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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 (O_3) precursor. Isoprene is also a precursor to peroxy acetyl nitrate (PAN) and thus affects partitioning among oxidized nitrogen (NO_y) species, shifting the balance towards PAN which more efficiently contributes to long-range transport relative to nitric acid (HNO_3) 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 20% changes in North American (NA) isoprene versus 20% changes in NA anthropogenic emissions (nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOC) and NO_x + NMVOC+carbon monoxide+aerosols). The regional NA surface O_3 response to a 20% increase in NA isoprene is approximately one third of the response (oppositely signed) to a 20% decrease in all NA anthropogenic emissions in summer. The intercontinental surface O_3 response over Europe and North Africa (EU region) to NA isoprene is more than half of the response to all NA anthropogenic emissions combined in summer and fall. During these seasons, natural inter-annual variations in NA isoprene emissions (estimated at ±10%) may modulate the responses of EU surface O_3, lower tropospheric PAN, and total NO_y deposition to a 20% decrease in NA anthropogenic emissions by ±25%, ±50%, and ±20%, respectively. Lower tropospheric PAN responds similarly for 20% perturbations to either NA isoprene or NA anthropogenic O_3 precursor emissions. This PAN response is at least twice as large as the relative changes in surface O_3, implying that long-term PAN measurements at high altitude sites may help to detect O_3 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 O_3 or oxidized nitrogen deposition, reported in the recent TF HTAP multi-model studies (TFHTAP, 2007).

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1 Introduction

A recent internationally coordinated effort has estimated hemispheric pollutant transport at northern mid-latitudes and assessed uncertainties in these estimates (TFHTAP, 2007; www.htap.org). Intended to inform future policy negotiations under the Convention on Long-Range Transboundary Air Pollution (CLRTAP), 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; Anenberg, 2009; Jonson et al., 2010) In regions heavily vegetated with isoprene-emitting plants, however, anthropogenic emissions of nitrogen oxides (NO_x) interact with isoprene, a highly reactive non-methane volatile organic compound (NMVOC), to produce ozone (O_3) 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 O_3 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_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 regions with abundant isoprene and NO_x, such as the Eastern United States (where July isoprene emissions have been estimated to be 4 to over 10 times higher than anthropogenic NMVOC (e.g., Fiore et al., 2005), isoprene thus has the potential to play a key role in hemispheric transport of O_3.

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In addition to O_3, various organic nitrates, including peroxy acetyl nitrate (PAN) which is particularly relevant for intercontinental transport, are produced during photochemical reactions involving isoprene and NO_x. Formation of PAN alters the balance between deposition and export of oxidized nitrogen (NO_y = NO_x+ HNO_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_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). Two pathways contribute approximate equally to intercontinental transport of O_3 pollution: (1) production of O_3 over the source region which is then exported, (2) export of precursors which then produce O_3 during transit to the downwind region (Jacob et al., 1999; Wild et al., 2004; West et al., 2009; Lin et al., 2010). Irrespective of the contribution of PAN to the latter pathway of intercontinental O_3 transport, PAN may also be a useful proxy for changes in O_3 precursor emissions, which may be detected more readily in observations of PAN than O_3 (Jaffe et al., 2007; Fischer et al., 2010).

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 ultimate impact of isoprene-NO_x-O_3 chemistry on foreign regions (Emmerson and Evans, 2009). Of particular relevance for O_3 produced in anthropogenic NO_x source regions is the uncertain interaction of isoprene with the NO_x budget via isoprene nitrate formation; the ultimate influence of isoprene (and changes in isoprene) on O_3 hinges 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

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responses of surface O_3 and NO_y deposition to anthropogenic emission perturbations, as reported in prior TF HTAP publications (Sanderson et al., 2008; Fiore et al., 2009; Reidmiller et al., 2009).

Though biogenic, isoprene 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 emitters) could dramatically alter future isoprene emissions and thereby air quality (e.g., Wiedinmyer et al., 2006; Avise et al., 2009; Chen et al., 2009). The strong temperature dependence of isoprene emissions implies that they will increase in a warmer climate, but accompanying increases in carbon dioxide may counteract this effect; the role of other environmental stressors such as drought, pollutant exposure, and insect herbivory is less well understood (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_3 pollution, we use the MOZART-2 global CTM (Sect. 2) to quantify the influence of NA isoprene on surface O_3, lower free tropospheric PAN, and NO_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_3 precursor emission changes (Sect. 4). We then evaluate the impact of isoprene emission variability, as well as uncertainties in isoprene emissions and chemistry, on estimates of hemispheric responses to NA anthropogenic emission controls (Sect. 5) and discuss the implications of our findings (Sect. 6).

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2 Model simulations

We use the MOZART-2 model (Horowitz et al., 2003) in the same configuration ("MOZARTGFDL-v2") as applied 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 the 4% yield of isoprene nitrates and 40% rate of recycling back to NO_x upon oxidation of these nitrates; these values are consistent with observed alkyl nitrates over the eastern United States in summer (Horowitz et al., 2007). The SYNOZ parameterization provides the stratospheric O_3 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 O_3 precursors were decreased by 20%, separately for NO_x, 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 NO_x (SR3NA), anthropogenic NMVOC (SR4NA), and all anthropogenic O_3 precursors plus aerosols combined (SR6NA). The differences between these perturbation simulations and SR1 provide an estimate of the response to changes in anthropogenic emissions.

Of the four continental source regions in Fig. 1, North America is the most abundant isoprene emitter in MOZART-2, with 35 Tg C a^{-1} as compared to 22, 12, and

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17 Tg C a^{-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 NO_x, CO and NMVOC from the NA region in MOZART-2 are 8.8 Tg N a^{-1}, 100 Tg a^{-1}, and 6.6 Tg C a^{-1}, respectively. The corresponding TF HTAP values (mean ±standard deviation across models) are 7.4±0.4 Tg N a^{-1}, 101±19 Tg $a^{-1}$and 16±7.1 Tg C a^{-1}. The lower anthropogenic NMVOC emissions and higher anthropogenic NO_x imply that O_3 and PAN formation in MOZART-2 may be more sensitive to NA isoprene vs. anthropogenic NMVOC emissions as 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 O_3 over NA is more sensitive to NA NO_x than NMVOC in the models participating in the TF HTAP multi-model studies from spring through fall (Fiore et al., 2009; their Fig. 4), we expect our results to be fairly robust to uncertainties in anthropogenic NMVOC emissions. The decline in eastern U.S. anthropogenic NO_x emissions over recent years will tend to decrease the sensitivity of O_3 formation to isoprene.

