Supplementary Information for:

Summertime State-Level Source-Receptor Relationships between NO\textsubscript{x} Emissions and Downwind Surface Ozone Concentrations over the Continental United States

Daniel Q. Tong (tong.daniel@epa.gov)\textsuperscript{1,2,3} 

and

Denise L. Mauzerall (mauzeral@princeton.edu)\textsuperscript{1,4,5}

11 pages, five Figures and one Table.
S1. CMAQ Model Configuration

CMAQ is configured with detailed implementation of horizontal and vertical advection based on the Piecewise Parabolic Method (PPM), turbulent diffusion based on K-theory, chemistry in the gas, liquid, and particulate phases using a modified version of the CBM-IV chemical mechanism (CB4-AQ-AE3) (Gery et al., 1994), dry deposition, and cloud physics and chemistry (CLOUD-RADM) (15). Hourly meteorological parameters, including temperature, wind velocities, humidity, surface pressure, and solar radiation, are obtained from the 5th Generation Mesoscale Model (MM5) (Grell et al., 1994). Anthropogenic emissions of nitrogen oxides (NO\textsubscript{x}), sulfur dioxide (SO\textsubscript{2}), carbon monoxide (CO), volatile organic compounds (VOCs), and ammonia (NH\textsubscript{3}) are obtained from the county level U.S. EPA 1996 National Emissions Trends inventory and processed with the Sparse Matrix Operator Kernel Emissions (SMOKE) model (Houyoux et al., 2000). Vehicle emissions of NO\textsubscript{x}, VOCs, CO and primary particulate matter (PM) are prepared using MOBILE5 (US EPA, 2003). Biogenic emissions, including NO\textsubscript{x} and VOCs, are obtained from the biogenic emissions inventory system, version 3 (BEIS3) (Pierce et al., 1998).

We chose 1996 emissions and meteorology because we have already carefully evaluated model results with observations using this data (16). Figure S1 shows the monthly mean surface wind in July 1996 over the continental U.S. obtained from the MM5 simulation which provides the meteorological fields for our CMAQ simulation. Ideally current emission data and meteorology would be used for analysis, particularly for NO\textsubscript{x} for which increasingly stringent controls on large stationary sources have been implemented over the last decade (23). However, at the time this work was started, even the 2002 National Emission Inventory (NEI), which did not fully account for the OTC emission reduction program, was not yet available.

S2. Biogenic NO\textsubscript{x} Emissions

Figure S2 shows the spatial distribution of isoprene and NO\textsubscript{x} emissions over our model domain. The figures show that while biogenic isoprene emissions are mostly
emitted from forested areas, biogenic NO\textsubscript{x} is emitted predominantly from agricultural lands. Over rural areas, soil-biogenic NO\textsubscript{x} emissions dominate other sources. Due to the human influence on emissions of soil-biogenic NO\textsubscript{x} via nitrogenous fertilizer application, we remove biogenic as well as direct anthropogenic emissions of NO\textsubscript{x} from our perturbation simulations in order to quantify the total effect a source state’s NO\textsubscript{x} emissions have on intra- and inter-state O\textsubscript{3} concentrations.

Unlike biogenic VOCs such as isoprene, trees are not a significant contributor to biogenic NO\textsubscript{x} emissions in regions other than tropical forests. Yienger and Levy (1995) estimated that forests only contribute 1–2\% of total biogenic NO\textsubscript{x} emissions in temperature regions. Previous field measurements in the U.S. revealed that forest emissions are one order of magnitude lower than those of grassland, which is about one tenth that of heavily fertilized soils (Williams and Fehsenfeld, 1991).

S3. Model Evaluation
Prior to using CMAQ to quantify source-receptor relationships we evaluated the ability of the model to simulate the surface distribution of tropospheric O\textsubscript{3} (16). A map of the model domain and measurement sites is shown in Figure S3. CMAQ reproduces surface O\textsubscript{3} for a wide range of conditions (30–80 ppbv) with a normalized mean error (NME) less than 35\% and normalized mean bias (NMB) lying between ±15\% for the whole domain. The NME is the averaged magnitude of the difference between model prediction and observation normalized by the observation. The NMB is defined similarly, but considers the actual difference, instead of the absolute value, allowing over- and under-estimation to cancel out. Although systematically over-predicting O\textsubscript{3} in the eastern US and coastal locations and under-predicting it in the California Central Valley and many locations in the western US, the model is able to reproduce 1-hour and 8-hour daily maxima with a cross-domain mean bias (MB) of 1 ppbv and 8 ppbv, or NMB of 8\% and 25\%, respectively.

