Some theoretical results concerning $O_3$-NO$_x$-VOC chemistry and NO$_x$-VOC indicators

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[1] A series of model results is shown pertaining to ozone, reactive nitrogen (NO$_x$), and peroxides in polluted regions. The results focus on ratios such as $O_3$/NO$_x$ and $H_2O_2$/HNO$_3$ that have been proposed as indicators for $O_3$-NO$_x$-VOC sensitivity. These ratios are shown to correlate with predicted NO$_x$-VOC sensitivity for a variety of zero-dimensional (0-D) and 3-D models, but the correlation varies in situations ranging from relatively clean to highly polluted. The previously identified NO$_x$-VOC transition values for indicators appear to be valid for moderately polluted conditions with 80–150 ppb $O_3$. Changes in indicator behavior are also correlated with the values of a test ratio, $O_3/(2H_2O_2+NO_2)$ which can be evaluated against measurements. Ratios of the form $\Delta O_3/\Delta NO_x$, representing differences relative to background values, are proposed for analyzing NO$_x$-VOC sensitivity in individual urban plumes. Comparisons are made to extent-of-reaction parameters, which have been proposed for evaluating NO$_x$-VOC sensitivity.

INDEX TERMS: 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 3210 Mathematical Geophysics: Modeling; KEYWORDS: ozone, nitrogen oxides, volatile organic compounds (VOC), hydrogen peroxide, photochemical smog

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1. Introduction

[2] The chemistry of ozone and its two main precursors, NO$_x$ and volatile organic compounds (VOC), continues to represent one of the major uncertainties in the field of atmospheric chemistry. In urban areas, uncertainty associated with $O_3$-NO$_x$-VOC chemistry can affect the design of control strategies to reduce ambient $O_3$. In the remote troposphere, $O_3$-NO$_x$-VOC chemistry affects evaluations of the ozone production efficiency per NO$_x$ as well as predicted responses to future changes in emissions.

[3] In recent years a number of works have analyzed the photochemical factors that determine the split into VOC-sensitive and NO$_x$-sensitive regimes [Sillman et al., 1990; Sillman, 1995; Kleinman, 1994; Kleinman et al., 1997; Tonnesen and Dennis, 2000a, 2000b; Jaegle et al., 1998, 2001]. Sillman [1995] and Sillman et al. [1998] proposed that $O_3$-NO$_x$-VOC chemistry could be linked to the ratios of certain measurable species which had different values for NO$_x$-sensitive and VOC-sensitive conditions. If successful, these "NO$_x$-VOC indicators" can provide a powerful tool for evaluating the chemical process leading to ozone formation. However, there is a range of theoretical and practical concerns associated with the proposed indicators. Contradictory results were reported by Lu and Chang [1998] and Chock et al. [1999]. It is especially unclear whether the indicator ratios would show similar behavior for a wide variety of conditions, as proposed by Sillman.

[4] Here, a series of model calculations is used to explore indicator behavior for a variety of conditions, ranging from rural to extremely polluted conditions. The calculations have two purposes: to identify how the behavior of indicator ratios may vary under different conditions; and to identify the link between the proposed indicator ratios and the chemistry of odd hydrogen radicals. The link between indicator ratios and odd hydrogen radicals, presented previously by Sillman [1995], Kleinman [1994], and Kleinman et al. [1997] will be used to explain variations in the behavior of indicator ratios for different conditions. Model results will also be used to identify broad correlation patterns among ozone, reactive nitrogen, and peroxides that are associated with NO$_x$-sensitive and VOC-sensitive chemistry.

[5] Results will be shown from both zero-dimensional (0-D) calculations and 3-D models. It should be emphasized that valid predictions for species concentrations must be based on 3-D models, which include more detailed representation of dynamical processes and which include comparison with measured values. The 0-D calculations are useful because they can extend previous analyses to new conditions (which do not match observed cases, but which may correspond to future situations) and because they allow
2. Theoretical Background

[6] The split between NO\(_x\)-sensitive and VOC-sensitive conditions is well-known, and illustrated by ozone isopleth plots (e.g., see Figure 1). For conditions with relatively high VOC and low NO\(_x\), O\(_3\) increases with increasing NO\(_x\) and is relatively insensitive to changes in VOC. For conditions with relatively low VOC and high NO\(_x\), O\(_3\) increases with increasing VOC and decreases with increasing NO\(_x\). An analogous split between “NO\(_x\)-sensitive” and “NO\(_x\)-saturated” regimes occurs in the remote troposphere, although for remote conditions O\(_3\) increases with increasing VOC even in the NO\(_x\)-sensitive regime [Jaegle et al., 1998, 2001].

[7] The split between NO\(_x\)-sensitive and VOC-sensitive regimes is driven by the chemistry of odd hydrogen radicals. As shown by Sillman et al. [1990] and Sillman [1995], the NO\(_x\)-VOC split was attributed to the relative rate of formation of peroxides (via HO\(_2\)-HO\(_2\) and HO\(_2\)-RO\(_2\) reactions) relative to nitric acid formation (via OH + NO\(_2\)). NO\(_x\)-sensitive conditions occur when peroxides dominate over nitric acid as radical sinks, while NO\(_x\)-saturated conditions occur when nitric acid dominates. As shown by Kleinman [1994], NO\(_x\)-VOC sensitivity was attributed to the relative source strengths of odd hydrogen radicals (S\(_H\)) and odd nitrogen (S\(_N\)), summed over the period of ozone production for an air parcel. (Abbreviations are summarized in section 8.) VOC-sensitive chemistry occurred when the odd nitrogen source exceeded the source of odd hydrogen. Subsequently Kleinman et al. [1997] found that the instantaneous rate of ozone production was VOC-sensitive whenever the instantaneous loss rate for odd nitrogen (L\(_N\)) was greater than half the total odd hydrogen source (L\(_H\)/Q > 0.5, as given by Kleinman et al. [1997]). This formulation is equivalent to that of Sillman [1995] if net formation of PAN and other organic nitrates is assumed to be zero. From Sillman [1995], odd hydrogen sources must be in steady state with its three major sinks:

\[
S_H = 2P_{perox} + P_{HNO3} + P_{PANs}
\]

where \(P_{perox}\) and \(P_{HNO3}\) represent production rates for peroxides (including H\(_2\)O\(_2\) and organic peroxides) and HNO\(_3\), and \(P_{PANs}\) represents net photochemical production of PAN and higher order analogues. VOC-sensitive chemistry would occur whenever \(P_{HNO3}\) exceeds 2\(P_{perox}\). In terms of \(S_H\), VOC-sensitive chemistry would occur for the following conditions:

\[
S_H < \xi L_N
\]

or

\[
S_H - P_{PANs} < 2P_{HNO3}
\]

[8] This modified form serves to emphasize that the NO\(_x\)-VOC split is associated with formation of nitric acid but is not affected by formation of PAN [Sillman et al., 1990; Tonnesen and Dennis, 2000b].

