North American isoprene influence on intercontinental ozone pollution

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Abstract. Changing land-use and climate may alter emissions of biogenic isoprene, a key ozone (O₃) precursor. Isoprene is also a precursor to peroxy acetyl nitrate (PAN) and thus affects partitioning among oxidized nitrogen (NOₓ) species, shifting the balance towards PAN, which more efficiently contributes to long-range transport relative to nitric acid (HNO₃) which rapidly deposits. With a suite of sensitivity simulations in the MOZART-2 global tropospheric chemistry model, we gauge the relative importance of the intercontinental influence of a 20% increase in North American (NA) isoprene and a 20% decrease in NA anthropogenic emissions (nitrogen oxides (NOₓ), non-methane volatile organic compounds (NMVOC) + carbon monoxide + aerosols). The surface O₃ response to NA isoprene emissions (ΔO₃-ISOP) in surface air over NA is about one third of the response to all NA anthropogenic emissions (ΔO₃-ANTH; although with different signs). Over intercontinental distances, ΔO₃-ISOP is relatively larger; in summer and fall, ΔO₃-ISOP in surface air over Europe and North Africa (EU region) is more than half of ΔO₃-ANTH. Future increases in NA isoprene emissions could thus offset decreases in EU surface O₃ resulting from controls on NA anthropogenic emissions. Over the EU region, ΔPAN-ISOP at 700 hPa is roughly the same magnitude as ΔPAN-ANTH (oppositely signed). Outside of the continental source region, the percentage changes in PAN are at least twice as large as for surface O₃, implying that long-term PAN measurements at high altitude sites may help to detect O₃ precursor emission changes. We find that neither the baseline level of isoprene emissions nor the fate of isoprene nitrates contributes to the large diversity in model estimates of the anthropogenic emission influence on intercontinental surface O₃ or oxidized nitrogen deposition reported in the recent TF HTAP multi-model studies (TFHTAP, 2007).

1 Introduction

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

Isoprene emissions increase strongly with temperature and sunlight and at northern mid-latitudes occur from spring through fall with a summer peak (e.g., Guenther et al., 2006). Global isoprene emissions are estimated to be at least five times higher than all anthropogenic NMVOC emissions and...
have been shown to enhance the tropospheric O\textsubscript{3} burden (e.g., Fuentes et al., 2000; Folberth et al., 2006; Guenther et al., 2006; Wild, 2007; Wu et al., 2007; Pfister et al., 2008). In the eastern United States, July isoprene emissions have been estimated to be 4 to over 10 times higher than anthropogenic NMVOC (e.g., Fiore et al., 2005). Isoprene, oxidized in the presence of the anthropogenic NO\textsubscript{x} available in this region, contributes as much as 15–25% to surface O\textsubscript{3} in summer as compared to ∼2% from anthropogenic NMVOC (Horowitz et al., 1998) and may play a key role in hemispheric transport of O\textsubscript{3}.

In addition to O\textsubscript{3}, various organic nitrates, including peroxy acetyl nitrate (PAN) which is particularly relevant for intercontinental transport, are produced during photochemical reactions involving isoprene (and to a lesser extent, other NMVOCs) and NO\textsubscript{x}. Formation of PAN alters the balance between deposition and export of oxidized nitrogen (NO\textsubscript{y} = NO\textsubscript{x} + HNO\textsubscript{3} + PAN + other minor oxidation products) from the NA region (e.g., Roberts et al., 1995; Horowitz et al., 1998). Frontal passages and convection, which ventilate the eastern NA boundary layer, can loft PAN to higher, colder altitudes where it is thermally stable and can undergo long-range transport and contribute to O\textsubscript{3} production upon decomposition in air masses that warm as they subside (e.g., Moxim et al., 1996; Liang et al., 1998; Val Martin et al., 2008; Fang et al., 2010; Fischer et al., 2010). Two pathways contribute approximately equally to intercontinental transport of O\textsubscript{3} pollution: (1) production of O\textsubscript{3} over the source region which is then exported, (2) export of precursors, PAN in particular, which then produce O\textsubscript{3} during transit to the downwind region (Liang et al., 1998; Jacob et al., 1999; Wild et al., 2004; West et al., 2009; Lin et al., 2010). PAN may also be a useful proxy for changes in O\textsubscript{3} precursor emissions, which may be detected more readily in observations of PAN than O\textsubscript{3} (Jaffe et al., 2007; Fischer et al., 2011).

