The influence of ozone precursor emissions from four world regions on tropospheric composition and radiative climate forcing

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[1] Ozone (O3) precursor emissions influence regional and global climate and air quality through changes in tropospheric O3 and oxidants, which also influence methane (CH4) and sulfate aerosols (SO42−). We examine changes in the tropospheric composition of O3, CH4, SO42− and global net radiative forcing (RF) for 20% reductions in global CH4 burden and in anthropogenic O3 precursor emissions (NOx, NMVOC, and CO) from four regions (East Asia, Europe and Northern Africa, North America, and South Asia) using the Task Force on Hemispheric Transport of Air Pollution Source-Receptor global chemical transport model (CTM) simulations, assessing uncertainty (mean ± 1 standard deviation) across multiple CTMs. We evaluate steady state O3 responses, including long-term feedbacks via CH4. With a radiative transfer model that includes greenhouse gases and the aerosol direct effect, we find that regional NOx reductions produce global, annually averaged positive net RFs (0.2 ± 0.6 to 1.7 ± 2 mWm−2/Tg N yr−1), with some variation among models. Negative net RFs result from reductions in global CH4 (−162.6 ± 2 mWm−2 for a change from 1760 to 1408 ppbv CH4) and regional NMVOC (−0.4 ± 0.2 to −0.7 ± 0.2 mWm−2/Tg C yr−1) and CO emissions (−0.13 ± 0.02 to −0.15 ± 0.02 mWm−2/Tg CO yr−1). Including the effect of O3 on CO2 uptake by vegetation likely makes these net RFs more negative by −1.9 to −5.2 mWm−2/Tg N yr−1, −0.2 to −0.7 mWm−2/Tg C yr−1, and −0.02 to −0.05 mWm−2/Tg CO yr−1. Net RF impacts reflect the distribution of concentration changes, where RF is affected locally by changes in SO42−, regionally to hemispherically by O3, and globally by CH4. Global annual average SO42− responses to oxidant changes range from 0.4 ± 2.6 to −1.9 ± 1.3 Gg for NOx reductions, 0.1 ± 1.2 to −0.9 ± 0.8 Gg for NMVOC reductions, and −0.09 ± 0.5 to −0.9 ± 0.8 Gg for CO reductions, suggesting additional research is needed. The 100-year global warming potentials (GWP100) are calculated for the global CH4 reduction (20.9 ± 3.7 without stratospheric O3 or water vapor, 24.2 ± 4.2 including those components), and for the regional NOx, NMVOC, and CO reductions (−18.7 ± 25.9 to −1.9 ± 8.7 for NOx, 4.8 ± 1.7 to 8.3 ± 1.9 for NMVOC, and 1.5 ± 0.4 to 1.7 ± 0.5 for CO). Variation in GWP100 for NOx, NMVOC, and CO suggests that regionally specific GWPs may be necessary and could support the inclusion of regionally specific GWP values.
of O₃ precursors in future policies that address air quality and climate change simultaneously. Both global net RF and GWP₁₀₀ are more sensitive to NOₓ and NMVOC reductions from South Asia than the other three regions.


1. Introduction

[2] Tropospheric ozone (O₃), methane (CH₄), and aerosols make important contributions to the global mean radiative forcing (RF) of climate [Forster et al., 2007; Ramaswamy et al., 2001]. Here we aim to quantify the net RF of these species due to regional changes in O₃ precursor emissions, across an ensemble of global chemical transport models (CTMs). We define net RF as the net (incoming minus outgoing) change in stratospheric temperatures to readjust [Forster et al., 2007]. The contribution of changes in tropospheric O₃ to the global mean RF since preindustrial times is an estimated 0.35 ± 0.15 W m⁻², which is approximately 21% of the RF due to changes in carbon dioxide (CO₂) [Forster et al., 2007]. Changes in CH₄ have contributed approximately 0.48 W m⁻², while those in sulfate aerosols (SO₄²⁻) have contributed approximately −0.4 ± 0.2 W m⁻² (direct effect only) [Forster et al., 2007].

[3] Changes in O₃ precursor emissions (nitrogen oxides [NOₓ], non-methane volatile organic compounds [NMVOC], carbon monoxide [CO], and CH₄) affect the abundance of gaseous species (O₂ and CH₄), and aerosols via changes in the availability of atmospheric oxidants (hydroxyl radical [OH], hydrogen peroxide [H₂O₂], O₃) [Pham et al., 1995; Unger et al., 2006; Shindell et al., 2009; Leibensperger et al., 2011]. These perturbations in turn influence the RF due to O₃ and CH₄ and inorganic aerosol-phase species [Ming et al., 2005; Unger et al., 2006; Naik et al., 2007; Shindell et al., 2009]. O₃ precursors also affect organic aerosols, including the formation of secondary organic aerosols (SOA) [Carlton et al., 2010], but the resulting RF remains to be quantified. O₃ decreases plant growth and hence reduces the removal of CO₂ from the atmosphere [Felszer et al., 2007; Stich et al., 2007; Collins et al., 2010], while NOₓ emissions influence nitrogen deposition and the subsequent uptake of CO₂ in terrestrial and oceanic ecosystems [Holland and Lamarque, 1997; Duve et al., 2008]. Because of these influences, actions to control O₃ precursor emissions affect both air quality and global climate [Fiore et al., 2002; Dentener et al., 2005; West et al., 2007].

