Effect of aqueous phase cloud chemistry on tropospheric ozone

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Effect of aqueous phase cloud chemistry on tropospheric ozone

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Abstract. The sensitivity of tropospheric O3 to aqueous HOx (OH + HO2) phase chemistry in clouds is examined using photochemical model calculations of the O3 production efficiency per unit NOx and the chemical lifetime of O3, combined with estimates for the residence time of air in clouds. It is found that the maximum perturbation to O3 from cloud chemistry in the tropics and midlatitudes summer is less than 3%. This result is supported by calculations using a three-dimensional, continental-scale model for North America.

1. Introduction

Clouds modify tropospheric chemistry by scattering UV radiation, by redistributing trace constituents vertically, and also by providing relatively large volumes of liquid water for scavenging of gases and aqueous phase chemistry to take place. Lelieveld and Crutzen [1990] pointed out that aqueous phase chemistry in a cloud causes O3 concentrations to decrease due to two rapid reactions involving HOx radicals: O2 + O3(aq) (consuming O3) and HO2(aq) + O2 (scavenging radicals). Several modeling studies have suggested that these reactions represent a significant sink for O3 in the troposphere [Lelieveld and Crutzen, 1990; Jonson and Isaksen, 1993; Dentener, 1993]. However, we present here model calculations indicating that the effect on O3 concentrations is at most a few percent, and we argue that the previous studies may have overestimated the effect.

Lelieveld and Crutzen [1990] based their analysis on photochemical model calculations of the net production minus loss rate of O3, (P - L)O3, in air parcels subjected to alternating periods of clear and cloudy conditions. They found that including aqueous phase radical chemistry in their model increased the net regional O3 loss averaged over clear and cloudy conditions by a factor of 1.3 to 2.3 under low-NOx conditions and decreased net O3 production by about 40% under high NOx conditions. On the basis of this result, they concluded that aqueous phase cloud chemistry represents a significant sink for O3 in the troposphere. It should, however, be noted that a large relative perturbation to (P - L)O3 may imply only a small perturbation to O3 concentrations, considering that P and L are of comparable magnitude in much of the troposphere [Chameides et al., 1987, 1989; Liu et al., 1992; Carroll and Thompson, 1995; Davis et al., 1996; Jacob et al., 1996], and that P is only weakly dependent on the O3 concentration while L is roughly first order. In addition, the effect of cloud chemistry on O3 cannot be decoupled from the effect on NOx, since NOx provides the limiting precursor for O3 production in the troposphere. Scavenging of HOx radicals by cloud droplets slows down the photochemical oxidation of NOx, so that O3 production downstream of the cloud may increase [Dentener, 1993]. A quantitative estimate of the effect of cloud chemistry on O3 concentrations can still be made within the simple air parcel modeling framework of Lelieveld and Crutzen [1990] by choosing suitable variables as diagnostics. We present results from such an approach below.

More definite assessment of the effect of cloud chemistry on O3 requires a chemical tracer model that can resolve the coupling between chemistry and transport. Jonson and Isaksen [1993] presented results from a two-dimensional (longitude-altitude) model for northern midlatitudes. They found that including cloud chemistry in their calculations (with effects on both radiation and chemistry) decreases O3 concentrations by 10-30% relative to a simulation with only gas phase chemistry, the largest effects (20-30%) being in the middle troposphere. Their simulation assumed unusually cloudy conditions, however, with one third of the 1 to 7-km column included in cloud at any given time. In comparison, Lelieveld et al. [1989] estimated that clouds occupy on average 15% of the northern midlatitudes atmosphere below 4 km and occupy less at higher altitudes, we argue below that even this estimate is too high. Jonson and Isaksen [1993] found that including aqueous phase chemistry in their model improved the simulation of O3 in the middle troposphere, but other O3 models without cloud chemistry do not show a systematic problem of excessive O3 in this part of the atmosphere [Crutzen and Zimmerman, 1991; Follows and Austin, 1992; Muller and Brasseur, 1995; Roelofs and Lelieveld, 1995].

In a pioneering study, Dentener [1993] included cloud chemistry in a coarse three-dimensional model with monthly averaged winds (MOGUNTIA) and compared results to a simulation including only gas phase chemistry and N2O5 hydrolysis in aerosols. He found that cloud chemistry causes a 4-15% decrease of O3 concentrations in the lower troposphere and a 7% global decrease in the O3 tropospheric inventory. We argue below that even this small effect may be an overestimate because the model assumed high liquid water abundances and high CH2O solubility.

We begin this paper (section 2) with a brief review of the aqueous phase chemistry affecting O3 in cloud. We follow in section 3 with a conceptual model for the tropospheric O3 budget using as variables the O3 production efficiency (c) and the pseudo first-order rate constant for chemical loss (k). We then present in section 4 a zero-dimensional photochemical model analysis of the sensitivity of c and k to cloud formation, and use this analysis to estimate the perturbation to O3 from cloud chemistry in different regions of the world. Supporting calculations using a three-dimensional model for North America are presented in section 5. Conclusions are presented in section 6.

2. Cloud Chemistry and Ozone

Ozone is produced and destroyed in the troposphere by reactions involving HOx radicals (defined as the ensemble of OH and peroxy radicals). Detailed discussions of cloud effects on HOx chemistry have been presented by Chameides and Davis [1982], Graedel and Goldberg [1983], Schwartz [1984], Jacob [1986],
and Lelieveld and Crutzen [1990], among others. The HO₂ radical is scavenged efficiently by cloud droplets as a result of acid-base dissociation of HO₂(aq) (pKₐ = 4.7):

\[ \text{HO}_2(g) = \text{HO}_2(aq) \]  
(1)

\[ \text{HO}_2(aq) = \text{H}^+ + \text{O}_2^- \]  
(2)

followed by electron transfer between HO₂(aq) and O₂:

\[ \text{HO}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{OH}^- \]  
(3)

and reaction of O₂ with O₃(aq):

\[ \text{O}_2 + \text{O}_3 \rightarrow 2\text{O}_2 + \text{OH} + \text{OH}^- \]  
(4)

Cloud water pH values are typically in the range 3-5 [Warneck, 1988]. Model calculations by Jacob [1986] indicate that HO₂(g) concentrations in a cloud of pH 4 are depleted by 70% relative to clear sky because of reactions (1)-(3); in a cloud of pH 5 the depletion is 85%. This depletion of HO₂(g) suppresses the gas phase reaction (5), which provides the major source of O₂ in the troposphere:

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  
(5)

\[ \text{NO}_2 + \text{hv} \rightarrow \text{O}_2 + \text{NO}_3 \]  
(6)

Contrary to HO₂, NO is not significantly soluble in water so that the HO₂ + NO reaction does not proceed significantly in the aqueous phase. The effect of HO₂ scavenging in suppressing (5) is partly compensated in summer by an increase in the NO/NO₃ ratio, as reaction with HO₂ is a significant pathway converting NO to NO₃ (reaction with O₃ dominates in winter).

Another important source of O₃ in the troposphere is (7):

\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{NO}_2 \]  
(7)

where CH₃O₂ is produced by oxidation of hydrocarbons, in particular methane. No data are available for the Henry’s law constant of CH₃O₂. We expect CH₃O₂ to be far less soluble than HO₂ because of its lower polarity. By analogy, the Henry’s law constant for CH₃OH is 300 times less than that for HO₂ [O’Sullivan et al., 1996]. Assuming the same ratio for the Henry’s law constants of CH₂O₂ and HO₂, one finds that scavenging of CH₃O₂ by cloud droplets is negligible (Jacob, 1986). The gas phase concentration of CH₂O₂ may actually increase in cloud due to suppression of the gas phase sink from

\[ \text{CH}_3\text{O}_2 + \text{HIO}_2 \rightarrow \text{CH}_2\text{O}_2\text{O}_2 + \text{O}_2 \]  
(8)

thus sustaining O₃ production in the cloud.

Scavenging of HO₂ by cloud droplets suppresses gas phase loss of O₃ by the reaction

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]  
(9)

but this effect may be more than compensated by aqueous phase reaction (4) which drives the cycling of HO₂ radicals in the aqueous phase (the aqueous phase reaction of HO₂ with O₃ is negligibly slow). The OH(aq) radical produced by (4) is recycled rapidly to HO₂(aq) by oxidation of hydrated formaldehyde and formate [Jacob, 1986], leading to a HO₂-catalyzed cycle for destruction of O₃ in the aqueous phase [Lelieveld and Crutzen, 1990]. The efficiency of this O₃ loss cycle is limited by the aqueous phase HO₂ sink from (3), which is considerably faster than the self-reaction of HO₂ in the gas phase. Reaction (3) facilitates the scavenging of HO₂ from the gas phase, on the one hand, and thus contributes to the suppression of O₃ production; on the other hand, it competes with (4) and moderates O₃ loss.

Cloud chemistry models indicate that OH(g) is depleted by 30-60% in cloud relative to clear sky conditions [Jacob, 1986; Lelieveld and Crutzen, 1990]. This depletion is due in part to direct uptake of OH by the cloud droplets and in part to the scavenging of HO₂ from the gas phase. The depletion of OH slows down NO₂ oxidation in the gas phase from the reaction

\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]  
(10)

This reaction is further slowed by the decrease in the daytime NO₂/NO₃ ratio resulting from the scavenging of HO₂ [Deniener, 1993]. Hence NO₂ may be preserved in cloud and remain available to produce O₃ by (5) and (7) after the cloud evaporates.

An additional mechanism for NO₂ loss in the troposphere is by nighttime reactions of NO₂ and N₂O₅ in aqueous aerosols:

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  
(11)

\[ \text{NO}_3 + \text{NO}_2 + \text{M} - \text{N}_2\text{O}_5 + \text{M} \]  
(12)

\[ \text{NO}_3 \rightarrow \text{NO}_3 + \text{X} \]  
(13)

\[ \text{N}_2\text{O}_5 \rightarrow 2\text{HNO}_3 \]  
(14)

where X is a suitable reductive (e.g., Cl⁻). In the daytime this mechanism is suppressed by photolysis of NO₂. Cloud formation causes a large increase in the rate constants for (13)-(14), because of the increase in the wet surface area [Lelieveld and Crutzen, 1990], but the nighttime rate of NO₂ loss may not be significantly affected as it is in general limited by (11). One possibly important rule of clouds is to enable the mechanism to proceed in the daytime. At the high surface areas found in cloud, (13) can compete with NO₃ photolysis, especially during winter when photolysis of NO₃ is weak.

3. A Conceptual Model for Tropospheric Ozone

Ozone production in the troposphere is limited in general by the availability of NO₃ [Chameides et al., 1992]. Liu et al. [1987] defined the O₃ production efficiency ε, as the total number of molecules of odd oxygen (O₃ − O₃ + O + NO₂ + HNO₃ + 2xNO₃ + 3xN₂O₅) produced per molecule of NO₃ oxidized to HNO₃. The idea is that a NO₃ molecule emitted to the atmosphere undergoes a number ε of peroxo + NO conversions, producing O₃ before it is oxidized to HNO₃ which is viewed as a terminal sink. In the lower troposphere at least, HNO₃ is removed principally by deposition. Consider a region sufficiently large that NO₃ is at steady state between its source $E_{NO₃}$ and its loss $L_{NO₃}$ (the lifetime of NO₃ against oxidation is of the order of 1 day). The O₃ production rate $P_{O₃}$ can be related to $E_{NO₃}$ by using a characteristic value of $ε$ for the region:

$$P_{O₃} = ε E_{NO₃}$$  
(15)

Chemical loss of O₃ takes place principally by the gas phase reactions O(¹D) + H₂O, HO₂ + O₃, and OH + O₃, and also in cloud by the aqueous phase reaction O₂ + O₃(aq). These reactions are approximately first order in O₃, and may therefore be grouped to define a pseudo first-order loss rate constant k for O₃. Oxidation of NO₃ to HNO₃ is an additional sink for O₃, but we do not include it in k because it is limited by $E_{NO₃}$ and not directly dependent on the O₃ concentration; this subtlety is of some importance because perturbation to NO₃ loss by aqueous phase chemistry should not be regarded as a real perturbation to the O₃ sink (although it perturbs the O₃ production efficiency). The loss rate $L_{NO₃}$ is thus given by

$$L_{NO₃} = k[O₃] + βE_{NO₃}$$  
(16)

where β is the number of O₃ molecules consumed in the oxidation of NO₃ to HNO₃ (β = 1 for NO₂ + OH, β = 1.5 for N₂O₅ hydrolysis), $β = 2$ for NO₃(aq) + X⁻.