Large uncertainties envelop the current understanding of the magnitude and distribution of isoprene emissions and subsequent oxidation chemistry (e.g., Steiner and Goldstein, 2007; Arneth et al., 2008; Carlton et al., 2009; Lelieveld et al., 2008). This uncertainty propagates into PAN formation and therefore the impact of isoprene-NO\textsubscript{x}-O\textsubscript{3} chemistry on foreign regions (Kuhn et al., 1998; Emmerson and Evans, 2009). Of particular relevance for O\textsubscript{3} produced in the source regions is the uncertain interaction of isoprene with the NO\textsubscript{x} budget via isoprene nitrate formation; the ultimate influence of isoprene on O\textsubscript{3} may hinge on the poorly understood fate of isoprene nitrates (e.g., von Kuhlmann et al., 2004; Ito et al., 2009; Perring et al., 2009; Paulot et al., 2009; Weaver et al., 2009). While we expect these uncertainties to contribute to model diversity in “baseline” simulations for the present atmosphere, it is unclear whether they are also contributing to the range in model estimates of the responses of surface O\textsubscript{3} and NO\textsubscript{x} deposition to anthropogenic emission perturbations, as reported in prior TF HTAP publications (Sanderson et al., 2008; Fiore et al., 2009; Reidmiller et al., 2009).

Although anthropogenic emissions of isoprene may be a major contributor to ambient isoprene in some urban settings, the biogenic source overwhelmingly dominates over much of the northern mid-latitudes during the warm season (Reimann et al., 2000; Guenther et al., 2006; Dollard et al., 2007). Even the biogenic isoprene source, however, is heavily influenced by human activities via land-use changes, as has occurred historically with changes in cropland areas (e.g., Lathière et al., 2010). Future decisions to establish poplar (a high isoprene-emitting species) plantations for biofuel or to convert vast forested regions to croplands (low isoprene emitters) could dramatically alter future isoprene emissions and thereby air quality (e.g., Wiedinmyer et al., 2006; Avis et al., 2009; Chen et al., 2009). The strong temperature dependence of isoprene emissions suggests that they will increase in a warmer climate, but other factors (higher carbon dioxide, drought, pollutant exposure, insect herbivory) could offset this increase (e.g., Pacifico et al., 2009; Rosenstiel et al., 2003; Guenther et al., 2006). The relative importance of future changes in climate and land-use on isoprene emissions is unclear, but the potential for humans to alter isoprene emissions deserves consideration.

As a first step towards understanding the role of isoprene emissions in intercontinental O\textsubscript{3} pollution, we use the MOZART-2 global CTM (Sect. 2) to quantify the influence of NA isoprene on O\textsubscript{3} and PAN in surface air and at 700 hPa, as well as NO\textsubscript{y}, deposition at northern mid-latitudes in August (Sect. 3) and throughout the year (Sect. 4). We also explore the potential for PAN measurements to detect O\textsubscript{3} precursor emission changes (Sect. 5). We then evaluate the impact of uncertainties in isoprene emissions and chemistry on estimates of hemispheric responses to NA anthropogenic emission controls (Sect. 6) and discuss the implications of our findings (Sect. 7).

## 2 Model simulations

We use the MOZART-2 model (Horowitz et al., 2003) in the same configuration (“MOZARTGFDFL-v2”) as applied to the year 2001 for the multi-model studies coordinated by the Task Force on Hemispheric Transport of Air Pollution (TFHTAP; www.htap.org) (e.g., TFHTAP, 2007). Briefly, the model meteorology is driven by the NCEP reanalysis (Kalnay et al., 1996) for the year 2001 with a horizontal resolution of 1.9° × 1.9° with 28 vertical levels. Emissions are as in Horowitz et al. (2003) except for biomass burning for which we use GFED version 2 (van der Werf et al., 2006) for the year 2001. Isoprene emissions are a monthly varying climatological inventory (Guenther et al., 1995; Horowitz et al., 2003). We modified the isoprene oxidation chemistry from that of Horowitz et al. (2003) to use a 4% yield of isoprene nitrates and 40% rate of recycling back to NO\textsubscript{x} upon oxidation of these nitrates; these values are consistent with observed alkyl and peroxy nitrates over the eastern United States in
summer (Horowitz et al., 2007). (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 NOx.) The SYNOZ parameterization provides the stratospheric O3 upper boundary condition (McLinden et al., 2000), implemented as described by Emmons et al. (2010). All simulations are spun up for seven months prior to the analysis year of 2001.

