

Impact of Wildland Fires and Prescribed Burns on Ground Level Ozone Concentration

Review of Current Science Concepts and Analytical Approaches

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Introduction

Satellite observations have shown that vegetation fires influence regularly Earth's atmosphere on a global scale (Fishman et al. 1991, 2003; Thompson et al. 2001; Torres et al. 2002; Bremer et al. 2004). Biomass burning releases nitrogen oxides (NO_x) and volatile organic compounds (VOCs) (Andreae and Merlet 2001; Sinha et al. 2003a; Christian et al., 2003), which react photo-chemically causing elevated ozone (O₃) concentrations in the troposphere (Fishman and Brackett 1997; Thompson et al., 2001; McKeen et al. 2002; Liu et al. 2006). Photochemical reactions and ozone production also occurs in individual smoke plumes on the timescale of hours or less (Hobbs et al. 2003; Goode et al. 2000; Takegawa et al. 2003; Yokelson et al. 2003). Studies have estimated that biomass burning contributes globally about 10% to the observed tropospheric ozone level (Lelieveld and Dentener 2000; Marufu et al. 2000; Galanter et al. 2000; Granier et al. 2000). However, on a regional scale close to the source area, vegetation fires can have a significantly stronger impact on ambient ozone concentration (Marufu et al. 2000; McKeen et al. 2002). For example, according to recent analysis, emissions from biomass burning account for nearly 24% of the observed O₃ in the planetary boundary layer over Africa during the dry season (Marufu et al. 2000).

Most biomass burning, and resulting impact on global ozone, is believed to occur in the tropics. Thus, several studies have specifically focused on understanding the impact of tropical burning on tropospheric ozone (Hauglustaine et al. 1998, 1999; Schultz et al. 1999; Galanter et al., 2000). A number of field experiments have been conducted to quantify biomass-burning emissions in different regions, e.g., the Southern Tropical Atlantic Region Experiment (STARE) (Andreae et al. 1996), the Experiment for Regional Sources and Sinks of Oxidants (EXPRESSO) (Delmas et al. 1999), the Smoke, Clouds, and Radiation-Brazil experiment (SCAR-B) (Kaufman et al. 1998), the Southern Oxidants Study (Wotawa and Trainer 2000), and the Southern African Regional Science Initiative (SAFARI 2000) (Swap et al. 2002, 2003). Several global and regional databases have been developed to estimate particulate and gaseous emissions from biomass burning (van der Werf et al. 2003; Hoelzemann et al. 2004; Ito and Penner 2004; Wiedinmyer et al. 2006).

Field observations indicate that biomass burning strongly influences the atmospheric composition in South America and Africa during the dry season (Artaxo et al. 1994; Anderson et al. 1996; Reid et al. 1998; Kirkman et al. 2000; Sinha et al. 2003). These studies also suggest that a significant fraction of the enhanced ozone concentration observed at the regional scale is attributable to photochemical ozone production in local smoke plumes before dispersion to the regional scale (Mauzerall et al. 1998; Kondo et al. 2004). Ozone production in young (fresh) smoke plumes has been often observed within tens of minutes to several hours after the smoke is released into the atmosphere in both tropical and boreal regions (Hobbs et al., 1996, 2003; Goode et al. 2000; Takegawa et al. 2003; Jost et al. 2003; Yokelson et al. 2003). Elevated ozone has often been detected several days downwind of large fires (Mauzerall et al. 1998; Wotawa and Trainer 2000; Forster et al. 2001).

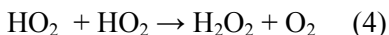
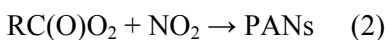
Modeling also confirms the important impact that fire emissions have on ozone levels at regional and global scales (Chatfield et al. 1998; Mauzerall et al. 1998; Lelieveld and Dentener 2000; Marufu et al. 2000; Peters et al. 2002; Duncan et al. 2003a, 2003b). Most global atmospheric photochemistry models consider emissions from biomass burning (e.g., Bey et al., 2001; Horowitz et al., 2003). Regional photochemical transport models have been used to study effects of intense fire activity on downwind ozone concentrations (Phadnis and Carmichael 2000; McKeen et al. 2002; Junquera et al., 2005). Individual smoke plume models have been employed to analyze the photochemical dynamics of biomass-burning smoke over the course of a few hours to several days (Jonquière et al. 1998; Taupin et al., 2002; Trentmann et al. 2003; Mason et al. 2006).

A new book is in press that will further add to the database of information about effects of vegetation fire on air pollution and tropospheric ozone in particular (A. Bytnerowicz, M. Arbaugh, A. Riebau and C. Andersen (eds), *Wildland Fires and Air Pollution*, Elsevier, In Press.)

Photochemistry of Ozone Production in Smoke Plumes

Ozone is a secondary product of biomass burning formed through the oxidation of non-methane hydrocarbons and other volatile organic compounds (VOCs) in the presence of elevated levels of nitrogen oxides (NO_x) (Jost et al. 2003). Here, we use the acronym VOC to refer collectively to both oxygenated organic compounds and hydrocarbons.

Tropospheric gas phase photochemistry is driven by sunlight and temperature, and is characterized by the oxidation of CO and VOCs catalyzed by NO_x with the formation of O₃ as a byproduct (Mason et al. 2001). The catalytic photochemical reaction cycle is controlled and maintained by radical species, which are introduced into the troposphere via photolytic radical reactions. Radical species and NO_x are removed from the photochemical cycle through termination reactions such as these (Mason et al. 2001):



The first three reactions consume NO_x as well as radical species, and are referred to as "Rad+NO_x" termination reactions, while the last two are recombination reactions and are called "Rad+Rad" termination reactions (Kleinman 1994). Which termination reactions are dominant depends on the relative availability of NO_x and radical species (Kleinman 1994).