The MOZART-2 SR1 simulation, which has previously been evaluated with observations of surface O_3 and O_3 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 U.S. and Europe and at low-altitude sites in the Northeastern US and central Europe during winter. Most pertinent to our study is the model overestimate of summertime surface O_3 over the eastern United States; this is pervasive across the current generation of CTMs (Fiore et al., 2009; Reidmiller et al., 2009) and investigations into its cause are

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ongoing. Although we do not yet understand the source(s) of this bias in surface O_3, the lack of a simple relationship between biases in individual models with respect to the observations and the modeled O_3 responses to emission changes (Reidmiller et al., 2009; Jonson et al., 2010) suggests that this bias alone is not a good test for discriminating among models of 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 up to 100–200 ppt; Fiore et al., 2010).

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 multi-model 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 centered on the role of NA isoprene emissions, 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). 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 difference in surface O_3 between ISOPNA and SR1 provides an estimate of the response to changes in NA isoprene which can be compared directly with the response to the TF HTAP SR anthropogenic emission perturbations. For testing the sensitivity of the

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relationships between surface O_3 and NA anthropogenic emissions (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 changes in isoprene emissions on the hemispheric O_3 response to a sustained 20% decrease in NA anthropogenic emissions. We then 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 the relationships between surface O_3 and anthropogenic emissions (SR1-SR6NA) reported in (Fiore et al., 2009) and for NO_y deposition reported in (Sanderson et al., 2008). Although we imposed oppositely signed perturbations to the isoprene and anthropogenic emissions, for ease of comparison we show the absolute changes; the O_3 response to a 20% increase versus decrease in emissions has been shown to be approximately linear for anthropogenic NMVOC and NO_x (Fiore et al., 2009; Wu et al., 2009).

3 Hemispheric influence of NA isoprene and anthropogenic emissions in August

Over foreign regions in the Northern Hemisphere, the changes in surface O_3 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). The spatial patterns of the O_3 response to NA isoprene and NA anthropogenic emissions correlate strongly ($r = 0.71$), reflecting the co-location of NO_x and isoprene sources in eastern NA and the role of meteorology in transporting O_3 from NA. 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).

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Changes in lower tropospheric PAN (model level centered at 694 hPa) due to isoprene and NA anthropogenic emission perturbations are similar in spatial pattern ($r = 0.98$) and in magnitude, with a slightly higher intercontinental response to NA isoprene versus anthropogenic emissions in August (Fig. 1). This stronger influence of isoprene on PAN as compared to O_3 is more clearly seen in Fig. 2, which shows the relative responses to the NA emission perturbations. These results demonstrate the key role isoprene plays in PAN formation over the NA region in summer (Horowitz et al., 1998; Pfister et al., 2008). If we extrapolate the results in Fig. 2 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 lower tropospheric PAN over Spain, the Mediterranean and Northern Africa is associated with NA isoprene emissions.

Since isoprene influences the NO_y partitioning between organic nitrates and nitric acid, we also examine the impacts of anthropogenic versus isoprene emission changes on NO_y deposition (Fig. 2). The changes from NA anthropogenic emissions are similar to those reported for the NA NO_x 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 HTAP regions. The NA isoprene influence on NO_y deposition in the foreign HTAP regions is less than 1%. Over NA, the response to NA isoprene emissions is of opposite sign to the emission perturbation since increasing isoprene favors PAN formation relative to nitric acid (HNO_3), in part due to the decrease in OH associated with increasing isoprene emissions in the model (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. 2 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 and the subsequent deposition of that nitrogen (as HNO_3) in air masses

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that subside as they circulate around the Bermuda and Pacific high pressure systems.

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. 3). We focus on the responses in the NA and EU regions to illustrate "regional" versus "intercontinental" responses. We note that the average values in Fig. 3 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 and 2. Isoprene consistently acts to depress local NO_y deposition but increase intercontinental NO_y deposition as seen in Fig. 2 (bottom row) throughout the isoprene emission season (not shown) and so we focus on seasonal variations in O_3 and PAN in this section.

The NA isoprene emission influence on surface O_3 is enhanced in autumn relative to spring (determined from the difference of the ISOPNA and SR1 simulations; green lines in Fig. 3), despite similar emissions in the two seasons (~4 Tg C in May and September, and ~2 Tg C in April and October). In contrast, the seasonal cycle of the NA O_3 response to the anthropogenic O_3 precursors (blue, red, and black lines in Fig. 2 for 20% decreases in NA anthropogenic NMVOC, NO_x, and all O_3 precursors, respectively) tends to be more symmetrically centered on the summer months; those emissions do not vary seasonally in the model so the O_3 responses are only influenced by seasonal changes in transport and chemistry. The larger influence of NA isoprene on surface O_3 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).

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Whereas O_3 responds more strongly to equivalent percentage changes in anthropogenic NO_xthan to isoprene emissions (red vs. green lines in Fig. 3), the opposite is true for PAN during May through December. Furthermore, the regional PAN response to isoprene exceeds that to all anthropogenic emissions in August (black vs. green lines in Fig. 3; see also Fig. 2) and is approximately equal in other non-winter months; the intercontinental response is equivalent from June through October. Imposing equivalent percentage reductions to isoprene and anthropogenic NMVOC emissions yields stronger O_3 and PAN responses for the isoprene perturbation over all regions from spring through late fall (green vs. blue lines in Fig. 3), 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).

The combined impact of NA isoprene and anthropogenic emission perturbations can be fairly well approximated by adding the results from the simulations which individually perturbed those emissions (black dot-dash versus dotted lines in Fig. 3). 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 in the response over the immediate source region as compared to intercontinental distances (particularly evident for PAN in Fig. 3) is consistent with the findings of Wild and Prather (2006).

We explore here the potential for PAN to indicate O_3 precursor emission changes. Comparing the O_3 and PAN responses in Fig. 2 indicates that the PAN changes, induced either by NA anthropogenic or isoprene emission perturbations, are more than twice as large as for O_3, with larger changes extending over wider regions. This finding supports the premise of Jaffe et al. (2007) and Fischer et al. (2010), 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. Unraveling the relative contributions of NO_x versus isoprene, however, will require additional source information, including a solid

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understanding of isoprene emission variations (near equivalence of red and green lines in Fig. 3). While isoprene clearly dominates PAN formation over anthropogenic NMVOC 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 emitting season.

5 Estimating NA anthropogenic influence: uncertainty from isoprene emissions and chemistry

We first estimate the impact of changes in isoprene emissions, as might be induced by changes in climate, land-use, or weather, on the surface O_3 response to anthropogenic emission controls sustained over many years. The difference of the base simulation (SR1) and the SR6ISOPNA simulation (black dash-dot line in Fig. 3) can be used to estimate such an impact. We do not consider changes in the spatial distribution of isoprene emissions relative to the simple, uniform scaling applied here, which may also alter the surface O_3 response to anthropogenic emissions. When isoprene increases by 20% in the model, as might occur in a warmer climate, the O_3 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). This smaller response, 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).