[9] The above results were derived by Sillman [1995] and Kleinman et al. [1997] based on the following simplified photochemistry. The ozone production sequence includes:

\[
\begin{align*}
(R1) & \quad VOC + OH \rightarrow RO2 \\
(R2) & \quad RO2 + NO \rightarrow NO2 + HO2 + intermediate VOC \\
(R3) & \quad HO2 + NO \rightarrow OH + NO2 \\
(R4) & \quad NO2 + h\nu \rightarrow NO + O3 \\
(R5) & \quad O3 + h\nu \rightarrow H2O2 \\
(R6) & \quad HCHO + h\nu \rightarrow 2H2O2 \\
(R7) & \quad HO2 + HO2 \rightarrow H2O2 \\
(R8) & \quad HO2 + RO2 \rightarrow ROOH \\
(R9) & \quad O3 + NO2 \rightarrow HNO3 \\
(R10) & \quad CH3CO3 + NO2 \rightarrow PAN
\end{align*}
\]

[10] Similar reaction sequences apply for many individual VOC, which produce various radical chains with the form RO\(_2\) and with subsequent reactions analogous to (R2). Reaction (R1) (VOC + OH) is the rate limiting step for this sequence, and its rate depends on the availability of OH. OH in turn depends on the balance of sources and sinks of odd hydrogen radicals (including OH, HO\(_2\) and RO\(_2\)), which includes the following sources:

\[
\begin{align*}
(R5) & \quad O3 + h\nu \rightarrow H2O2 \\
(R6) & \quad HCHO + h\nu \rightarrow 2H2O2 \\
(R7) & \quad HO2 + HO2 \rightarrow H2O2 \\
(R8) & \quad HO2 + RO2 \rightarrow ROOH \\
(R9) & \quad OH + NO2 \rightarrow HNO3 \\
(R10) & \quad CH3CO3 + NO2 \rightarrow PAN
\end{align*}
\]

[11] Other sources include the photolysis of higher aldehydes and various alkene-O\(_3\) reactions [Paulson and Orlando, 1996]. Sinks include the following.

\[
\begin{align*}
(R11) & \quad CH3CO3 + NO2 \rightarrow PAN
\end{align*}
\]

Figure 1. (opposite) Isopleths as a function of the average emission rate for NO\(_x\) and VOC (10\(^{12}\) molec. cm\(^{-2}\) s\(^{-1}\)) in 0-D calculations. The isopleths represent conditions in the first layer during the afternoon following 3-day calculations, at the hour corresponding to maximum O\(_3\). Isopleths are shown for (a) O\(_3\) (ppb); (b) S\(_H\)/S\(_N\); (c) (H\(_2\)O\(_2\) + ROOH)/HNO\(_3\); (d) O\(_3\)/HNO\(_3\); (e) O\(_3\)/NO\(_2\); (f) O\(_3\)/S\(_H\); (g) \(\Delta O3/\Delta HNO3\); (h) \(\Delta O3/\Delta NO2\); (i) \(\Delta O3/\Delta S_H\); (j) O\(_3\)/(2H\(_2\)O\(_2\) + 2ROOH + NO\(_2\)); (k) \(\Delta O3/\Delta(2H\(_2\)O\(_2\) + 2ROOH + NO\(_2\))\); and (l) O\(_3\)/PAN. Isopleths are shown as solid green lines. Isopleths for O\(_3\) (red dashed lines) are superimposed on the other isopleth plots. The short blue dashed line represents the transition from VOC-sensitive to NO\(_x\)-sensitive conditions.
forming reactions (R7) and (R8) are the dominant radical sinks, then the radical steady state reduces to

$$\text{HO}_2 \propto \sqrt{S_{H} - P_{\text{pan}}/\text{NO}_2}$$

(3)

where the similar but more complex RO2 has been omitted for simplicity. The production rate for O3 is approximately equal to the rate of reactions (R2) and (R3) (HO2 + NO, RO2 + NO). This rate increases with increasing NO3 but has little direct dependence on VOC. By contrast, when the reaction to form nitric acid (R9) is the dominant radical sink, then the radical steady state becomes

$$\text{OH} \propto (S_{H} - P_{\text{pan}})/\text{NO}_2$$

(4)

[12] The production rate for O3 is proportional to the rate of the VOC + OH reactions (R1), and this rate increases with increasing VOC and decreases with increasing NOx.

[13] Tonnesen and Dennis [2000a] presented a similar results with slightly different terminology. Tonnesen and Dennis analyzed ozone formation in terms of radical formation (equivalent to SH here), radical termination (through production of peroxides, HNO3 and organic nitrates) and radical propagation (through VOC + OH and HO2 + NO, reactions (R1), (R2), and (R3)). The radical propagation reactions are directly associated with ozone formation and were regarded as synonymous with ozone production in Sillman [1995].

[14] Kleinman et al. [1997], Tonnesen and Dennis [2000a], and Kirchner et al. [2001] have developed methods for evaluating whether the instantaneous rate of ozone production is sensitive to NOx or VOC. This instantaneous sensitivity should be distinguished from the sensitivity associated with ozone concentrations, which are affected by upwind emissions, transport, and photochemistry. As discussed by Kirchner et al. [2001], Sillman [1995] identified indicator ratios that relate specifically to the NOx-VOC sensitivity of ozone concentrations rather than instantaneous production rates. The subsequent results all relate to the NOx-VOC dependence of ozone concentrations, based on photochemical production over extended periods of time.

[15] The NOx-VOC indicators proposed by Sillman [1995] included the following: O3/NOx (where NOx represents total reactive nitrogen); O2/NOx (where NOx represents summed NOx reaction products, or NOx(NO3); O3/HNO3; H2O2/HNO3; H2O2/NO2; and the equivalent ratios with summed H2O2 and organic peroxides. The ratios involving peroxides were justified based on the role of peroxides and nitric acid as sinks for odd hydrogen radicals. It is more difficult to explain why ratios such as O3/NOx should be associated with NOx-VOC sensitivity. Sillman [1995] suggested that O3 was roughly proportional to the odd hydrogen source, S_H. The ratio O3/NOx is then analogous to S_H/L_S, which is related to NOx-VOC sensitivity for reasons given above. This will be discussed in more detail in section 4.

3. Methods

Results will be shown from a series of simplified 0-D calculations and from previously published 3-D model simulations. The 0-D calculations use 2-layer model [Sillman et al., 1990] which has been adapted from urban photochemical box models. The model consists of a lower layer, representing the ambient boundary layer, and an upper residual layer representing conditions aloft at night. During the morning hours the height of the lower layer expands and the contents of the residual layer become entrained into the model lower layer. During the evening hours the height of the lower layer decreases and the remainder becomes part of the residual layer. The height of the lower layer varies from 200 m. at night to 1500 m. in the afternoon, representing typical behavior for a boundary layer during pollution events. The model residual layer extends from the top of the lower layer up to 1600 m. Emissions are entered into the lower layer as concentrations based on specified emission rates and the layer height. Although this model includes some rudimentary dynamics in one (vertical) dimension, it will be referred to as a 0-D model, as realistic dynamics are not included.

