

Interactive comment on “Measurement of ambient NO₃ reactivity: Design, characterization and first deployment of a new instrument” by Jonathan M. Liebmann et al.

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General Comments

This paper describes the first demonstration of NO₃ radical reactivity and its use in ambient air. Reactivity measurements for HO_x radicals have become a routine feature of instruments that measure ambient HO_x concentrations, yet no analogous instrument has been developed for NO₃ until now. As such, the paper represents an important contribution that will be of interest to the readership of AMT and that may serve as a seminal work that stimulates a new generation of atmospheric instrumentation. With one exception (see below), the development is thorough and convincing. It should be published in AMT.

The major general comment is the lack of discussion of secondary chemistry in the NO₃ flow tube. While the authors thoroughly consider the effect of the NO₃-N₂O₅ equilibrium and the potential production of NO₃ from NO₂ + O₃ in the flow tube, they do not comment (unless I missed this point) on the potential perturbation to the NO₃ reactivity by the addition of NO₃ itself to the ambient air in the flow tube. For example, at the lower end of the measurement range, $k = 0.005 \text{ s}^{-1}$, only about 30 pptv of a typical monoterpene (α -pinene) would be required to produce this reactivity, smaller than the added NO₃. The procedure calls for addition of 50 pptv NO₃ at that start of the flow tube (and in some experiments, more was used). The NO₃ reaction would lead to $\sim 8\%$ reduction of the initial α -pinene mixing ratio during the 10.5 s flow tube residence time (taking kinetics as first order for simplicity, even though in this example they are actually second order), placing some bias on the derived reactivity. Furthermore, the rapid VOC degradation induced by NO₃ addition would presumably lead to formation of peroxy radicals and / or HOx that could further react with NO₃ or the ambient VOC levels. If reactivity were dominated by even more reactive VOCs (e.g., sesquiterpenes), these effects could become significant. The authors should consider the potential for such secondary chemistry to bias the NO₃ reactivity measurement under the chosen level of added NO₃.

Aside from this comment, the authors should consider the following more specific comments prior to publication.

Specific Comments

Line 32: should add the phrase “at elevated NO_x”, since in the absence of NO_x, O₃ is the major nighttime oxidizing agent for these compounds.

Line 66: Equation appears to be inverted. Units as written would be s, not s⁻¹, so this should be τ_{ss} , not $1/\tau_{ss}$

Lines 99-100: Both Fuchs et al. (Anal. Chem. 80, 6010, 2008) and Wagner et al. (AMT, 4, 1227, 2011) describe the use of crystalline N₂O₅ for calibration of NO₃ and

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N₂O₅ instruments in the field in which there is no significant NO₂ impurity. In-field synthesis and sample stability have also been achieved, albeit with some difficulty. While this reviewer agrees that the method is difficult and the in-situ generation source may be superior, it may be worth pointing out that it is not impossible. If achievable, the crystalline source would have the advantage of no O₃ and reduced NO₂.

Lines 104-105: Is the 0.93 ppbv mixing ratio of NO₂ before or after its dilution into the O₂ flow? Presumably after, but not clear from the way it is written.

Lines 108-111: The termolecular reaction of NO₂+NO₃ is not rate limiting in this system, so it is difficult to see (intuitively) why high pressure would make N₂O₅ production more efficient, or why the reactor would be sensitive to fluctuations in external pressure.

Line 114: Reaction does not go to completion in 5 minutes at 400 ppbv O₃, correct?

Line 122: NO₂ (1 ppbv) lower after the reactor than before? (see comment above) Must be an error in the numbers given above.

Line 229: “non-isothermal effects” is not clear

Line 252-262: The role of the N₂O₅ equilibrium and the excess O₃ in the flow tube should be obvious enough that explicit discussion of equation (6) and deviations from it are not really needed. Suggest omitting this simple expression in favor of the discussion of the more accurate numerical simulations to simplify the paper.

Lines 291-292: Is there any degradation of kw observed during field sampling in ambient air? If NO₃ has a large wall loss rate constant on glass, it would presumably also be lost readily to FEP coatings there were not pristine.

Line 297: Does expression (7) take radial diffusion limitation into account? Also, r and c are presumably the tube radius and mean molecular speed of NO₃, but should be defined in the text.

Line 360-362: Statement could be stronger than “we prefer”. The numerical simulation

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is obviously more accurate and more general, and can be described as such.

Line 371: Is this really the time for flushing reactive gases? Several minutes for a system with 10.5 s residence time?

Line369-382: The authors may elect to shorten this section, which could be conveyed in a sentence or two to state that an iterative fit was used.

Line 410: Is the 0.2 pptv 1-sigma?

Line 514, Figure 12a: Figure would be much more effective with the y-axis on a log scale to illustrate the difference between night and day. It is difficult to see the nighttime reactivity on this scale, and the quantitative day / night contrast should be of interest to the readers.

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