If we assume that surface O_3 responds approximately linearly to NA isoprene emission perturbations of 20% (as occurs for anthropogenic NO_x and NMVOC; Fiore et al., 2009; Wu et al., 2009), then our NA isoprene perturbation simulation captures the full range of inter-annual isoprene variability observed in formaldehyde columns from

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space (Abbot et al., 2003; Palmer et al., 2006). Since we imposed climatologically average isoprene emissions in our simulations, the 50% decrease in the EU O_3 response to NA anthropogenic emissions (black solid vs. black dash-dot lines in Fig. 3 upper panels) should be interpreted as a variability of ±25% relative to an average meteorological summer (i.e., ±25% variations relative to our estimate determined from SR1-SR6NA; solid black lines in Fig. 3). In a similar manner, we estimate that isoprene can modulate lower tropospheric PAN by ±50% and NO_y deposition by ±20% over the EU region.

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 (Kang et al., 2003; von Kuhlmann et al., 2004; Fiore et al., 2005; Ito et al., 2009). In Fig. 4, 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 approximately up to 2–6 ppb, 20–50 ppt, and 10–20% in surface O_3, PAN at 700 hPa, and NO_y deposition over the NA region in August (Fig. 4). These findings are consistent with earlier work (von Kuhlmann et al., 2004; Fiore et al., 2005). 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 larger than that shown in Figs. 1 and 2 (right columns).

We turn next to determine the impact of these uncertainties (in isoprene emissions and isoprene nitrate fate) on estimates of the O_3 response to NA anthropogenic emissions. Figure 5 shows that neither a 20% increase in the baseline NA isoprene emissions (solid vs. dashed lines) nor an increase in the NO_x recycling from isoprene nitrates (solid vs. dotted lines) changes the estimated impact of a 20% decrease in NA anthropogenic emissions on surface O_3 over the NA or EU regions. Clearly the differences in Fig. 5 cannot explain the factor of 2–3 spread across models reported in Fiore

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et al. (2009) and Reidmiller et al. (2009). This lack of sensitivity indicates that the O_3 production remains linearly dependent on NA anthropogenic emissions even when the baseline isoprene-NO_x-O_3 chemistry is perturbed.

A modest nonlinear response does emerge for PAN, with a larger sensitivity to anthropogenic NO_x emissions in the baseline simulation with higher isoprene emissions. This response reflects the strong sensitivity of PAN formation to the ratio of NO to NO_2 and the key role of OH levels in this partitioning, implying that models with higher baseline isoprene emissions amplify the PAN response to anthropogenic NO_x emission changes. 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. 5). 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 reported across models (Sanderson et al., 2008).

6 Discussion and conclusions

With the MOZART-2 global chemical transport model, we examined the influence of isoprene versus anthropogenic emissions from North America (NA) on intercontinental ozone pollution, lower free tropospheric PAN and oxidized nitrogen deposition. Our findings indicate that long-term, continuous observations of PAN may prove more useful than O_3 itself in detecting O_3 precursor emission changes. For example, Fig. 2 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). Our findings further suggest that the role of isoprene must be carefully considered alongside that of anthropogenic emissions in interpreting observed changes in PAN. In this regard, long-term measurements that can distinguish changes in the biogenic and

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anthropogenic sources of carbon and nitrogen alongside total 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 O_3 during ground-based, ship and aircraft field intensives (Roberts et al., 1998, 2002, 2006).

The comparable influences on hemispheric O_3 transport during the summer through fall from isoprene and anthropogenic emissions in the model 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_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).

Any changes in isoprene, whether induced by a warming climate, fluctuating weather, or changing land-use practices, may alter the influence of a sustained level of anthropogenic emission controls on intercontinental O_3 pollution. For example, we find that weather-driven variability in isoprene emissions can induce fluctuations of ±25% in the monthly mean EU surface O_3 response to NA anthropogenic emissions relative to the response in an average meteorological year. For lower tropospheric PAN and for NO_ydeposition, the corresponding ranges are ±50% and ±20%. This variability should also be considered in future assessments of hemispheric O_3 transport.

The simulated hemispheric responses of surface O_3 and oxidized nitrogen deposition to regional anthropogenic emission perturbations show little sensitivity to the level of isoprene emissions specified in the model or the extent to which isoprene nitrates serve as a terminal sink for NO_x. Although these uncertainties do contribute to the range in model estimates of surface O_3 and the tropospheric O_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_3 or oxidized nitrogen deposition to anthropogenic

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emission perturbations estimated in the TFHTAP studies (TFHTAP, 2007; Sanderson et al., 2008; Fiore et al., 2009; Reidmiller et al., 2009).

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References

Abbot, D. S., Palmer, P. I., Martin, R. V., Chance, K. V., Jacob, D. J., and Guenther, A.: Seasonal and interannual variability of North American isoprene emissions as determined by formaldehyde column measurements from space, Geophys. Res. Lett., 30, 1886, doi:10.1029/2003gl017336, 2003.

Anenberg, S. C., West, J. J., Fiore, A. M., Jaffe, D. A., Prather, M. J., Bergmann, D., Cuvelier, K., Dentener, F. J., Duncan, B. N., Gauss, M., Hess, P., Jonson, J. E., Lupu, A., MacKenzie, I. A., Marmer, E., Park, R. J., Sanderson, M. G., Schultz, M., Shindell, D. T., Szopa, S., Vivanco, M. G., Wild, O., and Zeng, G.: Intercontinental Impacts of Ozone Pollution on Human Mortality, Environ. Sci. Technol., 43, 6482–6487, doi:10.1021/es900518z, 2009.

Archibald, A. T., Cooke, M. C., Utembe, S. R., Shallcross, D. E., Derwent, R. G., and Jenkin, M. E.: Impacts of mechanistic changes on HOx formation and recycling in the oxidation of isoprene, Atmos. Chem. Phys., 10, 8097–8118, doi:doi:10.5194/acp-10-8097-2010, 2010.

Arneth, A., Monson, R. K., Schurgers, G., Niinemets, A., and Palmer, P. I.: Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes)?, Atmos. Chem. Phys., 8, 4605–4620, doi:10.5194/acp-8-4605-2008, 2008.

Avise, J., Chen, J., Lamb, B., Wiedinmyer, C., Guenther, A., Salathé, E., and Mass, C.: Attribution of projected changes in summertime US ozone and PM2.5 concentrations to global changes, Atmos. Chem. Phys., 9, 1111–1124, doi:10.5194/acp-9-1111-2009, 2009.

Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987–5005, doi:10.5194/acp-9-4987-2009, 2009.

Chameides, W. L., Lindsay, R. W., Richardson, J., and Kang, C. S.: The role of biogenic hydrocarbons in urban smog: Atlanta as a case study, Science, 241, 1473–1475, 1988.

