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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.

A. E. Perring et al.

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We thank referee #2 for the constructive comments. All of the technical corrections and typos noted will be addressed in the revised manuscript. We describe our detailed responses to scientific comments below. Both referees suggest looking at correlations between isoprene and total_ANs. We have omitted them in the current text because we believe such correlations are misleading, as we will clarify in the revised text. total_ANs should be correlated with the fraction of isoprene that has already been oxidized by OH and then reacted with NO or isoprene that has reacted with NO3 and not with isoprene itself. Formaldehyde is also connected to the same reaction channel. In the revised manuscript we will add text and a figure to clarify this point.

Reviewer comment: Isoprene oxidation pathways and the associated product yields (e.g., HCHO) depend on NOx. The authors should include a discussion of this and

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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).

Response: We do not investigate isoprene oxidation in this manuscript but rather we specifically investigate the yield of nitrates from the Isoprene-O2+NO reaction and constrain the lifetimes of the resulting nitrates. In the revised manuscript we will discuss this in more detail to clarify the general issue and also the possibility of uncorrelated H2CO sources.

Reviewer Comment: By combining everything into a single average the authors do not do justice to their data. Isoprene is highly variable and its effect on RONO2 should be as well. Figure 4 fails to give 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.

Response: As indicated above, we think isoprene itself is not the point of this manuscript. Nonetheless, we will add discussion to the revised manuscript showing the relationship between both ANs and isoprene and CH2O and isoprene. The specific figure proposed by the referee does not have sufficient statistics for us to be satisfied that it is meaningful. In the revised manuscript we will clarify where we use means and medians.

Reviewer comment: VOC dataset. It is not clear what if any VOC data were 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 cat-

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egory is said to include all measured non-methane hydrocarbons. Generally NMHC does not include OVOCs so this is all very confusing.

Response: The primary OVOCs that are relevant are MACR and MVK. In the revised paper we will clarify our use of terminology. We will also include the PANAK measurements in our calculation although the impacts on the result are negligible.

Reviewer Comment: 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.

Response: We will remove the comment in question from section 3.2.

Reviewer Comment: Also you should move the later discussion of observed vs. predicted OH reactivity here to make this point. Point out also that you 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 have already undergone significant oxidation before you could measure them.

Response: In the revised manuscript we will limit section 3.2 to a more qualitative discussion of why we might expect CH2O and total_ANs to be correlated and an introduction to the complications involved in the interpretation of this correlation. It is mainly intended as a lead-in to sections 3.3 and 3.4 where we discuss OH reactivity and lifetime effects in more detail.

Reviewer Comment: Finally, what does this mean? Is isoprene the dominant source of RONO2 everywhere, in the mean, some of the time? See variability comment above

Response: We have been careful not to talk about the distribution of total_ANs in this paper. In our opinion knowledge of the yield and lifetime allows a general analysis of where and when INs will be important if there is knowledge for a model of VOC reactivity and NOx.

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Reviewer Comment: L15: say would imply; since (as you show) you can not ignore those things.

Response: Noted and corrected.

Reviewer Comment: L17: known formaldehyde yield. There is 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 from 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.

Response: This comment refers to correlations of CH2O with isoprene emissions. As we discuss above and will expand upon in the text, our analysis does not start with isoprene but with isoprene oxidized by OH that subsequently reacts with NO. We do not think the referee's question can be addressed with the data available.

Reviewer Comment: P12322, L18-21. Suggest rewording since now it sounds like you are going to conclude that none of those effects matter and the yield is 6.8%. What about writing: 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.

Response: We will reword as suggested.

Reviewer Comment: 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.

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Response: We will rearrange and elaborate on the closure of the OH reactivity budget.

Reviewer Comment: Throughout, please do not say average since it is ambiguous. Say mean or median.

Response: All instances of average will be changed to mean. Medians will also be discussed in the revised manuscript.

Reviewer Comment: 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?

Response: We will clarify the statement so that it addresses the chemistry in question more specifically.

Reviewer Comment: 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.

Response: Yes, CH2O loss also should and will be included in a revised manuscript. Regression statistics for higher altitudes will be included in the revised text.

Reviewer Comment: 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.

Response: This was also noted by referee #1 and a more detailed discussion will be included in the revised manuscript. The uncertainty in the rate constants is likely not more than a factor of two, leading to an upper limit to the overall lifetime to oxidation of

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˜1 hour and a lower limit of ˜15 minutes. As discussed in response to reviewer #1, in the revised manuscript we will scale the NCAR and URI formaldehyde measurements to bring the two sets of observations into agreement with one another. This decreases the slope of the total_ANs-CH2O correlation and leads us to infer slightly longer lifetimes. The minimum lifetime (for a 12% branching ratio) is 2 hrs and the maximum lifetime (for a 4.4% branching ratio) is 8 hrs. Using these two extreme cases and the upper and lower limits of the calculated lifetime to oxidation the recycling rate is at least 50% and at most 97%.

Reviewer Comment: 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 is 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).

Response: We will rephrase to make this clearer. What we mean is that they all provide satisfactory fits to the data. No matter what uncertainties there are in both the formation rate and the lifetime to oxidation of isoprene nitrates, the conclusion that recycling rate is high remains firm. This wide range highlights current uncertainties in isoprene nitrate chemistry and indicates that getting the loss processes correct is as important to modeling isoprene nitrates as is getting the formation rate correct.

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

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