

Review of “Short lifetimes of organic nitrates in a sub-urban temperate forest indicate efficient assimilation of reactive nitrogen by the biosphere,” Andersen et al., EGU sphere (2024)

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Summary

This paper presents ground-based observations of trace gases in a temperate forest. They use a combination of simple models to calculate production rates of total alkyl nitrates and peroxyacyl nitrates, and they examine how these depend on different oxidants and how they vary between different periods. They use the residual between modeled and observed mixing ratios to infer physical loss rates, which they imply reflect loss of these compounds via dry deposition. The writing is good and the number and style of figures is appropriate.

As detailed below, I find several major flaws in this study, specifically with regards to 1) presumption of the nature of missing sinks, 2) inadequate treatment of uncertainty, and 3) missing chemical reactions and inadequate consideration of the applicability and limitations of the model for this particular environment. Any one of these would be cause for major revisions, but in sum I regret that they justify rejection (with encouragement to resubmit).

General Comments

The title is misleading. The results presented in this paper do not “indicate efficient assimilation of reactive nitrogen by the biosphere.” At best, results indicate that additional sinks are sometimes needed to square a steady state model with observed concentrations. No evidence is presented that can isolate these sinks. Indeed, L554 (last paragraph of the conclusions), states that deposition is “presumably” the cause. The title should be amended to reflect defensible conclusions.

Missing sinks: equating model-estimated “physical losses” with deposition is quite a leap. First, a steady-state 0-D box model cannot be expected to represent all processes accurately, or even sufficiently, within a forest where there are complex interactions of emissions, radiation, and chemistry. Numerous studies using 1-D canopy models support this. The transport timescale in a typical forest canopy is a few minutes, so anything with a lifetime longer than this would be affected by those processes. Second, it is possible to estimate the expected dry deposition rates using a range of reasonable deposition velocities (Nguyen et al., 2015, and other studies). For a 1 km boundary layer and $V_d = 1 - 3$ cm/s, the effective deposition lifetime is 9 – 27 h, which is much longer than the 1.5 h AN lifetime estimated here. Several studies have shown that aerosol formation is important (L69). OK, that’s the rant; the point is that the analysis could be improved by 1) estimating deposition loss rates based on literature, and 2) not presuming that “physical loss” means deposition.

Nighttime OH: L261 states that nighttime OH can be explained by ozonolysis, but analysis is never shown to support this. Later, L346 states that a major difference between this study and a previous

one is the nighttime OH data. This is not the first time nocturnal OH has been observed, and I suspect the jury is still out on the extent to which this might be a measurement artifact. Given this appears to be important, the paper should include some analysis of whether or not the observed nighttime OH is consistent with known chemistry.

Uncertainty: Measurement uncertainties are not propagated. This is especially important for any calculations using OH. Figures 6 C-D could use error bars or something in the text discussing how uncertain that balance is. Figure 8 A-B would also benefit from an uncertainty estimate on the modeled PAN – at least from known errors. This doesn't have to be fully rigorous to be useful.

Specific Comments

Sect. 3.2.1: What is the accuracy of the reactive N measurements?

L124: Corrected for what?

Sect. 3.2.2: how confident are you that the observed OH is representative of the average for the forest canopy or the larger environment that would contribute to VOC oxidation? If you are in a forest, presumably there is significant shading.

Sections 4.1 – 4.3 present theory that is used to analyze the results, not the results themselves. As such, this should be moved to Methods or a "Theory" section.

Sect. 4.1 does not include N₂O₅. This seems like a major omission, especially considering Sect. 3.2.1 states N₂O₅ was measured. This needs to be included in the NO₃ steady state calculation (including heterogeneous loss of N₂O₅), or a quantitative argument needs to be made on why it can be excluded.

L280: What is the basis for the generic rate coefficients?

L376: This is also consistent with another very different analysis of isoprene nitrates, which found lifetime of < 2h with losses dominated by aerosol uptake (Wolfe et al, 2015, Table S5).

L378: a potential implication of XO₂ over-prediction is that OH is too high. How would reduced OH alter your estimated AN lifetime? At a minimum, this should be considered from the standpoint of the presumed 25% uncertainty in observed OH.

L405: MPA radical can also isomerize (Crouse et al., 2012). Presumably this has a relatively minor impact on modeled PANs.

L465: This is also consistent with analysis of PAN fluxes above another forest (Wolfe et al., 2009), although in that study they found a downward flux driven by warmer temperatures at the surface (meaning that canopy transport was a net source of PAN).

Technical Comments

L29: Define "ACROSS"

L53: capitalize IUPAC

L146: suggest striking this sentence. I believe it is no longer acceptable to refer to an unwritten paper, especially since they often remain unwritten.

L160: define LISA

L230” delete “i.e. . . . terms.”

L269: OH addition, which is the dominant channel for alkenes, does not lead to H₂O formation.

L378: change “above” to “Sect. 3.3.”

L498: Fig. 8

References

Crouse, J. D., et al.: On the atmospheric fate of methacrolein: 1. Peroxy radical isomerization following addition of OH and O₂, *Journal Of Physical Chemistry A*, 116, 5756–5762, <https://doi.org/10.1021/jp211560u>, 2012.

Nguyen, T. B., Crouse, J. D., Teng, A. P., St. Clair, J. M., Paulot, F., Wolfe, G. M., and Wennberg, P. O.: Rapid deposition of oxidized biogenic compounds to a temperate forest, *Proceedings of the National Academy of Sciences*, 112, E392–E401, <https://doi.org/10.1073/pnas.1418702112>, 2015.

Wolfe, G. M., et al.: Eddy covariance fluxes of acyl peroxy nitrates (PAN, PPN and MPAN) above a Ponderosa pine forest, *Atmospheric Chemistry And Physics*, 9, 615–634, 2009.

Wolfe, G. M., et al.: Quantifying sources and sinks of reactive gases in the lower atmosphere using airborne flux observations, *Geophysical Research Letters*, 42, 8231–8240, <https://doi.org/10.1002/2015GL065839>, 2015.