In the TF HTAP “source-receptor (SR)” simulations, anthropogenic emissions of O3 precursors were decreased by 20%, separately for NOx, NMVOC, and carbon monoxide (CO), and for all three precursors together (plus aerosols), within each of the four major northern mid-latitude source regions in Fig. 1. We focus here on the NA source region, employing four MOZART-2 SR simulations (Table 1): base (denoted SR1) and perturbation simulations with 20% decreases in NA emissions, for anthropogenic NOx (SR3NA), anthropogenic NMVOC (SR4NA), and all anthropogenic O3 precursors plus aerosols combined (SR6NA). The differences between these perturbation simulations and SR1 provide an estimate of the response to changes in anthropogenic emissions. Hereafter, we refer to the decreases in O3 and PAN produced by the anthropogenic emission reductions as $\Delta O_3\text{ANTH}$ and $\Delta PAN\text{ANTH}$, respectively.

Of the four continental source regions in Fig. 1, North America is the most abundant isoprene emitter in MOZART-2, with 35 Tg Ca$^{-1}$ as compared to 22, 12, and 17 Tg Ca$^{-1}$ from East Asia, Europe, and South Asia, respectively. Qualitatively, this ranking is consistent with that for the multi-model average regional emissions of non-anthropogenic NMVOC from the models participating in the TF HTAP studies (determined as the differences between values reported in Tables A2 and A3 of Fiore et al., 2009). Anthropogenic emissions of NOx, CO and NMVOC from the NA region in MOZART-2 are $0.88 \times 10^1$ Tg N a$^{-1}$, $1.00 \times 10^2$ Tg a$^{-1}$, and $0.66 \times 10^1$ Tg Ca$^{-1}$, respectively. The corresponding TF HTAP values (mean ± standard deviation across models) are $0.74 \times 10^1 \pm 0.04 \times 10^1$ Tg N a$^{-1}$, $1.01 \times 10^2 \pm 0.19 \times 10^2$ Tg a$^{-1}$ and $0.16 \times 10^2 \pm 0.071 \times 10^2$ Tg Ca$^{-1}$ for NA anthropogenic emissions of NOx, CO and NMVOC, respectively (Table A3 of Fiore et al., 2009). The lower anthropogenic NMVOC emissions and higher anthropogenic NOx in MOZART-2 imply that O3 and PAN formation may be more sensitive to NA isoprene vs. anthropogenic NMVOC emissions compared to other CTMs. Given that (1) the NA isoprene emissions are still more than double the TF HTAP value for anthropogenic NMVOC emissions, (2) isoprene reactivity is generally several times higher than that for anthropogenic NMVOC (e.g., Fuentes et al., 2000), and (3) surface O3 over NA is more sensitive to NA NOx than anthropogenic NMVOC from spring through fall in the models participating in the TF HTAP multi-model studies (Fiore et al., 2009; their Fig. 4), we expect our results to be robust to uncertainties in anthropogenic NMVOC emissions. The decline in eastern US anthropogenic NOx 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.

The MOZART-2 SR1 simulation, which has previously been evaluated with observations of surface O3 and O3 profiles as part of the TF HTAP effort (Fiore et al., 2009;
Reidmiller et al., 2009; Jonson et al., 2010), generally captures observed distributions and seasonality over most regions. Notable exceptions include systematic high biases of 10–20 ppb in summertime surface O$_3$ over the eastern United States and Japan, and systematic low biases of ~15 ppb at mountainous sites in the western US and Europe and at low-altitude sites in the northeastern US and central Europe during winter. Most pertinent to our study is the model over-estimate of summertime surface O$_3$ over the eastern United States; this pervasive across the current generation of CTMs (Fiore et al., 2009; Reidmiller et al., 2009) and investigations into its cause are ongoing. Although we do not yet understand the source(s) of this bias in surface O$_3$, the lack of a simple relationship between model biases with respect to the observations and the simulated O$_3$ responses to either domestic or intercontinental emission changes (Reidmiller et al., 2009; Jonson et al., 2010) suggests that additional tests are needed to evaluate the capability of models to adequately resolve the key processes governing intercontinental O$_3$ pollution. Comparison with monthly mean PAN measured at mountain sites (2–4 km altitude) in western NA (Mt. Bachelor, Oregon, USA) and Europe (Jungfraujoch, Switzerland and Zugspitze, Germany) indicates that MOZART-2 falls within the observed range in most months, with a tendency to underestimate PAN from spring into early summer at the two European mountain sites (by 100–200 ppt; Fiore et al., 2011).

