



Review

Ozone production from wildfires: A critical review

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ABSTRACT

Tropospheric ozone (O_3) negatively impacts human health and ecosystems, and is a greenhouse gas. Wildfires are a source of tropospheric O_3 , and studies show that wildfires are increasing in North America. In this study, we present a critical review of O_3 production from wildfires focusing on three key topics: the influence of wildfire emissions on O_3 production; the influence of photochemistry on wildfire O_3 production; and regulatory issues associated with wildfire O_3 production in the United States. Observations of $\Delta O_3/\Delta CO$ range from approximately -0.1 to 0.9 , and are caused by the interplay of numerous factors including fire emissions, efficiency of combustion, chemical and photochemical reactions, aerosol effects on chemistry and radiation, and local and downwind meteorological patterns. Using average $\Delta O_3/\Delta CO$ ratios for major biomes, we estimate global wildfires produce approximately 170 Tg of O_3 per year, which is 3.5% of all global tropospheric O_3 production. Areas of uncertainty in wildfire O_3 production include the net effect of aerosols on chemical and photochemical reactions within a fire plume, the impact of oxygenated volatile organic compounds and nitrous acid on O_3 production, and the interplay of variables that lead to extreme $\Delta O_3/\Delta CO$ values. Because wildfire frequencies are likely increasing and have been shown to contribute to elevated O_3 at air quality monitoring sites, it is important to better understand the emissions, photochemistry and impacts of these fires.

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1. Introduction

Ozone (O_3) is an important secondary air pollutant with both health and climate implications (IPCC, 2007; NRC, 2008). Exposure to high concentrations of O_3 has also been linked to short-term mortality (Bell et al., 2004), irritates lungs and aggravates bronchitis, emphysema and asthma (Lippmann, 1991; McConnell et al., 2002).

Ozone is formed from the interaction of nitrogen oxides ($NO_x = NO + NO_2$) and non-methane organic carbons (NMOCs) in the presence of sunlight. For much of the troposphere there are sufficient natural sources of NMOCs, so NO_x is typically the limiting precursor in O_3 production. Since a large fraction of global NO_x

emissions are due to anthropogenic stationary and mobile sources, O_3 pollution is common in metropolitan areas. In urban environments, the details of NO_x –NMOC– O_3 photochemistry have been studied for several decades and are moderately well understood (e.g. Finlayson-Pitts and Pitts, 1986).

Wildfires also generate substantial emissions of O_3 precursors (Crutzen et al., 1979; Andreae and Merlet, 2001; Akagi et al., 2011) and the majority of observations suggest some degree of O_3 production from wildfires (e.g. Evans et al., 1974; Radke et al., 1978; Stith et al., 1981; Westberg et al., 1981; Delany et al., 1985; Fishman et al., 1990; Kaufman et al., 1992; Pickering et al., 1996; Thompson et al., 1996, 2001; Cheng et al., 1998; Jonquieres et al., 1998; Mauzerall et al., 1998; Fujiwara et al., 1999; Schultz et al., 1999; Galanter et al., 2000; Kita et al., 2000; Singh et al., 2000; Wotawa and Trainer, 2000; Forster et al., 2001; Jaffe et al., 2001, 2004; Liu et al., 2002; McKeen et al., 2002; Staudt et al., 2002; Chan et al., 2003; Sinha et al., 2003; Yokelson et al., 2003, 2009; Bertschi et al., 2004; Colarco et al., 2004; DeBell et al., 2004; Honrath et al., 2004; Kondo et al., 2004; Bertschi and Jaffe, 2005; Junquera et al., 2005; Lapina et al., 2006; Morris et al., 2006; Pfister et al., 2006, 2008; Val Martin et al., 2006, 2008; Real et al., 2007; Oltmans et al., 2010). However, a smaller number of studies, mainly in boreal regions, have found that O_3 is minimally enhanced or even depleted downwind of some biomass burning plumes (e.g. Tanimoto et al.,

Abbreviations: AOD, aerosol optical depth; AQS, Air Quality System; CARB, California Air Resources Board; CO, carbon monoxide; EPA, Environmental Protection Agency; HONO, nitrous acid; JNO_2 , photolysis rate of nitrogen dioxide; JO_3 , photolysis rate of ozone; MCE, modified combustion efficiency; NAAQS, National Ambient Air Quality Standards; NMHC, non-methane hydrocarbon; NMOC, non-methane organic carbon; NO, nitric oxide; NO_2 , nitrogen dioxide; NO_x , nitrogen oxides; O_3 , ozone; OVOC, oxygenated volatile organic compounds; PAN, peroxyacetyl nitrate; $PM_{2.5}$, particulate matter less than 2.5 microns in diameter; ppbv, parts per billion by volume; ppmv, parts per million by volume; Tg, teragram.

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2008; Paris et al., 2009; Verma et al., 2009; Alvarado et al., 2010). The low O₃ production in these plumes was likely caused by low mixing ratios of NO_x due to low emissions, sequestration of NO_x as PAN, and/or a reduction in photochemical reactions (especially due to aerosol effects). It is also important to note that in some cases, the question of O₃ production from wildfire emissions can be complicated by mixing with urban emissions (e.g. McKeen et al., 2002; Jaffe et al., 2004; Bein et al., 2008; Singh et al., 2010).

In the United States (US), the current air quality standard for O₃ is 75 parts per billion by volume (ppbv) for an 8-h average, and is evaluated using the 3-year running average of the fourth highest annual O₃ value. This standard has been made more stringent several times over the past two decades and may become even more stringent as a result of recommendations from the EPA's Clean Air Science Advisory Committee. As the standard is lowered, understanding all O₃ sources becomes increasingly important. Fires have been shown to contribute to exceedances of the US O₃ air quality standard (Jaffe et al., 2004; Junquera et al., 2005; Bein et al., 2008).

