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Chemical nonlinearities in relating intercontinental ozone pollution to anthropogenic emissions

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[1] Model studies typically estimate intercontinental influence on surface ozone by perturbing emissions from a source continent and diagnosing the ozone response in the receptor continent. Since the response to perturbations is non-linear due to chemistry, conclusions drawn from different studies may depend on the magnitude of the applied perturbation. We investigate this issue for intercontinental transport between North America, Europe, and Asia with sensitivity simulations in three global chemical transport models. In each region, we decrease anthropogenic emissions of NO_x and nonmethane volatile organic compounds (NMVOCs) by 20% and 100%. We find strong nonlinearity in the response to NO_x perturbations outside summer, reflecting transitions in the chemical regime for ozone production. In contrast, we find no significant nonlinearity to NO_x perturbations in summer or to NMVOC perturbations year-round. The relative benefit of decreasing NO_x vs. NMVOC from current levels to abate intercontinental pollution increases with the magnitude of emission reductions. **Citation:** Wu, S., B. N. Duncan, D. J. Jacob, A. M. Fiore, and O. Wild (2009), Chemical nonlinearities in relating intercontinental ozone pollution to anthropogenic emissions, *Geophys. Res. Lett.*, *36*, L05806, doi:10.1029/2008GL036607.

1. Introduction

[2] Ozone (O_3) in surface air is toxic to humans and vegetation. It is produced within the troposphere by photochemical oxidation of methane, non-methane volatile organic compounds (NMVOCs), and CO in the presence of nitrogen oxide radicals ($NO_x \equiv NO + NO_2$). The lifetime of tropospheric ozone varies from days to months, and the lifetimes of its precursors span an even wider range, so that ozone pollution can be transported on an intercontinental scale. This intercontinental influence is now emerging as a significant issue for northern mid-latitude countries attempting to meet their ozone air quality standards. The Task Force on Hemispheric Transport of Air Pollution (TF HTAP; www.htap.org) was recently established to coordinate a multi-model effort to better quantify intercontinental source-receptor relationships for O_3 and other air pollutants [*Task Force on Hemispheric Transport of Air Pollution*, 2007; *Fiore et al.*, 2009].

[3] A number of investigators have applied global chemical transport models (CTMs) to quantify intercontinental source-receptor relationships for ozone pollution. They have applied either of two approaches: source attribution using ozone tracers tagged by production region [e.g., *Wang et al.*, 1998; *Fiore et al.*, 2002; *Derwent et al.*, 2004; *Auvray and Bey*, 2005], or sensitivity studies perturbing the sources [e.g., *Jacob et al.*, 1999; *Yienger et al.*, 2000; *Wild and Akimoto*, 2001; *Fiore et al.*, 2009]. Because the dependence of ozone production on its NO_x and VOC precursors is strongly nonlinear [*Liu et al.*, 1987; *Lin et al.*, 1988; *Sillman et al.*, 1990], these approaches are expected to yield different sensitivities in the ozone response, making it difficult to generalize results from the literature. A number of previous studies [*Sillman et al.*, 1990; *Jacob et al.*, 1995; *Sillman*, 1999; *Kleinman et al.*, 2001; *Stein et al.*, 2005] have investigated the nonlinearities on the domestic scale but not on the intercontinental scale.

[4] Sensitivity studies with perturbed sources are of most policy relevance for addressing intercontinental pollution, but the magnitudes of perturbations applied in the literature vary across studies. Most turn off completely the anthropogenic emissions in the source continent [*Berntsen et al.*, 1999; *Fiore et al.*, 2002; *Liu et al.*, 2003; *Auvray and Bey*, 2005; *Guerova et al.*, 2006]. Others increase emissions two-fold or more to examine the implications of industrialization [*Jacob et al.*, 1999; *Zhang et al.*, 2008]. *Wild and Akimoto* [2001] investigate the effects of 10% increases to minimize nonlinearity relative to the base case.