Tropospheric ozone is formed through the photolysis of NO₂. However, most NO_x emissions into the atmosphere are in the form of NO, and the photolysis of NO₂ also regenerates NO. Thus, in order to obtain net cyclic formation of O₃, NO must be converted to NO₂ by a molecule other than O₃. This conversion is mainly performed by peroxy radical species via reactions such as this (Mason et al. 2001):



Depending on which reactant is limiting this reaction, the system may be sensitive to one or the other.

In the VOC sensitive state, the emission of NO_x exceeds the production of radical species. Radicals are thus rapidly removed from the system via reactions (1)-(3), limiting their availability to perform the NO-to-NO₂ conversion (as in reaction 6) and inhibiting O₃ production (Mason et al. 2001). In general, the VOC sensitive state is characterized by a decrease in O₃ concentration with increasing NO_x level, while an increase in VOC concentration increases radical production and therefore boosts O₃ formation (Sillman 1999).

In NO_x-sensitive situations, the NO-to-NO₂ conversion reactions (such as 6) are limited by the availability of nitrogen oxides. In this case, O₃ formation increases with higher NO_x concentration because radical species are readily available to convert NO to NO₂ (Kleinman 1994; Mason et al. 2001). Some studies conclude that O₃ production in this case is largely independent of VOC concentration due to the saturation of radical species (Sillman 1999). However, model simulations conducted by Mason et al. (2001) suggest that net O₃ formation can sometimes be VOC-dependent under NO_x-sensitive conditions due to VOC-induced removal of NO_x leading to reductions in both O₃ destruction and production. Modeling studies have shown that urban plumes undergo a transition from VOC-sensitive (close to the city center) to NO_x-sensitive photochemistry (in outlying rural areas) due to removal of NO_x from the plume by photochemical reactions and dilution (Sillman 1999). A similar phenomenon is observed in smoke plumes from biomass combustion (Mason et al. 2001).

In boreal fires, NO_x emissions per carbon consumed are nearly three times smaller compared to tropical and savannah fires. This causes a low efficiency of O₃ formation in the boreal region as reflected in the smaller regression slopes of observed O₃ versus CO data (McKeen et al. 2002). Thus, measurements obtained during the 1995 Southern Oxidants Study (SOS-95) in Canada revealed $\Delta\text{O}_3/\Delta\text{CO}$ ratios of about 0.1 within the CO plumes above the planetary boundary layer (Wotawa and Trainer, 2000), which is similar to such ratios observed in plumes from Alaskan fires by Goode et al. (2000). The value of 0.1 is about three times smaller than what is observed downwind of urban areas in the summer (Parrish et al. 1993), and a factor of 5 to 10 lower than in plumes from tropical fires that are several days old (Mauzerall et al., 1998; Singh et al., 2000).

In individual smoke plumes, photochemical production of O₃ is driven by the oxidation of VOCs via the hydroxy radical (OH) in the presence of high concentrations of NO_x (Trentmann et al. 2003). One important difference between urban and biomass-burning emissions is the large amount of oxygenated volatile organic compounds emitted by vegetation fires. The most important VOCs emitted from biomass burning are aldehydes (e.g. HCHO, CH₃CHO), organic acids (e.g. HCOOH, CH₃COOH), alcohols (e.g. CH₃OH), and ketones (e.g. CH₃COCH₃) (Trentmann et al. 2003).

VOCs released from prescribed burns and wildfires can boost radical species production, which has complex effects on the formation of O₃ and other photochemical products in a smoke plume. The amount of NO_x initially released by fires is oftentimes smaller compared to NO_x emitted by urban or industrial processes. While oxygenated compounds can increase the concentrations of radical species and the general level of photochemistry within a smoke plume, therefore acting to increase O₃ production, they can also accelerate the titration of NO_x out of the smoke plume via “Rad+NO_x” termination reactions resulting in the slowing of O₃ production and altering the product distribution profile. Thus, the net impact of directly emitted VOCs on O₃ depends on the complex balance between these two effects and may be either positive or negative (Mason et al. 2001).

The depletion of NO_x via the addition of VOCs in an environment, which is already NO_x-limited results in a complex behavior of O₃ and OH concentrations depending on initial NO_x levels and reaction rates, which are controlled by ambient temperature and incident solar radiation. When the initial NO_x concentration is large enough to compensate for the increased removal of NO_x, the addition of VOCs leads to an overall increase in the NO-to-NO₂ conversion reactions and therefore an increase in O₃ and OH formation. However, lower initial NO_x concentrations may not be able to compensate for the increased removal of NO_x, leading to a decrease in NO-to-NO₂ conversion and a subsequent decrease in O₃ and OH production. Mason et al. (2001) attribute this effect to the ability of the VOCs to photolyze, resulting in an additional direct source of radical species, which may not be compensated for by the NO_x emissions. Hence, studies intending to predict the increased O₃ production due to biomass combustion at the regional scale need to include both direct emissions of

VOCs and a realistic estimate of initial NO_x concentrations (Mason et al 2001). In addition, the release of acetone from biomass burning might be particularly important for atmospheric chemistry, because such acetone emissions are accompanied by NO_x emissions as well as convective activity (Jost et al. 2003). As acetone is most effective in changing the O₃ production in the upper troposphere under high NO_x conditions (Folkins and Chatfield 2000; Jaegle et al. 2001), acetone from biomass burning might be more important than acetone from other sources that are not associated with atmospheric convection and NO_x emissions such as organic matter decomposition (Warneke et al. 1999).

