VOC/NO\textsubscript{x} SENSITIVITY ANALYSIS FOR OZONE PRODUCTION USING CMAQ PROCESS ANALYSIS FOR THE PACIFIC NORTHWEST

Ying Xie*, Brian Lamb, and Tom Jobson
Department of Civil and Environmental Engineering, Washington State University, Pullman, WA, USA

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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{3})) and its relationship with precursors, namely NO\textsubscript{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\textsubscript{3})), and 3) to evaluate P(O\textsubscript{3}) sensitivity to changes in VOC and NO\textsubscript{x} emissions in the region using these indicators.

2. METHODOLOGY

The VOC/NO\textsubscript{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\textsubscript{3}), 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\textsubscript{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\textsubscript{3}).

To investigate ozone production rate (P(O\textsubscript{3})) and its relationship with precursors, P(O\textsubscript{3}) and radical production rate (Q) from process analysis along with NO\textsubscript{x} and total VOC reactivity (VOC\textsubscript{R}) were analyzed. Radical production rate (Q) is the sum of production rate of new radicals (OH+RO\textsubscript{2}+HO\textsubscript{2}). Total VOC reactivity (VOC\textsubscript{R}) was calculated based on OH reactivity.

To investigate the behavior of local indicators for instantaneous odd oxygen production rate (P(O\textsubscript{3})), two model sensitivity runs were conducted by decreasing the anthropogenic VOC and NO\textsubscript{x} emissions by 30% from the base case. The grid cells are related to VOC or NO\textsubscript{x} sensitive regimes according to the following criteria. Grid cells with \(\partial P(O_3)/\partial E_{NOx} = 0\) are close to ridgeline conditions. NO\textsubscript{x} sensitive cells are associated with \(\partial P(O_3)/\partial E_{NOx} > 0\), whereas VOC sensitive cells are linked to \(\partial P(O_3)/\partial E_{NOx} < 0\). Equal sensitivity is thought to

*Corresponding author: Ying Xie, Department of Civil & Environmental Engineering, Sloan Hall 101, Spokane Street, Washington State University, Pullman, WA 99164-2910; e-mail: ying_xie@wsu.edu
occur in these grid cells when 
\( \partial P(O_3)/\partial E_{NOx} = \partial P(O_3)/\partial E_{VOC} \).

The five indicators \( f_{OH\cdotHC}, f_{HO2\cdotNO}, P(H_2O_2)/P(HNO_3), O_3/NO_x, \) and \( L_V/Q \) 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.

4. THE BEHAVIOR OF LOCAL INDICATORS FOR P(O\(_3\))

Figure 3 shows \( \partial P(O_3)/\partial E \) as a function of \( f_{HO2\cdotNO} \) in the base case at 13 LST on July 26-28, 1998 within the Portland sub-domain. There is a narrow range \( f_{HO2\cdotNO} \) values associated with \( \partial P(O_3)/\partial E_{NOx} = 0 \), 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 \( f_{OH\cdotHC}, P(H_2O_2)/P(HNO_3), O_3/NO_x, \) and \( L_V/Q \) also appear to be able to clearly distinguish NO\(_x\) and VOC sensitive conditions (not shown).
5. SENSITIVITY TO VOC/NO\textsubscript{x} CHANGES BASED ON INDICATORS

Contour plot for \(f_{\text{HO}_2:NO}\) 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\textsubscript{x} limited, but not far from the ridgeline. The contour plots of other indicators show very consistent patterns regarding to VOC and NO\textsubscript{x} sensitive regions (not shown here).

![Contour plot](image)

Figure 4. Surface contour plot of \(f_{\text{HO}_2:NO}\) at 13 LST on July 27, 1998.

6. CONCLUSIONS

Maximum ozone production rate was found to be 30-40 ppb hr\textsuperscript{-1}, with NO\textsubscript{x} concentrations of 5-15 ppb and total VOC reactivity of 8-12 s\textsuperscript{-1}. All five indicators \((f_{\text{OH},\text{HO}_2}, f_{\text{HO}_2:NO}, P(H_2O_2)/P(HNO_3), O_3/NO\textsubscript{x}, \text{ and } L_{\text{NO}}/Q)\) appear to be able to distinguish NO\textsubscript{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\textsubscript{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.

7. REFERENCES


Sillman, S., 1995: The use of \(NO_\text{y}, HCHO, H_2O_2,\) and \(HNO_3\) as indicators for ozone-\(NO_\text{y}\)-hydrocarbon sensitivity in urban locations, J. Geophys. Res., 100, 14175-14188.

