Ozone Production from the 2004 North American Boreal Fires

G.G. Pfister¹, L.K. Emmons¹, P.G. Hess¹, R. Honrath², J.-F. Lamarque¹, M. Val Martin², R.C. Owen², M.A. Avery³, E.V. Browell¹, J.S. Holloway⁴, P. Nedelec⁵, R. Purvis⁶, T.B Ryerson⁴, G.W. Sachse³, H. Schlager⁷

¹ National Center for Atmospheric Research, Boulder, CO
² Michigan Technological University, Houghton, MI
³ NASA Langley Research Center, Hampton, VA
⁴ National Oceanic and Atmospheric Administration, Boulder, CO
⁵ Centre National de la Recherche Scientifique, Toulouse, France
⁶ Facility for Airborne Atmospheric Measurements, Cranfield, UK
⁷ German Aerospace Center, Oberpfaffenhofen, Germany

Abstract

We examine the ozone production from boreal forest fires based on a case study of wildfires in Alaska and Canada in summer 2004. The model simulations were performed with the chemistry transport model, MOZART-4, and were evaluated by comparison with a comprehensive set of aircraft measurements. In the analysis we use measurements and model simulations of carbon monoxide (CO) and ozone (O₃) at the PICO-NARE station located in the Azores within the pathway of North American outflow. The modeled mixing ratios were used to test the robustness of the enhancement ratio ΔO₃/ΔCO (defined as the excess O₃ mixing ratio normalized by the increase in CO) and the feasibility for using this ratio in estimating the O₃ production from the wildfires. Modeled
and observed enhancement ratios are about 0.25 ppbv/ppbv which is in the range of values found in the literature, and results in a global net $O_3$ production of $12.9\pm2$ Tg $O_3$ during summer 2004. This matches the net $O_3$ production calculated in the model for a region extending from Alaska to the East Atlantic (9–11 Tg $O_3$) indicating that observations at PICO-NARE representing photochemically well-aged plumes provide a good measure of the $O_3$ production of North American boreal fires. However, net chemical loss of fire related $O_3$ dominates in regions far downwind from the fires (e.g. Europe and Asia) resulting in a global net $O_3$ production of 6 Tg $O_3$ during the same time period. On average, the fires increased the $O_3$ burden (surface–300 mbar) over Alaska and Canada during summer 2004 by about 7–9%, and over Europe by about 2–3%.
1 Introduction

Ozone (O$_3$) plays a central role in tropospheric chemistry as a primary source of hydroxyl radicals and, by being toxic in nature, has negative impacts on human and plant health. It is also estimated to be the third most important anthropogenic greenhouse gas [Ramaswamy et al., 2001]. Anthropogenic sources and biomass burning release O$_3$ precursors including carbon monoxide (CO), nitrogen oxides (NO$_x$) and volatile organic compounds (VOCs) into the atmosphere. Photochemical reaction of CO and VOCs with the hydroxyl radical in the presence of NO$_x$ and sunlight results in the production of O$_3$.

The production of tropospheric ozone in the Northern mid-latitudes is largely impacted by anthropogenic sources [Chameides and Tan, 1981; Levy et al., 1985]. Significant ozone enhancements have been observed in individual plumes of boreal forest fires [Wofsy et al., 1992; Goode et al., 2000; Forster et al., 2001; McKeen et al., 2002; Jaffe et al., 2004; Honrath et al., 2004; Lapina et al., 2006], and measurements in combination with chemical transport simulations have been used in various studies to estimate the amount of ozone produced from boreal fires [Mauzerall et al., 1996; McKeen et al., 2002]. However, the large-scale impacts of high latitude biomass burning on the hemispheric tropospheric ozone budget are poorly quantified.

In here we apply a chemical transport model to evaluate various techniques used for estimating the ozone production from a specific source, and include various model tracers to gain a detailed insight into the limitations of these methods. We combine model analysis with observations of CO and O$_3$ to quantify contributions of boreal fires to Northern Hemispheric CO and O$_3$ burdens, a topic not very well explored so far. Our
analysis focuses on fires in Alaska and Canada in summer 2004. These fires were the
largest on record for Alaska, and the CO emissions for the North American boreal region
has been estimated as 30±5 Tg for June through August [Pfister et al., 2005]. A total of
about 11 million acres were burned in Alaska and Canada during that time period. The
study is supported by a comprehensive set of observations collected during the ICARTT
(International Consortium for Atmospheric Research on Transport and Transformation)
campaign.

CO is a long-lived tracer, and the relationship between mixing ratios of O₃ and CO in
transported regional plumes can be used as an indicator for the magnitude of net O₃
production from selected sources [Parrish et al., 1993]. It has been found that the
enhancement ratio (ΔO₃/ΔCO), given as the excess O₃ mixing ratio normalized by the
increase in CO concentrations, is typically smaller for boreal forest fires than for tropical
biomass and savannah burning or urban and industrial plumes, due to a lower NOₓ:CO
emission ratio in boreal forest fires compared to the other sources [e.g. Andreae et al.,
1994; Wofsy et al., 1992]. ΔO₃/ΔCO of fire plumes is also expected to change with plume
age. For example, Yokelson et al. [2003] found an increase from 0.09 ppbv/ppbv in fresh
tropical biomass burning plumes to 0.22 ppbv/ppbv for plumes 2–4 days old. Thus, O₃
production downwind from the source region must be accounted for.