Equations (15) and (16) can be combined to obtain a simple budget expression for the O₃ concentration at steady state in a
given region of the troposphere:

\[
[O_3] = [O_2] \frac{(\varepsilon - \beta)E_{NO_x} + F_{\text{in}}}{k + k'}
\]  

(17)

where \( F_{\text{in}} \) is the flux of \( O_3 \) into the region, and \( k' \) is a rate constant for export of \( O_3 \) out of the region including effects from both transport and deposition. In general, \( \beta << \varepsilon \), except for high latitudes in winter. If we consider a region sufficiently large and photochemically active, so that \( \varepsilon >> \beta \), \( \varepsilon E_{NO_x} \gg F_{\text{in}} \) and \( k >> k' \), then \( O_3 \) concentrations vary as \( \varepsilon/k \). Perturbations to \( \varepsilon \) and \( k \) from cloud chemistry, as computed from a zero-dimensional air parcel model [Lelieveld and Crutzen, 1990], can be translated directly into a corresponding perturbation to \( O_3 \), and we follow this approach in the next section.

4. Zero-Dimensional Photochemical Model

Model Description

We compute \( \varepsilon \) and \( k \) with a zero-dimensional photochemical model for 11 air parcels representative of a range of latitudes, altitudes, and seasons [Lelieveld and Crutzen, 1990] (Table 1). The composition of each air parcel is defined by specified concentrations of \( O_3 \), CO, CH\(_4\) (1.7 parts per million by volume), NO\(_x\), and H\(_2\)O, and under cloudy conditions by a specified liquid water content (LWC) and cloud water \( pH \). A relative humidity of 100\% is assumed under both clear-sky and cloudy conditions, in order to separate the effects of aqueous phase chemistry from that of changes in humidity. The rate constant \( k_p \) for (13) and (14) under cloud-free conditions is specified following Dentener and Crutzen [1993]. Cloud LWCs are specified with a temperature-dependent parameterization based on Somerville and Roper [1984]:

\[
\text{LWC} = 0.32 - 0.0060 (T - 273) \text{ g m}^{-3},
\]  

(18a)

for \( 293 \leq T \leq 280 \text{ K} \);

\[
\text{LWC} = 0.23 + 0.0065 (T - 273) \text{ g m}^{-3},
\]  

(18b)

for \( 280 \leq T \leq 248 \text{ K} \);

\[
\text{LWC} = 0.07 \text{ g m}^{-3}, \text{ for } T < 248 \text{ K}
\]  

(18c)

The cloud droplets are assumed to be monodisperse (radius = 10 \( \mu \text{m} \)) and of homogeneous composition, so that cloud water can be effectively modeled as a single phase defined by bulk LWC and \( pH \). This assumption can be made with no loss of generality (we will present calculations exploring the sensitivity to LWC and \( pH \)).

The model calculates the gas phase concentrations of \( O(1D) \), \( \text{OH} \), \( \text{HO}_2 \), \( \text{CH}_3O \), \( \text{H}_2O \), \( \text{CH}_2O \), \( \text{CH}_4 \), \( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{CO}_3 \), \( \text{NO}_x \), \( \text{NO}_y \), \( \text{NO}_z \), \( \text{N}_2\text{O}_5 \), \( \text{HNO}_4 \), and \( \text{HNO}_x \), and when a cloud is present the aqueous phase concentrations of \( \text{SO}_4 \), \( \text{OH} \), \( \text{HO}_2 \), \( \text{O}_2 \), \( \text{H}_2\text{O}_2 \), \( \text{H}_2\text{CO}_3 \), \( \text{HCOO}^- \), \( \text{CH}_3\text{O}^- \), and \( \text{CH}_2\text{O}OH^{aq} \). The gas phase chemical mechanism is from DeMore et al. [1994]. The aqueous phase chemical mechanism is from Jacob [1986], with updated rate constant \( k = 7.7x10^8 \text{ M}^{-1} \text{s}^{-1} \) for the oxidation of \( \text{H}_2\text{CO}(\text{OH})_2(\text{aq}) \) by \( \text{OH}(\text{aq}) \) [Chin and Wine, 1994]. Gas droplet mass transfer is computed as described by Jacob [1986]. Ultraviolet photon intensities are calculated with the clear sky radiative transfer code of Logan et al. [1981]. Changes in UV radiation due to cloud formation are not considered in order to focus attention on the changes in chemistry.

For each case in Table 1, we begin by integrating to die a steady state a clear sky simulation including only gas phase chemistry and reactions of \( \text{NO}_x \) and \( \text{N}_2\text{O}_5 \) in aerosols. Die a steady state is defined by 24-hour periodicity for the concentrations of all species being solved in the model. Once this steady state is reached, we cycle the air parcel intermittently through cloud for 7 days, using an alternating pattern of 2-hour cloudy periods followed by 12-hour cloud-free periods. This pattern was chosen to provide a cloud duration and frequency typical of the values employed by Lelieveld and Crutzen [1990] and also to sample cloudy conditions evenly over all times of day. Thus the 7-day simulation includes 24 hours in cloud spanning the full die cycle of UV radiation intensities.