[17] Photochemistry and dry deposition are as shown by Sillman et al. [1998]. The photochemical mechanism is based on the work of Lurmann et al. [1986] with various modifications, including updated reaction rates from DeMore et al. [1997], isoprene chemistry from Paulson and Seinfeld 1992], RO2-RO2 reactions from Kirchner and Stockwell [1996], and organic peroxide production rates from Stockwell et al. [1997]. Aerosol reactions are not included. One weakness of this photochemical representation is that it has not been tested against environmental chamber experiments. By contrast, the RACM [Stockwell et al., 1997] and SAPRC [Carter, 2000] have been extensively tested against chamber data. The current mechanism has been retained here because it includes many reactions that are important in the rural/remote troposphere. Also, because aerosol reactions are not included, the calculations do not account for the formation of aerosol nitrate (NO3) from heterogeneous reaction with ammonia. HNO3 in these calculations should be viewed as equivalent to the sum of HNO3 and NO3; Martilli et al., 2002].

[18] Calculations were performed for 3-day time periods with diurnally varying emissions, for a wide variety of anthropogenic VOC and NOx emission rates. Specification of VOC was based on average speciation in the NAPAP 1990 inventory [Environmental Protection Agency (EPA)], 1993]. Diurnal variations were based on average diurnal variations in the same inventory. In the standard series of calculations emissions rate were constant (except for the diurnal variation) throughout the 3-day period. Alternative calculations were performed with higher emissions on the third day, representing a situation in which processed rural air would enter an urban area on the third day. Initial conditions were typical for remote air in the U.S.: 40 ppb O3, 1 ppb H2O2, 15 ppt NO and NO2, and 5 ppb C VOC.

[19] The 3-D simulations are summarized in Table 1.

4. Results From 0-D Calculations

Figure 1 shows isopleths for O3 and for a series of species ratios, shown as a function of diurnal average emission rates for VOC and NOx. The plots represent
conditions during the afternoon of the third day of a 3-day
calculation, at the hour corresponding to maximum O$_3$.
Figure 1a is the standard isopleth plot for O$_3$ and illustrates
the well-known split between NO$_x$-sensitive and VOC-
sensitive (or NO$_x$-saturated) conditions. Figure 1a also
shows the “sensitivity transition” from NO$_x$-sensitive to
VOC-sensitive conditions, defined as follows:

$$\frac{1}{Q_N} \frac{\partial [O_3]}{\partial Q_N} = \frac{1}{Q_H} \frac{\partial [O_3]}{\partial Q_H}$$

(5)

where [O$_3$] represents ozone concentrations and Q$_N$ and Q$_H$
represent emission rates for NO$_x$ and VOC. Using this
definition, the sensitivity transition represents the point at
which a given percent reduction in either NO$_x$ or VOC
would result in the same reduction in O$_3$. As shown in
Figure 1a, reduced NO$_x$ would result in lower O$_3$ than an
equivalent percent reduction in VOC when Q$_H$/Q$_N$ is higher
than its value at the transition line. When Q$_H$/Q$_N$ is lower
than the transition value, then reduced VOC would result in
lower O$_3$ than an equivalent percent reduction in NO$_x$. The
same transition line is included for reference in the other
isopleth plots.

[21] Figure 1b shows the calculated ratio S$_H$/S$_N$, where
S$_H$ and S$_N$ represent calculated sums of the source of odd
hydrogen and odd nitrogen over the 3-day period. This ratio
is similar to the ratio used by Kleinman et al. [1997] to
analyze instantaneous ozone chemistry, but here they rep-
resent sums for an extended period of ozone production
(including nighttime) rather than an instantaneous condi-
tions. There is some ambiguity about this ratio in multiday
calculations, because the exact value of S$_H$/S$_N$ depend on
the time period over which S$_H$ is summed and because for
realistic conditions an air parcel will include a wide variety
of ozone production rates over its photochemical history. In
these simplified calculations, ozone production occurs con-
tinuously over the 3-day period with relatively little varia-
tion for each individual calculation. We have summed S$_H$
and S$_N$ over the full 3 days for both model layers as
molecules produced or emitted (rather than molecules per
volume). As shown below, this provides a useful way to
identify differences between calculations that represent
equivalent air mass histories but with very different amounts
of precursors.

[22] As shown in the figure, the ratio S$_H$/S$_N$ is closely
associated with NO$_x$-VOC sensitivity and the transition
from NO$_x$-sensitive to VOC-sensitive conditions is
associated with a specific value of S$_H$/S$_N$. This transition
value (S$_H$/S$_N = 2$) remains for emission rates varying by a
factor of 100, and for O$_3$ varying from 60 to 600 ppb. Higher
S$_H$/S$_N$ is associated with NO$_x$-sensitive conditions and
lower values with VOC-sensitive conditions. An equiva-

tent transition value (L$_H$/L$_N = 0.5$) was found by Kleinman
et al. [1997] for the NO$_x$-VOC variation of instantaneous
ozone production. The ratio S$_H$/S$_N$ cannot be measured,
but it provides a theoretical basis for identifying measur-
able species ratios as potential NO$_x$-VOC indicators.

[23] The region with S$_H$/S$_N < 1$ is also of interest, because
this corresponds to conditions in which the source of
radicals is not sufficient to oxidize the total amount of
NO$_x$ emitted into the air mass. In this region ozone
concentrations are sharply lower. The ratio NO$_x$/NO$_x$,
a measure of the extent of photochemical processing, increases
sharply for S$_H$/S$_N$ less than one (see Figure 7). This is
discussed more in section 6.

[24] Figure 1c shows the ratio (H$_2$O$_2$ + ROOH)/HNO$_3$.
The value of this ratio is also closely associated with NO$_x$-
VOC sensitivity, although the NO$_x$-VOC transition value is
not uniformly constant. The transition value is 0.5 for O$_3$
below 250 ppb. A slightly higher value (0.5–0.6) was
found in the 3-D model reported by Sillman et al. [1998].
At higher emission rates and higher O₃ the transition value drifts lower, reaching 0.2 at 500 ppb O₃. The NOₓ-sensitive and VOC-sensitive regions of the isopleth plot are associated respectively with much higher and lower values of the ratio.

[25] The ratio H₂O₂/HNO₃ shows a similar close association with NOₓ-VOC sensitivity, and again the NOₓ-VOC transition value tends to decrease at higher O₃ and higher emission rates. Referring to Figure 1c, the most useful information about these ratios is the value along the sensitivity transition of the isopleth plot. These values are shown plotted against O₃ along the sensitivity transition in Figure 2. The transition value for H₂O₂/HNO₃ varies from 0.3 at 100 ppb O₃ to 0.07 at 400 ppb O₃. The transition values at 150 ppb O₃ in these calculations all correspond closely with transition values in 3-D simulations reported by Sillman et al. [1998].

[26] The ratio O₃/HNO₃ (Figure 1d) both show a general correspondence with NOₓ-VOC sensitivity, but the correspondence is not as clear and the transition value shows greater variation. The ratio O₃/NOₓ (Figure 1e) shows a significantly worse correspondence with NOₓ-VOC sensitivity. There is a general (though imperfect) correspondence between O₃/NOₓ and NOₓ-VOC sensitivity for O₃ below 200 ppb, but the correspondence breaks down for higher O₃. When VOC emissions are high (corresponding to high O₃ at the sensitivity transition) the ratio O₃/NOₓ appears to vary in direct proportion to VOC emissions and does not increase (or may even decrease) with increasing NOₓ. The transition value of O₃/HNO₃ and O₃/NOₓ (i.e., the value along the NOₓ-VOC sensitivity transition) decreases as emission rates increase. This variation along the transition value is also shown in Figure 2b. Similar results were reported by Tommesen and Dennis [2000b] and Kirchner et al. [2001].