Importance of Scale for the Ozone Production due to Biomass Burning

Ozone production from biomass burning occurs at the scale of individual plumes due to the oxidation of short-lived chemical species such as alkenes and aldehydes, and at the regional scale due to the oxidation of longer-lived emissions such as CO and alkanes (Jost et al. 2003). In a large-scale model study of the impact of Canadian fires on ozone pollution levels over the Eastern US, McKeen et al. (2002) found that as fire NO_x/CO emission ratios increase above 0.014, the resulting change in O₃ concentration becomes increasingly more sensitive to the assumed fire ratio of non-methane hydrocarbons to CO. For fire NO_x/CO ratios of less than 0.025, the transported fraction of the O₃ increase is limited by NO_x availability. When a NO_x/CO emission ratio of 0.045 was assumed, the model predicted enough NO_x emissions to limit hydrogen radical chemistry downwind of the fires through the NO₂ + OH reaction to form nitric acid. This allowed higher levels of precursor CO and NO_x to arrive intact within the eastern United States resulting in a two times higher photochemical production rate compared to lower NO_x/CO ratios. Analysis of individual points showed that when the CO increase from fires exceeds 200 ppbv, then ΔO₃ is about 75% higher under moderately polluted conditions (NO_x ≈ 10 ppbv) compared to cleaner, more rural conditions (NO_x ≤ 2 ppbv). The O₃ enhancement for the more polluted regions exceeded locally 30 ppbv (McKeen et al. 2002). These results indicate that, at larger scales, the effect of fires on tropospheric ozone formation results from complex interaction between photochemical mechanisms and long-range atmospheric transport. Thus, Colarco et al. (2004) found that the elevated surface ozone concentrations (>125 ppbv) observed near Washington D.C. in July 2002 was caused by high altitude transport of pollutants from forest fires in Quebec (Canada). Their study concluded that the entrainment of a gradually subsiding plume into the PBL is an important mechanism for transporting pollutants from elevated layers to the surface.

Photochemical O₃ production also takes place in very young smoke plumes, i.e. within a few tens of minutes after the fire emissions are released (Goode et al. 2000; Hobbs et al. 2003; Yokelson et al. 2003; Jost et al. 2003). According to Mauzerall et al. (1998) and Jost et al. (2003), maximum gross O₃ production and loss due to biomass burning occurs at low altitudes and within young plumes. The O₃ production in individual biomass-burning plumes can be significant for the regional-scale ozone budget as it has been the case in the tropical region of South Atlantic (Mauzerall et al. 1998) and in the boreal region of northeastern Alberta, Canada (Cheng et al 1998). For example, Cheng et al. (1998) found that a large forest fire in 1995, which occurred north of Edmonton, the capital of the Alberta province, caused 50-150% increase in O₃ and NO_x concentrations some 300 km away. Since enhanced O₃ concentrations were observed during both daytime and nighttime hours, the authors conclude that ozone has been formed in the plume early on and then transported downwind.

The importance of ozone formation in individual young smoke plumes has been clearly demonstrated through observations and model simulations by Jost et al. (2003), Trentmann et al. (2003, 2005), and Mason et al. (2006). Close to the fire, ozone in the plume may be highly depleted compared to background concentrations, due to the reaction of ozone with the emitted NO. Trentmann et al. (2003) found that photochemical ozone production occurred in the plume of a prescribed fire in Brazil at a

rate of about 25 ppb h⁻¹ and the downwind ozone concentration increased well above the background level to about 70 ppb. In this study, photochemical ozone production was dominated by the reaction of HO₂ with NO (~69%). Peroxy radicals from the alkenes also contributed significantly to ozone production. Formation of nitrogen reservoir species was dominated by HNO₃, which accounted for about 60% of the NO_x production. Significant atmospheric oxidation of alkenes occurred within the first tens of minutes after their release into the atmosphere. Plume photochemistry was generally limited by the availability of radicals. Photochemical production of radical species occurred mainly from the photolysis of formaldehyde emitted from the fire. Secondary production from the oxidation of VOCs accounted for about 12% of the HCHO concentration.

Primary VOC emissions have been found critical for the formation of ozone in young smoke plumes (Trentmann et al. 2003). Neglecting or omitting VOC emissions in biomass-burning plumes may lead to significant underestimation of O₃ concentrations (Mason et al. 2006). Unfortunately, only about 70% of the VOCs present within a smoke plume can be identified with current technology (Christian et al. 2003). Simulation analysis conducted by Mason et al. (2006) suggest that VOCs with the highest emission ratios do not always have the strongest impact on predicted O₃ formation in a nascent smoke plume. The production of radicals through the photolysis of HCHO is crucially important for the formation of ozone and nitrogen reservoir species, and the oxidation of alkenes in fresh plumes (Trentmann et al. 2003). Any change in this source of radicals, e.g., through the neglect of primary HCHO emissions or through enhanced photolysis due to less aerosol absorption, has a significant effect on photochemistry. Enhanced radical production leads to enhanced ozone production, enhanced formation of nitrogen species, and higher oxidation efficiency (Trentmann et al. 2003).

Modeling Ozone Production due to Biomass Burning

The photochemistry of tropospheric ozone formation due to fires have been studied thus far using two distinct numerical approaches depending on the spatial and temporal scale of interest – (a) gridded meso-scale simulation systems and (b) individual smoke plume models.

Regional ozone production is typically analyzed with simulation systems that couple a 3-D atmospheric chemistry model such as CMAQ with a 3-D meso-scale atmospheric model such as MM5, and an Emission Inventory Estimator such as GloBEIS. The atmospheric model provides meteorological forcing necessary to drive the air-quality model, which is constrained by NO_x and VOC emissions supplied by the Emission Inventory Estimator. McKeen et al. (1991, 2002) developed such a 3-D model system to study the dynamics of surface ozone across the continental United States. The system simulates the meteorology of specific days using the MM5 meso-scale model, stores output at hourly intervals, and then applies a photochemical-transport model in a post-analysis mode. The models operate at 60-km horizontal grid spacing in sigma vertical coordinates using 23 unequally spaced layers, with seven layers below 2 km altitude and about 75 m resolution in the lowest layer. The photochemical-transport model employs mechanisms outlined by McKeen et al. (1991), and incorporates JPL-97 recommendations (DeMore et al. 1997) for reaction rates, photolysis cross sections, quantum and product yields of inorganic gas-phase compounds, as well as C₂ and C₃ hydrocarbons. The model also includes a complete oxidation mechanism for isoprene, and explicit treatments of acetylene and propane. McKeen et al. (2002) applied this modeling system to study the impact of 1995 summer wildfires in the boreal region of Canada on pollution levels and surface ozone concentrations over the Eastern USA. Model results indicated that the observed 10 to 30 ppbv enhancement of O₃ throughout a large region of the central and eastern United States was due to the Canadian fires.