At the same time, the frequency and intensity of wildfires is likely to increase in many regions due to climate change. Gillett et al. (2004) and Westerling et al. (2006) have shown that global warming has already impacted the frequency of the area burned for Canadian and US forests, respectively, over the past century. These changes were associated with earlier spring snowmelt, longer fire seasons and larger, more extreme wildfires. While land-use and land management practices are also important, both Gillett et al. (2004) and Westerling et al. (2006) conclude that climate change is the most important factor in explaining changes in fire frequency and intensity over recent decades. Similarly, Kasischke and Turetsky (2006) found that recent increases in burned area in the North American boreal region are due to climate change and alterations of the biome composition. In a comparison of modeled and observed changes in boreal ecosystems, Soja et al. (2007) found that the effects of climate change are apparent in this biome and have resulted in extreme fire years in Alaska, Canada and Russia during the last decade. Several studies have evaluated the possibility that fires will increase in the future under various global warming scenarios. Using past relationships between fires and meteorology along with projected future changes in climate, these studies show that fires are highly likely to continue to increase in the western US. Spracklen et al. (2009) estimate an increase in burned area of 54% by 2050 for the entire western US. These projected increases are even larger in the Pacific Northwest and Rocky Mountain regions, with changes of 78% and 175%, respectively. Amiro et al. (2009) project a 33% increase in fuel burned for Canadian wildfires for a doubling of anthropogenic CO₂ emissions. These results are qualitatively similar to those in Pechony and Shindell (2010). Thus it seems highly likely that air quality impacts from wildfires will grow in importance in North America.

For these reasons we have conducted a critical review of published papers focused on O₃ impacts from wildfires. Our review is organized around three key issues:

- 1) Influence of wildfire emissions on O₃ production;
- 2) Influence of photochemistry on wildfire O₃ production;
- 3) Regulatory issues associated with wildfire O₃ production in the US.

2. Influence of wildfire emissions on ozone production

Wildfires emit substantial amounts of NMOCs and NO_x, the primary O₃ precursors. A large number of NMOCs have been identified in smoke plumes. In the compilation of emission factors by Andreae and Merlet (2001), over 30 non-methane hydrocarbons (NMHCs) and 35 oxygenated volatile organic carbons (OVOCs) were quantified, although many of the values were based on only one or

two measurements or were estimated. Nonetheless, the authors estimated that more than half of volatile organic compound (VOC) mass was in the form of oxygenated compounds. More recent observations have identified many additional compounds and suggest that OVOCs are 60–80% of the total NMOC emissions (e.g. Singh et al., 2001; Christian et al., 2004; Yokelson et al., 2007a, 2008; Burling et al., 2010; Akagi et al., 2011). Akagi et al. (2011) identified over 90 individual compounds found in biomass burning smoke and a few classes of compounds (e.g. "C6 Carbonyls") that significantly increased the number of quantified OVOCs. Nonetheless, there is still significant uncertainty on the molecular form of the oxygenated compounds, as many of the compounds have not been identified (Singh et al., 1995; Warneke et al., 2011). New studies continue to quantify the breadth of compounds found in fire smoke (e.g. Simpson et al., 2011; Yokelson et al., 2011). In a study of biomass burning emission factors for atmospheric modeling, Akagi et al. (2011) reported total emission factors for NMOCs, including unidentified compounds of 51.9, 24.7, 58.7 and 23.7 g kg⁻¹ of fuel for tropical forests, savannah, boreal and temperate forests, respectively.

Biomass burning produces nitrogen compounds almost entirely from fuel nitrogen. This is different from fossil fuel production, where higher temperatures also promote oxidation of atmospheric N₂ to NO_x (e.g. Logan, 1983). A large number of gaseous nitrogen compounds have been identified in wildfire emissions including N₂, N₂O, NH₃, HONO, HNO₃, NO, NO₂, HCN, CH₃CN, amines (R–NH₂) and nitrates (R–ONO₂) (Lobert et al., 1990; Andreae and Merlet, 2001; Akagi et al., 2011). The nitrogen content of vegetation varies considerably, ranging from 0.2 to 4% (Lobert et al., 1991; Goode et al., 1999; Yokelson et al., 2008; McMeeking et al., 2009). There does not appear to be a systematic difference in fuel nitrogen content by biome (e.g. Laursen et al., 1992). Lacaux et al. (1996) have shown a positive correlation between fuel nitrogen content and NO_x emissions. Further, in a study of several fuel types, Goode et al. (1999) report that 67% of the wildfire fuel nitrogen was released to the atmosphere in some form, while Hurst et al. (1994) estimate that 89% of fuel nitrogen is released for savannah fires. However, it is important to note that some of the nitrogen content in wildfire fuels near urban areas may be enriched from deposition of anthropogenic pollutants (Yokelson et al., 2007b).

However, the nitrogen content of fuels is not the only influence on NO_x emissions; combustion efficiency is also an important factor. Wildfire combustion has been characterized by the unitless modified combustion efficiency (MCE) ratio (e.g. Ward and Radke, 1993; Ferek et al., 1998): $MCE = CO_2 / (CO + CO_2)$, where CO and CO₂ refer to mixing ratios or grams of carbon kg⁻¹ fuel burned for each species. The MCE can be influenced by fuel moisture, fuel load, temperature, relative humidity, winds and other meteorological parameters (e.g. Radke et al., 1991; Shea et al., 1996). Typical MCE values for vegetative combustion range between 0.80 and 1.00 (e.g. Yokelson et al., 1996, 2008; Ferek et al., 1998; Goode et al., 1999; McMeeking et al., 2009). MCE values closer to 0.80 represent fires with a higher proportion of smoldering, while MCE values approaching 1.0 represent fires dominated by flaming combustion. During flaming combustion, nitrogen compounds such as NO, N₂, and N₂O tend to be released in larger amounts due to greater oxidation of fuel nitrogen, while more reduced compounds such as NH₃ and HCN tend to be emitted in larger amounts during smoldering combustion (Cofer et al., 1989; Yokelson et al., 1996, 1997; Goode et al., 1999; Andreae and Merlet, 2001; McMeeking et al., 2009). Also, as the MCE decreases the fraction of OVOC emissions tends to increase (Yokelson et al., 1997; Goode et al., 2000). Using the emission factors from Akagi et al. (2011), we calculate average MCE values of 0.94, 0.92, 0.92 and 0.80 for savannah, tropical, temperate and boreal forest fires, respectively. However, it is important to note that the average MCE of a biome can change

during the fire season. One study suggests that boreal wildfires may be increasingly dominated by smoldering combustion as the fire season progresses, leading to lower NO_x emissions towards the end of the season (Lapina et al., 2008).

