Developments in Environmental Science, Volume 8
A. Bytnerowicz, M. Arbaugh, A. Riebau and C. Andersen (Editors)

ISSN: 1474-8177/DOI:10.1016/S1474-8177(08)00004-1

Chapter 4

Chemical Composition of Wildland Fire Emissions

*Shawn P. Urbanski, Wei Min Hao** *and Steve Baker*

AU :2

Abstract

Wildland fires are major sources of trace gases and aerosol, and these emissions are believed to significantly influence the chemical composition of the atmosphere and the earth's climate system. The wide variety of pollutants released by wildland fire include greenhouse gases, photochemically reactive compounds, and fine and coarse particulate matter. Through direct emissions and secondary chemical and physical processes, wildland fire can have a significant impact on tropospheric chemistry and serve as a major source of air pollution. We provide a synthesis of emission factor data from the literature and previously unpublished research for use in global, continental and regional scale studies investigating the role of wildland fire emissions in atmospheric chemistry and climate. The emission factor data is presented by geographic zones (boreal, temperate, and tropical) and vegetation group (forest and savanna/rangeland), allowing researchers to account for the different emission characteristics exhibited by biomass burning in these disparate regions. A brief overview of the wildland fuel combustion process as related to emissions production is also provided. The atmospheric fate of wildland fire emissions is briefly discussed and related to the production of secondary air pollutants. Previously unpublished results from a series of fire emission studies in the United States and Canada is presented in an appendix.

---

*Corresponding author: E-mail: whao@fs.fed.us

4.1. Introduction

Wildland fires emit large amounts of trace gases and particles (Ito & Penner, 2004; Michel et al., 2005; van der Werf et al., 2006; Wiedinmyer et al., 2006), and these emissions are believed to significantly influence the chemical composition of the atmosphere (Lapina et al., 2006; Simpson et al., 2006) and the earth's climate system. The wide variety of pollutants released by wildland fire include greenhouse gases (carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O)), photochemically reactive compounds (e.g., carbon monoxide (CO), nonmethane volatile organic carbon (NMVOC), nitrogen oxides (NO_x)), and fine and coarse particulate matter (PM). Wildland fires influence climate both directly, through the emission of greenhouse gases and aerosols, and indirectly, via secondary effects on atmospheric chemistry (e.g., ozone (O_3) formation) and aerosol and cloud microphysical properties and processes (e.g., the "Twomey" cloud albedo effect; Lohmann & Feichter, 2005; Naik et al., 2007). Wildland fire emissions contribute to air pollution by increasing the atmospheric levels of pollutants that are detrimental to human health and ecosystems and degrade visibility, leading to hazardous or general nuisance conditions. The air quality impacts occur through the emission of primary pollutants (e.g., PM, CO, NO_x) and the production of secondary pollutants (e.g., O_3, secondary organic aerosol (SOA)) when NMVOC and NO_x released by fires undergo photochemical processing. Air quality can be degraded through local (Muhle et al., 2007; Phuleria et al., 2005), regional (DeBell et al., 2004; Sapakota et al., 2005), and continental (Morris et al., 2006) scale transport and transformation of fire emissions.

AU :3

The air quality impact of wildland fires depends on meteorology, fire plume dynamics, the amount and chemical composition of the emissions, and the atmosphere into which the emissions are dispersed. Fresh smoke from burning wildland fuel is a complex mixture of gases and aerosols. The amount and composition of fire emissions depends on a wide range of variables related to fuel characteristics (type, structure, loading, chemistry, moisture) and fire behavior (Christian et al., 2003). Fuel characteristics are ecosystem-specific properties that are heavily influenced by land use history and environmental conditions (e.g., seasonal weather patterns that drive fuel moisture or anthropogenic nitrogen and sulfur deposition that impact fuel chemistry). It is fuel characteristics in conjunction with meteorology and topography that control fire behavior (Albini, 1976; Anderson, 1983; Rothermal, 1972).

This chapter provides an overview of the wildland fuel combustion process as related to emissions production and provides a synthesis of emissions data from the literature and previously unpublished research for global and continental scale studies of atmospheric chemistry and climate. We also briefly discuss the atmospheric fate of wildland fire emissions and how it is related to the production of secondary air pollutants. Last, we include an appendix of previously unpublished results from a series of fire emission studies in the United States and Canada.

4.2. Wildland fuel combustion process and emissions

Given an ignition, wildland fire propagates through heat transfer from the open flame and burning region of a fuelbed to the unburned components of the fuelbed. Heat transfer can occur through direct flame contact, convective heating, radiative heating, and firebrand contact (Morvan & Dupuy, 2001). The unburned material is thermally degraded producing volatile gases that mix with air to form a combustible mixture ahead of the flaming front. Ignition of the combustible mixture by the flame spreads the flaming front (Benkoussas et al., 2007; Morvan & Dupuy, 2001). In the wake of the flaming front, combustion continues in the fuelbed, with regions of intermittent open flame. The combustion of wildland fuels may be divided into several phases: distillation/drying, pyrolysis, char oxidation, and flaming combustion (Benkoussas et al., 2007).

Laboratory studies investigating the combustion of wildland fuels and biomass provide valuable insight into the relationship between the character of fire emissions and the combustion process. Distillation involves volatilization of compounds stored in liquid pools as the vegetation is heated. Distillation of freshly harvested live foliage has been observed to emit a variety of volatile organic compounds (VOC; Greenberg et al., 2006). Greenberg et al. (2006) measured emission rates of terpenes, methanol, acetaldehyde, acetic acid, and methyl acetate from five different vegetation species when heated from 60°C to 200°C.

Minimal thermal decomposition of lignocelluosic biomass occurs prior to about 200°C, where pyrolysis begins (~250 °C for whole wood; Rowell & LeVan–Green, 2005). Below 300 °C, pyrolysis mainly leads to the production of volatile gases and the formation of reactive char (Rowell & LeVan–Green, 2005). Low temperature pyrolysis (200–300 °C) of freshly harvested live foliage and woody tissue produces CO, CO_2, and a host of oxygenated-VOC (OVOC), including methanol, acetic acid, acetone, 1,3-butadione, furan, and 2-furyladehyde (Greenberg et al., 2006). Oxidation of the reactive char leads to smoldering or glowing combustion. Pyrolysis and char oxidation create flammable gas mixtures that form the flame. The flaming combustion process produces gas-phase emissions that are dominated by highly oxidized compounds (CO_2, NO_x, sulfur dioxide (SO_2)) (Lobert et al., 1991; Yokelson et al., 1997) and aerosol with a significant, but highly variable fraction of elemental carbon (Chen et al., 2007; Radke et al., 1991; Reid et al., 2005).

After flaming combustion has ceased, oxidation of residual char results in glowing combustion. As the heat intensity decreases and the levels of combustible gases decrease, char oxidation initiates smoldering combustion (Rowell & LeVan–Green, 2005). Large scale, open fires in laboratory combustion chambers have identified several products of pyrolysis and char oxidation occurring following the cessation of open flame; these incomplete combustion products include CO, CH_4, ammonia (NH_3), C2–C3 hydrocarbons, methanol, formic and acetic acids, and formaldehyde (Bertschi et al., 2003; Yokelson et al., 1996, 1997).

During a wildland fire event, the complex thermal degradation processes (distillation, pyrolysis, char oxidation, and the oxidation of the resultant gas products in flaming combustion) occur simultaneously and often in close proximity. Thermal degradation of fuels occurs ahead and along the fireline, while pockets of intermittent open flame often persist well behind the flaming front. However, for purposes of characterizing emissions, wildland fire behavior is usually described based on the presence or absence of an open flame: "flaming" or "smoldering" combustion. While this taxonomy is imperfect, it does provide a basis for objectively describing the fire behavior associated with emission measurements. The relative amount of flaming and smoldering combustion in a wildland fire may be described using the combustion efficiency (CE) or modified combustion efficiency (MCE) indices (see Section 4.3). Numerous laboratory studies demonstrate flaming combustion is characterized by high CE and MCE (Chen et al., 2007; Goode et al., 1999; Yokelson et al., 1996). These studies demonstrate that values of CE and MCE approach 1 when flaming combustion dominates—for a bed of fine fuels (grass or conifer needles) completely engulfed in flame, MCE is about 0.99 (Chen et al., 2007; Yokelson et al., 1996).

The presence of open flame—flaming combustion—has a significant impact on the chemical composition of emissions and the plume dynamics of the fire. Volatile gases created by thermal degradation of the fuels are oxidized in the flame, generating more highly oxidized emissions (Lobert et al., 1991; Yokelson et al., 1997). Flaming combustion is a highly exothermic process that produces high-temperature gases and subsequent convective lofting of emissions. Consumption of the fuel leads to a reduced rate of pyrolysis and eventual cessation of the open flame.

The continued thermal degradation of fuels in the postfrontal fuelbed is the phase of fire commonly labeled "smoldering combustion." During the smoldering phase, the reduced rate of pyrolysis results in lower heat production and fuel consumption rates (Freeborn et al., 2007; Lobert & Warnatz, 1993; Ottmar, 2002; Rowell & LeVan–Green, 2005). The energy AU :4 available to drive convective lofting of emissions is greatly diminished, and the smoke often remains close to the ground (Ottmar, 2002; Ottmar et al., 2002).

The convective updraft of a fire's flaming front often entrains emissions from smoldering combustion along the fire front and in the postfrontal fuelbed, resulting in a smoke plume that is a mixture of emissions created by flaming and smoldering combustion. It is these convectively lofted emissions that have the greatest potential for impacting air pollution beyond the local vicinity of a fire. Most field studies of fire emissions have employed aircraft or towers as sampling platforms and have measured the fresh smoke plumes of fire convective updrafts. Smoldering combustion that is not entrained in the convective updraft or is sustained without open flame is referred to as residual smoldering combustion (RSC; Bertschi et al., 2003; Wade & Lunsford, 1989). RSC generally involves the combustion of large diameter fuels AU :5 and belowground biomass (e.g., peat, duff, and roots) and may persist for days or weeks after flaming combustion has ceased (Ward et al., 1992). Emissions from RSC can be quite significant; in boreal and temperate forests RSC may comprise 50% or more of the biomass consumed in some fire events (Kasischke et al., 2000; Reinhardt et al., 1991).

