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Comment on acp-2021-310

Anonymous Referee #1

Referee comment on "Urban inland wintertime N_2O_5 and $ClNO_2$ influenced by snow-covered ground, air turbulence, and precipitation" by Kathryn D. Kulju et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-310-RC2>, 2021

Kulju et al. present measurements of N_2O_5 and $ClNO_2$ in Kalamazoo, Michigan, from January - February 2018. This paper follows up on earlier papers on the same data set (McNamara et al., ACS Earth and Space Chemistry, doi 10.1021/acsearthspacechem.0c00317, 2021 and Chen et al., ACS Earth and Space Chemistry 3(5), 811-822, 2019). In this paper, the authors focus on how meteorological events (fog, snow and rain) and turbulence affected N_2O_5 and $ClNO_2$ concentrations, which are interesting and understudied topics. Low mixing ratios of N_2O_5 and $ClNO_2$ during precipitation events have been observed before; this paper aims to extend these observations with simultaneous measurements of friction velocities using a sonic anemometer.

The paper is written well and thorough in citing related work and appropriate references. However, the analysis is not robust.

In general, concentrations of molecules in air change because of chemical production (P), chemical loss (L), and transport (E) terms. Kulju et al. present an analysis that essentially neglects the P and E terms and attributes observed rates in concentration changes entirely to L. It is inappropriate to neglect transport during precipitation events as a possible reason for concentration changes via rapid vertical mixing - see, for example, Winkler et al. Radiat. Environ. Biophys., 40, 115-123, 10.1007/s004110100096, 2001, who observed this effect for radioactive tracers. Further, the L term is, incorrectly, attributed in its entirety to scavenging by precipitation even though other reactions may contribute such as the indirect loss of N_2O_5 via NO_3 chemistry (see, for example, the 'steady state lifetime' approach pioneered by Brown et al., J. Geophys. Res., 108, 4539, 10.1029/2003JD003407, 2003, and J. Geophys. Res., 114, D00F10, 10.1029/2008jd011679, 2009 (equation 6)). It would have been useful for the authors to explore the use of box models to better constrain the precipitation loss term. Unfortunately, it does not appear that the necessary auxiliary data (such as concentrations of NO and NO_2) are available to extend the analysis in this direction.

As already stated, the data set has already been partially described elsewhere, such that

this manuscript's value rests largely with its analysis, which is in poor shape. Considerable and major revisions would be required to make this manuscript acceptable for publication. I hence recommend rejection of this article, though it would be acceptable in my opinion for the editor to reconsider a revised version if the authors believe they can address the issues raised below.

Major comments

(1) One cannot simply compare N_2O_5 (and $ClNO_2$) abundances with meteorological conditions as presented in this manuscript (rain, snow, fog - Figure 2, lines 215-216; turbulence - Figure 4, line 360) unless the rates of NO_3 production, $P(NO_3) = k_4[O_3][NO_2]$, the NO_3 loss rates to VOCs and NO, temperature and $[NO_2]$ (which affect N_2O_5 concentration via equilibrium K_3), and aerosol surface area chloride abundances were of similar magnitude for these events. It is not at all likely that all of these variables were identical. In fact, Table 3 shows that temperatures were very different, indeed.

(2) The calculation of "gas-phase scavenging coefficients" (Table 2) is questionable as one needs to assume the absence of production and transport terms that also affect mole ratios. The examples cited (lines 280-283) are for molecules (SO_2 and NH_3) that are relatively unreactive and are mainly primary in origin, but that is not the case for $ClNO_2$ and certainly not for N_2O_5 . Furthermore, the analysis is not robust because vastly different values are obtained depending over what time period the scavenging coefficients are calculated. For example, the data in Figure 3d show an increase in $ClNO_2$ mixing ratios during a rain episode - does this imply that the scavenging coefficient would be negative, and the rain is a source of $ClNO_2$?

