

1 North American isoprene influence on intercontinental ozone 2 pollution

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8 9 Abstract

10 Changing land-use and climate may alter emissions of biogenic isoprene, a key ozone (O₃)
11 precursor. Isoprene is also a precursor to peroxy acetyl nitrate (PAN) and thus affects
12 partitioning among oxidized nitrogen (NO_y) species, shifting the balance towards PAN which
13 more efficiently contributes to long-range transport relative to nitric acid (HNO₃) which rapidly
14 deposits. With a suite of sensitivity simulations in the MOZART-2 global tropospheric
15 chemistry model, we gauge the relative importance of the intercontinental influence of a 20%
16 increase in North American (NA) isoprene and a 20% decrease in NA anthropogenic emissions
17 (nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOC) and
18 NO_x+NMVOC+carbon monoxide+aerosols). The surface O₃ response to NA isoprene
19 emissions (ΔO_3_{ISOP}) in surface air over NA is about one third of the response to all NA
20 anthropogenic emissions (ΔO_3_{ANTH} ; although with different signs). Over intercontinental
21 distances, ΔO_3_{ISOP} is relatively larger; in summer and fall, ΔO_3_{ISOP} in surface air over
22 Europe and North Africa (EU region) is more than half of ΔO_3_{ANTH} . Future increases in NA
23 isoprene emissions could thus offset decreases in EU surface O₃ resulting from controls on NA
24 anthropogenic emissions. Over the EU region, ΔPAN_{ISOP} at 700 hPa is roughly the same
25 magnitude as ΔPAN_{ANTH} (oppositely signed). Outside of the continental source region, the
26 percentage changes in PAN are at least twice as large as for surface O₃, implying that long-term
27 PAN measurements at high altitude sites may help to detect O₃ precursor emission changes. We
28 find that neither the baseline level of isoprene emissions nor the fate of isoprene nitrates

1 contributes to the large diversity in model estimates of the anthropogenic emission influence on
2 intercontinental surface O₃ or oxidized nitrogen deposition reported in the recent TF HTAP
3 multi-model studies (TFHTAP, 2007).

4

5 **1 Introduction**

6 A recent internationally coordinated effort has estimated hemispheric pollutant transport at
7 northern mid-latitudes and assessed uncertainties in these estimates (TFHTAP, 2007). Intended
8 to inform future policy negotiations under the Convention on Long-Range Transboundary Air
9 Pollution (CLRTAP), work to date has largely focused on “source-receptor” (SR) relationships
10 (*i.e.*, the pollutant response in a receptor region to an emissions perturbation within a source
11 region) for anthropogenic emissions (TFHTAP, 2007; Sanderson et al., 2008; Shindell et al.,
12 2008; Fiore et al., 2009; Reidmiller et al., 2009; Jonson et al., 2010; Anenberg et al., 2009). In
13 regions heavily vegetated with isoprene-emitting plants, however, anthropogenic emissions of
14 nitrogen oxides (NO_x) interact with isoprene, a highly reactive non-methane volatile organic
15 compound (NMVOC), to produce ozone (O₃) and thereby contribute to urban and regional air
16 pollution (*e.g.*, Trainer et al., 1987; Chameides et al., 1988). Below, we describe our application
17 of a three-dimensional global chemical transport model (CTM) to examine the sensitivity of
18 intercontinental O₃ pollution to changes in NA isoprene emissions and chemistry alongside
19 changes in NA anthropogenic emissions.

20 Isoprene emissions increase strongly with temperature and sunlight and at northern mid-latitudes
21 occur from spring through fall with a summer peak (*e.g.*, Guenther et al., 2006). Global isoprene
22 emissions are estimated to be at least five times higher than all anthropogenic NMVOC
23 emissions and have been shown to enhance the tropospheric O₃ burden (*e.g.*, Fuentes et al., 2000;
24 Folberth et al., 2006; Guenther et al., 2006; Wild, 2007; Wu et al., 2007; Pfister et al., 2008). In
25 the eastern United States, July isoprene emissions have been estimated to be 4 to over 10 times
26 higher than anthropogenic NMVOC (*e.g.*, Fiore et al., 2005). Isoprene, oxidized in the presence
27 of the anthropogenic NO_x available in this region, contributes as much as 15-25% to surface O₃
28 in summer as compared to ~2% from anthropogenic NMVOC (Horowitz et al., 1998) and may
29 play a key role in hemispheric transport of O₃.

1 In addition to O₃, various organic nitrates, including peroxy acetyl nitrate (PAN) which is
2 particularly relevant for intercontinental transport, are produced during photochemical reactions
3 involving isoprene (and to a lesser extent, other NMVOCs) and NO_x. Formation of PAN alters
4 the balance between deposition and export of oxidized nitrogen (NO_y = NO_x+ HNO₃ + PAN +
5 other minor oxidation products) from the NA region (*e.g.*, Roberts et al., 1995; Horowitz et al.,
6 1998). Frontal passages and convection, which ventilate the eastern NA boundary layer, can loft
7 PAN to higher, colder altitudes where it is thermally stable and can undergo long-range transport
8 and contribute to O₃ production upon decomposition in air masses that warm as they subside
9 (*e.g.*, Moxim et al., 1996; Liang et al., 1998; Val Martin et al., 2008; Fang et al., 2010; Fischer et
10 al., 2010a). Two pathways contribute approximately equally to intercontinental transport of O₃
11 pollution: (1) production of O₃ over the source region which is then exported, (2) export of
12 precursors, PAN in particular, which then produce O₃ during transit to the downwind region
13 (Liang et al., 1998; Jacob et al., 1999; Wild et al., 2004; West et al., 2009; Lin et al., 2010).
14 PAN may also be a useful proxy for changes in O₃ precursor emissions, which may be detected
15 more readily in observations of PAN than O₃ (Jaffe et al., 2007; Fischer et al., 2010b).

16 Large uncertainties envelop the current understanding of the magnitude and distribution of
17 isoprene emissions and subsequent oxidation chemistry (*e.g.*, Steiner and Goldstein, 2007; Arneth
18 et al., 2008; Carlton et al., 2009; Lelieveld et al., 2008). This uncertainty propagates into PAN
19 formation and therefore the impact of isoprene-NO_x-O₃ chemistry on foreign regions (Kuhn et
20 al., 1998; Emmerson and Evans, 2009). Of particular relevance for O₃ produced in the source
21 regions is the uncertain interaction of isoprene with the NO_x budget via isoprene nitrate
22 formation; the ultimate influence of isoprene on O₃ may hinge on the poorly understood fate of
23 isoprene nitrates (*e.g.*, von Kuhlmann et al., 2004; Ito et al., 2009; Perring et al., 2009; Paulot et
24 al., 2009; Weaver et al., 2009). While we expect these uncertainties to contribute to model
25 diversity in “baseline” simulations for the present atmosphere, it is unclear whether they are also
26 contributing to the range in model estimates of the responses of surface O₃ and NO_y deposition to
27 anthropogenic emission perturbations, as reported in prior TF HTAP publications (Sanderson et
28 al., 2008; Fiore et al., 2009; Reidmiller et al., 2009).

29 Although anthropogenic emissions of isoprene may be a major contributor to ambient isoprene in
30 some urban settings, the biogenic source overwhelmingly dominates over much of the northern
31 mid-latitudes during the warm season (Reimann et al., 2000; Guenther et al., 2006; Dollard et al.,

1 2007). Even the biogenic isoprene source, however, is heavily influenced by human activities
2 via land-use changes, as has occurred historically with changes in cropland areas (*e.g.*, Lathière
3 et al., 2010). Future decisions to establish poplar (a high isoprene-emitting species) plantations
4 for biofuel or to convert vast forested regions to croplands (low isoprene emitters) could
5 dramatically alter future isoprene emissions and thereby air quality (*e.g.*, Wiedinmyer et al.,
6 2006; Avise et al., 2009; Chen et al., 2009). The strong temperature dependence of isoprene
7 emissions suggests that they will increase in a warmer climate, but other factors (higher carbon
8 dioxide, drought, pollutant exposure, insect herbivory) could offset this increase (*e.g.* Pacifico et
9 al., 2009; Rosenstiel et al., 2003; Guenther et al., 2006). The relative importance of future
10 changes in climate and land-use on isoprene emissions is unclear, but the potential for humans to
11 alter isoprene emissions deserves consideration.