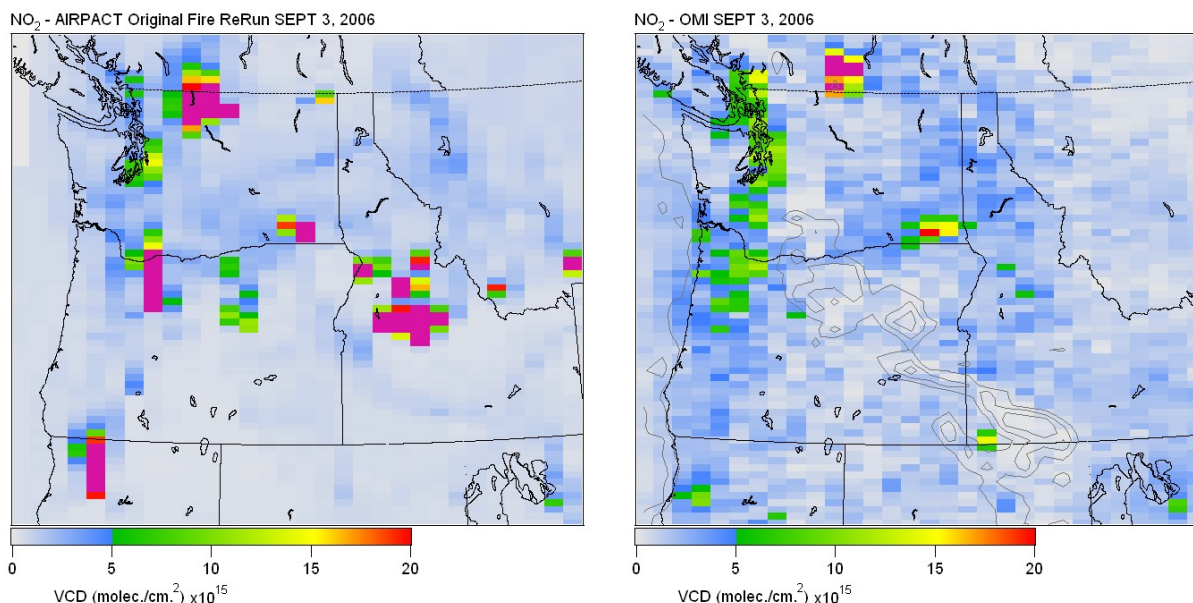


Figure 1. Comparison of NO₂ atmospheric fields predicted by the AIRPACT system (left) and observed by the OMI satellite (right) in the Northwest on Sep 3, 2006 (O'Neill and Herron-Thorpe, personal communication).

Vaughan et al. (2004) developed a numerical regional air quality forecast system (AIRPACT-3) for the Pacific Northwest that runs daily and predicts ozone, particulate matter and other pollutants from both anthropogenic and biogenic sources. The system is based on the Community Multi-scale Air-Quality (CMAQ) model (Byun and Schere 2006) running at 12-km horizontal resolution with anthropogenic emissions provided by the EPA 2002 National Emissions Inventory and biogenic emissions supplied by the EPA Biogenic Emissions Inventory System (BEIS version 3). Atmospheric photochemistry is driven by weather data from the MM5 mesoscale model. CMAQ explicitly simulates the photochemistry of gas phase emissions (including ozone), the fate of aerosol-phase species, and the deposition of both gas and aerosol species. AIRPACT outputs ambient pollutant concentrations and deposition rates at hourly time step. In the summer of 2006, Lamb et al. (2007, unpublished manuscript) enhanced AIRPACT-3 to ingest pollutant emission estimates for wildfires generated by the *BlueSky* smoke modeling system (O'Neill et al. 2005). *BlueSky*'s EPM/CONSUME module predicts fine and coarse particulate matter (PM_{2.5} and PM₁₀ respectively), as well as emissions of carbon monoxide, ammonia, total nitrogen oxides (NO_x), and total non-methane hydrocarbons (NMHC). At present, EPM/CONSUME emission calculations do not provide species differentiation for NO_x and NMHC. Lamb et al. (2007) found that wildfires had a significant impact on predicted ozone formation in the region. Thus, NO_x emissions from fires caused a near-surface O₃ enhancement of more than 30 ppbv. AIRPACT-3 simulations have been verified against observations whenever possible. Figure 1 compares NO₂ fields predicted by AIRPACT and observed by the OMI satellite for the Pacific Northwest on September 3, 2006 (O'Neill and Herron-Thorpe, personal communication).

To analyze long-range transport of smoke and its impact on local ozone production, some studies employed particle dispersion models such FLEXPART (Stohl et al. 1998). Thus, Morris et al. (2006) used FLEXPART along with ozone observations and satellite data to prove that smoke containing ozone and ozone precursor species generated by forest fires burning in Alaska and western Canada can travel as far as southern Texas and substantially contribute to increases in ozone pollution levels

above Houston, where concentrations in excess of 125 ppbv were measured at the surface and over 150 ppbv at 2 km in the atmosphere.