4.3. Emission data

The standard metric employed in the measurement of fire emissions is the excess mixing ratio, ΔX, defined as

$$\Delta X = X_{\text{plume}} - X_{\text{bkgd}} \tag{4.1}$$

where X_{plume} and X_{bkgd} are the mixing ratio of compound X in the fresh smoke plume and the background air, respectively (Ward & Radke, 1993). Emission data is typically reported as emission ratios ($\mathrm{ER}_{\mathrm{X/Y}}$) or emission factors ($\mathrm{EF}_{\mathrm{X}}$). The $\mathrm{ER}_{\mathrm{X/Y}}$ is the excess mixing ratio of species X normalized to the excess ratio of a reference species Y, typically CO or CO_2:

$$\mathrm{ER}_{\mathrm{X/Y}} = \frac{\Delta X}{\Delta Y} \tag{4.2}$$

This chapter presents emission data as emission factors, calculated using the carbon mass balance method (Ward & Radke, 1993), and defined as the mass of a compound released per mass of dry fuel consumed, in units of $\text{g}\,\text{kg}^{-1}$. The emission factor for compound X, EF_X, may be estimated using

$$\text{EF}_\text{X} = F_\text{C} \times 1000 \times \frac{\text{MM}_\text{X}}{12} \times \frac{\Delta X}{C_\text{T}} \tag{4.3}$$

$$C_\text{T} = \sum_{j=1}^{n} N_j \times \Delta C_j \tag{4.4}$$

where ΔX is the excess molar mixing ratio of compound X (Eq. (4.1)), C_T the total excess molar mixing ratio of carbon emitted, MM_X the molecular mass of compound X ($\text{g}\,\text{mole}^{-1}$), 12 the molar mass of carbon ($\text{g}\,\text{mole}^{-1}$), F_C the mass fraction of carbon in the dry fuel, and 1000 ($\text{g}\,\text{kg}^{-1}$) a unit conversion factor (Yokelson et al., 1999). Elemental analysis of wildland fuels from a wide range of vegetation types and ecosystems shows F_C falls between 0.45 and 0.55 (Chen et al., 2007; Lobert et al., 1991; Susott et al., 1991, 1996). A detailed discussion on the elemental analysis of wildland fuels is provided by Susott et al. (1996). C_T may be calculated using Eq. (4.4), where n is the number of emitted species measured, N the number of moles of carbon in species j, and ΔC_j is the excess mixing ratio measured for species j.

The creation of wildland fire source terms for chemical transport or air quality modeling generally requires a mass emission estimate, which EF_X provides. Emission data reported as $\text{ER}_{\text{X/Y}}$ can be converted to EF_X using

$$\text{EF}_\text{X} = \text{ER}_{\text{X/Y}} \times \frac{\text{MM}_\text{X}}{\text{MM}_\text{Y}} \times \text{EF}_\text{Y} \tag{4.5}$$

where $\text{ER}_{\text{X/Y}}$ is the molar emission ratio of compound X to a reference compound Y (as defined in Eq. (4.2), MM_X and MM_Y are the molecular mass of compounds X and Y ($\text{g}\,\text{mole}^{-1}$), and EF_Y is the emission factor for reference compound Y (Eq. (4.3)).

The fire behavior associated with emissions is often characterized using the CE or the MCE, indices that describe the relative amount of flaming and smoldering combustion in a biomass fire (Ward & Radke, 1993). The CE is the molar ratio of CO_2 emitted to the total moles of carbon emitted. CE may be expressed as the ratio of excess moles of carbon emitted as CO_2 to the molar sum of carbon (C) emitted, C_T (Eq. (4.6)). MCE is defined as the ratio of CO_2 emitted to the sum of emitted CO and CO_2

(Eq. (4.7); Ward & Radke, 1993).

$$\mathrm{CE} = \frac{\Delta \mathrm{CO}_2}{C_\mathrm{T}} \tag{4.6}$$

$$\mathrm{MCE} = \frac{\Delta \mathrm{CO}_2}{\Delta \mathrm{CO}_2 + \Delta \mathrm{CO}} \tag{4.7}$$

4.4. Emissions factors for global and continental scale modeling

4.4.1. Introduction

In this section, we provide a synthesis of emissions data from the literature and previously unpublished research for use in global to continental scale studies investigating the role of wildland fire emissions in atmospheric chemistry and climate. Since the research of Andreae and Merlet (2001), knowledge of emissions from wildland fires in tropical regions has increased greatly through extensive field campaigns in southern Africa (SAFARI-2000) (Swap et al., 2003) and Brazil (e.g., The Tropical Forest and Fire Emissions Experiment; Yokelson et al., 2007). The synthesis presented here includes previously unpublished emissions data from field studies of 56 fires covering a broad range North American ecosystems. The emission data is presented by geographic zones (boreal, temperate, and tropical) and vegetation group (forest and savanna/rangeland), allowing modelers to account for the different emission characteristics exhibited by biomass burning in these disparate regions.

Numerous global to continental scale studies using global chemical transport models have sought to elucidate the role of biomass burning in atmospheric chemistry and climate. Recent studies include the role of African biomass burning on tropical O_3 in the Atlantic (Jourdain et al., 2007), the global impacts of aerosol emitted from major source regions (Koch et al., 2007), and the influence of biomass burning on radiative forcing via aerosol and O_3 production (Naik et al., 2007). These studies consider the large-scale influence of widespread, seasonal, regional burning. The coarse grids ($1^\circ \times 1^\circ$ to $6^\circ \times 6^\circ$) of global chemical transport models used in such studies integrate fire activity across a heterogeneous mix of ecosystems (e.g. grasslands, shrublands, and open woodlands; Hely et al., 2003; Sinha et al., 2003). Emission factors for generalized vegetation types (e.g., tropical savanna), which synthesize data from studies encompassing a broad range of geographic regions (e.g., western and southern Africa, Brazil, Australia), ecosystems, and land use modes, are appropriate for global to continental scale investigations using global chemical transport models.

Biomass burning in the tropics is dominated by anthropogenic activities associated with agriculture (Fearnside, 1990; Hao & Liu, 1994; Kauffman et al., 2003, Roberts & Wooster, 2007). In the tropics, fire activity occurs largely within a region's "burning season" (e.g., June through November in the southern Africa; Giglio et al., 2006). The tropical savanna vegetation group represents grassland, shrubland, and woodland savanna ecosystems found in South America, Africa, India, Mainland Southeast Asia, and Australia. The tropical savanna and tropical forest emission data synthesizes an extensive collection of studies conducted in Brazil, Africa, and Australia.

AU :6

The wildland fire activity in temperate zones includes wildfire and prescribed burning (see Section 4.4.2). Prescribed fires are defined as fires ignited by management actions to meet specific, nonagricultural objectives, such as fuel reduction and ecosystem management and restoration (Finney et al., 2005; Hardy et al., 2002). Wildfires are unplanned wildland fires. The temperate zone emission data has been grouped as forest or rangeland (grassland/shrubland). Temperate zone wildfires often occur during a region's wildfire season when meteorological and fuel conditions favor high intensity, rapidly spreading fires (e.g., July through September in the interior mountain west of the United States and Canada). Conversely, prescribed fire is typically employed under meteorological and fuel conditions favorable for low-intensity fires and selective fuel reduction (Fernandes & Botelho, 2004; Finney et al., 2005; Hardy et al., 2002; Price et al., 2007; Smith et al., 2004). Published emission studies for wildland fire in Europe and Central Asia are extremely sparse. As a result, the temperate zone emission data draws mostly from field studies of wildfires and prescribed fires in the United States and southwestern Canada.

Wildfires occurring in the boreal regions of Russia, Canada, and Alaska are estimated to comprise about 20% of annual global biomass burning emissions (van der Werf et al., 2006). Due to the lack of published emission studies, boreal zone emission data is given only for forests, and relies largely on data collected in Canada and Alaska. Despite the significance of boreal fires in Russia, published emission studies for fires in this region are extremely limited.

AU :7

4.4.2. Methods

The emission data is presented here as emission factors (see Section 4.3). Emission factors defined following Eq. (4.3) were used unchanged.

Emission factors given as the fraction of carbon burned were adjusted using the fuel carbon content (F_C) provided by the authors. In the absence of an author provided F_C, a value of 0.50 was used. The F_C value of 0.50 is consistent with F_C measurements for a wide range of vegetation types and ecosystems and is likely accurate to within ±10% (Chen et al., 2007; Lobert et al., 1991; Susott et al., 1991, 1996). When emission data was provided as $ER_{X/Y}$, the data was converted to EF_X using Eq. (4.5). When EF_Y was not supplied by the authors, it was either calculated from the reported data if possible (using Eqs. (4.1–4.4)) or estimated based on EF_Y data for the appropriate vegetation cover group.

Most of the available emission data was obtained from near source, airborne sampling that measures an integrated mixture of emissions from flaming and smoldering combustion. Because the different fire phases often occur simultaneously and in close proximity, differentiating emissions by phase is problematic, even for ground-based measurements. Therefore, we have not attempted to tabulate emission factors by fire phase. When emission data was reported by flaming and smoldering phases, average emission factors were calculated by weighting the phases to achieve an MCE equal to the average MCE of the appropriate vegetation cover group.

The combination of data from wildfires and prescribed fires for temperate zone EFs may seem inappropriate given their different fire behavior characteristics. Temperate zone wildfires are generally more intense than prescribed fires, exhibiting higher rates of spread, greater flame lengths and fire line intensities, and sometimes crown fire (Fernandes & Botelho, 2004; Finney et al., 2005). The greater intensity of wildfires might be expected to result in greater CE compared to lower intensity for prescribed burns. However, during the temperate zone wildfire season, the combination of low fuel moistures (in particular for large diameter woody surface fuels and duff) and high-intensity fire fronts facilitates postfrontal consumption of large woody surface fuels and duff (Albini & Reinhardt, 1995). While pockets of intermittent open flame do persists in postfrontal combustion, low-efficiency, smoldering combustion dominates fuel consumption (Albini & Reinhardt, 1995; Ottmar, 2002; Ottmar et al., 2002). Postfrontal combustion of woody fuels and duff may comprise a significant portion of the total fuel consumed in a fire event (Reinhardt et al., 1991). Conversely, prescribed burning in temperate zones of North America and Europe is generally typified by low-intensity fire occurring under conditions when large woody surface fuels and duff moistures are moderate (Fernandes & Botelho, 2004; Finney et al., 2005; Hardy et al., 2002). These conditions minimize consumption of the large woody fuels and duff, which limits the detrimental fire effects on the

AU :8

ecosystem (Reinhardt et al., 2001), a key management objective of prescribed fire.

In a wildfire event, the convective plume integration of emissions from the high-intensity flaming front and a portion of the emissions from postfrontal smoldering combustion result in fire average combustion efficiencies similar to those of prescribed fires, where flaming combustion comprises a larger fraction of the total fuel consumption. For example, airborne measurements of conifer forest wildfire smoke plumes in the western United States observed MCE of 0.89–0.94 (Babbit et al., 1994; Friedli et al., 2001) compared with an average MCE of 0.92 from studies of 21 prescribed fires in western conifer forests (see Appendix A). Numerous laboratory and field studies (both ground-based and airborne) have shown EFs for a wide range of compounds are linearly correlated with MCE, particularly within vegetation types (Hao et al., 1996; Korontzi et al., 2003; Sinha et al., 2003; Yokelson et al., 2003). Therefore, the similar MCE of wildfires and prescribed fires suggests the aggregation of emissions data from these fire events is appropriate for estimating EFs for use in global to continental scale modeling.

