

Review of Sobanski et al, “Day- and Night-time Formation of Organic Nitrates at a Forested Mountain site in South West Germany”

This paper presents two summer field campaigns (2011 and 2015) of organic nitrate data at an urban-influenced mountain site, focusing on measurements of alkyl nitrate formation and implications for production of ozone, and measurements of peroxy nitrates, both using a thermal dissociation – cavity ringdown instrument, which detects these species via thermal dissociation and then detection of NO_2 . Reference is made to an earlier instrument paper for the measurement methodology and data corrections to account for some known interferences, the focus in this paper is in interpreting the field observations, including comparing across two years with different meteorological conditions. This paper presents a novel combined dataset that will be of interest to the atmospheric chemistry community. I do see a few opportunities to extend the analysis and to compare to additional available measurements, which I mention below, and recommend publication after these revisions.

Major suggestions:

1) There are a few additional studies that I would suggest citing to inform your analysis, and to enable comparisons with your data:

- Kiendler-Scarr et al (2016) have just published a series of measurements of aerosol-phase RONO_2 around Europe using AMS, and they comment on the ubiquity of NO_3 sourced nitrates – this would be a good point of comparison. (“Organic nitrates from night-time chemistry are ubiquitous in the European submicron aerosol,” *Geophys Res Lett*, 10.1002/2016GL069239, 2016.)
- Fry et al. (2013) measured ΣPNs and ΣANs at an urban-influenced Colorado site, also in summertime, including doing the same O_3 / ANs slope analysis to assess nitrate branching and relevance to O_3 formation. Compare yield and VOC mix? (“Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011,” *Atmos. Chem. Phys.*, 13, 8585-8605, 2013.)
- The Ng et al. 2016 review paper that you cite discussed some observations and general trends about organonitrate losses, including hydrolysis, that would be valuable to consider in the context of your claims that nighttime nitrates may be lost more rapidly under damp and foggy conditions during NOTOMO, in contrast to the first year. There are several primary papers cited in Ng that might be relevant here, for example Boyd et al 2015 (“Secondary organic aerosol formation from the β -pinene+ NO_3 system: effect of humidity and peroxy radical fate,” *Atmos. Chem. Phys.*, 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.) – but in general I think the conclusions here would be at odds with your observations: nighttime NO_3 +terpene produced organonitrates are expected to be mostly primary and secondary nitrates, which appear to have longer lifetimes, not shorter, than daytime produced OH-initiated nitrates (which would include more tertiary nitrates)

2) In my view, the weakest point in the paper is the explanation of the difference in PAN/AN ratio and apparent O_3 AN branching ratio across the two years. It would be great to find more evidence to support and interpret this difference. For example:

- even though you don't have VOC measurements in year 2 (bummer!), could you look at e.g. temperature / sunshine differences correlated with VOCs measured within

the PARADE period where you DO have the GCs running, and then extrapolate to the conditions during the second year of measurements?

- Or even use any other GC data taken at that site, whenever, to be able to say something about the potential range of year- over- year variability?
- Can you find literature to point to on how oxidized VOCs like nitrates deposition depends on met conditions (your claim at the top of p. 13)?
- Does the NO: NO₂ ratio during the two years support the apparent differences in PAN vs. ANs formation rate?
- Can you find any NO_x emissions data or traffic counts or similar to suggest that the NO_y mix arriving at the site might be different across the 2 years?