[5] The recent HTAP intercomparison of 21 global CTMs for intercontinental ozone pollution [*Fiore et al.*, 2009] applied 20% reductions in anthropogenic emissions of ozone precursors separately to North America, Europe, and Asia to ensure a detectable signal while minimizing non-linearity. Changes over the past decade have in fact been larger, either upward (East China) or downward (Europe) [e.g., *Richter et al.*, 2005]. The surface ozone sensitivities to changes in intercontinental anthropogenic NO_x emissions derived from the HTAP results are significantly weaker compared to previous studies with zero anthropogenic emissions but are closer to those with small perturbations. We present in this paper a general analysis of

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Table 1. Anthropogenic Emissions of NO_x and NMVOCs[a]

Emissions		North America (NA; 125W–60W and 15N–55N)	Europe (EU; 10W–50E and 25N–65N)	East Asia (EA; 95E–160E and 15N–60N)
NO_x ($Tg\ N\ a^{-1}$)	FRSGC/UCI	7.3	7.4	5.5
	GMI	7.5	6.8	5.4
	MOZARTGFDL-v2	8.8	8.3	4.7
NMVOC ($Tg\ C\ a^{-1}$)	FRSGC/UCI	15.6	21.3	19.2
	GMI	12.4	6.2	13.2
	MOZARTGFDL-v2	6.6	10.6	7.8

[a]As used in the standard model simulations (control runs).

the nonlinear response of surface ozone to changes in emissions from other continents.

2. Approach

[6] We focus our analysis on the intercontinental transport of ozone pollution between North America (NA), Europe (EU), and East Asia (EA). Regions are defined as given by *Fiore et al.* [2009] and geographical information is given in Table 1. We investigate the effect of perturbations to anthropogenic NO_x and NMVOC emissions in each continent. *Fiore et al.* [2009] previously showed that perturbations to CO emissions have negligible effects on intercontinental ozone pollution. Methane is an important global precursor of ozone but is not at present subject to air quality regulations.. We expect methane and NMVOCs to show similar linear behavior.

[7] We use the Global Modeling Initiative's Chemical Transport Model (GMI CTM) (http://gmi.gsfc.nasa.gov/intro_to_models.html) for sensitivity simulations. The GMI CTM participated in the HTAP study [*Fiore et al.*, 2009]. Its simulation of tropospheric ozone chemistry largely follows that of the GEOS-Chem CTM [*Bey et al.*, 2001]. The GMI simulation of global tropospheric ozone has been evaluated in previous studies [*Ziemke et al.*, 2006; *Duncan et al.*, 2007, 2008]. We use meteorological fields for 2001 from the Goddard Modeling and Assimilation Office (GMAO) GEOS-4 data assimilation system (GEOS-4-DAS) [*Bloom et al.*, 2004]. The meteorological fields were regridded to a horizontal resolution of 2° latitude by 2.5° longitude and 42 vertical levels extending up to 0.01 hPa. The anthropogenic emission inventories used in GMI (Table 1) are as those of *Duncan et al.* [2008].

[8] The model results from GMI are compared here with two other models that participated in the HTAP study: FRSGC/UCI [*Wild et al.*, 2004; *Wild*, 2007] and MOZARTGFDL-v2 [*Horowitz et al.*, 2003; *Fiore et al.*, 2005]. Both FRSGC/UCI and MOZARTGFDL-v2 have been evaluated against observations in previous studies. All three models performed the same sensitivity simulations by reducing the EU anthropogenic emissions by 20% and 100%, respectively. As we will see in the next section, perturbations to EU anthropogenic NO_x emissions show the strongest nonlinearities.

3. Nonlinearity in Intercontinental Ozone Response

[9] Figure 1 (top) shows the decreases of intercontinental enhancement in monthly mean surface ozone resulting from