We presently lack observational constraints on the O$_3$ response to emission perturbations, so we briefly summarize the comparison of MOZART-2 estimates with the multimodel mean in the HTAP studies. With respect to the intercontinental O$_3$ response to the combined 20% decreases in anthropogenic NO$_x$ + CO + NMVOC + aerosols emissions, MOZART-2 estimates fall below the multi-model average (e.g., Fig. A2 of Fiore et al., 2009). The MOZART-2 annual NO$_y$ export fraction from NA is estimated to be 0.23, slightly higher than the multi-model mean of 0.18; the summertime NA NO$_y$ export fraction of 0.13, more relevant for our study, is close to the multi-model mean (Sanderson et al., 2008; see their Table 1 and Fig. 2).

In order to examine the relative importance of isoprene versus anthropogenic O$_3$ precursor emissions on hemispheric O$_3$ levels, we conduct additional sensitivity simulations (Table 1). Relative to SR1, we impose a 20% increase in NA isoprene emissions (denoted ISOPNA). Our rationale for imposing oppositely signed perturbations to isoprene versus anthropogenic emissions is based on the strong temperature dependence of isoprene (which suggests that its emissions may increase in a warming climate), while we expect future efforts to abate air pollution to yield additional decreases in NA anthropogenic emissions. We note caveats on this scenario, which include the potential for rising carbon dioxide abundances or other factors to cause NA isoprene emissions to decline in future years (e.g., Rosenstiel et al., 2003; Avise et al., 2009; Chen et al., 2009) For context, the 20% perturbation we impose on NA isoprene emissions is equivalent to observed year-to-year fluctuations, estimated at ~20–30% from formaldehyde columns retrieved from space (Abbot et al., 2003; Palmer et al., 2006). The differences in O$_3$ and PAN between ISOPNA and SR1 provides an estimate of the response to changes in NA isoprene (hereafter referred to as $\Delta$O$_3$ISOP and $\Delta$PANISOP) which can be compared directly with the response to the TF HTAP SR anthropogenic emission perturbations.

For testing the sensitivity of $\Delta$O$_3$ANTH in surface air (diagnosed by differencing SR1 and SR6NA) to isoprene emissions and their interactions with NO$_x$, we conduct three additional simulations: (1) a combined 20% increase in NA isoprene and 20% decrease in NA anthropogenic emissions (SR6ISOPNA), (2) SR1 but with 100% recycling of NO$_x$ from isoprene nitrates (SR1_r100), and (3) SR6NA but with 100% isoprene nitrate recycling (SR6NA_r100). We use the difference between the SR6ISOPNA and SR1 simulations to gauge the potential impacts of a coincident 20% increase in NA isoprene and 20% decrease in all NA anthropogenic emissions, referred to hereafter as $\Delta$O$_3$ANTHISOP and $\Delta$PANANTHISOP. The difference between these simulations also allows for an estimate of the “noise” associated with inter-annual variability in isoprene emissions surrounding the “signal” of a sustained reduction in NA anthropogenic

### Table 1. MOZART-2 Simulations.

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR1</td>
<td>Base case (see Sect. 2 for details)</td>
</tr>
<tr>
<td>SR3NA</td>
<td>SR1 but with anthropogenic NO$_x$ emissions within NA decreased by 20%</td>
</tr>
<tr>
<td>SR4NA</td>
<td>SR1 but with anthropogenic NMVOC emissions within NA decreased by 20%</td>
</tr>
<tr>
<td>SR6NA</td>
<td>SR1 but with anthropogenic emissions of all O$_3$ precursors (NO$_x$+CO+NMVOC plus aerosols within NA decreased by 20%</td>
</tr>
<tr>
<td>ISOPNA</td>
<td>SR1 but with isoprene emissions within NA increased by 20%</td>
</tr>
<tr>
<td>SR6ISOPNA</td>
<td>SR6NA but with isoprene emissions within NA increased by 20%</td>
</tr>
<tr>
<td>SR1_r100</td>
<td>SR1 but with an isoprene nitrate recycling rate of 100% (up from 40% in SR1)</td>
</tr>
<tr>
<td>SR6NA_r100</td>
<td>SR6NA but with an isoprene nitrate recycling rate of 100%</td>
</tr>
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</table>
emissions. Such an estimate is useful, for example, if one were trying to detect the influence of changes in NA emissions on O\textsubscript{3}. We next estimate the potential contribution of different baseline isoprene emission levels (ISOPNA-SR6ISOPNA) and different treatments of isoprene nitrate chemistry (SR1\_r100-SR6NA\_r100) to the model spread in \(\Delta O\textsubscript{3}\)\_ANTH reported in Fiore et al. (2009) and for NO\textsubscript{y} deposition reported in Sanderson et al. (2008). Table 1 summarizes the model simulations used in this analysis.