The structure of this paper is the following. After the Introduction we discuss the
model simulations and model evaluation in Sections 2 and 3, respectively. In Section 4
we describe CO and O₃ in-situ measurements taken at the PICO-NARE station located in
the Azores. These observations were used in combination with model simulations to
investigate the O₃ production from the fires in Alaska and Canada in summer 2004.
Section 5 discusses and evaluates different techniques for calculating the enhancement ratio and analyzes the O$_3$ production due to emissions from the fires. The analysis is supported by incorporating fire tracers for CO and O$_3$ into the model and by performing model simulations with and without fire emissions. Finally, we investigate the contributions these fires had on the Northern Hemispheric and regional budgets of CO and O$_3$. Section 6 summarizes our findings.
2 Model Simulation

The Model for OZone And Related chemical Tracers (MOZART) chemistry transport model has been developed at the National Center for Atmospheric Research, the Geophysical Fluid Dynamics Laboratory and the Max-Planck Institute for Meteorology. In this study we are using Version 4 [any other reference for Mozart with aerosols?, Emmons et al., Sensitivity of chemical budgets to meteorology in MOZART-4, in preparation]. Modifications from Version 2 published in Horowitz et al. [2003] include, amongst others, a more complete description of anthropogenic hydrocarbon chemistry, the inclusion of tropospheric aerosols, and on-line calculations of dry deposition, H$_2$O, and biogenic emissions.

We run the model at a horizontal resolution of ~2.8 degrees by 2.8 degrees. The meteorological fields for 2004 for driving MOZART were taken from the National Centers for Environmental Prediction (NCEP) National Center for Atmospheric Research Re-Analysis [Kistler et al., 2001] and were interpolated from a 6-hour time resolution to the 20-minute time steps of the simulations. The vertical resolution of the meteorological fields and hence the model consists of 28 hybrid levels ranging from the surface up to 2 hPa.

Biofuel and fossil fuel emissions used in this study were taken from the European Union project POET (Precursors of Ozone and their Effects in the Troposphere) [Granier et al., 2004]. Over the continental US, the anthropogenic emissions are based on the U.S. EPA NEI-99 inventory (National Emissions Inventory, base year 1999, version 3) [EPA, 2004]. For the Alaska and Canada region, the biomass burning emissions for CO for 2004
were taken from an inverse modeling study [Pfister et al., 2005], and emissions for NOx and VOCs were deduced from this inventory by applying emission factors based on 
Andreae and Merlet [2001]. At the time these simulations were run, an emissions inventory for the year 2004 for biomass burning sources outside North America was not available. A comparison of CO data from the Measurements Of Pollution In The Troposphere (MOPITT) remote sensing instrument for 2000 – 2004 showed that the global biomass burning activity in summer 2004 was similar to 2002 and for this reason we used a 2002 biomass burning inventory based on ATSR fire counts [Granier et al., 2004].

Our model simulations cover the months from June through August 2004 with a spin-up phase beginning in August 2003. We performed three different simulations. Two of these include emissions from the Alaskan and Canadian wildfires, and are abbreviated as BB in the following. In one of these simulations (BBsurf), the wildfire emissions were released at the lowest model layer and distributed in the boundary layer by the model boundary layer scheme. Studies [Fromm et al., 2005; Damoah et al., 2006] have shown that fire induced convective clouds might transport fire emissions rapidly to higher altitude. To test the sensitivity of our model to the emissions injection height, we performed another simulation (BBvert), where the emissions were distributed evenly with regard to number density between the surface and 9 km altitude. The 9 km altitude represents an upper limit for the injection height based on estimates derived from the Multi-Angle Imaging Spectro-Radiometer (MISR) and the Moderate Resolution Imaging Spectro-Radiometer (MODIS) [Averill et al., 2005]. In a third simulation (noBB) used as a reference, the emissions of the wildfires in Alaska and Canada were set to zero.
We included two fire tracers in the model. Tracers are emitted or produced from a specific source, but undergo the same transport, chemistry, and physical processes as the standard species. The first tracer incorporated into the simulations is a CO fire tracer (COf), i.e. CO released from the Alaska/Canada wildfires. For the second tracer we tagged the O₃ production resulting from hydrocarbon or CO oxidation in association with the emissions of NOₓ from the fires. We refer to this tracer as \( O_3^{NO_x} \) in the following. The tagging technique for \( O_3^{NO_x} \) takes into account the re-cycling of NOₓ from reservoirs such as PAN by applying tags to all nitrogen-containing species. Although there are some minor pathways to create O₃ without the presence of NOₓ, the accuracy of the tagging technique has been estimated as better than 95% on a monthly basis [Lamarque et al., 2005]. The statistical analysis we perform using \( O_3^{NO_x} \) in this study is expected to give a comparable accuracy.
3 Model Evaluation

MOZART-4 simulations (BBsrf and BBvert) have been evaluated by comparison with aircraft measurements taken in the framework of the ICARTT campaign during summer 2004. Table 1 includes a list of the platforms, instrumentation, and corresponding references. Measurements with the NASA DC-8 covered large parts of North America and the Northern Atlantic, the NOAA-P3 flights were focused on the Eastern United States, the British BAE146 performed most flights over the Atlantic, and the German Falcon covered mostly Europe. The Measurements of OZone aboard Airbus In-service airCraft (MOZAIC) data set has global coverage, but we are including only measurements over North America, the Northern Atlantic and Europe in accordance with the regions covered by the other aircraft. Most low altitude measurements for this data set are from take-offs and landings over airports in Europe and the US. For a more detailed description of all flight patterns we refer to Fehsenfeld et al. [International Consortium for Atmospheric Research on Transport and Transformation (ICARTT): North America to Europe: Overview of the 2004 summer field study, submitted to J. Geophys. Res., 2006].