[27] The behavior of O₃/NOₓ and O₃/HNO₃ can be understood by regarding them as an imperfect surrogate for Kleinman’s ratios Sₓ/Sₙ or Sₓ/Lₓ. It was shown above that Sₓ/Sₙ is correlated with NOₓ-VOC sensitivity for the entire range of 0-D calculations used here. O₃/NOₓ can be expressed as a function of Sₓ/Lₓ as follows:

\[
\frac{O₃}{NOₓ} = \frac{Sₓ}{Lₓ} \left[ \frac{Lₓ}{NOₓ} \right] \left[ \frac{O₃}{Sₓ} \right]
\]

[28] Based on Figure 1b, if O₃/NOₓ were directly proportional to Sₓ/Sₙ it would be expected to correlate with NOₓ-VOC sensitivity and show a near-constant value along the sensitivity transition throughout the range of model calculations. To the extent that O₃/NOₓ shows a different pattern, the differences should be associated with the terms Lₓ/NOₓ and O₃/Sₓ in equation (6a). Therefore, Lₓ/NOₓ and O₃/Sₓ may be regarded as sources of error for O₃/NOₓ as a NOₓ-VOC indicator.

[29] The ratio Lₓ/NOₓ relates the rate of removal of NOₓ (primarily through conversion to the species included in NOₓ) to the NOₓ concentration. As an source of error, this relates to the removal rate of NOₓ. The ratio O₃/Sₓ is more important as a source of error in the indicator concept. Sillman [1995] assumed that Sₓ was likely to be proportional to O₃ because O₃ is a major precursor of odd hydro-

Figure 2. Values of ratios along the NOₓ-VOC transition line shown in Figure 1, for 0-D calculations. Values are shown for (a) (H₂O₂ + ROOH)/HNO₃, (H₂O₂ + ROOH)/ NOₓ, H₂O₂/HNO₃, and H₂O₂/NOₓ; (b) O₃/HNO₃, O₃/NOₓ, O₃/(2H₂O₂ + NOₓ), and O₃/(2H₂O₂ + 2ROOH + NOₓ) (listed in order from highest to lowest); and (c) ΔO₃/ΔH(NO₃), ΔO₃/ΔNOₓ, ΔO₃/ΔNO₂, ΔO₃/Δ(NOₓ + NO₂), ΔO₃/Δ(2H₂O₂ + NOₓ), and ΔO₃/Δ(2H₂O₂ + 2ROOH + NOₓ). The sum H₂O₂ + ROOH is abbreviated as “perox” in the figure labels.
ogen radicals. However, VOC are also important radical sources, so that O3/SH can be expected to decrease with increasing VOC. O3/SH can also vary photochemical age, since SH here represents the summed source over the period of ozone production. The ratio O3/NOx (included in Figure 2b) is useful in this regard because it indirectly accounts for photochemical aging. O3/NOx can be viewed as O3/NO2 multiplied by an aging term (NOx/NOx).

[30] As shown in Figure 1f, the ratio O3/SH decreases with increasing VOC emissions along the sensitivity transition. The change in O3/SH is proportional to the change in O3/NOx along the sensitivity transition, and thus explains much of the change in the transition value of O3/NOx from low to high emissions.

[31] As an alternative approach, it is possible to use difference ratios such as ΔO3/ΔNOx, where ΔO3 and ΔNOx represent differences relative to background values (O3,NO2). The difference ratio is related to the O3/NOx slope, which has been used to evaluate the ozone production efficiency per NOx [Trainor et al., 1993]. The difference ratio is related to Kleinman’s SH/LN as follows:

\[
\frac{\Delta O_3}{\Delta NO_x} = \frac{S_H}{L_N} \frac{L_N}{\Delta NO_x} \frac{\Delta O_3}{S_H} \tag{6b}
\]

[32] The error term is now ΔO3/SH. This term can be interpreted as an ozone production efficiency per primary radical production [see Daum et al., 2000a]. However, since the reaction sequence leading to production of radicals from secondary hydrocarbons is similar to the reaction sequence leading to production of O3, it is possible to view ΔO3/SH as a ratio of two closely related photochemical processes. As such, this ratio is likely to show little variation over a wide range of photochemical conditions. The ratio ΔO3/SH is also related to the “chain length”, the ratio of chain propagation to chain termination described by Tonnesen and Dennis [2000a], if chain propagation is viewed as being proportional to production of O3.

[33] As shown in Figures 1g, 1h, and 2c, the ratios ΔO3/ΔHNO3, ΔO3/ΔNO2, and ΔO3/ΔNOx show a good correlation with NOx-VOC sensitivity for O3 below 250 ppb. The values of these ratios along the sensitivity transition still vary from low to high emissions. The correlation between these ratios and NOx-VOC sensitivity becomes substantially worse for O3 higher than 250 ppb, suggesting that these ratios may behave differently in highly polluted environments. The test ratio ΔO3/SH (Figure 1i) also remains nearly constant along the sensitivity transition for O3 below 250 ppb, and decreases with increasing emissions for higher O3. This ratio can also be interpreted as net ozone production efficiency per primary radical production (OPEQ) and compared with previous results from Daum et al. [2000]. Daum et al. reported OPEQ from 1 to 4, higher than the values shown here. However, Daum’s values represent production only and do not include loss terms.

[34] The ratios O3/(2H2O2 + NO2) and O3/(2H2O2 + 2ROOH + NO2) are especially significant because they are directly related to the error terms in equation (6a). The relation can be expressed as follows:

\[
\frac{O_3}{(2H_2O_2 + NO_2)} = \frac{S_H}{L_N} \frac{L_N}{\Delta NO_x} \frac{\Delta O_3}{S_H} \tag{7a}
\]

or, in difference form

\[
\frac{\Delta O_3}{\Delta (2H_2O_2 + NO_2)} = \frac{S_H}{L_N} \frac{L_N}{\Delta NO_x} \frac{\Delta O_3}{S_H} \tag{7b}
\]

[35] Since H2O2 and NO2 represent the major radical sinks, the ratio S_H/(2H2O2 + NO2) is determined almost entirely by the removal rate of H2O2 and NO2. This is analogous to the term L_N/NOx in equation (6a), which is determined by the removal rate of NO2. The terms O3/SH and ΔO3/SH appear identically in equations (6a), (6b), (7a), and (7b). Thus, the ratios O3/(2H2O2 + NO2) and O3/(2H2O2 + 2ROOH + NO2) can be interpreted as a test for errors in the indicator ratio O3/NOx. Because they are associated with ΔO3/SH, these ratios can also be associated with ozone production efficiency per primary radical production and with chain length.

