Ozone formation in biomass burning plumes: Influence of atmospheric dilution

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Abstract. Biomass burning in the tropics contributes substantially to the emission of organic compounds and nitrogen oxides into the troposphere and has an important impact on the global budget of ozone in the troposphere. Since ozone formation is a nonlinear chemical process the rate of formation is also influenced by atmospheric dilution and transport. This paper addresses the production of ozone in a plume emerging from a biomass burning site. Atmospheric mixing processes downwind the fire are expected to influence the total amount of ozone produced. A sensitivity study to assess the influence of dilution on the maximum ozone mixing ratio and on the amount of ozone formed in the entire plume (excess ozone) reveals that both quantities depend strongly on the time scale and the final value of the dilution. Up to 70 % difference of the excess ozone as function of the characteristic time of the dilution was observed. Since many global models do not treat the early development of the plume with sufficient resolution in space and time a substantial uncertainty of model predicted ozone formation from biomass burning plumes is to be expected.

Introduction

Photooxidant formation in particular chemical production of ozone in the plume of a biomass burning event is a substantial contribution to the photooxidant budget in the tropics (Chatfield and Delany [1990] and Lelieveld et al. [1996]). It is estimated that roughly 15 % of the global ozone formation in the tropics is due to the impact of natural and anthropogenic biomass fires.

The purpose of the present paper is to shed some light on the role of atmospheric transport in particular dilution by mixing with chemically unperturbed air on the temporal evolution and the amount of ozone that is formed. We use the experimental data from the SAFARI campaign in 1992, where mixing ratios of hydrocarbons, ozone, NOx, and a couple of other parameters were measured in several plumes of biomass fires in southern Africa (Koppmann et al. [1997] and references therein).

Chatfield and Delany [1990] have already discussed the influence of transport on the formation of ozone. They distinguished between two cases. Fresh emissions within the plume are first chemically processed and then mixed ("cook-then-mix") and the other limiting case where at the early stages dilution takes place and most of the chemistry occurs at later times ("mix-then-cook"). They concluded from calculations with a one dimensional model that model predictions always tend to overpredict ozone from biomass burning events.

Here we will present some simple model simulations that indicate a non monotonic dependence of the total amount of ozone formed in a plume on the total dilution and the time constant that is associated with the expansion of the plume downwind the fire.

Chemical Ozone Formation

Ozone is chemically formed by the photolysis of NO2 and subsequent reaction of the emerging ground state oxygen atom with molecular oxygen.

\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \] (1)

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \] (2)

On the other hand, ozone reacts with NO

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \] (3)

Considering only reactions (1-3), the sum of [O3] and [NO2] is constant. Thus the reaction chain above is a zero cycle for O3. An efficient ozone formation in the atmosphere can only be achieved in reactions that oxidize NO to NO2 without consuming simultaneously O3. The reactions of NO with \( \text{HO}_2 \)

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \] (4)

and with organic peroxy radicals, \( \text{RO}_2 \),

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

are of this kind. Assuming stationary mixing ratios for NO which are usually attained during daytime within minutes the production of ozone from these reactions is given by

\[ \frac{d[\text{O}_3]}{dt} = k_4[\text{NO}][\text{HO}_2] + k_5[\text{NO}][\text{RO}_2] \] (6)

Since \( \text{HO}_2 \) and \( \text{RO}_2 \) are formed by reaction of \( \text{CO} \) and hy-
drocarbons with \( \text{OH} \) the rate in eq(6) is basically proportional to the abundance of \( \text{OH} \). Adopting steady state approximations for the short lived species with relaxation times of less than several minutes the \( \text{OH} \) concentration and the momentary rate of ozone formation can be calculated. In figure 1 results from a simple box model calculation using the RADM2 gas-phase chemistry by Stockwell et al. [1990] are shown. Both \( \text{OH} \) and the chemical production of \( \text{O}_3 \) vary in parallel as function of \( \text{NO}_x \). The nitrogen oxides are obviously a very important parameter controlling the ozone formation. At early stages of the fire shortly after leaving the burning site \([\text{NO}_x]\) is large thereby allowing for only small \( \text{OH} \) concentrations. Therefore, despite the large hydrocarbon mixing ratios, the photochemical activity is low. During aging of the plume the abundance of \( \text{NO}_x \) decreases due to chemical degradation mainly in reaction of \( \text{OH} \) with \( \text{NO}_2 \) but also by heterogeneous removal and dilution. This leads to increasing ozone formation until a maximum ozone formation is reached at \( \text{NO}_x \) mixing ratios of several ppb. For \([\text{NO}_x]\) < 50 ppb ozone losses via reaction with \( \text{HO}_2 \) and the photolytic production of \( \text{OH}, \text{P}_{\text{OH}} \), exceed the formation of ozone from reactions(4-5) and results in net ozone destruction.

