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, NO_x, 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 dis-

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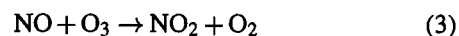
Here we will present some simple model simulations that indicate a non monotonic dependence of the total amount of ozone formed in a plume on the total dilution and the time constant that is associated with the expansion of the plume downwind the fire.

Chemical Ozone Formation

Ozone is chemically formed by the photolysis of NO_2 and subsequent reaction of the emerging ground state oxygen atom with molecular oxygen.

$$NO_2 + h\nu \rightarrow NO + O \qquad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$
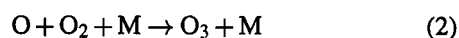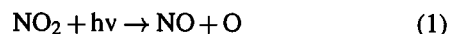
On the other hand, ozone reacts with NO

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (3)$$

Considering only reactions(1-3), the sum of $[O_3]$ and $[NO_2]$ is constant. Thus the reaction chain above is a zero cycle for O_3. An efficient ozone formation in the atmosphere can only be achieved in reactions that oxidize NO to NO_2 without consuming simultaneously O_3. The reactions of NO with HO_2

$$NO + HO_2 \rightarrow NO_2 + OH \qquad (4)$$
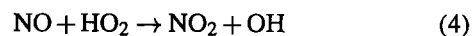
and with organic peroxy radicals, RO_2,

$$NO + RO_2 \rightarrow NO_2 + RO \qquad (5)$$
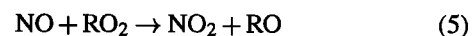
are of this kind. Assuming stationary mixing ratios for NO which are usually attained during daytime within minutes the production of ozone from these reactions is given by

$$\frac{d[O_3]}{dt} = k_4[NO][HO_2] + k_5[NO][RO_2] \qquad (6)$$

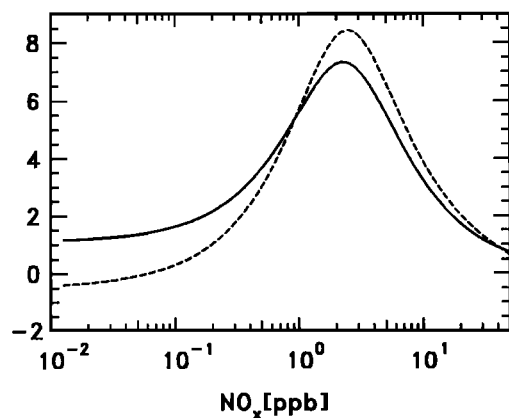Since HO_2 and RO_2 are formed by reaction of CO and hy-

Figure 1. Local chemical production of O_3 (in ppb/h, dashed line) and the OH concentration (in $10^6 cm^{-3}$, solid line) as function of the NO_x mixing ratio. Calculations were performed with the gas-phase chemistry RADM2 of the Regional Acid Deposition Model.

drocarbons with OH the rate in eq(6) is basically proportional to the abundance of OH. Adopting steady state approximations for the short lived species with relaxation times of less than several minutes the 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 OH and the chemical production of O_3 vary in parallel as function of 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 $[NO_x]$ is large thereby allowing for only small OH concentrations. Therefore, despite the large hydrocarbon mixing ratios, the photochemical activity is low. During aging of the plume the abundance of NO_x decreases due to chemical degradation mainly in reaction of OH with NO_2 but also by heterogeneous removal and dilution. This leads to increasing ozone formation until a maximum ozone formation is reached at NO_x mixing ratios of several ppb. For $[NO_x] < 50 ppt$ ozone losses via reaction with HO_2 and the photolytic production of OH, P_{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 form 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 O_3 stays low. The removal rate of NO_x due to formation of HNO_3 is slow since it cannot exceed the production of OH from photolytic sources. Ozone starts to increase rapidly (faster than exponentially with time) as soon as NO_x is in the range of several ppb. After processing nearly all NO_x to the inactive compounds of NO_y the O_3 mixing ratio finally decreases. The onset of efficient formation of ozone
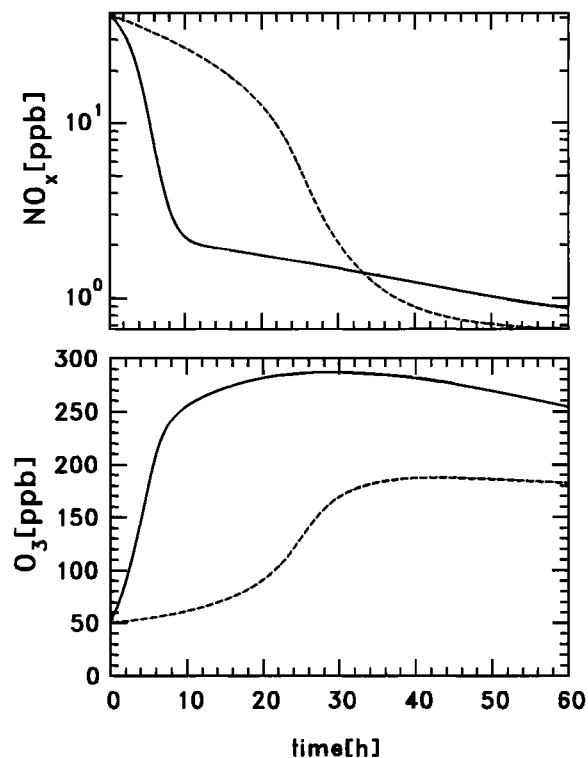

Figure 2. Time dependence of the ozone and NO_x mixing ratios. Initial condition were taken from the Drakensberg record. Solid (dashed) curve includes (excludes) the non methane hydrocarbons. The gas-phase chemistry RADM2 was used. No dilution was applied.

