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Sensitivity of ozone production rate to ozone precursors

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Abstract. The photochemical equations describing O_3 formation in the lower troposphere contain 2 major sink terms for free radicals; combination reactions and reactions with NO_x. Knowing the fraction of radicals removed by reactions with NO_x, termed L_N/Q, allows one to predict the sensitivity of O_3 production to NO and VOCs. We derive an analytic formula that gives L_N/Q in terms of readily measured O_3 precursors and test this formula using constrained steady state calculations based on field observations gathered in Phoenix, Arizona. The formula quantifies well-known results regarding the effects of dilution, oxidation, and the production of oxidants on the transition from VOC to NO_x sensitive behavior as an air parcel is advected away from an urban source.

1. Introduction

Ozone is formed in the lower atmosphere by a sequence of chemical reactions requiring sunlight, NO_x ($NO + NO_2$), and VOCs. Determining the relation between O_3 and its precursors has been the object of more than 4 decades of research [*NARSTO*, 2000]. It has been found that O_3 formation depends on NO_x and VOC emissions in a complicated and non-linear way. Several qualitative generalizations are, however, possible. In an urban plume O_3 becomes more VOC sensitive (i.e., more responsive to a change in VOCs) at high NO_x to VOC ratios and at high absolute concentrations. As an urban plume is advected away from its source it tends to become more dilute and have a lower NO_x to VOC ratio. For both reasons a plume will evolve in the direction of being VOC sensitive near its source to being NO_x sensitive far away [*Staffelbach et al.*, 1997; *Duncan and Chameides*, 1998; *Sillman*, 1999].

In this article we consider the sensitivity of the rate of O_3 production, $P(O_3)$, to changes in atmospheric concentrations of NO_x and VOCs. This problem is a prerequisite to the more complicated problem of determining the response of O_3 to an emissions change. The behavior of $P(O_3)$ is a property of an air mass and can be characterized reasonably well by means of chemical measurements. In contrast, a sensitivity to an emissions change is not a local property [*Kleinman*, 2000]. It depends on the entire time history of an air mass and therefore cannot be directly observed, although several indirect techniques are available [*Cardelino and Chameides*, 1995; *Sillman*, 1995]. In a general sense, we know that the two problems must be related as O_3 concentration is due to O_3 production occurring over the time history of an air mass.

We showed in a previous study [*Kleinman et al.*, 1997] that the sensitivity of $P(O_3)$ to NO and VOCs is given by a simple analytic function of L_N/Q, the fraction of free radicals removed by reactions with NO_x. L_N/Q enters our equations from a starting point which is a conservation statement for free radicals (also known as odd-hydrogen and consisting primarily of OH, HO_2, and RO_2s). Production of free radicals occurs principally from photolysis reactions. Radicals are removed by two major categories of reactions; combination reactions between radicals, including $HO_2 + HO_2 \rightarrow H_2O_2$; and reactions between radicals and NO_x, principally $OH + NO_2 \rightarrow HNO_3$. The conservation statement for free radicals can be written as,

$$Q = L_R + L_N \quad (1)$$

where Q is the production rate, L_R is the loss rate due to radical-radical reactions, and L_N is the loss rate due to all reactions of radicals with NO_x.

In this study we examine the variable L_N/Q. We provide an analytic formula that gives L_N/Q in terms of O_3 precursors. This formula can be used to estimate NO_x and VOC sensitivity based on readily measured concentrations. From the analytic expression for L_N/Q it is easy to show how NO_x and VOC sensitivity depends on the NO_x to VOC ratio and on absolute concentration.

2. Experiment

During the late spring of 1998, the Atmospheric Chemistry Program of DOE in collaboration with the Arizona Department of Environmental Quality conducted a photochemistry field campaign in the Phoenix metropolitan area. The DOE G-1 aircraft was used to sample the atmosphere upwind, over, and downwind of the metropolitan area. Measurements included, O_3, CO, VOCs, NO, NO_2, NO_y, HCHO, H_2O_2, organic peroxides, actinic flux, temperature, and dew point. We will use these observations to illustrate and check a series of analytic results that we believe are generally applicable to urban plumes.