[36] As shown in Figures 1j and 2b, the ratios O3/(2H2O2 + NO2) and O3/(2H2O2 + 2ROOH + NO2) show patterns of variation that are very similar to O3/SH. Previous results from 3-D models and measurements [Sillman et al., 1998] suggested that these ratios should have a near-constant value in photochemically aged air. The results here show a broader pattern of variation. The ratio tends to decrease with increasing O3 along the sensitivity transition, and also decreases (though not consistently) with increasing VOC. The range of ratio values identified by Sillman et al. [1998] (O3/(2H2O2 + NO2) = 6–8) are comparable with the values shown in Figure 2c for the appropriate range of O3 (80–140 ppb). The difference ratio ΔO3/Δ(2H2O2 + 2ROOH + NO2) (Figures 1k and 2c) shows a pattern of variation that is comparable to ΔO3/SH.

[37] Figure 2b shows a direct comparison between the values of O3/NOx, O3/(2H2O2 + NO2) and other similar ratios along the NOx-VOC transition. As shown, these ratios all show a similar tendency to decrease as conditions range from relatively clean to highly polluted. This result is important because it suggests that O3/(2H2O2 + NO2) provides a measurement-based test for the NOx-VOC transition value associated with the indicator ratios. The NOx-VOC transition values for indicators represent model predictions and cannot be tested readily against measurements. Since O3/(2H2O2 + NO2) and O3/(2H2O2 + 2ROOH + NO2) are correlated to the indicator transition values but are not themselves correlated with NOx-VOC sensitivity, they provide an indirect test for the transition values. A similar correlation is found for the difference ratios (Figure 2c).

[38] The behavior of O3/NOx at high VOC is also influenced by the increasingly dominant role of PAN and other organic nitrates. In contrast with HNO3, the ratio O3/PAN does not correlate with NOx-VOC sensitivity (see Figure 1k) [see also Tonnesen and Dennis, 2000b]. At warm temperatures and relatively high NOx (>0.5 ppb) PAN formation reaches an approximate steady state that is proportional to O3, and the ratio O3/PAN decreases with increasing VOC [see Sillman et al., 1990]. The correlation between O3/NOx and NOx-VOC sensitivity breaks down
when PAN and other organic nitrates become the dominant component of NO₂.

[39] In summary, several of the ratios previously identified by Sillman [1995] as NOx-VOC indicators (especially O₃/NO₂ and O₃/HNO₃) appear to show systematic variations in behavior as conditions vary from relatively clean to highly polluted. These variations can be understood conceptually if ratios are viewed as imperfect representations of the theoretical ratio SH/LN, which appears to correlate closely with NOx-VOC sensitivity both in these 0-D calculations and in previous work by Kleinman et al. [1997]. Variations in the behavior of indicator ratios in models is also associated with predicted variations in the ratios O₃/(2H₂O₂ + NO₂) and O₃/(2H₂O₂ + 2ROOH + NO₂), which might be compared with ambient measurements. The next section shows equivalent results from 3-D models.

5. Results From 3-D Calculations

[40] Figure 3 shows O₃ versus NOₓ (afternoon values at the surface) from a composite of 3-D simulations (see summary in Table 1). The simulations include a series of regional-scale simulations in the eastern U.S. (with horizontal extent 1000 km or larger and horizontal resolution 20 × 20 km or 5 × 5 km) and for the San Joaquin valley (California), and urban-scale simulations (with horizontal extent 150–250 km) for Atlanta and Los Angeles. The figure includes results from a modified form of the simulation from Lu and Chang [1998] [see Sillman et al., 2001], which included results that contradicted the original analysis of indicator ratios by Sillman [1995]. Results represent afternoon hours (1500–1600 LST).

[41] The figure also shows predicted NOₓ-VOC sensitivity for each location, based on differences between O₃ in each model base case and in equivalent scenarios with 25% or 35% reductions in anthropogenic VOC and in NOₓ. Locations have been classified according to the following definitions:

1. NOₓ-sensitive: O₃ in the scenario with reduced NOₓ is lower than O₃ in both the base case and in the scenario with reduced VOC at the specified location and hour by at least 5 ppb.
2. VOC-sensitive: O₃ in the scenario with reduced VOC is lower than O₃ in both the base case and in the scenario with reduced NOₓ by at least 5 ppb.
3. Mixed: The scenarios with reduced NOₓ and reduced VOC have O₃ within 5 ppb of each other, and both have O₃ lower than in the base case by at least 5 ppb.
4. NO\textsubscript{x}-titration: O\textsubscript{3} in the scenario with reduced NO\textsubscript{x} is larger than O\textsubscript{3} in the base case by at least 5 ppb, and O\textsubscript{3} in the simulation with reduced VOC is not lower by 5 ppb or more relative to the base case.

[42] All other locations are viewed as insensitive to NO\textsubscript{x} and VOC in the context of the model domain. These typically represent locations with O\textsubscript{3} dominated by transport from outside the model boundary rather than calculated photochemical production.

[43] The locations dominated by NO\textsubscript{x}-titration are usually near large sources of NO. These locations typically have relatively low O\textsubscript{3}, and O\textsubscript{3} has been affected primarily by the reaction O\textsubscript{3} + NO \rightarrow NO\textsubscript{2} in the presence of directly emitted NO rather than by ozone production chemistry. Indicator ratios in these locations can be misleading because the indicator ratios involve photochemical reaction products associated with ozone formation rather than removal. Evaluation of indicator ratios will be based on the ability to distinguish between NO\textsubscript{x}-sensitive and VOC-sensitive ozone production, ignoring the locations dominated by NO\textsubscript{x}-titration.

[44] As shown in Figure 3, NO\textsubscript{x}-sensitive and VOC-sensitive locations are associated with a different range of values in the correlation plots for O\textsubscript{3} versus NO\textsubscript{x} and other ratios. The mixed locations occupy intermediate values between the NO\textsubscript{x}-sensitive and VOC-sensitive locations. Results for peroxides versus HNO\textsubscript{3} are especially useful for identifying NO\textsubscript{x}-VOC sensitivity because there is a large difference between model values associated with NO\textsubscript{x}-sensitive and VOC-sensitive locations. For O\textsubscript{3}/NO\textsubscript{x}, O\textsubscript{3}/ NO\textsubscript{2} and O\textsubscript{3}/HNO\textsubscript{3} the difference between NO\textsubscript{x}-sensitive and VOC-sensitive locations is smaller and therefore more likely to be affected by model uncertainties. Also, locations dominated by NO\textsubscript{x} titration cannot be distinguished from other locations based on peroxides versus HNO\textsubscript{3}, because the process of NO\textsubscript{x} titration has little impact on peroxides or HNO\textsubscript{3}. NO\textsubscript{x}-titration locations are clearly identifiable in the plot of O\textsubscript{3} versus NO\textsubscript{x}.