3 Hemispheric influence of NA isoprene and anthropogenic emissions in August

Over foreign regions in the Northern Hemisphere, \(\Delta O\textsubscript{3}\)\_ISOP is at least half as large (but opposite in sign) as \(\Delta O\textsubscript{3}\)\_ANTH during August (Fig. 1). The intercontinental \(\Delta PAN\)\_ISOP and \(\Delta PAN\)\_ANTH at the surface is negligible (Fig. 1), reflecting the strong thermal instability of PAN in warmer, surface air. The spatial patterns of the surface \(\Delta O\textsubscript{3}\)\_ISOP and \(\Delta O\textsubscript{3}\)\_ANTH correlate strongly \((r = 0.71)\); both of these sources are predominantly located in eastern NA and are subject to the same meteorology which exports \(O\textsubscript{3}\) from the NA continental boundary layer. NA emissions exert the largest intercontinental influence on Europe and North Africa (EU), the nearest downwind region, a robust result across models (Fiore et al., 2009).

We next examine changes in \(O\textsubscript{3}\) 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. At 700 hPa in August, \(\Delta PAN\)\_ISOP and \(\Delta PAN\)\_ANTH are more strongly correlated spatially \((r = 0.99;\) Fig. 2) than \(\Delta O\textsubscript{3}\)\_ISOP and \(\Delta O\textsubscript{3}\)\_ANTH \((r = 0.81)\). Both at the surface and at 700 hPa, \(\Delta O\textsubscript{3}\)\_ANTH is generally larger in magnitude than \(\Delta O\textsubscript{3}\)\_ISOP (Figs. 1, 2 and 3). In contrast, the 700 hPa \(\Delta PAN\)\_ISOP is equivalent in magnitude or larger than \(\Delta PAN\)\_ANTH Figs. 2 and 3). The slightly larger \(\Delta PAN\)\_ISOP at 700 hPa over the EU region may partially reflect the transport of hydroxyacetone, an intermediate isoprene oxidation product with a 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\textsubscript{y} (e.g., from regional emissions; not shown). These results demonstrate the key role that isoprene plays in PAN formation at northern mid-latitudes in summer (Horowitz et al., 1998; Pfister et al., 2008). If we extrapolate the results in Fig. 3 assuming that PAN responds linearly to isoprene emission changes (i.e., multiplying the response to a 20% perturbation by five to estimate 100% contribution), then we estimate that up to 25% of 700 hPa PAN over Spain, the Mediterranean and Northern Africa in August is associated with NA isoprene emissions.

Since isoprene influences the NO\textsubscript{y} partitioning between organic nitrates and nitric acid, we also examine the impacts of anthropogenic versus isoprene emission changes on NO\textsubscript{y} deposition (Fig. 3). The changes from NA anthropogenic emissions are similar to those reported for the NA NO\textsubscript{y} perturbations in Sanderson et al. (2008), with changes in deposition largely concentrated within the source region, and small (a few percent) changes in the foreign TFHTAP regions. The NA isoprene influence on NO\textsubscript{y} deposition in the foreign TFHTAP regions is less than 1%. Over NA, NO\textsubscript{y} deposition decreases when isoprene emissions increase since isoprene is a direct precursor to the peroxy acetyl radical, thus favoring PAN formation relative to nitric acid (HNO\textsubscript{3}); the decrease in OH associated with increasing isoprene emissions in the model would also tend to decrease HNO\textsubscript{3} production (Horowitz et al., 1998). We emphasize that the influence of
isoprene on OH is the subject of much debate and ongoing research and is likely not well represented in mechanisms available in current generation CTMs (e.g., Lelieveld et al., 2008; Ren et al., 2008; Paulot et al., 2009; Archibald et al., 2010). Nevertheless, we see from Fig. 3 the interaction of isoprene oxidation products with meteorology, which leads to more NO$_y$ deposition in the North Atlantic and North Pacific oceans. These regions are influenced by PAN decomposition in air masses that subside as they circulate around the Bermuda and Pacific high pressure systems, and the subsequent deposition of that nitrogen (mainly as HNO$_3$).