ACPD

10, 24821–24851, 2010

Chen, J., Avise, J., Lamb, B., Salath, E., Mass, C., Guenther, A., Wiedinmyer, C., Lamarque, J. F., O'Neill, S., McKenzie, D., and Larkin, N.: The effects of global changes upon regional ozone pollution in the United States, Atmos. Chem. Phys., 9, 1125–1141, doi:10.5194/acp-9-1125-2009, 2009.

Emmerson, K. M. and Evans, M. J.: Comparison of tropospheric gas-phase chemistry schemes for use within global models, Atmos. Chem. Phys., 9, 1831–1845, doi:10.5194/acp-9-1831-2009, 2009.

Emmons, L. K., Walters, S., Hess, P. G., Lamarque, J. F., Pfister, G. G., Fillmore, D., Granier, C., Guenther, A., Kinnison, D., Laepple, T., Orlando, J., Tie, X., Tyndall, G., Wiedinmyer, C., Baughcum, S. L., and Kloster, S.: Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4), Geosci. Model Dev., 3, 43–67, doi:10.5194/gmd-3-43-2010, 2010.

Fang, Y., Fiore, A. M., Horowitz, L. W., Levy, H., II, Hu, Y., and Russell, A. G.: Sensitivity of the NO_y budget over the United States to anthropogenic and lightning NO_x in summer, J. Geophys. Res., AGU, D18, doi:10.1029/2010jd014079, 2010.

Fiore, A. M., Horowitz, L. W., Purves, D. W., Levy, H., II, Evans, M. J., Wang, Y., Li, Q., and Yantosca, R. M.: Evaluating the contribution of changes in isoprene emissions to surface ozone trends over the eastern United States, J. Geophys. Res., 110, D12303, doi:10.1029/2004jd005485, 2005.

Fiore, A. M., Dentener, F. J., Wild, O., Cuvelier, C., Schultz, M. G., Hess, P., Textor, C., Schulz, M., Doherty, R. M., Horowitz, L. W., MacKenzie, I. A., Sanderson, M. G., Shindell, D. T., Stevenson, D. S., Szopa, S., Van Dingenen, R., Zeng, G., Atherton, C., Bergmann, D., Bey, I., Carmichael, G., Collins, W. J., Duncan, B. N., Faluvegi, G., Folberth, G., Gauss, M., Gong, S., Hauglustaine, D., Holloway, T., Isaksen, I. S. A., Jacob, D. J., Jonson, J. E., Kaminski, J. W., Keating, T. J., Lupu, A., Marmer, E., Montanaro, V., Park, R. J., Pitari, G., Pringle, K. J., Pyle, J. A., Schroeder, S., Vivanco, M. G., Wind, P., Wojcik, G., Wu, S., and Zuber, A.: Multimodel estimates of intercontinental source-receptor relationships for ozone pollution, J. Geophys. Res., 114, D04301, 10.1029/2008jd010816, 2009.

Fiore, A. M., Fischer, E. V., Jaffe, D. J., Pandey, S., and Staehelin, J.: Hemispheric and regional pollution signatures in PAN at northern mid-latitude mountain sites, in preparation, 2010.

Fischer, E. V., Jaffe, D. A., and Weatherhead, E. C.: Free tropospheric Peroxyacetyl Nitrate (PAN) and Ozone at Mount Bachelor: Causes of Variability and Timescale for Trend Detection, Atmospheric Chemistry and Physics, in preparation, 2010.

ACPD

10, 24821–24851, 2010

Folberth, G. A., Hauglustaine, D. A., Lathière, J., and Brocheton, F.: Interactive chemistry in the Laboratoire de Météorologie Dynamique general circulation model: model description and impact analysis of biogenic hydrocarbons on tropospheric chemistry, Atmos. Chem. Phys., 6, 2273–2319, doi:10.5194/acp-6-2273-2006, 2006.

Fuentes, J. D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J. W., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T. D., and Stockwell, W.: Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review, Bull. Amer. Meteor. Soc., 81, 1537–1575, 2000.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, doi:10.1029/94jd02950, 1995.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Honrath, R. E., Owen, R. C., Val Martin, M., Reid, J. S., Lapina, K., Fialho, P., Dziobak, M. P., Kleissel, J., and Westphal, D. L.: Regional and hemispheric impacts of anthropogenic and biomass burning emissions on summertime CO and O3 in the North Atlantic lower free troposphere, J. Geophys. Res., 109, D24310, doi:10.1029/2004JD005147, 2004.

Horowitz, L. W., Liang, J., Gardner, G. M., and Jacob, D. J.: Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, J. Geophys. Res., 103, 13451–13476, doi:10.1029/97jd03142, 1998.

Horowitz, L. W., Walters, S., Mauzerall, D. L., Emmons, L. K., Rasch, P. J., Granier, C., Tie, X., Lamarque, J.-F., Schultz, M. G., Tyndall, G. S., Orlando, J. J., and Brasseur, G. P.: A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, J. Geophys. Res., 108, 4784, doi:10.1029/2002jd002853, 2003.

Horowitz, L. W., Fiore, A. M., Milly, G. P., Cohen, R. C., Perring, A., Wooldridge, P. J., Hess, P. G., Emmons, L. K., and Lamarque, J.-F.: Observational constraints on the chemistry of isoprene nitrates over the eastern United States, J. Geophys. Res., 112, D12S08, doi:10.1029/2006jd007747, 2007.

Ito, A., Sillman, S., and Penner, J. E.: Global chemical transport model study of ozone response to changes in chemical kinetics and biogenic volatile organic compounds emissions due to