[4] Past studies have shown that both regional and global reductions in NOₓ surface emissions produce an overall positive RF from global CH₄ increases via decreases in OH, which outweigh the negative forcing from tropospheric O₃ decreases. The magnitude of forcing, however, depends on the location or sector of emission reduction [Fuglestvedt et al., 1999; Wild et al., 2001; Berntsen et al., 2005; Naik et al., 2005; West et al., 2007; Derwent et al., 2008]. In contrast, CO, NMVOC, and CH₄ reductions contribute an overall negative RF by decreasing tropospheric O₃ and increasing OH, leading to global CH₄ decreases [Prather, 1996; Wild et al., 2001; Fiore et al., 2002; Naik et al., 2005]. Global anthropogenic CH₄ emission reductions were shown to produce the most negative RF of the O₃ precursors, mainly due to direct reductions in CH₄ forcing [Fiore et al., 2002; Shindell et al., 2005; West et al., 2007].

[5] Because of the short atmospheric lifetimes of O₃, aerosols, and their precursors (apart from CH₄), studies of regional O₃ precursor reductions show that air quality and RF effects depend strongly on the geographical location of emissions [Fuglestvedt et al., 1999; Berntsen et al., 2005; Naik et al., 2005]. The dependence on location, however, has made it difficult to include O₃ precursors in emissions trading schemes or international climate agreements [Rypdal et al., 2005], and to evaluate the co-benefits of actions to reduce O₃ for slowing global climate change. Studies have shown substantial dependence of O₃ concentrations and RF on the region of NOₓ emissions [Fuglestvedt et al., 1999; Berntsen et al., 2005; Naik et al., 2005; Derwent et al., 2008; Fuglestvedt et al., 2010], where O₃ and RF are more sensitive to NOₓ reductions from tropical regions, yet positive global annual average net RFs result from NOₓ reductions in each of nine world regions [Naik et al., 2005]. While NMVOCs typically have atmospheric lifetimes comparable to NOₓ, CO has a longer atmospheric lifetime of 1–3 months [Seinfeld and Pandis, 2006], suggesting that the influence of CO on O₃ and OH may be less dependent on reduction region [Berntsen et al., 2005; Rypdal et al., 2005]. Apart from Naik et al. [2005], who also examined combined reductions in NOₓ, CO, and NMVOCs from three regions, and Berntsen et al. [2005], who evaluated CO changes from two regions, less attention has been placed on regional CO and NMVOC emissions and their effects on tropospheric O₃, CH₄, and SO₄²⁻ and global and regional net RF. In response to nonuniform forcings, some regional climate responses are also sensitive to the location and distribution of O₃, aerosols, and RF [Shindell and Faluvegi, 2009].

[6] Here we investigate the effects of a 20% reduction in global CH₄ abundance and 20% reductions in anthropogenic emissions of NOₓ, NMVOC, and CO, individually and combined, from four world regions on tropospheric O₃, CH₄, and SO₄²⁻ concentrations and on the resulting distribution and magnitude of global net RF for all precursor-region pairs. We use results from an ensemble of global CTMs that participated in the Task Force on Hemispheric Transport of Air Pollution (TF HTAP) multimodel intercomparison study of Source-Receptor (SR) sensitivity [Fiore et al., 2009], which allows for an assessment of uncertainty as the spread across CTMs. We examine the regional dependency of RF and global warming potential (GWP) to individual precursors by comparing estimates across the four regions of reduction.

2. Methodology

[7] We use the results from an ensemble of 11 global CTMs [Task Force on Hemispheric Transport of Air
Table 1. HTAP Source-Receptor Sensitivity Simulations, Where the Four Regions of Reduction are East Asia, Europe, North America, and South Asia for SR3 Through SR6

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
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<tbody>
<tr>
<td>SR1</td>
<td>Base simulation</td>
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<tr>
<td>SR2</td>
<td>20% reduction in global CH4 mixing ratio</td>
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<tr>
<td>SR3</td>
<td>20% reduction in regional NOx emissions</td>
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<tr>
<td>SR4</td>
<td>20% reduction in regional NMVOC emissions</td>
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<tr>
<td>SR5</td>
<td>20% reduction in regional CO emissions</td>
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<tr>
<td>SR6</td>
<td>20% reduction in regional NOx, NMVOC, CO, and aerosol emissions</td>
</tr>
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</table>

2.1. HTAP CTM Simulations

[8] The SR simulations performed by each CTM are outlined in Table 1. We analyze O3 and CH4 results from 11 CTMs and SO42− using the standalone radiative transfer model (RTM) developed by the National Oceanographic and Atmospheric Administration (NOAA) Geophysical Fluid Dynamics Laboratory (GFDL) [Schwarz et al., 1999; GFDL, Global Atmospheric Model Development Team (GFDL, GAMDT), 2004]. We estimate the RF due to SO42−, as SO42− responds to oxidant changes, considering only its direct effects on radiation [Naik et al., 2007]; few CTMs reported other aerosol species for all reduction scenarios. Although we account for variability across the CTM ensemble in the O3, CH4, and SO42− results from four CTMs (Table 2). Each CTM utilized its own emissions inventory and prescribed meteorological fields for the year 2001 [Fiore et al., 2009]. Anthropogenic emissions of NOx, NMVOCs, and CO, and all precursors combined were reduced by 20% in each of four world regions: East Asia (EA), Europe and Northern Africa (EU), North America (NA), and South Asia (SA). For CH4, the present-day abundance (1760 parts per billion by volume [ppbv]) was imposed in all simulations except for the CH4 control simulation (SR2), where global CH4 abundance was decreased by 20% to 1408 ppbv. All simulations were performed for a full year (2001), after an initial spin-up of at least six months [Fiore et al., 2009].

[9] The multimodel mean ± 1 standard deviation changes in the anthropogenic emissions of NOx, NMVOCs, and CO, across 11 CTMs, are presented in Table 3. There is considerable variability in the emission reduction magnitudes across CTMs. Coefficients of variation (CVs) (standard deviation/mean) are lowest for NOx emissions from EU, NA, and SA, while there is more variability in NMVOC and CO emissions from the four regions, consistent with the comparison of current global emission inventories by Granier et al. [2011].

