Supplement of

The long-term trend and production sensitivity change in the US ozone pollution from observations and model simulations

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Evaluation of the O$_3$/NO$_y$ ratio threshold

In our study, we could not access the research grade NO$_y$ observations from the EPA observations and did not conduct long-term sensitivity experiments of CMAQ with reduced emissions rates. So we have to rely on results from the previous studies. Sillman explored the concept using photochemical indicators including O$_3$/NO$_y$ to identify the regime of ozone photochemical production, finding that the link between the ozone production sensitivity and these indicators is largely unaffected by changes in model assumptions, including emission rates of anthropogenic and biogenic species (Sillman, 1995; Sillman et al., 1997). Observations from urban areas of Atlanta, New York, and Los Angeles was compared with modeling results from the Urban Airshed Model at urban scales, and threshold of 7 was proposed for using O$_3$/NO$_y$ ratio as the photochemical indicator (Sillman et al., 1997). Zhang et al. (2009) expanded the study to the CONUS with 1-year CMAQ simulations, and suggested a threshold of 15 for O$_3$/NO$_y$ ratio. Zhang et al. (2009) used previous CMAQ version 4.4 for 1-yr CONUS simulations of 2001 at a coarse spatial resolution (36 km) which is close to our 30-km CONUS domain, so we adopted their proposed threshold and evaluated it with the following approach.

We selected hourly O$_3$, NO$_y$, and NO$_x$ concentrations from CMAQ in the afternoon (defined as 12 pm to 4 pm) in 2004, and calculated the O$_3$/NO$_y$ ratios. Figure S1a shows scatter density of O$_3$/NO$_y$ ratios vs. NO$_x$ concentrations, which is calculated based on a 100 × 100 bins with NO$_x$ from 0-20 ppbv NO$_x$ (i.e., 0.2 ppbv per bin) and 0-100 O$_3$/NO$_y$ ratios (i.e., 1 per bin). In the afternoon over the CONUS, the ozone production is mainly in high O$_3$/NO$_y$ (>15) and low NO$_x$ (less than 2 ppbv) environment, i.e., in the NO$_x$-sensitive regions by thresholds proposed by both Sillman et al. (1997) and Zhang et al. (2009). Figure S1b shows the same density plot, but the color stands for mean O$_3$ concentrations. Both low and high ozone concentrations exist in high NO$_x$ region (NO$_x$ > 4 ppbv), which are usually urban or suburban. Then we calculated the weighted ozone concentrations which equals to the product of O$_3$/NO$_y$ and NO$_x$ scatter density (Fig. 4a) and mean O$_3$ concentrations (Fig. S1b), which stands for the O$_3$ sensitivity with respect to O$_3$/NO$_y$ ratios and NO$_y$ concentrations over the CONUS (Fig. S1c). At the national scale, when the weighted ozone concentrations increase with CMAQ NO$_x$ levels, the photochemical production is NO$_x$-sensitive. The region with O$_3$/NO$_y$ higher than 7 and 11 both have this characteristics, while due to low probability (Fig. S1a) and urban environment (Fig. S1b) we believe the O$_3$/NO$_y$ threshold of 7 stands for the urban environment. The O$_3$/NO$_y$ ratio threshold of 15 is more proper for the CONUS scale analysis. This analysis qualitatively supports our application of O$_3$/NO$_y$ threshold from Zhang et al. (2009).
Figure S1. Afternoon O$_3$/NO$_y$ ratios vs. NO$_x$ concentrations simulated by CMAQ in 2014. a) Scatter density, the color contour stands for the probability for each bin; b) O$_3$ concentrations, the color contour stands for the mean O$_3$ over the bins; c) Weighted O$_3$ concentrations. Two black lines stand for the O$_3$/NO$_y$ ratios of 7 and 11.

References:

