ASSESMENT OF VOCS AND NO2 PREDICTIONS IN U.S. URBAN AREAS: POTENTIAL IMPLICATIONS FOR O3 CONTROL STRATEGIES

Kirk R. Baker*
U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, 109 TW Alexander Dr., Research Triangle Park, NC 27711

Annmarie G. Carlton
U.S. Environmental Protection Agency, Office of Research and Development, 109 TW Alexander Dr., Research Triangle Park, NC 27711

1. INTRODUCTION

The United States Environmental Protection Agency (US EPA) is currently considering lowering the 8-hr National Ambient Air Quality Standard (NAAQS) for ozone (O_3). A new standard below the current 85 ppb level will result in many new areas being designated as nonattainment. Nonattainment areas, the new ones in particular, will need to rely on conventional photochemical modeling and routinely available ambient data to develop effective air quality management plans that employ O_3 control scenarios based on the current mix of precursors, nitrogen oxides (NO_X) and volatile organic compounds (VOC), in their area (Jones et al., 2005).

Ozone production in urban areas is typically considered to be limited by VOC (or TNMOC) availability, meaning control strategies should focus on local VOC controls and areas outside urban cores are considered NO_X limited and should focus on NO_X controls (Milford et al., 1994a; Milford et al., 1994b; Milford et al., 1989). Most field studies assessing ozone formation were conducted more than 10 years ago while emission reductions in response to regulations/legislation for large stationary point and mobile source emissions may have changed the mix of O_3 precursors. Further, previous studies in non-attainment areas like Los Angeles may not adequately describe O_3 production regimes in new nonattainment areas. These newly classified areas have not had the benefit of intensive measurement campaigns or sophisticated modeling studies.

The relative mix of O_3 precursors can be estimated from the ratio of total non-methane organic compounds (TNMOC) to nitrogen dioxide (NO_2). The tendency of a particular area's ozone formation to be limited by NO_x or VOC emissions can be inferred from the TNMOC/NO_2 ratio (Ran et al., 2009). For example, when the instantaneous TNMOC:NO_2 ratio is above 5.5:1 (using a carbon-based mixing ratio for TNMOC and based on OH reactivity) for an average urban atmosphere, the system is said to be NO_x-limited, because a further decrease in NO_x compounds would favor peroxy-peroxy reactions, limiting O_3 formation (Seinfeld and Pandis, 1998) through removal of free radicals (e.g., OH). Conversely, when the instantaneous TNMOC:NO_2 ratio is less than 5.5:1 the system is said to be VOC-limited because OH reacts predominantly with NO_2 to remove radicals and limit O_3 formation.

Comparisons of observed and photochemical model estimates of TNMOC:NO_2 can provide insight as to whether the model adequately describes the relative mix of VOCs and NO_2 for a particular area. This type of assessment helps develop confidence for the tool to be used for areas that lack routine measurements of O_3 precursors. From a dynamic model evaluation perspective, if simulated ratios substantially differ from actual conditions, the model may not adequately characterize the O_3 production regime and as a consequence predictions of O_3 for future years may not appropriately respond to emission controls, making the modeling system appear "stiff" to emissions adjustments (Gilliland et al., 2008). Future year estimates of TNMOC:NO_2 from the CMAQ model are compared to the baseline predictions to provide an indication about how O_3 formation regimes may differ after the continued implementation of Federal Rules and vehicle fleet turnover.

One shortcoming of evaluating the TNMOC:NO_2 ratio is that some compounds may contribute a small amount to the total VOC mass inventory in a particular area, but the same compound could contribute a large fraction of the total reactivity. This comparison is problematic because speciated VOC measurements are not

made routinely, nor are all VOCs explicitly modeled. It is also important to consider whether TNMOC:NO_2 ratios provide useful information about whether an area would realize air quality benefits from NO_X or VOC control. Near-surface VOC and NO_X emissions are each reduced by 75% and model response is compared to the TNMOC:NO_2 ratio to evaluate the usefulness of this indicator for predicting ozone response.

2. METHODS

The Community Multi-scale Air Quality (CMAQ) model v4.7.1 (www.cmaq-model.org) is a state of the science three-dimensional Eularian "one-atmosphere" photochemical transport model (Appel et al., 2007; Byun and Schere, 2006) used to estimate air quality. The CMAQ model is applied with RADM aqueous phase chemistry (Chang et al., 1987) and the carbon-bond 2005 (CB05) gas-phase chemistry module (Gery et al., 1989).

The 2005 emission inputs are based on the 2005 National Emission Inventory (NEI) version 3 (Strum, 2008). All emissions were processed using the Sparse Matrix Operator Kernel Emissions (SMOKE) Modeling System (Houyoux et al., 2000). Daily hour-specific biogenic emissions based on 2005 meteorology data are generated using the BEIS 3.13 model. Additional simulations for July 2005 were conducted where VOC and NO_X emissions were each reduced by 75% for the area, onroad, and nonroad emissions sectors.