[10] Previous publications based on the HTAP SR experiments have emphasized the effects of long-range transport on surface O3, and other components, and comparisons with observations [Sanderson et al., 2008; Shindell et al., 2008; Fiore et al., 2009; Jonson et al., 2010; Reidmiller et al., 2009]. Fiore et al. [2009] found that the HTAP ensemble mean surface O3 concentrations compared well with observations over EU for the year 2001, but overestimated measurements by more than 10 ppb during the summer and fall over the eastern United States and Japan. Jonson et al. [2010] compared simulated vertical O3 profiles with observed ozoneonde profiles, finding that the spread in CTM results (and their over and underestimation of O3 soundings) increases in the spring and summer with more active chemistry. In the winter and spring, seasonal averages for most CTMs were within 20% of sonde measurements in the upper and middle troposphere. Simulated SO42− concentrations at the surface for the base simulation (SR1) also have been compared to observations (M. Schulz, personal communication, 2011, preliminary results available at http://aerocom.met.no/cgi-bin/aerocom/surfobs_annualrs.pl), where the results show that the CTMs are generally realistic.

[11] Short-lived O3 precursors affect tropospheric O3 within hours to weeks after their emission; however, they also affect OH, which influences the lifetime of CH4 and in turn, O3 in the long term [Prather, 1996; Wild et al., 2001; Berntsen et al., 2005; Naik et al., 2005]. Global CH4 changes were calculated by Fiore et al. [2009], based on the CH4 loss by tropospheric OH diagnostic reported for each CTM and SR3 through SR6, relative to the fixed CH4 abundance of 1760 ppbv. Long-term O3 responses are then calculated in each grid cell, following West et al. [2007, 2009b], by scaling the change in O3 from the CH4 control simulation (SR2 minus SR1) to the calculated global CH4 change for...
each SR simulation and CTM. We then add the long-term O3 responses to the simulated short-term O3 responses to give O3 concentrations at steady state.

Since the HTAP CTMs were typically not designed to model stratospheric chemistry, we use the same three-dimensional monthly mean O3 concentrations in the stratosphere and merge these with calculated steady state (short-term + long-term) tropospheric O3 concentrations for each simulation and CTM. Stratospheric O3 is taken for the year 2001 from the AC&C/SPARC O3 database prepared for CMIP5 (Available: http://pcmdi-cmip.llnl.gov/cmip5/forcing.html).

Søvde et al. [2011] found that around 15% of the RF from O3 precursors is due to O3 changes in the lower stratosphere, using a single model with both standard and updated chemistry. Since we ignore lower stratospheric O3 changes, our RF estimates may underestimate the full effect of O3 precursors. After each CTM’s O3 and SO4\(^2\) results are interpolated to a common resolution (longitude \(\times\) latitude \(\times\) level) as required by the RTM (72 \(\times\) 37 \(\times\) 33 for O3; 96 \(\times\) 80 \(\times\) 14 for SO4\(^2\)), the HTAP ensemble mean \(\pm 1\) standard deviation O3 and SO4\(^2\) distributions are calculated in each grid cell and month in three dimensions, in addition to the ensemble mean \(\pm 1\) standard deviation global CH4 abundances (derived from the CH4 loss by tropospheric OH diagnostics). Global O3, CH4, and SO4\(^2\) changes are calculated for each CTM as perturbation (SR2 to SR6) minus base (SR1) values.

2.2. GFDL Radiative Transfer Model

We employ the GFDL RTM to estimate the net RF at steady state due to the changes in atmospheric gases (O3 and CH4) alone and due to combined changes in O3, CH4, and SO4\(^2\) aerosols. The GFDL RTM is a module of the GFDL coupled atmospheric-ocean model (AM2) and simulates solar and infrared radiative transfer [GFDL GAMDT, 2004; Naik et al., 2005, 2007]. It has been used in studies of long-lived greenhouse gases [Schwarzkopf and Ramaswamy, 1999] and short-lived forcing agents such as O3 and aerosols [Naik et al., 2005, 2007; West et al., 2007; Fiore et al., 2008; Saikawa et al., 2009]. Here the RTM is employed as for Naik et al. [2007] and Saikawa et al. [2009], at 144 \(\times\) 90 \(\times\) 24 levels, except for the following changes. We update well-mixed greenhouse gas concentrations based on observations for the year 2001 included as part of the historical period (1750–2005) of the CMIP5 Representative Concentration Pathways (RCP) database [Meinshausen et al., 2011] (Available: http://www.iiasa.ac.at/web-apps/tnt/RcpDb/dsd?Action=htmlpage&page=download). We also update the solar data used by the RTM to the CMIP5 solar forcing data (Available: http://www.geo.fu-berlin.de/en/met/ag/strat/forschung/SOLARIS/Input_data/CMIP5_solar_irradiance.html). The RTM simulations do not include the indirect effects of aerosols on clouds or the internal mixing of aerosols. RF contributions from changes in nitrate aerosols, changes in stratospheric O3 and water vapor, changes to the carbon cycle via O3 and nitrogen deposition, and changes to CO2 from CH4, CO, and NMVOC oxidation are also omitted in the RTM simulations.