### Values of \( \varepsilon \) and \( k \) in Cloud

Values of \( \varepsilon \) and \( k \) are retrieved from the model as

\[
\varepsilon = \frac{P_{\text{O}_3}}{L_{\text{NO}_x}}
\]  

(19)

\[
k = \frac{L_{\text{O}_3} - \beta L_{\text{NO}_x}}{[\text{O}_3]}
\]  

(20)

where the quantities on the right-hand side are 24-hour averages from the 7-day simulation, and \( P \) and \( L \) are chemical production and loss rates. Equation (20) is simply a rearrangement of (16) assuming steady state for \( \text{NO}_x \), \( L_{\text{NO}_x} = L_{\text{O}_3} \). We calculate "wish-cloud" values \( k_w \) and \( \varepsilon_w \) by sampling continuously the 7-

### Table 1. Air Parcel Definitions Used in Zero-Dimensional Model

<table>
<thead>
<tr>
<th>Case</th>
<th>Altitude (km)</th>
<th>T (K)</th>
<th>LWC (g m(^{-3}))</th>
<th>pH</th>
<th>NO(_x) (ppt)</th>
<th>O(_3) (ppb)</th>
<th>CO(_2) (ppb)</th>
<th>O(_3) Volume (DU)</th>
<th>( k_p ) (10(^{-5}) s(^{-1}))</th>
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<tr>
<td>1</td>
<td>45°S, winter</td>
<td>1.5</td>
<td>268</td>
<td>0.20</td>
<td>5.0</td>
<td>10</td>
<td>25</td>
<td>70</td>
<td>325</td>
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<tr>
<td>2</td>
<td>45°S, winter</td>
<td>3.0</td>
<td>260</td>
<td>0.15</td>
<td>5.0</td>
<td>10</td>
<td>25</td>
<td>65</td>
<td>325</td>
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<tr>
<td>3</td>
<td>45°S, summer</td>
<td>1.5</td>
<td>285</td>
<td>0.25</td>
<td>5.0</td>
<td>7</td>
<td>15</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
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<td>3.0</td>
<td>277</td>
<td>0.26</td>
<td>5.0</td>
<td>7</td>
<td>15</td>
<td>50</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>equator</td>
<td>1.5</td>
<td>291</td>
<td>0.22</td>
<td>5.0</td>
<td>40</td>
<td>30</td>
<td>85</td>
<td>255</td>
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<td>6</td>
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<td>283</td>
<td>0.27</td>
<td>5.0</td>
<td>30</td>
<td>30</td>
<td>75</td>
<td>255</td>
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<tr>
<td>7</td>
<td>equator</td>
<td>5.0</td>
<td>270</td>
<td>0.21</td>
<td>5.0</td>
<td>20</td>
<td>30</td>
<td>70</td>
<td>255</td>
</tr>
<tr>
<td>8</td>
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<td>1.5</td>
<td>268</td>
<td>0.20</td>
<td>4.5</td>
<td>780</td>
<td>30</td>
<td>130</td>
<td>350</td>
</tr>
<tr>
<td>9</td>
<td>45°N, winter</td>
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<td>260</td>
<td>0.15</td>
<td>4.5</td>
<td>400</td>
<td>30</td>
<td>115</td>
<td>350</td>
</tr>
<tr>
<td>10</td>
<td>45°N, summer</td>
<td>1.5</td>
<td>285</td>
<td>0.25</td>
<td>4.5</td>
<td>135</td>
<td>40</td>
<td>90</td>
<td>315</td>
</tr>
<tr>
<td>11</td>
<td>45°N, summer</td>
<td>3.0</td>
<td>277</td>
<td>0.26</td>
<td>4.5</td>
<td>100</td>
<td>40</td>
<td>85</td>
<td>315</td>
</tr>
</tbody>
</table>

The air parcel compositions are from Lelieveld and Crutzen [1990]. The cloud liquid water contents (LWC) are from equation (18). The rate constants \( k_p \) for conversion of \( \text{NO}_x \) and \( \text{N}_2\text{O}_5 \) to \( \text{HNO}_x \) in aerosols under noncloudy conditions are from Dentener and Crutzen [1993]. Abbreviation ppt, parts per trillion volume; ppb, parts per billion volume; DU, Dobson units (1 DU = 2.687 \times 10^{19} \text{ molecules cm}^{-2} \).
acrosol chemistry but no aqueous phase HO$_2$ radical chemistry in cloud. This "no-cloud" simulation still accounts for the increased loss of NO$_3$ and N$_2$O$_5$ in intermittent clouds due to the surface-limited reactions (13) and (14); assessment of a cloud effect associated with these reactions would be ambiguous as it depends on the aerosol surface area assumed to represent cloud-free conditions. The rate constants $k_d$ for (13)-(14) given in Table 1 are based on average relative humidity conditions [Denning and Crutzen, 1993] and would underestimate values for a pre-cloud atmosphere at 100% relative humidity.

Figure 1 shows the sensitivities of $k$ and $r$ in cloud to aqueous phase radical chemistry, as expressed by the ratios of "cloudy" to "no-cloud" values,

$$\begin{align*}
  r_e &= \frac{e_{cl}}{e_{nc}} \\
  r_k &= \frac{k_{cl}}{k_{nc}}
\end{align*}$$

(21)

(22)

for the air parcel of case 5 (equator, 1.5-km altitude) as a function of cloud LWC and pH. We see from Figure 1 that aqueous phase chemistry has less than 20% effects on in-cloud values of $k$ and $r$ over the usual range of LWC (0.1-0.5 g m$^{-3}$) and pH (3-5). These weak effects reflect in part the compensating factors discussed in section 2. Another factor moderating the effect on $k$ is that most of the gas phase loss of O$_3$ is by the reaction O($^1D$)+H$_2$O, which is unaffected by cloud chemistry. For pH values above 5 (pH > $pK_a$(HO$_2$/O$_2$)) the effect of cloud chemistry on $k$ increases rapidly with pH because of (2) and (4) and also because of the suppression of (3) which competes with (4). Results in Figure 1 indicate that $k$ may increase by as much as 50% relative to clear sky inside a dense cloud with pH 5, such as in the upward regions of convective storms [Barth et al., 1992]. However, air spends little time in such dense clouds, which occupy little atmospheric volume.