12 As a first step towards understanding the role of isoprene emissions in intercontinental O₃
13 pollution, we use the MOZART-2 global CTM (Section 2) to quantify the influence of NA
14 isoprene on O₃ and PAN in surface air and at 700 hPa, as well as NO_y deposition at northern
15 mid-latitudes in August (Sections 3) and throughout the year (Section 4). We also explore the
16 potential for PAN measurements to detect O₃ precursor emission changes (Section 5). We then
17 evaluate the impact of uncertainties in isoprene emissions and chemistry on estimates of
18 hemispheric responses to NA anthropogenic emission controls (Section 6) and discuss the
19 implications of our findings (Section 7).

20

21 **2 Model Simulations**

22 We use the MOZART-2 model (Horowitz et al., 2003) in the same configuration
23 (“MOZARTGFDL-v2”) as applied to the year 2001 for the multi-model studies coordinated by
24 the Task Force on Hemispheric Transport of Air Pollution (TFHTAP; www.htap.org) (*e.g.*,
25 TFHTAP, 2007). Briefly, the model meteorology is driven by the NCEP reanalysis (Kalnay et
26 al., 1996) for the year 2001 with a horizontal resolution of 1.9°x1.9° with 28 vertical levels.
27 Emissions are as in Horowitz et al. (2003) except for biomass burning for which we use GFED
28 version 2 (van der Werf et al., 2006) for the year 2001. Isoprene emissions are a monthly
29 varying climatological inventory (Guenther et al., 1995; Horowitz et al., 2003). We modified the
30 isoprene oxidation chemistry from that of Horowitz et al. (2003) to use a 4% yield of isoprene

1 nitrates and 40% rate of recycling back to NO_x upon oxidation of these nitrates; these values are
2 consistent with observed alkyl and peroxy nitrates over the eastern United States in summer
3 (Horowitz et al., 2007). (Note that we do not explicitly track secondary multi-functional organic
4 nitrates which serve as a terminal sink in Horowitz et al. (2007) but we do increase the
5 hydroxycarbonyl yield to match that of NO_x .) The SYNOZ parameterization provides the
6 stratospheric O_3 upper boundary condition (McLinden et al., 2000), implemented as described by
7 Emmons et al. (2010). All simulations are spun up for seven months prior to the analysis year of
8 2001.

9 In the TF HTAP “source-receptor (SR)” simulations, anthropogenic emissions of O_3 precursors
10 were decreased by 20%, separately for NO_x , NMVOC, and carbon monoxide (CO), and for all
11 three precursors together (plus aerosols), within each of the four major northern mid-latitude
12 source regions in Fig. 1. We focus here on the NA source region, employing four MOZART-2
13 SR simulations (Table 1): base (denoted SR1) and perturbation simulations with 20% decreases
14 in NA emissions, for anthropogenic NO_x (SR3NA), anthropogenic NMVOC (SR4NA), and all
15 anthropogenic O_3 precursors plus aerosols combined (SR6NA). The differences between these
16 perturbation simulations and SR1 provide an estimate of the response to changes in
17 anthropogenic emissions. Hereafter, we refer to the decreases in O_3 and PAN produced by the
18 anthropogenic emission reductions as ΔO_3_ANTH and $\Delta\text{PAN_ANTH}$, respectively.

19 Of the four continental source regions in Fig. 1, North America is the most abundant isoprene
20 emitter in MOZART-2, with 35 Tg C a^{-1} as compared to 22, 12, and 17 Tg C a^{-1} from East Asia,
21 Europe, and South Asia, respectively. Qualitatively, this ranking is consistent with that for the
22 multi-model average regional emissions of non-anthropogenic NMVOC from the models
23 participating in the TF HTAP studies (determined as the differences between values reported in
24 Tables A2 and A3 of Fiore et al. (2009)). Anthropogenic emissions of NO_x , CO and NMVOC
25 from the NA region in MOZART-2 are $0.88 \times 10^1 \text{ Tg N a}^{-1}$, $1.00 \times 10^2 \text{ Tg a}^{-1}$, and $0.66 \times 10^1 \text{ Tg C}$
26 a^{-1} , respectively. The corresponding TF HTAP values (mean \pm standard deviation across models)
27 are $0.74 \times 10^1 \pm 0.04 \times 10^1 \text{ Tg N a}^{-1}$, $1.01 \times 10^2 \pm 0.19 \times 10^2 \text{ Tg a}^{-1}$ and $0.16 \times 10^2 \pm 0.071 \times 10^2 \text{ Tg C a}^{-1}$
28 for NA anthropogenic emissions of NO_x , CO and NMVOC, respectively (Table A3 of Fiore et
29 al., 2009). The lower anthropogenic NMVOC emissions and higher anthropogenic NO_x in
30 MOZART-2 imply that O_3 and PAN formation may be more sensitive to NA isoprene vs.
31 anthropogenic NMVOC emissions compared to other CTMs. Given that (1) the NA isoprene

1 emissions are still more than double the TF HTAP value for anthropogenic NMVOC emissions,
2 (2) isoprene reactivity is generally several times higher than that for anthropogenic NMVOC
3 (*e.g.*, Fuentes et al., 2000), and (3) surface O₃ over NA is more sensitive to NA NO_x than
4 anthropogenic NMVOC from spring through fall in the models participating in the TF HTAP
5 multi-model studies (Fiore et al., 2009; their Figure 4), we expect our results to be robust to
6 uncertainties in anthropogenic NMVOC emissions. The decline in eastern U.S. anthropogenic
7 NO_x emissions over recent years, which occurred after 2001, will tend to decrease the sensitivity
8 of O₃ formation to isoprene, suggesting that the current O₃ sensitivity to NA isoprene emissions
9 may be smaller than that estimated below.

10 The MOZART-2 SR1 simulation, which has previously been evaluated with observations of
11 surface O₃ and O₃ profiles as part of the TF HTAP effort (Fiore et al., 2009; Reidmiller et al.,
12 2009; Jonson et al., 2010), generally captures observed distributions and seasonality over most
13 regions. Notable exceptions include systematic high biases of 10-20 ppb in summertime surface
14 O₃ over the eastern United States and Japan, and systematic low biases of ~15 ppb at
15 mountainous sites in the western U.S. and Europe and at low-altitude sites in the northeastern
16 U.S. and central Europe during winter. Most pertinent to our study is the model overestimate of
17 summertime surface O₃ over the eastern United States; this is pervasive across the current
18 generation of CTMs (Fiore et al., 2009; Reidmiller et al., 2009) and investigations into its cause
19 are ongoing. Although we do not yet understand the source(s) of this bias in surface O₃, the lack
20 of a simple relationship between model biases with respect to the observations and the simulated
21 O₃ responses to either domestic or intercontinental emission changes (Reidmiller et al., 2009;
22 Jonson et al., 2010) suggests that additional tests are needed to evaluate the capability of models
23 to adequately resolve the key processes governing intercontinental O₃ pollution. Comparison
24 with monthly mean PAN measured at mountain sites (2-4 km altitude) in western NA (Mt.
25 Bachelor, Oregon, U.S.A.) and Europe (Jungfrauoch, Switzerland and Zugspitze, Germany)
26 indicates that MOZART-2 falls within the observed range in most months, with a tendency to
27 underestimate PAN from spring into early summer at the two European mountain sites (by 100-
28 200 ppt; Fiore et al., 2011).