At their current state of development, 3-D regional photochemistry models do not adequately simulate important local processes controlling the variance and time evolution of ozone (McKeen et al. 2002). For example, large-scale models cannot account for the O₃ production within individual biomass-burning plumes, because of their limited spatial and temporal resolution. Biomass burning emissions in these models are homogeneously distributed over grid boxes with sizes of 16 to 100 km. Therefore, chemical processing of the emissions may occur at concentrations too low compared to the situation in individual plumes. Due to the non-linearity of photochemical reactions, this can lead to an overestimation or an underestimation of the O₃ production depending on the dilution rate (Pope et al. 1998; Liang and Jacobson 2000; McKeen et al. 2002). The observed fast O₃ production in young smoke plumes, which is not accounted for in larger-scale model simulations, might be, at least in part, responsible for the discrepancy between observations of tropical tropospheric O₃ and global model estimates during the dry season. (Emmons et al. 2000; McKeen et al. 2002; Peters et al. 2002).

Smoke plume models simulate the photochemical evolution of rising individual smoke plumes and are designed for applications at small temporal and spatial scales. These models can be either zero- or three- dimensional. Trentmann et al. (2003) applied a 3-D non-hydrostatic plume model to investigate the formation of ozone during the first tens of minutes in a biomass-burning plume from a prescribed fire conducted during the Smoke Cloud, and Radiation-C experiment in Brazil. The model was a modified version of the Active Tracer High Resolution Atmospheric Model (ATHAM) (Herzog et al. 1998; Graf et al. 1999). ATHAM has a modular structure and contains mechanisms for simulating transport, turbulence, radiation, emissions, and photochemistry. The turbulent quantities are calculated using a modified Kolmogorov-Prandtl formulation. The solar radiation is predicted with the 2-stream Practical Improved Flux Method (PIFM) of Zdunkowski et al. (1982), which simulates radiative effects of gases and aerosol particles. “The chemical mechanism includes the oxidation of the primary emissions from biomass burning, i.e. CO, CH₄, C₂H₆, C₂H₄, C₃H₆, HCHO, CH₃CHO, HCOOH, CH₃COOH, and CH₃COCH₃. Oxidation by OH is considered for all emitted species. Photolysis of aldehydes and acetone is included as well as ozonolysis of the alkenes.” “Two heterogeneous reactions on aerosol particles are simulated, i.e. the reaction of NO₂ to yield HONO, and that of N₂O₅ to yield HNO₃” (Trentmann et al. 2003). Photolysis frequencies, which include the effect of absorption and scattering by molecules and aerosol particles, are estimated using the actinic flux calculated with PIFM version 2 (PIFM; Zdunkowski et al. 1982).

Zero-dimensional (box) plume models are designed to study the detailed photochemistry of very young (0-3 hour old) fast evolving smoke plumes. These models incorporate sophisticated photochemical mechanisms and require comprehensive measurements (information) of fire emissions and passive tracers (such as CO) to constrain them (Mason et al. 2006). Time-dependent horizontal dilution of the smoke plume (and chemical species in it) is simulated using a Gaussian expansion formulation, which requires foreknowledge of the horizontal diffusion coefficient. This coefficient is typically estimated by tuning the box model to reproduce the observed time evolution of a passive tracer such as CO. Recent examples of box plume models include ‘Fredonia’ and ‘Mainz’.

The ‘Fredonia’ plume model was originally developed at the University of Montana (Mason et al. 2001). It currently runs at the State University of New York College at Fredonia (SUNY – Fredonia). ‘Fredonia’ is based the Master Mechanism developed at the National Center for Atmospheric Research (NCAR) (Madronich and Calvert 1989). The photochemical mechanism of the model includes 1,300 chemical species, and simulates 3,650 reactions, of which 400 are photolytic. Photolysis frequencies are computed externally to the smoke plume simulation based on calculation of the actinic flux (Mason et al. 2006) using the NCAR Tropospheric Ultraviolet and Visible (TUV)

radiation model (Madronich and Flocke 1998). Predicted photolysis frequencies are tabulated at 15 min intervals and linear interpolation is used to compute values at intermediate points.

The ‘Mainz’ plume model was first developed at the Max Planck Institute for Chemistry in Mainz, Germany to study the atmospheric oxidation of major compounds emitted from vegetation fires under high NO_x conditions (Jost et al. 2003; Trentmann et al. 2005; Mason et al. 2006). The model simulates 640 reactions (of which 117 photolytic) involving some 250 chemical species. The calculation of photolysis frequencies is based upon the method of Landgraf and Crutzen (1998), using the two-stream PIFM algorithm of Zdunkowski et al. (1982) for the calculation of the actinic flux. Jost et al. (2003) and Trentmann et al. (2005) provide further details on reaction rates and the treatment of particular chemical species. The Mainz model has been used in smoke plume simulation studies constrained by observations for several data sets (Jost et al. 2003; Trentmann et al. 2005; Mason et al. 2006).

Fire emissions and their atmospheric evolution are often characterized in individual smoke plumes via ‘enhancement ratios’ (e.g., Yokelson et al., 1996, 1997; Andreae and Merlet, 2001). Mason et al. (2006) define the enhancement ratio of a compound X as “the difference between its concentration in the plume and the ambient air (i.e., ΔX , the excess mixing ratio), normalized by the corresponding difference for CO”:

$$\Delta X/\Delta \text{CO} = (X_{\text{plume}} - X_{\text{ambient}})/(\text{CO}_{\text{plume}} - \text{CO}_{\text{ambient}})$$

When such a ratio is applied to measurements of emitted chemical species taken close to the fire, it is often called ‘emission ratio’. The CO concentrations are used as a reference here, because CO is chemically inert in the atmosphere on time-scales of days. Thus, at the scale of individual smoke plume, any decrease in the CO excess mixing ratio (ΔCO) is due to the dilution of the plume with ambient air. By dividing the excess mixing ratio of species X (ΔX) by that of CO (ΔCO), the effects of dilution on species X (due to the mixing of ambient air) are removed. Hence, changes of the $\Delta X/\Delta \text{CO}$ ratio in a young smoke plume are mainly due to physicochemical processes (Mason et al. 2006). For measurements taken downwind of the fire, this ratio is typically referred to as ‘enhancement ratio’. Studies have also called it “normalized excess mixing ratio” (e.g. Hobbs et al. 2003) since some chemical species are subject to net destruction or a null effect in terms of their plume concentrations rather than being ‘enhanced’.

