Review of Yu et al. "Characterization of nighttime formation of particulate organic nitrates based on high-resolution aerosol mass spectrometry in an urban atmosphere in China"

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Description:

This manuscript describes measurements of OA and organic nitrate aerosol in an urban area in south China using AMS during 4 seasons. The AMS nitrate is separated into organic and inorganic nitrate using 2 methods (NOx+ ratio and PMF) and compared. Organic nitrate aerosol is estimated to be a substantial fraction of total nitrate and of OA during the three warmer seasons. OA is also separated into different source factors using PMF. The organic nitrates are shown to correlate with fresher SOA (LO-OOA from PMF) with slightly better correlations during nighttime. NO3 radical concentrations are calculated based on a steady-stated model of production from O3+NO2 and reaction with two terpenes and conclude that the NO3 radical reaction is the dominant loss of the two terpenes. They model the SOA formation from NO3 + two terpenes and seem to argue that it is consistent with the organic nitrate aerosol measurements and that nighttime NO3 + BVOC is the dominant overall source of particle organic nitrates.

Some of the methods are reasonably well described and follow on methods developed and described in the literature, although additional details are needed for several aspects. However, overall nothing new seems to be offered in terms of method development nor advancement in understanding of atmospheric science (which Ref #2 recognized as well). The conclusions the authors arrive at are not surprising and have been previously published. Thus, it largely comes across as a data report, where measurements were made, previous methods are applied and the scientific analysis/interpretation is conducted in this case with less rigor than prior publications. Thus the value to the literature essentially amounts a report of measurements and simple calculations conducted in a different location. The results section consists of only a few figures and ~2 pages of 1.5-space text, a reflection of the thin-ness of new content. Importantly, some conclusions are overstated with insufficient evidence or even faulty logic presented, so in present form is in fact misleading. Therefore, publication in ACP does not seem appropriate. Details are provided below.

Main Issues:

Text/Clarity:

Text was generally readable but there are lots of grammar errors. A few pervasive errors include the addition or omission of articles (e.g. "the", "a") or plurality when not needed or needed. Reviewing by native English speaker BEFORE submission is recommended. Much of the text is written clearly, while in many cases insufficient details were provided to understand exactly what was done.

PMF details:

I agree with Referee 1 that there is not sufficient detail provided on the PMF (both justification of solutions, as well as summary of results). This should also include the NOx+ ratios for each factor, discussion of the meaning and/or possible biases related to the HOA factor containing nitrates and the inorganic factor having a different NOx+ ratios than calibrations. Correlations of organic nitrates vs all of the factors should be presented (ideally a version of Fig. 3 for each factor in the supplementary). Simply showing that organic nitrates correlate with LO-OOA does not make a convincing case that they are related since often all concentrations largely increase and decrease at a given sampling site together. Additionally diurnal cycles should be shown for all factors

Organic nitrate quantification:
Evidence is thin to install confidence that the methods for separation of organic nitrates is producing meaningful separation. While the methods have been applied before in other papers, the methods may be prone to substantial error and potentially bias when organic nitrates are a small fraction of total nitrate, as is the case here for all seasons except summertime. Diurnal cycles of the total nitrate and inorganic and organic nitrates calculated by the different methods would be helpful. Showing correlations of both the organic AND inorganic nitrate with the PMF factors may also be informative.

NO3 radical calculation:
The NO3 radical concentration calculation is bewildering. The loss in the steady-state calculation is based on only a-pinene and limonene with no justification for this choice (Section 2.4, Table S1). Then the concentrations are neither reported nor shown, it is unclear if they are calculated for only one fixed value or as a time series. What season was this done for? What season does Table S1 pertain to? This is a critical calculation since the conclusion that NO3 dominates over O3 for BVOC losses and for the SOA modeling. The calculation that NO3 accounts for nearly 100% of the BVOC loss at night is a little surprising and also from which major conclusions of this manuscript flow. For the Xu et al. (2015b) study (referenced in the manuscript), they calculated that only 20%/38% of the reacted a/b-binene was with NO3 at night. Might the NO3 calculated here be biased high since only two VOC losses were considered?

NO3-BVOC SOA modeling and conclusions drawn:
As Referee 2 points out regarding the analysis in Sect. 3.3 on the estimation of pON formation, the sources of measured pON depend on reacted VOCs, not on the amount of VOCs present in the atmosphere. The authors seem to be equating the two. Essentially the authors appear to be calculating the relative amounts of production expected if the sampled airmass was allowed to react to completion with no further emissions. This does not equate to the regional productions since it would systematically underweight more reactive compounds and the two metrics may only be loosely connected.