29 We presently lack observational constraints on the O₃ response to emission perturbations, so we
30 briefly summarize the comparison of MOZART-2 estimates with the multi-model mean in the
31 HTAP studies. With respect to the intercontinental O₃ response to the combined 20% decreases

1 in anthropogenic NO_x+CO+NMVOC+aerosols emissions, MOZART-2 estimates fall below the
2 multi-model average (*e.g.*, Figure A2 of Fiore et al., 2009). The MOZART-2 annual NO_y export
3 fraction from NA is estimated to be 0.23, slightly higher than the multi-model mean of 0.18; the
4 summertime NA NO_y export fraction of 0.13, more relevant for our study, is close to the multi-
5 model mean (Sanderson et al., 2008; see their Table 1 and Figure 2).

6 In order to examine the relative importance of isoprene versus anthropogenic O₃ precursor
7 emissions on hemispheric O₃ levels, we conduct additional sensitivity simulations (Table 1).
8 Relative to SR1, we impose a 20% increase in NA isoprene emissions (denoted ISOPNA). Our
9 rationale for imposing oppositely signed perturbations to isoprene versus anthropogenic
10 emissions is based on the strong temperature dependence of isoprene (which suggests that its
11 emissions may increase in a warming climate), while we expect future efforts to abate air
12 pollution to yield additional decreases in NA anthropogenic emissions. We note caveats on this
13 scenario, which include the potential for rising carbon dioxide abundances or other factors to
14 cause NA isoprene emissions to decline in future years (*e.g.*, Rosenstiel et al., 2003, Avise et al.,
15 2009; Chen et al., 2009) For context, the 20% perturbation we impose on NA isoprene
16 emissions is equivalent to observed year-to-year fluctuations, estimated at ~20-30% from
17 formaldehyde columns retrieved from space (Abbot et al., 2003; Palmer et al., 2006). The
18 differences in O₃ and PAN between ISOPNA and SR1 provides an estimate of the response to
19 changes in NA isoprene (hereafter referred to as ΔO_3_ISOP and ΔPAN_ISOP) which can be
20 compared directly with the response to the TF HTAP SR anthropogenic emission perturbations.

21 For testing the sensitivity of ΔO_3_ANTH in surface air (diagnosed by differencing SR1 and
22 SR6NA) to isoprene emissions and their interactions with NO_x, we conduct three additional
23 simulations: (1) A combined 20% increase in NA isoprene and 20% decrease in NA
24 anthropogenic emissions (SR6ISOPNA), (2) SR1 but with 100% recycling of NO_x from isoprene
25 nitrates (SR1_r100), and (3) SR6NA but with 100% isoprene nitrate recycling (SR6NA_r100).
26 We use the difference between the SR6ISOPNA and SR1 simulations to gauge the potential
27 impacts of a coincident 20% increase in NA isoprene and 20% decrease in all NA anthropogenic
28 emissions, referred to hereafter as $\Delta O_3_ANTHISOP$ and $\Delta PAN_ANTHISOP$. The difference
29 between these simulations also allows for an estimate of the “noise” associated with inter-annual
30 variability in isoprene emissions surrounding the “signal” of a sustained reduction in NA
31 anthropogenic emissions. Such an estimate is useful, for example, if one were trying to detect

1 the influence of changes in NA emissions on O₃. We next estimate the potential contribution of
2 different baseline isoprene emission levels (ISOPNA-SR6ISOPNA) and different treatments of
3 isoprene nitrate chemistry (SR1_r100-SR6NA_r100) to the model spread in ΔO₃_ANTH
4 reported in Fiore et al. (2009) and for NO_y deposition reported in Sanderson et al. (2008). Table
5 1 summarizes the model simulations used in this analysis.

6
7 **3 Hemispheric influence of NA isoprene and anthropogenic emissions in**
8 **August**

9 Over foreign regions in the northern hemisphere, ΔO₃_ISOP is at least half as large (but opposite
10 in sign) as ΔO₃_ANTH during August (Fig. 1). The intercontinental ΔPAN_ISOP and
11 ΔPAN_ANTH at the surface is negligible (Fig. 1), reflecting the strong thermal instability of
12 PAN in warmer, surface air. The spatial patterns of the surface ΔO₃_ISOP and ΔO₃_ANTH
13 correlate strongly (r=0.71); both of these sources are predominantly located in eastern NA and
14 are subject to the same meteorology which exports O₃ from the NA continental boundary layer.
15 NA emissions exert the largest intercontinental influence on Europe and North Africa (EU), the
16 nearest downwind region, a robust result across models (Fiore et al., 2009).

17 We next examine changes in O₃ and PAN at the model level centered at 694 hPa, hereafter
18 referred to as “700 hPa”, for two reasons: (1) this level should reside in the lower free
19 troposphere and thus reflect the composition of air masses that are available to subside and mix
20 into the continental boundary layer, and (2) this altitude is a region of the atmosphere that can be
21 sampled with ground-based instruments in mountainous regions. At 700 hPa in August,
22 ΔPAN_ISOP and ΔPAN_ANTH are more strongly correlated spatially (r=0.99; Fig. 2) than
23 ΔO₃_ISOP and ΔO₃_ANTH (r=0.81). Both at the surface and at 700 hPa, ΔO₃_ANTH is
24 generally larger in magnitude than ΔO₃_ISOP (Figs. 1, 2 and 3). In contrast, the 700 hPa
25 ΔPAN_ISOP is equivalent in magnitude or larger than ΔPAN_ANTH (Figs. 2 and 3). The
26 slightly larger ΔPAN_ISOP at 700 hPa over the EU region may partially reflect the transport of
27 hydroxyacetone, an intermediate isoprene oxidation product with a lifetime of days, which
28 further reacts to produce methyl glyoxal and the peroxy acetyl radical, which may lead to
29 additional PAN formation in the presence of NO_x (e.g., from regional emissions; not shown).
30 These results demonstrate the key role that isoprene plays in PAN formation at northern mid-

1 latitudes in summer (Horowitz et al., 1998; Pfister et al., 2008). If we extrapolate the results in
2 Fig. 3 assuming that PAN responds linearly to isoprene emission changes (i.e., multiplying the
3 response to a 20% perturbation by five to estimate 100% contribution), then we estimate that up
4 to 25% of 700 hPa PAN over Spain, the Mediterranean and Northern Africa in August is
5 associated with NA isoprene emissions.

6 Since isoprene influences the NO_y partitioning between organic nitrates and nitric acid, we also
7 examine the impacts of anthropogenic versus isoprene emission changes on NO_y deposition (Fig.
8 3). The changes from NA anthropogenic emissions are similar to those reported for the NA NO_x
9 perturbations in Sanderson et al. (2008), with changes in deposition largely concentrated within
10 the source region, and small (a few percent) changes in the foreign TFHTAP regions. The NA
11 isoprene influence on NO_y deposition in the foreign TFHTAP regions is less than 1%. Over NA,
12 NO_y deposition decreases when isoprene emissions increase since isoprene is a direct precursor
13 to the peroxy acetyl radical, thus favoring PAN formation relative to nitric acid (HNO_3); the
14 decrease in OH associated with increasing isoprene emissions in the model would also tend to
15 decrease HNO_3 production (Horowitz et al., 1998). We emphasize that the influence of isoprene
16 on OH is the subject of much debate and ongoing research and is likely not well represented in
17 mechanisms available in current generation CTMs (e.g., Lelieveld et al., 2008; Ren et al., 2008;
18 Paulot et al., 2009; Archibald et al., 2010). Nevertheless, we see from Fig. 3 the interaction of
19 isoprene oxidation products with meteorology, which leads to more NO_y deposition in the North
20 Atlantic and North Pacific oceans. These regions are influenced by PAN decomposition in air
21 masses that subside as they circulate around the Bermuda and Pacific high pressure systems, and
22 the subsequent deposition of that nitrogen (mainly as HNO_3).