[45] Previously Sillman [1995] associated NO\textsubscript{x}-sensitive and VOC-sensitive conditions with high and low values of indicator ratios (O\textsubscript{3}/NO\textsubscript{x}, etc.) and identified transition values that separated NO\textsubscript{x}-sensitive and VOC-sensitive locations (O\textsubscript{3}/NO\textsubscript{x} = 6–8, O\textsubscript{3}/NO\textsubscript{2} = 8–10, O\textsubscript{3}/HNO\textsubscript{3} = 12–15). A careful examination of Figure 3 shows that the NO\textsubscript{x}-VOC transition does not correspond exactly to these transition values, and that the transition values of indicator ratios decreases with increasing O\textsubscript{3}. The change in indicator transition values is especially noticeable for O\textsubscript{3} less than 80 ppb (with NO\textsubscript{x}-VOC transitions at O\textsubscript{3}/NO\textsubscript{x} = 11–15, O\textsubscript{3}/NO\textsubscript{2} = 15–20). For O\textsubscript{3} greater than 100 ppb the NO\textsubscript{x}-VOC transition corresponds to the ratio values previously identified by Sillman [1995]. By contrast, NO\textsubscript{x}-VOC transition for ratios involving peroxides (H\textsubscript{2}O\textsubscript{2}/HNO\textsubscript{3} = 0.2–0.3; total peroxides/HNO\textsubscript{3} = 0.3–0.45) do not appear to vary for the range of clean and polluted conditions shown here.

[46] Figure 4 shows the same results in different format, with the indicator ratio O\textsubscript{3}/NO\textsubscript{x} plotted versus O\textsubscript{3} for NO\textsubscript{x}-sensitive and VOC-sensitive locations. This variation in transition ratios in Figures 3 and 4 is broadly consistent with the indicator transition values identified from the 0-D simulations (see Figure 2).

[47] From Figure 3 it appears that the NO\textsubscript{x}-VOC transition might fit more closely to an indicator ratio of the form \( \Delta O_3/\Delta NO_x \), where \( \Delta O_3 \) represents the difference between O\textsubscript{3} at the location in question and the model background O\textsubscript{3} (40 ppb). Indicator ratios of the form \( \Delta O_3/\Delta NO_x \) would also be advantageous for evaluating NO\textsubscript{x}-VOC sensitivity in specific urban areas that include significant transport of O\textsubscript{3} from upwind. As pointed out by Dommen et al. [1999] measured indicator values in plumes from relatively small cities reflect NO\textsubscript{x}-VOC sensitivity associated with region-wide production of O\textsubscript{3} rather than the impact of emissions in the individual urban center. Indicators with the form \( \Delta O_3/\Delta NO_x \) could provide information about individual metropolitan area emissions as well as region-wide conditions. However, determination of background values provides an additional uncertainty for indicators with this form.

[48] In order to identify background concentrations to be used in forming these ratios, the following formalism will be used: background concentrations will be based on the model grid with minimum NO\textsubscript{x} over the relevant portion of the model domain at the hour of interest. Here, we assume that the region of interest might be either (1) an urban plume surrounded by “background” rural concentrations; or (2) a polluted region (such as the eastern half of the U.S.) with well defined upwind conditions. We also assume that there is a specified (afternoon) hour of interest, at a time when surface conditions reflect photochemical production of O\textsubscript{3} in a well-mixed layer. Background concentrations will be set equal to conditions in the model grid with minimum NO\textsubscript{x} at the same hour and for a specified altitude. The location with minimum NO\textsubscript{x} is selected based on a horizontal domain that includes the rural background region surrounding the plume or polluted region. As suggested by Blanchard and Stoeckenius [2001], the model impact of reduced NO\textsubscript{x} and VOC predicted for the location with minimum NO\textsubscript{x} is subtracted from the model impact of reduced NO\textsubscript{x} and VOC at other locations, so that the analysis will not include sensitivity to emissions upwind of the boundary point. Although somewhat arbitrary, this
method is advantageous because the same ratios and equivalent background values can easily be determined from a network of measurements that includes samples within an urban plume and the surrounding rural region. It also avoids the use of morning values to determine background, because these values are influenced by the nocturnal boundary layer and uncertain rates of entrainment from aloft. We have also avoided using the O$_3$/NO$_x$ slope, which is often reported for measured data sets, because the value of this slope is often unclear and may depend on the precise location of the measurements.

The $\Delta$O$_3$/ΔNO$_x$ and other ratios defined in this manner provide specific values at each model location (or at each measurement site) other than the site identified as the rural background. In the subsequent analysis we will use the above formalism to define background values for urban and regional subdomains of individual model scenarios. The model indicator ratios based on these background values will be compared with the predicted impact of reduced NO$_x$ and VOC emissions within the equivalent subdomain.

As shown in Figure 5, the ratio $\Delta$O$_3$/ΔNO$_x$ is strongly correlated with NO$_x$-VOC sensitivity for the group of 3-D simulations included here. There is some overlap between NO$_x$-sensitive and VOC-sensitive locations, with NO$_x$-sensitive values as low as 3 and VOC-sensitive values as high as 5. The NO$_x$-VOC transition value appears to be similar for locations with high and low O$_3$, although the value of $\Delta$O$_3$/ΔNO$_x$ for O$_3$ below 60 ppb is especially sensitive to the assumed background value.

The information in Figure 5 can be conveniently summarized and evaluated by reporting the distribution of ratio values associated with NO$_x$-sensitive and VOC-sensitive locations. In Figure 5 the indicator values for VOC-sensitive locations are lower than values for NO$_x$-sensitive locations, and there is little overlap between the ranges of values. Locations with mixed sensitivity typically have intermediate indicator values. As was done in Sillman et al. [1998] the indicator results for individual simulations are summarized by recording the 5th, 50th and 95th percentile indicator values for NO$_x$-sensitive and VOC-sensitive locations. A NO$_x$-VOC indicator is successful if the 95th percentile value for VOC-sensitive locations is equal to or less than the 5th percentile value for NO$_x$-sensitive locations, and if the transition values remain similar in models for different locations and assumptions. These 95th percentile and 5th percentile values identify the transition from NO$_x$-sensitive to VOC-sensitive conditions.

As shown in Table 2, the ratios $\Delta$O$_3$/ΔNO$_x$, $\Delta$O$_3$/ΔNO$_2$, and $\Delta$O$_3$/ΔHNO$_3$ (where HNO$_3$ is interpreted to include aerosol nitrate) are potentially useful as NO$_x$-VOC indicators. These ratios are correlated with NO$_x$-VOC sensitivity both at the regional scale and within urban subsets of model domains, with ΔO$_3$, etc. relative to the appropriate background for the subdomain. Median values of the ratios for NO$_x$-sensitive locations are often twice as high as median values for VOC-sensitive locations, and the 95th percentile NO$_x$-VOC sensitive value and 5th percentile NO$_x$-sensitive value are generally comparable. Ratio values at the NO$_x$-VOC transition are: $\Delta$O$_3$/ΔNO$_x$ = 4–6; $\Delta$O$_3$/ΔNO$_2$ = 5–7; and $\Delta$O$_3$/ΔHNO$_3$ = 8–10. It is noteworthy that range of values from the model for San Joaquin reported by Lu and Chang [1998] are generally comparable to the others. Results for O$_3$/NO$_x$ from this model differed sharply from the indicator results in Sillman [1995], probably because the scenario reported by San Joaquin had different boundary conditions [see Sillman et al., 2001]. When ratios such as $\Delta$O$_3$/ΔNO$_x$ along with the described procedure for identifying background values are used, model boundary conditions are less important.

