VOC/NO_X SENSITIVITY ANALYSIS FOR OZONE PRODUCTION USING CMAQ PROCESS ANALYSIS FOR THE PACIFIC NORTHWEST

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1. INTRODUCTION

The Cascadia region of the Pacific Northwest periodically experiences elevated ozone levels downwind of major urban areas. Most of the modeling studies conducted in the region have involved direct comparisons of predicted and measured ozone levels (Barna et al., 2000). It is well known that photochemical production of ozone is a highly nonlinear system where the predicted peak ozone level is not dependent on a unique set of VOC and NO_x concentrations, and therefore, the model might predict incorrect sensitivities to changes in precursors even while correctly predicting ozone levels (Sillman, 1995). The uncertainties in ozone sensitivity have led to the development of various chemical indicators for ozone sensitivity to changes in VOC and NO_x emissions (Sillman, 1995; Kleinman et al., 1997, 2005; Tonnesen and Dennis, 2000a, 2000b). The general thought is that those measurable indicators would have different values related to NO_x sensitive and VOC sensitive conditions, so that model predicted sensitivity could be evaluated by comparing to measured indicator values or ozone sensitivity could be evaluated directly from measurements. Although there have been a number of studies (Kleinman et al., 1997; Lu and Chang, 1998; Sillman and He, 2002; Sillman et al., 2003) of these indicators, there is considerable uncertainty about how the indicators might behave under different conditions, and with different models and photochemical mechanisms. For the Pacific Northwest region, these indicators haven't been widely tested, and therefore it is unclear about their effectiveness and whether the ranges of values related to ozone sensitivity are similar or different compared to other urban areas.

The goal of this study is 1) to investigate ozone production rate ($P(O_3)$) and its relationship with precursors, namely NO_x, VOC reactivity, and radical production rate in the Pacific Northwest, 2) to investigate the behavior of local indicators for instantaneous odd oxygen production rate ($P(O_x)$), and 3) to evaluate $P(O_x)$ sensitivity to changes in VOC and NO_x emissions in the region using these indicators.

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2. METHODOLOGY

The VOC/NO_x sensitivity analysis for ozone production was studied by using the MM5/SMOKE/CMAQ modeling system with 4 km grid size for a region encompassing the I-5 corridor of western Washington and Oregon for an ozone episode that occurred in July, 1998. The integrated reaction rate analysis (IRR) (Gipson, 1999) was used to output production rate of selected species such as ozone, odd oxygen (O_x), new radical (Q), as well as important propagation and termination pathways. Model output within the Portland sub-domain at 13 LST from July 26 to July 28, 1998 was selected for data analysis, which correspond to the periods when maximum ozone production rates ($P(O_3)$) were predicted. This sub-domain (as shown in the black box in Figure 1) covers Portland urban area and downwind regions with high $P(O_3)$.

To investigate ozone production rate ($P(O_3)$) and its relationship with precursors, $P(O_3)$ and radical production rate (Q) from process analysis along with NO_x and total VOC reactivity (VOC_R) were analyzed. Radical production rate (Q) is the sum of production rate of new radicals ($OH+RO_2+HO_2$). Total VOC reactivity (VOC_R) was calculated based on OH reactivity.

To investigate the behavior of local indicators for instantaneous odd oxygen production rate ($P(O_x)$), two model sensitivity runs were conducted by decreasing the anthropogenic VOC and NO_x emissions by 30% from the base case. The grid cells are related to VOC or NO_x sensitive regimes according to the following criteria. Grid cells with $\partial P(O_x)/\partial E_{NOx}=0$ are close to ridgeline conditions. NO_x sensitive cells are associated with $\partial P(O_x)/\partial E_{NOx}>0$, whereas VOC sensitive cells are linked to $\partial P(O_x)/\partial E_{NOx}<0$. Equal sensitivity is thought to occur in these grid cells when $\partial P(O_x)/\partial E_{NOx}=\partial P(O_x)/\partial E_{VOC}$.

The five indicators (f_{OH+HC}, f_{HO2+NO}, $P(H_2O_2)/P(HNO_3)$, O_3/NO_x, and L_N/Q) are defined using similar definition as Tonnesen and Dennis (2000a) and Kleinman et al. (1997, 2005).

3. OZONE PRODUCTION RATE AND ITS PRECURSORS

Contour maps of model predicted ozone production rate is plotted in Figure 1 at 13 LST on July 27, 1998. As shown in Figure 1, maximum ozone production rate close to 35 ppb hr^{-1} was predicted downwind of the Portland and Seattle urban area. For the urban cores, negative values were predicted as a result of high NO_x concentrations.

Ozone production rate as a function of total VOC reactivity and NO_x concentration is plotted in Figure 2 as color-coded symbols using data within the Portland sub-domain at 13 LST from July 26 to July 28, 1998. For $P(O_3)$ > 20 ppb h^{-1}, the data points (red and pink) appear to generally follow an upward slope, indicating similar VOC_R/NO_x ratios between those data points. For the data points with $P(O_3)$ >30 ppb h^{-1}, VOC_R ranges mostly between 8-12 s^{-1} and NO_x ranges mostly between 5-15 ppb. There is much more scatter for the low $P(O_3)$ data points (<10 ppb h^{-1}) which exist at both low and high end of VOC_R and NO_x values.