For the comparison of the model with the observations, 2-hour average model data have been linearly interpolated to the time and location of the aircraft data. The time resolution of the observations is 1 minute. Statistics have been calculated for the individual aircraft data sets and binned onto a 2-km wide altitude grid. The results for BBvert, BBsrf, and for comparison, noBB, are shown in Figure 1 for CO and in Figure 2 for O3, respectively. The agreement with observations for CO as well as O3 is generally
better in the simulations with fires than in the simulation without fires. CO and O₃ mixing ratios are clearly different between the BB and noBB simulations for all platforms, also for the UK BAE146 and DLR Falcon. This indicates that plumes from the Alaska and Canada fires reached all the way to Europe. We list statistics for modeled CO and O₃ concentrations for the different platforms in Table 2. The data included in the statistics corresponds to those shown in Figures 1 and 2, but in here we consider the entire altitude range from the surface to 8 km. The T-test significance levels for simulations with and without fire emissions are above 99% for all platforms indicating the samples have significantly different means. It is interesting to note that the T-test statistics comparing BBvert and BBsrf show a somewhat higher significance level for O₃ compared to CO. This suggests the modeled O₃ production from the fires is slightly more sensitive to the injection height than the concentration fields of CO.

For most altitudes and platforms, the CO bias between model and observations is less than 10% for both BBsrf and BBvert (see Figure 1). The mean bias as well as the correlation improved upon adding fire emissions into the model, with the only exception being the highest altitude bin for the NOAA P3 and DLR Falcon data set. We believe this can partly be explained by the small data sample in these bins, and, associated with that, the comparison is more strongly impacted by single events. This might also contribute to the large bias in the 4-6 km bin for the DLR Falcon. The comparison for O₃ (Figure 2) shows an agreement of better than 10% for all platforms and altitude bins when fire emissions are included in the simulations. No clear conclusion can be drawn from the evaluation if either BBsrf or BBvert lead to better general agreement. The comparison for individual fire plumes give a better agreement for either the one or the other simulation.
This reflects the combination of crown, smoldering, and peat burning of the Alaska fires. The two cases we ran do not represent the full complexity of fire behavior, but are probably better regarded as sensitivity tests to the vertical distribution of emissions.
4 Impact of Biomass Burning on CO and O$_3$ at PICO-NARE

For the analysis of the O$_3$ production from the wildfires in Alaska and Canada we made use of in-situ measurements at the PICO-NARE station. The station is located on the summit caldera of Pico mountain on Pico Island in the Azores, Portugal (2225 m above sea level, 38.47N, 28.40W) and is well suited for studying North American pollution outflow. Air masses at this location typically arrive from North America, but frequently originate from high latitude regions such as Alaska and Siberia [Honrath et al., 2004], often with enhancements in CO and O$_3$ that have been attributed to boreal fire impacts [Lapina et al., 2006]. The advantage of measurements at PICO-NARE compared with other locations on the continent is its remote location allowing the sampling of chemically well processed air masses.

CO at PICO-NARE was measured using a non-dispersive infrared absorption instrument (Thermo Environmental, Inc., Model 48C-TL) modified as described by Parrish et al. [1994]. O$_3$ was measured with a commercial ultraviolet absorption instrument (Thermo Environmental Instruments Inc., Franklin, Massachusetts, Model 49C). Data are available as 1-minute averages. For the 2-hour averages used in this study the precision for CO is estimated to be better than 9 ppbv and for O$_3$ better than 1 ppbv. For a description of the station and the measurement techniques we refer to Honrath et al. [2004] and Owen et al. [2006].

For comparing the model simulations with the observations at PICO-NARE, the observations have been averaged in time to match the 2-hour window of the simulations, and the model data have then been linearly interpolated to the location and pressure level
of the observations. Due to the coarse model resolution, the simulations do not resolve
upslope events occurring at the mountain site. Observations potentially affected by
upslope flow were small during summer 2004. We identified these periods as described
by Kleissl et al. [2006] [The occurrence of upslope flows at the Pico mountain-top
observatory: a case study of orographic flows on a small, volcanic island, submitted to J.
Geophys. Res.] and omitted them from the analysis.

Figure 3 shows the time series for modeled and measured CO and O₃ at PICO-NARE.
In addition to results from the BB model simulations, we also include results from the
noBB simulation to emphasize the impact of the Alaskan/Canadian wildfires. For clarity,
we reduced the temporal resolution in the graphs to daily average values, however, our
analysis refers to the 2-hour average values. A detailed analysis of PICO-NARE 30-
minute observations in the 2004 fire season is provided by Val Martin et al. [Significant
Enhancement of Nitrogen Oxides, Black Carbon, and Ozone in the North Atlantic Lower
Free Troposphere Resulting from North American Boreal Wildfires, submitted to J.
Geophys. Res. (hereinafter Val Martin et al., submitted)]. As can be seen in Figure 3, the
model closely matches the observed temporal variability, and also captures the
magnitudes fairly well. The mean bias between modeled (BBsurf) and observed mixing
ratios is -3±16 ppbv for CO and 6±12 ppbv for O₃. The corresponding biases for the
simulation without fire emissions are −12±19 ppbv for CO and 4±12 ppbv for O₃,
respectively. Daily CO fire tracers in the model estimate a typical transport time on the
order of 1–2 weeks for biomass burning plumes reaching PICO-NARE.

The time series for CO from the simulations BB and noBB indicate a clear impact from
the fires at PICO-NARE throughout the months of July and August with the most
extreme period from the end of July to mid-August. This is a combination of the most intense fire activity occurring in mid to end of July [Pfister et al., 2005] and the transport time of 1–2 weeks. The period from July 22–24 had the highest half-hour average CO levels yet recorded at the PICO-NARE station [Val Martin et al., submitted]. The impact of the fires on the O$_3$ concentrations is less pronounced, but differences between BB and noBB of up to 10 ppbv are evident during some of the intense episodes. The difference in CO and O$_3$ concentrations by subtracting noBB from BBsrf gives an average enhancement due to the fires of 8 ppbv (8%) for CO and 2 ppbv (4%) for O$_3$.