### 4 Seasonal variations in regional and intercontinental influences of NA emissions

We turn next to seasonal variations in the surface O$_3$ and lower free tropospheric PAN responses to changes in NA isoprene versus anthropogenic emissions. Following the approach of Fiore et al. (2009), we construct monthly SR relationships for surface O$_3$ and PAN at 700 hPa by spatially averaging over the continental-scale regions (Fig. 4). We focus on the NA and EU regions to illustrate “regional” versus “intercontinental” responses. We note that the average values in Fig. 4 mask a large sub-regional variability in the O$_3$ response to emission perturbations (Reidmiller et al., 2009; Lin et al., 2010), evident in Figs. 1, 2 and 3. Increases in isoprene consistently act to depress local NO$_y$ deposition but increase intercontinental NO$_y$ deposition as seen in Fig. 3 (bottom row) throughout the isoprene emission season (not shown) and so we focus on seasonal variations in O$_3$ and PAN in this section.

Over the NA and EU regions, $\Delta$O$_3$ ISOP in surface air (Fig. 4) is enhanced in autumn relative to spring, despite similar emissions in the two seasons ($\sim$4 Tg C in May and September, and $\sim$2 Tg C in April and October). In contrast, the seasonal cycle of $\Delta$O$_3$ ANTH tends to be more symmetrically centered on the summer months (Fig. 4); those emissions do not vary seasonally in the model so the O$_3$ responses are only influenced by seasonal changes in transport...
and photochemistry. The larger $\Delta O_3$ ISOP in autumn relative to spring is consistent with a transition in $O_3$ formation from NO$_x$-sensitive to hydrocarbon-sensitive over the eastern United States in September, resulting from the seasonal decline in UV radiation (maximum in June) and humidity (maximum in summer) (Kleinman, 1991; Jacob et al., 1995; Liang et al., 1998).

Whereas surface (and 700 hPa) $O_3$ responds more strongly to equivalent percentage changes in anthropogenic NO$_x$ than to isoprene emissions (Fig. 4; see also Fig. 3), the opposite is true for 700 hPa PAN during May through December. Furthermore, the regional $\Delta$PAN.ISOP at 700 hPa exceeds that to $\Delta$PAN.ANTH in August (Fig. 4) and is approximately equal in other non-winter months; the intercontinental response is equivalent from June through October. Imposing equivalent percentage reductions to NA isoprene and anthropogenic NMVOC emissions yields stronger $O_3$ and PAN responses for the isoprene perturbation over both regions from spring through late fall (Fig. 4), as expected since the absolute perturbation is an order of magnitude larger for isoprene. Even in winter, NA isoprene contributes to hemispheric $O_3$ and PAN, likely due to production from emissions in the southern-most portion of the NA domain as well as the longer chemical lifetimes during this season (e.g., Wang et al., 1998).

5 PAN as a proxy for regional changes in $O_3$ precursor emissions

We explore here the potential for PAN to indicate $O_3$ precursor emission changes. Both NA anthropogenic and isoprene emission changes exert a larger relative influence on PAN, both at the surface and at 700 hPa, as compared to $O_3$ (Fig. 3). Indeed, outside of the NA source region, both $\Delta$PAN.ANTH and $\Delta$PAN.ISOP are more than twice as large as $\Delta O_3$ ANTH and $\Delta O_3$ ISOP, with larger changes extending over wider regions.