Characteristics of the Phoenix air basin during the field campaign were a very low humidity, high temperature and solar

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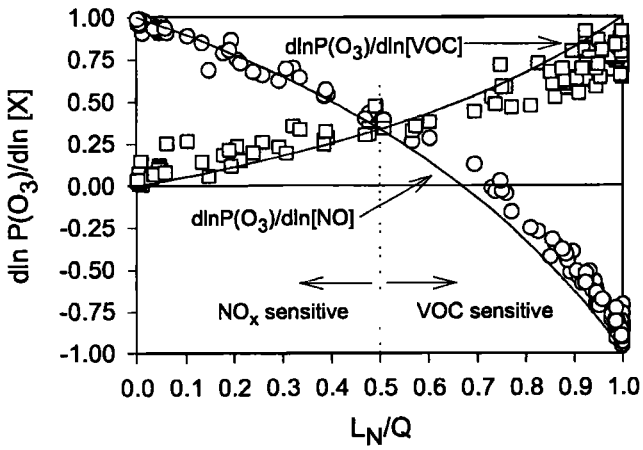

Figure 1. The relative sensitivity of O_3 production rate to [NO] and [VOC], $dlnP(O_3)/dln[NO]$ and $dlnP(O_3)/dln[VOC]$, as a function of the fraction of radicals removed by reactions with NO or NO_2, L_N/Q. Symbols are from CSS calculation. Lines are the analytic functions (2) and (3). A value of 1 (-1) for $dlnP(O_3)/dln[X]$ means that an n% increase in [X] produces an n% increase (decrease) in $P(O_3)$.

insolation, an emissions mixture dominated by transportation sources, and low biogenic emissions. Twenty two flights were conducted with about half of the flight time used for sampling over high emission rate regions. Clean air was observed in the early morning in the nighttime residual layer and later in the day above the convective boundary layer. A wide range of chemical concentrations were encountered. For example NO_x concentration varied from 70 ppt to 39 ppb, O_3 from 29 to 92 ppb, and CO from a background of about 120 ppb to 470 ppb. Results are presented in greater detail elsewhere [*Fast et al.*, 2000].

3. Model

We have applied a constrained steady state (CSS) photochemical box model to the Phoenix observations. This model uses as input the trace gas concentrations (excluding NO_2) observed from the DOE G-1. The limiting factor in the use of this model is the availability of VOC data which is determined from discrete canister samples. Model predictions include the concentrations of free radicals and NO_2 that are in rapid equilibrium with the observed mixture of trace gases. Of particular importance to this study are predictions of the production rate of O_3, $P(O_3)$; the formation rate of free radicals, Q; and the rate at which radicals are lost by different reaction pathways, L_N and L_R. The kinetic equations in the model are from the chemical mechanisms of *Stockwell et al.* [1990] and *Paulson and Seinfeld* [1992]. PAN is not a calculated variable as it is assumed to be in steady state. The CSS model is the same as previously used and is described in more detail elsewhere [*Kleinman et al.*, 1997; 2000].

CSS calculations have been performed for 123 locations during the Phoenix field campaign. Calculations were repeated with perturbed values of NO or VOCs. A finite difference formula was used to determine the relative sensitivity of $P(O_3)$ to NO and VOCs. In Figure 1 we compare those results with sensitivities calculated from the following formulas derived by *Kleinman et al.* [1997]:

$$dlnP(O_3)/dln[NO] = (1 - 3/2\ L_N/Q)/(1 - 1/2\ L_N/Q) \quad (2)$$

$$dlnP(O_3)/dln[VOC] = (1/2\ L_N/Q)/(1 - 1/2\ L_N/Q) \quad (3)$$

It is seen that the variable L_N/Q provides information on NO_x and VOC sensitivity similar to that obtained from the CSS calculations. A low value of L_N/Q yields NO_x sensitive chemistry; a high value VOC sensitive chemistry. The tendency to produce peroxides under NO_x sensitive conditions and HNO_3 under VOC sensitive conditions was first noted by *Sillman* [1995] and forms the basis of an Indicator Species method. Similar results have already been presented for Nashville, Tennessee and the New York City metropolitan area [*Kleinman et al.*, 1997; 2000].

4. Theory

The derivation of an analytic formula for L_N/Q begins with the conservation condition for free radicals expressed in (1). L_R includes contributions from peroxide formation and biomolecular radical-radical destruction reactions such as $OH + HO_2$. The later reactions are generally less important and will be ignored. As in previous work we express the rate of peroxide formation using an effective rate constant, k_{eff}, defined in terms of the ratio of $[HO_2]$ to $[RO_2]$ and the individual rate constants for forming H_2O_2 and ROOH [*Kleinman et al.*, 1997]. $RO_2 + RO_2'$ reactions are ignored in the analytic equations but not in the CSS model. For each peroxide molecule formed, 2 radicals are lost and

$$L_R = 2\ k_{eff}\ ([HO_2] + [RO_2])^2 \quad (4)$$

Combining (1) and (4), we obtain

$$2\ k_{eff}\ ([HO_2] + [RO_2])^2 = Q(1 - L_N/Q) \quad (5)$$

The primary NO_x - radical reaction is

$$OH + NO_2 \rightarrow HNO_3 \quad (R1)$$

and we approximate L_N as

$$L_N = k_1\ [OH]\ [NO_2] \quad (6)$$

So far we have dealt with sources and sinks of radicals. Under many conditions each radical that is formed participates in a multi-step chain reaction before that radical is removed [e.g., *Sillman et al.*, 1990; *Jeffries and Tonnesen*, 1994; *Seinfeld and Pandis*, 1997; *Tonnesen and Dennis*, 2000]. The chain contains the following 2 links