Although the ratios $\Delta$O$_3$/ΔNO$_x$, etc. effectively separate NO$_x$-sensitive and VOC-sensitive conditions for many of the 3-D simulations, there were some situations with ambiguous results. The ratios $\Delta$O$_3$/ΔNO$_2$ and $\Delta$O$_3$/ΔHNO$_3$ performed poorly in the models for Los Angeles, San Joaquin and in one Nashville case. In the ambiguous cases, the ratio $\Delta$O$_3$/ΔNO$_x$ value for NO$_x$-sensitive locations is comparable to the median value for VOC-sensitive locations, suggesting significant overlap of values between NO$_x$-sensitive and VOC-sensitive conditions. Performance is significantly better for $\Delta$O$_3$/ΔNO$_x$ in these locations. Indicator results are especially poor for the model for Los Angeles reported by Chock et al. [1999]. Transition values can also be shifted by 20% in response to changes in dry deposition rates.

Table 2 also includes results for the original indicator ratios (O$_3$/NO$_x$, H$_2$O$_2$/HNO$_3$, etc.) from Sillman [1995]. These ratios generally show a larger separation between NO$_x$-sensitive and VOC-sensitive locations than the ratios with the form $\Delta$O$_3$/ΔNO$_x$, etc. They also avoid the uncertainty associated with background values for $\Delta$O$_3$/ΔNO$_x$. As described above, the NO$_x$-VOC transition for the ratios O$_3$/NO$_x$, O$_3$/NO$_2$, and O$_3$/HNO$_3$ are much higher in the models for San Joaquin and in the model for Los Angeles reported by Chock et al. than in other cases.

The ratio H$_2$O$_2$/HNO$_3$ and similar ratios involving summed peroxides generally show the strongest correlation with NO$_x$-VOC sensitivity and the smallest variation among individual models. However, the difference ratio relative to background ($\Delta$H$_2$O$_2$/ΔHNO$_3$) does not correlate with NO$_x$-VOC sensitivity. Typically, H$_2$O$_2$ is lower inside an urban plume relative to the surrounding rural area [Weinstein-
Table 2. Distribution of Indicator Values for NO$_x$- and VOC-Sensitive Locations in 3-D Simulations

<table>
<thead>
<tr>
<th>Indicator</th>
<th>VOC-Sensitive Locations</th>
<th>NO$_x$-Sensitive Locations</th>
</tr>
</thead>
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<td></td>
<td>5th Percentile</td>
<td>50th Percentile</td>
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<tr>
<td>/C1NO3/C1NOy</td>
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<tr>
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<tr>
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</tr>
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<td>3.4</td>
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<td>2.8</td>
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<tr>
<td>San Joaquin (Sillman)</td>
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<td>2.8</td>
</tr>
<tr>
<td>Sainte (Lu and Chang)</td>
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</tr>
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</tr>
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This decrease in H$_2$O$_2$ may suggest that the urban plume has VOC-sensitive chemistry, but it may also occur because the surrounding rural area has strongly NO$_x$-sensitive conditions. A correlation with urban NO$_x$-VOC chemistry independent of conditions in the surrounding rural region does not appear to be possible. H$_2$O$_2$/HNO$_3$ and similar ratios correlate with NO$_x$-VOC sensitivity on regional scales, where most of the H$_2$O$_2$ and HNO$_3$ has been produced within the model domain of interest.

### Table 2. (continued)

<table>
<thead>
<tr>
<th>Indicator</th>
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The table shows 5th, 50th, and 95th percentile indicator values (with percentile ordering by indicator value) for VOC-sensitive locations and NO$_x$-sensitive locations as defined in the text. The terms ΔO$_3$, ΔNO$_x$, ΔNO$_y$, and ΔHNO$_3$ represent the difference between values at specified locations and background values. In some cases results are shown separately for (a) the full model domain and (b) an urban subdomain. In these cases NO$_x$-VOC sensitivity is defined relative to changed emissions within the model subdomain and background values are determined relative to the same subdomain. Models are described in Table 1.

$^a$The Nashville high-deposition scenario has dry deposition rates of 5 cm$^2$ s$^{-1}$ for H$_2$O$_2$ and HNO$_3$, as opposed to 2.5 cm$^2$ s$^{-1}$ in the standard scenario.

$^b$In models with CB-4 chemistry, “H$_2$O$_2$” is interpreted as a surrogate for the sum of H$_2$O$_2$ and organic peroxides.

The results of the previous section should be viewed in the context of the need to identify the range of conditions for which the proposed NO$_x$-VOC indicators are valid. The general pattern of correlation between indicators and NO$_x$-VOC sensitivity appears to apply for a very wide range of conditions, as illustrated in Figures 3 and 4. As pointed out by Lu and Chang [1998], the NO$_x$-VOC transition values for some indicator ratios can vary significantly. However, this does not appear to be just a random variation among different models or locations. Rather, it is part of a systematic variation from relatively clean to highly polluted conditions, which is imperfectly captured by the indicator ratios. This variation can be explained in terms of the radical chemistry that drives the split into NO$_x$-sensitive and VOC-sensitive conditions.
calculations shown here suggest that some indicator ratios (O₃/NOₓ) may not be applicable for more highly polluted conditions, and others may have different NOₓ-VOC transition values. This finding is especially important in connection to investigations of the chemistry of ozone formation in Mexico City. Sosa et al. [2000] reported that the ratio O₃/NOₓ did not correlate well with NOₓ-VOC sensitivity in 3-D models for Mexico City.

From the calculations shown here, the indicator ratios involving peroxides appear to be more robust than the ratios involving O₃. Lu and Chang [1998] and Chock et al. [1999] reported transition values for H₂O₂/HNO₃ that differed from previously reported results.

It may be possible to derive more robust ratios by using the form ΔO₃/ΔNOₓ rather than the simpler O₃/NOₓ. Indicator ratios of this form are more consistent with the pattern of variation among NOₓ-sensitive and VOC-sensitive locations shown in Figure 3. However, this would introduce additional uncertainty concerning the value of the background concentrations, which are needed to determine ΔO₃. In addition, ratios with this form still show significant variation and in models for different locations. It is perhaps more useful to interpret measured indicator ratios by directly comparing correlations with the broad pattern of NOₓ-VOC variation in Figure 3. A direct comparison of correlation plots would also help to establish the validity of using specific sets of measurements in combination with these theoretical results.