Thus both the combustion type (e.g. MCE) and the fuel nitrogen content dictate the overall NO_x emissions. However, a typical large wildfire does not comprise one type of vegetation nor a single value of MCE, but rather a mix of fuels and combustion efficiencies, both of which change over time. Andreae and Merlet (2001) summarize emission factors from many studies to derive average values of 1.6, 3.9 and 3.0 g NO kg⁻¹ dry fuel burned for tropical, savannah/grasslands and extra-tropical forests, respectively. Akagi et al. (2011) summarize a set of studies meeting specific criteria (e.g. young smoke plumes) to report values of 2.6, 3.9 and 1.2 g NO kg⁻¹ fuel burned for tropical, savannah and extra-tropical fires, respectively, and further split the extra-tropical category into boreal (including peat) and temperate forests at 0.9 and 2.5 g kg⁻¹, respectively. The much lower NO_x emissions from extra-tropical fires in this study reflect the large weighting given to smoldering, boreal fires (Akagi et al., 2011) and are consistent with observations from high latitude regions (e.g. McKeen et al., 2002; Alvarado et al., 2010).

Using the average emissions from Akagi et al. (2011), we calculate an average molar NMOC/NO_x emission ratio for savannah, tropical, temperate and boreal forest fires of approximately 15, 50, 20 and 150, respectively. Thus NO_x is typically the limiting O₃ precursor in wildfire plumes, as is also shown in other studies (e.g. Mauzerall et al., 1998). While the average emission factors for a biome may be useful to generate overall emissions, they do not reflect the spatial and temporal variability of wildfires. The wide range in observed emissions, even from a single fire, reflects the variable and changing combustion conditions. Ultimately, the level of temporal and spatial requirements for the emissions determines the level of detail needed on MCE and fuel nitrogen content, making modeling of O₃ production challenging. Studies focusing on understanding instantaneous O₃ production will require detailed information on emissions, which depends on high resolution fuel nitrogen content and wildfire MCE data.

3. Influence of photochemistry on wildfire ozone production

Wildfires emit myriad gases and aerosols, and the relative proportion of each emitted species depends on the variables mentioned in Section 2. Chemical and photochemical reactions involving these species occur rapidly and continue downwind. An additional complexity is that O₃ production rates can change magnitude and sign as the plume ages and crosses other emissions sources. All of these factors make clear identification of the O₃ production from wildfires challenging.

In wildfires, NO_x is emitted primarily as NO, which is quickly converted to NO₂ (Lobert and Warnatz, 1993; Andreae and Merlet, 2001). Once emitted, the partitioning of reactive nitrogen species is set by the local photochemical environment and will determine the O₃ production in a wildfire plume: NO_x can be converted to HNO₃ (g), aerosol NO₃⁻ and peroxyacetyl nitrate (PAN), among other species. The lifetime of emitted NO_x depends on numerous factors including concentrations of OH and hydrocarbons (especially peroxyacetyl radicals), temperature, humidity and sunlight. Formation of gaseous HNO₃ or aerosol NO₃⁻ is largely a one-way conversion, whereas PAN can regenerate NO_x far downwind due to thermal decomposition. HNO₃ is formed from the reaction of NO₂ with OH during the day and from the hydrolysis of N₂O₅ on aerosols at night. PAN forms from the reversible reaction of NO₂ with the peroxyacetyl radical during the daytime. Ambient temperature is also important for O₃ formation.

PAN is the most abundant form of peroxy-carboxylic nitric anhydrides in the atmosphere and can act as a long-term reservoir

for NO_y. At high latitudes, fires burn at cooler temperatures and often with lower MCE values, which leads to larger emissions of NMOCs, especially oxygenated compounds. Thus, at high latitudes a significant proportion of NO_x emitted from wildfires can be rapidly converted to PAN (e.g. Jacob et al., 1992). In a study of boreal wildfires, Alvarado et al. (2010) found that 40% of emitted NO_x was converted to PAN within hours. This process can also occur in the tropics (Mauzerall et al., 1998), although to a lesser extent due to the generally warmer temperatures. In addition, Alvarado et al. (2010) found from observations and modeling that as the molar ratio of NO_x/CO is reduced, a greater fraction of the NO_x is sequestered in the form of PAN. This likely occurs due to depletion of the peroxyacetyl radicals at higher NO_x concentrations. By limiting NO_x availability, the rapid conversion of NO_x to PAN is a key limit on the local in-situ O₃ production. However, PAN will eventually decompose and lead to O₃ production far downwind (e.g. Mauzerall et al., 1998; Jaffe et al., 2004; Val Martin et al., 2006, 2008; Real et al., 2007; Fischer et al., 2010). Mason et al. (2006) used several box models to examine chemistry in a plume from one Alaskan boreal fire and one African savannah fire. In both cases, the model showed significant O₃ production and NO_x loss; this took place within one hour for the African case and up to several hours for the Alaskan case. The major difference was that in the Alaskan case the model suggested an accumulation of up to 8 ppbv of PAN versus only about 1 ppbv of PAN for the African fire, despite higher NO_x emissions. This suggests a significant difference in the downstream O₃ production for boreal fires due to conversion of NO_x to PAN. Further, in a study of high latitude fires 6–15 days downwind, Val Martin et al. (2006) found enhanced NO_x (>0.1 ppbv) in fire plumes. Since NO_x has a lifetime of only a few days in the free troposphere, the source for this NO_x was almost certainly PAN decomposition, which contributed to the high O₃ production seen in these plumes.