4.4.3. Results and discussion

Emission factor data has been compiled in Table 4.1 according to five generalized vegetation cover groups: temperate forest, temperate rangelands, tropical savanna, tropical forest, and boreal forest. In most instances, the values listed in Table 4.1 are the average of the values obtained from the cited literature and previously unpublished data presented in Appendix A. The scope of Table 4.1 has been limited to compounds that dominate wildland fire emissions or that have a significant potential to impact atmospheric chemistry. Table 4.1 is not an all inclusive list of species that have been observed in wildland fire emissions (e.g., halocarbons are known to be minor products of wildland fire; Andreae & Merlet, 2001 but are not included). For the species considered in our synthesis, the data coverage is thorough for temperate and tropical forests and tropical savannas. The boreal forest data lacks measurements of nonmethane hydrocarbons (NMHC) and heavy OVOC. The temperate rangeland data does not include emission factors for formic acid, acetic acid, and formaldehyde. These three compounds, along with methanol, comprise a large fraction of both OVOC emissions and total NMVOC emissions in the other vegetation cover groups. We report emissions factors for $PM_{2.5}$; however, a detailed discussion of the complex topic of aerosol properties (size distributions, chemistry, thermodynamics) is beyond the scope of this chapter. Reid et al. (2005)

Table 4.1. Emission factors data from wildland fires according to five generalized vegetation cover groups

Species	Temperate forest	Temperate rangeland	Tropical savannas	Tropical forest	Boreal forest	References[a]
	EF ($g\,kg^{-1}$)[b]					
MCE[c]	0.919 ± 0.017	0.939 ± 0.015	0.935 ± 0.019	0.897 ± 0.017	0.906 ± 0.044	1–6,8–13,29–33
Carbon dioxide (CO_2)	1619 ± 112	1684 ± 45	1661 ± 66	1604 ± 50	1604 ± 119	1–6,8–13,29–33
Carbon monoxide (CO)	89.6 ± 13.2	69 ± 17	75 ± 20	117 ± 19	105 ± 45	1–6,8–13,14–27,28,29–33
Methane (CH_4)	3.41 ± 0.90	2.31 ± 1.08	2.7 ± 1.1	6.7 ± 1.1	4.5 ± 2.3	1–7,8–13,14–27,29–33
Ethane (C_2H_6)	0.49 ± 0.24	0.27 ± 0.13	0.42 ± 0.20	0.75 ± 0.23	0.97 ± 0.69	1–3,5,7,8,13,14,16–21,23,24,29–33
Ethene (C_2H_4)	1.11 ± 0.13	1.11 ± 0.44	1.25 ± 0.49	1.20 ± 0.40	2.52 ± 1.02	1–4,7,8,13,14–21,23,24,29,32,33
Ethyne (C_2H_2)	0.29 ± 0.05	0.38 ± 0.15	0.38 ± 0.28	0.21–0.28	0.38 ± 0.23	1–3,5,7,8,13,14–20,22–24,29,32
Propane (C_3H_8)	0.19 ± 0.10	0.09 ± 0.06	0.20 ± 0.28	0.15–0.99	0.31 ± 0.20	1–3,5,7,8,13,14,16–21,23,24,29,33
Propene (C_3H_6)	0.48 ± 0.14	0.40 ± 0.25	0.41 ± 0.15	0.97 ± 0.60	1.05 ± 0.69	1–3,5,7,8,13,14,16–21,24,29,32,33
Propyne (C_3H_4)	0.06 ± 0.02	0.06 ± 0.02				1–3,13
n-butane (n-C_4H_{10})	0.019–0.104	0.03	0.040 ± 0.032	0.04		1,7,14,16,19,22,23
i-butane (i-C_4H_{10})	0.006–0.027	0.008	0.008 ± 0.002	0.02		1,7,14,16,19,23
1+i-butene (C_4H_8)	0.115–0.270	0.06				1,7
1-butene (C_4H_8)			0.075 ± 0.024	0.02–0.13		14,16,17,19,32
i-butene (C_4H_8)			0.062 ± 0.012	0.11		16,17,19
t-2-butene (C_4H_8)	0.018–0.051	0.02	0.026 ± 0.009	0.02–0.05		1,7,14,16,17,23,32
c-2-butene (C_4H_8)	0.014–0.131	0.04	0.020 ± 0.008	0.02–0.04		1,7,14,16,17,23,32
1,3 butadiene (C_4H_6)	0.059–0.065	0.037	0.065 ± 0.069			1,7,14,17,23
n-pentane (n-C_5H_{12})	0.009–0.051	0.011	0.015 ± 0.013	0.014		1,7,14,16,23
i-pentane (i-C_5H_{12})	0.026	0.006	0.075 ± 0.084	0.007		1,16,17,22,23
1-pentene (C_5H_{10})	0.068	0.02	0.020	0.059		7,17,23,28
cis-2-pentene (C_5H_{10})	0.010		0.027 ± 0.006			1,14
trans-2-pentene (C_5H_{10})	0.019	0.003	0.003			1
2-methyl-1-butene (C_5H_{10})			0.006–0.029	0.031		14,17,28
2-methyl-2-butene (C_5H_{10})	0.033	0.027	0.005–0.010	0.046		1,14,28
3-methyl-1-butene (C_5H_{10})	0.019	0.01	0.005			1,14
Cyclopentene (C_5H_8)	0.019	0.005				1
Isoprene (C_5H_8)	0.044–0.114	0.03	0.011–0.042	0.02–0.37		1,7,14,16,17,32

Table 4.1. (*Continued*)

Species	Temperate forest	Temperate rangeland	Tropical savannas	Tropical forest	Boreal forest	References[a]
	EF (g kg^{-1})[b]					
1,3-pentadiene (C_5H_8)	0.028	0.01				1
1,3-cyclopentadiene (C_5H_6)	0.025	0.03				1
Hexane (C_6H_{14})	0.005–0.033	0.006	0.010–0.013	0.067		1,7,14,23,28
Methylcyclopentane (C_6H_{12})	0.006					1
1-hexene (C_6H_{12})	0.102	0.03	0.030–0.046	0.042		1,23,28
trans-2-hexene (C_6H_{12})	0.014					1
cis-2-hexene (C_6H_{12})	0.004					1
2-methylpentene (C_6H_{12})	0.009		0.004			1
Heptane (C_7H_{16})	0.004–0.032	0.005	0.007	0.013		1,7,14,28
Octane (C_8H_{18})	0.017	0.003		0.012		1,28
1-octene (C_8H_{16})	0.018	0.003	0.009			1,14
1-nonene (C_9H_{18})	0.019	0.003				1
Decane ($C_{10}H_{22}$)	0.027	0.002				1
Benzene (C_6H_6)	0.250–0.440	0.22	0.29±0.10	0.38±0.08		1,7,14,16,20–23,28,32
Toluene (C_7H_8)	0.150–0.510	0.13	0.15±0.04	0.23±0.04		1,7,14,16,20,23,28,32
m+p-xylene (C_8H_{10})	0.171	0.039	0.04	0.050		1,16,23
o-xylene (C_8H_{10})	0.051	0.009	0.009–0.012	0.014–0.017		1,16,28
Xylenes (C_8H_{10})				0.13		32
Ethylbenzene (C_8H_{10})	0.020–0.051	0.02	0.009–0.024	0.04±0.03		1,7,16,28,32
Methanol (CH_4O)	0.31–2.03	0.14	1.17	2.57	1.23–1.57	1,4,15,29,32
Phenol				0.01–0.37		32
Formic acid (CH_2O_2)	1.17		0.62	0.59	0.71–1.57	4,15,29,32
Acetic acid (CH_4O_2)	3.11		2.42	3.43	1.61–3.38	4,15,29,32
Formaldehyde (CH_2O)	2.25		0.24–1.10	1.66	1.50–2.38	4,15,21,29,32
Acetaldehyde (C_2H_4O)	0.24	0.25	0.53–0.97	1.38		1,21,22,32
Propanal (C_3H_6O)	0.035	0.01		0.09		1,32
Propenal (C_3H_4O)	0.123	0.08		0.58		1,32
2-methylpropanal (C_4H_8O)	0.206			0.01–0.16		1,32
2-methylbutanal ($C_5H_{10}O$)	0.015					1

Acetone (C_3H_6O)	0.347	0.25		0.57		1,32
2-butanone (C_4H_8O)	0.40	0.26				1
2,3-butanedione ($C_4H_6O_2$)	1.5			0.66		1,32
2-pentanone ($C_5H_{10}O$)	0.079	0.01		0.07		1,32
Cyclopentanone (C_5H_8O)	0.014					1
Furan (C_4H_4O)	0.445	0.1	0.36	0.27–0.33		1,20,32
2-methyl-furan (C_5H_6O)	0.521		0.051–0.24	0.11±0.07		1,20,28,32
3-methyl-furan (C_5H_6O)	0.052		0.012	0.03–0.28		1,28,32
2-ethylfuran (C_6H_8O)	0.006		0.001	0.004		1,28
2,5-dimethyl-furan (C_6H_8O)	0.053					1
2-vinyl-furan (C_6H_6O)	0.013					1
Benzofuran (C_8H_6O)	0.038		0.015	0.016		1,28
Nitrogen oxides (as NO)	1.7		2.3±1.0	1.77	1.1–3.3	5,15,21,22,27,32
Nitric oxide (NO)			1.1	0.74–1.8	1.5–2.3	25,29,32
Nitrous oxide (N_2O)	0.16	0.32	0.12–0.18		0.14–0.41	5,10,22,26,30,33
Ammonia (NH_3)	0.56–1.13		0.26–1.77	1.08	0.10–0.49	4,5,15,21,22,29,32
Hydrogen cyanide (HCN)			0.03–0.53	0.68		15,21,22,32
Aectonitrile (CH_3CN)			0.03–0.13	0.37		21,22,32
Sulfur dioxide (SO_2)			0.43			14
Carbonyl sulfide (OCS)	0.03	0.01		0.02		1,32
$PM_{2.5}$	11.7±5.0	9.7±4.3	4.4	8.5	1.5–7.2	2,3,6,13,24,25,31

Notes: $\mu \pm \sigma$ (mean ± one standard deviation).

[a] References: a. temperate forest, b. temperate rangeland, c. tropical savanna, d. tropical forest, e. boreal forest; 1. Friedli et al. (2001) (a, b); 2. Appendix A, western U.S. conifer forests (a); 3. Appendix A, southeastern U.S. conifer forests (a); 4. Yokelson et al. (1999) (a); 5. Nance et al. (1993) (a,b,e); 6. Babbit et al. (1994) (a); 7. Lee et al. (2005) (a); 8. Radke et al. (1991) (a, b, e); 9. Cofer et al. (1998) (e); 10. Cofer et al. (1990) (b); 11. Hardy et al. (1996) (b); 12. Ward and Hardy 1989 (b); 13. Appendix A, U.S. grassland and shrublands (b); 14. Sinha et al. (2003) (c); 15. Yokelsin et al. (2003) (c); 16. Ferek et al. (1998) (c,d); 17. Bonsang et al. (1991) (c); 18. Rudolph et al. (1995) (c); 19. Bonsang et al. (1995) (c); 20. Greenberg et al. (1984) (c,d); 21. Hurst et al. (1994A) (c); 22. Hurst et al. (1994B) (c); 23. Hao et al. (1996) (c); 24. Ward et al. (1996) (c); 25. Ward et al. (1992) (c,d); 26. Cofer et al. (1996) (c); 27. Lacaux et al. (1996) (c); 28. Koppmann et al. (1996) (c,d); 29. Goode et al. (2000) (e); 30. Cofer et al. (1998) (e); 31. Appendix A, Alaska boreal forest (e); 32. Yokelson et al. (2007) (d); 33. Cofer et al. (1990) (b).

[b] Emission factors are in units of gram of compound emitted per kilogram of dry fuel consumed.

[c] MCE (modified combustion efficiency) = $\Delta CO_2/(\Delta CO+\Delta CO_2)$.

provide a thorough review of biomass burning aerosol. Due to the lack of published data for coarse aerosol (e.g., diameter $< 10\,\mu m$ or total particulate matter) emissions from wildland fire, we have not included EF for coarse aerosol.