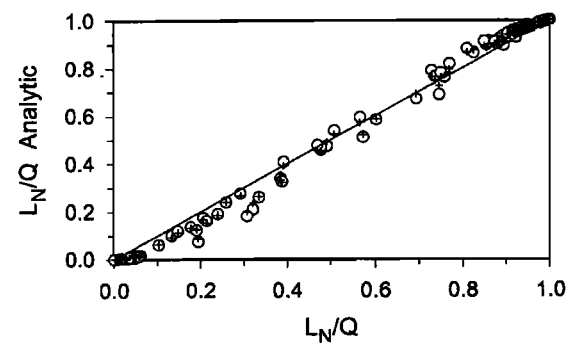

Figure 2. A comparison between L_N/Q calculated from the analytic formula, (12-13), and CSS model. Open symbols use model derived values for HO_2 to RO_2 ratio. Plus signs use a value of 2:1 for this ratio. Line shows 1 to 1 agreement.

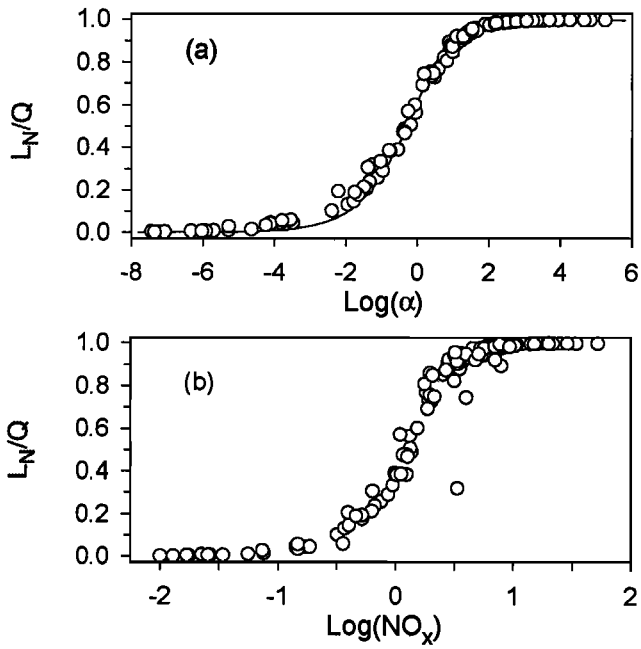

Figure 3. (a) The dependence of L_N/Q on log (α). Solid line is the analytic relation in (12). Data points are determined from Phoenix observations which yield values for α. CSS calculations yield the corresponding values of L_N/Q. (b) The dependence of L_N/Q on log(NO_x).

$$OH + VOC \rightarrow HO_2 \quad (R2)$$

$$HO_2 + NO \rightarrow OH \quad (R3)$$

Note that the full reaction sequence can be more complicated as OH+VOC can produce RO_2s, but eventually (in the absence of a radical loss event) an HO_2 will be produced to regenerate OH. In the limit that chain propagation is much more important than chain initiation (or equivalently, chain termination) we obtain

$$k_2 [OH] [VOC] = k_3 [HO_2] [NO] \quad (7)$$

The term k_2[VOC] in (7) is an abbreviation for a summation over all VOCs, including CO and CH_4, which can participate in (R2).

From this point on no additional approximations are made. A "constant" γ is defined by

$$\gamma = [HO_2]/[HO_2 + RO_2] \quad (8)$$

Substituting (8) into (5), we get

$$2k_{eff} ([HO_2]/\gamma)^2 = Q (1-L_N/Q) \quad (9)$$

Combining (6) and (7) to eliminate [OH] yields

$$[HO_2] = k_2[VOC] L_N/(k_3[NO] k_1[NO_2]) \quad (10)$$

Substituting (10)into (9) gives a quadratic equation for L_N/Q

$$(1-L_N/Q) = \frac{2k_{eff}Q}{\gamma^2}\left[\frac{k_2[VOC]}{k_3[NO]k_1[NO_2]}\right]^2 (L_N/Q)^2 \quad (11)$$

with solution

$$L_N/Q = -\alpha/2 + (\alpha^2 + 4\alpha)^{1/2}/2 \quad (12)$$

where

$$\alpha = \left(\frac{k_1[NO_2]k_3\gamma[NO]}{k_2[VOC]}\right)^2\left(\frac{1}{2Qk_{eff}}\right) \quad (13)$$

Equations (12-13) give L_N/Q in terms of concentrations and parameters which can be readily observed or estimated. Q can be determined to reasonable accuracy by measuring O_3, H_2O, HCHO, and solar intensity. k_{eff} and γ depend on the HO_2 to RO_2 ratio which can be estimated based on specific model calculations or on general experience with similar chemical environments.

