

Interactive comment on “North American isoprene influence on intercontinental ozone pollution” by A. M. Fiore et al.

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The specific comments from Reviewer 1 are surrounded by **. We are grateful for this careful review which we believe has greatly strengthened our manuscript.

1. General comments

We have carefully revised the manuscript, attempting to clarify ambiguous discussions (e.g., replace “change” with “increase” or “decrease”. To further aid comprehension, we have revised Figure 3 (now Figure 4) to plot the response to isoprene emission increases on the right-hand axis (shown in green). We also include an expanded discussion of the results as suggested by the reviewer.

2. Specific comments **1. The discussion of percent changes in O₃ and PAN resulting

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Discussion Paper



from changed emissions (Figure 2) is a central finding of the paper. It is odd, however, that the manuscript only shows O₃ at the surface in comparison with PAN at 700 hPa rather than comparing O₃ and PAN at the same vertical layer. There are good reasons for this choice: surface O₃ is of direct interest, while 700 hPa PAN shows the strongest percent change in response to precursors. However the comparison of responses to O₃ and PAN in Figure 2 is difficult because of the obviously different transport patterns (and photochemical lifetimes) between the surface and 700 hPa. I suggest that the authors consider expanding Figure 2 to include percent changes of O₃ at 700 hPa and PAN at the surface, in addition to the current content (O₃ at the surface and PAN at 700 hPa).**

We now better motivate our selection of the 700 hPa level, which was not for the reason assumed by the reviewer. We now explain our reasoning in Section 3: “We next examine changes in O₃ and PAN at the model level centered at 694 hPa, hereafter referred to as “700 hPa”, for two reasons: (1) this level should reside in the lower free troposphere and thus reflect the composition of air masses that are available to subside and mix into the continental boundary layer, and (2) this altitude is a region of the atmosphere that can be sampled with ground-based instruments in mountainous regions.”

We also expand Figure 2 (now Figure 3) to include percentage ozone changes at 700 hPa and the surface, along with 700 hPa PAN and NO_y deposition. In addition, we have included absolute changes in PAN at the surface in Figure 1 (along with the base simulation surface O₃ and PAN abundances, as requested below) and created a new Figure 2 that includes base simulation 700 hPa O₃ and PAN abundances, as well as the absolute changes at 700 hPa from the NA emissions perturbations. Section 3 has been revised to include discussion of these additional figures.

**Specifically, the manuscript states (p. 24832, line 25): “Comparing the O₃ and PAN responses in Fig. 2 indicates that the PAN changes, induced either by NA anthropogenic or isoprene emission perturbations, are more than twice as large as for O₃,

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with larger changes extending over wider regions." This is definitely true for the O₃ and PAN responses to isoprene, and it is true for the responses to anthropogenic emissions over the oceans (where long-distance transport is important). However it does not appear to be true over the US. **

This discussion has been moved into a new Section 5, as requested by referee #2 ("PAN as a proxy for regional changes in O₃ precursor emissions") and the revised text reads, "Indeed, outside of the NA source region, the magnitude of the PAN changes, induced either by NA anthropogenic or isoprene emission perturbations, is more than twice as large as for O₃, with larger changes extending over wider regions."

Since transport is generally stronger at 700 hPa than at the surface, it is not clear whether the response to anthropogenic emissions is stronger for PAN in an equivalent comparison (surface-to-surface and/or 700 hPa to 700 hPa). The rationale for a stronger PAN response is also much more clear for isoprene than for anthropogenic emissions. (Isoprene emissions are direct PAN precursors and increase the effective yield of PAN resulting from the combined organic+OH atmospheric reactions. Increases in anthropogenic HC, CO and NO_x may also lead to greater increases in PAN than O₃, but this would be due to complex O₃-NO_x-PAN chemistry rather than a shift in the atmospheric CO-HC content in the direction of greater PAN formation relative to O₃ formation).) So it would be useful to show a direct comparison for O₃ and PAN responses at 700 hPa. Also, does the PAN response disappear at the surface (where PAN is short-lived)? Results for PAN at the surface would show this. Adding these extensions to Figure 2 (O₃ at 700 hPa and PAN at the surface) would be most useful. The authors may consider adding equivalent figures to Fig 1 and Fig 4 (and possibly the equivalent base case O₃ and PAN for comparison) as supplementary files, if that is possible through ACP.

We have included these suggested Figure expansions as described in our response to the point 1 above.