The modeling domain covers the eastern and western U.S. using 12 km^2 sized grid cells. The vertical atmosphere up to approximately 15 km above ground level is resolved with 14 layers with the most resolution in the boundary layer. CMAQ was applied for annual simulations using 2005 meteorology with 2005 based emissions and again with projected 2020 based emissions. Initial conditions and hourly boundary conditions were extracted from annual CMAQ simulations that have a larger and coarser (36 km^2) domain using 2005 meteorology and emissions based on 2005 and 2020.

Hourly PAMS measurements of O_3 and TNMOC:NO_2 ratios are compared to model estimates from the grid cell containing the monitor. Previous research has shown that chemiluminescense monitor measurements of NO_2 often include additional nitrogen species, most notably PAN and nitric acid (HNO_3) (Dunlea et al., 2007; Ryerson et al., 2000). Model estimates of NO_2 include the sum of modeled NO_2, PAN, and HNO_3 in order to better match measurements. Model estimates are not manipulated in any way to account for known artifacts related to VOC canister sampling (McClenny et al., 2002).

3. RESULTS

The modeling system tends to under-estimate the highest observed O_3 mixing ratios at the PAMS network locations. Mean observed and model estimated TNMOC:NO_2 ratio when observed O_3 is greater than 70 ppb is shown for each monitor location in Figure 1. The color scale provides a qualitative indication about whether O_3 production may be VOC limited (blue) or NO_x limited (red). Transitional areas suggest both VOCs and NO_x may limit O_3 production at a particular location.

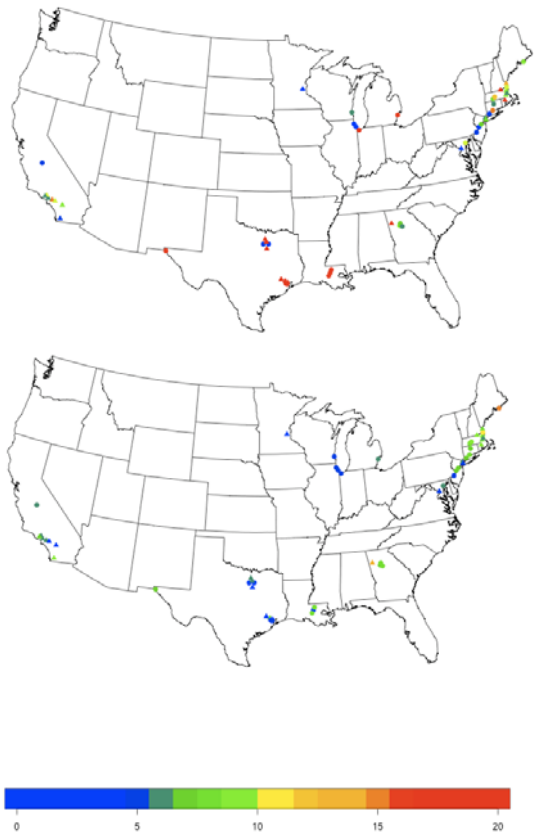

Fig 1. Observed (top) and modeled (bottom) TNMOC:NO_2 averaged over all hours where observed O_3 concentrations are ≥ 70 ppb (Triangle indicates N<10, circle indicates N ≥ 10).

The modeling system tends to be in a VOC limited regime for O_3 formation more often than suggested by measurements. This is most apparent at monitors located just outside urban cores (i.e. Dallas, Chicago, New York/Boston). Pooled domain wide hourly predictions and observations of TNMOC:NO_2 are shown by hour of the day in and day of the week in Figure 2. The modeling system tends to capture the diurnal and day-to-day variation in the TNMOC:NO_2 ratio.

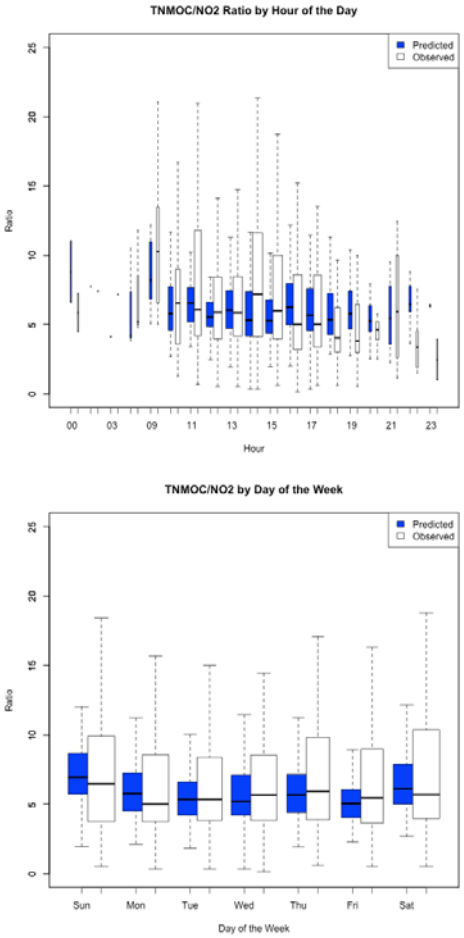

Fig 2. Distribution of observed and estimated TNMOC:NO_2 ratio by hour of the day (top) and day of the week (bottom).