The correlation between the CO mixing ratios from the simulation BBsrf and the observations is $r=0.64$ compared to a correlation of $r=0.48$ between noBB and the observations. During times of intense biomass burning impact, the noBB run actually shows slight enhancement in the CO concentrations as well, indicating that these outflow events transported pollution from the fires together with elevated pollution from likely North American anthropogenic sources.

The correlation between the measured and modeled O$_3$ is $r=0.51$ for the simulation noBB and increases only slightly for the BB runs ($r=0.54$), an indication of the less pronounced or more complex [Val Martin et al., submitted] effect of the fires on the O$_3$ burden compared to the CO burden. While the model is picking up the higher O$_3$ values moderately well, neither the BB nor the noBB simulations capture the low end of the observed O$_3$ concentrations. This is likely due to the positive O$_3$ bias in the model over the US, leading to an overestimate of North American outflow of O$_3$ and to an overestimate in the modeled O$_3$ mixing ratio of maritime background air. In agreement with the conclusions drawn from the model evaluation in Section 3 it cannot be stated if
either $BB_{srf}$ or $BB_{vert}$ results in better agreement with the observations. Unless otherwise mentioned, we will focus in the following analysis on results for $BB_{srf}$. 
5 Ozone Production from Boreal Fires

Assuming a linear relationship between CO emissions and net O$_3$ production, the relationship between tropospheric CO and O$_3$ concentrations might be used as an estimate for the net O$_3$ production in regional plumes [Parrish et al., 1993; Forster et al., 2001]. The enhancement ratio $\Delta$O$_3$/ΔCO is defined as the difference between the O$_3$ concentrations in a polluted air mass from that of background air, normalized by the excess mixing ratio of CO. In the case of biomass burning plumes, the background defines concentrations of CO and O$_3$ not linked to the fire emissions.

The change in the Northern Hemispheric net O$_3$ production rate due to the fires, calculated by differencing net O$_3$ production rates in the BB and the noBB simulation, is estimated as 6 Tg O$_3$ for June through August. This is contribution of 3% to the Northern Hemispheric net ozone production. Normalizing by the total CO emissions for this time period (30±5 Tg CO) yields a global average enhancement ratio for the fires in Alaska and Canada of 0.12 ppbv/ppbv. In the following Sections we examine the feasibility of estimating the O$_3$ production of North American boreal fires by using enhancement ratios based on observed and modeled mixing ratios of CO and O$_3$ at PICO-NARE.

5.1 Determining the Enhancement Ratio from CO and O$_3$ Observations

There are two common ways to calculate $\Delta$O$_3$/ΔCO. The first, in the following referred to as the “scatter technique”, determines the enhancement ratio from the slope of the linear fit of O$_3$ versus CO mixing ratios [Parrish et al., 1993]. The second, termed as “enhancement technique”, infers “background” concentrations of CO and O$_3$ from air
masses not affected by the considered pollution source (in our case the wildfires in
Alaska and Canada) and calculates the corresponding excess mixing ratios by subtracting
background concentrations from total concentrations [Mauzerall et al., 1998]. Both
two methods are discussed in the following.

5.1.1 Scatter Technique

This technique has been applied in Figure 4 showing CO-O₃ scatter plots for observed
and modeled concentrations at PICO-NARE. The data were grouped into air masses with
varying biomass burning impact by using the magnitude of the observed CO mixing ratio
as the threshold. Studies by Honrath et al. [2004] and Lapina et al. [2006] show that
periods of extreme summertime CO concentrations frequently coincide with airflow from
Northern latitudes transporting pollution from wildfires in Siberia, Alaska and Canada to
PICO-NARE. To allow comparison with the observations, we applied two methods to the
model data: 1) we used a threshold derived from the simulated CO, and 2) we used the
relative contribution of the fire tracer COf. The second method gives in some sense the
true solution, as it is not impacted by sources of high CO other than the wildfires. The
thresholds, specified in the graphs, were chosen in a way that the number of data points
was roughly equal in the different subsets. The coarse spatial resolution in the model
results in a more pronounced dilution of biomass burning plumes and this explains the
smaller threshold in total CO applied to the subset of high intense plumes in the model
compared to the observations.

The fitting technique applied is a reduced major axis reduction (RMA). It uses the
geometric mean of the slopes of the standard linear regression of y versus x and of x
versus y [Draper and Smith, 1998] thus taking into account the variability in both
abscissa and ordinate. The mean slope and the corresponding standard deviation are specified in Figure 4.