In general, Section 3.3. is highly undersupported and speculative considering the evidence shown. It is not clear what the modeled SOA (blue trace in Fig. 5) even is. Is that the amount produced per unit time from the model? It cannot be the cumulative production since it increases and decreases (and the model does not have dynamics, dilution, mixing, etc.). In any case, the features of organic nitrates and the ambiguous modeled SOA don't match all that well. Also, it seems likely that the day-to-day variability may be of similar or larger magnitude to the variations in the average diurnal cycle (variability bars such as standard deviations would be helpful here). Potentially the very rough similarities may be an averaging artifact? Thus, the diurnal cycle should be supplemented additional evidence, such as time series of the relevant metrics and correlations plots to make a convincing case that the model may be indeed be representing the key processes and explain the measurements. Also, inclusion of inorganic nitrates together with the organic nitrates (diurnal cycle and other relevant plots), would help make a stronger case that the separation of the organic nitrates is meaningful and robust. Based on this section, the authors conclude (as stated in the abstract) that BVOC + NO3 at night are the dominant formation pathway of organic nitrates in the polluted atmosphere. This simply has not been demonstrated.

Moreover, it appears that the authors are equating boundary layer concentration with overall regional production importance. As the authors note in Sect. 3.3, the boundary layer is expected to be lower during nighttime. Consequently, the concentrations observed represent a smaller volume of air, so equating lower concentrations during daytime with lower overall (column integrated, regional) importance is faulty logic. BL-effects were not considered here nor production during the daytime modeled, thus no conclusions beyond nighttime boundary layer concentrations and production should be drawn based on this analysis. Yet, this manuscript seems to do just that – an example of the vastly overstated implications claimed.

New results:

Kiendler Scharr et al. (2016), Ng et al. (2017), Xu et al. (2015a, 2015b) and others have reported that at many sites throughout the US and Europe, including polluted urban areas, organic nitrates can be substantial fractions of aerosol nitrates and NO3+BVOC reactions can be an important source. The manuscript fails to make a case for what new information this study from one polluted city provides and how it would add to the body of atmospheric literature.

Regional Implications:

The authors broadly refer to their results as pertaining to “South China” which is a large and diverse areas. Unless there is evidence that this site is generally representative of that geographic area, text and conclusions should be limited to just this one urban area. This is an example of overselling the story without providing the supporting analysis.

Detailed Comments:

L32-3: “Play a larger role” for what? Reference?

L40-41: The Rollins et al. (2002) paper demonstrated the application of the aerosol-only organic nitrate measurement. The technique for total nitrates was developed and demonstrated a decade earlier (Day et al., 2002).

L41: “measured” would be better than “obtained”

L66: “to obtain more representative samples” seems vague. Clarify.

L74: “literatures” should not be plural.

L82-4: state if the RIE of ammonium was calibrated or assumed.

L105-6: Site Xu et al. (2015a) since isn't this is exactly what they did?

L107-8: Stating that negative calculated organic nitrates means that concentrations must be low is not very analytically sound. E.g., can't this just mean the method isn't working well or there are large uncertainties due a variety of possible factors? Please revise to be more precise and inclusive of the possible causes.

L127: Fry et al. 2013 is not the proper reference for heterogeneous N_2O_5 reaction with aerosol. They just performed the calculation.

L130: Units for velocity are wrong.

L131: Where did the aerosol surface area concentration for the modeling come from? It does not appear that an aerosol sizing instrument was used in the study.

L133-135: Why do the authors include the calculation of the $N_2O_5+H_2O$ gas-phase reaction? The lifetime is 500 years!

L145: “6.82 and 19.38 ppb”: Too many significant figures. It would be more useful to report averages and standard deviations.

L159: "<u>may</u> explain" instead? Without any quantitative assessment, it is not justified to say that it does explain it.

L165: “adequate” for what or by what measure? Too vague – needs clarification.

L173-4: Statement points out that the organic nitrate is similar to SE US “even though” BC and NO_x are higher in S. China. How is this meaningful? If terpenes are dominantly reacting with NO_3 then the production would be largely controlled by the amount of terpenes present - which appear to be quite modest at this location. Statements like this need more context/discussion to be meaningful. Or remove such comparisons if not informative and making a clear point.

L180: “both organic spectra” should instead read “both OOA spectra”?

L180-2: Unclear. Is this referring to running PMF with and without the NO_x ions? Please clarify.

182-3: Please report these correlations (table?) and show the correlations in the SI (i.e. duplicate Fig. 3 for MO-OOA and HOA).

L196-198: Limonene and a-pinene shown to account for 90% of NO_3 loss? Assuming the authors are referring to Sect. 2.4 (not 2.3 as written), this is not shown there – or anywhere else. Only 2 compounds were considered according to the text (which references Table S1).

Table 1: “NO_3^-“: Is that inorganic nitrate or total nitrate? If total, then the ionic denotation isn’t appropriate.

Figure 5: beta-pinene misspelled.

Table S1: a-pinene SOA yield: Why was this single reference value picked, considering that there is a substantial range reported in the literature? See Table 2 in Ng et al. (2017). A range would seem more appropriate here unless the authors justify why this particular one is more appropriate for this study.

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