[60] It is useful to compare indicator ratios described here with the “extent-of-reaction” parameters developed by Johnson et al. [1990] and Blanchard et al. [1999; Blanchard and Stoeckenius, 2001] [see also Olzyna et al., 1994; T. Chang et al., 1997]. Extent-of-reaction parameters were derived from smog chamber experiments, and are based on the finding that ozone in photochemically aged air is sensitive to NOₓ while ozone in air with relatively unprocessed emissions is sensitive to VOC. Although the rationale is different, the extent-of-reaction parameters are often similar to the ratio ΔO₃/ΔNOₓ used here. Blanchard et al. [1999] developed the following parameters for extent of reaction (modified here to account for dry deposition of NOₓ):

\[
\text{Extent}_1 = \frac{1.1O_3 - O_2b - NO + 1.23 NO_y}{22NO_y^{0.67}} \tag{8a}
\]

\[
\text{Extent}_2 = \left[ 1 - \frac{NO_x}{1.3NO_y} \right]^{0.67} \tag{8b}
\]

[61] Figure 6 shows how the extent parameters vary for NOₓ-sensitive and VOC-sensitive locations for the ensemble of models used here. The first extent parameter (based on ΔO₃/ΔNOₓ) effectively separates NOₓ-sensitive from VOC-sensitive locations, but the NOₓ-VOC transition tends to vary from low to high O₃. A better correlation with NOₓ-VOC sensitivity would be obtained using the original extent parameter developed by Johnson et al. [1990] (based on ΔO₃/ΔNOₓ), although the original parameter would need to be modified to account for removal of NOₓ by dry deposition. Blanchard et al. [1999] described how the 0.67 exponent was added based on results from 0-D calculations and smog chamber experiments. Based on the isopleths in Figure 1 and 2b, it is possible that the form ΔO₃/ΔNOₓ may be more appropriate for highly polluted environments. The NOₓ-VOC transition in the isopleth plots (see Figure 2b) correlates more closely to ΔO₃/ΔNOₓ than to ΔO₃/ΔNOₓ for highly polluted conditions (O₃ > 150 ppb).

[62] The second extent parameter (based on 1-NOₓ/NO₃) is loosely correlated with NOₓ-VOC sensitivity but there are a large number of exceptions, with VOC-sensitive chemistry and extent of reaction close to 1. A similar analysis was done by Blanchard and Stoeckenius [2001]. We also found poor performance for a third extent parameter, reported by Blanchard et al. [1999], based on O₃ and NOₓ. The poor correlation for this parameter may be related to a flaw in the extent-of-reaction concept. Figure 7 shows isopleths for NOₓ/NO₃ in comparison with O₃ from the 0-D calculations (equivalent to Figure 1). As shown in the figure, high NOₓ/
NO\textsubscript{x} ratios are associated with strongly VOC-sensitive chemistry in which ozone production is sharply limited by excess NO\textsubscript{x}. The high NO\textsubscript{y}/NO\textsubscript{x} also corresponds to S\textsubscript{H}/S\textsubscript{N} < 1 in Figure 1a. Low NO\textsubscript{y}/NO\textsubscript{x} ratios in Figure 7 correspond both to NO\textsubscript{x}-sensitive conditions and to VOC-sensitive conditions that have relatively high rates of ozone production. In the 3-D simulations also a low value of the extent parameter (corresponding to high NO\textsubscript{y}/NO\textsubscript{x}) is associated with strongly VOC-sensitive chemistry, but a high value (corresponding to low NO\textsubscript{y}/NO\textsubscript{x}) can be associated with either NO\textsubscript{x}-sensitive or VOC-sensitive conditions. The exceptional VOC-sensitive cases occur mainly in the simulation for Lake Michigan, in which a strongly VOC-sensitive plume from Chicago moves downwind and remains sensitive to VOC even after it ages. The extent-of-reaction parameters based on \(\Delta O_3/\Delta NO_x\) show a closer correlation with NO\textsubscript{x}-VOC sensitivity in models, possibly because \(\Delta O_3/\Delta NO_x\) is associated with Kleiman’s radical ratio (S\textsubscript{H}/L\textsubscript{N}, discussed in sections 2 and 4) rather than just the photochemical age.

7. Conclusion

[63] The above analysis has resulted in the following new findings concerning the use of secondary species NO\textsubscript{x}-VOC indicators.

1. The behavior of some proposed indicator ratios tends to be different for relatively clean environments (O\textsubscript{3} < 80 ppb), moderately polluted (100–200 ppb O\textsubscript{3}) and highly polluted environments (O\textsubscript{3} > 200 ppb). This is especially true for O\textsubscript{3}/NO\textsubscript{2}. Previously reported results from Sillman [1995] and Sillman et al. [1998] were based on moderately polluted conditions.

2. The correlation with NO\textsubscript{x}-VOC sensitivity is stronger and more consistent for ratios involving peroxides (H\textsubscript{2}O\textsubscript{2}/HNO\textsubscript{3}, etc.) than for ratios such as O\textsubscript{3}/NO\textsubscript{2}.

3. The ratios \(O_3/(2H_2O_2 + NO_x)\) and \(O_3/(2H_2O_2 + 2ROOH + NO_x)\) should also vary from clean to highly polluted environments. These ratios provide a measurement-based test of indicator NO\textsubscript{x}-VOC transition values.

4. Indicator ratios with the form \(\Delta O_3/\Delta NO_x\) (where \(\Delta O_3\) and \(\Delta NO_x\) represents the difference between values at a specific location and background values) are proposed for evaluating local NO\textsubscript{x}-VOC sensitivity in urban plumes with well-defined background concentrations. This ratio is generally correlated with O\textsubscript{3}-NO\textsubscript{x}-VOC sensitivity in models, but there is significant variation among models for different locations.

5. Variations in indicator behavior are analytically linked to variations in the ozone production efficiency per primary radical production (O\textsubscript{3}/S\textsubscript{N}).

6. The “extent-of-reaction” parameter (\(\Delta O_3/\Delta NO_x\)) also correlates with NO\textsubscript{x}-VOC sensitivity in models, but its behavior shows a systematic variation with O\textsubscript{3}. Extent parameters based on NO\textsubscript{x}/NO\textsubscript{y} do not correlate with model NO\textsubscript{x}-VOC sensitivity.

[64] The indicator ratios discussed here are a potentially useful method for identifying NO\textsubscript{x}-sensitive and VOC-sensitive conditions in the ambient atmosphere, but they are also subject to many uncertainties. These include: uncertain dry deposition rates, wet deposition, aerosol interactions, measurement error, and case-to-case variations. It is especially important to recognize that many of the results shown here depend on the mechanism used to represent photochemistry. Derived ratios such as the ozone production per primary radical production may depend on the detailed representation of reaction sequences of VOC, which are often highly parameterized. It is important to compare these values for different photochemical representations and compare them with measurements (including both smog chamber experiments).

[65] Perhaps the biggest weakness is the difficulty in testing the predicted indicator-NO\textsubscript{x}-VOC relationship against ambient measurements. Comparisons between measured data sets and the predicted patterns of correlation in Figure 3 are likely to be more useful in establishing the validity of indicator ratios.

8. Notation

\begin{itemize}
  \item NO\textsubscript{x} NO\textsubscript{x} reaction products, or NO\textsubscript{2}-NO\textsubscript{x}.
  \item S\textsubscript{H}, Q summed source of odd hydrogen radicals, including OH, HO\textsubscript{2} and RO\textsubscript{2} (referred to as Q in Kleiman et al., 1997).
  \item S\textsubscript{N} summed source of NO\textsubscript{x}.
  \item L\textsubscript{N} summed rate of photochemical removal of NO\textsubscript{x}, also equal to the rate of production of NO\textsubscript{2}.
  \item OPE\textsubscript{N} ozone production efficiency per NO\textsubscript{x}.
  \item OPE\textsubscript{P} ozone production efficiency per primary radical production.
\end{itemize}

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has not been subjected to peer and administrative review by either agency, and therefore may not necessarily reflect the views of the agencies, and no official endorsement should be inferred.

References