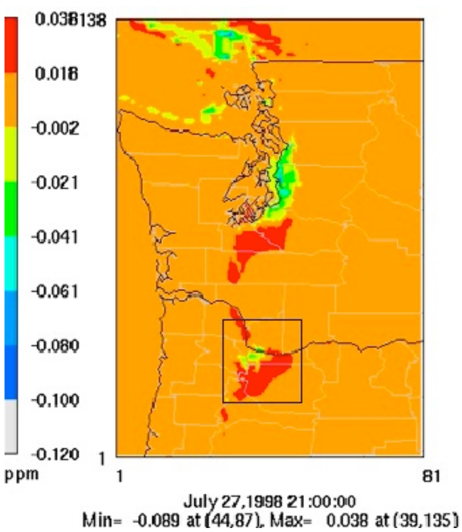

Figure 1. Surface $P(O_3)$ contours at 13 LST on July 27,1998 for the entire modeling domain. The inner black box shows the location of Portland sub-domain.

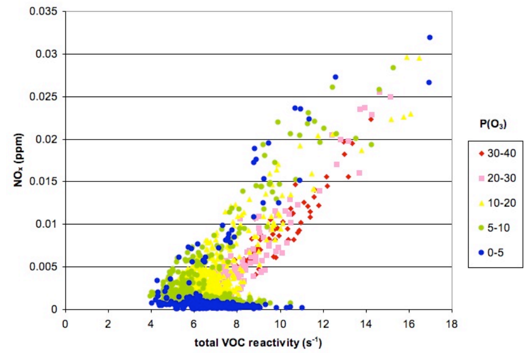

Figure 2. Ozone production rate as a function of NO_x and total VOC reactivity at 13 LST on July 26-28, 1998 within the Portland sub-domain.

4. THE BEHAVIOR OF LOCAL INDICATORS FOR $P(O_X)$

Figure 3 shows $\partial P(O_x)/\partial E$ as a function of f_{HO2+NO} in the base case at 13 LST on July 26-28, 1998 within the Portland sub-domain. There is a narrow range f_{HO2+NO} values associated with $\partial P(O_x)/\partial E_{NOx}$ =0, primarily between 0.96-0.97 indicating ridgeline values. Here cells with values greater than 0.97 are mainly VOC limited, whereas cells with values less than 0.92 are mostly NO_x limited. Values between 0.92-0.95 are linked to cells having equal sensitivity to VOC and NO_x. The other four indicators (f_{OH+HC}, $P(H_2O_2)/P(HNO_3)$, O_3/NO_x, and L_N/Q) also appear to be able to clearly distinguish NO_x and VOC sensitive conditions (not shown).

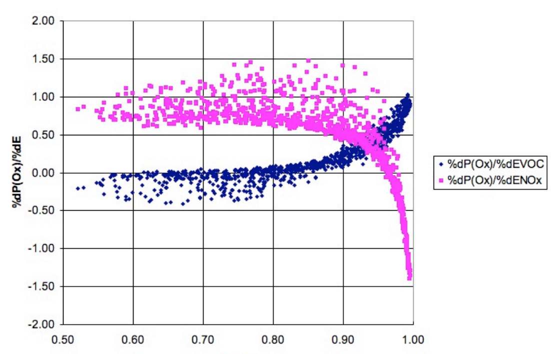

Figure 3. $\partial P(O_x)/\partial E$ as a function of f_{HO2+NO} at 13 LST on July 26-28, 1998 within the Portland sub-domain.

5. SENSITIVITY TO VOC/NO_X CHANGES BASED ON INDICATORS

Contour plot for f_{HO2+NO} is plotted at 13 LST on July 27, 1998 for the entire modeling domain as shown in Figure 4. On the maps, the color tiles around the ridgeline value are plotted in black and white, so that the intersection zone of the two colors could be viewed as where the ridgeline approximately sits. Both Portland and Seattle urban cores appear to be VOC limited in that hour, with Seattle being further more limited by radicals. Cells with high $P(O_3)$ (as shown in Figure 1) are primarily NO_x limited, but not far from the ridgeline. The contour plots of other indicators show very consistent patterns regarding to VOC and NO_x sensitive regions (not shown here).

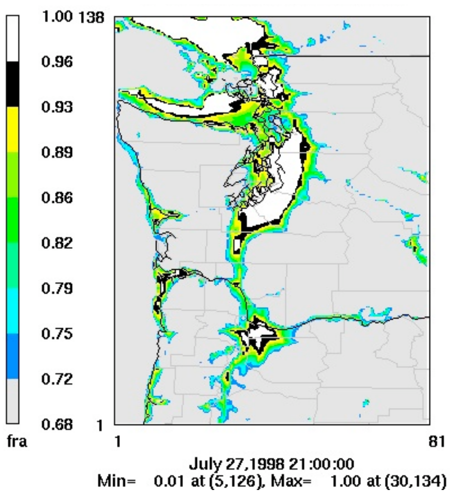

Figure 4. Surface contour plot of f_{HO2+NO} at 13 LST on July 27, 1998.

6. CONCLUSIONS

Maximum ozone production rate was found to be 30-40 ppb hr^{-1}, with NO_x concentrations of 5-15 ppb and total VOC reactivity of 8-12 s^{-1}. All five indicators (f_{OH+HC}, f_{HO2+NO}, $P(H_2O_2)/P(HNO_3)$, O_3/NO_x, and L_N/Q) appear to be able to distinguish NO_x and VOC sensitive conditions and suggest similar results regarding the location of ozone ridgeline. When $P(O_3)$ reaches maximum levels, Portland and Seattle urban cores both appear to be VOC limited; the grid cells with maximum $P(O_3)$ are located downwind of the urban core and mainly NO_x limited based on the indicator values. Further analysis using selected indicators is underway to compare model predicted ozone sensitivity with observations using aircraft and ground based measurements from PNW2001 field study.

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