Table 2 shows the effects of cloud chemistry on $r$ and $k$ for different regions and seasons, as illustrated by the 11 cases of Table 1. Aqueous phase chemistry decreases in-cloud values of $r$ by 0.40% in the tropics and midlatitudes summer, and by 50-70% in midlatitudes winter; $k$ increases by 0-30% in the former cases and by 70-90% in the latter cases. In winter the compensating factor on $k$ from reduced photochemical loss of NO$_3$ is relatively small because nighttime reactions of NO$_3$ and N$_2$O$_5$ in aerosols provide the principal sink for NO$_3$ [Denning and Crutzen, 1993].

### Table 2. Effect of Cloud Chemistry on O$_3$ concentrations

<table>
<thead>
<tr>
<th>Case</th>
<th>$P_{O_3}^{cl}$/P_{O_3}^{nc}</th>
<th>L_{O_3}^{cl}/L_{O_3}^{nc}</th>
<th>$e_{nc}$</th>
<th>$e_{cl}$</th>
<th>$k_{nc}$</th>
<th>$k_{cl}$</th>
<th>$f^*$</th>
<th>max(-$\Delta$[O$_3$]/[O$_3$]), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.33</td>
<td>0.24</td>
<td>0.94</td>
<td>0.92</td>
<td>0.45</td>
<td>4.5</td>
<td>0.0009</td>
<td>0.017</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>0.22</td>
<td>0.95</td>
<td>0.93</td>
<td>3.3</td>
<td>3.3</td>
<td>0.0069</td>
<td>0.013</td>
</tr>
<tr>
<td>3</td>
<td>0.83</td>
<td>0.71</td>
<td>0.64</td>
<td>0.73</td>
<td>66</td>
<td>80</td>
<td>0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>4</td>
<td>0.71</td>
<td>0.59</td>
<td>0.88</td>
<td>0.73</td>
<td>82</td>
<td>82</td>
<td>0.11</td>
<td>0.14</td>
</tr>
<tr>
<td>5</td>
<td>0.70</td>
<td>0.69</td>
<td>0.95</td>
<td>0.79</td>
<td>75</td>
<td>75</td>
<td>0.23</td>
<td>0.28</td>
</tr>
<tr>
<td>6</td>
<td>0.73</td>
<td>0.70</td>
<td>0.82</td>
<td>0.73</td>
<td>29</td>
<td>29</td>
<td>0.24</td>
<td>0.28</td>
</tr>
<tr>
<td>7</td>
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<td>0.57</td>
<td>0.82</td>
<td>0.70</td>
<td>44</td>
<td>44</td>
<td>0.12</td>
<td>0.15</td>
</tr>
<tr>
<td>8</td>
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<td>0.86</td>
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<td>1.8</td>
<td>1.8</td>
<td>0.0062</td>
<td>0.012</td>
</tr>
<tr>
<td>9</td>
<td>0.22</td>
<td>0.07</td>
<td>0.77</td>
<td>0.22</td>
<td>4.5</td>
<td>4.5</td>
<td>0.0068</td>
<td>0.013</td>
</tr>
<tr>
<td>10</td>
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<td>0.01</td>
<td>0.70</td>
<td>0.17</td>
<td>17</td>
<td>17</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>11</td>
<td>0.83</td>
<td>0.01</td>
<td>0.63</td>
<td>0.07</td>
<td>24</td>
<td>24</td>
<td>0.13</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Results are shown for the 11 air parcel cases of Table 1. The indices "cl" and "nc" refer to 24-hour average quantities computed in cloudy air parcels, with and without consideration of aqueous phase radical chemistry, respectively. max(-$\Delta$[O$_3$]/[O$_3$]) is the theoretical maximum relative decrease of the regional O$_3$ concentration due to cloud chemistry, as calculated from (28), assuming that clouds occupy a volume fraction of $f$ of the regional atmosphere.
During winter, uptake of NO$_3$ and N$_2$O$_5$ by cloud droplets can compete with NO$_3$ photolysis during daytime hours, further reducing the importance of OH as a NO$_3$ oxidant. Despite the relatively high perturbations to $\epsilon$ and $k$, the effect of cloud chemistry on O$_3$ concentrations in winter should be weak considering that the chemical lifetime of O$_3$ is several months, even in cloud (Table 2).

Ozone Budget Perturbation

The above discussion focused on the perturbation to in-cloud values of $\epsilon$ and $k$ from aqueous phase chemistry. However, an air parcel is cloudy only a fraction of the time. The perturbation to O$_3$ concentrations from intermittent cloud chemistry in the 11 cases of Table 1 can be estimated from (17) by using “with-cloud” versus “no-cloud” values of (c-$\beta$) (hereinafter denoted as $\epsilon$ for simplicity of notation) and $k$. The magnitude of the perturbation depends on the fraction $f$ of time that the air parcel is cloudy. We find in our model that a simple linear relationship can be used to relate the average “with-cloud” values ($\epsilon_{wc}$, $k_{wc}$) to the previously discussed “cloudy” values ($\epsilon_{cl}$, $k_{cl}$) and “no-cloud” values ($\epsilon_{nc}$, $k_{nc}$):

$$\epsilon_{wc} = \frac{(1-f)\epsilon_{nc} + f\epsilon_{cl}}{(1-f)\epsilon_{NO} + f\epsilon_{NO}} = w \epsilon_{nc} + (1-w) \epsilon_{cl}$$

$$k_{wc} = (1-f)k_{nc} + f k_{cl}$$

where

$$w = \frac{1}{1-f}$$

$$r_L = \frac{L_{NO}}{L_{NO}}$$

and the indices “cl” and “nc” refer to the “cloudy” and “no-cloud” values as previously defined. Replacing into our O$_3$ budget equation (17), we obtain the following expression for the relative decrease of O$_3$ in the air parcel due to cloud chemistry:

$$\frac{[O_3]_{wc} - [O_3]_{nc}}{[O_3]_{nc}} = \frac{\Delta [O_3]}{[O_3]} = 1 - \frac{w (1-w) r_k}{1 + \frac{F_{in}}{\epsilon_{nc} E_{NO_3}}}$$