23

24 **4 Seasonal variations in regional and intercontinental influences of NA** 25 **emissions**

26 We turn next to seasonal variations in the surface O_3 and lower free tropospheric PAN responses
27 to changes in NA isoprene versus anthropogenic emissions. Following the approach of Fiore et
28 al. (2009), we construct monthly SR relationships for surface O_3 and PAN at 700 hPa by spatially
29 averaging over the continental-scale regions (Fig. 4). We focus on the NA and EU regions to
30 illustrate “regional” versus “intercontinental” responses. We note that the average values in Fig.

1 4 mask a large sub-regional variability in the O₃ response to emission perturbations (Reidmiller
2 et al., 2009; Lin et al., 2010), evident in Figs. 1, 2 and 3. Increases in isoprene consistently act to
3 depress local NO_y deposition but increase intercontinental NO_y deposition as seen in Fig. 3
4 (bottom row) throughout the isoprene emission season (not shown) and so we focus on seasonal
5 variations in O₃ and PAN in this section.

6 Over the NA and EU regions, ΔO_3_{ISOP} in surface air (Fig. 4) is enhanced in autumn relative to
7 spring, despite similar emissions in the two seasons (~4 Tg C in May and September, and ~2 Tg
8 C in April and October). In contrast, the seasonal cycle of ΔO_3_{ANTH} tends to be more
9 symmetrically centered on the summer months (Fig. 4); those emissions do not vary seasonally
10 in the model so the O₃ responses are only influenced by seasonal changes in transport and
11 photochemistry. The larger ΔO_3_{ISOP} in autumn relative to spring is consistent with a transition
12 in O₃ formation from NO_x-sensitive to hydrocarbon-sensitive over the eastern United States in
13 September, resulting from the seasonal decline in UV radiation (maximum in June) and humidity
14 (maximum in summer) (Kleinman, 1991; Jacob et al., 1995; Liang et al., 1998).

15 Whereas surface (and 700 hPa) O₃ responds more strongly to equivalent percentage changes in
16 anthropogenic NO_x than to isoprene emissions (Fig. 4; see also Fig. 3), the opposite is true for
17 700 hPa PAN during May through December. Furthermore, the regional ΔPAN_{ISOP} at 700
18 hPa exceeds that to ΔPAN_{ANTH} in August (Fig. 4) and is approximately equal in other non-
19 winter months; the intercontinental response is equivalent from June through October. Imposing
20 equivalent percentage reductions to NA isoprene and anthropogenic NMVOC emissions yields
21 stronger O₃ and PAN responses for the isoprene perturbation over both regions from spring
22 through late fall (Fig. 4), as expected since the absolute perturbation is an order of magnitude
23 larger for isoprene. Even in winter, NA isoprene contributes to hemispheric O₃ and PAN, likely
24 due to production from emissions in the southern-most portion of the NA domain as well as the
25 longer chemical lifetimes during this season (*e.g.*, Wang et al., 1998).

26

27 **5 PAN as a proxy for regional changes in O₃ precursor emissions**

28 We explore here the potential for PAN to indicate O₃ precursor emission changes. Both NA
29 anthropogenic and isoprene emission changes exert a larger relative influence on PAN, both at
30 the surface and at 700 hPa, as compared to O₃ (Fig. 3). Indeed, outside of the NA source region,

1 both $\Delta\text{PAN_ANTH}$ and $\Delta\text{PAN_ISOP}$ are more than twice as large as $\Delta\text{O}_3\text{-ANTH}$ and
2 $\Delta\text{O}_3\text{-ISOP}$, with larger changes extending over wider regions.

3 This finding supports the premise of Jaffe et al. (2007) and Fischer et al. (2010b), that long-term
4 PAN observations at remote sites may be more useful than O_3 itself in detecting large-scale
5 trends in O_3 precursor emissions. Fischer et al. (2010b), however, estimate that the larger
6 variability in PAN observed at the Mount Bachelor site in western NA compensates for the
7 larger relative signal such that the same length of time is needed to determine an emission-driven
8 trend in O_3 as for PAN. Given that measured O_3 can additionally be influenced by changes in
9 the stratospheric O_3 source and chemical losses (whereas the major sink for PAN in the lower
10 troposphere is thermal decomposition), it may be desirable to establish a few key long term sites
11 to measure PAN, ideally with coincident O_3 measurements, to aid in detecting changes in O_3 that
12 can be attributed with confidence to regional changes in O_3 precursor emissions. For example,
13 Fig. 3 suggests that long-term observations at the Pico station in the Azores could identify
14 changes in NA anthropogenic and biogenic emissions (Honrath et al., 2004). Such
15 measurements would also provide much needed constraints on major uncertainties in PAN
16 formation chemistry as represented in chemical mechanisms (Kuhn et al., 1998; Emmerson and
17 Evans, 2009; Henderson et al., 2011).

18 Our findings further suggest that the role of isoprene must be carefully considered alongside that
19 of anthropogenic emissions in interpreting observed changes in PAN. We use the difference
20 between the SR6ISOPNA and SR1 simulations to estimate the “noise” associated with trying to
21 detect the “signal” of $\Delta\text{O}_3\text{-ANTH}$ or $\Delta\text{PAN_ANTH}$ over Europe in light of year-to-year
22 variability in isoprene emissions. For this calculation, we first note that our NA isoprene
23 perturbation simulation captures the full range of inter-annual isoprene variability observed in
24 formaldehyde columns from space (Abbot et al., 2003; Palmer et al., 2006). Second, our
25 simulations use climatologically average isoprene emissions. Third, we assume that surface O_3
26 responds approximately linearly to NA isoprene emission perturbations of 20% as occurs for
27 anthropogenic NMVOC and for small perturbations (generally within 20%) to anthropogenic
28 NO_x (Fiore et al., 2009; Wu et al., 2009). Our finding that $\Delta\text{O}_3\text{-ANTHISOP}$ is half of
29 $\Delta\text{O}_3\text{-ANTH}$ over EU in summer (Fig. 5 upper panels) can thus be interpreted as a variability of
30 $\pm 25\%$ relative to the climatologically average isoprene emissions (*i.e.*, $\pm 25\%$ variations relative
31 to our $\Delta\text{O}_3\text{-ANTH}$ estimate determined from SR1-SR6NA; Figs. 4 and 5). In a similar manner,

1 we estimate that inter-annual variability in NA isoprene emissions can induce fluctuations of
2 $\pm 50\%$ around the decrease in EU $\Delta\text{PAN_ANTH}$ at 700 hPa.

3 Unraveling the relative contributions of NO_x versus isoprene or other NMVOC to observed
4 variability in measured PAN requires additional source information, including a solid
5 understanding of isoprene emission variations (near equivalence of red and green lines in Fig. 4).
6 While isoprene clearly dominates over anthropogenic NMVOC with regard to PAN formation in
7 the model in summer and fall, anthropogenic NMVOC precursors to PAN are likely important in
8 some regions (e.g., Liu et al., 2010) as well as outside the isoprene emission season. In this
9 regard, long-term measurements that can distinguish changes in the biogenic and anthropogenic
10 sources of carbon and nitrogen alongside PAN concentrations would be valuable. For example,
11 coincident measurements of individual PAN species (MPAN and PPN) have enabled attribution
12 of anthropogenic versus biogenic carbon contributions to PAN and O_3 during ground-based, ship
13 and aircraft field intensives (Roberts et al., 1998; 2002; 2006).