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

Our findings further suggest that the role of isoprene must be carefully considered alongside that of anthropogenic emissions in interpreting observed changes in PAN. We use the difference between the SR6ISOPNA and SR1 simulations to estimate the “noise” associated with trying to detect the “signal” of ΔO3_ANTH or ΔPAN_ANTH over Europe in light of year-to-year variability in isoprene emissions. For this calculation, we first note that our NA isoprene perturbation simulation captures the full range of inter-annual isoprene variability observed in formaldehyde columns from space (Abbot et al., 2003; Palmer et al., 2006). Second, our simulations use climatologically average isoprene emissions. Third, we assume that surface O3 responds approximately linearly to NA isoprene emission perturbations of 20% as occurs for anthropogenic NMVOC and for small perturbations (generally within 20%) to anthropogenic NOx (Fiore et al., 2009; Wu et al., 2009). Our finding that ΔO3_ANTHISOP is half of ΔO3_ANTH over EU in summer (Fig. 5 upper panels) can thus be interpreted as a variability of ±25% relative to the climatologically average isoprene emissions (i.e., ±25% variations relative to our ΔO3_ANTH estimate determined from SR1-SR6NA; Figs. 4 and 5). In a similar manner, we estimate that inter-annual variability in NA isoprene emissions can induce fluctuations of ±50% around the decrease in EU ΔPAN_ANTH at 700 hPa.

Unraveling the relative contributions of NOx versus isoprene or other NMVOC to observed variability in measured PAN requires additional source information, including a solid understanding of isoprene emission variations (near equivalence of red and green lines in Fig. 4). While isoprene clearly dominates over anthropogenic NMVOC with regard to PAN formation in the model in summer and fall, anthropogenic NMVOC precursors to PAN are likely important in some regions (e.g., Liu et al., 2010) as well as outside the isoprene emission season. In this regard, long-term measurements that can distinguish changes in the biogenic and anthropogenic sources of carbon and nitrogen alongside PAN concentrations would be valuable. For example, coincident measurements of individual PAN species (MPAN and PPN) have enabled attribution of anthropogenic versus biogenic carbon contributions to PAN and O3 during ground-based, ship and aircraft field intensives (Roberts et al., 1998, 2002, 2006).

6 Estimating NA anthropogenic influence: uncertainty due to isoprene emissions and chemistry

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 difference between ΔO3_ANTH and ΔO3_ANTHISOP (Fig. 5) provides an estimate of the offset. 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, ΔO3_ANTH is offset by approximately half over foreign regions and by one third over the NA region from summer into fall. This result, taken in isolation, implies that additional controls on anthropogenic emissions would be needed.
to sustain a desired level of hemispheric O$_3$ abatement if isoprene emissions increase. We note that other changes in a warmer climate (e.g., more water vapor) not considered here are expected to lessen the overall intercontinental influence (e.g., Johnson et al., 1999; Murazaki and Hess, 2006; TFHTAP, 2007). 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 (Fig. 5). This additivity was previously shown to occur for the surface O$_3$ responses to anthropogenic NO$_x$, CO, and NMVOC emission perturbations (Fiore et al., 2009). The larger divergence from additivity over the immediate source region as compared to intercontinental distances (particularly evident for PAN in Fig. 5) is consistent with the findings of Wild and Prather (2006).

Prior work has demonstrated a large sensitivity of surface O$_3$ to the choice of isoprene emission inventories and the fate of nitrates formed during isoprene oxidation (Horowitz et al., 1998; Kang et al., 2003; von Kuhlmann et al., 2004; Fiore et al., 2005; Ito et al., 2009). Evaluation of eastern US isoprene emission inventories with observations suggests an uncertainty of within a factor of two (Warneke et al., 2010). We do not have a good estimate of the range of NA isoprene emissions in the models participating in the TF HTAP study, but we expect that the 20% increase in NA isoprene emissions that we imposed is conservative and so the range of responses is likely significantly larger than that shown in Figs 1, 2 and 3 (right columns). In Fig. 6, we illustrate the changes in the baseline simulations resulting from increasing the isoprene nitrate recycling from 40% to 100% during August. Doubling the response to isoprene nitrate recycling to approximate the full range of 0 to 100% recycling as occurs in current CTMs (e.g., Fiore et al., 2005), we estimate uncertainty ranges (reflecting spatial variability) of 2–6 ppb, 10–50 ppt, and 5–20% in surface O$_3$, 700 hPa PAN and NO$_y$ deposition, respectively, over the NA region in August (Fig. 6). These findings are consistent with earlier work (von Kuhlmann et al., 2004; Fiore et al., 2005).

