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Atmospheric Chemistry and Physics Discussions



# *Interactive comment on* "Airborne observations of total $RONO_2$: new constraints on the yield and lifetime of isoprene nitrates" *by* A. E. Perring et al.

**Anonymous Referee #2**

Received and published: 30 June 2008

Review of Perring et al.:

Perring and coauthors present an analysis of organic nitrates measured by TD-LIF over North America during INTEX. The paper is stimulating and well written, and addresses an important and appropriate topic for ACP. The findings are generally presented in a way that avoids false precision but still provides useful information to the community. The paper can be improved in certain ways as per the comments below. Once the comments below are addressed the paper should certainly be published and I look forward to seeing it in print.

General comments:

Isoprene oxidation pathways and the associated product yields (e.g., HCHO) depend



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on NOx. The authors should include a discussion of this and whether it has a significant effect on their analysis. To what extent would you expect the IN yield to depend on NOx? It might be a small effect relative to the large uncertainty on IN yield, but it is an important effect for HCHO (see below).

By combining everything into a single average the authors dont do justice to their data. Isoprene is highly variable and its effect on RONO2 should be as well. Figure 4 fails to give an appreciation of that. Are those means or medians plotted? Given isoprenes skewed distribution I would expect it to make a difference. Either way you are obscuring useful information. Instead of two bars, I propose plotting that data as a stack plot, with [isoprene] on the x-axis. Generally I would like to see a more thoughtful treatment/discussion of isoprene/RONO2 variability.

VOC dataset. It is not clear what if any VOC data was used aside from the canister data. Were OVOCs from the PANAK instrument included (acetaldehyde, acetone, MEK, methanol, ethanol, etc) in the RONO2 production & OH reactivity calculations? If not they need to be. PANAK/OVOCs are not mentioned in the methods or anywhere else, except in reference to Fig 4 it says "the second most important ... is OVOCs (acronym not defined). In figure 4 OVOCs are not mentioned; the "Other" category is said to include all measured non-methane hydrocarbons. Generally NMHC does not include OVOC so this is all very confusing.

P12322, L11-12 "isoprene is indeed the dominant source of SANs". A bit too flippant. You need to convince us first that the VOC dataset is close to complete, first by addressing the previous comment. Also you should move the later discussion of observed vs. predicted OH reactivity here to make this point. Point out also that your calculation uses a yield on the low end, which will bolster your point. Also consider adding a brief discussion of the effects of lifetime on this; e.g. the extent to which the influence of short-lived compounds is understated in Fig 4 because they've already undergone significant oxidation before you could measure them. Finally, what does this mean? Is isoprene the dominant source of RONO2 everywhere, in the mean, some of



ACPD

8, S4274–S4278, 2008



the time? See variability comment above.

", L15: say "would imply"; since (as you show) you can't ignore those things.

", L17: "known formaldehyde yield". There's a problem here in that the effect of variability & uncertainty in the HCHO yield from isoprene is not acknowledged. Palmer et al. [2006] showed that predicted yield varies 20-50% depending on the model used and the NOx concentration. It also is time dependent. Some discussion is needed. What yield did you use, given its dependence on NOx, time, and chemical model? An average molar yield of 1.6 was estimated for INTEX-A based on HCHO and isoprene observations [Millet et al., 2006], is your assumption consistent with that?

On a related note, the HCHO yield from isoprene is time-dependent and so I expect is the IN yield. How would you expect that to play out? This might be worth a bit of discussion.

P12322, L18-21. Suggest rewording this since now it sounds like you're going to conclude that none of those effects matter and the yield is 6.8%. What about "In what follows, we examine the role these processes play in modifying the SANs/HCHO correlation, and the constraints that can be placed on the IN yield, lifetime, and NOx-recycling capacity."

P12323, L7-9. OH reactivity, see earlier suggestion for moving up to earlier discussion of VOC suite. Also, since this is a central point, I think a few more details should be given.

Throughout, please don't say "average" since it is ambiguous. Say "mean" or "median".

P12324, L4-7. Again this type of statement is problematic since it implies this is the case (isoprene dominant source of RONO2/HCHO) universally when it is not (though it may be in the mean). The case of HCHO has been investigated already specifically for the INTEX data, and isoprene was the dominant source when HCHO was high, but not at other times (longer-lived compounds dominated). Is the same true for RONO2?



ACPD

8, S4274–S4278, 2008

", L8: and HCHO loss too, right? Though this is well-constrained.

", L11-14. This argument might be convincing if you gave us the regression statistics for the >2km data.

P12326, L14-20: I think this can be phrased to make your point more clearly: a <1 hour lifetime, which would indicate prompt NOx recycling, is not consistent with the observations.

P12326. It seems that you could make a definitive and useful statement that based on your data ANs have a recycling rate of 75-92%. But how robust is this based on the assumed OH, O3 rate constants? I think it would be useful if you could give an estimated bound on this quantity that included a reasonable range for the rate constants.

P12327, L25-27, and Abstract, L20-22: "We recommend sets of ..." This is unclear and I think should be phrased differently. From how you state it, it's not clear whether you think that all 3 are physically feasible sets of values that could occur in the environment, or whether any of those combinations would provide a satisfactory fit to the ensemble of the INTEX data. (I guess you mean the latter).

Technical / editorial comments:

Punctuation and in-text citations are messed up in places.

P12315, L4: Say "potentially large" since unmeasured

", L9: "multifunctional"

", L10: VOC not defined

", L16: 76% seems like arbitrary precision. What about 3/4, or 75%.

", L24: "partially maintained". based on your findings it seems you could say something stronger/more specific- At least 75%?

P12316, L13: clarify that the tetrols were observed in aerosol



ACPD

8, S4274–S4278, 2008

", L20-22: refer to Table 1 in this sentence to show the range of closure achieved

P12318, L16: "photochemical processing"?

", L23: "in the summer" or "during summer"

", L26-29: but point out that the sensitivity will be double (on a molecular basis) if another ONO2 group is added

P12319, L17 "for each compound class"

", L18-19: "Each channel..."; this sentence is grammatically incorrect

P12321, L1: "580C channel."

P12321, L17-18: 1-minute merged, but point out that the canister data is less frequent than that.

P12322, L10-11: suggest "we would expect a strong correlation between them in ambient samples, depending on their relative lifetimes and the age of the sampled air"

P12322, L16: this equation needs an equals sign

", L24: None of those papers actually inferred isoprene emissions from satellite data. Here are some that did: Palmer et al., 2003; Abbot et al., 2003; Shim et al., 2005; Palmer et al., 2006; Fu et al., 2007; Millet et al., 2008.

P12323, L11: give value for assumed rate constant

P12324, L18-20: presumably this is based on measured OH and J-values; please note this.

", L25-28: A bit awkward. How about "... weighted according to the product yields of the individual isomers..."

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 12313, 2008.



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8, S4274–S4278, 2008

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