14

15 **6 Estimating NA anthropogenic influence: Uncertainty due to isoprene** 16 **emissions and chemistry**

17 We first estimate the degree to which NA isoprene emission increases, as might be induced by
18 changes in climate or land-use (e.g., Sanderson et al., 2003; Wiedinmyer et al., 2006; Weaver et
19 al., 2009), would offset the decreases in surface O_3 resulting from NA anthropogenic emission
20 controls. The difference between ΔO_3_ANTH and $\Delta\text{O}_3_ANTHISOP$ (Fig. 5) provides an
21 estimate of the offset. We do not consider changes in the spatial distribution of isoprene
22 emissions relative to the simple, uniform scaling applied here, which may also alter the surface
23 O_3 response to anthropogenic emissions. When isoprene increases by 20% in the model,
24 ΔO_3_ANTH is offset by approximately half over foreign regions and by one third over the NA
25 region from summer into fall. This result, taken in isolation, implies that additional controls on
26 anthropogenic emissions would be needed to sustain a desired level of hemispheric O_3 abatement
27 if isoprene emissions increase. We note that other changes in a warmer climate (e.g., more water
28 vapor) not considered here are expected to lessen the overall intercontinental influence (e.g.,
29 Johnson et al., 1999; Murazaki and Hess, 2006; TFHTAP, 2007). We further note that the
30 combined impact of NA isoprene and anthropogenic emission perturbations can be approximated

1 by adding the differences between pairs of simulations in which we perturbed those emissions
2 individually (Fig. 5). This additivity was previously shown to occur for the surface O₃ responses
3 to anthropogenic NO_x, CO, and NMVOC emission perturbations (Fiore et al., 2009). The larger
4 divergence from additivity over the immediate source region as compared to intercontinental
5 distances (particularly evident for PAN in Fig. 5) is consistent with the findings of Wild and
6 Prather (2006).

7 Prior work has demonstrated a large sensitivity of surface O₃ to the choice of isoprene emission
8 inventories and the fate of nitrates formed during isoprene oxidation (Horowitz et al., 1998;
9 Kang et al., 2003; von Kuhlmann et al., 2004; Fiore et al., 2005; Ito et al., 2009). Evaluation of
10 eastern U.S. isoprene emission inventories with observations suggests an uncertainty of within a
11 factor of two (Warneke et al., 2010). We do not have a good estimate of the range of NA
12 isoprene emissions in the models participating in the TF HTAP study, but we expect that the
13 20% increase in NA isoprene emissions that we imposed is conservative and so the range of
14 responses is likely significantly larger than that shown in Figs 1, 2 and 3 (right columns). In Fig.
15 6, we illustrate the changes in the baseline simulations resulting from increasing the isoprene
16 nitrate recycling from 40% to 100% during August. Doubling the response to isoprene nitrate
17 recycling to approximate the full range of 0 to 100% recycling as occurs in current CTMs
18 (*e.g.*, Fiore et al., 2005), we estimate uncertainty ranges (reflecting spatial variability) of 2-6 ppb,
19 10-50 ppt, and 5-20% in surface O₃, 700 hPa PAN and NO_y deposition, respectively, over the
20 NA region in August (Fig. 6). These findings are consistent with earlier work (von Kuhlmann et
21 al., 2004; Fiore et al., 2005).

22 We next determine the impact of these uncertainties in isoprene emissions and isoprene nitrate
23 fate on estimates of ΔO_3_ANTH . Fig. 7 shows that neither a 20% increase in the baseline NA
24 isoprene emissions nor an increase in the NO_x recycling from isoprene nitrates changes
25 ΔO_3_ANTH significantly in surface air over the NA or EU regions. Clearly the differences in
26 Fig. 7 cannot explain the factor of 2-3 spread in EU surface ΔO_3_ANTH across models reported
27 in Fiore et al. (2009) and Reidmiller et al. (2009). This lack of sensitivity indicates that the
28 dependence of O₃ production on precursor emissions, at least for the 20% decreases to NA
29 anthropogenic emissions considered here, is not changed by perturbations to isoprene-NO_x-O₃
30 chemistry.

1 A modest nonlinear response does emerge for PAN, with larger Δ PAN_ANTH in the simulations
2 with higher isoprene emissions. This response reflects the strong sensitivity of PAN formation
3 to the production of peroxy acetyl radicals from isoprene as well as the ratio of NO to NO₂ and
4 the key role of OH levels in this partitioning. This sensitivity implies that models with higher
5 baseline isoprene emissions may amplify Δ PAN_ANTH. In contrast, the NO_y deposition
6 sensitivity, defined as the change in total (wet plus dry) NO_y deposition over a region divided by
7 the change in NA NO_x emissions (Sanderson et al., 2008), is relatively insensitive to the
8 uncertainties in isoprene emissions and chemistry tested here. The maximum difference among
9 pairs of simulations is 2% over NA and 0.06% over EU in summer (bottom panels of Fig. 7).
10 Even if the full range of uncertainty would allow for a doubling of these values, they are still
11 insufficient to explain the 5% and 0.8% standard deviations (full ranges of 10% and 1.6%)
12 reported across models (Sanderson et al., 2008).

13

14 **7 Conclusions**

15 With the MOZART-2 global chemical transport model, we examined the influence of isoprene
16 versus anthropogenic emissions from North America (NA) on intercontinental O₃ pollution, PAN
17 at 700 hPa and oxidized nitrogen deposition. Sensitivity simulations in the model indicate that
18 any increases in isoprene, whether induced by a warming climate or changing land-use practices,
19 could offset the regional and intercontinental surface O₃ decreases produced by controls on NA
20 anthropogenic emissions during the summer through fall. These results imply a need to include
21 the role of biogenic NMVOC alongside that of anthropogenic emissions in discussions of
22 hemispheric air pollution management. In addition to raising hemispheric O₃ levels, biogenic
23 isoprene emissions enhance organic aerosol burdens in the atmosphere with corresponding
24 implications for climate and air quality (*e.g.*, Carlton et al., 2009). In light of the potentially
25 large impacts on biogenic emissions, plausible land-use options merit inclusion in anthropogenic
26 emission scenarios used to project future air quality and climate (*e.g.*, Wiedinmyer et al., 2006;
27 Avise et al., 2009).

28 We further interpret our findings to show that long-term, continuous observations of PAN in the
29 lower free troposphere may prove useful in detecting O₃ precursor emission changes. We find
30 that the role of isoprene should be carefully considered if one is attributing observed changes in

1 PAN (or O₃) to anthropogenic emission changes. Long-term PAN measurements would also
2 provide crucial constraints on our uncertain understanding of PAN formation chemistry (Kuhn et
3 al., 1998; Emmerson and Evans, 2009; Henderson et al., 2011).

4 The simulated hemispheric responses of surface O₃ and oxidized nitrogen deposition to regional
5 anthropogenic emission perturbations show little sensitivity to the level of isoprene emissions
6 specified in the model (within the 20% uncertainty range considered here) or the extent to which
7 isoprene nitrates serve as a terminal sink for NO_x. Although these uncertainties do contribute to
8 the range in model estimates of surface O₃ and the tropospheric O₃ budget (von Kuhlmann et al.,
9 2004; Wu et al., 2007), we find that they are not a major driver of the inter-model spread in the
10 responses of surface O₃ or oxidized nitrogen deposition to anthropogenic emission perturbations
11 estimated in the TFHTAP studies (TFHTAP, 2007; Sanderson et al., 2008; Fiore et al., 2009;
12 Reidmiller et al., 2009).