Conclusions

- ❑ Ozone is a secondary product of biomass burning formed through the oxidation of non-methane hydrocarbons and oxygenated volatile organic compounds in the presence of elevated concentrations of nitrogen oxides acting as catalysts. Ozone production occurs at the scale of individual smoke plumes due to the oxidation of short-lived chemical species such as alkenes and aldehydes, and at the regional scale due to the oxidation of longer-lived emissions such as CO and alkanes.
- ❑ Ozone production from fires is very complex as it depends on the amounts of various chemical reactants and catalysts available, the radiation loading and air temperature, the persistence and size of the source, the chemical composition of the burning biomass, the intensity of the fire, and the weather-controlled dispersion of the plume. Many of these interactions are non-linear with threshold responses for some processes but not for others.
- ❑ Globally, ozone precursors (e.g. VOCs and NO_x) emitted by vegetation fires are responsible for about 10% enhancement of tropospheric ozone levels. Regionally, however, biomass

burning can temporally increase background surface ozone concentrations by 24% to well over 100% causing exceedence of regulatory standards. Ozone formed in smoke plumes along with its precursors and aerosol particles emitted from large fires can be transported by weather systems over large distances spanning continental scales. When brought down toward the surface via smoke plume entrainment into the planetary boundary layer, fire-generated VOCs and NO_x can cause severe ozone episodes over metropolitan areas that are hundreds and even thousands of miles away from the fire locations.

- ❑ Field observations and modeling studies have demonstrated that a significant fraction of the enhanced ozone concentration at the regional scale is due to photochemical production of ozone in local smoke plumes before dispersion to the regional scale. Ozone production rates of about 25 ppb h⁻¹ have been observed in plumes of prescribed fires.
- ❑ The photochemistry of ozone formation in very young (0-3 hr old) smoke plumes and its impact on regional ozone levels has been the topic of several investigations. Studies have revealed that the chemical evolution of young smoke plumes is an important and complex phenomenon with VOCs (emitted from biomass burning) playing a critical role in the formation of secondary pollutants such as ozone. The production of radicals through the photolysis of HCHO appears to be particularly important for the formation of ozone and nitrogen reservoir species, and the oxidation of alkenes. In young smoke plumes, enhanced radical production leads to an enhanced ozone production, enhanced formation of nitrogen reservoir species, and higher oxidation efficiency. VOCs become even more important when considering that current technology can only identify about 70% of all VOCs present within a smoke plume, and VOCs with the highest emission ratios may not have the strongest impact on ozone formation. All this requires that the prediction of ozone production from biomass burning be conducted through process-oriented simulation models.
- ❑ The photochemistry of tropospheric ozone formation due to biomass burning has been studied at the regional level through gridded mesoscale simulation systems, and at the scale of individual fires through smoke-plume models. Mesoscale systems typically consist of linked 3-D models simulating meteorological forcing (e.g. pressure, winds, temperature, relative humidity, solar radiation), atmospheric photochemistry and smoke dispersion, and emissions of hydrocarbons and nitrogen oxides from both fires and other biogenic and anthropogenic sources. Plume models predict the detailed photochemical evolution of individual smoke plumes, and can be either 3-dimensional or zero-dimensional (box) models.
- ❑ Regional photochemical models are limited in their ability to simulate important local processes controlling the variance and time evolution of ozone. Because of their coarse spatial resolution (typically 16 km – 100 km), these models do not currently account for the ozone production within individual biomass-burning plumes. Due to non-linear effects of VOCs and NO_x concentrations on ozone formation, regional models are prone to aggregation errors in their projections resulting from spatial averaging of species concentrations within a grid cell.
- ❑ Individual smoke-plume models resolve the limitations of regional models. However, their application is limited by the availability of detailed fire emission inventories and high-resolution data on plume dispersion and/or the meteorological environment in the immediate vicinity of the fire. The computationally intensive nature of their algorithms also poses a potential constraint on the application of these models at the regional scale.

Recommendations to the FS FCAMMS Program

In order to build a national FCAMMS capability to evaluate the effects of prescribed burns and wildfires on tropospheric ozone, we recommend (based on the foregoing literature review) the development of an FCAMMS Ozone Forecasting & Analysis System (FCAMMS-OFAS). The System will be assembled along the following concept.