The multimodel monthly mean \(\pm 1\) standard deviation O3, CH4, and SO4\(^2\) concentrations are used as input in the RTM simulations, along with meteorological fields from GFDL’s atmosphere model (AM2) and land model (LM2), sampled one day per month at midmonth for the year 2001 to represent monthly mean conditions [Naik et al., 2005]. Substantial variability in the SO4\(^2\) estimates across only four CTMs precluded evaluating the mean \(\pm\) 1 standard deviation for SO4\(^2\) (e.g., several grid cells had standard deviations exceeding the mean). We simulate the monthly mean net radiation fluxes for the base and perturbed cases and calculate the net RF as the difference between the perturbed and...
base net fluxes (net shortwave minus net longwave) at the
tropopause, after allowing stratospheric temperatures to
readjust to radiative equilibrium [Naik et al., 2007; Saikawa
et al., 2009].

3. Tropospheric Composition Changes
3.1. Tropospheric Ozone Changes

[15] Figure 1 shows the changes in global annually aver-
aged steady state tropospheric O3 burden and its variability
across 11 HTAP CTMs. Full troposphere and upper tropo-
sphere (UT) O3 burdens are distinguished because O3 in the
UT has a higher RF efficiency on a per molecule basis [Lacis
et al., 1990; Wang et al., 1993; Forster and Shine, 1997].
For each CTM’s regridded O3 distributions that have been
blended with CMIP5 stratospheric O3 values (section 2.1),
the UT is defined from 500 hPa to the tropopause, where the
tropopause is identified at the 150 ppbv O3 level.

[16] The largest changes in full troposphere and UT O3
burden are found for the 20% CH4 reduction, followed
by the 20% combined precursor reductions from NA and
EA, respectively. However, there is considerable diversity
among the 11 CTMs’ estimates of full troposphere and UT
O3 burden changes. In these 17 SR simulations relative
to the base case, the change in UT O3 burden per change
in full troposphere O3 burden (UT O3/full troposphere O3) is
largest for reductions in global CH4 (0.36 to 0.47) and regional
CO emissions (0.19 to 0.53), and smallest for regional
NMVOC reductions (0.16 to 0.42) across the 11 CTMs,
reflecting the longer lifetimes of CO and CH4 in comparison to
NMVOCs and NOx. UT O3/full troposphere O3 is also largest
for individual O3 precursor (NOx, NMVOC, and CO) reduc-
tions from SA in comparison to the other regions.

[17] To evaluate regional sensitivities, we consider how
changes in full troposphere and UT O3 burdens per unit
change in emissions vary by region for each precursor
(Figure 2). The CTMs mostly agree that the SA NOx
reduction produces the greatest change in full troposphere
and UT O3 burden per change in emissions out of the four
regions, which can be attributed to more rapid vertical
mixing, stronger photochemistry, and greater sensitivity of
O3 to precursor emissions from the tropics and southern
hemisphere (SH) [Kunhikrishnan et al., 2004; West et al.,
2009a]. We find less variability across the four regions in
reducing full troposphere and UT O3 burden per change
in NMVOC and CO emissions (Figure 2), but six CTMs show
that SA NMVOC and CO reductions produce the largest
reductions in UT O3 burden per change in emissions.

[18] For each regional reduction, the greatest changes in
steady state tropospheric total column O3 occur over the
reduction region, in each individual CTM and across the
HTAP ensemble (Figure 3). For NOx reductions from each
region, slight increases in O3 burden occur in the SH, in
contrast to overall decreases in the northern hemisphere
(NH), due to long-term O3 increases via CH4 that are glob-
ally distributed (according to the pattern of O3 response to
CH4) [West et al., 2007, 2009b] (see section 3.2). As SA is
further south than the other regions, the largest O3 decreases
occur near the tropics and do not extend as far north.
The slightly higher increases in O3 in the SH from the NA
NOx reduction correspond to this region producing greater
increases in global CH4 (Figure 4). For NMVOC and CO
reductions from the four regions, we find decreases in total
column O3 in both the SH and NH, as sustained decreases
in these precursors cause both short- and long-term global
O3 decreases. NMVOC reductions also reduce global annual
average peroxy acetyl nitrate (PAN) burdens from the four
regions by 1.4 ± 0.6% (SR4EA), 2.0 ± 0.8% (SR4EU),
1.5 ± 0.5% (SR4NA), and 0.5 ± 0.2% (SR4SA), relative to
the base, through which NMVOCs can influence the nitro-
gen cycle and therefore long-range O3. Across the 11 CTMs,
we find that tropospheric PAN decreases are correlated
to the changes in NMVOC emissions for the EA, EU,
and NA reductions.

3.2. Tropospheric Methane Changes

[19] Although global CH4 was held constant by each CTM
in all perturbations, we analyze the changes in global
tropospheric CH4 calculated off-line for each perturbation. NOx reductions from all four regions increase global CH4 abundance via decreases in OH, while NMVOC and CO reductions from all four regions decrease global CH4 (Figure 4). These changes in CH4 drive the long-term O3 changes discussed in the previous section. For particular precursors, reductions from certain regions, e.g., CO reductions from EA, are slightly more effective at decreasing global CH4 than other regions. However, there is noticeable variability among the CTMs’ changes in global CH4 (Figure 4), which is partly explained by variance in CTM emissions for CO, but not for NOx and NMVOCs.

For several CTMs, some emissions perturbations had minimal impact on global OH, resulting in calculated steady state CH4 changes of zero. In addition, the CVs of CH4 change are lowest in magnitude for NOx reductions (0.22 to 0.39) and highest for NMVOC reductions (−0.40 to −1.12), perhaps reflecting differing NMVOC speciation and chemical schemes among the CTMs [Collins et al., 2002].