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15

16 Table 1. MOZART-2 Simulations.

Name	Description
SR1	Base case (see Section 2 for details)
SR3NA	SR1 but with anthropogenic NO _x emissions within NA decreased by 20%
SR4NA	SR1 but with anthropogenic NMVOC emissions within NA decreased by 20%
SR6NA	SR1 but with anthropogenic emissions of all O ₃ precursors (NO _x +CO+NMVOC) plus aerosols within NA decreased by 20%
ISOPNA	SR1 but with isoprene emissions within NA increased by 20%
SR6ISOPNA	SR6NA but with isoprene emissions within NA increased by 20%
SR1_r100	SR1 but with an isoprene nitrate recycling rate of 100% (up from 40% in SR1)
SR6NA_r100	SR6NA but with an isoprene nitrate recycling rate of 100%

17

18

19 **Figure Captions**

1 Fig. 1. August 2001 surface mixing ratio of O₃ (top) and PAN (bottom) in the MOZART-2 base
2 (SR1) simulation (left); ΔO_3_ANTH (top) and ΔPAN_ANTH (bottom) diagnosed as the
3 difference between the SR1 and SR6NA simulations (middle); and ΔO_3_ISOP (top) and
4 ΔPAN_ISOP (bottom) diagnosed as the difference between the ISOPNA and SR1 simulations
5 (right). Regions outlined in black, from left to right are: North America (NA), Europe and North
6 Africa (EU), South Asia (SA), and East Asia (EA), as in TFHTAP (2007). Note the different
7 scales on each color bar. Areas below the minimum values are shown in white.

8 Fig. 2. Same as Fig. 1 but for 700 hPa.

9 Fig. 3. Percentage decrease (left) and increase (right) in surface O₃ (first row), O₃ at 700 hPa
10 (second row), PAN at 700 hPa (third row), and NO_y deposition (bottom row) resulting from
11 20% decreases in NA anthropogenic O₃ precursor emissions (SR1-SR6NA simulations; left) and
12 20% increases in biogenic isoprene emissions (ISOPNA-SR1; right) in the MOZART-2 model
13 during August of 2001. Note the different scales on each color bar. Areas in white fall below
14 the minimum value shown.

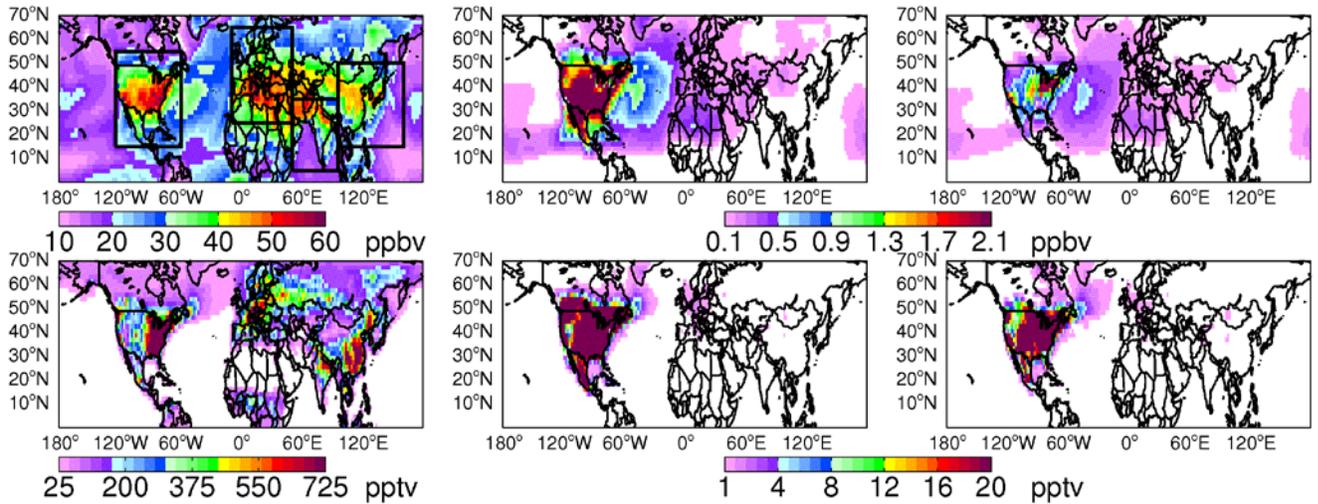
15 Fig. 4. Monthly mean regional (left) and intercontinental (right) ΔO_3_ANTH in surface air (top)
16 and ΔPAN_ANTH at 700 hPa (bottom), as determined by differencing the spatially averaged
17 surface O₃ over NA and EU (Fig. 1) in the baseline simulation and in sensitivity simulations in
18 which NA anthropogenic emissions of NO_x (red), NMVOC (blue), and all O₃ precursors
19 combined (black) are decreased by 20% (left axis). Also shown are ΔO_3_ISOP and ΔPAN_ISOP
20 (green; right axis).

21 Fig. 5. Monthly mean regional (left) and intercontinental (right) ΔO_3_ANTH (solid; as in Fig. 4)
22 and $\Delta O_3_ANTHISOP$ (dash-dot) in surface air (top), and ΔPAN_ANTH (solid; as in Fig. 4) and
23 $\Delta PAN_ANTHISOP$ (dash-dot) at 700 hPa (bottom), diagnosed as the difference between
24 sensitivity simulations as in Fig. 4. Also shown are $\Delta O_3_ANTH + \Delta O_3_ISOP$ and
25 $\Delta PAN_ANTH + \Delta PAN_ISOP$ (dotted).

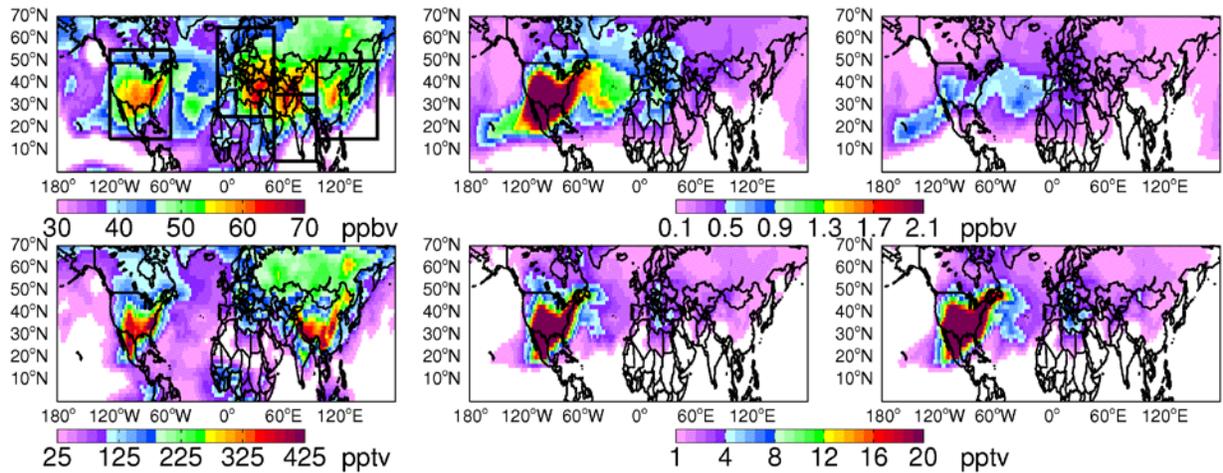
26 Fig. 6. Change in August mean surface O₃ (top), lower free tropospheric PAN (middle), and NO_y
27 deposition (bottom) when global isoprene nitrate recycling increases from 40% to 100%
28 (SR1_r100-SR1).

1 Fig. 7. The monthly mean regional (left) and intercontinental (right) ΔO_3_ANTH in surface air
2 (top), ΔPAN_ANTH at 700 hPa (middle), and NO_y deposition sensitivity (bottom) with different
3 model baselines: as in Fig. 4 (solid; SR1-SR6NA), with NA isoprene emissions increased by
4 20% (dashed; ISOPNA-SR6ISOPNA), and with the isoprene nitrate recycling rate increased
5 from 40% (as in SR1) to 100% (dotted; SR1_r100-SR6NA_r100). NO_y deposition sensitivity is
6 defined as the regional change in NO_y deposition divided by the change in NA NO_x emissions
7 (Sanderson et al., 2008).

