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

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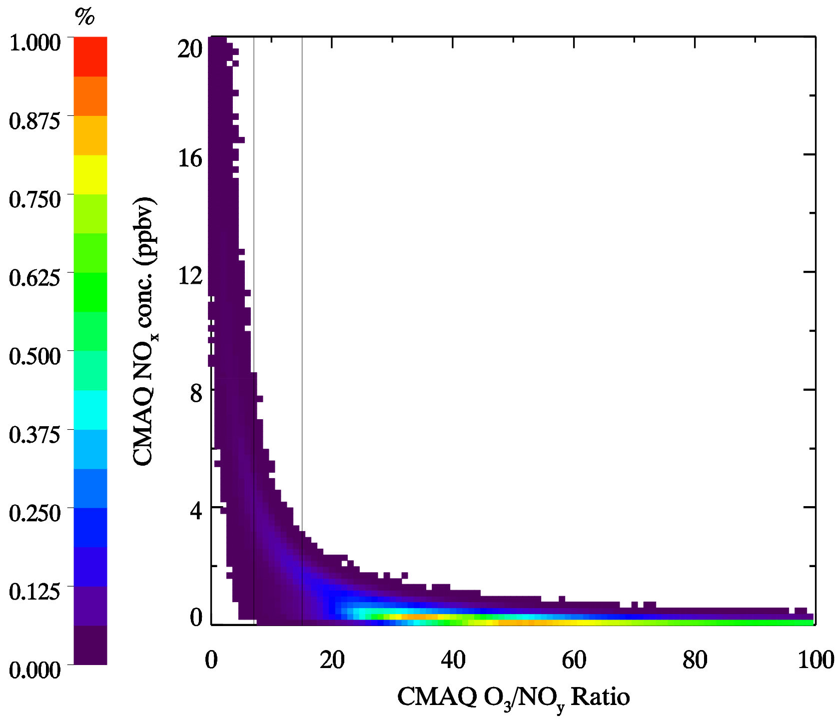
Evaluation of the O_3/NO_y ratio threshold

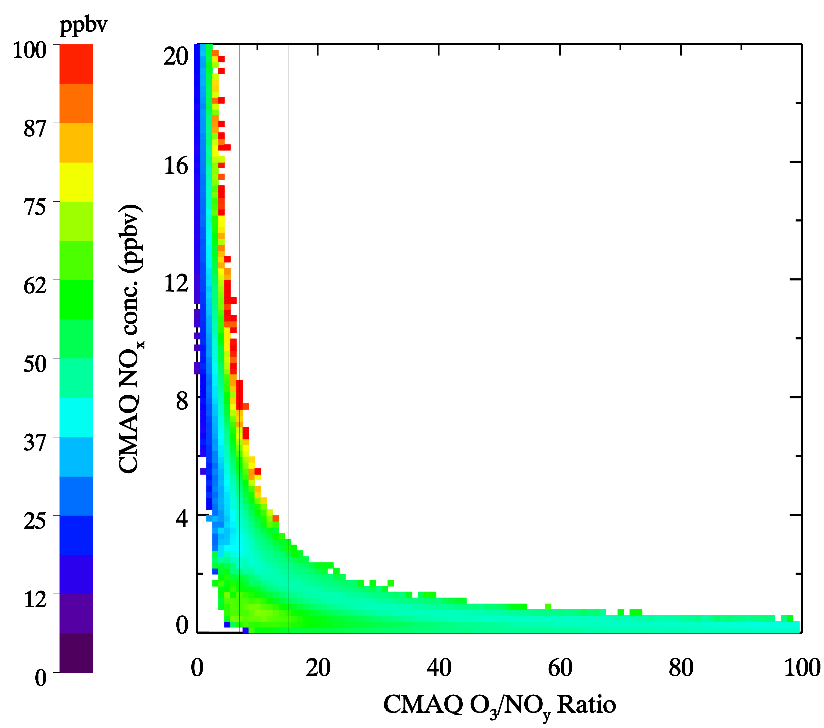
In our study, we could not access the research grade NO_y observations from the EPA observations and did not conduct long-term sensitivity experiments of CMAQ with reduced emissions rates. So we have to rely on results from the previous studies. Sillman explored the concept using photochemical indicators 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 indictor (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).

a)


%
1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
CMAQ NO_x conc. (ppbv)
20
16
12
8
4
0
0
20
40
60
80
100
CMAQ O_3/NO_y Ratio

b)


ppbv
100
87
75
62
50
37
25
12
0
CMAQ NO_x conc. (ppbv)
20
16
12
8
4
0
0
20
40
60
80
100
CMAQ O_3/NO_y Ratio

c)

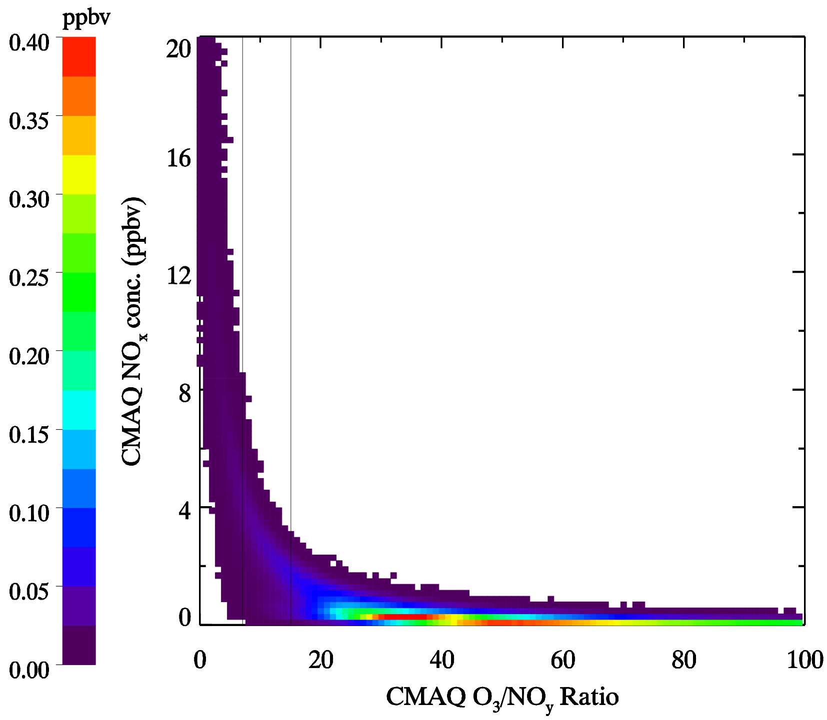


Figure S1. Afternoon O_3/NO_y ratios vs. NO_x concentrations simulated by CMAQ in 2014. a) Scatter density, the color contour stands for the probability for each bin; b) O_3 concentrations, the color contour stands for the mean O_3 over the bins; c) Weighted O_3 concentrations. Two black lines stand for the O_3/NO_y ratios of 7 and 11.

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