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 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*

Table 1. Summarized initial conditions for the model calculations for the Drakensberg fire of SAFARI 92 (*Koppmann et al.* [1997]), $T = 295K$, solar zenith angle $\chi = 22°$, $R.H. = 30\%$. First order losses for HNO_3 and NO_2 with time constants of 2 days and for H_2O_2 with 1 day were incorporated. Entries in brackets indicate modified initial mixing ratios for calculations without $NMHC$.

Species	Drakensberg	background
NO_x [ppb]	40	0.01
ozone [ppb]	50	50
CO [ppb]	2321	70
CH_4 [ppb]	1981	1700
alkanes [ppbC]	72(5)	5
alkenes [ppbC]	39(1)	0
aromates [ppbC]	33(0)	0

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

$$\left(\frac{dC_i}{dt}\right)_{dilution} = -\frac{1}{v(t)}\frac{dv(t)}{dt}(C_i - c_i) \qquad (7)$$

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

$$v(t) = ae^{t/\tau} + b \qquad (8)$$

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 $\tau \ll t_e$ the expansion varies exponentially with t with the time constant τ while for $\tau \gg t_e$ 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 parametrisation of the expansion since they address the plume at later stages.

Both parameters were infered 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 $E(t)$

$$E(t) = v(t)([O_3(t)]^{plume} - [O_3(t)]^{background}). \qquad (9)$$

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_{max}. The time of maximum E is less than $35h$, depends only slightly on τ and decreases with increasing V to values less than $10h$ for the largest V considered. Results for E_{max} are given as function of τ and V in figure 3 for an initial
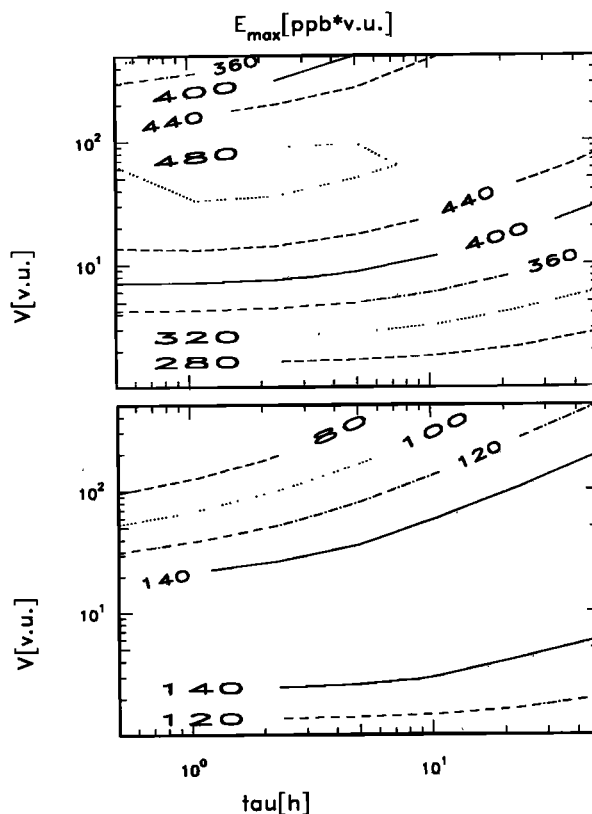

Figure 3. Isolines of the maximum excess of ozone E_{max} produced in a plume as function of the dilution time constant τ and the expansion ratio V. E_{max} is given in $ppb * v.u..$ Upper panel:Initial $NO_x=40ppb$ (Drakensberg case). Lower panel:Initial $NO_x=8ppb$.

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_{max} increases with increasing V until a maximum is reached. Larger V lead to lower E_{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 τ one finds by comparing the smallest with the largest E_{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 τ is only small for $\tau < 10h$. For larger τ the E_{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_{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_{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

Liu et al. [1987], *Lin et al.* [1988], and *Trainer et al.* [1993]) is approximately given by

$$y(t) \approx \frac{E(t)}{[NO_x^{plume}(0)]v(0)} \quad (10)$$

where small contributions in the denominator from $NO_x^{background}(0)$ and $NO_x^{plume}(t_e)$ were neglected. For the Drakensberg fire (see figure 3) we obtain $7 < y_{max} < 12$. For $NO_x = 8ppb$ the yield is slightly larger ($8 < y_{max} < 18$). It is tempting to estimate the contribution of the global net formation of ozone from biomass burning, $G(O_3)$, to the tropospheric ozone budget by multiplying the global annual NO_x source strength $S(NO_x)$, from biomass fires with the yield. Adopting $S(NO_x) = 4Tg(N)/y$ (average of the data of *Crutzen and M.O.Andreae* [1990]) and y_{max} from the Drakensberg fire, we obtain an upper bound for $G(O_3) = 96 - 164Tg(O_3)/y$. 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 global ozone budget. From the non monotonic change of E_{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_{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_x mixing ratio E_{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 ($\tau = 0$) 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^2, large fires can cover several tens of km^2. However, even a regional CTM, like the Regional Acid Deposition Model (*Chang et al.* [1987]) with a horizontal resolution of typically $100km * 100km$, confines the fire to a single box. The dependence of E_{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 $10°$ by $10°$ 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 *Sillman 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_{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.

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