The scatter in the data and the uncertainties in the slopes are explained by the mixture of different air masses, variability in the background CO and O$_3$ levels, and differing pathways and photochemical ages in the sampled plumes. The slopes are also somewhat dependent on the fitting technique applied. The calculated $\Delta$O$_3$/\Delta CO is independent of air mass age if the tracers used have similar lifetimes or have lifetimes much longer than the transport time, but this assumption is not entirely fulfilled in the case of CO and O$_3$. However, in a statistical sense, a clear distinction between the different types of air masses is evident with the smallest O$_3$ enhancements per unit CO for the most intense plumes in both model and data. The decrease in the slopes with increasing biomass burning impact is seen in both the model data (Figure 4b) and the observations (Figure 4a). However, the model does not capture the measured $\Delta$O$_3$/\Delta CO due to the impact of mixing in the model. As a result, the calculated slope has a rather large value with, at the same time, a high uncertainty. Applying the ratio CO$_f$/CO as a selection criteria instead (Figure 4c) we achieved a clearly stricter separation of the fire impact for the modeled plumes. The slope calculated for the most biomass burning impacted subset is then 0.44±0.08 with a correlation of $r=0.54$ instead of a slope of 0.77±0.57 and a correlation of $r=0.28$ when applying total CO mixing ratios as threshold. This slope is still higher than the observed one and this is likely due to more strongly diluted plumes in the model resulting from the coarse spatial resolution. As will be shown in Section 5.2, the selection of more intense model fire plumes reduces the estimated slope.
The generally higher slopes for air masses least impacted by biomass burning sources (defined as “non-fire plumes” here and characterized strongly by anthropogenic pollution sources) compared to those more strongly impacted by the wildfires is consistent with earlier studies \cite{Wofsy et al., 1992; Andreae et al., 1994, McKeen et al., 2002} and have been explained by a lower NO\textsubscript{x}:CO emission ratio in boreal fires relative to urban and industrial sources. In Figure 4c we include results from a simulation where the NO\textsubscript{x}:CO emission ratio for the wildfire emissions in the model was increased by a factor of 10 to match the emission ratio of anthropogenic sources. The pronounced difference between air masses with weak and with strong biomass burning impact is diminished in this case supporting the hypothesis that the difference between \textit{O}_3 production of anthropogenic and biomass burning plumes can largely be explained by a difference in NO\textsubscript{x}:CO emission ratios.

It is evident from Figure 4 that the limitations used in the selection of biomass burning impacted air masses and the degree of mixing in the considered air masses have an effect on the calculation of \textit{ΔO}_3/\textit{ΔCO}. The observed and modeled correlations also indicate that the enhancement ratio decreases the more strict the selection criteria applied are, and this dependence will be looked into more closely in Section 5.2.

\textbf{5.1.2 Enhancement Technique}

The enhancement technique requires knowledge of the background concentrations, and large uncertainties might be introduced if the background and its variability are not well known. For modeling studies, however, the variability in background concentrations can be determined accurately from a simulation where the considered emission source is omitted.
Figure 5 shows observed and modeled excess mixing ratios of O\textsubscript{3} versus CO for the air mass separation applied earlier (Section 5.1.1). For Figures 5a and 5b we estimated the background by averaging CO and O\textsubscript{3} mixing ratios over the subset of non-fire impacted air flow, which explains the existence of negative excess mixing ratios in this subset of data. For the observations the derived background values are 82 ppbv for CO and 37 ppbv for O\textsubscript{3}; for the model data we obtain 81 ppbv for CO and 45 ppbv for O\textsubscript{3}. The derived slopes for the air masses impacted by biomass burning are nearly identical to the values derived from the scatter technique showing that the background value we assumed in the enhancement technique is similar to the one implied in the scatter technique. The difference in the slopes for observed and modeled CO-O\textsubscript{3} relationships (Figures 5a and 5b) suggests this method is also sensitive to the amount of mixing.

Figure 5c shows modeled slopes when the background is estimated from the simulation without fire emissions. In some sense, this is the result one would obtain assuming perfect data, i.e. if the excess mixing ratios of CO and O\textsubscript{3} are precisely known. For each data point in the BB\textsubscript{srf} simulation a corresponding background value is derived from the noBB run, thus the temporal variability in the background is accounted for. The standard deviation of the background mixing ratios as determined from the noBB simulation is on the order of 5 ppbv for the biomass burning plumes. Compared to the scatter technique and the enhancement technique with a constant background, the excess mixing ratios for CO and O\textsubscript{3} derived with this technique are more strongly correlated and the calculated slopes are much less sensitive to the selection of the air mass. \(\Delta\text{O}_3/\Delta\text{CO}\) for the biomass burning plumes at PICO-NARE derived from this technique is 0.28 ppbv/ppbv when the air masses are filtered for the points most impacted by biomass.
burning, and 0.23 ppbv/ppbv for all data points. These values are lower than those calculated with the scattering technique for the model data and match the observed \( \Delta O_3/\Delta CO \). This concludes that the modeled fire plumes are more diluted compared to observed plumes because of the coarse model resolution, and still carry characteristics of non-fire related pollution. This impact only cancels out by considering the contribution of time-varying non-fire related background air. When the sensitivity to model mixing is removed, the model captures the observed enhancement ratio.

Thus, provided accurate information about the variability in the background levels is available, the enhancement technique allows a more accurate determination of \( \Delta O_3/\Delta CO \) than the scatter technique. The same technique applied to the model simulation in which the NO\textsubscript{x} fire emissions were increased by a factor of 10 yields slopes on the order of 0.8, i.e. close to the enhancement ratio estimated for anthropogenic sources.

5.2 Enhancement Ratios and O\textsubscript{3} Production

We used the model data to test the sensitivity of \( \Delta O_3/\Delta CO \) derived with both the scatter and the enhancement techniques to the degree to which air masses are impacted by biomass burning. For the enhancement technique the background was derived from the \textit{noBB} simulation. Figure 6 shows \( \Delta O_3/\Delta CO \) as a function of the magnitude of biomass burning impact indicated by selecting air masses based on a lower limit of the fraction of CO\textsubscript{f} to total CO. The enhancement technique shows a weak dependence on the selected air masses and the variations seen reflect the variability in O\textsubscript{3} production in biomass burning plumes due to changes in O\textsubscript{3} chemistry, transport pathways and times, and a combination of these or more processes. The average \( \Delta O_3/\Delta CO \) is calculated as 0.25
ppbv/ppbv for $BB_{sr}$ and a slightly higher value, 0.27 ppbv/ppbv, is calculated for $BB_{vt}$. This value is close to the enhancement ratio of 0.26 derived from the observations when intense plumes are selected only (Figure 4).

