

Interactive comment on “Secondary Organic Aerosol (SOA) yields from NO₃ radical + isoprene based on nighttime aircraft power plant plume transects” by Juliane L. Fry et al.

Anonymous Referee #3

Received and published: 5 May 2018

Fry et al use airborne observations from the SENEX campaign to infer SOA yields for the reaction of isoprene with NO₃ radicals. Specifically they show that night time transects through power plant plumes capture conditions in which the loss of NO₃ is dominated by the reaction with isoprene. Comparisons of out of plume isoprene and particle phase nitrate measurements with values observed in the seconds to minutes long in-plume parts of the flight, are used to calculate SOA molar and mass yields. While the approach of using field data to evaluate SOA yields in “wall free” environments is interesting, the data analysis is based on highly speculative assumptions and the SOA yields can therefore not be taken as reliable real world reference. The paper needs major modifications before it can be published.

C1

Major Points

The particulate organic nitrate mass concentration is evaluated according to an established method using AMS observed NO₂⁺/NO⁺ ion ratios. While this method has been used before for high resolution data sets, the authors have to apply corrections for unknown organic interferences to their C-TOF-AMS dataset, subtracting 55% and 33% of the total measured signal on m/z 30 and 46, respectively. As shown in Figure S2 e (lower panel), the thus derived UMR corrected NO₂⁺/NO⁺ ratio agrees relatively well with the HR ratio, except for periods in which the total nitrate signal is low. The authors should have a look into this feature and derive from it a threshold total nitrate mass concentration below which no reliable analysis of organic nitrate is possible. Note that the values for R ammonium nitrate and R organic nitrate indicated in Figure S2 do not match with the values of 0.49 and 0.175 reported in the paper and in Figure 3.

The use of a value R=0.175 of NO₂⁺/NO⁺ for organic nitrates is justified with reference to Day et al 2017, a paper in preparation. As the R-value directly affects the calculated mass concentration of organic nitrates, basing its justification on unpublished work is not acceptable. In a more conservative approach the authors should instead use the organic nitrate R-value of 0.1, which will lead to a lower estimate of organic nitrate mass concentration. Implementing this value for the data set in Table 2 would lead to a reduction of organic nitrate mass concentration by ~ 25%, directly reducing the SOA molar and mass yields by the same percentage. Noteworthy, the use of R=0.1 for organic nitrates would also increase slightly the mass concentration of ammonium nitrate. As for many plumes the authors calculate negative ammonium nitrate mass concentration, this negative bias for the ammonium nitrate would be overcome, further supporting the use of R=0.1 instead of R=0.175. As mentioned above, the use of R=0.1 would reduce organic nitrate mass concentration and therefore the SOA mass yield would be reduced to ~20% instead of the current 27%. Accounting for the 2/3 organic mass the SOA mass yield presented here would translate into an organic mass yield of 13%, well comparable to the literature data cited by the authors.

C2

The discussion on urban plumes, although acknowledging uncertainties, is far too speculative and should be removed from the manuscript.

In view of the uncertainties in organic nitrate mass determination, the SOA molar and mass yields have to be reconsidered, accounting for above approach.

Other points (in order of appearance in the manuscript)

Page 5, line 172, 174: "0.7 μgm^{-3} ...a factor of three lower than 1.7 μgm^{-3} " the numbers don't match up, check for consistency.

Page 13, line 469: the nitrate radical production rate that was used to identify in-plume parts of the flight needs justification

Page 16, line 567 and following: To justify the statement, the authors need to show calibration data for deriving RIE of NH_4 and show the precision of ion balance in the calibration aerosol.

Although the authors cite, that NO_3 loss is dominated by reaction with isoprene, they could use the calculated potential for inorganic nitrate formation from N_2O_5 uptake to support the interpretation of most in-plume particulate nitrate formation having organic sources.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-255>, 2018.