Aerosols and clouds can also have a significant impact on O₃ production within a fire plume. High aerosol optical depths (AOD) can greatly reduce transmission of solar radiation through a wildfire plume and therefore limit formation of OH. Real et al. (2007) calculated that aerosols in a biomass plume from an Alaskan fire reduced the photolysis rates of NO₂ and O₃ (JNO₂ and JO₃) by approximately 20% over a 5 day transport time. Duncan et al. (2003) estimated reductions of 10–20% in monthly mean photolysis rates over Indonesia during a strong fire season. These reductions depend on the aerosol concentrations and intensive properties, such as the single scattering albedo and size distribution (Duncan et al., 2003; Real et al., 2007). However, the impact of lower photolysis rates on O₃ production is not clear. Real et al. (2007) show that reducing the photolysis rates can either increase or decrease the net O₃ production by changing both the O₃ production and loss rates. In contrast, Verma et al. (2009) found a strong reduction in net O₃ production due to optically thick plumes (e.g. AOD > 3). Hauglustaine et al. (1999) found a decrease of 5–35% for JNO₂ in the boundary layer for Indonesian fires with AODs of 1–3, and an increase in the free troposphere of 5–6% due to increased back scattering. Cloud processing has also been shown to effect concentrations of NMOCs in fire plumes, reducing soluble compounds and increasing other compounds, such as formaldehyde (Yokelson et al., 2003; de Gouw et al., 2006). Additionally, heterogeneous reactions of O₃ and HO_x radicals can be an important mechanism for O₃ loss (de Gouw and Lovejoy, 1998; Thomas et al., 2001; Duncan et al., 2003).

Since O₃ and CO are often correlated in wildfire plumes, the excess ratio ($\Delta\text{O}_3/\Delta\text{CO}$) can be used to characterize O₃ production in smoke plumes. For a set of inert compounds, this ratio would be preserved during downwind dilution so long as the dilution air remains constant (Jaffe et al., 2005). The ratio is usually calculated using a linear regression of observed data or occasionally by

calculating the enhancement above an assumed background value. Regardless of which method is used, the calculation assumes that the background mixing ratios do not vary over the range of observations. Close to a fire, we expect this ratio to be low or even negative due to NO titration of O₃. The ratio should grow to a peak value downstream of the fire, reflecting the maximum O₃ production when NO_x has decreased to very low mixing ratios. In some cases, the ratio in the free troposphere may be stable or change slowly for several days during transport, only to increase again when NO_x is released from PAN decomposition. Thus, the observed $\Delta\text{O}_3/\Delta\text{CO}$ ratio is strongly influenced by the travel time between the fire and measurement location.

Table 1 shows a summary of reported $\Delta\text{O}_3/\Delta\text{CO}$ values arranged by biome type and by reported plume age. By arranging the data in this way, two features become apparent. First, $\Delta\text{O}_3/\Delta\text{CO}$ ratios tend to increase with plume age, which is reasonable given that we expect O₃ production to proceed as long as NO_x is elevated to any significant extent (e.g. >0.1 ppbv). Second, tropical and equatorial regions tend to have significantly greater $\Delta\text{O}_3/\Delta\text{CO}$ ratios, which likely reflects the much greater NO_x emissions associated with higher MCE values. However, the excess ratio is not a perfect measure of O₃ production. Mauzerall et al. (1998) point out that this

ratio can be biased high by up to 20% due to photochemical loss of CO during long-distance transport of biomass plumes over a week. Typical values for the $\Delta\text{O}_3/\Delta\text{CO}$ ratio in aged plumes are between 0.1 and 0.7 although values as high as 0.9 have been reported for some plumes associated with tropical fires (Andreae et al., 1994; Mauzerall et al., 1998) and boreal fires (Honrath et al., 2004; Bertschi and Jaffe, 2005). However it is not clear if these high values reflect the actual O₃ production in the plume or mixing of airmasses. For example, Bertschi and Jaffe (2005) report very high ratios (up to 0.84) in long-distance plumes from Siberian fires sampled by aircraft near the US west coast. The most likely explanation for these very high ratios is the fact that O₃ production at low NO_x mixing ratios is very efficient. While a typical lifetime for NO_x in the boundary layer is less than one day, sequestration of NO_x in the form of PAN, and the subsequent decomposition of that PAN, can lead to NO_x mixing ratios of 0.1 ppbv to a few ppbv far downwind. Hudman et al. (2004) and Fischer et al. (2010) found O₃ production rates in excess of 40 ppbv O₃ per ppbv of NO_x at low NO_x mixing ratios in the free troposphere based on both observations and modeling. Thus long-range transport and decomposition of a few ppbv of PAN would be sufficient to explain the high $\Delta\text{O}_3/\Delta\text{CO}$ values reported in a number of studies (e.g. Andreae et al., 1994; Mauzerall

Table 1
Observations of wildfire $\Delta\text{O}_3/\Delta\text{CO}$ by biome and plume age. Where multiple plumes were encountered, we report the mean or range and the number of independent plumes encountered.