The inhibition and promotion of the build-up of ozone is shown in a time dependent (zero dimensional) model calculation (see figure 2). Initial conditions were taken from the Drakensberg data set (summarized in table 1). Transport or dilution processes were not considered. Also the diurnal cycle of the photolysis frequencies is not taken into account. If the nonmethane hydrocarbons (NMHC) are neglected one observes an incubation period of several sunlit days during which \( \text{O}_3 \) stays low. The removal rate of \( \text{NO}_x \) due to formation of \( \text{HNO}_3 \) is slow since it cannot exceed the production of \( \text{OH} \) from photolytic sources. Ozone starts to increase rapidly (faster than exponentially with time) as soon as \( \text{NO}_x \) is in the range of several ppb. After processing nearly all \( \text{NO}_x \) to the inactive compounds of \( \text{NO}_y \) the \( \text{O}_3 \) mixing ratio finally decreases. The onset of efficient formation of ozone depends on amount and reactivity of the hydrocarbons in the plume. For the Drakensberg fire very reactive alkenes in particular isoprene provide an earlier increase of \( \text{O}_3 \) after 10 h. Also the maximum ozone mixing ratio increases from 180 ppb to 280 ppb, which is in both cases much larger than the observed ozone levels during SAFARI92.

Obviously chemical ozone formation is a nonlinear process, which as such is expected to be influenced by atmospheric mixing. Most relevant for an emerging plume is dilution with ambient chemically unperturbed air (Chatfield

![Figure 1](image1.png)

**Figure 1.** Local chemical production of \( \text{O}_3 \) (in ppb/h, dashed line) and the \( \text{OH} \) concentration (in \( 10^6 \text{cm}^{-3} \), solid line) as function of the \( \text{NO}_x \) mixing ratio. Calculations were performed with the gas-phase chemistry RADM2 of the Regional Acid Deposition Model.

![Figure 2](image2.png)

**Figure 2.** Time dependence of the ozone and \( \text{NO}_x \) mixing ratios. Initial condition were taken from the Drakensberg record. Solid (dashed) curve includes (excludes) the nonmethane hydrocarbons. The gas-phase chemistry RADM2 was used. No dilution was applied.

<table>
<thead>
<tr>
<th>Species</th>
<th>Drakensberg</th>
<th>background</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NO}_x ) [ppb]</td>
<td>40</td>
<td>0.01</td>
</tr>
<tr>
<td>ozone [ppb]</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>( \text{CO} ) [ppb]</td>
<td>2321</td>
<td>70</td>
</tr>
<tr>
<td>( \text{CH}_4 ) [ppb]</td>
<td>1981</td>
<td>1700</td>
</tr>
<tr>
<td>alkanes [ppbC]</td>
<td>72(5)</td>
<td>5</td>
</tr>
<tr>
<td>alkenes [ppbC]</td>
<td>39(1)</td>
<td>0</td>
</tr>
<tr>
<td>aromates [ppbC]</td>
<td>33(0)</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1. Summarized initial conditions for the model calculations for the Drakensberg fire of SAFARI 92 (Koppmann et al. [1997]), \( T = 295 \text{K}, \) solar zenith angle \( \chi = 22^\circ, \) R.H. = 30%. First order losses for \( \text{HNO}_3 \) and \( \text{NO}_2 \) with time constants of 2 days and for \( \text{H}_2\text{O}_2 \) with 1 day were incorporated. Entries in brackets indicate modified initial mixing ratios for calculations without NMHC.
and Delany [1990] and Mauzerall et al. [1998]). A sensitivity study was conducted to assess the impact on the maximum ozone mixing ratio and the total amount of ozone being formed. We utilize a simple box model treatment where trace gases are confined to a box of volume $v(t)$ that expands during time thereby incorporating background air. The extra term in the balance equation for a compound $i$ reads

$$\frac{dC_i}{dt}_{\text{dilution}} = -\frac{1}{v(t)} \frac{dv(t)}{dt} (C_i - c_i)$$