We compare the change in global CH4 from the combined precursor reductions to the sum of global CH4 changes from NOx, NMVOC, CO, and combined. Based on the HTAP multimodel mean results, global CH4 changes from SA and NA combined precursor reductions are approximately 59% and 75%, respectively, of the sum of CH4 changes from individual precursor reductions, while global CH4 changes from EA and EU combined precursor reductions are slightly negative in contrast to small positive global CH4 changes from the sum. The three (of 11) CTMs that did not include reductions in SO2 and aerosols in the SR6 experiments [Fiore et al., 2009] show global CH4...
changes from the combined precursor reductions close to the sum of CH₄ changes from individual NOₓ, NMVOC, and CO reductions. This suggests that deviations from additivity may be due to reductions in SO₂ and aerosols (in SR6) affecting CH₄.

### 3.3. Tropospheric Sulfate Changes

[22] There is considerable variability and disagreement in the sign of SO₄²⁻ responses among the four CTMs evaluated (Figure 5). The greatest variability in global SO₄²⁻ burden across the CTMs occurs for the CH₄ reduction and for NOₓ reductions from all four regions. There is less variability across CTMs for NMVOC and CO reductions, but still differences in the sign of change.

[23] The four CTMs analyzed here account for SO₄²⁻ formation through two main oxidation pathways: 1) gas-phase oxidation of sulfur dioxide (SO₂) by OH, and 2) aqueous-phase oxidation of SO₂ by H₂O₂ or O₃ [Houweling et al., 1998; Jeukén et al., 1999, 2001; Barth et al., 2000; Rasch et al., 2000; Horowitz et al., 2003; Rotman et al., 2004; Tie et al., 2005]. Since CH₄, NMVOC, and CO reductions increase OH concentrations, SO₂ oxidation via pathway (1) is expected to increase tropospheric SO₄²⁻ formation. At the same time, increases in H₂O₂ (occurring with increases in OH) are expected to increase SO₂ oxidation via pathway (2), but decreases in O₃ may decrease oxidation (also pathway (2)). NOₓ reductions not only decrease O₃, but can also decrease OH and H₂O₂, which leads to decreases in

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**Figure 4.** Global annual multimodel changes (perturbation minus 1760 ppbv) in tropospheric CH₄ (ppbv) for −20% regional emissions of NOₓ, NMVOC, CO, and combined: median (black bars), mean (red points), mean ± 1 SD (boxes), and max and min (whiskers) for the HTAP ensemble of 11 models, estimated directly from the CH₄ loss by tropospheric OH archived by each HTAP CTM [Fiore et al., 2009]. Tropospheric CH₄ changes were not available from INCA-vSSz for SA 20% NMVOC reduction and from LLNL-IMPACT-T5a for 20% NOₓ reductions (EA, EU, NA, SA); these models are excluded from the multimodel CH₄ changes for these perturbations.

**Figure 5.** Global annual multimodel changes (perturbation minus base) in short-term tropospheric SO₄²⁻ (Gg) for −20% CH₄ burden and −20% regional emissions of NOₓ, NMVOC, and CO: mean (red bars) and mean ± 1 SD (boxes) across the HTAP ensemble of four models. The individual model results are shown in black (pluses).
SO$_2^{2-}$ formation by pathways (1) and (2). Figure 5 shows that the sign of SO$_2^{2-}$ response is not consistent across all four CTMs, suggesting uncertainty in the modeled effects of O$_3$ precursors on oxidants, the relative importance of these oxidation pathways, and the lifetime and removal of SO$_2$ and SO$_2^{2-}$.

The global distributions of tropospheric total column SO$_2^{2-}$ changes (Figure 6) show the greatest changes in SO$_2^{2-}$ over the region of emission change, with only slight changes globally. The individual CTMs and HTAP ensemble mean results show that NOx reductions from EA, EU, and NA cause both increases and decreases in SO$_2^{2-}$ over the reduction region, which correspond to changes in oxidants (OH, H$_2$O$_2$, O$_3$); localized decreases in SO$_2^{2-}$ are due in part, to localized decreases in OH (auxiliary material Figure S5) and decreases in O$_3$. The distributions of H$_2$O$_2$ are not analyzed, as they were not reported in the CTM simulations. NMVOC reductions from EU increase SO$_2^{2-}$ over northeastern Africa and decrease SO$_2^{2-}$ over western Europe in three of the CTMs and the ensemble mean. All four CTMs consistently show that the EA NMVOC reduction decreases SO$_2^{2-}$ and the SA NMVOC reduction increases SO$_2^{2-}$ regionally, while two CTMs show SO$_2^{2-}$ decreases over the eastern U.S. from the NA NMVOC reduction. For CO reductions from all four regions, the ensemble mean shows localized increases, while the individual CTMs differ in the sign of regional SO$_2^{2-}$ change for all CO reductions except SA. Regional increases in SO$_2^{2-}$ from the NMVOC and CO reductions can be explained partly by localized increases in OH (Figure S5); however, decreases in SO$_2^{2-}$ may be related to the differing effects on oxidants (including H$_2$O$_2$) and on the SO$_2$ oxidation pathways in each CTM, as discussed in the previous paragraph.