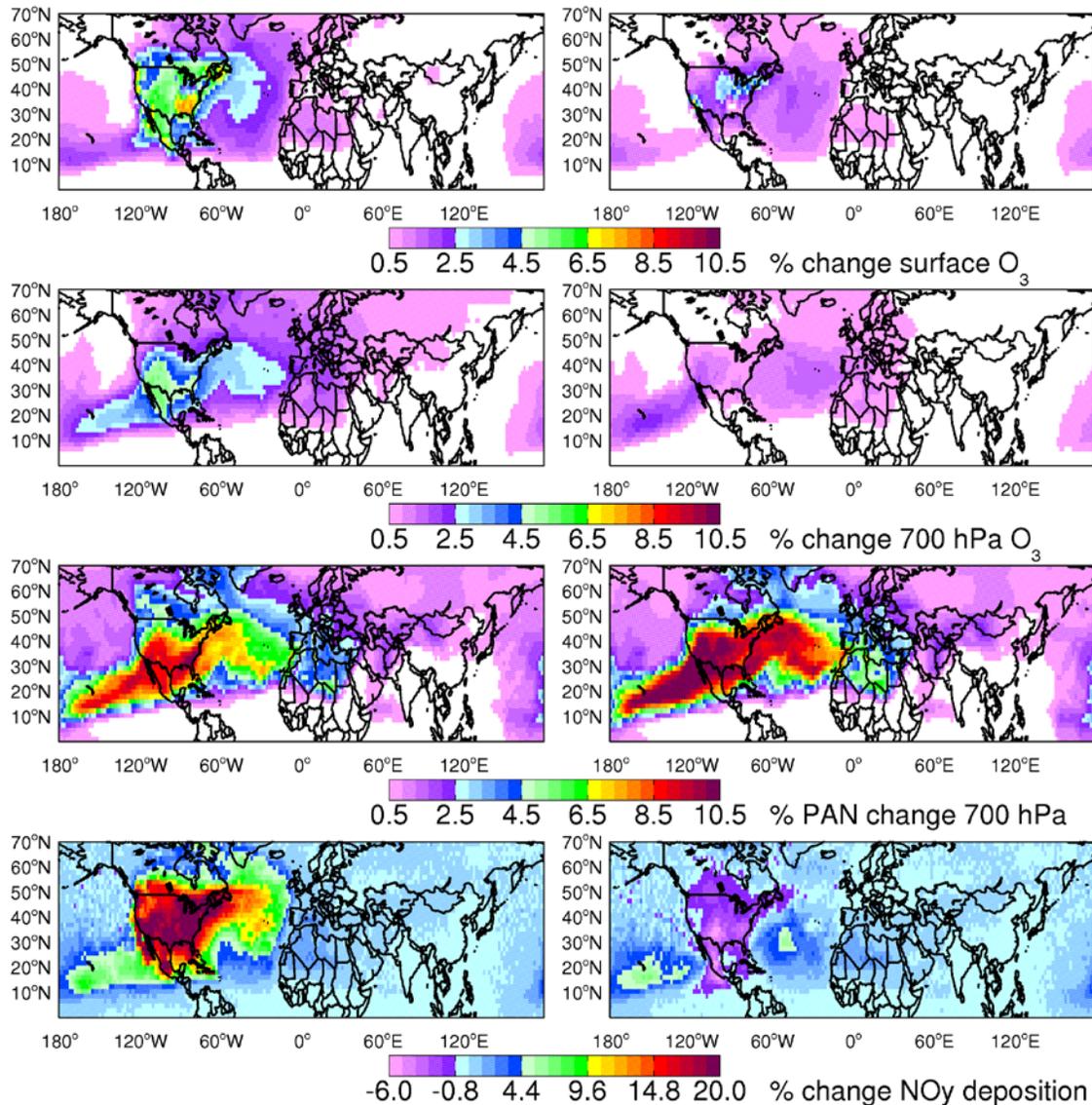
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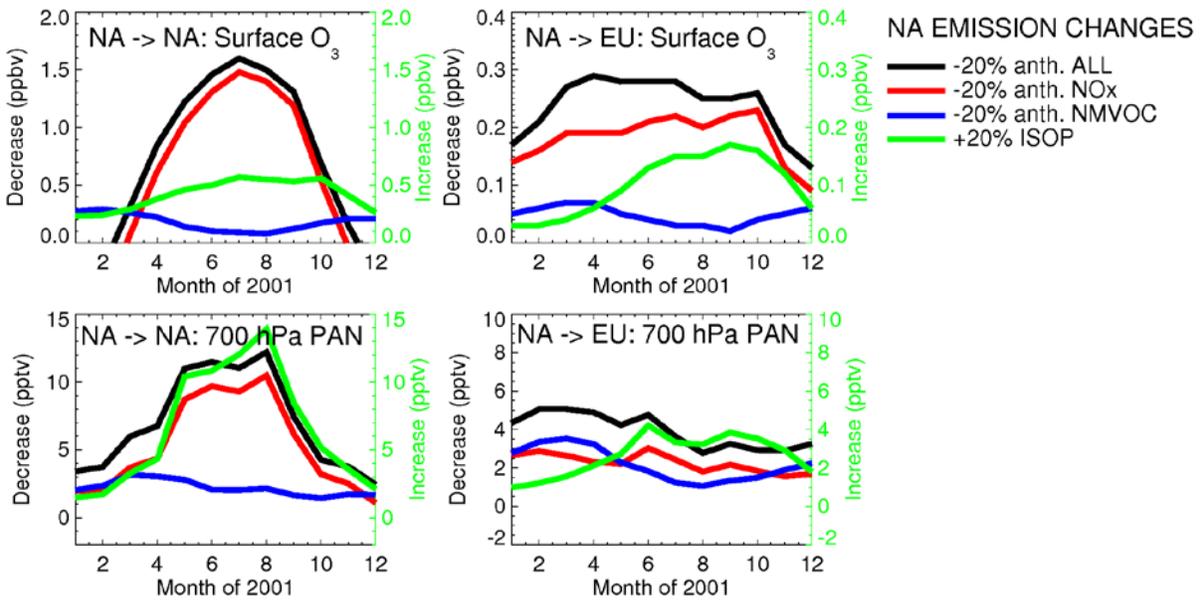
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 7 Africa (EU), South Asia (SA), and East Asia (EA), as in TFHTAP (2007). Note the different
 8 scales on each color bar. Areas below the minimum values are shown in white.



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 10 Fig. 2. Same as Fig. 1 but for 700 hPa.