5. Comparisons with CSS results

We use the CSS calculations to test the analytic equations for L_N/Q. Figure 2 shows a comparison between L_N/Q obtained from (12-13) and that obtained from a complete CSS calculation. Two sets of results are shown. In one case (12-13) is evaluated using model predictions for the HO_2 to RO_2 ratio. In the other case the evaluation is done without this information using a representative value of 2 to 1 for the ratio. The later calculation is done to assess the utility of applying (12-13) using commonly available measurements. Both cases show reasonable agreement.

Equations (12) and (13) show how L_N/Q depends on NO_x, VOCs, and Q. Perhaps the easiest way to visualize the relation is to note that L_N/Q is a monotonic, increasing function of α. Alpha, in turn, is proportional to $(NO_x^2/VOC)^2/Q$, assuming that both NO and NO_2 are proportional to NO_x. Thus, L_N/Q varies in the same sense as $(NO_x^2/VOC)^2/Q$; i.e., an increase in NO_x yields a higher value of L_N/Q (more VOC sensitive) while an increase in VOCs or Q yields a lower value of L_N/Q (more NO_x sensitive). Because NO_x appears to the 4th power in α and VOCs only to the −2 power, L_N/Q will be affected more by a change in NO_x than by a change in VOCs. Note that, according to (13), it is not the VOC concentration itself that is relevant but the VOC reactivity, k_2[VOC].

Figure 3a illustrates the monotonic dependence of L_N/Q on α. The solid line is the analytic relation given by (12). The data points show the range of values of α observed in Phoenix and the corresponding values of L_N/Q calculated from the CSS model. There is a good correspondence between analytic and calculated points. In the Phoenix data set α varies by 13 orders of magnitude. High values occur in samples taken over the downtown high emission rate region, while the lowest values are from the clean free troposphere. As shown in Figure 3b, most of the variability in α (and hence L_N/Q) is due to NO_x which appears as a 4th power and furthermore varies by almost 3 orders of magnitude. VOC reactivity and radical production rate affect L_N/Q as described by (12-13). However, these variables are less important than NO_x because they appear to a lower power in α and also, for the Phoenix data set, their range of values is relatively small. Figure 3b shows that L_N/Q is near 1 for values of NO_x between the maximum and about 3 ppb. Within this concentration range, $P(O_3)$ is very VOC sensitive and remains so, until NO_x is lowered past the 3 ppb threshold value. This threshold depends on chemical conditions, specifically the concentration of VOCs and the rate of radical production. Further decreases in NO_x are accompanied by a large change in L_N/Q and hence a transition between VOC and NO_x sensitivity.

6. Discussion and Conclusions

As an air parcel is advected away from its source region, concentrations will change due to oxidation of primary pollutants, dilution and the mixing-in of background air, and the formation of secondary pollutants. We can see how these factors affect L_N/Q by expressing α as proportional to NO_x^2 $(NO_x/VOC)^2/Q$. Oxidation reactions will decrease NO_x^2 and also decrease $(NO_x/VOC)^2$ because NO_x is more reactive than the average VOC [*Duncan and Chameides*, 1998]. Dilution, accompanied by the mixing-in of background air, will decrease NO_x^2 and also $(NO_x/VOC)^2$. The later decrease is due to the circumstance that background air tends to have very little NO_x but can have significant VOC reactivity due to CO and CH_4. Production of O_3 and other photochemical oxidation products such as HCHO will increase Q. All of these factors lead to a decrease in L_N/Q and therefore contribute to the transition from VOC to NO_x sensitive behavior as a plume ages.

L_N/Q is in some ways analogous to photochemical age [e.g., *McKeen et al.*, 1990] in that it is a progress variable that specifies where an air mass is in its chemical and dynamic evolution. Input of fresh emissions into the plume can of course upset the monotonic decrease in L_N/Q.

The photochemical equations used in typical calculations treat tens to thousands of discrete species. Recently, the photochemical equations have been treated as a dynamical system and the question has been asked as to what number of species is needed to reproduce the behavior of the full set of equations [*Field et al.*, 2001]. Here we are interested in a related question, the number of variables needed to describe steady states. By working with a radical budget equation we are able to write equations for quantities such as $P(O_3)$ in terms of only 3 variables, NO_x, VOCs, and Q [*Kleinman et al.*, 1997; *Daum et al.*, 2000]. One variable, namely L_N/Q, is sufficient to quantify the NO_x and VOC sensitivity of $P(O_3)$. As we have shown here that variable can be evaluated based on readily measured concentrations.

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