Plume age category	Study	Boreal and temperate regions	Approximate plume age	Range of $\Delta\text{O}_3/\Delta\text{CO}$ (ppbv/ppbv) (number of measurements)	Mean $\Delta\text{O}_3/\Delta\text{CO}$ (ppbv/ppbv)
$\leq 1-2$ days	Alvarado et al., 2010	Canada	4–10 h	−0.032–0.052 ($n = 16$)	0.005 ± 0.019
	Alvarado et al., 2010	Canada	14 h–2 days	−0.94–0.34 ($n = 15$)	−0.06 ± 0.28
	Goode et al., 2000	Alaska	2 h	0.064–0.089 ($n = 3$)	0.079 ± 0.024
	Singh et al., 2010	Siberia/North America	<1 day	range not specified ($n = 18$)	0.03 ± 0.04
	DeBell et al., 2004	Canada	1–3 days	0.014–0.062 ($n = 3$)	0.035
average					0.018
2–5 days	Mauzerall et al., 1996	Canada	not specified ^a	0.00–0.66 ($n = 9$)	0.13
	Paris et al., 2009	Siberia	2 days	0.14 ($n = 1$)	0.14 ± 0.50
	Singh et al., 2010	Siberia/North America	1–5 days	range not specified ($n = 20$)	0.11 ± 0.09 ^b
	Tanimoto et al., 2008	Siberia	≤ 5 days	−0.07–0.42 ($n = 8$)	0.17
	Wofsy et al., 1992	Alaska/Canada	not specified ^a	0.18 ($n = 1$)	0.18
average					0.15
≥ 5 days	Alvarado et al., 2010	Canada	2–11 days	−0.20–0.00 ($n = 3$)	−0.07 ± 0.12
	Bertschi et al., 2004	Siberia	6–10 days	0.22–0.36 ($n = 5$)	0.27
	Bertschi & Jaffe, 2005	Siberia	7–10 days	0.15–0.84 ($n = 5$)	0.44
	Honrath et al., 2004	Siberia	13–15 days	0.45–0.93 ($n = 4$)	0.59
	Paris et al., 2009	Siberia	13 days	−0.04 ($n = 1$)	−0.04
	Pfister et al., 2006	Alaska/Canada	not specified ^a	range/number not specified	0.25
	Real et al., 2007	Alaska	6–9 days	−0.0088–0.078 ($n = 2$)	0.035
	Val Martin et al., 2006	northern North America	6–15 days	−0.42–0.89 ($n = 9$)	0.27
	average				
Plume age category	Study	Tropics/subtropics	Approximate plume age	Range of $\Delta\text{O}_3/\Delta\text{CO}$ (ppbv/ppbv) (number of measurements)	Mean $\Delta\text{O}_3/\Delta\text{CO}$ (ppbv/ppbv)
$\leq 1-2$ days	Hobbs et al., 2003	Southern Africa	<1 h	−0.009–0.090 ($n = 11$)	0.036
	Jonquieres et al., 1998	northern Africa	≤ 2 days	0.13–0.37 ($n = 4$)	0.23
	Mauzerall et al., 1998	Brazil/southern Africa	<0.5 days	range not specified ($n = 4$)	0.15 ± 0.37
	Mauzerall et al., 1998	Brazil/southern Africa	0.5–1 day	range not specified ($n = 4$)	0.32 ± 0.76
	Yokelson et al., 2003	southern Africa	<1 day	−0.060–0.090 ($n = 32$)	0.006
	Yokelson et al., 2009	Mexico	<2 h	0.019–0.17 ($n = 4$)	0.078
average					0.14
2–5 days	Bertschi et al., 2004	Southeast Asia	4–5 days	0.26–0.42 ($n = 3$)	0.33 ^b
	Kondo et al., 2004	Southeast Asia	2–3 days	range/number not specified	0.20 ± 0.01
	Mauzerall et al., 1998	Brazil/southern Africa	1–5 days	range not specified ($n = 10$)	0.71 ± 0.12
	Sanhueza et al., 1999	Venezuela	not specified ^a	range/number not specified	0.17 ± 0.01
average					0.35
≥ 5 days	Andreae et al., 1994	Africa/South America	10 days	0.19–0.87 ($n = 10$)	0.41 ± 0.20
	Mauzerall et al., 1998	Brazil/southern Africa	5–7 days	range not specified ($n = 8$)	0.74 ± 0.9
	Singh et al., 2000	South Africa/South America	≤ 10 days	range/number not specified	0.75
average					0.63

^a For studies where the plume age was not specifically listed, information provided within the study was used to estimate the age.

^b These studies note that the biomass burning plumes observed are likely mixed with anthropogenic pollutants.

et al., 1996, 1998; Honrath et al., 2004; Bertschi and Jaffe, 2005; Singh et al., 2010). An alternate explanation is that mixing of air from the middle and upper troposphere could enhance O₃ downwind of source regions. However, by enhancing the O₃ background, dilution with air from the middle and upper troposphere will reduce the slope in the O₃–CO regression. This suggests that we need a chemical explanation, rather than one based on mixing, to explain the high $\Delta\text{O}_3/\Delta\text{CO}$ ratios. While we cannot conclude that mixing is unimportant, our current understanding would suggest that these high $\Delta\text{O}_3/\Delta\text{CO}$ values are most likely due to very efficient O₃ production following long-range transport of PAN. This remains an important question that impacts our understanding of the global O₃ production from wildfires.

Regardless of the distance traveled, O₃ production in wildfire plumes can be enhanced by mixing with external air masses. Junquera et al. (2005) used modeling to study two US wildfire plumes: one transported over a large urban region and one transported over forested areas. They found enhanced O₃ production in the former plume due to mixing with urban NO_x emissions. Ozone production was NO_x-limited in the latter plume, and due to the low NMOC emissions from the wildfire, the majority of the NMOCs involved in photochemical O₃ production were emitted from forests downwind of the fires. Other studies have also found significant O₃ enhancements in wildfire plumes that mix with urban NO_x emissions (e.g. McKeen et al., 2002; Morris et al., 2006; Singh et al., 2010). In a study of arctic wildfire plumes, Singh et al. (2010) found molar ratios of $\Delta\text{O}_3/\Delta\text{CO}$ of approximately 0.03 and 0.11 for fresh biomass burning plumes and aged plumes mixed with urban emissions, respectively. As described above, it is not clear whether the difference in these two categories is solely due to mixing with urban air masses or also due to suppression of O₃ production near the fire source.