We next determine the impact of these uncertainties in isoprene emissions and isoprene nitrate fate on estimates of $\Delta$O$_3$ ANTH. Figure 7 shows that neither a 20% increase in the baseline NA isoprene emissions nor an increase in the NO$_y$ recycling from isoprene nitrates changes $\Delta$O$_3$ ANTH significantly in surface air over the NA or EU regions. Clearly the differences in Fig. 7 cannot explain the factor of 2–3 spread in EU surface $\Delta$O$_3$ ANTH across models reported in Fiore et al. (2009) and Reidmiller et al. (2009). This lack of sensitivity indicates that the dependence of O$_3$ production on precursor emissions, at least for the 20% decreases to NA anthropogenic emissions considered here, is not changed by perturbations to isoprene-NO$_y$-O$_3$ chemistry. A modest nonlinear response does emerge for PAN, with larger $\Delta$PAN ANTH in the simulations with higher isoprene emissions. This response reflects the strong sensitivity of PAN formation to the production of peroxy acetyl radicals from isoprene as well as the ratio of NO to NO$_2$ and the key role of OH levels in this partitioning. This sensitivity implies that models with higher baseline isoprene emissions may amplify $\Delta$PAN ANTH. In contrast, the NO$_y$ deposition sensitivity, defined as the change in total (wet plus dry) NO$_y$ deposition over a region divided by the change in NA NO$_x$ emissions (Sanderson et al., 2008), is relatively insensitive to the uncertainties in isoprene emissions and chemistry tested here. The maximum difference among pairs of simulations is 2% over NA and 0.06% over EU in summer (bottom panels of Fig. 7). Even if the full range of uncertainty would allow for a doubling of these values, they are still insufficient to explain the 5% and 0.8% standard deviations (full ranges of 10% and 1.6%) reported across models (Sanderson et al., 2008).

7 Conclusions

With the MOZART-2 global chemical transport model, we examined the influence of isoprene versus anthropogenic emissions from North America (NA) on intercontinental O$_3$
pollution, PAN at 700 hPa and oxidized nitrogen deposition. Sensitivity simulations in the model indicate that any increases in isoprene, whether induced by a warming climate or changing land-use practices, could offset the regional and intercontinental surface O\textsubscript{3} decreases produced by controls on NA anthropogenic emissions during the summer through fall. These results imply a need to include the role of biogenic NMVOC alongside that of anthropogenic emissions in discussions of hemispheric air pollution management. In addition to raising hemispheric O\textsubscript{3} levels, biogenic isoprene emissions enhance organic aerosol burdens in the atmosphere with corresponding implications for climate and air quality (e.g., Carlton et al., 2009). In light of the potentially large impacts on biogenic emissions, plausible land-use options merit inclusion in anthropogenic emission scenarios used to project future air quality and climate (e.g., Wiedinmyer et al., 2006; Avise et al., 2009).

We further interpret our findings to show that long-term, continuous observations of PAN in the lower free troposphere may prove useful in detecting O\textsubscript{3} precursor emission changes. We find that the role of isoprene should be carefully considered if one is attributing observed changes in PAN (or O\textsubscript{3}) to anthropogenic emission changes. Long-term PAN measurements would also provide crucial constraints on our uncertain understanding of PAN formation chemistry (Kuhn et al., 1998; Emmerson and Evans, 2009; Henderson et al., 2011).

The simulated hemispheric responses of surface O\textsubscript{3} and oxidized nitrogen deposition to regional anthropogenic emission perturbations show little sensitivity to the level of isoprene emissions specified in the model (within the 20% uncertainty range considered here) or the extent to which isoprene nitrates serve as a terminal sink for NO\textsubscript{x}. Although these uncertainties do contribute to the range in model estimates of surface O\textsubscript{3} and the tropospheric O\textsubscript{3} budget (von Kuhlmann et al., 2004; Wu et al., 2007), we find that they are not a major driver of the inter-model spread in the responses of surface O\textsubscript{3} or oxidized nitrogen deposition to anthropogenic emission perturbations estimated in the TFHTAP studies (TFHTAP, 2007; Sanderson et al., 2008; Fiore et al., 2009; Reidmiller et al., 2009).

Acknowledgements. We thank M. Lin (Princeton), B. Duncan (NASA GSFC), and L. Horowitz (NOAA GFDL) for thoughtful comments on an earlier draft, M. Evans (Leeds), E. Fischer (U Washington) and J. Orlando (NCAR) for useful discussions, two anonymous reviewers, and the editor.

Edited by: D. Simpson
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Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Sein-
A. M. Fiore et al.: North American isoprene influence on intercontinental ozone pollution 1709