1. Tropospheric ozone production due to biomass burning is a complex phenomenon and its prediction requires mechanistic (process-oriented) models of atmospheric dynamics, fire intensity and emissions, atmospheric photochemistry and long-range transport. Emission calculations should provide sufficient speciation profiles for oxygenated organic compounds, non-methane hydrocarbons, and nitrogen oxides to ensure reliable estimates by the photochemical models.
2. FCAMMS-OFAS can be built upon an existing modeling framework such as AIRPACT-3, a numerical air quality forecast system for the Pacific Northwest (Vaughan et al. (2004). AIRPACT has been recently enhanced by Lamb et al. (2007, unpublished manuscript) to ingest fire emissions from the *BlueSky* smoke dispersion modeling system.
3. FCAMMS-OFAS will have a hierarchical structure, which embodies components and features not currently present in AIRPACT. These are shown on the conceptual OFAS flowchart depicted in Figure 2. Specifically:
 - (i) OFAS will implement a photochemical smoke Plume Model, which account for the rapid production of ozone and secondary ozone precursors in young smoke plumes. The Plume Model will essentially simulate sub-grid photochemical processes within the Regional Air-Quality and Transport Model (e.g. CMAQ), thus, helping resolve current aggregation errors in the large-scale model caused by spatial averaging of pollutant concentrations and non-linear photochemical reactions. The Plume Model will be chemically constrained by the Regional Model and driven by meteorological data from the Mesoscale Atmospheric (weather) Model;
 - (ii) The Fire Emissions Model will be enhanced beyond the current BlueSky capability to produce speciation profiles for NO_x, NMHC, and VOCs needed as input to the smoke Plume Model;
 - (iii) The Atmospheric Model will utilize an advanced surface scheme that allows prediction of ozone deposition velocities as a function of vegetation type (i.e. plant eco-physiology), canopy leaf area index (LAI), meteorological conditions, and soil physical environment. The new MFF model developed (upon MM5) by the USFS Rocky Mountain Center (Nikolov et al. 2006) implements such a surface scheme based on FORFLUX, a detailed biophysical model of terrestrial ecosystem-atmosphere trace-gas and energy exchange (Zeller and Nikolov 2000; Nikolov and Zeller 2003; see also www.FireWeather.info). MFF uses a 1-km resolution biome-independent dataset of seasonal LAI retrieved from satellite images (Nikolov and Zeller 2006). Compared to MM5, MFF delivers improved forecasts of mixing height, temperature, relative humidity, and precipitation. An alternative to using separate models for atmospheric dynamics and photochemistry (e.g. MFF and CMAQ) would be to employ the coupled weather/air-quality model WRF-Chem (see <http://cprm.acd.ucar.edu/Models/WRF-Chem/>). Figure 3 depicts a proposed OFAS flowchart using WRF-Chem. In this case, FORFLUX will be linked to WRF-Chem replacing the current NOAA surface scheme, and a new data layer of seasonal LAI will be ingested into WRF-Chem. FORFLUX will provide feedback to the Weather

Model through more accurate simulation of the surface energy partitioning, and to the Air-Quality Model through improved estimates of ozone removal rates from the atmosphere (i.e. total ozone deposition);

- (iv) OFAS will use predicted surface ozone concentrations to estimate the actual ozone uptake by vegetation employing FORFLUX. It is now widely recognized that the ozone entering leaf stomata is more important for plant response than ambient concentration. Biochemical processes within the leaf are altered by ozone, reducing photosynthesis and ultimately leading to loss of plant productivity. By predicting vegetation ozone uptake, OFAS will be able to address the important question: What is the actual impact of enhanced tropospheric ozone from biomass burning on terrestrial ecosystems?

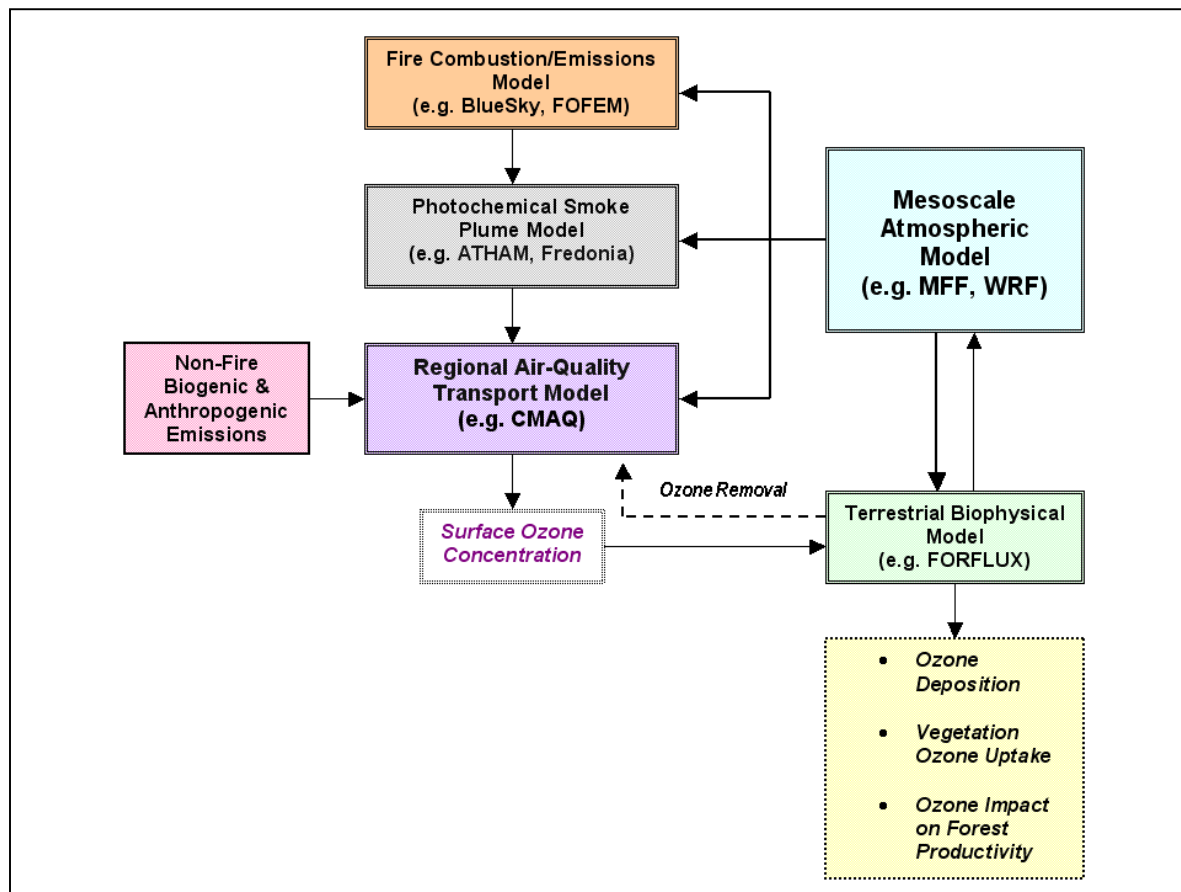


Figure 2. Conceptual flowchart of the proposed FCAMMS Ozone Forecasting & Analysis System (FCAMMS-OFAS) using separate models for regional atmospheric dynamics and photochemistry.