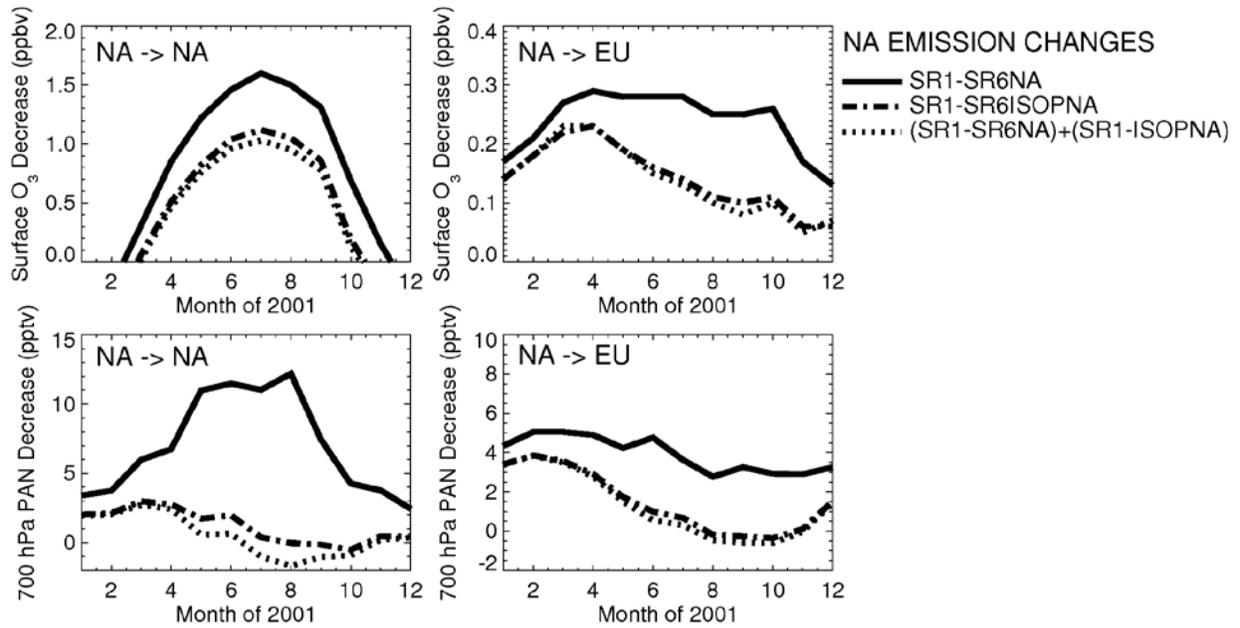


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 6 combined (black) are decreased by 20% (left axis). Also shown are ΔO_3_ISOP and ΔPAN_ISOP
 7 (green; right axis).

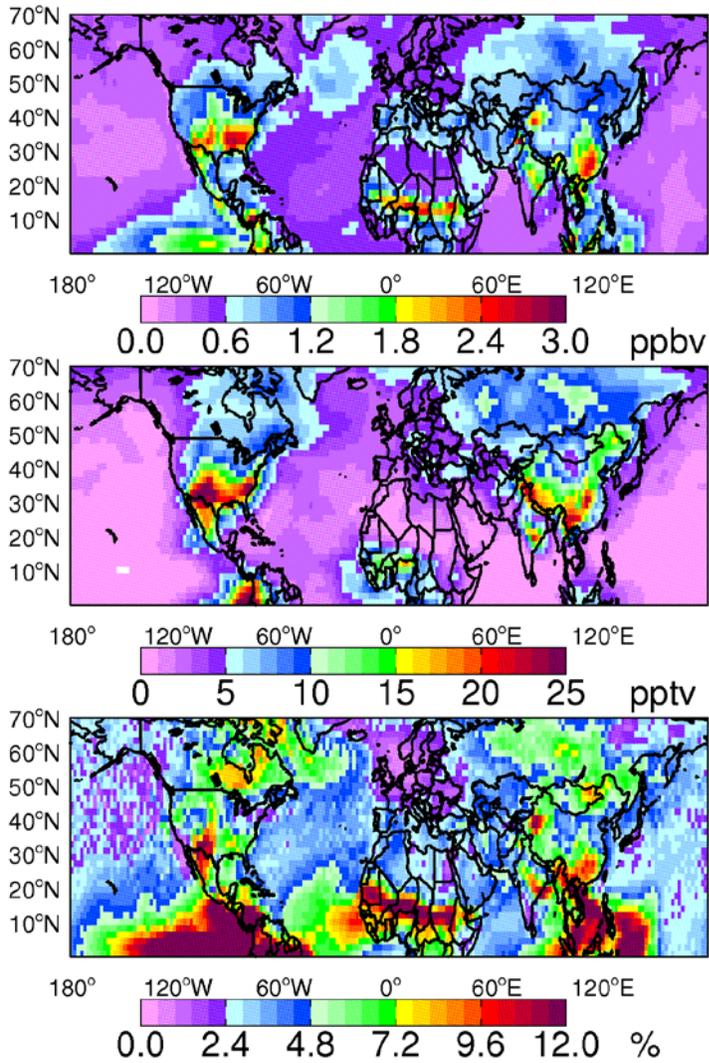
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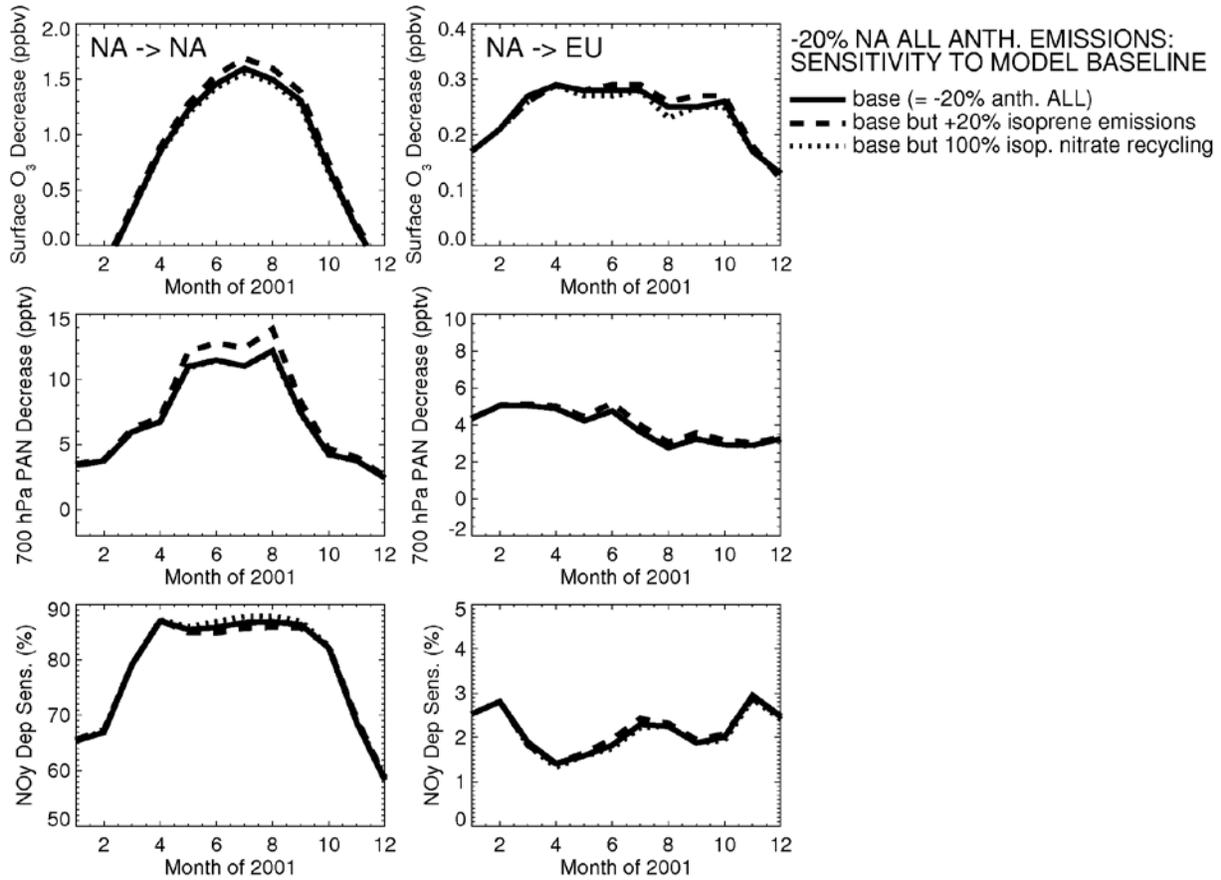
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 3 and $\Delta O_3_ANTHISOP$ (dash-dot) in surface air (top), and ΔPAN_ANTH (solid; as in Fig. 4) and
 4 $\Delta PAN_ANTHISOP$ (dash-dot) at 700 hPa (bottom), diagnosed as the difference between
 5 sensitivity simulations as in Fig. 4. Also shown are $\Delta O_3_ANTH + \Delta O_3_ISOP$ and
 6 $\Delta PAN_ANTH + \Delta PAN_ISOP$ (dotted).

7



1
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