Emissions are dominated by CO_2 and CO, which comprise 92–95% (87–92% of C burned) and 4–7% (6–10% of C burned) of total emissions, respectively. As discussed in Section 4.2, the MCE provides a measure of the relative amount of flaming and smoldering combustion in a wildland fire. The MCE is highest for tropical savannas and temperate rangelands and lowest for tropical forests. The high MCE of the savanna and rangeland vegetation cover groups reflects the dominance of flaming combustion in the burning of herbaceous fuels. The heat required for ignition of a fuel element depends on the fuel element's surface area-to-volume ratio (a larger surface area-to-volume ratio requires less heat for ignition) and the moisture content of the fuel (Rothermel, 1972). The large surface area-to-volume ratio of grasses makes these fuels prone to ignition and favors rapid and thorough consumption in open flames. Low-fuel moistures also favor flaming combustion in herbaceous fuels. During a region's dry season, herbaceous vegetation, especially annual grasses, typically have very low moisture content.

AU :9

Boreal forests exhibited the greatest variability in MCE (0.78–0.95) (Cofer et al., 1998; Nance et al., 1993). The lower end of this range reflects the contribution of smoldering duff in the postfrontal fuelbed, which burns with a low MCE (Bertschi et al., 2003; Goode et al., 1999; Yokelson et al., 1997) and can be a significant component of fuel loading in boreal ecosystems (French et al., 2004). The strong convective updrafts often accompanying boreal crown fires can effectively entrain emissions from postfrontal combustion (Trentmann et al., 2006). The low MCE observed for some boreal fires may reflect significant entrainment of postfrontal duff combustion into the convective plumes sampled in airborne studies. Based on their observations of high CO emissions from extremely intense (overall fire intensity of $38{,}400\,kW\,m^{-1}$) flaming crown fires, Cofer et al. (1998) have suggested that intense crown fires may behave as a fuel-rich combustion system with an associated low combustion efficiency.

After CO_2 and CO, the species accounting for the next largest share of emissions is $PM_{2.5}$, followed by CH_4. The $EF_{PM2.5}$ in Table 4.1 is based on tower measurements obtained in the convective updrafts of fires at 3–15 m above the surface (see Appendix A). Numerous airborne studies provide aerosol emission data for a wide range of ecosystems (Reid et al., 2005). However, the EFs measured in these studies encompass aerosol with diameters up to 3.5 or $4\,\mu m$. Because these measurements include aerosol with diameters outside the traditional definition of fine aerosol (diameter $< 2.5\,\mu m$), these studies are not included in Table 4.1.

Emissions of CH_4 from wildland fires appear to have a significant impact on the global levels of this important greenhouse gas (Simpson et al., 2006). Tropical forests have the highest EF_{CH_4} and the highest CH_4:CO EF ratio (0.056 vs. 0.033–0.043). The high CH_4 emissions for tropical forests may reflect the nature of deforestation burns, which typically involve slashed and dried vegetation with large woody fuels being a significant portion of the vegetation consumed (Fearnside, 1990; Kauffmann et al., 2003). Boreal fires involving similar, intentionally arranged fuelbeds, such as slash/tramp or chained fuels (Cofer et al., 1998; Nance et al., 1993; Radke et al., 1991), exhibit similar CH_4:CO EF ratios. Unlike burning in tropical forests, fires in intentionally arranged fuels is not a significant fraction of boreal fire activity (French et al., 2004).

Total emissions of NMVOC exceed that of $PM_{2.5}$ and CH_4 combined and account for 1–2% of fuel C burned (excluding temperate rangelands for which the lack of OVOC measurements prohibits a meaningful assessment). OVOC account for ~60–70% of NMVOC emission and exceed NMHC emissions even on a carbon mass basis. Methanol, acetic acid, formic acid, and formaldehyde dominate OVOC; emissions of these four compounds alone equals or surpasses emissions of NMHC. Figure 4.1 gives the emissions of NMVOC functional classes as a percent of total NMVOC emissions on a carbon basis.

NMVOC of importance in tropospheric chemistry may be grouped into four major classes: alkanes, alkenes, aromatic hydrocarbons, and oxygenated compounds. Oxygenated compounds encompass a diverse range of chemical species that include aldehydes, ketones, alcohols, furans, and acids. In the atmosphere, NMVOC are subjected to a number of physical and chemical processes that lead to their transformation or removal. Wet and dry deposition remove NMVOC from the atmosphere (Seinfeld & Pandis, 1998). Transformation of NMVOC occurs through photochemical processing, initiated by photolysis or reaction with OH radical, NO_3 radical, or O_3 (Atkinson & Arey, 2003). The atmospheric oxidation of NMVOC is an extremely complex process that is closely coupled with the formation of both O_3 and SOA (Ito et al., 2007; Tsigaridis & Kanakidou, 2003; reviews of tropospheric VOC chemistry and SOA can be found in Atkinson & Arey, 2003 and Kanakidou et al., 2005, respectively).

The NMVOC emitted by wildland fires is dominated by oxygenated compounds and unsaturated hydrocarbons (Fig. 4.1). This mix of

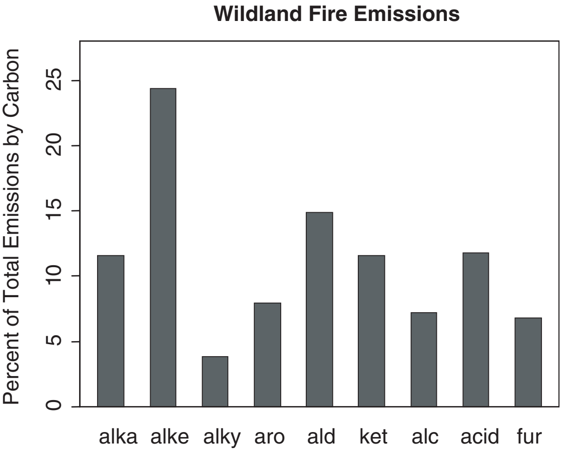

Figure 4.1. Wildland fire emissions aggregated by compound class and given as a percent of total emissions on a carbon basis. Based on an average of temperate and tropical forests and tropical savanna data from Table 4.1. Boreal forest and temperate rangeland data was not included due to insufficient data coverage. Compound classes listed on the *x*-axis are defined as follows: alka, alkanes; alke, alkenes; alky, alkynes; aro, aromatic hydrocarbons; ald, aldehydes; ket, ketones; alc, methanol; acid, formic and acetic acids; and fur, furans.

emissions is highly reactive, as demonstrated by the relatively short atmospheric lifetimes of many of these compounds with respect to gas phase reaction or photolysis (Table 4.2). The highly reactive nature of wildland fire emissions gives wildland fires a significant potential to influence tropospheric chemistry and degrade air quality. Through VOC–NO_x photochemistry, wildland fire emissions lead to O_3 formation on time scales of hours to days and over local to intercontinental distances (Real et al., 2007; Sudo & Akimoto, 2007; Trentmann et al., 2005). In addition to O_3 formation, the gas-phase oxidation of NMVOC can generate semivolatile oxygenated compounds. These semivolatile oxygenated compounds contribute to atmospheric aerosol loading through the formation of new aerosol via gas-to-particle conversion and by condensation on preexisting aerosol (de Gouw et al., 2005; Heald et al., 2005; Tsigaridis & Kanakidou, 2003). SOA formation resulting from the photochemical processing of wildland fire emissions can be quite significant relative to other sources (Heald et al., 2006). The formation of SOA can be quite rapid: wildland fire aerosol mass has been observed to increase by a factor of 1.5–2 over a period of a few days (Reid et al., 1998, 2005).

AU :10

Table 4.2. Estimated lifetimes of dominant emissions from wildfire[a]

Lifetime due to reaction or photolysis[b]	OH[c]	NO_3[d]	O_3[e]	Photolysis[f]
Ethene	1.4 days	225 days	10 days	
Formaldehyde	1.2 days	80 days	>4.5 years	4 hours
Methanol[g]	12 days	1 year		
Acetic acid[h,i]	14.5 days			
Ethane	46.7 days			
Propene	5.3 hours	4.9 days	1.6 days	
Ethyne	13.2 days			
Acetadehyde	8.8 hours	17 days	>4.5 years	6 days
Propane	10 days	~7 years	>4500 years	
2,3-butadione	49 days			1 hour
Formic acid[h,i]	25.7 days			
Benzene	9.4 days	>4 years	>4.5 years	

Notes: The compounds listed comprise ~80% of the total emissions on a molar basis.

[a] Wildland fire emissions are an average of temperate and tropical forest and tropical savanna data from Table 4.1, following conversion to moles.

[b] All lifetime data from Atkinson (2000), or estimated based on rate coefficients from Atkinson and Ayer (2003), unless otherwise noted.

[c] For a 12-hour daytime average OH concentration of 2.0×10^6 molec cm^{-3}.

[d] For a 12-hour daytime average NO_3 concentration of 5.0×10^8 molec cm^{-3}.

[e] For a 24-hour daytime average O_3 concentration of 7.0×10^{11} molec cm^{-3}g.

[f] For overhead sun.

[g] In a study of the global budget of methanol, Jacob et al. (2005) estimate the atmospheric lifetime of methanol is 7 days with removal processes being: 63% reaction with OH, 26% dry deposition, 6% wet deposition, 5% ocean deposition.

[h] Rate coefficient data from Atkinson et al. (2001).

[i] Dry and wet deposition is believed to be an important removal process for formic and acetic acids. Sanhuzea et al. (1996) report similar atmospheric lifetimes for formic and acetic acids: ~5 days for dry deposition and ~5 days for wet deposition.

4.5. Conclusions

Wildland fire emissions data from the literature and an extensive series of previously unpublished field experiments has been synthesized according to generalized vegetation cover groups, providing a dataset for use in global to continental scale studies of atmospheric chemistry and climate. Emissions from wildland fires are a rich and complex mixture of gases and aerosols. Primary pollutants emitted from wildland fires include greenhouse gases (CO_2, CH_4), NMVOC, NO_x, and aerosol. The NMVOC mixture produced by wildland fires is highly reactive. Participation of NMVOC fire emissions in VOC–NO_x photochemistry leads to the formation of O_3 and SOA. Through direct emissions and secondary chemical and physical processes, wildland fire can have a significant impact on tropospheric chemistry and serve as a major source of air pollution.

Uncited references

Albini and Reinhardt, 1997; Atkinson, 2000; Atkinson et al., 2001; Cofer et al., 1989; Hobbs et al., 1996; Jacob et al., 2005; Mason et al., 2005; Sanhueza et al., 1996.

REFERENCES

Albini, F.A. 1976. Estimating wildfire behavior and effects. General Technical Report, INT-30. USDA Forest Service, Intermountain Forest and Range Experiment Station, Ogden, Utah.

Albini, F.A., and Reinhardt, E.D. 1995. Calibration of a large fuel burnout model. Int. J. Wildland Fire 5, 173–192.

Albini, F.A., and Reinhardt, E.D. 1997. Improved calibration of a large fuel burnout model. Int. J. Wildland Fire 7, 21–28.

Anderson, H.E. 1983. Predicting wind–driven wildland fire size and shape. Research Paper INT–305. USDA Forest Service, Intermountain Forest and Range Experiment Station, Ogden, Utah.