ACPD
10, 24821–24851, 2010

increasing temperatures: Sensitivities to isoprene nitrate chemistry and grid resolution, J. Geophys. Res., 114, D09301, doi:10.1029/2008jd011254, 2009.
Jacob, D. J., Horowitz, L. W., Munger, J. W., Heikes, B. G., Dickerson, R. R., Artz, R. S., and Keene, W. C.: Seasonal transition from NO_x- to hydrocarbon-limited conditions for ozone production over the eastern United States in September, J. Geophys. Res., 100, 9315–9324, doi:10.1029/94jd03125, 1995.
Jacob, D. J., Logan, J. A., and Murti, P. P.: Effect of rising Asian emissions on surface ozone in the United States, Geophys. Res. Lett., 26, 2175–2178, doi:10.1029/1999gl900450, 1999.
Jaffe, D., Thornton, J., Wolfe, G., Reidmiller, D., Fischer, E. V., Jacob, D. J., Cohen, R., Singh, H., Weinheimer, A., and Flocke, F.: Can we Detect an Influence over North America From Increasing Asian NO_x Emissions?, EOS Trans. AGU, 88(52), Fall Meet. Suppl., Abstract A51E-04, 2007.
Johnson, C. E., Collins, W. J., Stevenson, D. S., and Derwent, R. G.: Relative roles of climate and emissions changes on future tropospheric oxidant concentrations, J. Geophys. Res., 104, 18631–18645, doi:10.1029/1999jd900204, 1999.
Jonson, J. E., Stohl, A., Fiore, A. M., Hess, P., Szopa, S., Wild, O., Zeng, G., Dentener, F. J., Lupu, A., Schultz, M. G., Duncan, B. N., Sudo, K., Wind, P., Schulz, M., Marmer, E., Cuvelier, C., Keating, T., Zuber, A., Valdebenito, A., Dorokhov, V., De Backer, H., Davies, J., Chen, G. H., Johnson, B., Tarasick, D. W., Stübi, R., Newchurch, M. J., von der Gathen, P., Steinbrecht, W., and Claude, H.: A multi-model analysis of vertical ozone profiles, Atmos. Chem. Phys., 10, 5759–5783, doi:10.5194/acp-10-5759-2010, 2010.
Kalnay, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Iredell, M., Saha, S., White, G., Woollen, J., Zhu, Y., Leetmaa, A., Reynolds, R., Chelliah, M., Ebisuzaki, W., Higgins, W., Janowiak, J., Mo, K. C., Ropelewski, C., Wang, J., Jenne, R., and Joseph, D.: The NCEP/NCAR 40-Year Reanalysis Project, Bulletin of the American Meteorological Society, 77, 437–471, doi:10.1175/1520-0477(1996)077<0437:TNYRP>2.0.CO;2, 1996.
Kang, D., Aneja, V. P., Mathur, R., and Ray, J. D.: Nonmethane hydrocarbons and ozone in three rural southeast United States national parks: A model sensitivity analysis and comparison to measurements, J. Geophys. Res., 108, 4604, doi:10.1029/2002jd003054, 2003.
Kleinman, L. I.: Seasonal Dependence of Boundary Layer Peroxide Concentration: The Low and High NO_x Regimes, J. Geophys. Res., 96, 20721–20733, doi:10.1029/91jd02040, 1991.
Lathière, J., Hewitt, C. N., and Beerling, D. J.: Sensitivity of isoprene emissions from the terrestrial biosphere to 20th century changes in atmospheric CO2 concentration, climate, and

ACPD
10, 24821–24851, 2010

land use, Global Biogeochem. Cycles, 24, GB1004, doi:10.1029/2009gb003548, 2010.
Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, Nature, 452, 737–740, 2008.
Liang, J., Horowitz, L. W., Jacob, D. J., Wang, Y., Fiore, A. M., Logan, J. A., Gardner, G. M., and Munger, J. W.: Seasonal budgets of reactive nitrogen species and ozone over the United States, and export fluxes to the global atmosphere, J. Geophys. Res., 103, 13435–13450, doi:10.1029/97jd03126, 1998.
Lin, M., Holloway, T., Carmichael, G. R., and Fiore, A. M.: Quantifying pollution inflow and outflow over East Asia in spring with regional and global models, Atmos. Chem. Phys., 10, 4221–4239, doi:10.5194/acp-10-4221-2010, 2010.
Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L. G., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L., Liu, S.-C., Chang, C.-C., Amoroso, A., and Costabile, F.: Evidence of Reactive Aromatics As a Major Source of Peroxy Acetyl Nitrate over China, Environ. Sci. Technol., 44, 7017–7022, doi:10.1021/es1007966, 2010.
McLinden, C. A., Olsen, S. C., Hannegan, B., Wild, O., Prather, M. J., and Sundet, J.: Stratospheric ozone in 3-D models: A simple chemistry and the cross-tropopause flux, J. Geophys. Res., 105, 14653–14665, doi:10.1029/2000jd900124, 2000.
Moxim, W. J., Levy, H., II, and Kasibhatla, P. S.: Simulated global tropospheric PAN: Its transport and impact on NO_x, J. Geophys. Res., 101, 12621–12638, doi:10.1029/96jd00338, 1996.
Murazaki, K. and Hess, P.: How does climate change contribute to surface ozone change over the United States?, J. Geophys. Res., 111, D05301, doi:10.1029/2005jd005873, 2006.
Pacifico, F., Harrison, S. P., Jones, C. D., and Sitch, S.: Isoprene emissions and climate, Atmos. Environ., 43, 6121–6135, 2009.
Palmer, P. I., Abbot, D. S., Fu, T.-M., Jacob, D. J., Chance, K., Kurosu, T. P., Guenther, A., Wiedinmyer, C., Stanton, J. C., Pilling, M. J., Pressley, S. N., Lamb, B., and Sumner, A. L.: Quantifying the seasonal and interannual variability of North American isoprene emissions using satellite observations of the formaldehyde column, J. Geophys. Res., 111, D12315, doi:10.1029/2005jd006689, 2006.
Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, Atmos. Chem. Phys., 9, 1479–1501, doi:10.5194/acp-9-1479-2009, 2009.
Perring, A. E., Bertram, T. H., Wooldridge, P. J., Fried, A., Heikes, B. G., Dibb, J., Crounse, J.

ACPD
10, 24821–24851, 2010

D., Wennberg, P. O., Blake, N. J., Blake, D. R., Brune, W. H., Singh, H. B., and Cohen, R. C.: Airborne observations of total RONO2: new constraints on the yield and lifetime of isoprene nitrates, Atmos. Chem. Phys., 9, 1451–1463, doi:10.5194/acp-9-1451-2009, 2009.

Pfister, G. G., Emmons, L. K., Hess, P. G., Lamarque, J. F., Orlando, J. J., Walters, S., Guenther, A., Palmer, P. I., and Lawrence, P. J.: Contribution of isoprene to chemical budgets: A model tracer study with the NCAR CTM MOZART-4, J. Geophys. Res., 113, D05308, doi:10.1029/2007jd008948, 2008.

Reidmiller, D. R., Fiore, A. M., Jaffe, D. A., Bergmann, D., Cuvelier, C., Dentener, F. J., Duncan, B. N., Folberth, G., Gauss, M., Gong, S., Hess, P., Jonson, J. E., Keating, T., Lupu, A., Marmer, E., Park, R., Schultz, M. G., Shindell, D. T., Szopa, S., Vivanco, M. G., Wild, O., and Zuber, A.: The influence of foreign vs. North American emissions on surface ozone in the US, Atmos. Chem. Phys., 9, 5027–5042, doi:10.5194/acp-9-5027-2009, 2009.

Ren, X., Olson, J. R., Crawford, J. H., Brune, W. H., Mao, J., Long, R. B., Chen, Z., Chen, G., Avery, M. A., Sachse, G. W., Barrick, J. D., Diskin, G. S., Huey, L. G., Fried, A., Cohen, R. C., Heikes, B., Wennberg, P. O., Singh, H. B., Blake, D. R., and Shetter, R. E.: HOx chemistry during INTEX-A 2004: Observation, model calculation, and comparison with previous studies, J. Geophys. Res., 113, D05310, doi:10.1029/2007jd009166, 2008.

