ATMS 458 Problem Set #4: Urban Photochemistry Data Analysis

Due: November 24, 2010 (see also the overview document)

O_3 Production Rate And its Dependence on the HO_x Production Rate and NO_x in an Urban Area

I. O_3 Production Rate

Here we will use observations to calculate the rate of ozone production outside of Nashville, TN to examine how the rate changes on the hourly and daily timescale and what environmental parameters it depends on.

1. $NO + O_3 \rightarrow NO_2 + O_2$ $k_1 = 2.2 \times 10^{-12} \exp(-1430/T)$ $cm^3\ molec^{-1}\ s^{-1}$
2. $NO_2 + hv \rightarrow NO + O$
3. $O + O_2 + M \rightarrow O_3$
7. $NO + HO_2 \rightarrow OH + NO_2$ $k_7 = 3.6 \times 10^{-12} \exp(250/T)$ $cm^3\ molec^{-1}\ s^{-1}$
8. $NO + RO_2 \rightarrow RO + NO_2$

1. Write a steady state expression for NO or NO_2 that says the rate of $NO \rightarrow NO_2$ conversion is equal to the rate of $NO_2 \rightarrow NO$ conversion, including explicitly the role of HO_2 and RO_2 radicals (using the variable "k_8" to designate the rate constant for reaction 8).

2. If the rate constant for reaction 8 is equivalent to that for reaction 7 (i.e. $k_8 = k_7$), write an expression which shows that you can calculate the O_3 production rate (P_{O3}) only knowing k1, NO, NO_2, O_3 and j_{NO2}. P_{O3} was derived in lecture. You should also note that you could solve for the quantity $XO_2 = HO_2 + RO_2$ (the sum total peroxy radicals).

3. Use the above expression to calculate P_{O3} at Cornelia Fort. For convenience convert this calculation to units of "ppb/hr". Plot this quantity vs. sos_time and zoom in on 2-3 days. What type of behavior do you see over the day, is it the same day-to-day? Plot P_{O3} versus sos_tod. What time does P_{O3} typically reach a maximum? What is a *typical* maximum value at this time?

4. In your plot of P_{O3} vs. sos_time, do you notice a period or periods of time where P_{O3} values are generally unphysical? That is, a period of time when the average P_{O3} is likely negative? Why do you think that is? *Hint* What assumption did you make to calculate P_{O3}, and what factors are leading to invalidate that assumption?

II. HO_x Production Rate

A primary source of HO_x radicals is the photolysis of O_3 to $O(^1D)$ which subsequently reacts with H_2O to form two OH.

1. O_3 + hv → $O(^1D)$ + O_2 j_o3
2. $O(^1D)$ + N_2→ $O(^3P)$ + N_2 k_{10} = 1.8 x 10^{-11}.*exp(110../T) cm^3 $molec^{-1}$ s^{-1}
3. $O(^1D)$ + O_2→ $O(^3P)$ + O_2 k_{11} = 3.2 x 10^{-11}.*exp(70../T) cm^3 $molec^{-1}$ s^{-1}
4. $O(^1D)$ + H_2O → 2OH k_{12} = 2.2 x 10^{-10} cm^3 $molec^{-1}$ s^{-1}

1. Plot j_o3 (this is for O^1D production) and j_no2 versus sos_tod on separate plots (or a subplot if you remember how to do that). Offer explanations of similarities and differences between the shapes and variations of the j-values vs time of day.

2. Write a rate expression for the production rate of OH (p_oh_o1d) in terms of $O(^1D)$, H_2O and the necessary rate constants.

3. Assume $O(^1D)$ is in a steady-state, write an expression for its concentration using the above reactions, and then write a new expression for the OH production rate using the expression of $[O(^1D)]_{ss}$.

4. Using the above expression for the OH production rate from $O(^1D)$+H_2O, calculate p_oh_o1d at Cornelia Fort. For convenience convert this to units of **ppt/s.** Plot this quantity versus sos_tod. What is the typical daily behavior of p_oh_o1d? When does it maximize? Is this similar to the time P_{O3} maximizes? What is a typical maximum for p_oh_o1d?

5. The photolysis of oxygenated compounds such as formaldehyde can also be a significant source of HO_x radicals. Calculate the HO_x production rate via the photolysis of formaldehyde assuming that the photolytic reaction is H_2CO + hv (+2O_2)→ 2HO_2 + CO. Note that O_2 doesn't enter into the rate calculation. Convert this quantity (p_hox_h2co) into units of ppt/s. How does this HO_x source compare on average to p_oh_o1d? Is one consistently larger? Does the importance of this HO_x source depend on time of day, and why or why not?

6. Create a vector for the total HOx production rate, p_hox = p_oh_o1d+p_hox_h2co; Plot the percent contribution of H_2CO photolysis to the total HO_x production rate versus sos_tod. What is a typical contribution of this HO_x source during the day? Is there a time of day when it is generally more important? If so, why?

7. Finally, plot OH mixing ratios versus the total HO_x production rate. What type of general behavior do you observe?

III. Dependence of P_{O3} on P_{HOx} and NO

1. Plot P_{O3} versus no_ppb. What do you see? Can you discern any behavior that is significant?

2. To help understand what causes the spread of P_{O3} versus NO, group PO3 into three categories: 1. when p_hox > 0.7, 2. when p_hox > 0.4 and p_hox < 0.6, 3. p_hox > 0.1 and p_hox < 0.3.

Matlab hint: ***high = find(p_hox>0.7); med=find(p_hox > 0.4 & p_hox < 0.6); low = find(p_hox > 0.1 & p_hox < 0.3);***
Excel hint: ***=IF(AA5>0.7,V5," "); =IF(AND(AA5>0.4,AA5<0.6),V5," "); =IF(AND(AA5>0.1,AA5<0.3),V5," ")*** *where AA5 is p_hox and v5 is p_o3*

Make sure your p_hox is in units of ppt/s. **Explain** how these indices will help you examine the dependence of P_{O3} on NO?

3. Plot P_{O3} vs NO for each regime represented by the above indices on a semi-log scale.
Matlab hint: ***semilogx(no_ppb(high),po3(high),'bo', no_ppb(med),po3(med),'g*', no_ppb(low),po3(low),'rs');grid on;zoom on***

The above command should be all on one line. *Zoom in on your plot so that the x axis is between ~ 0.01 ppb and 2 ppb, and so you can clearly see the bulk of variance on the y-axis.* Describe the behavior of P_{O3} versus NO in the three regimes. Is there a regime where P_{O3} is highest, on average? Does P_{O3} in different regimes show different sensitivity to NO? Is there evidence that the behavior matches with the theoretical behavior presented during lectures?

4. From your above plot, is it fair to say that ozone production at Cornelia Fort is generally NO_x limited? Is there an NO concentration above which the plot indicates ozone production might be NO_x-saturated for a given regime? *It is helpful to examine the P_{O3} vs NO for each individual regime.*