Andreae, M.O., and Merlet, P. 2001. Emissions of trace gases and aerosol from biomass burning. Global Biogeochem. Cy. 15, 955–966.

Atkinson, R. 2000. Atmospheric chemistry of VOC's and NOx. Atmos. Environ. 34, 2063–2101.

Atkinson, R., and Arey, J. 2003. Atmospheric degradation of volatile organic compounds. Chem. Rev. 103, 4605–4638.

Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F. Jr., Kerr, J.A., Rossi, M.J., and Troe, J. 2001. In: Carver, G.D., and Cox, R.A., eds. Summary of evaluated kinetic and photochemical data for atmospheric chemistry. IUPAC Subcommittee on Gas Kinetic Evaluation for Atmospheric Chemistry, University of Cambridge, Cambridge, pp. 1–56.

Babbit, R.E., Ward, D.E., Susott, R.A., Hao, W.M., and Baker, S.P. 1994. Smoke from western wildfires, 1994. In: Proceedings, annual meeting of Interior West Fire Council. November, 1994, Coeur d'Alene, Idaho.

Benkoussas, B., Consalvi, J.-L., Porterie, B., Sarody, N., and Loraud, J.-C. 2007. Modelling thermal degradation of woody fuel particles. Int. J. Therm. Sci. 46, 319–327.

Bertschi, I.T., Yokelson, R.J., Ward, D.E., Goode, J.G., Babbitt, R., Susott, R.A., and Hao, W.M. 2003. The trace gas and particle emissions from fires in large–diameter and belowground biomass fuels. J. Geophys. Res. 108, 8472.

Bonsang, B., Boissard, C., Le Cloarec, M.F., Rudolph, J., and Lacaux, J.P. 1995. Methane, carbon monoxide and light non methane hydrocarbon emissions from African savanna burnings during the FOS/DECAFE experiment. J. Atmos. Chem. 22, 149–162.

Bonsang, B., Lambert, G., and Boissard, C.C. 1991. Light hydrocarbons emissions from African savanna burnings. In: Levine, J.S., ed. Global biomass burning: Atmospheric, climatic and biospheric implications. MIT Press, Cambridge, pp. 155–161.

Chen, L.-W.A., Moosmüller, H., Arnott, W.P., Chow, J.C., Watson, J.G., Susott, R.A., Babbitt, R.E., Wold, C.E., Lincoln, E.N., and Hao, W.M. 2007. Emissions from laboratory combustion of wildland fuels: Emission factors and source profiles. Environ. Sci. Technol. 41, 4317–4325.

Christian, T.J., Kleiss, B., Yokelson, R.J., Holzinger, R., Crutzen, P.J., Hao, W.M., Saharjo, B.H., and Ward, D.E. 2003. Comprehensive laboratory measurements of biomass–burning emissions: 1. Emissions from Indonesian, African, and other fuels. J. Geophys. Res. 108, 4719.

Cofer, W.R. III, Levine, J.S., Sebacher, D.I., Winstead, E.L., Riggan, P.J., Stocks, B.J., Brass, J.A., Ambrosia, V.G., and Boston, P.J. 1989. Trace gas emissions from Chaparral and Boreal forest fires. J. Geophys. Res. 94, 2255–2259.

Cofer, W.R. III, Levine, J.S., Winstead, E.L., Cahoon, D.R., Sebacher, D.I., Pinto, J.P., and Stocks, B.J. 1996. Source composition of trace gases released during African savanna fires. J. Geophys. Res. 101, 23597–23602.

Cofer, W.R. III, Levine, J.S., Winstead, E.L., Lebel, P.J., Koller, A.M. Jr., and Hinkle, C.R. 1990. Trace gas emissions from burning Florida wetlands. J. Geophys. Res. 95, 1865–1870.

Cofer, W.R. III, Winstead, E.L., Stocks, B.J., Goldammer, J.G., and Cahoon, D.R. 1998. Crown fire emissions of CO_2, CO, H_2, CH_4, and TNMHC from a dense jack pine boreal forest fire. Geophys. Res. Lett. 25, 3919–3922.

DeBell, L.J., Talbot, R.W., Dibb, J.E., Munger, J.W., Fischer, E.V., and Frolking, S.E. 2004. A major regional air pollution event in the northeastern United States caused by extensive forest fires in Quebec, Canada. J. Geophys. Res. 109, D19305.

de Gouw, J.A., Middlebrook, A.M., Warneke, C., Goldan, P.D., Kuster, W.C., Roberts, J.M., Fehsenfeld, F.C., Worsnop, D.R., Canagaratna, M.R., Pszennym, A.A.P., Keene, W.C., Marchewka, M., Bertman, S.B., and Bates, T.S. 2005. Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002. J. Geophys. Res. 110, D16305.

Fearnside, P.M. 1990. Fire in the tropical rain forest of the Amazon basin. In: Goldhammer, J.G., ed. Fire in the Tropical Biota: Ecosystem Processes and Global Challenges. Springer–Verlag, Berlin, pp. 106–116.

Ferek, R.J., Reid, J.S., Hobbs, P.V., Blake, D.R., and Liousse, C. 1998. Emission factors of hydrocarbons, halocarbons, trace gases, and particles from biomass burning in Brazil. J. Geophys. Res. 103, 32107–32118.

Fernandes, P., and Botelho, H. 2004. Analysis of the prescribed burning practice in pine forest of northwestern Portugal. Environ. Manage. 70, 15–26.

Finney, M.A., McHugh, C.W., and Grenfell, I.C. 2005. Stand– and landscape–level effects of prescribed burning on two Arizona wildfires. Can. J. For. Res. 35, 1714–1722.

Freeborn, P.H., Wooster, M.J., Hao, W.M., Ryan, C.A., Nordgren, B.L., Baer, S.P., and Ichoku, C. 2007. Relationships between energy release, fuel mass loss, and trace gas and aerosol emissions during laboratory biomass fires. *J. Geophys. Res.*, [In press]. AU :11

French, N.H.F., Goovaerts, P., and Kasischke, E.S. 2004. Uncertainty in estimating carbon emissions from boreal forest fires. J. Geophys. Res. 109, D14S08.

Friedli, H.R., Atlas, E., Stroud, V.R., Giovanni, L., Campos, T., and Radke, L.F. 2001. Volatile organic trace gases emitted from North American wildfires. Global Biogeochem. Cy. 15, 435–452.

Giglio, L., Csiszar, I., and Justice, C.O. 2006. Global distribution and seasonality of active fires as observed with the terra and aqua moderate resolution imagining spectroradiometer (MODIS) sensors. J. Geophys. Res. 111, G02016.

Goode, J.G., Yokelson, R.J., Susott, R.A., and Ward, D.E. 1999. Trace gas emissions from laboratory biomass fires measured by open–path Fourier transform infrared spectroscopy: Fires in grass and surface fuels. J. Geophys. Res. 104, 21237–21245.

Goode, J.G., Yokelson, R.J., Ward, D.E., Susott, R.A., Babbitt, R.E., Davies, M.A., and Hao, W.M. 2000. Measurements of excess O_3, CO_2, CO, CH_4, C_2H_4, C_2H_2, HCN, NO, NH_3, HCOOH, CH_3COOH, HCHO, and CH_3OH in 1997 Alaskan biomass burning plumes by airborne Fourier transform infrared spectroscopy (AFTIR). J. Geophys. Res. 105, 22147–22166.

Greenberg, J.P., Zimmerman, P.R., Heidt, L., and Pollock, W. 1984. Hydrocarbon and carbon monoxide emissions from biomass burning in Brazil. J. Geophys. Res. 89, 1350–1354.

Greenberg, J.P., Friedli, H., Guenther, A.B., Hanson, D., Harley, P., and Karl, T. 2006. Volatile organic emissions from the distillation and pyrolysis of vegetation. Atmos. Chem. Phys. 6, 81–91.

Hao, W.M., and Liu, M.H. 1994. Spatial and temporal distribution of tropical biomass burning. Global Biogeochem. Cy. 8, 495–503.

Hao, W.M., Ward, D.E., Olbu, G., and Baker, S.P. 1996. Emissions of CO_2, CO and hydrocarbons from fires in diverse African savanna ecosystems. J. Geophys. Res. 101, 23577–23584.

Hardy, C.C., Hermann, S.M., and Mutch, R.E. 2002. The wildland fire imperative. In: Hardy, C.C., Ottmar, R.D., Peterson, J.L., Core, J.C., and Seamon, P., eds. Smoke management guide for prescribed and wildland fire: 2001 edition. National Wildfire Coordination Group, National Interagency Fire Center, Boise, 11–19.

Heald, C.L., Jacob, D.J., Park, R.J., Russell, L.M., Huebert, B.J., Seinfeld, J.H., Liao, H., and Weber, R.J. 2005. A large organic aerosol source in the free troposphere missing from current models. Geophys. Res. Lett. 32, L18809.

Heald, C.L., Jacob, D.J., Turquety, S., Hudman, R.C., Weber, R.J., Sullivan, A.P., Peltier, R.E., Atlas, E.L., de Gouw, J.A., Warneke, C., Holloway, J.S., Neuman, J.A., Flocke, F.M., and Seinfeld, J.H. 2006. Concentrations and sources of organic carbon aerosols in the free troposphere over North America. J. Geophys. Res. 111, D23S47.

Hely, C., Dowdy, P.R., Alleaume, S., Caylor, K.K., Korontzi, S., Swap, R.J., Shugart, H.H., and Justice, C.O. 2003. Regional fuel load for two climatically contrasting years in southern Africa. J. Geophys. Res. 108, 8375.

Hobbs, P.V., Reid, J.S., Herring, J.A., Nance, J.D., Weiss, R.E., Ross, J.L., Hegg, D.A., Ottmar, R.D., and Liousse, C. 1996. Particle and trace–gas measurements in the smoke from prescribed burns of forest products in the Pacific Northwest. In: Levine, J.S., ed. Global biomass burning: Atmospheric, climatic and biospheric Implications. MIT Press, Cambridge, pp. 697–715.

Hurst, D.F., Griffith, D.W.T., Carras, J.N., Williams, D.J., and Fraser, P.J. 1994a. Measurements of trace gases emitted by Australian savanna fires during the 1990 dry season. J. Atmos. Chem. 18, 33–56.

Hurst, D.F., Griffith, D.W.T., and Cook, G.D. 1994b. Trace gas emissions from biomass burning in tropical Australian savannas. J. Geophys. Res. 99, 16441–16456.

Ito, A., and Penner, J.E. 2004. Global estimates of biomass burning emissions based on satellite imagery for the year 2000. J. Geophys. Res. 109, D14S05.

Ito, A., Sillman, S., and Penner, J.E. 2007. Effects of additional nonmethane volatile organic compounds, organic nitrates, and direct emissions of oxygenated organic species on global troposhperic chemistry. J. Geophys. Res. 112, D06309.

Jacob, D.J., Field, B.D., Li, Q., Blake, D.R., de Gouw, J., Warneke, C., Hansel, A., Wisthaler, A., Singh, H.B., and Guenther, A. 2005. Global budget of methanol: Constraints from atmospheric observations. J. Geophys. Res. 110, D08303.