### 4. Radiative Forcing due to Precursor Emission Changes

Figure 7 (and Table S1 in auxiliary material Text S1) show the global annual net RF due to O$_3$, CH$_4$, and SO$_2^{2-}$, estimated from RTM simulations, first for multimodel mean O$_3$ and CH$_4$, and second for multimodel mean O$_3$, CH$_4$, and SO$_2^{2-}$, for each SR scenario relative to the base case. We calculated the net RF distributions for each perturbation scenario (SR2 through SR6) by subtracting (in each grid cell and month) the simulated radiative fluxes for the base case (SR1) from those for each perturbation. To estimate the contribution of the multimodel mean SO$_2^{2-}$ to the global annual net RF, we subtracted the net RF results due to O$_3$ and CH$_4$ from the net RF due to O$_3$, CH$_4$, and SO$_2^{2-}$ for each SR scenario, assuming the effects of O$_3$, CH$_4$, and SO$_2^{2-}$ are additive. To distinguish the contributions of O$_3$ and CH$_4$ to the global annual net RF, we estimated the net RF due to the multimodel mean CH$_4$ for each SR scenario, using the formula of Ramaswamy et al. [2001], attributing the difference to O$_3$ RF.
Figure 7. (a) Global annual average RF (mW m\(^{-2}\)) for the HTAP ensembles of 11 models (for O\(_3\) and CH\(_4\) forcing) and four models (for SO\(_4^{2-}\) forcing) due to multimodel mean changes in steady state O\(_3\), CH\(_4\), and SO\(_4^{2-}\). Vertical black bars represent the uncertainty in net RF across models, calculated as the net RF of the multimodel mean ± 1 standard deviation O\(_3\) and CH\(_4\), for each perturbation (−20% CH\(_4\) burden, and −20% regional emissions of NO\(_x\), NMVOC, CO, and combined), relative to the base simulation. The uncertainty estimates for −20% CH\(_4\) account only for the variability in simulated O\(_3\) changes across the CTMs, since all CTMs uniformly reduced CH\(_4\) (1760 ppbv to 1408 ppbv). Vertical green bars represent the upper uncertainty bound of SO\(_4^{2-}\) RF across models. (b) Global, annual average RF per multimodel mean change in emissions (mW m\(^{-2}\)/Tg emissions per year) due to multimodel mean changes in steady state O\(_3\), CH\(_4\), and SO\(_4^{2-}\), and uncertainty (vertical black bars) as the net RF of the multimodel mean ± 1 standard deviation changes in O\(_3\) and CH\(_4\) per unit change in emissions for each perturbation, relative to the base simulation. Vertical green bars represent the upper uncertainty bound of SO\(_4^{2-}\) RF per unit change in emissions across models.
Computational limitations prevented us from simulating the RFs individually for each CTM’s 18 SR scenarios. Instead, we simulate RFs for multimodel means, and for the multimodel mean ±1 standard deviation O3 and CH4 and the multimodel mean +1 standard deviation SO4 to account for uncertainty in the net RF due to differences in the CTMs. We show uncertainty (mean ±1 standard deviation) for the resulting net RF, which includes the uncertainty in O3 and CH4 RFs, as changes in O3 and CH4 are not strongly correlated among the 11 CTMs for most scenarios (Figure S4). For NOx reductions, because the RF due to O3 opposes that of CH4, a broader uncertainty range would have resulted had we instead simulated together the multimodel mean +1 standard deviation O3 and the multimodel mean −1 standard deviation CH4 (and the reverse) to estimate uncertainty.

Figure 7 shows that O3 and CH4 RFs have the same sign as the tropospheric composition changes in section 3; since SO4 is cooling, SO4 RF has the opposite sign. NOx reductions from all four regions produce an overall positive net RF due to increases in CH4, which outweigh the negative net RF due to decreases in O3 (Figure 7a). Negative global net RFs are produced by CO and NMVOC reductions, due to O3 and CH4 decreases, and also by the combined precursor reductions, as increases in CH4 from NOx reductions roughly cancel CH4 decreases from NMVOC and CO reductions [Fiore et al., 2009]. The net RF due to the combined precursor reduction is 98% to 117% of the sum of the net RFs of O3 and CH4 due to reductions of each individual precursor, across the four regions, showing approximate additivity for the different precursors.

Consistent with the SO4 changes in Figure 5, NOx reductions from EU and SA contribute a positive SO4 RF, while EA and NA NOx reductions produce negative SO4 RF. The SO4 RFs for NMVOC and CO reductions vary in magnitude and sign across the four regions, corresponding to the disagreement in SO4 response across the CTMs (Figure 5). We do not estimate the contribution of SO4 to net RF for the combined reductions, since many of these perturbations included 20% reductions in SO2 and aerosols, making it difficult to isolate the effect of NOx, NMVOC, and CO on SO4 RF.

Figure 7 also shows an estimate of the RF due to the CO2 equivalent emission resulting from the influence of surface O3 on plants’ ability to remove CO2 from the atmosphere. Figure 8. Annual average net RF distributions (mW m−2), calculated as the annual shortwave radiation minus the annual longwave radiation, due to tropospheric O3, CH4, and SO4 for the multimodel mean, for each of the precursor reduction simulations (−20% CH4 burden and −20% regional emissions of NOx, NMVOC, CO, and combined) minus the base simulation. Note the difference in scale between the −20% regional (NOx, NMVOC, CO, combined) and −20% CH4 reduction scenarios.
atmosphere, from Collins et al. [2010], based on one HTAP CTM (STOCHEM) and not the HTAP ensemble. The CO2 responses to pulse changes from Collins et al. [2010] were converted to equilibrium responses by integrating over 100 years. The range of CO2 RF represents high to low sensitivity of vegetation to O3. With the additional consideration of CO2 RF, the global annual net RF due to regional NOx reductions changes sign to an overall net climate cooling (−0.83 to −4.28 mW m−2 for all four regions), while the negative net RFs for regional NMVOC and CO reductions are reinforced by the addition of CO2 RF (Table S1 in auxiliary material Text S1).

[30] We normalize the global annual net RF estimates (Figure 7a) by each region’s reduction in emissions (Table 3). The net RF per unit change in NOx and NMVOC emissions is greatest for SA reductions out of the four regions (Figure 7b), corresponding to the sensitivity findings in section 3.1. For CO reductions, all four regions are approximately as effective at reducing global net RF per unit CO emissions, consistent with CO’s longer atmospheric lifetime.

