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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol" *by* S. S. Brown et al.

Anonymous Referee #1

Received and published: 7 January 2009

The paper by Brown et al. presents a very nice set of data regarding measurements of isoprene and NO3, along with the isoprene oxidation products MVK and methacrolein, and other NOy components, from a set of nighttime aircraft flights over the relatively anthropogenically polluted northeastern U.S. coastline. The data allow for calculation of the fraction of isoprene oxidized (by NO3) after sunset, the fraction of the organic nitrates that might be produced from NO3 + isoprene in this polluted environment, and the contribution of the NO3 + isoprene reaction to SOA production. The data are clearly and cleverly presented and interpreted, and I think the paper is interesting and impor-

tant. Given the uniqueness of the data set, and the generally well-written character of the paper, I feel that it should be published, after relatively minor revisions. However, the paper has one significant omission, and one serious flaw, that I feel must be corrected before publication. To the omission - while the paper presents very nice data, for many difficult to measure species, there is virtually no description of the methods at all in the paper. Considering the central nature of NO3 to the paper, and the fact that sampling issues for NO3 (and other NOy species) may well be important, at a minimum, the details of how these species were sampled, and at least some description of the analytical methods employed is essential, and, I think, obvious. Losses and how they were estimated for species like HNO3 and aerosols should be discussed, as well as interferences and thus estimated uncertainties for the PTRMS data. It should always be recognized that, for species at low concentrations, like isoprene in this case, there are no guarantees that the PTRMS data are without significant interferences. Regarding the flaw: this paper calculates and presents in Figure 8 the total isoprene nitrates that result from NO3 reaction with isoprene. But that calculation is just the calculated amount that is produced (assuming a production yield), while ignoring consumption of these nitrates. However, these nitrates are olefinic, and thus highly reactive to ozone and NO3. Thus the calculated isoprene nitrates could be a substantial overestimate, or, if considering NO3 reaction, even an underestimate. The literature does indicate that some substituted alkenes can have enhanced ozonolysis rate constants, so this issue is potentially very important. Indeed, it is important to any ultimate conclusions that might be drawn about the impact of NO3 chemistry on the transport of reactive nitrogen in the form of these nitrates, as they are likely very short lived, and so what is likely more important is whether their oxidation retains the nitrooxy group. This issue and the associated uncertainties (and interesting questions) must be addressed in the revision.

More minor issues are listed below in the order they arose in the paper.

1. Figure 4: it is clearly non-linear and should have a non-linear fit, as this is what we

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would expect. Obviously, when 1/tau(NO3) = 0, k1[isoprene] must be zero, so the line for the plot should go through zero. And, it makes no sense that phi is a constant. In the limit of large isoprene, phi approaches 1, and it is clear that the curve in Figure 4 bends upward as it should. Perhaps this Figure should have a second order fit, and the text should discuss that phi(isop) should not be regarded as a constant.

2. Page 8 bottom paragraph - I think this section should state clearly that it is assuming no OH at night; that is important, given that there have been measurements (whether correct or not) of significant nighttime OH.

3. Page 9 line 2: should say ...presence of isoprene chemistry...

4. Page 9, middle: (open quote) showed agreement (close quote)is vague; specify or delete.

5. Page 9, referring to Figure 5, and in other places, the paper should state the times for all the flights.

6. Top of page 10, re estimation of [isoprene] present at sunset: this calculation treats sunset as a hard quantity in terms of [OH], which is likely not the case at all. Perhaps the paper should cite cases when OH was measured at this time, and discuss the uncertainty introduced by the assumption that OH goes to zero for SZA$>$90.

7. Page 12, paragraph 2, third line: should say ...emissions were calculated to sometimes be....

8. Bottom of page 12: I would expect this fraction (22%) is a function of NOx, but not so much a function of isoprene emissions. Explain?

9. Mid-page 14: explain the extent to which (and how) N2O5 hydrolysis, which occurs on aerosols, contributes to gas phase HNO3.

10. Bottom of page 14: the isoprene nitrates derived from NO3 reaction with isoprene absolutely are not long lived. This discussion should be stricken, or substantially rewrit-

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ten.

11. Bottom of page 16 - should say ....the calculated isoprene SOA mass...

12. Page 17: the calculations of the contribution of NO3 chemistry to aerosol yields dont take into account the impact of environmental conditions on the literature aerosol yields, specifically, temperature and humidity. This should be recognized.

13. Page 17, near bottom: explain the statement that aerosol production from anthropogenic VOCs during the preceding day could produce (open quote)much larger amounts of organic aerosol (close quote), and provide references.

14. I suggest that you delete the first paragraph of the Summary and Conclusions. To summarize what you just said in the paper seems unnecessary, unless it wasnt said clearly enough, in which case, the latter should be fixed.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 225, 2009.