Jourdain, L., Worden, H.M., Worden, J.R., Bowman, K., Li, Q., Eldering, A., Kulawik, S.S., Osterman, G., Boersma, K.F., Fisher, B., Rinsland, C.P., Beer, R., and Gunson, M. 2007. Tropospheric vertical distribution of tropical Atlantic ozone observed by TES during the northern Africa biomass burning season. Geophys. Res. Lett. 34, L04810.

Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., and Wilson, J. 2005. Organic aerosol and global climate modelling: A review. Atmos. Chem. Phys. 5, 1053–1123.

Kasischke, E.S., O'Neill, K.P., French, N.H.F., and Bourgeau–Chavez, L.L. 2000. Controls on patterns of biomass burning in Alaskan boreal forests. In: Kasischke, E.S., and Stocks, B.J., eds. Fire, climate change, and carbon cycling in the North American boreal forest. Springer–Verlag, New York, 173–196.

Kauffman, J.B., Steele, M.D., Cummings, D.L., and Jaramillo, V.J. 2003. Biomass dynamics associated with deforestation, fire, and conversion to cattle pasture in a Mexican tropical dry forest. For. Ecol. Manage. 176, 1–12.

Koch, D., Bond, T.C., Streets, D., Unger, N., and van der Werf, G.R. 2007. Global impacts of aerosols from particular source regions and sectors. J. Geophys. Res. 112, D02205.

Koppmann, R., Khedim, A., Rudolph, J., Helas, G., Welling, M., and Zenker, T. 1996. Airborne measurements of organic trace gases from savanna fires in southern Africa during SAFARI–92. In: Levine, J.S., ed. Global biomass burning: Atmospheric, climatic and biospheric implications. MIT Press, Cambridge, pp. 309–319.

Korontzi, S., Ward, D.E., Susott, R.A., Yokelson, R.J., Justice, C.O., Hobbs, P.V., Smithwick, E.A.H., and Hao, W.M. 2003. Seasonal variation and ecosystem dependence of emission factors for selected trace gases and PM2.5 for southern African savanna fires. J. Geophys. Res. 108, 4758.

Lacaux, J.-P., Delmas, R., Jambert, C., and Kuhlbusch, T.A.J. 1996. NOx emissions from African savanna fires. J. Geophys. Res. 101, 23585–23596.

Lapina, K., Honrath, R.E., Owen, R.C., Val Martín, M., and Pfister, G. 2006. Evidence of significant large–scale impacts of boreal fires on ozone levels in the midlatitude Northern Hemisphere free troposphere. Geophys. Res. Lett. 33, L10815.

Lee, S., Baumann, K., Schauer, J.J., Sheesley, R.J., Naeher, L.P., Meinardi, S., Blake, D.R., Edgerton, E.S., Russell, A.G., and Clements, M. 2005. Gaseous and particulate emissions from prescribed burning in Georgia. Environ. Sci. Technol. 39, 9049–9056.

Lobert, J.M., and Warnatz, J. 1993. Emissions from the combustion process in vegetation. In: Crutzen, P.J., and Goldammer, J.G., eds. Fire in the environment: The ecological, atmospheric, and climatic importance of vegetation fires. Wiley, New York, pp. 15–37.

Lobert, J.M., Scharffe, D.H., Hao, W.M., Kuhlbusch, T.A., Seuwen, R., Warneck, P., and Crutzen, P.J. 1991. Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds. In: Levine, J.S., ed. Global biomass burning: Atmospheric, climatic and biospheric implications. MIT Press, Cambridge, pp. 289–304.

Lohmann, U., and Feichter, J. 2005. Global indirect aerosol effects: A review. Atmos. Chem. Phys. 5, 715–737.

Mason, S.A., Trentmann, J., Winterrath, T., Yokelson, R.J., Christian, T.J., Carlson, L.J., Warner, T.R., Wolfe, L.C., and Andreae, M.O. 2005. Intercomparison of two box models of the chemical evolution in biomass–burning smoke plumes. J. Atmos. Chem. 55, 273–297.

Michel, C., Liousse, C., Gregoire, J.M., Tansey, K., Carmichael, G.R., and Woo, J.H. 2005. Biomass burning emission inventory from burnt area data given by the

SPOT–VEGETATION system in the frame of TRACE–P and ACE–Asia campaigns. J. Geophys. Res. 110, D09304.

Morris, G.A., Hersey, S., Thompson, A.M., Pawson, S., Nielson, J.E., Colarco, P.R., McMillan, W.W., Stohl, A., Turquety, S., Warner, J., Johnson, B.J., Kucsera, T.L., Larko, D.E., Oltmans, S.J., and Witte, J.C. 2006. Alaskan and Canadian forest fires exacerbate ozone pollution over Houston, Texas, on 19 and 20 July 2004. J. Geophys. Res. 111, D24S03.

Morvan, D., and Dupuy, J.L. 2001. Modeling of fire spread through a forest fuel bed using a multiphase formulation. Combust. Flame 127, 1981–1994.

Muhle, J., Lueker, T.J., Su, Y., Miller, B.R., Prather, K.A., and Weiss, R.F. 2007. Trace gas and particulate emissions from the 2003 southern California wildfires. J. Geophys. Res. 112, D03307.

Naik, V., Mauzerall, D.L., Horowitz, L.W., Schwarzkopf, M.D., Ramaswamy, V., and Oppenheimer, M. 2007. On the sensitivity of radiative forcing from biomass burning aerosols and ozone to emission location. Geophys. Res. Lett. 34, L03818.

Nance, J.D., Hobbs, P.V., Radke, L.F., and Ward, D.E. 1993. Airborne measurements of gases and particles from an Alaskan wildfire. J. Geophys. Res. 98, 14873–14882.

Ottmar, R.D. 2002. Smoke source characteristics. In: Hardy, C.C., Ottmar, R.D., Peterson, J.L., Core, J.C., and Seamon, P., eds. Smoke management guide for prescribed and wildland fire: 2001 edition. National Wildfire Coordination Group, National Interagency Fire Center, Boise, 89–106.

Ottmar, R.D., Peterson, J.L., Leenhouts, B., and Core, J.E., 2002. Smoke management techniques. In: Hardy, C.C., Ottmar, R.D., Peterson, J.L., Core, J.C., and Seamon, P., eds. Smoke management guide for prescribed and wildland fire: 2001 edition. National Wildfire Coordination Group, National Interagency Fire Center, Boise, 141–160.

Phuleria, H.C., Fine, P.M., Zhu, Y., and Sioutas, C. 2005. Air quality impacts of the October 2003 Southern California wildfires. J. Geophys. Res. 110, D07S20.

Price, O.F., Edwards, A.C., and Russell–Smith, J. 2007. Efficacy of permanent firebreaks and aerial prescribed burning in western Arnhem Land, Northern Territory, Australia. Int. J. Wildland Fire 16, 295–307.

Radke, L.F., Hegg, D.A., Hobbs, P.V., Nance, J.D., Lyons, J.H., Laursen, K.K., Weiss, R.E., Riggan, P.J., and Ward, D.E. 1991. Particulate and trace gas emissions from large biomass fires in North America. In: Levine, J.S., ed. Global biomass burning: Atmospheric, climatic and biospheric Implications. MIT Press, Cambridge, pp. 209–224.

Real, E., Law, K.S., Weinzierl, B., Fiebig, M., Petzold, A., Wild, O., Methven, J., Arnold, S., Stohl, A., Huntrieser, H., Roiger, A., Schlager, H., Stewart, D., Avery, M., Sachse, G., Browell, E., Ferrare, R., and Blake, D. 2007. J. Geophys. Res. 112, D10S41.

Reid, J.S., Hobbs, P.V., Ferek, R.J., Blake, D.R., Martins, J.V., Dunlap, M.R., and Liousse, C. 1998. Physical, chemical and optical properties of regional hazes dominated by smoke in Brazil. J. Geophys. Res. 103, 32059–32080.

Reid, J.S., Koppmann, R., Eck, T.F., and Eleuterio, D.P. 2005. A review of biomass burning emissions part II: Intensive physical properties of biomass burning particles. Atmos. Chem. Phys. 5, 799–825.

Reinhardt, E.D., Brown, J.K., Fischer, W.C., and Graham, R.T. 1991. Woody fuel and duff consumption by prescribed fire in northern Idaho mixed conifer logging slash. Research Paper INT–443. USDA Forest Service, Intermountain Research Station, Ogden, Utah.

Reinhardt, E.D., Keane, R.E., and Brown, J.K. 2001. Modeling fire effects. Int. J. Wildland Fire 10, 373–380.

Roberts, G., and Wooster, M.J. 2007. New perspectives on African biomass burning dynamics. EOS Transactions 88, 369–370.

Rothermal, R.C. 1972. A mathematical model for predicting fire spread in wildand fuels. Research Paper INT–115. USDA Forest Service, Intermountain Forest and Range Experiment Station, Ogden, Utah.

Rowell, R.M., and LeVan–Green, S.L. 2005. Thermal properties. In: Rowell, R.M., ed. Handbook of wood chemistry and wood composites. CRC Press, Boca Raton, FL, pp. 121–138.

Rudolph, J., Khedim, A., Koppmann, R., and Bonsang, B. 1995. Field study of the emissions of methyl chloride and other halocarbons from biomass burning in western Africa. J. Atmos. Chem. 22, 67–80.

Sanhueza, E., Figueroa, L., and Santana, M. 1996. Atmospheric formic and acetic acids in Venezuela. Atmos. Environ. 30, 1861–1873.

Sapakota, A., Symons, J.M., Kleissl, J., Wang, L., Parlange, M.B., Ondov, J., Breysse, P.N., Diette, G.B., Eggleston, P.A., and Buckley, T.J. 2005. Impact of the 2002 Canadian forest fires on particulate matter air quality in Baltimore City. Environ. Sci. Technol. 39, 24–32.

Seinfeld, J.H., and Pandis, S.N. 1998. Atmospheric chemistry and physics: from air pollution to climate change. Wiley, New York.

Simpson, I.J., Rowland, F.S., Meinardi, S., and Blake, D.R. 2006. Influence of biomass burning during recent fluctuations in the slow growth of global tropospheric methane. Geophys. Res. Lett. 33, L22808.

Sinha, P., Hobbs, P.V., Yokelson, R.J., Bertschi, I.T., Blake, D.R., Simpson, I.J., Gao, S., Kirchstetter, T.W., and Novakov, T. 2003. Emissions of trace gases and particles from savanna fires in southern Africa. J. Geophys. Res. 108, 8487.

Smith, M.A., Grant, C.D., Loneragan, W.A., and Koch, J.M. 2004. Fire management implications for fuel loads and vegetation structure in jarrah forest restoration on bauxite mines in Western Australia. For. Ecol. Manage. 187, 247–266.

Sudo, K., and Akimoto, K. 2007. Global source attribution of tropospheric ozone: Long–range transport from various source regions. J. Geophys. Res. 112, D12302.

Susott, R.A., Ward, D.E., Babbit, R.E., and Latham, D.J. 1991. The measurement of trace emissions and combustion characteristics for a mass fire. In: Levine, J.S., ed. Global biomass burning: Atmospheric, climatic and biospheric implications. MIT Press, Cambridge, pp. 245–257.

Susott, R.A., Olbu, G.J., Baker, S.P., Ward, D.E., Kauffmann, J.B., and Shea, R.W. 1996. Carbon, hydrogen, nitrogen, and thermogravimetric analysis of tropical ecosystem biomass. In: Levine, J.S., ed. Biomass burning and global change. MIT Press, Cambridge, Vol. 1, pp. 249–259.