Comparisons of vertical profiles of simulated O\textsubscript{3} with ozonesonde data show a consistent under-prediction in the upper troposphere even when lateral boundary conditions from MOZART-2 are used (16). The discrepancy can be attributed to the use of a zero-flux upper boundary condition in CMAQ with a relatively low model top
(200mb) (16). In addition, missing sources of NO\(_x\) emissions, such as transported NO\(_x\) from the stratosphere, lightning and aircraft discharges, may play an important role in determining O\(_3\) concentrations in the upper troposphere. Lightning accounts for roughly 14\% of NO\(_x\) emissions in July over the continental U.S., and its emissions have been shown to contribute a significant fraction to O\(_3\) concentrations in the middle and upper troposphere (Zhang et al., 2003 and references therein). Aircraft emissions increase background NO\(_x\) concentrations by 0.05-0.07 ppbv in the upper troposphere over North America, and contribute up to 3 ppbv to upper troposphere O\(_3\) levels in July (Kentarchos et al., 2002). Although air traffic related emissions near the surface are included in the model input, aircraft emissions at high altitudes are not. The under-prediction of O\(_3\) at high altitudes may raise questions about the ability of CMAQ to simulate continental scale pollution transport. Long-distance transport of air pollution at mid-latitudes is generally associated with lifting of surface emissions to the free troposphere by frontal systems or convection followed by rapid advection in the free troposphere westerlies and subsidence at downwind locations (Bey et al., 2001; Cooper et al., 2003). O\(_3\) is the primary precursor of the hydroxyl radical which in turn determines the lifetime of most atmospheric constituents. Therefore, the underestimation of upper tropospheric O\(_3\) concentrations may change the lifetime of O\(_3\) and its precursors in the upper troposphere and thus change the distance of transport and the source-receptor relationships. However, as the major objective of this study is to examine the impact of large NO\(_x\) emissions on downwind surface locations, the long-distance transport processes in the upper troposphere are less important than advection and photochemistry near the surface. Mauzerall et al. (1996) has shown that photochemistry largely controls O\(_3\) concentrations in the polluted boundary layer. We expect the underestimation of upper tropospheric O\(_3\) due to exclusion of the influx of stratospheric O\(_3\) to have only a small effect on our results.

**S4. Spatial distribution of surface O\(_3\) in source and receptor states**

Figure S4 shows the spatial distribution of changes in mean July all-hour O\(_3\) concentrations resulting from NO\(_x\) emissions from ten states distributed across the U.S.
These states include the five largest NO\textsubscript{x} emitters (TX, CA, OH, IL, and FL), two ranked in the top 25% (PA and TN), and three with moderate emissions (NY, NJ and CO).

**S5. Time Series of Hourly O\textsubscript{3} Concentrations over Trenton, NJ**

To illustrate the different sensitivities between peak 8-hour and 24-hour O\textsubscript{3} concentrations to NO\textsubscript{x} emission changes, we provide a time series showing hourly O\textsubscript{3} concentrations with and without New Jersey NO\textsubscript{x} emissions over Trenton, NJ. Figure S5 shows that most days local NO\textsubscript{x} emissions reduce surface O\textsubscript{3} concentrations at night and in early morning but increase peak O\textsubscript{3} concentrations during the day. Although the relative magnitude of increases or decreases caused by local emissions vary spatially and depend upon meteorological conditions, the general trends with and without intrastate emissions are similar. As a result, the state-averaged 24-hour and peak 8-hour metrics display different responses to NO\textsubscript{x} emission changes.

**References:**


Figure S1. Monthly mean surface winds in July 1996 over the continental United States. Winds are from the MM5 simulation that provides the meteorological fields used for CMAQ.
Figure S2. Spatial distribution of mean July 1996 a) biogenic NO\textsubscript{x} emissions, b) biogenic isoprene emissions, c) the ratio of biogenic NO\textsubscript{x} emissions to total surface NO\textsubscript{x} emissions and d) the ratio of NO\textsubscript{x} emissions to total VOC emissions over our domain.
Figure S3. Map of modeling domain and locations of measurements used for model evaluation. Open circles are AQS monitors, filled triangles are CASTNet sites, and filled circles are two ozonesonde stations located at Boulder, CO and Wallops Island, VA.
Figure S4. Changes in monthly mean all-hour O$_3$ concentrations resulting from NO$_x$ emissions from: (a) California; (b) Colorado; (c) Texas; (d) Illinois; (e) Tennessee; (f) Florida; (g) Ohio; (h) Pennsylvania; (i) New York and (j) New Jersey.
Figure S5. Time series of surface $O_3$ concentrations at Trenton, NJ during the July 1996 simulations. Baseline emissions with and without NJ NO$_x$ emissions are plotted in black and red, respectively. Vertical lines indicate midnight on a given day.
Table S1. Maximum contribution to monthly mean peak 8-hour O₃ concentrations within a single grid cell over each receptor state resulting from a source state’s NOₓ emissions during July 1996.