[31] We compare our ensemble mean global annual net RF estimates per unit NOx emissions to those of Naik et al. [2005], who used a single CTM and analyzed 10% NOx reductions. Our estimates are approximately 32% to 63% (EU, NA, SA) and 16% (EA) of those reported by Naik et al. [2005], but these differences in net RF (CH4 and O3 RF combined) are small in comparison to the magnitudes of CH4 and O3 forcing individually.

[32] The net RF distributions (Figure 8) correspond to the distributions of total column O3 (Figure 3) and SO2− changes (Figure 6), where regional to hemispheric RF corresponds to O3 changes and more localized RF is dominated by SO2− changes, as illustrated by shortwave forcings (Figure S2). Changes in CH4 influence net RF globally, since a uniform CH4 mixing ratio was specified in each RTM simulation. For NOx reductions, we find positive net RFs in the SH due to CH4 and long-term O3 increases globally, but in the NH these positive RFs are outweighed by the negative RF of O3 decreases (Figure 8). For CH4, NMVOC, CO, and combined reductions, negative net RFs from O3 decreases in the NH overlay negative RFs globally due to CH4. While Figure 7 presents globally averaged forcings, the regionally inhomogeneous forcings in Figure 8 are also relevant for regional climate change [Shindell et al., 2009]. However, regional RF patterns resulting from changes in tropospheric loadings do not directly translate to regional climate responses [Levy et al., 2008; Shindell et al., 2010].

5. Global Warming Potentials

[34] Beyond analyzing RF, the climate impacts of O3 precursor emissions can be compared with each other, and

Figure 9. Radiative forcing efficiency of O3 for the 16 SR simulations (SR3 through SR6) for the multi-model mean, showing the global, annual average O3 net RF (mW m−2), calculated as the difference between the simulated net RF due to O3 and CH4 and estimated net RF due to CH4 [Ramaswamy et al., 2001], versus the global, annual average steady state changes in tropospheric O3 burden (Tg). The SR simulations are distinguished by precursor (color) and region (shape).
with the emissions of other species using climate metrics such as the global warming potential (GWP). Forster et al. [2007] suggest that there are serious limitations to the use of GWPs for comparing short-lived species. While other metrics have been proposed to compare climate effects, such as the global temperature potential (GTP) [Shine et al., 2005, 2007], none are as widely used as the GWP. We choose to analyze the GWP here for comparison with earlier studies.

[35] The basis for the GWP calculation is the integrated RF following a pulse emission. In section 4, O3 RF was calculated for equilibrium conditions for the sum of the short and long-term O3 responses (Figure 7, and Table S1 in auxiliary material Text S1). Here long-term O3 RF is calculated by scaling O3 RF from SR2 by the ratio of steady state O3 burden change in a particular SR scenario (SR minus base) to those of SR2 (SR minus base). The short-term O3 RF is then the difference between the steady state RF (section 4) and long-term RF. Following Collins et al. [2010], RF as a function of time is calculated for a one-year emissions perturbation, for each SR scenario. The short-term RF components (SO4 and short-term O3) are assumed to be constant over the one-year pulse and then drop to zero instantaneously; whereas, the long-term components (CH4 and long-term O3) respond and decay with the multimodel mean CH4 perturbation lifetime (11.65 years). For the 20% CH4 reduction (SR2), an analytical expression is used to calculate the impact of a one-year emissions pulse and subsequent decay [Collins et al., 2010]. This CH4 perturbation is used to scale the SO4 and O3 RFs from SR2 in Figure 7. The formula by Ramaswamy et al. [2001] is used to calculate the CH4 RF.

[36] GWP100 is given by the RF integrated out to a time horizon $H$ and normalized by the change in emissions, divided by the equivalent for CO2. In Figure 10, and Table S2 in auxiliary material Text S1, we present GWPs for the 20- and 100-year time horizons (GWP20 and GWP100). The uncertainties are dominated by the variation in CH4 response across the CTMs. For NOx emissions, this uncertainty is sufficiently large that it is not possible to identify the sign of the GWPs. The patterns of GWP100 are very similar to those of Forster et al. [2007] and Fuglestvedt et al. [2010], though substantially smaller than those provided by Shindell et al. [2009]. The O3 contribution from Asian NOx, found by Berntsen et al. [2005] is within the range of the HTAP CTMs’ results, but slightly higher than the HTAP multimodel mean. We neglect RFs of nitrate aerosols, but Bauer et al. [2007] suggest nitrate contributions to NOx GWPs on the order of −80 for GWP20 and −20 for GWP100. The NMVOC GWPs (Figure 10) are generally smaller than those of Collins et al. [2002]; however, Collins et al. [2002] covered a range of individual NMVOCs. For CO, the GWPs are comparable to those of Derwent et al. [2001], but smaller than those of Berntsen et al. [2005], largely due to the lower O3 response of the HTAP multimodel mean; the O3 response to Asian CO emissions of Berntsen et al. [2005], however, is within the range of the HTAP CTMs. The CO GWP100 estimates are also smaller than the no-aerosol results of Shindell et al. [2009], due to a lower CH4 response. The O3 contribution to GWP100 for CH4 is smaller in this multimodel study (21% of the direct CH4 contribution) than the 25% assumed by Forster et al. [2007], mostly because changes in O3 above the tropopause are neglected. Adding in the contribution of O3 in the lower stratosphere (15% of O3 RF) [Søvde et al., 2011], and that for stratospheric water vapor (15% of the CH4 contribution) would give a total GWP100 for CH4 of 24.2 ± 4.2.