Our values for $\Delta O_3/\Delta CO$ are in the range of values found in the literature. Mauzerall et al. [1996] calculated enhancement ratios for aged boreal fire plumes on the order of 0.1±0.2 ppbv/ppbv. A value of 0.1 ppbv/ppbv was encountered during SOS-95 by Wotawa and Trainer [2000] and similar values during ABLE-3 for Alaska fires [Jacob et al., 1992]. McKeen et al. [2002] report enhancement ratios of 0.17 ppbv/ppbv. Higher averaged enhancement ratios are estimated by Bertschi and Jaffe [2005] and Honrath et al. [2004] for highly aged boreal fire plumes: 0.4 ppbv/ppbv and 0.7 ppbv/ppbv, respectively.

In the case of the scatter technique it is evident that $\Delta O_3/\Delta CO$ is higher for the weakly impacted plumes due to the mixing of the biomass burning impact with the impact of other pollution sources. As mentioned earlier, during times of intense fire plumes, increased pollution was also transported to PICO-NARE (Figure 3). The average $O_3$ concentration for the noBB simulation is 44±9 ppbv for $CO_f/CO<0.01$, but 47±5 ppbv and 47±4 ppbv for $CO_f/CO>0.1$ and $CO_f/CO>0.2$, respectively. Corresponding CO concentrations are 77±8 ppbv, 84±6 ppbv, and 82±6 ppbv. When air masses with at least 20% biomass burning impact are selected, the slopes calculated with the two different techniques approaches a similar range. However, towards stricter limitations the number of data points is small and the fitting technique is less reliable.

By using $\Delta O_3/\Delta CO = 0.25$ ppbv/ppbv as derived from the enhancement technique, an approximation for the total $O_3$ produced from the fires can be made [Parrish et al., 1993;
Mauzerall et al., 1996]. With 30±5 Tg CO emitted by the fires from June through August as stated by Pfister et al. [2005], an O₃ production of 10.7–15 Tg O₃ is estimated for the same time period (30±5 Tg CO multiplied by 0.25 ppbv ppbv⁻¹ and corrected by the ratio of O₃ (48 g mol⁻¹) to CO (28 g mol⁻¹) molecular weights).

This value is larger than the Northern Hemispheric net chemical production rate of 6 Tg O₃ in the model as mentioned earlier. The discrepancy can be explained in that ΔO₃/ΔCO at the location of PICO-NARE is not representative for the total net change in O₃, but rather for the net O₃ production rate covering the region from the source location to the Azores. Close to the source region net chemical production of fire-related O₃ dominates, while further downwind from the source (e.g. Europe and Asia) net chemical loss dominates. The modeled net O₃ production calculated over a region representative for air masses reaching PICO-NARE (stretching from 180W to 20W and from 40N to 70N) is 9 Tg O₃ for BBstrf and 11 Tg O₃ for BBvert, i.e. in the range of the estimate based on ΔO₃/ΔCO. These results demonstrate that the measurements and model simulations at the location of PICO-NARE being representative of aged biomass burning plumes indeed give a good measure of the O₃ production of fires in North America. Differences between the ΔO₃/ΔCO based estimate and the model calculated production are explained by uncertainties in the calculation of the slopes and differing pathways and chemical ages for plumes reaching PICO-NARE.

As mentioned earlier, our model simulations not only include a CO fire tracer, but also an O₃ fire tracer $O₃^{NOx}$ that tracks the amount of O₃ produced from the NOₓ fire emissions. One might assume that the global net O₃ production for this tracer equals the amount derived when subtracting results for simulations with and without fire emissions.
as has been done above (6 Tg O₃). However, the net O₃ production rate for the Northern Hemisphere calculated from the O₃ fire tracer is higher, close to 9 Tg O₃. The reasons for this are due to the non-linearity in O₃ chemistry and are explored in the following Section.

5.3 Changes in the O₃ Chemistry due to Fire Emissions

In Figure 7 we show correlations between the model CO and O₃ fire tracers and the difference in O₃ and CO mixing ratios from BBsrf and noBB simulations defined as dO₃ and dCO, respectively. As can be seen, the correlation for CO is close to the 1:1 line, but for O₃ the mixing ratios of O₃NOx are clearly larger compared to dO₃ indicating that O₃ production related to the fires must have been offset by an increased loss of O₃.

To explore the mechanisms behind the O₃ production from the fire emissions, we compared O₃ concentrations, production and loss terms in the model for the simulations BBsrf and noBB. The data set has been split into three groups of varying fire impact determined by the ratio COf/CO. Statistics for the individual subsets are plotted in Figure 8. The maps (Figure 8a) denote the geographical coverage of the selected data with red indicating a high, and blue a low, concentration of data points. The most intense plumes are concentrated near the source location, but plumes of high fire impact can also be seen all the way to Europe. The high intensity plumes are mostly located near the surface (Figure 8b) as expected when the emissions are released at the lowest model level. With time, atmospheric transport and convection spread plumes over a larger altitude range.

Figure 8c shows that O₃ levels without fire emissions (O₃noBB) are mostly below 40 ppbv over the source regions, i.e. the fires occurred in an area of low O₃ concentrations.
The additional NO\textsubscript{x} from the fires causes a shift in the distribution of O\textsubscript{3} concentrations towards higher values. The effect is most pronounced over the source region, but a slight positive shift is also evident for the subset of least impacted plumes.

The increase in O\textsubscript{3} is caused by a strong net production of the fire tracer $O_{3}^{NOx}$ in the most impacted plumes with the magnitude decreasing with decreasing plume intensity. This is shown in Figure 8d where we illustrate histograms for the $O_{3}^{NOx}$ net chemical production. Even though the strongest production takes place close to the source region, continuing production is also evident in regions further downwind from the source. For the subset of least impacted plumes (and most aged plumes), there are a significant number of data points with net chemical loss of $O_{3}^{NOx}$.