4. The development of OFAS will fully utilize FCAMMS' existing computational and modeling infrastructure. Thus, RMC can contribute its supercomputing capabilities and the MFF atmospheric model, which implements the new FORFLUX surface scheme. At present, RMC runs MFF operationally twice a day at 12-km resolution for the Continental US, and at 8-km resolution for the Western portion of the country. In addition, RMC produces 48-h smoke dispersion forecasts also twice a day using the *BlueSky* System for both Continental US (at 12 km), and the West (at 8 km), see <http://FireWeather.info/>.

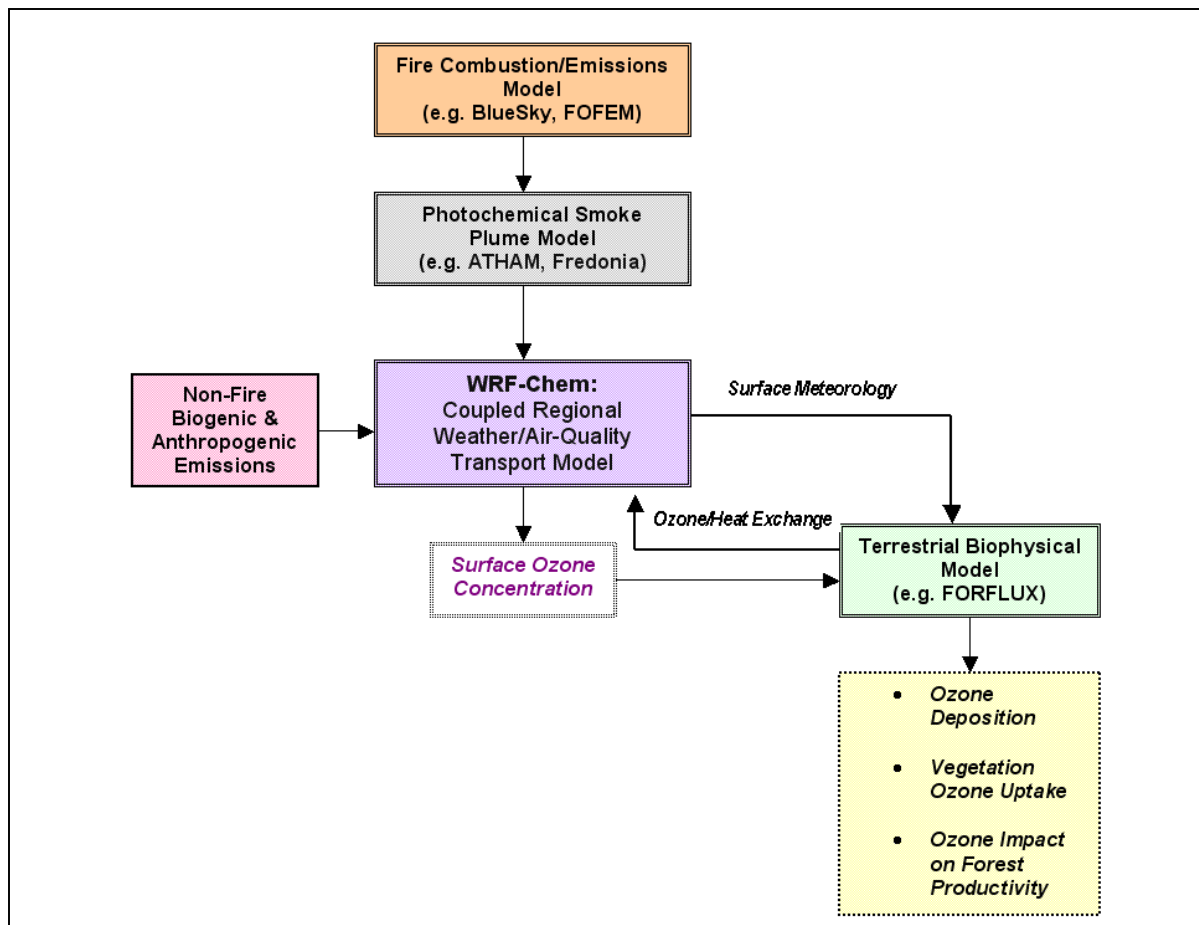


Figure 3. Conceptual flowchart of the proposed FCAMMS Ozone Forecasting & Analysis System (FCAMMS-OFAS) using the coupled weather/air-quality regional model *WRF-Chem*.

Other FCAMMS Centers could contribute to this effort as well. The Missoula Fire Lab could assist RMC in coupling FORFLUX with WRF-Chem and implementing WRF-Chem-FF at 12-km resolution for the Continental US. The Southeast Center (SHRMC) could provide algorithms and expertise for the smoke-plume modeling effort. The Pacific Northwest Center (NWRMC) could deliver enhancements to the *BlueSky* system in terms of fire emission speciation, and share its expertise in working with the AIRPACT system. The Eastern Area Modeling Consortium (EAMC) could provide algorithms for improved simulation of fire-atmosphere interactions in terms of heat release, combustion, and fire spread. The Southwest Center (at the FS Fire Lab in Riverside, CA) could synthesize published data on plant ozone uptake and its impact on plant eco-physiology to be used in a model development to simulate the feedback between canopy ozone uptake and stomatal closure. Such a feedback algorithm would improve the FORFLUX capability to predict regional ozone deposition.

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