**2. The text (p. 24830) states that "we estimate that up to 25 % of lower tropospheric

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PAN over Spain, the Mediterranean and Northern Africa is associated with NA isoprene emissions." The phrase "lower tropospheric PAN" seems to suggest that NA isoprene is a significant source of PAN even at the surface, and even in regions with local isoprene and anthropogenic emissions (Spain). This may just be a problem with wording. The authors may be referring only to 700 hPa and not to the surface. Can this be clarified?*

Yes, we have reworded to specify "at 700 hPa".

Also in this context: Do the PAN precursors (specifically methyl glyoxal, HYDRALD and hydroxyacetone, if included) also show sensitivity to NA isoprene in this region? If so, are they large enough to contribute significantly to reformation of PAN? Or is transport limited to PAN in regions where it is long-lived (700 hPa and higher)? If the model predicts a significant signal from PAN near the surface, then it should also show a change in PAN precursors, enough to contribute to the re-formation of PAN. This may be beyond the scope of the paper but it would be useful to know.

Interesting point, and the simulations for these species nicely illustrate the difference between isoprene, a major precursor to the PAN precursors mentioned here, versus the anthropogenic emissions which are not (at least in the model). For the anthropogenic emissions, changes in methyl glyoxal and hydroxyacetone are confined mainly to the continental source region, whereas the longer-lived hydroxyacetone product of isoprene oxidation enables the isoprene emission increase to impact hydroxyacetone and thereby methyl glyoxal far downwind, contributing to the stronger PAN response to isoprene relative to ozone for the isoprene versus anthropogenic emission perturbations. We have added some discussion of this to the manuscript, in Section 3: "In the case of O₃ (both at the surface and at 700 hPa), the decrease in response to the 20% reduction of NA anthropogenic emissions is generally larger in magnitude than the O₃ increase from the 20% increase in NA isoprene emissions (Figs. 1,2 and 3). In contrast, the 700 hPa PAN enhancements from the 20% increase in NA isoprene emissions are equivalent in magnitude or larger than the 700 hPa PAN decreases from

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the 20% reduction in NA anthropogenic emissions (Figs. 1,2 and 3). The slightly larger response of 700 hPa PAN over the EU region to NA isoprene may partially reflect the transport of hydroxyacetone, an intermediate isoprene oxidation product (lifetime of days) which further reacts to produce methyl glyoxal and the peroxy acetyl radical, which may lead to additional PAN formation in the presence of NO_x (e.g., from regional emissions; not shown).”

3. The following concerns clarity of presentation and possible confusion over the direction of changes: An essential piece of background information needed for reading this paper is the knowledge that increased emissions leads primarily to increased reaction products (ozone and PAN) throughout the study, and decreased emissions lead to decreased ozone and PAN. I think this is not stated clearly enough. Results in the figures typically present both increases-from-increases and decreasesfrom- decreases as positive numbers, sometimes on the same graph (Figure 3). The figures are OK but only if they are very clearly explained. After all, it is not always true that increased biogenics lead to increased O₃ - in some environments O₃ decreases in response to increased isoprene. I think it would be most useful to state this at the start of the discussion of results (p.24829, start of Section 3). Also, it would help if the authors referred specifically to "increase" or "decrease" in referring to perturbations and responses, so that readers can keep track of the directionality of the changes.

We fully agree and have attempted to clarify throughout the text. Most notably, the revised Figure 3 (now Figure 4), shows the O₃ and PAN decreases resulting from the 20% decreases in NA anthropogenic emissions on the left-hand axis (in black), and the increases from the 20% NA isoprene emission increase plotted on the right hand axis (in green). This should aid in better communicating our results.

**Here are specific examples: p. 24833 line 15 "When isoprene increases by 20% in the model, as might occur in a warmer climate, the O₃ sensitivity to NA anthropogenic emissions reductions is cut by approximately half over foreign regions and by one third over the NA region from summer into fall (black solid vs. dash-dot lines in Fig. 3)." |

would interpret the phrase "sensitivity to NA anthropogenic emissions reductions" as referring to the change in O₃ between two cases with identical biogenic VOC – base case vs -20 % anthro (solid black line in Fig. 3) or +20% isop versus +20 % isop, -20 % anthro (sum of green line and broken black lines). These are almost identical (compare the broken black line with the linear sum line). The authors probably intend to say that the combination of reduced anthropogenic emissions and increased isoprene will reduce O₃, but the reductions are smaller than would be achieved by a reduction in anthropogenic emissions with no change in isoprene. The wording needs to be clarified.**