Figures 8e to 8g show the changes to background O\textsubscript{3} levels when fire emissions are injected into the system. Figure 8e denotes the distribution for production of $O_{3}^{noBB}$ and of background O\textsubscript{3} with fire emissions; the latter defined as $O_{3}B$. $O_{3}B$ is calculated by subtracting the O\textsubscript{3} fire tracer from the total O\textsubscript{3}. The production of $O_{3}B$ is less than the production of $O_{3}^{noBB}$. Thus, by adding fire emissions to the system, the production of background O\textsubscript{3} is reduced in the simulations. This is explained by reduced background levels of peroxy radicals (not shown here). Peroxy radicals play an important role in ozone production by reacting with NO to form NO\textsubscript{2} which then is photolyzed to give atomic oxygen necessary in the O\textsubscript{3} formation. Changes are most pronounced over the source region, but differences are also evident in less impacted plumes.

In addition to a reduced production of $O_{3}B$, the loss of $O_{3}B$ is increased over that of $O_{3}^{noBB}$, reflected in a reduction in the chemical lifetime (Figure 8f). The reduced production and increased loss of background O\textsubscript{3} result in lower concentrations of $O_{3}B$.
compared to $O_3^{noBB}$. In Figure 8g we show the corresponding frequency distributions for $O_3^{NOx}$, $O_3B$ and $dO_3$. When compared to Figure 8c we see that over the source region $O_3B$ has on average ~80% smaller values compared to $O_3^{noBB}$ and most of the $O_3$ present is in the form of $O_3^{NOx}$, i.e. $O_3$ due to the NO$_x$ fire emissions.

The strong reduction of background $O_3$ levels when fire emissions are included explains why concentrations of $O_3^{NOx}$ are larger than the difference in $O_3$ concentrations between runs with and without fire emissions. In contrast, the CO chemistry has a first-order linearity, thus the concentrations of the fire tracer $CO_f$ are close to the difference of CO concentrations simulated with and without fire emissions (Figure 7). However, the fires also impacted background levels of atmospheric CO to some extent. The high VOC and CO emissions from the fires result in a reduction in average OH concentrations. This in turn reduces the rate of oxidation of CO and results in increased background CO levels. This increase has been estimated in the model by comparing the background CO with fire emissions (calculated by subtracting $CO_f$ from total CO concentrations in $BB_{srf}$) to the CO field without fire emissions. For the Northern Hemisphere we calculate an increase in the burden of background CO of up to 1 Tg CO.

5.4 Impact of Alaska/Canada Wildfires on the $O_3$ Budget

Finally, using the model results, we examine how increases in the CO and $O_3$ concentration fields related to the wildfires affected the Northern Hemispheric and the regional trace gas budgets. In Figure 9 we show the time series for the modeled Northern Hemispheric CO and $O_3$ burden (surface – 300 hPa) and the changes related to the emissions from the fires. The change in the CO burden reaches close to 10% around the end of July. The corresponding changes in the $O_3$ burden are on the order of up to 4%. On
average, the Northern Hemispheric CO and O₃ burden during the summer 2004 were
increased due to emissions by the fires by 4–5% and 2%, respectively.

As expected, the largest changes in the atmospheric burden occurred over Alaska and
Canada (50–70N, 180E–60W) with an average increase in the O₃ burden of 7–9% for the
altitude range surface–300 hPa, and 11–12% for the range surface–800 hPa. For
comparison, over the altitude range up to 300 hPa, this is slightly smaller than the
estimated contribution of stratospheric O₃ (11%) in the model, but for the range up to 800
hPa exceeds the contribution of stratospheric O₃ (3%).

Due to the transport of O₃ and its precursors, effects from the fires are also expected
far downwind of the source location. Over Europe (35–70N, 20W–20E) we estimate a
contribution of O₃ from the fires of up to 10% around the end of July for the surface–300
hPa range and up to 8% for the range surface–800 hPa. Averaged over the summer, the
contributions are on the order of 3% for both altitude ranges considered. These results
show that even though the fires had a rather small contribution to the large-scale
hemispheric budget of O₃, over certain regions and altitudes, even far downwind from the
source itself, the impact is significant.
6 Conclusion

We have determined the amount of O$_3$ produced from the wildfires in Alaska and Canada in summer of 2004 by using a combination of model simulations and observations. The modeled CO and O$_3$ fields have been evaluated by comparison with a comprehensive set of aircraft measurements taken during the ICARTT campaign.

In analyzing the O$_3$ production from North American boreal fires we used measured and modeled CO and O$_3$ mixing ratios at the PICO-NARE station in the Azores. The results show that the enhancement ratio $\Delta$O$_3$/ΔCO, defined as the increase in O$_3$ per unit increase in CO, derived from observed and modeled concentrations at PICO-NARE is a good measure for the O$_3$ production from the Alaska and Canada fires. However, we also show that this measure can be very sensitive to the selected air masses. Our analysis yields enhancement ratios of 0.25 ppbv/ppbv for aged plumes of Alaskan and Canadian wildfires, which is in the range of values found in the literature. The enhancement ratio found for boreal biomass burning plumes is about a factor of 3–4 smaller than that of anthropogenic plumes. We have also performed a sensitivity simulation that clearly showed that the difference in the enhancement ratio for anthropogenic and boreal fire biomass burning plumes is a result of the difference in the NO$_x$/CO emissions ratios for these sources.