(7)

were $C_i$ and $c_i$ denote the concentrations inside and outside the box, respectively. The balance equations of the background chemistry were also integrated in time. The initial values for the background roughly represent the average conditions observed during SAFARI outside biomass burning plumes. All initial conditions for the calculations are compiled in table 1.

The size of the box $v(t)$ increases with time. This dilution function $v(t)$ (in arbitrary volume units) is parameterized by

$$v(t) = a e^{\tau t} + b$$

(8)

where $a$ and $b$ are determined from $v(0) = 1$ and the expansion ratio $V = v(t_e)/v(0)$, where $v(t_e)$ is the final volume at the end of the integration period $t_e$, with $t_e = 120h$. For $\tau << t_e$ the expansion varies exponentially with time while for $\tau >> t_e$ the volume depends approximately linearly on time. Using an exponential time dependence allows for rapid dilution in the immediate vicinity of the fire, where the Drakensberg data were taken, that are used as initial conditions for the model calculations. Sillman et al. [1990] used a similar approach, however, with a different parameterization of the expansion since they address the plume at later stages.

Both parameters were inferred from the Drakensberg data to $V = 2$ and $\tau = 2h$ using the measured excess $CO_2$ mixing ratio in the plume relative to the local background which was 10ppm above the hemispherical average (Koppmann et al. [1997]). Comparison with calculations without dilution shows that dilution favours the formation of ozone at earlier times in particular in the case without the NMHC. In the presence of NMHC the dilution has only a rather small impact. This is probably due to the high reactivity resulting from the presence of highly reactive NMHC. The maximum O$_3$ mixing ratio is lowered to 180ppb, which is, however, still larger than the experimental data.

The impact on the atmospheric ozone budget is related to the total amount of ozone formed in the entire plume rather than to the ozone mixing ratio. We define $E(t)$

$$E(t) = v(t) ([O_3(t)]^{\text{plume}} - [O_3(t)]^{\text{background}}).$$

(9)

which may be considered the "excess ozone" amount resulting from the chemical ozone formation in the expanding plume. $E(t)$ has a maximum as function of time denoted by $E_{\text{max}}$. The time of maximum $E$ is less than 35h, depends only slightly on $\tau$ and decreases with increasing $V$ to values less than 10h for the largest $V$ considered. Results for $E_{\text{max}}$ are given as function of $\tau$ and $V$ in figure 3 for an initial burden of $NO_x$ of 40ppb as determined for the Drakensberg case. Small $V$ corresponds to the case "cook and then mix" where the net formation of ozone is low. $E_{\text{max}}$ increases with increasing $V$ until a maximum is reached. Larger $V$ lead to lower $E_{\text{max}}$ because now dilution in particular for $NO_x$ is so fast, the time spent with $NO_x$ around 1ppb with maximum ozone production rates is so short, that the amount of ozone summed over the plume decreases. For small $\tau$ one finds by comparing the smallest with the largest $E_{\text{max}}$ that the enhancement of ozone due to dilution is up to 70% and is therefore not a negligible quantity. For $V < 10$ the dependence on the characteristic dilution time $\tau$ is only small for $\tau < 10h$. For larger $\tau$ the $E_{\text{max}}$ increases and is shifted towards larger values of $V$. A similar behaviour with a shift of the maximum towards larger values of $V$ is observed if the hydrocarbons are neglected.

