

Review of Liebmann et al., “Alkyl nitrates in the boreal forest: Formation via the NO₃, OH and O₃ induced oxidation of BVOCs and ambient lifetimes,” for ACP May 2019

This concise and clear paper reports on measurements of alkyl nitrates in the boreal forest, with coincident measurements of organic trace gases enabling an assessment of the relative source strength of OH, NO₃, and O₃ oxidation in producing these alkyl nitrates. In this NO_x-limited environment, NO₃ oxidation is found to be the dominant source of alkyl nitrates both night and day. The paper is clearly written and the figures are helpful. I suggest addition of a bit more auxiliary data to enable readers to better interpret the conclusions.

General comments:

- 1) As I read this paper and sought to understand the key observations, I found myself wondering about the [NO] and relative concentrations of different organic trace gases. These data are perhaps in other papers cited, but for convenience of the reader I urge the authors to include this data here. I suggest to include an NO trace in the top panel of Figure 2, and add a panel to that figure showing BVOC timeseries, perhaps split out by isoprene and summed terpenes since they likely have different diel patterns, and since their relative reactivities is different and can help the reader interpret the day/night observations.
- 2) For similar reasons, it would be helpful to add another panel to the diel average figure 4, showing NO₂ and BVOC traces. In particular, I was curious why the NO₃-initiated production of ANs would peak at 19:00 local time and then decrease? Given your statement that monoterpene concentrations build up overnight, I might have expected this to continue increasing. Is it that the NO₂ is fully consumed by then?
- 3) I agree with Jacqui, Figure 5 is not necessary.
- 4) Abstract line 22: “strongly controlled by biogenic emissions” – ? seems inconsistent with your discussion in the manuscript body. There, you describe this as due to rapid deposition to particles?
- 5) Around p. 3 line 23-24: Could you list the dominant terpenes here? (and / or, on p. 5 around line 13 where you state that only a handful contributed significantly to reactivity – include a brief ranked list?) Also, what anthropogenic emissions are observed from the cities & sawmill – just NO_x, or NO_x and SO₂?
- 6) On p. 8 around line 18: say something about why the NO₃ initiated formation of ANs peaks at 19:00
- 7) On Figure 6, the error bars on the bottom panel look very large compared to the reported slope uncertainty of +/- 0.5 hr. Please explain how this error bar is determined – it looks to me like the slope could even be negative within the uncertainties.
- 8) Figure 7 makes me wonder whether it's possible that different sensitivities of I- CIMs to daytime vs. nighttime BVOC mixes could explain the different amplitude of the diel cycle. Can you add anything additional information on this?

Technical corrections/suggestions:

p. 2 line 21: "OH radicals are largely absent"

line 27: "Reaction 6a is a composite"

p. 3 line 10: suggest to add reference to Ayres 2015 (<https://www.atmos-chem-phys.net/15/13377/2015/>): this NO₃ + BVOC dominance during the day was also observed at SOAS 2013.

p. 3 line 30 "reached 100% during many nights"

end p. 3 / top of p. 4: Is 300 pptv the average NO_x level for the whole campaign? Maybe also mention the [NO_x] during the events where airmasses arrive from the industrial sources.

p. 4 line 4 "photolysis frequency, and the"

line 21: remove extra ")"

lines 25-26: "OH concentrations have an associated uncertainty of ~ 50%"

line 33: add citation for I- CIMS high sensitivity to nitrates

p. 5 Eq. 2: It's a little confusing that you use the average alpha in the equation but then talk about the individual ones first below the equation, and then define the average in Eq 3 below. Maybe combine Eq. 3 into 2 so you see the average and the summation simultaneously? Also, after the current Eq. 3, define the C_i term.

Eqn 4: k₃ should be k₅?

Line 24 "total measured reactivity"

p. 6 Eqn R12: meaning of the "delta" term is unclear

line 27: "UTC). In order to account for this competition with HO₂ reactions, equation (7) can be modified to:"

p. 7 line 3: "the local sawmill, likely due to elevated reactivity with?"

Line 4-5: This sentence sounds like you're drawing a contrast to NO₃, but I think this is true in that case as well. Perhaps make this sentence the first sentence of the next paragraph instead?

Line 11: "We show below that even if unattributed OH-reactivity reaches 50%, this would not significantly"

Line 13: insert space "from [C_i]"

Line 20: "Similarly as for OH-reactions,"

p. 8 line 2: "was estimated to be ~ 60%"

line 10: "is rather consistent with"

line 24: "ANs production rate occurs exclusively via NO₃-initiated reactions."

p. 9 line 1 "which was 570 m"

line 2: omit extra ")"

line 7: "which is not the case (Eerdekens"

line 20: "overall uncertainty represented by error bars, there"

line 27: "well-mixed daytime boundary"

line 28: include units on V_{dep} (here and in the line below "V_{dep} ~ 2")

line 32: "can be assessed"

p. 10 line 3: "For typical alkyl nitrate"

line 18 & below: Shouldn't the CIMS be designated the "I- CIMS" and not "I-CIMS"?

p. 11 top 2 lines: C₉ shows up in two categories ?

line 11: "lifetimes are entirely consistent"