Controversies exist in the understanding of the importance of O$_3$ production from boreal forest fires. The total net O$_3$ production from the boreal fires in Alaska and Canada in the summer of 2004 in our model is estimated as 6 Tg O$_3$ which gives a contribution of about 3% to the Northern Hemispheric budget. Considering only a region spanning from...
the source to the Azores, a net chemical production of 9–11 Tg O₃ is calculated in the model. This is in agreement with the estimate derived from enhancement ratios based on model simulations and observations at PICO-NARE (10.7–15 Tg O₃). Large increases in the O₃ burden are observed downwind of the fires due to transport of O₃ produced near the fires as well as due to continuing O₃ production in the fire plumes. Modeling studies show that the increase in the atmospheric burden of O₃ is a combination of a strong O₃ production due to precursors emitted by the fires, and an increased destruction of O₃ background levels resulting from reduced peroxy radical concentrations.

While the availability of satellite measurements of tropospheric CO concentrations puts constraints on the CO emissions, uncertainties remain in how to constrain the emissions of NOₓ and VOCs resulting in uncertainties in the estimated O₃ production. Another unknown is the emissions injection height of the fires.

The results of this study indicate that fires in the boreal region can have a significant impact on the O₃ production over large parts of the Northern Hemisphere. We focused our investigations on the wildfires in Canada and Alaska from summer 2004, that have been a record for this region, but comparable or even larger impacts might occur from fires in Siberia. With climate change and the possibility of increased fire activity in the Northern latitudes as a result of more frequent and/or more severe droughts and increased direct human impact [Mollicone et al., 2006], O₃ production from boreal fires might gain in importance in the future.

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<td>CO</td>
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Table 1: List of aircraft measurements included in the evaluation of the model simulations. The NOAA-P3 O₃ instrument is a new installation, but similar to the one described in the listed reference.
Table 2: Statistics over the altitude range 0-8 km for the model simulations $BB_{srf}$, $BB_{vert}$ and $noBB$ and the platforms listed in Table 1. Mean and standard deviation for CO and $O_3$ concentrations and the significance level of the Student’s T-Statistics comparing $BB_{srf}$ to $noBB$, $BB_{vert}$ to $noBB$, and $BB_{srf}$ to $BB_{vert}$ are shown.

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<td>117±35</td>
<td>106±31</td>
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<td>&lt; 0.01</td>
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<tr>
<td>P-3</td>
<td>140±41</td>
<td>139±41</td>
<td>124±39</td>
<td>&lt; 0.01</td>
<td>&lt; 0.01</td>
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<tr>
<td>BAE146</td>
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<td>99±23</td>
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<tr>
<td>Falcon</td>
<td>110±24</td>
<td>108±23</td>
<td>85±11</td>
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<td>&lt; 0.01</td>
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<td>117±39</td>
<td>116±39</td>
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<tr>
<td>MOZAIC</td>
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<td>63±13 60±13</td>
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<td>DIAL</td>
<td>54±8</td>
<td>56±9   53±8</td>
<td>&lt; 0.01 &lt; 0.01 &lt; 0.01</td>
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Figure 1: Model evaluation with aircraft data for CO (blue diamonds: observations, black crosses: model with fire emissions injected at surface; green squares: model simulations with fire emissions injected over 0-9 km; red triangles: no fire emissions). The mean percent bias and standard deviation (model minus measurement), correlation coefficient r and number of data points for 2-km wide altitude bins are specified.
Figure 2: As Figure 1, but for $O_3$. 
Figure 3: Measured and modeled time series of CO and O₃ mixing ratios at PICO-NARE (daily averages are shown).
Figure 4: Observed (a) and modeled (b,c) CO-O₃ relationships at PICO-NARE. Air masses are separated into three groups: mostly non-fire related origin (blue), some biomass burning impact (green), pronounced biomass burning impact (red). In (c) results are also shown for a simulation where the NOₓ fire emissions were increased by a factor of 10.
Figure 5: Observed (a) and modeled (b,c) CO-O_3 excess mixing ratios. In (a) and (b) a constant background (bg) is calculated from the subset of non-fire impacted airmasses, in (c) the background is derived from the noBB simulation.
Figure 6: Enhancement Ratio (mean slope and standard deviation) determined by the scatter and the enhancement technique as a function of intensity of biomass burning influence of considered air masses. The number of selected data points is represented by the shaded area. Results for the BBsrfl simulation.
Figure 7: Correlation between the model fire tracers $CO_f$ and $O_3^{NOx}$ and the difference in CO and O$_3$ mixing ratios between the simulations $BB_{surf}$ and $noBB$ (defined as $dCO$ and $dO_3$) at PICO-NARE.
Figure 8: Statistics for ozone concentrations and ozone production and loss terms for three different subsets of fire plume intensity as characterized by the ratio of COf/CO. (a) Spatial distribution for selected data points. (b) Frequency distribution for the height of the selected data points (c) Frequency distribution of the volume mixing ratios $O_3^{\text{noBB}}$ and $O_3$. (d) Net O3 production rate for the fire tracer $O_3^{\text{NOx}}$ (e) Frequency distribution of the O3 production rate for $O_3^{\text{noBB}}$ and $O_3^B$ (background O3 estimated by subtracting $O_3$ and $O_3^{\text{NOx}}$). (f) as (e) but for the chemical lifetime (g). Frequency distribution of the volume mixing ratios $O_3^{\text{NOx}}$, $dO_3$ and $O_3^B$. 


Figure 9: Northern Hemispheric burden of CO and O$_3$ for the altitude range surface-300 mbar. Model results for simulations $BB_{srf}$ (solid line) and $noBB$ (dotted line). The dash-dotted line denotes the percentage difference between simulations $BB$ and $noBB$ (shown on the secondary ordinate).