Roberts, J. M., Tanner, R. L., Newman, L., Bowersox, V. C., Bottenheim, J. W., Anlauf, K. G., Brice, K. A., Parrish, D. D., Fehsenfeld, F. C., Buhr, M. P., Meagher, J. F., and Bailey, E. M.: Relationships between PAN and ozone at sites in eastern North America, J. Geophys. Res., 100, 22821–22830, doi:10.1029/95jd01221, 1995.

Roberts, J. M., Williams, J., Baumann, K., Buhr, M. P., Goldan, P. D., Holloway, J., Hübler, G., Kuster, W. C., McKeen, S. A., Ryerson, T. B., Trainer, M., Williams, E. J., Fehsenfeld, F. C., Bertman, S. B., Nouaime, G., Seaver, C., Grodzinsky, G., Rodgers, M., and Young, V. L.: Measurements of PAN, PPN, and MPAN made during the 1994 and 1995 Nashville Intensives of the Southern Oxidant Study: Implications for regional ozone production from biogenic hydrocarbons, J. Geophys. Res., 103, 22473–22490, 10.1029/98jd01637, 1998.

Roberts, J. M., Flocke, F., Stroud, C. A., Hereid, D., Williams, E., Fehsenfeld, F., Brune, W., Martinez, M., and Harder, H.: Ground-based measurements of peroxycarboxylic nitric anhydrides (PANs) during the 1999 Southern Oxidants Study Nashville Intensive, J. Geophys. Res., 107, 4554, doi:10.1029/2001jd000947, 2002.

Roberts, J. M., Marchewka, M., Bertman, S. B., Goldan, P., Kuster, W., de Gouw, J., Warneke, C., Williams, E., Lerner, B., Murphy, P., Apel, E., and Fehsenfeld, F. C.: Analysis of the

ACPD
10, 24821–24851, 2010

isoprene chemistry observed during the New England Air Quality Study (NEAQS) 2002 intensive experiment, J. Geophys. Res., 111, D23S12, doi:10.1029/2006jd007570, 2006.
Rosenstiel, T. N., Potosnak, M. J., Griffin, K. L., Fall, R., and Monson, R. K.: Increased CO_2 uncouples growth from isoprene emission in an agriforest ecosystem, Nature, 421, 256–259, 2003.
Sanderson, M. G., Dentener, F. J., Fiore, A. M., Cuvelier, C., Keating, T. J., Zuber, A., Atherton, C. S., Bergmann, D. J., Diehl, T., Doherty, R. M., Duncan, B. N., Hess, P., Horowitz, L. W., Jacob, D. J., Jonson, J. E., Kaminski, J. W., Lupu, A., MacKenzie, I. A., Mancini, E., Marmer, E., Park, R., Pitari, G., Prather, M. J., Pringle, K. J., Schroeder, S., Schultz, M. G., Shindell, D. T., Szopa, S., Wild, O., and Wind, P.: A multi-model study of the hemispheric transport and deposition of oxidised nitrogen, Geophys. Res. Lett., 35, L17815, doi:10.1029/2008gl035389, 2008.
Shindell, D. T., Chin, M., Dentener, F., Doherty, R. M., Faluvegi, G., Fiore, A. M., Hess, P., Koch, D. M., MacKenzie, I. A., Sanderson, M. G., Schultz, M. G., Schulz, M., Stevenson, D. S., Teich, H., Textor, C., Wild, O., Bergmann, D. J., Bey, I., Bian, H., Cuvelier, C., Duncan, B. N., Folberth, G., Horowitz, L. W., Jonson, J., Kaminski, J. W., Marmer, E., Park, R., Pringle, K. J., Schroeder, S., Szopa, S., Takemura, T., Zeng, G., Keating, T. J., and Zuber, A.: A multi-model assessment of pollution transport to the Arctic, Atmos. Chem. Phys., 8, 5353–5372, doi:10.5194/acp-8-5353-2008, 2008.
Steiner, A. L. and Goldstein, A. H.: Biogenic volatile organic compounds, in: Volatile Organic Compounds in the Atmosphere, edited by: Koppmann, R., Blackwell Publishing, Ltd., 82–128, 2007.
TFHTAP: Task Force on Hemispheric Transport of Air Pollution 2007 Interim Report, in: Air Pollution Studies, edited by: Keating, T. J. and Zuber, A., United Nations Economic Commission for Europe, New York and Geneva, 2007.
Trainer, M., Williams, E. J., Parrish, D. D., Buhr, M. P., Allwine, E. J., Westberg, H. H., Fehsenfeld, F. C., and Liu, S. C.: Models and observations of the impact of natural hydrocarbons on rural ozone, Nature, 329, 705–707, 1987.
Val Martin, M., Honrath, R. E., Owen, R. C., and Lapina, K.: Large-scale impacts of anthropogenic pollution and boreal wildfires on the nitrogen oxide levels over the central North Atlantic region, J. Geophys. Res., 113, D17308, doi:10.1029/2007JD009689, 2008.
van der Werf, G. R., Randerson, J. T., Giglio, L., Collatz, G. J., Kasibhatla, P. S., and Arellano Jr, A. F.: Interannual variability in global biomass burning emissions from 1997 to 2004, Atmos.