For all our cases except case 3, $r_k < 1$ and $r_K > 1$, so that the ozone perturbation is largest when the regional O$_3$ budget is controlled solely by chemical production and loss ($\epsilon E_{NO_3} >> F_{in}$, $k >> K'$). From (27) we obtain the following upper limit for the relative decrease of O$_3$ concentrations due to cloud chemistry:

$$\text{max}(\frac{\Delta [O_3]}{[O_3]}) = 1 - \frac{w (1-w) r_k}{1 + f r_k}$$

In case 3, $r_k > 1$ and $r_K > 1$, so that the O$_3$ perturbation is largest when the regional O$_3$ budget is controlled solely by transport and chemical loss ($F_{in} >> E_{NO_3}$, $k >> K'$). The upper limit for the perturbation in this case is

$$\text{max}(\frac{\Delta [O_3]}{[O_3]}) = 1 - \frac{1}{1 + f r_k}$$

We estimate values of $f$ for cases 1-11 in Table 1 by constraining the resulting time-averaged liquid water in the 0- to 5-km column to match global satellite observations of liquid water columns reported by Greenwald et al. [1993] for that latitude (Figure 2). This approach yields values of $f$ ranging from 3 to 11% depending on the case, with most around 10%. The resulting maximum decrease of O$_3$ concentrations from cloud chemistry is only 1-3% in the tropics and midlatitudes summer (Table 2). Larger values for the maximum decrease are found for midlatitudes winter; however, transport terms dominate the O$_3$ budget during that time of year [Levy et al., 1985], so that the actual perturbation to O$_3$ is certainly much less than the theoretical maximum.

The perturbations to O$_3$ from cloud chemistry reported here are much smaller than in the previous modeling studies of Lelieveld and Crutzen [1990], Jonson and Isaksen [1993], and Dentener [1993]. The assumption of large liquid water abundances in these studies is an important factor in the discrepancy. We compare in Figure 2 the liquid water column climatologies assumed by Lelieveld and Crutzen [1990] and Dentener [1993] to the satellite observations of Greenwald et al. [1993] and Njoku and Swanson [1983]; the observations are consistently lower. As pointed out in the Introduction, the model study of Jonson and Isaksen [1993] assumed even higher liquid water columns.

Figure 2. Zonally averaged atmospheric liquid water columns in (top) August and (bottom) February as a function of latitude. Satellite observations (oceans only) from Greenwald et al. [1993] and Njoku and Swanson [1983] are shown as "G" and "N" symbols, respectively. The seasonal climatologies used in the models of Lelieveld and Crutzen [1990] (as given by Lelieveld et al. [1989]) and Dentener [1993] are shown as "L" and "D" symbols, respectively. The solid line shows the GISS GCM values calculated as described in section 5. The two thick vertical lines bracket the latitudes analyzed in our three-dimensional model.
Another factor responsible for the higher sensitivities of \( O_3 \) to cloud chemistry found in previous modeling studies is that these studies assumed a high Henry's law constant (\( K \)) for \( CH_3O_2 \), equal to that of \( HO_2 \) (\( K_{CH_3O_2} = K_{HO_2} = 2000 \text{ M atm}^{-1} \) at \( T=298 \text{ K} \)). As pointed out in section 2, the Henry's law constant for \( CH_3O_2 \) is likely less than that for \( HO_2 \). We have used \( K_{CH_3O_2} = 5.9 \text{ M atm}^{-1} \) (at \( T=298 \text{ K} \)) in our standard model by assuming that the ratio of the Henry's law constants for \( CH_3O_2 \) and \( HO_2 \) is equal to that for \( CH_3OOH \) and \( H_2O \) [(Jacob, 1986)]. We conducted a sensitivity test for the cases in Table 1 using \( K_{CH_3O_2} = 2000 \text{ M atm}^{-1} \) (at \( T=298 \text{ K} \)) and \( CH_3O_2(aq) \) chemistry in cloud based on similarity with \( HO_2(aq) \) [Jacob, 1986]. The production of \( O_3 \) in cloud is more strongly suppressed than in our standard model, with \( r_e = 0.47-0.73 \) in the tropics and midlatitudes summer. The perturbation to \( k \) is unaffected. The maximum decrease of \( O_3 \) concentrations from cloud chemistry is 2.5% in the tropics and midlatitudes summer, about twice the values computed in our standard model.

The Henry's law constant for \( HO_2 \) has an uncertainty of about a factor of 2 [Schwartz, 1984]. To evaluate the effect of this uncertainty, we performed another sensitivity test for the cases in Table 1 by doubling the Henry's law constant of \( HO_2 \). We find that the perturbation to \( O_3 \) from cloud chemistry is not sensibly increased over that in our standard model, an expected result since the solubility of \( HO_2 \) in our standard model is already sufficiently high for efficient scavenging of \( HO_2 \) from the gas phase.

5. Three-Dimensional Model for North America

Our conceptual model analysis of sections 3.4 oversimplifies the chemistry of tropospheric \( O_3 \) by treating the atmosphere as regionally homogeneous and neglecting the coupling between chemistry and transport. As a test of our conclusions from this conceptual model, we examine here the sensitivity of \( O_3 \) to cloud chemistry with a three-dimensional continental-scale model for North America originally described by Jacob et al. [1993]. The version of the model used here features a number of improvements, particularly in the formulation and integration of the chemical mechanism.