Ozone production in some biomass burning plumes can be extremely rapid. For a fire in South Africa, Hobbs et al. (2003) show rapid O₃ loss, followed by O₃ enhancements of 98 ppbv in less than thirty minutes. This results in a remarkable net O₃ production rate of more than 200 ppbv h⁻¹. Some of the more reactive compounds appear to accelerate the photochemistry in biomass plumes. Both HONO (Trentmann et al., 2005; Keene et al., 2006; Burling et al., 2010) and formaldehyde (Holzinger et al., 1999; Yokelson et al., 1999; Trentmann et al., 2003) are emitted in significant quantities and can provide an important HO_x radical source. These will offset, to some extent, the reductions in photolysis in the plumes. Hobbs et al. (2003) also compare their South African results to similar observations from Alaska and the Pacific Northwest and find, not surprisingly, that the O₃ build-up is much faster for the South African case compared to the higher latitude cases.

Studies of O₃ formation in wildfire plumes have involved a variety of models including GEOS-CHEM (e.g. Martin et al., 2002; Duncan et al., 2003; Jaffe et al., 2004; Sinha et al., 2004; Nassar et al., 2009), MOZART-4 (e.g. Pfister et al., 2006, 2008), p-TOMCAT (e.g. Cook et al., 2007), STEM (e.g. Phadnis and Carmichael, 2000); CiTTYCAT (e.g. Real et al., 2007) and GRACES (e.g. Chatfield et al., 1996). Modeling O₃ production is especially challenging due to the impacts from the wide range of NMOCs emitted, difficulty in simulating radical production, heterogeneous interactions, aerosol radiative effects and the model resolution needed to adequately capture plume dynamics and chemistry. Most models report some degree of O₃ production, but have difficulty in reproducing O₃ mixing ratios quantitatively. Phadnis and Carmichael (2000) found that differences between modeled and observed O₃ concentrations are likely due to uncertainties in the concentration, timing and dispersion of fire emissions. Alvarado and Prinn (2009) show reasonable success in modeling the O₃ formation in plumes from African and Alaskan fires using a Lagrangian parcel model combined with the ASP aerosol model; however one simulation did

not produce sufficient O₃ due to modeled values of OH that were lower than observations. Cook et al. (2007) modeled O₃ formation during long-range transport of plumes from Alaskan and Canadian fires to the North Atlantic and found discrepancies between modeled and observed PAN, NO_x and O₃, likely due to inaccurate NMOC and NO_x emissions in the model. The authors improved model agreement with observations in part by lowering the NO₂/CO emission ratio for these boreal fires. McKeen et al. (2002) also found that changes in NO_x and NMOC emission factors contribute to model bias, and Nassar et al. (2009) found that disparities between modeled and observed O₃ over Indonesia in 2006 were partly due to an underestimation of NO_x emissions. In a study comparing two models' ability to capture the O₃ production from African and Alaskan fires, Mason et al. (2006) found that NMOC emissions data is the most significant factor in model accuracy, due to its effect on reaction mechanisms. Trentmann et al. (2003) modeled the first ten minutes of a fire plume and found unrealistically low O₃ values resulted from underestimation of OVOC emissions. Trentmann et al. (2005) used a photochemical box-model with dilution to examine O₃ production in a savannah fire plume. They found that O₃ mixing ratios were underestimated by up to 60 ppbv in the first hour, likely due to an incomplete understanding of the oxygenated emissions and photochemical reactions. Similarly, using the GEOS-CHEM model Alvarado et al. (2010) were able to track biomass burning plumes, but had difficulty simulating the rapid production of PAN, likely due to inadequate treatment of the NMOCs.

Modeled O₃ concentrations are affected by mixing and dilution (Cook et al., 2007; Real et al., 2007; Nassar et al., 2009). Chatfield and Delany (1990) postulate that models will significantly overestimate O₃ production if the vertical mixing and dilution are subject to extensive spatial averaging. Similarly, Leung et al. (2007) find much greater O₃ production for emissions lofted above the boundary layer due to greater dispersion of NO_x, and note that column and surface observations of CO must be used to define the injection height of the plume. When fire emissions are diluted into large grid cells, as in global chemical transport models, significant errors can result (Pfister et al., 2006; Alvarado et al., 2009). Sinha et al. (2004) found negative biases of approximately 10–25% downwind of African fires and approximately 30% near the fires' sources, resulting from coarse spatial and temporal resolutions. In addition, Hauglustaine et al. (1999) found that while their model simulation of the 1997 Indonesian fires reproduced O₃ concentrations fairly well, the transport pathways of the fire plumes differed from observations due to the use of a mean climatology in place of higher resolution meteorological data. All of these studies highlight the difficulties of modeling O₃, and demonstrate that chemistry schemes must be complex enough to capture the breadth of photochemical reactions occurring in wildfire plumes, the emission factors of the region modeled and the dynamics of the plume transport.

Wildfires can make a significant contribution to O₃ both regionally and globally. Table 2 shows estimated O₃ production from several prior studies along with our estimates. Our calculations are based on the annual CO emission inventory for 1997–2010 for all categories of biomass consumption given by van der Werf et al. (2010). To estimate global O₃ production, we use a method similar to that described by Mauzerall et al. (1996). For the $\Delta\text{O}_3/\Delta\text{CO}$ ratio we used a value of 0.4 for equatorial and tropical regions and a value of 0.2 for all other regions, similar to the average values given in Table 1 for plumes greater than 2 days old for each region. As mentioned earlier, the much greater O₃ production (per unit CO emission) from tropical and equatorial regions is due to the much higher NO_x emissions per unit of fuel consumed. With these assumptions, we estimate global O₃ production of 174 Tg year⁻¹ due to wildfires, with an uncertainty of approximately 50% due to

Table 2
Global and regional estimates of O₃ production from wildfires.