(3) A large portion of the analytical methods, data set and analysis have been presented elsewhere. The authors should avoid unnecessary repetition (e.g., line 128 - section 2.2. N_2O_5 and $ClNO_2$ measurements using chemical ionization mass spectrometry (CIMS)). Rather than restating everything here, please simply cite the earlier paper(s) where possible, briefly summarize and note deviations from the earlier work.

(4) Throughout the manuscript, there are statements such as " N_2O_5 was fairly stable" and " $ClNO_2$ increasing steadily", which is grammatically incorrect since molecules cannot be referred to in this way, only their abundances. Consider rephrasing to "Mole ratios of N_2O_5 ..." or "Mixing ratio of $ClNO_2$ ".

(5) The manuscript would benefit from more data as only one of each snowfall, fog and rainfall events were described in the main paper yet more were observed (Figure S2). It is thus unclear how representative the events selected in the main manuscript are.

Specific comments

lines 153-54. "N₂O₅ and ClNO₂ were calibrated offline relative to Cl₂ as described in McNamara et al. (2019b)." A better way to say this is "the instrument response for N₂O₅ and ClNO₂ was calibrated ..." as a compound cannot be calibrated.

McNamara et al. (2019b) did not describe a calibration "relative to Cl₂" which would not be accurate since Cl₂ does not convert quantitatively to ClNO₂ (and cannot be used to calibrate for N₂O₅); instead, they described a titration method for N₂O₅ and thermal dissociation method for ClNO₂.

Please clarify how response factors were obtained in this work and state how accurate the derived calibration factors were.

N₂O₅ is not quantitatively transmitted through inlets. What was assumed for its inlet transmission efficiency? How uncertain and variable is the inlet transmission efficiency?

line 164. "Cl₂ was monitored" appears under the heading "N₂O₅ and ClNO₂ measurements ..." Please address this (minor) organizational issue.

line 226 Table 1, caption "±95% confidence interval". These are very small confidence intervals, too small to be credible in my opinion. How were the CI calculated? Do the values in the table take uncertainties in calibration factors and inlet transmission factors into account, or are they were merely calculated based on (averaged?) measurement precision?

line 253 / Figure 3. One of the axis titles is missing an oxygen.

For the snowfall case (Figure 3b) there appears to be a sustained loss throughout the episode with a consistent loss rate coefficient, but for the other cases (fog - 3c and rain 3d) the mole ratios sometimes increase during the episode. Please explain why this might be and how this affects the subsequent analysis.

line 280-281. "one hour fog period". Where all scavenging coefficients calculated over 1-hr long periods? How did the authors decide over what periods the loss rates should be calculated?

line 289 / Table 2. Uncertainty estimates should be added to Table 2. Please indicate (in Figure 3) over what periods the scavenging coefficients were calculated, as the derived values depend on it.

line 300. "Although precipitation rates were used to inform time periods used for calculations during the rainfall case, a more thorough characterization of scavenging with respect to precipitation rate and intensity is beyond the scope of this discussion." This would have been useful, imo.

line 360. Here, N_2O_5 mole ratios are compared to turbulence conditions. However, this analysis is not sound as it is not clear if the production from oxidation (via reaction of NO_2 with O_3 to NO_3 and subsequent reaction with NO_2), sinks (e.g., aerosol surface area, VOC abundance) and temperature (which shifts the $NO_2/NO_3/N_2O_5$ equilibrium and has a large effect on N_2O_5 concentration and loss rates) are identical for the high and low turbulence cases.

line 464. The N_2O_5 mixing ratios observed were small; how much additional nitrate would be expected if all of it were taken up (i.e., if the production of N_2O_5 via NO_3 , i.e., R4, were integrated)?

line 565 - strike "Received"

Figure S1 - please state uncertainty of the slope. What is the theoretical value based on? Note that the $^{37}Cl : ^{35}Cl$ isotope ratio is known to higher precision than shown.