It has been noted earlier that $NO_x$ influences the temporal evolution of the ozone mixing ratio in the plume (Koppmann et al. [1997]). Smaller initial $NO_x$ burden (see figure 3) leads to smaller $E_{\text{max}}$ and the maximum as function of $V$ is shifted to smaller $V$. The much larger $NO_x$ burden of 80ppb (not shown here) causes some increase in $E_{\text{max}}$ and the maximum as function of $V$ is now shifted to an even larger $V$. The chemical formation of ozone is clearly $NO_x$-dependent. The total yield of ozone produced per $NO_x$ consumed (see also
where small contributions in the denominators from NO\textsubscript{x,background} and NO\textsubscript{x,plume}(t\textsubscript{e}) were neglected. For the Drakensberg fire (see figure 3) we obtain 7 < y\textsubscript{max} < 12. For NO\textsubscript{x} = 8ppb the yield is slightly larger (8 < y\textsubscript{max} < 18). It is tempting to estimate the contribution of the global net formation of ozone from biomass burning, G(O\textsubscript{3}), to the tropospheric ozone budget by multiplying the global annual NO\textsubscript{x} source strength S(NO\textsubscript{x}), from biomass fires with the yield. Adopting S(NO\textsubscript{x}) = 4Tg(N)/y (average of the data of Crutzen and M.O.Andreae [1990]) and y\textsubscript{max} from the Drakensberg fire, we obtain an upper bound for G(O\textsubscript{3}) = 96 - 164Tg(O\textsubscript{3})/y. Though the figures are consistent with the model estimates by Lelieveld et al. [1996], the agreement may be purely accidental. Still, these results show that the amounts of ozone formed in the early development stages of biomass burning plumes contribute substantially to the global ozone budget. Consequently details of the mixing and dilution processes in developing plumes will have a significant impact on the overall ozone budget. From the non-monotonic change of E\textsubscript{max} as function of the dilution parameters it is evident that the consideration of limiting cases such as extremely fast or very slow dilution is not sufficient to put constraints on the amount of ozone formed from biomass burning. The general behaviour of E\textsubscript{max} is only slightly influenced by the chemistry in the background. Calculations with background mixing ratios fixed to their initial values show also a maximum. Due to the then neglected chemical ozone losses because of the low NO\textsubscript{x} mixing ratio E\textsubscript{max} is somewhat smaller.

Mixing of plumes in the real atmosphere is a complex process that is only poorly described by the simple homogeneous dilution approach, that is used here. Nevertheless, our sensitivity study demonstrates that atmospheric transport has a substantial impact on the formation of ozone. There is a similar influence on other chemical intermediates like peroxides and the aldehydes (not discussed here).

Many numerical chemical tracer models (CTM) have a horizontal resolution that is larger than the scale of the plume in the early stage. The emission from the plume is often instantaneously (t = 0) smeared out over the (Eulerian) box in which the biomass burning takes place. Depending on the volume of a box (parameterized in our model by V) in the CTM this can lead to substantial errors of the modeled ozone. Small biomass fires extend over several km\textsuperscript{2}, large fires can cover several tens of km\textsuperscript{2}. However, even a regional CTM, like the Regional Acid Deposition Model (Chang et al. [1987]) with a horizontal resolution of typically 100 km \cdot 100 km, confines the fire to a single box. The dependence of E\textsubscript{max} on V indicates that different spatial resolutions can be already responsible for substantial deviations between model results. For CTMs on the global scale with a typical horizontal resolution of 10\textdegree\textsuperscript{2} by 10\textdegree\textsuperscript{2} the deviations could even be larger. From figure 3 it is evident that for a fast dilution the excess ozone formation depends strongly on the expansion ratio. This supports the findings of Chatfield and Delany [1990] and also Siliman et al. [1990] that an unrealistically fast expansion such as instantaneous dilution in a model over a grid box will result in an overestimate of ozone formation if small and medium expansion ratios are compared. However, a comparison of medium and high expansion ratios suggests the opposite. Our results show substantially lower excess ozone formation for expansion ratios around ten than for expansion ratios around fifty (cf. figure 3). The monotonic decrease of E\textsubscript{max} for very high expansion factors suggests, that there exist plausible conditions where simulations on a global scale may underestimate the impact of biomass burning on the ozone budget.

References
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