Fire/time period	CO emissions	O ₃ production	Method	Reference
Southern Hemisphere (Africa and South America)/during the dry season	17 Tg month ⁻¹	17 Tg month ⁻¹	1	Mauzerall et al., 1998
Alaska and Canada/summer 2004	30 Tg	11–15 Tg	2	Pfister et al., 2006
Boreal Northern Hemisphere	38 Tg year ⁻¹	13 Tg year ⁻¹	3	This work
Temperate Northern Hemisphere	9 Tg year ⁻¹	3 Tg year ⁻¹	3	This work
Northern Hemisphere Tropical and Equatorial Region (10° S–30° N)	151 Tg year ⁻¹	103 Tg year ⁻¹	3	This work
Southern Hemisphere south of 10° S	158 Tg year ⁻¹	54 Tg year ⁻¹	3	This work
Global total	356 Tg year ⁻¹	174 Tg year ⁻¹	3	This work

1: Total biomass burned (Tg)*CO Tg⁻¹ biomass burned*observed ΔO₃/ΔCO ratio. Mauzerall et al. (1998) used a relatively low biomass consumption for the southern hemisphere (SH) of 294 Tg month⁻¹, but a relatively high ΔO₃/ΔCO of 0.59.

2: Total biomass burned (Tg)*CO Tg⁻¹ biomass burned*observed and modeled ΔO₃/ΔCO ratio.

3: For our estimates, we used the average CO emissions given by van der Werf et al. (2010) for 1997–2010 and a ΔO₃/ΔCO ratio of 0.4 for equatorial and tropical regions and a value of 0.2 for all other regions. We used the van der Werf et al. (2010) classifications as follows: Boreal northern hemisphere (NH) (BONA, BOAS); Temperate NH (TENA, EURO, CEAS); NH Tropical and Equatorial Region (CEAM, NHSA, MIDE, NHAF, SEAS, EQAS) and SH (south of 10S, SHSA, SHAF, AUST).

uncertainty in the mean ΔO₃/ΔCO ratios and total CO production. This calculation yields a value that is 3.5% of the global in-situ tropospheric O₃ production of approximately 5000 Tg year⁻¹ (Bey et al., 2001). Similarly, Ziemke et al. (2009) calculate that biomass burning increases the global tropospheric burden of O₃ by 4–5% using a global model. But in contrast to the global photochemical production from all sources, the production from wildfire plumes is more regionally concentrated (e.g. Jaffe et al., 2008; Nassar et al., 2009). In our estimates, more than half of the global O₃ production from biomass burning occurs in the northern tropics and equatorial regions due to the greater degree of biomass burning and higher ΔO₃/ΔCO ratios in these regions. Additionally, in some years the amount of global biomass burning can be much higher (e.g. Cahoon et al., 1994; McKeen et al., 2002). This is especially true during El Niño periods both for tropical (e.g. Chandra et al., 2009; Fujiwara et al., 1999) and boreal regions (e.g. Kasischke and Bruhwiler, 2002; Jaffe et al., 2004). Akagi et al. (2011) estimate that the overall emissions from fires during El Niño years can be up two times larger than other years, which would lead to a proportional increase in O₃ production during those years.

Our calculations (Table 2) indicate that O₃ production in temperate regions is the lowest of all regions, at only 3 Tg year⁻¹. Yet, this amount of production can still be important for surface air quality. For example, Jaffe et al. (2008) show that wildfires add an additional 10 ppbv to the boundary layer in a large portion of the western US during high fire years. Using this value we can estimate the O₃ production required to sustain this mixing ratio in the boundary layer for the western US region considered by Jaffe et al. (2008), approximately 1500 km × 1500 km. Using a boundary layer height of 1 km and an O₃ lifetime of 5 days, we calculate an O₃ production rate of 0.27 Tg month⁻¹ to sustain a 10 ppbv enhancement in the boundary layer of the western US. To sustain this enhancement over a 3 month fire season would require O₃ production of approximately 0.9 Tg. This shows that the estimated O₃ production shown in Table 2 is sufficient to sustain significant O₃ enhancements in the boundary layer across major wildfire regions.

4. Regulatory issues associated with wildfire ozone production in the US

In the US, the National Ambient Air Quality Standards (NAAQS) are a set of standards that should not be violated for six criteria pollutants. The O₃ exceedance level has become increasingly strict over the past several decades, changing from a 1-h average of 0.12 ppmv to an 8-h average of 0.08 ppmv in 1997 (which was legally interpreted as 85 ppbv) to an 8-h average of 75 ppbv in 2008. A county or metropolitan area is in exceedance of the standard if the 3 year average of the annual fourth highest daily maximum 8-h average exceeds this level. Only measurements

made by official air quality sites—known as Air Quality System (AQS) sites—are considered in the attainment/non-attainment designation. Numerous studies have shown that emissions from wildfires have contributed to O₃ mixing ratios in urban areas that are greater than these exceedance levels (e.g. Jaffe et al., 2004, 2008; Jaffe, 2011; Morris et al., 2006; Pfister et al., 2008).

Several approaches have been used to identify the contribution of wildfires emissions to elevated O₃ levels. Jaffe et al. (2004) identified long-range transport of smoke from Siberia to the west coast of the US during 2003, a huge fire year in Siberia. They then evaluated O₃ data from Washington State to develop a statistical model to predict O₃ mixing ratios based on daily maximum temperature. This relationship was then applied to estimate the enhanced O₃ due to the fire influence on days with clear evidence of forest fire smoke. Morris et al. (2006) used a combination of satellite data, modeling and surface observations to identify smoke impacts in Houston from long-range transport of emissions from Alaskan and Canadian fires. Pfister et al. (2008) demonstrate how wildfires in 2008 enhanced O₃ by more than 10 ppbv at a number of air quality monitoring stations in California. Jaffe et al. (2008) show that wildfires in the Rocky Mountain region of the US have strong interannual variations, and impact O₃ concentrations at numerous air quality monitoring sites in the region. They also showed that temperature played a relatively minor role in explaining the O₃ variability at these sites. Continuing this analysis, Jaffe (2011) demonstrates how the number of days with an 8-h average O₃ mixing ratio greater than 75 ppbv (the current US O₃ exceedance level) has a strong interannual variation that largely depends on the density of wildfires in the western US.