Model estimates of TNMOC:NO_2 using emissions projected to 2020 are more NO_X limited than ratios estimated using 2005 emissions at locations in the central and eastern United States (Figure 3). Emissions used in this modeling assessment for the eastern United States decreased by 13% for VOC and by 44% for NO_X between 2005 and 2020. The comparatively larger projected NO_X emissions decrease compared to VOC results in a mix of precursors that may favor NO_X emissions control strategies in the future. A mischaracterization of O_3 formation regime in the current year may be magnified by emissions projections estimates and result in a modeling system that may not be fully responsive to controls.

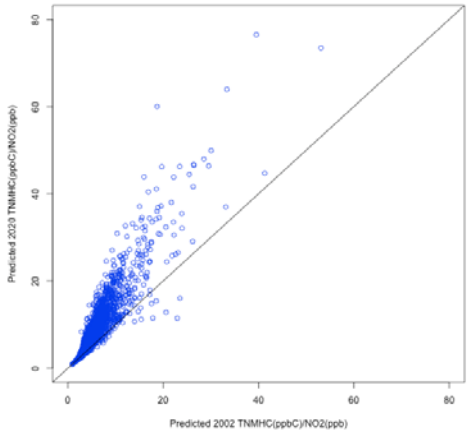

Fig 3. Model estimated TNMOC:NO_2 ratio for 2005 and 2020 where observed ozone > 70 ppb in 2005.

The 75% reduction in VOC and NO_X emissions to near ground level emitting sources (area and mobile) show greater benefit from NO_X control, particularly during the middle of the week (Figure 4). The VOC sensitivity showed the most response in ozone during the weekend days, although there were few days in July 2005 with ozone concentrations > 70 ppb.

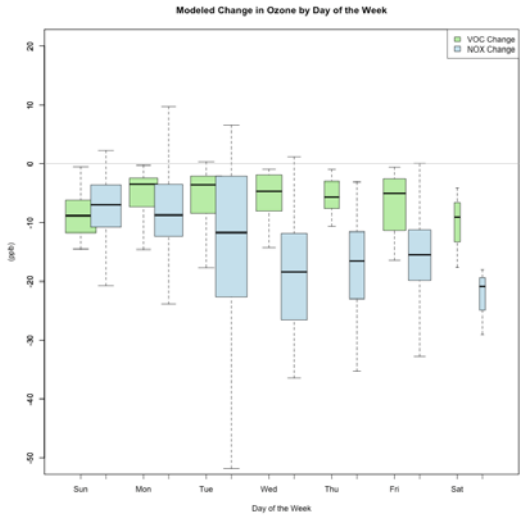

Figure 4. Modeled change in ozone where predicted ozone > 70 ppb by day of the week.

When modeled ozone reductions are compared to modeled TNMOC:NO_2 ratio the utility of this indicator becomes questionable. Ozone reductions are shown for both NO_X and VOC regardless of the magnitude of the indicator ratio (Figure 5). In this evaluation NO_2 does not include any additional modeled nitrogen species.

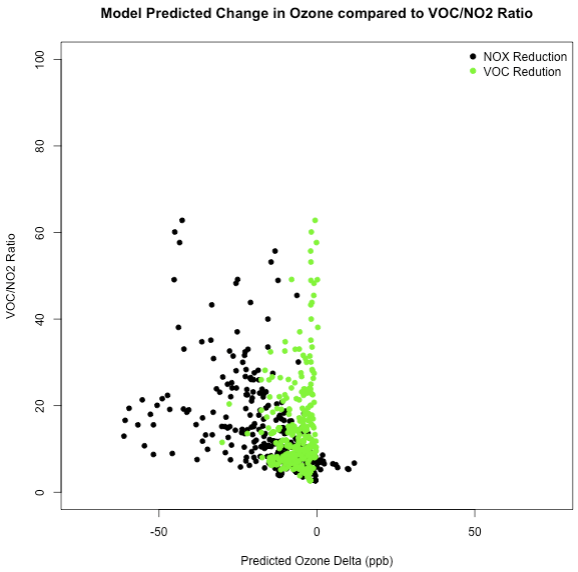

Fig 5. Modeled change in ozone where predicted ozone > 70 ppb compared to the model estimated TNMOC:NO_2 ratio.

Regional transport may confound this type of comparison but the sensitivity approach was designed to minimize the influence of transport. The emissions adjustments are made to local near-surface emitting sectors (mobile and area) and evaluated using an urban-centric monitor network.

4. CONCLUSIONS

The observed mix of TNMOC:NO_2 ratios varies considerably from one urban area to another. Variability is shown within region in many places including Chicago-Milwaukee and southern California. The modeling system does an adequate job of qualitatively capturing the spatial variability of the TNMOC:NO_2 indicator ratio. The modeling system appears to be a useful tool to characterize the relative mix of TNMOC:NO_2 which strengthens confidence that the model will respond appropriately to changes in precursor emissions. It is not clear that the TNMOC:NO_2 ratio provides useful information about whether NO_X or VOC controls are needed to reduce ozone. Model sensitivity simulations suggest most areas benefit from both NO_X and VOC reductions in local areas.

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