Model Description

The model simulates \( O_3 \), \( NO_x \), \( CO \)-hydrocarbon chemistry over a domain extending horizontally from the mid-Pacific (162.5°W) to the mid-Atlantic (27.5°W), from the tropics (4°N) to the subarctic (56°N), and vertically from the surface to the stratosphere. The grid resolution is \( 4° \times 5° \) in the horizontal, with nine layers in the vertical and a time step of 4 hours. The four lowest layers are centered at 980, 915, 810, and 655 hPa for a grid square at sea level. A subgrid nested scheme accounts for chemical nonlinearities in urban and industrial plumes [Sillman et al., 1990]. Meteorological input including cloud optical depths in individual grid boxes is provided by an archive of 4-hour resolution data from a general circulation model (GCM) developed at the Goddard Institute of Space Studies (GISS) [Hansen et al., 1983]. Boundary conditions for \( O_3 \) and other tracers at the edges of the model domain are specified by observed concentrations over the western Pacific from the Pacific Exploratory Mission PEM-West(A) [Davis et al., 1996]. These observations are interpolated on the latitude-altitude grid of the model.

Twenty one tracers are transported in the model including \( O_3 \), \( CO \), \( NO_x \), four nonmethane hydrocarbons (propane, butane, propene, isoprene), and their oxidation products. The gas phase chemical mechanism is based on recent compilations [DeMore et al., 1994; Atkinson, 1994; Atkinson et al., 1993]. Photolysis rates are calculated with a radiative transfer code [Logan et al., 1981], including cloud albedos at 800, 500, and 200 hPa inferred from GCM cloud optical depths. Conversion of \( NO_x \) and \( N_2O_5 \) in aerosols is treated by assuming a reaction probability of 0.1 at the aerosol surface [Dentener and Crutzen, 1993]. The aerosol surface area is estimated from a three-dimensional simulation of sulfate employing the GCM meteorological environment [Chin et al., 1996] and assuming the aerosol to be \( NH_4HSO_4 \cdot nH_2O \) (where \( n \) is defined by the local relative humidity). The aqueous phase cloud chemistry mechanism is the same as in section 4. A cloud water pH of 4.5 is assumed. Over a 4-hour model time step a grid box is assumed to be 100% cloudy for a fraction \( f \) of the time corresponding to the cloud volume fraction of the grid box, and 100% clear for a fraction \( 1 - f \) of the time. The calculation of \( f \) is described below.

Anthropogenic emissions of \( NO_x \), hydrocarbons, and CO in North America are from a high resolution inventory for 1985 produced by the U.S. Environmental Protection Agency (EPA) [1989] and are scaled to national estimates of emissions for 1990 [EPA, 1993]. Biogenic emission of isoprene is calculated using the inventory of Guenther et al. [1995]. Dry deposition fluxes of species are computed following Wesely [1989], and scavenging of \( HNO_3 \) and \( H_2O_5 \) by precipitation is computed following Balkanski et al. [1993]. Integration of the chemical mechanism including emission and dry deposition is done with a fast Gear solver [Jacobson and Turco, 1994]; an implicit finite difference method [Wofsy, 1978] is employed in cases involving aqueous phase chemistry where the Gear solver requires excessively small time steps for integration. Because of the short lifetime of \( OH(aq) \), aqueous phase chemistry greatly enhances the stiffness of the model chemical system.

The cloud volume fraction \( f \) of a grid box for a given time step is calculated from the liquid water column \( \Lambda \) (g m\(^{-2}\)) in the grid box, the vertical thickness \( \Delta Z \) (meters) of the grid box, and the LWC (g m\(^{-3}\)) from (18):

\[
f = \frac{\Lambda}{\Delta Z \text{ LWC}}
\]

(29)

We retrieve \( \Lambda \) from the cloud optical depth \( \tau \) in the grid box as follows [Lin and Rosson, 1994]:

\[
\Lambda = \frac{4 \tau \rho_w}{3 \alpha \text{sat}}
\]

(30)

where \( \rho_w = 1 \text{ g cm}^{-3} \) is the density of liquid water, \( \alpha \text{sat} = 2 \) is the extinction coefficient, and \( \tau \) is an effective cloud droplet radius. For liquid water clouds \( \tau = 10 \mu \text{m} \) is appropriate [Lin and Rosson, 1994].

We compare in Figure 2 the resulting zonal mean liquid water columns computed from the GISS GCM to the satellite observations of Njoku and Swanson [1983] and Greenwald et al. [1993]. The GCM values in August agree well with Njoku and Swanson [1983] but both are smaller than Greenwald et al.'s [1993] by up to 50%. The GCM values for February are also smaller by up to 50% than those of Greenwald et al. [1993]. Although the discrepancy is within the uncertainty of the measurements, estimated at 50 m g\(^{-2}\) [Greenwald et al., 1993], it appears that the GCM may underestimate cloud water abundances. Sensitivity simulations with increased cloud water abundances will be presented below.

Results

We conducted simulations for two 2-month periods, June-July and January-February, starting from the boundary conditions as initial conditions. The first month was used for initialization (1 month is sufficient to ventilate the model domain). We present results for July and February. Figure 3 shows the monthly mean concentrations of \( O_3 \) and \( NO_x \) simulated for these 2 months. We focus our attention on the U.S. boundary layer, defined as the
region extending horizontally from 24°N to 48°N and from 127.5°W to 67.5°W (Figure 3), and vertically to the top of the third model layer (about 740 hPa, or 2.6 km altitude). This region is far from the boundaries of the model domain and receives high NO$_x$ emissions, so that NO$_x$ concentrations are not significantly affected by advection of boundary conditions.