In deciding if a region is in compliance with the NAAQS, EPA can consider if an air quality event was due to factors that are beyond the control of domestic regulations. These events are called “exceptional events” by EPA. A state regulatory agency must petition EPA to have a particular day or days excluded from their calculation of NAAQS attainment. These rules are intended to cover events such as natural dust events, long-range transport of pollution from outside national boundaries, entrainment of stratospheric airmasses and wildfires. To date, most exceptional events proposed for exclusion by state agencies have focused on particulate matter less than 2.5 microns in diameter (PM_{2.5}) due to wildfires. The EPA has a partial list of cases that have been presented by state agencies at: <http://www.epa.gov/ttn/analysis/exevents.htm>.

One case in this list focused on wildfire impacts on O₃. This case was presented by the California Air Resources Board (CARB) for fires that occurred in Sacramento County in 2008. The evidence presented by CARB was extensive and included monitoring data, satellite data, air parcel trajectories and photochemical modeling. A key element of the analysis was a statistical model to estimate O₃ mixing ratios in the absence of wildfires. This fulfills the EPA requirement to demonstrate that the event would have met the air

quality standard “but for” the exceptional event. In this case CARB used historical O₃ and meteorological data to develop a predictive model of daily maximum O₃ mixing ratios. With this model, CARB could show the amount of additional O₃ that was due to the wildfires.

In general, demonstrating and quantifying the O₃ impacts from wildfires in an urban area is challenging. This reflects the fact that O₃ is a secondary pollutant, so that while most pollutants emitted by a wildfire decrease with distance, O₃ can increase. In addition, nonlinearities in the plume photochemistry and wildfire fuel emissions described in Sections 2 and 3 add to these complexities. Nonetheless, as wildfires continue to impact populated areas and as the air quality standards are tightened it will become increasingly important to identify the sources of O₃ in populated areas.

5. Conclusions

Ozone production from wildfires is a complex process involving numerous variables including fire emissions, chemical and photochemical reactions, aerosol effects on chemistry and radiation, and local and downwind meteorological patterns. While O₃ production requires both NO_x and NMOCs, wildfires tend to be NO_x-limited. We calculate that the average molar ratio of emitted NMOC/NO_x in savannah, tropical, temperate and boreal forests is 15, 50, 20 and 150, respectively. However, NMOC emissions are not well quantified. Recent findings suggest that OVOCs compose more than half of total NMOC emissions from fires, although the molecular form of many of these species is unknown. Nitrogen emissions from wildfires are a function of fuel nitrogen content, which typically ranges from 0.2 to 4.0%, and the efficiency of combustion, which correlates with NO_x emissions. MCE, a unitless ratio, can be used to quantify combustion efficiency, and typical MCE values for individual fires range between 0.80 and 1.00. We calculate that average MCE values for savannah, tropical, temperate and boreal forests are 0.94, 0.92, 0.92 and 0.80, respectively, indicating that boreal wildfires are likely to produce less NO_x on average than fires in other biomes.

Chemical and photochemical reactions also significantly impact O₃ production in wildfire plumes. HNO₃ and aerosol NO₃⁻ are largely sinks for NO_x, while PAN acts as a NO_x reservoir. Thermal decomposition of PAN up to two weeks downwind of wildfires has been linked to O₃ production. The colder temperatures of high latitudes favor sequestration of NO_x in the form of PAN, although tropical wildfire plumes also show evidence of this. Modeling of O₃ production is very challenging due to the interplay and complexity of emissions, photochemistry and dynamics. A model's ability to reproduce observed O₃ concentrations is affected by the accuracy of the emissions, heterogeneous and radiative impacts, photochemical scheme used, model resolution and accuracy of the dynamics. Because of the variation in fuels and chemical reaction pathways in fire plumes at different latitudes, regional and local models may provide a better quantitative estimate of O₃ production compared to global models, which are likely to overestimate O₃ production due to coarse grid resolution.

For this review, we have compiled a number of studies that report ΔO₃/ΔCO ratios in wildfire plumes (see Table 1). The majority of studies show that O₃ is produced from wildfires, and typical ΔO₃/ΔCO values range from nearly zero to 0.7. Using average ΔO₃/ΔCO ratios of 0.4 for tropical and equatorial biomes and 0.2 for other regions, we estimate global wildfires produce approximately 170 Tg of O₃ per year, which is 3.5% of all global tropospheric O₃ production. Generally, we find that the ΔO₃/ΔCO ratio increases with plume age, as expected, and is greater in tropical and equatorial regions, which is consistent with greater NO_x emissions per unit of fuel consumed. A number of other factors contribute to the observed ΔO₃/ΔCO in a wildfire plume. Recent studies have identified oxygenated

compounds, such as HONO and formaldehyde, which dramatically accelerate O₃ production. In addition, decreased transmission of solar radiation due to aerosols can reduce photolysis rates significantly in a fire plume. Cloud processing and heterogeneous reactions involving aerosols have also been shown to affect the concentration of compounds involved in O₃ production and loss reactions. Further, mixing of wildfire plumes with airmasses containing natural and anthropogenic O₃ precursors has been shown to enhance O₃ production. However, there are still uncertainties surrounding the ΔO₃/ΔCO ratios that fall outside of the typical range. Some studies have documented negative ΔO₃/ΔCO values, even far downwind of the fire source, and others have found values up to 0.9. Additional research is needed to better understand the interplay of fire emissions, chemical reactions, aerosol effects and atmospheric dynamics that explain these ratios.

A clear understanding of O₃ production from wildfires is increasingly important in the US due to the tightening of the NAAQS for O₃. Wildfires have been shown to contribute to background O₃ levels and to days that exceed the air quality standard. However, identification of fire influence on O₃ production is complicated because O₃ is a secondary pollutant which peaks only downwind of the fire location. Thus, while particulate aerosol concentrations will decrease with distance from a fire, O₃ mixing ratios can increase. Because of this, it will be important to continue to analyze O₃ production from wildfires, focusing both on AQS sites and additional urban and rural measurement sites that can provide a broad dataset for analysis of changing O₃ concentrations and health impacts.

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