentration of Cl<sub>2</sub> from the cylinder and/or consider the potential loss of Cl<sub>2</sub> in the calibration system, e.g. the loss on the regulator of the cylinder or tubing? This is crucial for the determination of ClNO<sub>2</sub> calibration factor and estimation of measurement uncertainty, which can affect the reported levels of ClNO<sub>2</sub> and maybe the conclusions of this study
- Line 279: Specify the humidity (RH) of the humidified chamber air
- Line 300: 'no corrections are needed for the interpretation of ClNO<sub>2</sub> measurements'. I

am wondering if this variation has been considered in the estimation of the measurement uncertainty.

- Line 367: As shown in this figure, the ClNO<sub>2</sub> and related parameters are separated into long-range transport and region transport. The classification of long-range and regional has been described in the text. A lacking information here is the 'age' of different air masses. My question is will the 'age' of air masses play important role in the observed levels of ClNO<sub>2</sub>? I think this should also be addressed in the discussion since the 'age' of air mass may affect the NO<sub>2</sub> and O<sub>3</sub> concentrations
- Line 387: Section 3.3 describes the nocturnal vertical stratification and summarize that the JULIAC inlet (50 m) is most often located within the nocturnal boundary layer and on top of the surface layer. What does it means by most often? At this point, I am not so convince yet that the ClNO<sub>2</sub> are often measured above the nocturnal boundary layer with the discussion and provide only one day example (Fig.4). Please provide more evidence (of different seasons) and discussion in the main text or supporting info to support this argument. This is an important information for the validity of the calculation made from Eq7 (Line 465)
- Line 541–542: The measured aerosol surface area is an essential parameter for the calculation. This should be included in the supporting info. Can the authors justify why setting the aerosol surface area to constant value in the model since they have measurement data?
- Line 577–578: Temperature also plays an important role for the value of the ClNO<sub>2</sub> production efficiency due to the shift of the equilibrium between NO<sub>3</sub> to N<sub>2</sub>O<sub>5</sub>. The temperature shift may also affect the humidity which has been shown in previous studies to promote N<sub>2</sub>O<sub>5</sub> uptake and production of ClNO<sub>2</sub>. How can the authors separate the effect of humidity with the effect of temperature?
- Line 691: Please provide a proper reference here rather than citing the general website of IUPAC
- Supporting Information Figure S2: Explain why the response of ClNO<sub>2</sub> decrease with H<sub>2</sub>O concentration (a)? Show the correlation coefficient for this linear fitting (b) as the points are spreading wide from the fitted-line.