[38] For NOx and NMVOCs, SA emissions have a larger impact than emissions from the other regions. This suggests that some latitudinal dependence may be appropriate for GWPs of O3 precursors. Note that equatorial or SH emission changes were not considered in this study, but Fuglestvedt et al. [2010] found a dependence on latitude. European NOx emissions have a more negative GWP than other regions in the northern midlatitudes, as O3 production in this NOx-saturated region is lower.

6. Conclusions

[39] We quantified the magnitude and distribution of global net RF due to changes in O3, CH4, and SO4 for 20% reductions in global CH4 and regional NOx, NMVOC, CO, and combined precursor emissions. We find that the 20% NOx reductions produce global, annually averaged positive net RFs, as positive CH4 RFs outweigh negative O3 RFs, consistent with previous studies [Fuglestvedt et al., 1999; Wild et al., 2001; Naik et al., 2005; West et al., 2007]. For CH4, NMVOC, and CO reductions, O3 and CH4 GWPs are synergistic, yielding overall negative net RFs, consistent with previous global-scale studies [Fiore et al., 2002; West et al., 2007; Shindell et al., 2009]. Including the effects of O3 on plant growth and the carbon cycle may change the sign of net RF for NOx reductions to an overall net climate cooling, in contrast to previous results that neglect this effect, while reinforcing the negative net RFs due to NMVOC and CO reductions, but future research is needed to better quantify this effect.

[40] By normalizing the net RF estimates by changes in emissions (for NOx, NMVOC, and CO), we find that RF is more sensitive to NOx and NMVOC emission reductions from regions closer to the equator (i.e., SA), consistent with our findings that changes in O3 burden per change in emissions (full troposphere and UT O3 for NOx, and UT O3 for NMVOC) are greatest for SA reductions. RF is more uniformly sensitive to CO emission reductions from each of the four regions, which agrees with O3 burden changes per unit CO being less variable across the four regions. The trends in GWP100 across the four regions, for each precursor, reflect the normalized net RF results. Compared to GWP100, the GWP20 patterns are influenced more by short-term O3 and SO4. The large uncertainties in the NOx GWP estimates, mainly from the variation in calculated CH4 responses across the CTMs, limit the determination of the sign of NOx GWPs. The estimated GWPs for individual regions are from the largest model ensemble that has been analyzed to date, and are broadly comparable to previous studies.
We find that regional RFs correspond to localized increases and decreases in SO$_4^{2-}$/CO$_2$ burden. O$_3$ changes are most important for RF on the regional to hemispheric scales, and CH$_4$ influences RF globally, dominating the RF response in the SH. The estimated contribution of SO$_4^{2-}$/CO$_2$ (direct effect only) to net RF is small compared to the RF of O$_3$ and CH$_4$.

Shindell et al. [2009] found with a single CTM that for global NOx, CO, and VOC emissions, changes in SO$_4^{2-}$/CO$_2$ contributed a RF more comparable in magnitude to the RFs of O$_3$ and CH$_4$. Our findings contrast with those of Shindell et al. [2009] on the importance of SO$_4^{2-}$ RF due to O$_3$ precursors. However, the robustness of these results is limited, since there was substantial variability in SO$_4^{2-}$ among only four HTAP CTMs. The effects of O$_3$ precursors on SO$_4^{2-}$ via oxidants merit further research, using newer models that include improved treatment of oxidant-aerosol interactions.

[41] We account for variability in O$_3$, CH$_4$, and SO$_4^{2-}$/CO$_2$ across the ensemble of CTMs, but our estimates of uncertainty only include the variability in CTMs, using a single RTM for all RF estimates. We therefore understate the uncertainty in net RF. In addition, while we capture the most important forcings, a more complete analysis of RF could include RFs due to changes in nitrate aerosols (likely important for NO$_x$ reductions), the indirect effect of aerosols, internal mixing of aerosols, changes in stratospheric O$_3$.

Figure 10. GWPs for time horizons of (a) 20 years and (b) 100 years for the -20% CH$_4$ burden and -20% regional emissions of NO$_x$, NMVOC, and CO scenarios. The four regions’ estimates (labeled “All”) represent the GWP due to the sum of the four regions’ responses (to O$_3$, CH$_4$, SO$_4^{2-}$, and all three species [Total GWP]). Uncertainty analysis is as in Figure 7, but also includes the uncertainty in the CH$_4$ lifetimes for the base simulation (SR1) (supporting data available in Table S2 in auxiliary material Text S1).

[42] We account for variability in O$_3$, CH$_4$, and SO$_4^{2-}$ across the ensemble of CTMs, but our estimates of uncertainty only include the variability in CTMs, using a single RTM for all RF estimates. We therefore understate the uncertainty in net RF. In addition, while we capture the most important forcings, a more complete analysis of RF could include RFs due to changes in nitrate aerosols (likely important for NO$_x$ reductions), the indirect effect of aerosols, internal mixing of aerosols, changes in stratospheric O$_3$.
and water vapor, and changes to the carbon cycle via nitrogen deposition. Finally, we estimate RF due to changes in the radiative budget of the global atmosphere, but do not estimate the full climate response to regional forcings. Future research should link global and regional RF to climate responses.

[43] Our analysis contributes to the understanding of the effects of O₃ precursors on global and regional RF, and provides motivation for evaluating the climate benefits of policies addressing tropospheric O₃ and its precursors. We show that among short-lived O₃ precursors, NMVOC and CO emission reductions most effectively reduce RF. Our GWP estimates would be important. For CO, the consistency in RF per unit emissions and GWP₁₀₀ across the four regions implies that the error in using a uniform GWP for CO may be small. However, the RF per unit CO emissions may differ in other regions not studied here. Future studies should analyze additional source regions, such as near the equator and in the SH, as other precursors show greater sensitivity in these regions [e.g., Naik et al., 2005].

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