ACPD
10, 24821–24851, 2010

Chem. Phys., 6, 3423–3441, doi:10.5194/acp-6-3423-2006, 2006.
von Kuhlmann, R., Lawrence, M. G., Pöschl, U., and Crutzen, P. J.: Sensitivities in global scale modeling of isoprene, Atmos. Chem. Phys., 4, 1–17, doi:10.5194/acp-4-1-2004, 2004.
Wang, Y., Jacob, D. J., and Logan, J. A.: Global simulation of tropospheric O3-NO x - hydrocarbon chemistry 3. Origin of tropospheric ozone and effects of nonmethane hydrocarbons, J. Geophys. Res., 103, 10757–10767, doi:10.1029/98jd00156, 1998.
Weaver, C. P., Cooter, E., Gilliam, R., Gilliland, A., Grambsch, A., Grano, D., Hemming, B., Hunt, S. W., Nolte, C., Winner, D. A., Liang, X.-Z., Zhu, J., Caughey, M., Kunkel, K., Lin, J.-T., Tao, Z., Williams, A., Wuebbles, D. J., Adams, P. J., Dawson, J. P., Amar, P., He, S., Avise, J., Chen, J., Cohen, R. C., Goldstein, A. H., Harley, R. A., Steiner, A. L., Tonse, S., Guenther, A., Lamarque, J.-F., Wiedinmyer, C., Gustafson, W. I., Leung, L. R., Hogrefe, C., Huang, H.-C., Jacob, D. J., Mickley, L. J., Wu, S., Kinney, P. L., Lamb, B., Larkin, N. K., McKenzie, D., Liao, K.-J., Manomaiphiboon, K., Russell, A. G., Tagaris, E., Lynn, B. H., Mass, C., Salath, E., O'neill, S. M., Pandis, S. N., Racherla, P. N., Rosenzweig, C., and Woo, J.-H.: A Preliminary Synthesis of Modeled Climate Change Impacts on US Regional Ozone Concentrations, B. Am. Meteorol. Soc., 90, 1843–1863, doi:10.1175/2009BAMS2568.1, 2009.
West, J. J., Naik, V., Horowitz, L. W., and Fiore, A. M.: Effect of regional precursor emission controls on long-range ozone transport, Part 1: Short-term changes in ozone air quality, Atmos. Chem. Phys., 9, 6077–6093, doi:10.5194/acp-9-6077-2009, 2009.
Wiedinmyer, C., Tie, X., Guenther, A., Neilson, R., and Granier, C.: Future Changes in Biogenic Isoprene Emissions: How Might They Affect Regional and Global Atmospheric Chemistry?, Earth Interact., 10, 1–19, doi:10.1175/EI174.1, 2006.
Wild, O., Prather, M. J., Akimoto, H., Sundet, J. K., Isaksen, I. S. A., Crawford, J. H., Davis, D. D., Avery, M. A., Kondo, Y., Sachse, G. W., and Sandholm, S. T.: Chemical transport model ozone simulations for spring 2001 over the western Pacific: Regional ozone production and its global impacts, J. Geophys. Res., 109, D15S02, doi:10.1029/2003jd004041, 2004.
Wild, O. and Prather, M. J.: Global tropospheric ozone modeling: Quantifying errors due to grid resolution, J. Geophys. Res., 111, D11305, doi:10.1029/2005jd006605, 2006.
Wild, O.: Modelling the global tropospheric ozone budget: exploring the variability in current models, Atmos. Chem. Phys., 7, 2643–2660, doi:10.5194/acp-7-2643-2007, 2007.
Wu, S., Mickley, L. J., Jacob, D. J., Logan, J. A., Yantosca, R. M., and Rind, D.: Why are there large differences between models in global budgets of tropospheric ozone?, J. Geophys. Res., 112, D05302, doi:10.1029/2006jd007801, 2007.

ACPD
10, 24821–24851, 2010

Wu, S., Duncan, B. N., Jacob, D. J., Fiore, A. M., and Wild, O.: Chemical nonlinearities in relating intercontinental ozone pollution to anthropogenic emissions, Geophys. Res. Lett., 36, L05806, doi:10.1029/2008gl036607, 2009.

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10, 24821–24851, 2010

Table 1. MOZART-2 Simulations.

Name	Description
SR1	Base case (see Sect. 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%

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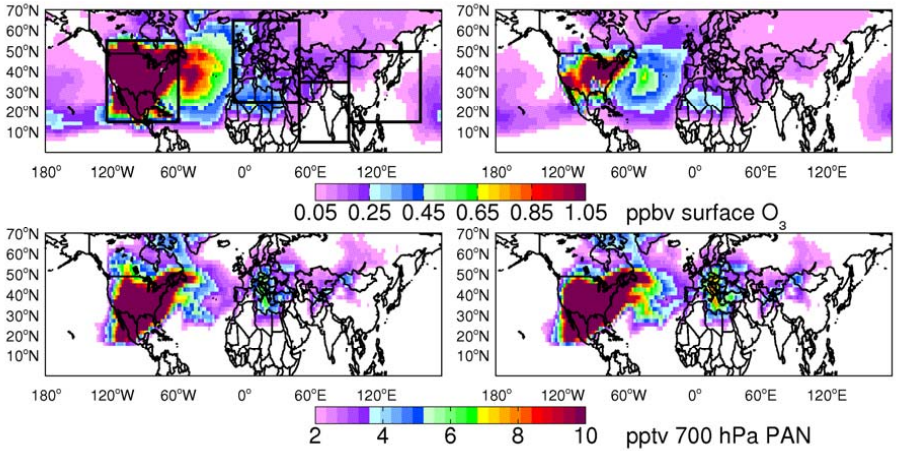

Fig. 1. Changes in (top) surface O_3 and (bottom) PAN at 700 hPa resulting from 20% perturbations to (left) North American anthropogenic O_3 precursor emissions (SR1-SR6NA simulations) and (right) biogenic isoprene emissions (ISOPNA-SR1) in the MOZART-2 model during August of 2001. Regions outlined in black, from left to right are: North America (NA), Europe and North Africa (EU), South Asia (SA), and East Asia (EA), as in TFHTAP (2007). Note the different scales on each color bar.

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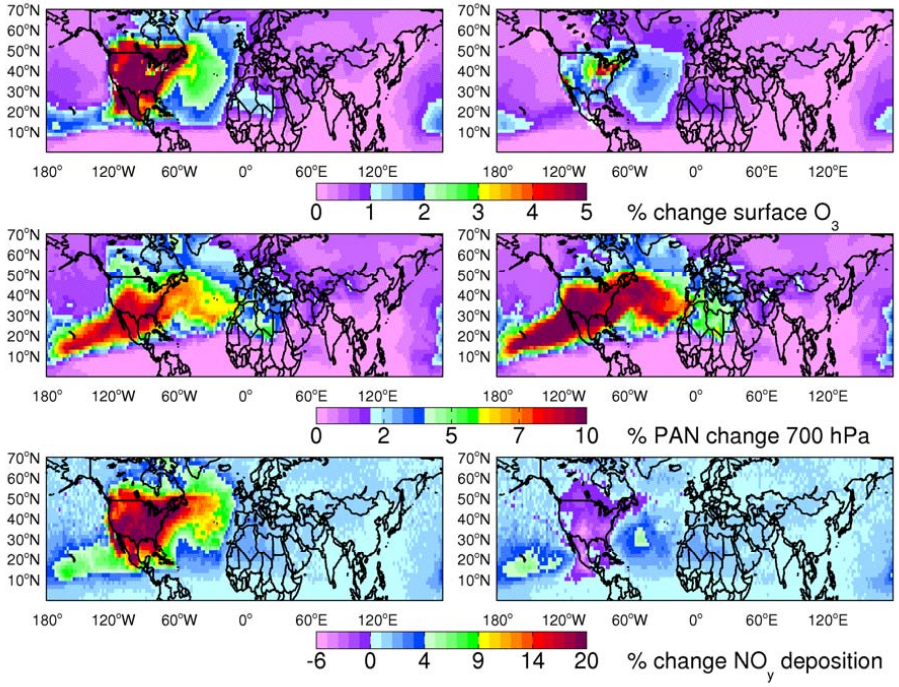

Fig. 2. Percentage changes in (top) surface O_3, (middle) lower free tropospheric PAN, and (bottom) NO_y deposition resulting from 20% perturbations to (left) North American anthropogenic O_3 precursor emissions (SR1-SR6NA simulations) and (right) biogenic isoprene emissions (ISOPNA-SR1) in the MOZART-2 model during August of 2001. Note the different scales on each color bar.