Swap, R.J., Annegarn, H.J., Suttles, J.T., King, M.D., Platnick, S., Privette, J.L., and Scholes, R.J. 2003. Africa burning: A thematic analysis of the Southern African Regional Science Initiative (SAFARI 2000). J. Geophys. Res. 108, 8465.

Trentmann, J., Yokelson, R.J., Hobbs, P.V., Winterrath, T., Christian, T.J., Andreae, M.O., and Mason, S.A. 2005. An analysis of the chemical processes in the smoke plume from a savanna fire. J. Geophys. Res. 110, D12301.

Trentmann, J., Luderer, G., Winterrath, T., Fromm, M.D., Servranckx, R., Textor, C., Herzog, M., Graf, H.-F., and Andreae, M.O. 2006. Modeling of biomass smoke injection into the lower stratosphere by a large forest fire (part I): Reference simulation. Atmos. Chem. Phys. 6, 5247–5260.

Tsigaridis, K., and Kanakidou, M. 2003. Global modelling of secondary organic aerosol in the troposphere: A sensitivity analysis. Atmos. Chem. Phys. 3, 1849–1869.

van der Werf, G.R., Randerson, J.T., Giglio, L., Collatz, G.J., Kasibhatla, P.S., and Arellano, A.F. Jr. 2006. Interannual variability in global biomass burning emissions from 1997 to 2004. Atmos. Chem. Phys. 6, 3423–3441.

Wade, D.D., and Lunsford, J.D. 1989. A guide for prescribed fire in southern forests. Technical Report, R8–TP–11. USDA Forest Service, Southern Region, Atlanta, Georgia.

Ward, D.E., Hao, W.M., Susott, R.A., Babbitt, R.A., Shea, R.W., Kauffman, J.B., and Justice, C.O. 1996. Effect of fuel composition on combustion efficiency and emission factors for African savanna ecosystems. J. Geophys. Res. 101, 23569–23576.

Ward, D.E., and Radke, L.F. 1993. Emission measurements from vegetation fires: A comparative evaluation of methods and results. In: Crutzen, P.J., and Goldammer, J.G., eds. Fire in the environment: The ecological, atmospheric, and climatic importance of vegetation fires. Wiley, New York, pp. 53–76.

Ward, D.E., Susott, R.A., Kauffman, J.B., Babbitt, R.E., Cummings, D.L., Dias, B., Holben, B.N., Kaufman, Y.J., Rasmussen, R.A., and Setzer, A.W. 1992. Smoke and fire characteristics for cerrado and deforestation burns in Brazil: BASE–B experiment. J. Geophys. Res. 97, 14601–14619.

Wiedinmyer, C., Quayle, B., Geron, C., Belote, A., McKenzie, D., Zhang, X., O'Neill, S., and Wynne, K.K. 2006. Estimating emissions from fires in North America for air quality modeling. Atmos. Environ. 40, 3419–3432.

Yokelson, R.J., Bertschi, I.T., Christian, T.J., Hobbs, P.V., Ward, D.E., and Hao, W.M. 2003. Trace gas measurements in nascent, aged, and cloud–processed smoke from African savanna fires by airborne Fourier transform infrared spectroscopy (AFTIR). J. Geophys. Res. 108, 8478.

Yokelson, R.J., Goode, J.G., Ward, D.E., Susott, R.A., Babbitt, R.E., Wade, D.D., Bertschi, I., Griffith, D.W.T., and Hao, W.M. 1999. Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy. J. Geophys. Res. 104, 30109–30125.

Yokelson, R.J., Griffith, D.W.T., and Ward, D.E. 1996. Open–path Fourier transform infrared studies of large–scale laboratory biomass fires. J. Geophys. Res. 101, 21067–21080.

Yokelson, R.J., Karl, T., Artaxo, P., Blake, D.R., Christian, T.J., Griffith, D.W.T., Guenther, A., and Hao, W.M. 2007. The tropical forest and fire emissions experiment: Overview and airborne fire emission factor measurements. Atmos. Chem. Phys. 7, 5175–5196.

Yokelson, R.J., Susott, R., Ward, D.E., Reardon, J., and Griffith, D.W.T. 1997. Emissions from smoldering combustion of biomass measured by open–path Fourier transform infrared spectroscopy. J. Geophys. Res. 102, 18865–18877.

Appendix A. Emission factors for North America ecosystems

This appendix presents previously unpublished results from emission studies of prescribed fires in the southeastern, mid-western, and western United States, western Canada, and Alaska. The prescribed fire emissions data may be used to estimate emissions of several key primary pollutants from fires in a broad range of North American ecosystems for which prescribed fire is an essential land management tool. The prescribed fire studies indicate emission factors for many pollutants exhibit significant variability across vegetation types. These findings suggest modeling studies to assess the air quality impact of wildland fire at the local to regional scales may benefit from data that captures interecosystem variations in EFs. This may be particularly important for quantifying the incremental contribution of wildland fire emissions to air pollution in urban areas.

The coarsely grouped EFs in Table 4.1 will often be adequate for continental and global scales studies of atmospheric chemistry, biogeochemical cycling, and climate. However, the generalized nature of the data synthesis may not provide the differentiation among ecosystems that is necessary to accurately assess and predict the impact of wildand fire on air quality at the local to regional scale. The ecosystem specific emissions data presented in this section is representative of the information land management agencies and air quality managers may find necessary to successfully address the air quality issues presented by wildland fire.

A.1. Field sites and methods

Emission data was obtained for 56 prescribed fires in 9 states and 1 province (Table A1). The emission studies cover a wide range of ecosystems types, but may be aggregated as southeastern conifer forest (mostly pine, a few pine-hardwood mix), interior mountain west conifer forest (ponderosa pine and Douglas-fir), grassland (mostly wetland grasses) shrubland (southeastern), and boreal forest vegetation groups. The prescribed burns in southeastern and interior mountain west were low- to moderate-intensity understory burns. The two boreal forest fires sampled in Alaska were high-intensity burn-out fires employed as a fire suppression tactic during the intense Alaska fire season of 2004. The burn-out fires involved surface and canopy fuels. These high-intensity crown fires were representative of the fire activity during June and July of 2004 when 6 million acres were burned in Alaska.

The emission studies used the Fire Atmosphere Sampling System (FASS) (Hao et al., 1996). Briefly, the FASS instrument uses a 3–15 m tower to obtain in situ measurements of gases, particulate matter, vertical velocity, and air temperature. The FASS collects integrated $PM_{2.5}$ filter and gas canister samples for background air, primarily flaming combustion, the transition from flaming to smoldering combustion, and mostly smoldering combustion. The $PM_{2.5}$ filter samples are analyzed for total mass, organic and elemental carbon. The canister samples are analyzed for CO_2, CO, CH_4, and C2–C3 alkanes, alkenes, and alkynes. The FASS also provides continuous measurements of CO, CO_2, vertical velocity, and air temperature, which gives a unique, useful time-series of the fire from a point "within" the burn.

Two to six FASS instrument towers were deployed within the burn perimeter for each prescribed fire. The carbon mass balance method (Ward & Radke, 1993) was used for calculating EFs with an assumed fuel carbon content of 50%. The F_C value of 0.50 is consistent with in situ F_C measurements for a wide range of vegetation types and is likely accurate to within ±10% (Lobert et al., 1991; Susott et al., 1991, 1996). Particulate matter was assumed to be 60% carbon by weight. The simultaneous measurements of plume vertical velocity, flux of emissions, and carbon were used to determine the rate of fuel consumption, which provides the weighting factors applied to the integrated $PM_{2.5}$ filter and canister samples to obtain fire average EFs for each FASS tower. The mean of the EFs produced from each FASS tower deployed during the fire were averaged to obtain an EF value for the fire as a whole.

A.2. Results

Emission factors were measured for $PM_{2.5}$, CO_2, CO, CH_4, and C2–C3 hydrocarbons. MCE and EFs for each fire are given in Table A1. Following CO_2 and CO, $PM_{2.5}$ is the dominant species emitted from prescribed fires, consistent with previous findings for a wide range of ecosystems, fire types, and measurement techniques (see references from Table 4.1). Fire weighted average $EF_{PM2.5}$ exhibits significant variability within vegetation groups. The $EF_{PM2.5}$ for the grassland and shrub cover group is lowest ($10.2\,g\,kg^{-1}$) and differs significantly from the average values of the forest cover groups ($p < 0.001$ or better for Welch two sample t-test and Wilcoxon rank sum test). Emissions of C2 and C3 hydrocarbons equal 78–114% of CH_4 emissions. Alkene emissions exceed emissions of their respective alkanes for all individual fires, which appears to be a common characteristic of biomass burning (see Table 4.1 and related references). These light hydrocarbons (C2–C3) typically comprise about half of the total NMHC emissions from wildland fire (see Table 4.1).

The CH_4, C_2H_6, C_3H_6, and C_3H_8 emissions for the interior mountain west conifer forests are significantly higher than those for the southeastern conifer forests and the grassland/shrubland vegetation groups ($p < 0.05$ or better for Welch two sample t-test and Wilcoxon rank sum test). The lower MCE of the interior mountain west conifer fires suggests this difference may be a function of fire behavior. Emission factors for CH_4 and many hydrocarbons often exhibit a strong linear relationship with MCE (Sinha et al., 2003; Yokelson et al., 2003). The EFs for C_2H_2, C_2H_4, and C_3H_4 are not statistically different across the vegetation groups.

Table A1. Fire weighted average emission factors (g of compound emitted per kg of dry fuel consumed)

Fire ID	Vegetation type	Location[a]	MCE[b]	CO_2	CO	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_3H_4	$PM_{2.5}$
		Grasslands and shrublands of southeastern and mid-western United States											
EB1	Sandhill shrub	Eglin AFB, FL	0.921	1652	89.7	2.62	0.32	1.01	0.23	0.11	0.47	0.03	11.9
EB2	Palmetto, turkey oak	Eglin AFB, FL	0.938	1695	71.1	1.65	0.18	1.13	0.49	0.02	0.31	0.05	6.9
FL5	Palmetto	Okefenokee NWR, FL	0.933	1665	76.4	2.13	0.23	1.12	0.35	0.08	0.45	0.05	15.7
NC3	Pacosin	Camp Lejune, NC	0.943	1683	64.2	1.84	0.22	1.35	0.36	0.11	0.46	0.06	16.7
SC9	Pacosin	Savannah River Site, SC	0.935	1682	75.0	2.66	0.30	0.98	0.34	0.10	0.39	0.05	8.9
EP1	Sawgrass	Panther WR, FL	0.914	1635	98.3	4.12	0.59	1.60	0.49	0.23	0.79	0.08	9.1
EP2A	Sawgrass	Big Cypress NWP, FL	0.936	1689	73.5	2.27	0.25	1.61	0.63	0.09	0.40	0.06	5.9
EP2B	Muley grass	Big Cypress NWP, FL	0.961	1743	45.5	1.54	0.19	0.95	0.36	0.08	0.30	0.05	3.7
MI1	Sawgrass	Merrit Island NWR, FL	0.97	1752	34.7	0.90	0.07	0.52	0.21	0.02	0.10	0.02	9.9
MN1	Freshwater grass	Bluestern Prarie, MN	0.948	1716	59.7	1.50	0.21	1.16	0.39	0.05	0.37	0.07	5.3
MN2	Freshwater grass	Bluestern Prarie, MN	0.933	1652	75.6	2.68	0.44	2.07	0.60	0.14	1.03	0.10	18.8
MN3	Freshwater grass	Sherburne NWP, MN	0.95	1705	57.1	1.53	0.15	1.22	0.46	0.07	0.23		11.8
MN4	Freshwater grass	Camp Ripley, MN	0.962	1750	44.4	1.07	0.12	0.55	0.20	0.02	0.04		3.6
FS1	Wiregrass	Fort Stewart, GA	0.936	1681	73.5	2.16	0.21	1.42	0.64	0.06	0.42	0.07	9.7
ICI3	Wiregrass	Ichuway, GA	0.912	1626	99.5	3.34	0.44	1.15	0.25	0.20	0.64	0.05	15.3
		Mean	0.939	1688	69.2	2.13	0.26	1.19	0.40	0.09	0.43	0.06	10.2
		Standard deviation	0.017	40	18.9	0.86	0.14	0.40	0.15	0.06	0.35	0.02	4.8
		Conifer forests of southeastern United States											
FL1	Longleaf pine, palmetto	Osceola NF, FL	0.952	1712	55.3	1.41	0.18	1.34	0.74	0.01	0.37	0.09	10.0
FL2	Longleaf pine, palmetto	Osceola NF, FL	0.94	1690	68.5	1.26	0.14	0.94	0.40	0.01	0.35	0.00	11.3
FL4	Longleaf pine, palmetto	Osceola NF, FL	0.934	1681	75.2	1.45	0.13	0.97	0.45		0.37	0.04	11.1