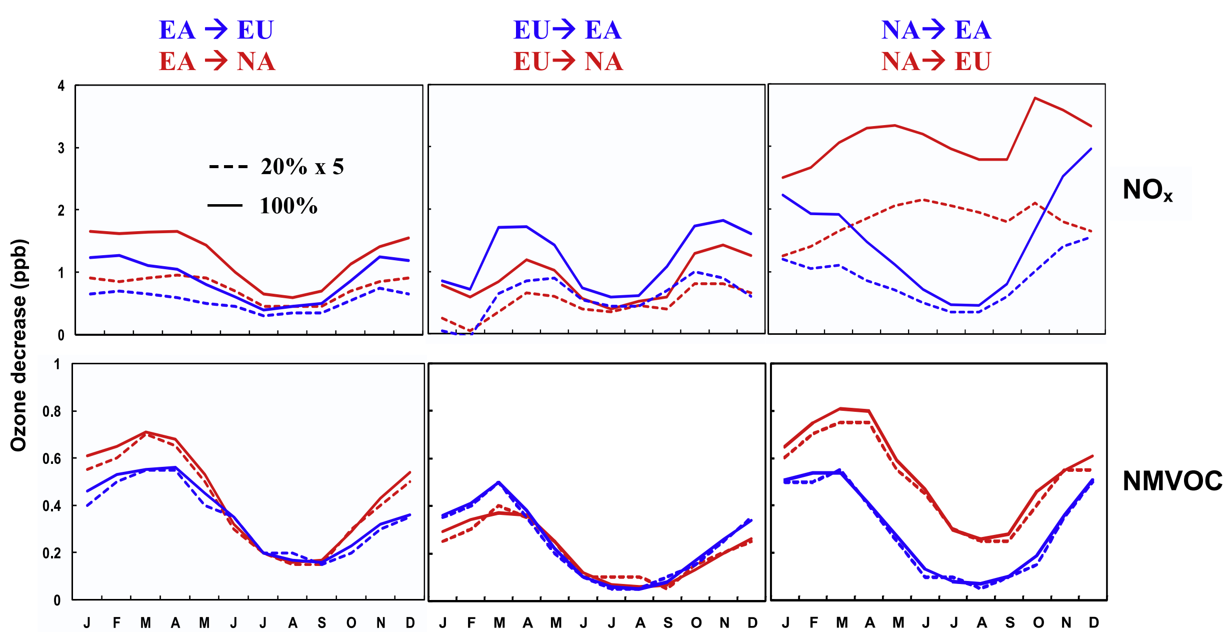

Figure 1. Decreases in monthly mean surface ozone concentrations over receptor regions resulting from reductions in anthropogenic emissions of (top)NO_x and (bottom) NMVOCs in source regions calculated by the GMI model. The source and receptor regions (EA, EU, and NA) are as defined in Table 1. The solid lines denote the perturbations due to 100% reductions and dashed lines represent 5 times the perturbations from the 20% reductions.

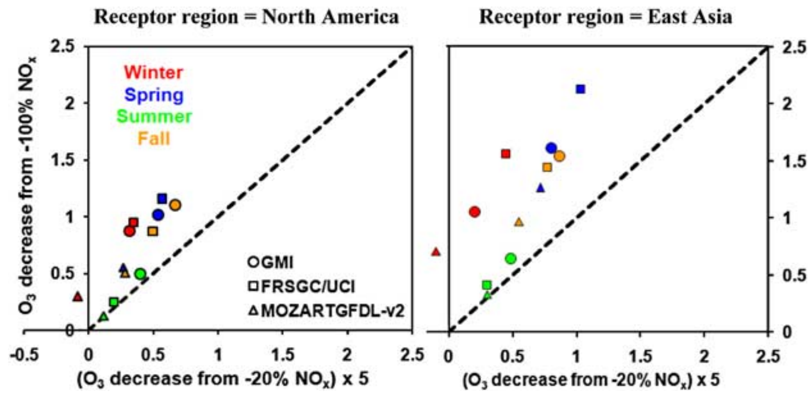

Figure 2. Changes in seasonal mean surface ozone over (left) NA and (right) EA in response to anthropogenic NO_x emission reductions in EU calculated with three different models: FRSGC/UCI (squares); GMI (circles) and MOZARTGFDL-v2 (triangles). The ordinate shows the perturbations from 100% reductions and the abscissa for 5 × 20% reductions. The dashed 1:1 line indicates linearity in the relationship.

20% and 100% reductions in anthropogenic (excluding emissions from biomass burning and soils) NO_x emissions for all different EU, EA, NA pairs calculated with the GMI model. Intercontinental influence is generally weakest in summer, reflecting the short lifetime of ozone and the weak circulation. The secondary minimum for European influence in winter is due to NO_x loss by the dark N_2O_5 hydrolysis pathway and associated regional titration of ozone [*Duncan et al.*, 2008]. The intercontinental influence for the NA → EU pair is strongest throughout the year, and shows little decrease in summer, reflecting the short intercontinental transport distance.

[10] Figure 1 shows that for any source-receptor pair and any season, the perturbation from a 100% NO_x emission reduction always results in ozone responses greater than 5 times the 20% NO_x emission reductions. The nonlinearity is strongest from November to April when the effect of the 100% NO_x reduction is often more than twice that of the 5 × 20% NO_x reduction. This can be understood in terms of the seasonal transition between NO_x-limited and NO_x-saturated regimes for ozone production, which depends on the relative supply of NO_x and photochemically generated hydrogen oxide radicals (HO_x) [*Kleinman*, 1991; *Jacob et al.*, 1995]. Ozone production in the continental boundary layer during November–April tends to be NO_x-saturated at current NO_x emission levels [*Jacob et al.*, 1995; *Carmichael et al.*, 1998], and 100% reduction of anthropogenic emissions causes a switch to NO_x-limited conditions. Nonlinearity is much weaker in summer when ozone production tends to be NO_x-limited at current emission levels.