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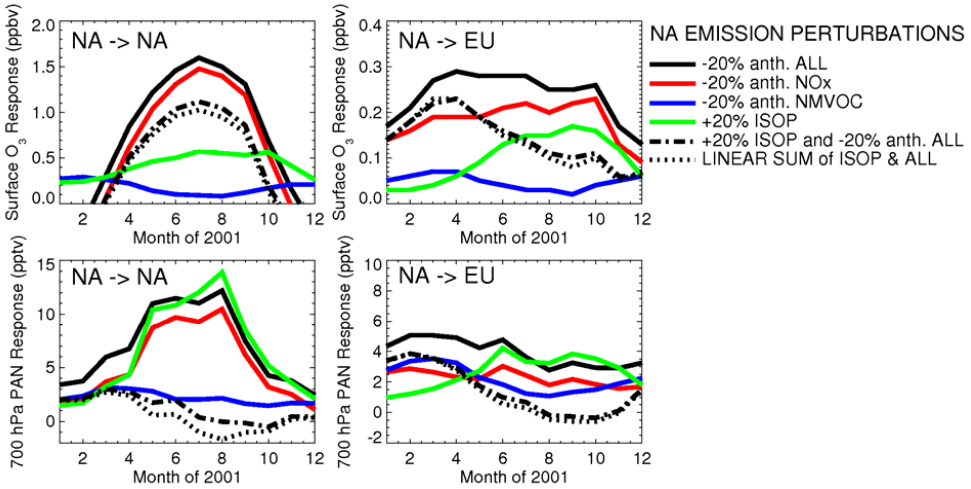

Fig. 3. Monthly mean (left) regional and (right) intercontinental (top) surface O_3 and (bottom) 700 hPa PAN response to North American (NA) emission perturbations, as determined by differencing the spatially averaged surface O_3 over NA and EU (Fig. 1) in the baseline simulation and in sensitivity simulations in which NA O_3 precursor emissions are perturbed individually by 20% (solid colored lines; note sign reversal for +20% ISOP). Also shown is the impact of a 20% increase in NA isoprene emissions combined with a 20% reduction in all NA anthropogenic O_3 precursors (dot-dashed; SR1-SR6ISOPNA) and the linear sum of these two changes imposed separately (dotted line; i.e., SR1-ISOPNA + SR1-SR6NA).

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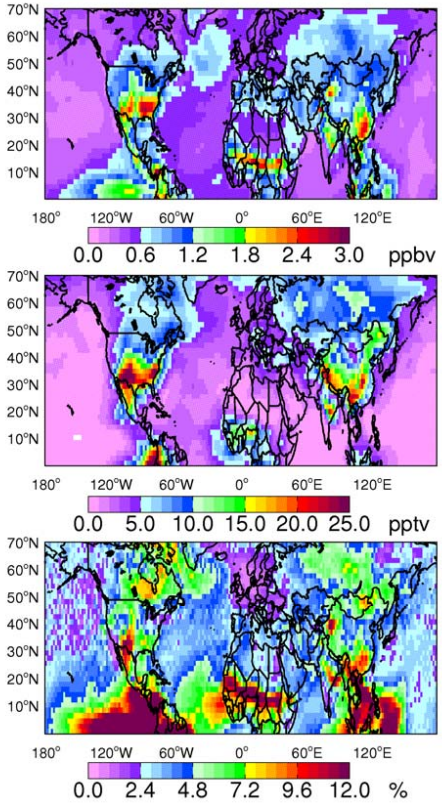

Fig. 4. Change in August mean (top) surface O_3, (middle) lower free tropospheric PAN and (bottom) NO_y deposition when global isoprene nitrate recycling increases from 40% to 100% (SR1_r100-SR1).

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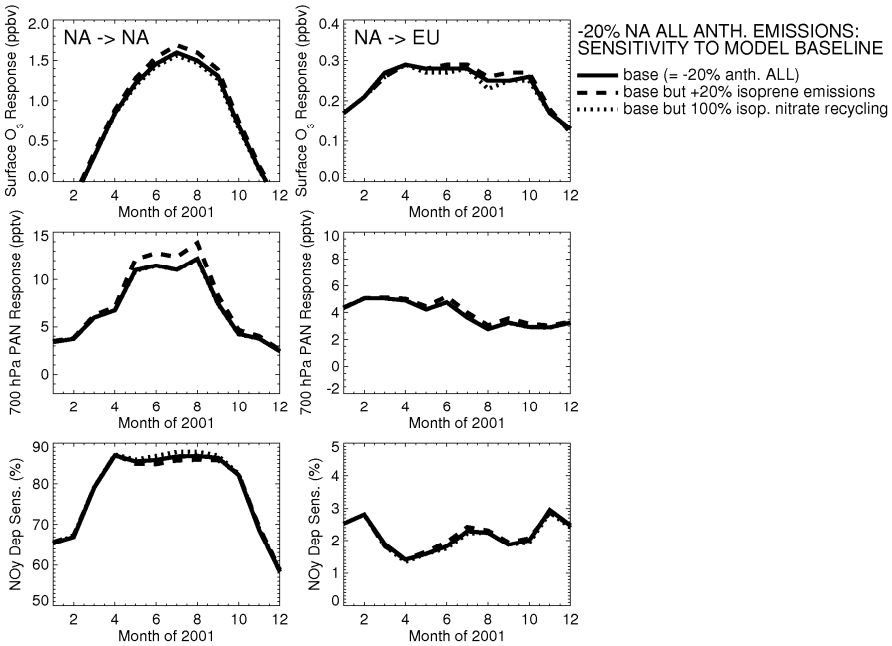

Fig. 5. The monthly mean regional (left) and intercontinental (right) response of (top) surface O_3 (middle) 700 hPa PAN and (bottom) NO_y sensitivity to a 20% decrease in all NA anthropogenic O_3 precursor emissions with different baselines: as in Fig. 3 (solid; SR1-SR6NA), with NA isoprene emissions increased by 20% (dashed; ISOPNA-SR6ISOPNA), and with the isoprene nitrate recycling rate increased from 40% (as in SR1) to 100% (dotted; SR1_r100-SR6NA_r100). NO_y sensitivity is defined as the regional change in NO_y deposition divided by the change in NA NO_x emissions (Sanderson et al., 2008).

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