3) Figure suggestions

- It would be valuable to see some of the VOC variability in addition to reporting the mean noontime values in table 1. Could you add the reactively most important VOC or two to Fig. 1, to enable readers to see whether periods of high ANs/PNs correlate with higher VOC? Also, suggest to add the diurnally averaged version to Fig. 4 as well. Are all daytime-peaking or some nighttime? Could target trying to ID the dominant NO₃+BVOC source of organonitrates at night vs. daytime RO₂+NO source, which will help you put the ideas about hydrolysis lifetime and its structure dependence in context.
- On Fig. 3, can you format the points so they don't obscure one another? it looks like the black points are behind the red, so it's hard to see their spread. Maybe use "+"s instead? Or bin /average data so there aren't so many points on the plot?
- Please "squish" Fig. 4 and 5 on the horizontal axis (or equivalently, make them taller) so they are the same width as Fig. 6, where the diurnal pattern is easier to see because of the larger height to width aspect ratio
- Suggest to rethink color scheme on figures. Red/black don't always means the same thing, leading to confusion. For example, could do dots vs solid for years, consistently, and always use color to refer to left/right axis?
- Suggest to add NO to figure 4.
- In caption to Fig. 5, briefly described how you separate out the rush-hour influenced days
- Fig. 7: how did you choose 11-13 UTC for the O₃ vs ANs slopes? Did you check consistency using different time periods? Also, could the iterative correction procedure that makes the ANs data look binned on fig. 7 be the reason for lower ANs concentration measurements, too? What is the relative error on these measurements in each campaign, based on the correction procedure? Could you put error bars on these plots? (Again, might be best to bin first to avoid having a too-busy plot)

Minor or technical edits:

1) p. 2 line 1: "during the night (R6) (see below) to produce peroxy radicals which subsequently produce stable organonitrates by any radical terminal reaction. Organic peroxy radicals are also formed in..."

2) p. 2 lin 12 "ultimate to O₃ formation."

- 3) p. 2 line 31-32: suggest to include chemical formulae for each PAN, PPN, MPAN, analogous to how you show $\text{RC(O)O}_2\text{NO}_2$ on line 5 of this page.
- 4) p 3 line 4: “first measurements of total ΣPNs and ...”
- 5) p 3 line 32: clarify that the long observed NO_3 lifetime here is presumed due to low VOC mixing ratio – correct? If so, could you note the mixing ratio compared to another time where you’re not sampling the residual layer?
- 6) p 5 line 32 what does “HLUG” mean?
- 7) p. 6 line 10-11. This is unclear. Add symbols to help reader correlate to table 1, e.g. “alkyl nitrate yields ($\alpha\text{(ANs)}$) and production rate of alkyl nitrates (P(ANs)) and ozone ($\text{P(O}_3\text{)}$). The phrase “for ANs and PNs, respectively” I don’t understand – $\text{P(O}_3\text{)}$ is just based on ANs – what do you mean by the PNs part?
- 8) p. 6 line 16. HLUG again - ?? and typo in “summarizes”
- 9) suggest to find/replace “see later” and change to “see below”, or vice versa, to make all consistent.
- 10) p. 7 line 6: Maybe check if Lee et al’s SOAS paper also does the sumANS / individual ANs comparison that Beaver’s paper did? I think in the supplemental:
<http://www.pnas.org/content/113/6/1516>
- 11) p. 7 line 16-18: is this a chemical clock? Can you correlate with wind speed?
- 12) p. 7 line 22: “this site. Furthermore, the temperature dependence suggest that ..” (because it’s the T-dependent that suggests this, right? Not the $f(\text{NO}_x)$ values). Also, the last sentence of this paragraph offers an alternative explanation, so maybe start with “However, note that low temperatures also increase ...” and then put some more evidence for one of the other potential explanations, from Major Suggestions #1 above, below in this section.
- 13) p. 7 line 31: typo “emissions”
- 14) p. 8 line 1: unclear. do you mean the mean and daily maxima of each variable? reword.
- 15) p. 9 line 4: give number for the PARADE campaign too to compare.
- 16) p. 9 line 15: typo “[NO_3] and”
- 17) p. 9 line 25-26: are you accounting for differences in rate here too, or assuming there is abundant NO_3 to fully oxidize all VOCs? Elaborate.
- 18) p. 10 line 15 typo “environment”
- 19) p. 10 line 23: SOA yields could be even higher – see summary table in Ng 2016 paper.
- 20) p. 11 line 24: “than the loss terms, D and E, and Eq. 5 ...”