Agreed. We have revised our prose to better communicate this point, and further, separated out the lines showing these results from Figure 3 into a completely separate figure (now Figure 5). Discussion in the text (opening section of Section 6, "Estimating NA anthropogenic influence: Uncertainty from isoprene emissions and chemistry ") now reads: "We first estimate the degree to which NA isoprene emission increases, as might be induced by changes in climate or land-use (e.g., Sanderson et al., 2003; Wiedinmyer et al., 2006; Weaver et al., 2009), would offset the decreases in surface O₃ resulting from NA anthropogenic emission controls. The differences between two pairs of simulations, SR1-SR6NA (solid black line in Fig. 5) and SR1- SR6ISOPNA simulation (black dash-dot line in Fig. 5) provide an estimate of such an impact. We do not consider changes in the spatial distribution of isoprene emissions relative to the simple, uniform scaling applied here, which may also alter the surface O₃ response to anthropogenic emissions. When isoprene increases by 20% in the model, the surface O₃ decrease in response to the 20% reduction in NA anthropogenic emissions is offset by approximately half over foreign regions and by one third over the NA region from summer into fall." And later in that paragraph: "We further note that the combined impact of NA isoprene and anthropogenic emission perturbations can be approximated by adding the differences between pairs of simulations in which we perturbed those emissions individually (black dot-dash versus dotted lines in Fig. 5)."

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****Abstract:** "The regional NA surface O3 response to a 20 % increase in NA isoprene is approximately one third of the response (oppositely signed) to a 20 % decrease in all NA anthro- pogenic emissions in summer. " This would be easier to follow if the text stated specifically that surface O3 increased in response to increased isoprene and decreased in response to decreased anthropogenics. ******

Agreed, revised as suggested.

****p. 24829 line 20:** "Over foreign regions in the Northern Hemisphere, the changes in surface O3 resulting from a 20 % perturbation to NA isoprene emissions are at least half as large as those from a 20 % perturbation to all NA anthropogenic emissions during August (Fig. 1). " Here it would be much clearer if the text referred specifically to increases and decreases rather than perturbations. This would be a good place to state that increased isoprene leads to increased model ozone, and that decreases in anthropogenics lead to decreased ozone. ******

Agreed, revised accordingly.

****p. 24829, line 13:** "Although we imposed oppositely signed perturbations to the isoprene and anthropogenic emissions..." This sentence would also be easier to understand if placed in a context of increased O3 in response to increased isoprene, decreased O3 in response to decreased emissions, etc. Readers familiar with the previous work by Fiore et al. and HTAP will understand this sentence, but it would be useful to add an explanation. ******

Done.

****4. NOx recycling from isoprene nitrates:** It is not clear whether the change from 40 % to 100 % recycling case releases only NOx or whether it also releases organics. From Horowitz et al., 2007, the relevant reactions are $\text{ONITR} + \text{OH} \rightarrow 0.4 \cdot \text{HYDRALD} + 0.4 \cdot \text{NO}_2 + \text{HO}_2 + 0.6 \cdot \text{XNITR}$ $\text{ONITR} + \text{O}_3 \rightarrow 0.4 \cdot \text{HYDRALD} + 0.4 \cdot \text{NO}_2 + \text{HO}_2 + 0.6 \cdot \text{XNITR}$ Does the case with 100% NOx recycling change the yield of HYDRALD and

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XNITR as well as NO₂? XNITR does not undergo further reaction, but HYDRALD can contribute to subsequent chemistry. Please clarify.**

Thank you for pointing this out. We are using an older chemical mechanism (MOZART-2 [Horowitz et al., 2003]) that does not explicitly track XNITR or include the ONITR+O₃ reaction, however we do indeed increase the HYDRALD yield to match the changes to NO_x (ONITR+OH → HYDRALD + NO₂ + HO₂). We now clarify with a parenthetical statement in the text: “(Note that we do not explicitly track secondary multi-functional organic nitrates which serve as a terminal sink in Horowitz et al. (2007) but we do increase the hydroxycarbonyl yield to match that of NO_x.)”

3. Technical corrections p. 24827 line 10: "The lower anthropogenic NMVOC emissions and higher anthropogenic NO_x imply that O₃ and PAN formation in MOZART-2 may be more sensitive to NA isoprene vs. anthropogenic NMVOC emissions as compared to other CTMs. " Awkward wording - it is hard to figure out what this sentence means.

Rewritten to, “The decline in eastern U.S. anthropogenic NO_x emissions over recent years, which occurred after 2001, will tend to decrease the sensitivity of O₃ formation to isoprene, suggesting that the current O₃ sensitivity to NA isoprene emissions may be smaller than that estimated below.”

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 24821, 2010.

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