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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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1. General comments

The manuscript addresses several issues associated with the impact of isoprene on global O3. This is a continuation of a series of papers on hemispheric transport of air pollutants and presents useful information. Results are not strikingly new, but the paper provides a useful expansion and clarification of the authors' previous results. Several features are interesting: the near-linear response of O3 and PAN to combined perturbations; the strong response of PAN to changes in biogenic emissions; the unchanged results with different NOx recycling from isoprene nitrates; and the general comparison of impact from perturbed biogenic versus anthropogenic sources. The near-linear response to perturbations is especially important because it suggests that the current model uncertainties (different performance versus measured O3 and isoprene nitrate

chemistry) are unlikely to affect policy-relevant findings with regard to transport. I recommend publication.

There are some places where the manuscript is confusing and should be worded more carefully. These are related primarily to the way the authors describe precursor responses: increased O3 and PAN from increased isoprene, decreased O3 and PAN from decreased anthropogenic emissions, etc. The text sometimes does not clearly identify the direction of the changes (increases causing increases, etc.) and occasionally the authors seem to even trip themselves up in summing the combined effects of increases and decreases.

The comments below also include suggestions for minor expansions of the results. These would be useful but are not necessary. It depends on how far the authors want to go.

2. Specific comments

1. The discussion of percent changes in O3 and PAN resulting 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).

Specifically, the manuscript states (p. 24832, line 25):

"Comparing the O3 and PAN responses in Fig. 2 indicates that the PAN changes, in

duced either by NA anthropogenic or isoprene emission perturbations, are more than twice as large as for O3, 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. 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 fo 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 NOx may also lead to greater increases in PAN than O3, but this would be due to complex O3-NOx-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.

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

thors may be referring only to 700 hPa and not to the surface. Can this be clarified?

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.

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 decreases-from-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.

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)."

I 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.

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.

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.

p. 24829, line 13: "Although we imposed oppositely signed perturbations to the iso-

prene 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.

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

ONITR + OH -> 0.4*HYDRALD + 0.4*NO2 + HO2 + 0.6*XNITR

ONITR + O3 -> 0.4*HYDRALD + 0.4*NO2 + HO2 + 0.6*XNITR

Does the case with 100% NOx recycling change the yield of HYDRALD and XNITR as well as NO2? XNITR does not undergo further reaction, but HYDRALD can contribute to subsequent chemistry. Please clarify.

3. Technical corrections

p. 24827 line 10: "The lower anthropogenic NMVOC emissions and higher anthropogenic NOx 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.

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