[11] Figure 1 (bottom) shows the ozone response to 20% and 100% reductions in anthropogenic NMVOC emissions for different source - receptor pairs. In contrast to NO_x perturbations, there is no significant non-linearity for any source-receptor pair or any season. This is consistent with *Wang and Jacob* [1998], who found that the ozone production efficiency referenced to NMVOCs is only weakly dependent on NMVOC levels so that near-linear behavior is expected. Anthropogenic NMVOCs account for a relatively small fraction of the total NMVOCs (dominated by biogenic emissions) and the perturbations to anthropogenic NMVOC emissions do not change the chemical regime of ozone production. For NO_x-saturated conditions as in winter EU, 100% reduction in anthropogenic NMVOCs does not change the regime because methane and CO are still present.

[12] We also conducted sensitivity simulations with 20% and 100% perturbations to anthropogenic NO_x and NMVOCs combined (not shown). The perturbations to individual ozone precursors are largely additive [*Shindell et al.*, 2005; *Fiore et al.*, 2009] and the nonlinearity for combined perturbations follows that of NO_x. This is expected since the responses to anthropogenic NMVOC perturbations are linear, as shown above, and the transition between NO_x-limited and NO_x-saturated regimes does not depend on the supply of anthropogenic NMVOCs but rather on the relative sources of NO_x and HO_x [*Jacob et al.*, 1995].

[13] We compare in Figure 2 the changes in seasonal mean surface ozone over NA and EA due to perturbations in EU anthropogenic NO_x emissions simulated by three different models: FRSGC/UCI, GMI and MOZARTGFDL-v2. The models show large differences in their simulated responses to intercontinental pollution, partly reflecting differences in emissions including the NO_x:NMVOC ratios (Table 1), as discussed by *Fiore et al.* [2009]. In addition, the models use different meteorological data products and treatments of atmospheric processes such as convection that would affect the ozone response. However, they are consistent in their non-linearities. All models show little non-linearity in summer and large non-linearity in other seasons. The strongest non-linearity is in winter for all three models.

[14] Differing nonlinearity of ozone response to NO_x and NMVOC emissions implies that the perceived relative benefit of controlling NO_x vs. NMVOCs increases with the magnitude of reductions from current emission levels. This is illustrated in Figure 3, which shows the decreases in surface ozone for each region in spring due to 100% and 20% reductions in emissions from the other regions calculated with the GMI model. For the North America receptor region, the relative benefit of reducing NO_x vs. NMVOC emissions in Europe and East Asia is a factor of 1.5 for a 20% perturbation but 2.7 for a 100% perturbation. In summary, simulations of intercontinental ozone pollution in current models show a large nonlinear response (often

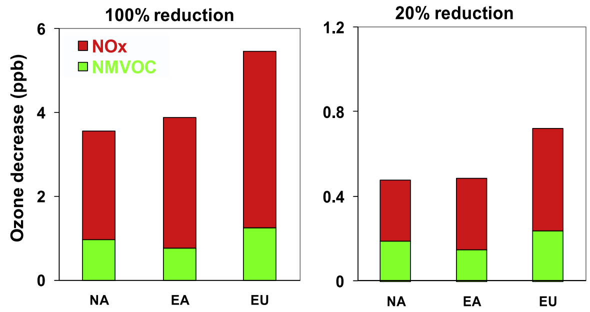

Figure 3. Decreases in springtime (MAM) mean surface ozone over NA, EA and EU due to (left) 100% and (right) 20% reductions in anthropogenic NO_x or NMVOC emissions from the other regions. Note the different scales between Figures 3 (left) and 3 (right) which would lead to equal height bars on both if the responses were linear.

exceeding a factor of two) in the response of surface ozone in the receptor continent to anthropogenic emissions of NO_x in the source continent outside summer. In contrast, there is no significant non-linearity in the response to NO_x emissions in summer or to anthropogenic NMVOC emissions year round. The nonlinearity in spring, when intercontinental influence is the greatest, is an important consideration in interpreting results from past model perturbation studies. Studies that eliminate anthropogenic NO_x emissions completely from the source continent overestimate the effect from a more realistic source perturbation.

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