

We thank the reviewer for the detailed and helpful comments. We have provided our response below, together with specific comments of the reviewers in italics.

1) Missing NO_y. The authors demonstrate that the model in both simulations (and presumably all the sensitivity studies) simulates NO_y which is lower than observed, but Σ AN's which is much higher. What are the likely reasons for this? One would imagine that NO_y is dominated by HONO₂, PAN and the (Sum)AN's.

Observed NO_y is largely composed of HNO₃, peroxy nitrates, NO_x, and alkyl nitrates. Underestimation of NO_y in the model is caused by underestimation of HNO₃. Both the base (−44%) and IS scheme (−33%) show low bias of HNO₃, which might be related to errors in the deposition process of HNO₃. The INTEX experiment included two measurements of HNO₃. For our analysis, we followed the approach in Bertram et al. (2007) and multiplied the UNH measurement by 1.2 and the CIT measurement by 0.8. Using either the UNH or CIT measurements alone did not substantially change the result.

We have added the following sentence to page 27185, line 2: “HNO₃ (not shown) is biased low in both cases (−44% for the base, −33% for IS scheme).”

2) Constraints on "global" importance of NO₃+Isoprene as source of ISON. It strikes me as interesting that the reaction between NO₃ and isoprene should really have such a large role to play on the formation of isoprene nitrates given that not much isoprene is emitted/exists at night. Do the authors think this could be a (general) model artifact (I note that this result has been observed in other modelling studies) or is there any observational evidence for enhanced formation of ISON during the night?

Based on aircraft measurements and laboratory observed nitrates yield (80%), Brown et al. (2009) inferred organic nitrates formed from isoprene+NO₃ reactions accounted for 2-9% of NO_y in the Northeast US. Direct evidence for enhanced formation from this pathway is rare, as ambient observations have been largely limited to mono-functional alkyl nitrates and total alkyl nitrates (Buhr et al., 1990; Flocke et al., 1998; Rosen et al., 2004; Cleary et al., 2005; Day et al., 2009), and few cases, isoprene hydroxynitrates (Grossenbacher et al., 2001, 2004). Recently at a rural forested site in California, the main products from isoprene+NO₃ reactions (i.e. nitrooxycarbonyl and nitrooxyhydroperoxide) were tentatively identified (Beaver et al., 2012). The elevated concentrations of these species (up to ~70 ppt) indicated the importance of nighttime isoprene chemistry. Nevertheless, more ambient measurements of individual multifunctional organic nitrates are needed to verify model predictions.

We will add the following sentence to page 27189, line 19 “...however, direct

evidence for enhanced formation from this pathway is rare. Ambient observations have been largely limited to mono-functional alkyl nitrates and total alkyl nitrates (Buhr et al., 1990; Flocke et al., 1998; Rosen et al., 2004; Cleary et al., 2005; Day et al., 2009). Only in a few cases the diurnal profiles of specific individual multifunctional organic nitrates have been quantified (Grossenbacher et al., 2001, 2004; Beaver et al., 2012). More ambient measurements are needed to verify model predictions.”

3) *Computational overheads. It would be interesting to know how much more demanding the IS simulations were relative to the base case.*

The IS simulations are 10 – 40% slower than the base case, depending on the numerical solver used in the chemistry routines. This is due to a combination of more processor time in the chemical solver due to more reactions, more processor time in the advection routines because of the expanded number of chemical species, and more input / output disk time because more species were saved. We have not examined this under different configurations of the parallelization, so a user’s experience may differ.

Technical corrections.

The following corrections refer to the page and line numbers in the ACPD paper:

27180-16: Use lower case k for rate constant.

It has been corrected as suggested.

27181-27: Add reference to da Silva 2009.

We think the reviewer refers to da Silva et al. (2010). “**da Silva, G., Graham, C., and Wang, Z. F.: Unimolecular β -Hydroperoxy Radical Decomposition with OH Recycling in the Photochemical Oxidation of Isoprene, Environ. Sci. Technol., 44, 250–256, 2010.**” The reviewer suggested adding the reference in the following sentence. “**The measured isomerization rate from Crouse et al. (2011) is used, which is ~50 times slower than that predicted from theoretical calculations (Peeters et al., 2009; Peeters and Müller, 2010).**”

The experimental work by Crouse et al. (2011) characterized 1,6-H-shift isomerization rate for δ -isoprene peroxy radicals. In our manuscript, we used this rate in the IS mechanism and compared it (as shown above) with those predicted from theoretical calculations (Peeters et al., 2009; Peeters and Müller, 2010). In contrast, da Silva et al. (2010) calculated 1,5-H-shift isomerization rates for β -isoprene peroxy radicals. This channel wasn’t implemented in IS scheme, as several studies (Crouse et al., 2011; Stone et al., 2011) concluded the process likely plays a minor role in the atmosphere. We think it will cause confusion if we add the reference as the reviewer suggested, as we only intend to compare the 1,6-H-shift isomerization rates.

27185-15: *You may want to add a comma after "from isoprene" and after "(MACR)".*

This has been corrected as suggested.

27188-18: *Add reference to Archibald et al., 2010 (this was included in the ref list but I couldn't see it in the main text).*

The reference has been added at page 27188, line 18 as suggested.

27189-9: *Add reference to Orland and Tyndall, 2012.*

The reference has been added at page 27189, line 9 as recommended.

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