Table A1. (*Continued*)

Fire ID	Vegetation type	Location[a]	MCE[b]	CO_2	CO	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_3H_4	$PM_{2.5}$
ICI1	Loblolly pine, wiregrass	Ichuway, GA	0.942	1687	66.5	1.78	0.26	1.27	0.42	0.10	0.45	0.05	13.2
ICI2	Loblolly pine, wiregrass	Ichuway, GA	0.928	1657	81.5	2.31	0.28	1.19	0.33	0.11	0.46	0.07	15.6
NC1	Mixed pine, wax myrtle	Camp Lejune, NC	0.904	1621	109.4	3.00	0.23	0.83	0.28	0.06	0.38	0.04	10.4
SC1	Oak, pine, grass	Piedmont WR, SC	0.921	1647	90.2	2.15	0.25	1.17	0.36	0.09	0.49	0.06	14.1
Conifer forests of southeastern United States (continued)													
SC12a	Oak, pine, grass	Piedmont WR, SC	0.942	1688	65.9	1.75	0.21	0.97	0.32	0.08	0.40	0.05	14.4
SC12b	Oak, pine, grass	Piedmont WR, SC	0.923	1651	87.5	2.26	0.28	1.01	0.28	0.10	0.46	0.05	14.5
SC3	Mixed pine, wiregrass	Camp Lejune, NC	0.936	1682	73.1	1.99	0.22	0.86	0.23	0.09	0.37	0.09	11.4
SC4	Loblolly pine	Savannah River Site, SC	0.936	1679	73.3	1.64	0.21	1.13	0.41	0.05	0.42	0.07	12.2
SC5	Longleaf pine	Savannah River Site, SC	0.941	1683	66.9	1.59	0.14	0.74	0.24	0.05	0.28	0.04	15.4
SC6	Loblolly pine	Savannah River Site, SC	0.932	1651	77.2	2.04	0.26	1.12	0.29	0.08	0.47	0.04	21.9
SC7	Mixed pine, hardwood	Sumter NF, SC	0.915	1630	96.4	2.89	0.37	1.13	0.24	0.14	0.59	0.05	16.2
SC8	Longleaf pine	Savannah River Site, SC	0.918	1653	94.0	3.39	0.39	0.95	0.30	0.11	0.50	0.05	11.5
		Mean	0.931	1667	78.7	2.06	0.24	1.04	0.35	0.08	0.42	0.05	13.5
		Standard Deviation	0.013	25	14.4	0.62	0.08	0.17	0.13	0.04	0.08	0.02	3.07
Interior west mountain conifer forests of United States and southwestern Canada													
AZ1	Ponderosa pine	Chimney Springs, AZ	0.941	1698	67.7	3.20							6.1
AZ2	Ponderosa pine	Limestone Flats, AZ	0.890	1605	126.7	4.86							21.4
AZ3	Ponderosa pine	Mormon Lake RD, AZ	0.924	1658	86.8	2.26	0.33	0.92	0.27	0.07	0.48	0.02	11.9
AZ4	Ponderosa pine	Limestone Flats, AZ	0.932	1668	77.9	2.29	0.31	0.99	0.28	0.12	0.49	0.08	13.4
AZ5	Ponderosa pine	Chimney Springs, AZ	0.910	1607	100.6	4.37	0.55	1.27	0.34	0.23	0.69	0.08	20.9
AZ6	Ponderosa pine	Peaks RD, AZ	0.924	1648	86.6	3.12	0.49	1.03	0.30	0.22	0.57	0.12	14.5

AZ7	Ponderosa pine	Chimney Springs, AZ	0.918	1640	93.1	3.53	0.55	1.07	0.32	0.22	0.60	0.11	13.0
AZ8	Ponderosa pine	Chimney Springs, AZ	0.926	1650	84.2	3.32	0.49	1.06	0.25	0.20	0.57	0.07	15.4
AZ9	Ponderosa pine	Peaks RD, AZ	0.919	1639	92.3	3.53	0.45	1.09	0.31	0.11	0.56		14.4
AZ10	Ponderosa pine	Limestone Flats, AZ	0.938	1678	70.1	2.49	0.34	0.87	0.26	0.07	0.41		14.8
AZ11	Ponderosa pine	Chimney Springs, AZ	0.948	1717	59.4	1.62	0.22	0.87	0.29		0.34		6.2
AZ12	Ponderosa pine	Chimney Springs, AZ	0.916	1622	94.2	3.22	0.43	1.19	0.34	0.14	0.56	0.03	20.8
BC1	Ponderosa pine	Clearwater, BC, Canada	0.894	1542	116.9	5.71	0.92	2.13	0.51	0.33	1.11	0.17	29.0
BC2	Ponderosa pine	Clearwater, BC, Canada	0.889	1568	125.1	6.47	1.19	1.62	0.30	0.55	1.27	0.10	16.0
Interior west mountain conifer forests of United States and southwestern Canada (continued)													
MT1	Ponderosa pine	Bitteroot NF, MT	0.914	1632	97.4	4.02	0.60	1.10	0.24	0.24	0.66	0.08	12.7
MT2	Ponderosa pine	Bitteroot NF, MT	0.904	1584	107.1	3.26	0.48	1.04	0.24	0.22	0.58	0.06	15.3
MT3	Ponderosa pine	Bitteroot NF, MT	0.918	1640	92.9	4.38	0.64	1.19	0.20	0.16	0.45	0.05	11.7
MT4	Ponderosa pine	Bitteroot NF, MT	0.910	1610	101.4	4.44	0.63	1.23	0.31	0.12	0.44	0.05	19.5
OR1	Ponderosa pine Douglas-fir, white fir	Hepner RD, OR	0.906	1601	106.0	3.85	0.57	1.33	0.41	0.24	0.70	0.14	20.3
OR2	Ponderosa pine Douglasfir, white fir	Hepner RD, OR	0.900	1603	113.6	5.23	0.63	1.16	0.33	0.23	0.67	0.08	14.5
OR3	Ponderosa pine Douglasfir, white fir	Hepner RD, OR	0.916	1609	93.7	4.01	0.61	1.35	0.45	0.22	0.69	0.12	15.7
		Mean	0.916	1629	94.9	3.77	0.55	1.19	0.31	0.21	0.62	0.07	15.6
		Standard deviation	0.016	42	17.7	1.18	0.22	0.29	0.08	0.11	0.23	0.04	5.2
Boreal forest of southeastern Alaska													
AK1	Black spruce	Chicken, AK	0.91	1616	105.0	4.39	1.12	1.74	0.26	0.34	1.04	0.03	7.23
AK2	Black spruce	Tetlin Junction, AK	0.92	1671	86.0	9.43	2.00	3.61	0.66	0.58	2.05	0.10	2.97
Pine-oak forests of mid-western United States													
MN4	Oak savanna	Camp Ripley, MN	0.953	1716.6	54.0	1.50	0.20	0.89	0.23	0.03	0.37	0.02	10.1
MN5	Oak	Chippewa NF, MN	0.936	1684.3	72.8	2.28	0.31	0.93	0.22	0.09	0.43	0.04	10.0
MN6	Redpine	Chippewa NF, MN	0.942	1692.9	65.9	2.07	0.26	0.87	0.23	0.08	0.41	0.04	11.5

---

[a] AFB, air force base; NWR, National Wildlife Refuge; NWP, national wildlife preserve; NF, national forest; WR, wildlife refuge; RD, ranger district.

[b] MCE (modified combustion efficiency) = $\Delta CO_2/(\Delta CO+\Delta CO_2)$.

AUTHOR QUERY FORM

ELSEVIER	**Book: DENS-V008** **Chapter: 4**	**Please eail or fax your responses and any corrections to:** **Eail:** **Fax:**

Dear Author,

During the preparation of your manuscript for typesetting, some questions may have arisen. These are listed below. Please check your typeset proof carefully and mark any corrections in the margin of the proof or compile them as a separate list*.

Disk use
Sometimes we are unable to process the electronic file of your article and/or artwork. If this is the case, we have proceeded by:

☐ Scanning (parts of) your article ☐ Rekeying (parts of) your article
☐ Scanning the artwork

Bibliography
If discrepancies were noted between the literature list and the text references, the following may apply:

☐ The references listed below were noted in the text but appear to be missing from your literature list. Please complete the list or remove the references from the text.
☐ *Uncited references:* This section comprises references that occur in the reference list but not in the body of the text. Please position each reference in the text or delete it. Any reference not dealt with will be retained inthis section

Queries and/or remarks

Location in Article	Query / remark	Response
AU:1	Please provide complete bibliographic details for the references Hardy et al. (1996), Ward and Hardy (1989), Yokelsin et al. (2003)	
AU:2	Please confirm the name of the corresponding author for Chapter 4 as two author names ‘Shawn P. Urbanski’ and ‘Wei Min Hao’ have been given in the ’Corresponding author list’ .	
AU:3	The spelling of the author ’Lohman’ has been changed to ’Lohmann’ based on the reference list. Please check.	

AU:4	The reference Lobert et al. (1993) has been changed to Lobert and Warnatz (1993) based on the reference list. Please check.	
AU:5	The spelling of the author ’Lundsford’ has been changed to ’Lunsford’ based on the reference list. Please check.	
AU:6	The spelling of the author ’Kaufman’ has been changed to ’Kauffman’ based on the reference list. Please check.	
AU:7	The spelling of the author ’van def Werf’ has been changed to ’van der Werf’ based on the reference list. Please check.	
AU:8	The reference Albini et al. (1995) has been changed to Albini and Reinhardt (1995) based on the reference list. Please check.	
AU:9	Rothermel (1972) is not in the reference list, please provide complete bibliographic detail of the same or delete its citation from the text.",4,0,4?>	