Table 3 shows model results for the U.S. boundary layer obtained for (1) a standard "gas-aerosol-cloud" simulation using the model as described above; (2) a "gas-aerosol" simulation ignoring aqueous phase chemistry in cloud; (3) a "gas-only" simulation ignoring also the reactions of NO$_x$ and N$_2$O$_5$ in aerosols; and (4) a "gas-cloud" simulation ignoring the reactions of NO$_x$ and N$_2$O$_5$ in aerosols but including aqueous phase chemistry in cloud. The "gas-aerosol-cloud" simulation was conducted for the standard specifications of cloud abundances and pH described above and also for sensitivity cases with tripled cloud volume and pH increased to 7. Changes in O$_3$ concentrations between the different simulations are minuscule (Table 3), in part due to the advection of O$_3$ from the model boundaries. We focus our comparisons on the regional O$_3$ production rate and the lifetime of O$_3$ against chemical loss (r) in winter; the lifetime of O$_3$ against chemical loss decreases by less than 1% in summer and by only 2% in winter. Including cloud chemistry in the model without reactions in aerosols ("gas-cloud" versus "gas-only"), or without nonmethane hydrocarbons (not shown), has similarly small effects. Tripling the cloud volumes (f×3) in the summer case roughly triples the O$_3$ perturbation; the effect is still small. As an extreme case, we conducted a sensitivity simulation with tripled cloud volume and a cloud water pH of 7 (f×3, pH=7) in summer. Only then does the effect of cloud chemistry on O$_3$ become significant, as shown in Table 3 (21% decrease in the chemical lifetime of O$_3$ relative to the gas-aerosol simulation).

6. Conclusions

We examined the sensitivity of tropospheric O$_3$ to aqueous phase HNO$_3$ chemistry in clouds by conducting zero-dimensional model calculations of the O$_3$ production efficiency per unit NO$_x$ consumed (r) and of the lifetime of O$_3$ against chemical loss (1/r) with and without aqueous phase chemistry. Results for the tropics and for midlatitudes summer indicate that aqueous phase chemistry causes in-cloud values of r to decrease by 0-40% and the in-cloud chemical lifetime of O$_3$ to decrease by 0-25%. Cloud formation suppresses O$_3$ production (mainly by scavenging of HNO$_3$) but also slows down the loss of NO$_x$ (due to scavenging of...
Table 3. Three-Dimensional Model Budgets of O₃ and NO₃ in the U.S. Boundary Layer

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Production of O₃, ppb d⁻¹</th>
<th>Loss of O₃, ppb d⁻¹</th>
<th>O₃, ppb</th>
<th>NO₃, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>July</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-only</td>
<td>12.8</td>
<td>7.34</td>
<td>49.1</td>
<td>0.236</td>
</tr>
<tr>
<td>Gas-cloud</td>
<td>12.7</td>
<td>7.34</td>
<td>48.8</td>
<td>0.237</td>
</tr>
<tr>
<td>Gas-aerosol</td>
<td>12.2</td>
<td>7.18</td>
<td>48.1</td>
<td>0.217</td>
</tr>
<tr>
<td>Gas-aerosol-cloud</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard (f = 0.04, pH=4.5)</td>
<td>12.1</td>
<td>7.18</td>
<td>47.8</td>
<td>0.218</td>
</tr>
<tr>
<td>f × 3, pH=4.5</td>
<td>11.9</td>
<td>7.19</td>
<td>46.9</td>
<td>0.217</td>
</tr>
<tr>
<td>f × 3, pH=7</td>
<td>12.0</td>
<td>8.17</td>
<td>43.3</td>
<td>0.228</td>
</tr>
<tr>
<td><strong>February</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-only</td>
<td>2.61</td>
<td>1.99</td>
<td>38.3</td>
<td>0.866</td>
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<tr>
<td>Gas-cloud</td>
<td>2.47</td>
<td>2.00</td>
<td>37.9</td>
<td>0.893</td>
</tr>
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<td>2.02</td>
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<tr>
<td>Gas-aerosol-cloud</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard (f = 0.00, pH=4.5)</td>
<td>2.33</td>
<td>2.03</td>
<td>37.5</td>
<td>0.813</td>
</tr>
</tbody>
</table>

All quantities are monthly averages for the U.S. boundary layer calculated with the continental-scale three-dimensional model. The "no aerosol" simulation includes no aerosol or cloud reactions. The "no-cloud" simulation includes aqueous phase chemistry with no aerosol reactions. The "gas-aerosol" simulation includes reactions of NO₃ and NO₂ in aerosols but no cloud chemistry. The "gas-aerosol-cloud" simulation includes both cloud chemistry and reactions of NO₃ and NO₂ in aerosols; results of sensitivity calculations with increased cloud water pH and increased cloud water volume fraction (f) are also shown.

References


OII), moderating the effect on the O₃ production efficiency. Based on typical frequencies of air processing by clouds, we estimate that the maximum perturbation to O₃ concentrations from cloud chemistry in the tropics and midlatitudes summer is 1-3%. Calculations with a three-dimensional model for North America support this result.

Our estimates of the perturbation to O₃ from aqueous phase cloud chemistry are considerably lower than reported in previous model studies [Lelieveld and Crutzen, 1990; Dentener, 1993; Jonson and Isaksen, 1993]. The difference reflects in part our use of lower cloud liquid water abundances constrained with recent observations. Another contributing factor is that our study assumes a much smaller, and we argue more realistic, solubility of CH₂O₂.

We conclude that based on current chemical knowledge there is little justification for including aqueous phase H₂O₂ chemistry in regional and global models of tropospheric O₃, particularly in view of the computational penalty associated with the increased stiffness of the chemical system. Hydrolysis of NO₃ and NO₂ in aerosols and clouds is far more important for modifying O₃ concentrations and can be included in models as a surface-limited process without explicit consideration of aqueous phase chemical reactions [Dentener, 1993; Dentener and Crutzen, 1993].

Our conclusion needs to be qualified in two ways. First, significant perturbation to O₃ concentrations from aqueous phase cloud chemistry might be found in regions such as status-capped marine boundary layers in the tropics where clouds occupy a large volume fraction and where UV radiation is particularly intense near cloud top. Second, important aqueous phase radical sources might be missing from current cloud chemistry mechanisms, for example, photochemical reactions involving trace metals or dissolved organic compounds [Graedel et al., 1986; Faust et al., 1993; Zuo and Hoigne, 1993; Siefert et al., 1996]. Not enough is known presently about these missing reactions to allow quantitative inclusion in models. As more information becomes available, an assessment of their effects on tropospheric O₃ can be made using the simple zero-dimensional modeling approach described in this paper.

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