CHAPTER 3

Combustion Chemistry and Smoke

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I. INTRODUCTION

Fires burning in vegetative fuels, whether prescribed or wildfires, emit a complex mixture of particles and gases into the atmosphere. The diversity in composition of combustion products results from wide ranges in fuel types, fuel chemistry, and fire behavior. This chapter discusses the state of knowledge concerning the effect of these variables on the characteristics of smoke. In addition, the chemical and physical characteristics of the vegetation affect the rate of combustion and influence the overall fire behavior.

The need to bring fire back into ecosystems that, historically, have been dependent on fire has created a great deal of concern over the smoke released and the effect of the smoke on air quality values in both urban and nonurban settings. This has resulted in a need to develop methods for estimating the rate of release of smoke and for methods of burning to minimize smoke production consistent with achieving goals of the managers. Air Quality Regulations have been the main drivers for improving guidelines needed for reducing smoke emissions and managing the dispersion of smoke in the atmosphere. Many of the principles discussed in detail in this chapter have direct application in reducing smoke from wildland fires or understanding the toxicity of the smoke to humans.

Relatively little biomass is burned in the United States in comparison to the rest of the world. The total biomass consumed globally is currently estimated to be on the order of 5–8 Pg (1 Pg equals 10^{15} g) per year (Crutzen and Andreae, 1990). In comparison, 1988 was one of the most extreme "fire years" in recent history in the United States with almost 2 million ha of land burned by wildfires, including the large fires of Yellowstone National Park. If we consider the average fuel consumption per ha to be 45 t (1 metric tonne is 10^6 g), the total fuel consumed by wildfires in the United States in 1988 would have been ~90 Tg (1 Tg is 10^{12} g). In addition, Ward *et al.* (1993) estimated that prescribed fires for 1989 consumed about 40 Tg of fuel in the United States. The total of ~130 Tg of fuel consumed per year is ~2% of the total burned globally. It is interesting that more than 80% of all biomass burning takes place in tropical countries (Hao and Liu, 1994).

The discussion in this chapter will focus on the chemistry of natural ecosystem fuels important from an emissions production standpoint; then combustion processes will be discussed; and finally a general discussion of the chemistry of smoke from fires in natural vegetation fuels will be presented. Process level mechanistic approaches have not been as useful for explaining the range and mix of emissions resulting from the burning of biomass in the open environment as has proven beneficial for studying the mix of emissions from the combustion of hydrocarbon and coal (Glassman, 1977). For wildland fires, the chemistry of fuels is very complex, the distribution of fuel elements is random but highly variable, and weather influences are nonlinear and exceptionally difficult to quantify with moisture gradients occurring throughout the fuel complex. Outstanding use has been made of controlled environment combustion laboratory experiments to simulate field conditions (Yokelson *et al.*, 1996). Correlation and linear regression modeling techniques have been used almost exclusively in establishing the influence of independent variables on smoke production. Generally, approaches used in studying smoke emissions can be broken into four levels of investigation based on scale and control of variables. These are:

1. Highly controlled microcombustion or pyrolysis devices (Ward, 1979; Clements and McMahon, 1980; Susott, 1980),
2. Laboratory experiments (Lobert *et al.*, 1991; Reinhardt and Ward, 1995; Yokelson *et al.*, 1997),

3. Field-based tower experiments, generally used for studying smoke emissions from small plots (Ward and Hardy, 1991; Ward *et al.*, 1992; Hoffa *et al.*, 1999), and
4. Airborne studies of full-scale fires burning under ambient atmospheric conditions (Radke *et al.*, 1991; Nance *et al.*, 1993; Reid *et al.*, 1998; Yokelson *et al.*, 1999).

The characterizations of fuels and resulting emissions discussed in the following sections draws heavily from all four scales of research.

II. FUEL CHEMISTRY AND COMBUSTION

A. FUEL

Plant material consists of polymeric organic compounds, generally described by the chemical formula $C_6H_9O_4$ (Byram, 1959), although we know that this generalized chemical formula varies depending on whether we are interested in the carbon content of grass or wood or material that is undergoing decay. Regardless, plant tissue is approximately 50% carbon, 44% oxygen, and 5% hydrogen by weight. The content of most wood varies between 41% and 53% cellulose, between 15% and 25% hemicellulose, and between 16% and 33% lignin (Browning, 1963). The lignin content of wood is much higher (up to 65%) in decaying (punky) wood, in which the cell wall polysaccharides are partially removed by biological degradation.

Dead plant material accumulates on the forest floor or in lakes and bogs. This material is rich in nutrients and is transformed by microorganisms into humus in which individual plant parts are no longer identifiable. In the process, sulfur and nitrogen accumulate in the organic matter because many of the microorganisms require these elements for growth and reproduction. In addition, tree needles and leaves generally have a higher composition of nitrogen and sulfur than woody stems and limbs. Allen (1974) reported sulfur content values between 0.08% and 0.5% for plant material and 0.03% and 0.4% for organic soils. Nitrogen is one of the most dominant of the macronutrients and is of primary concern because of the large number of nitrogen-based compounds produced when biomass is burned. Nitrogen makes up as much as 0.2% of the older wood of some species, 1% of needles of some pines, and up to 2.7% of fallen hardwood leaves (Clements and McMahon, 1980). We will discuss the nitrogenous products of combustion in Section III.C under the topic of emissions of trace gases (Ward *et al.*, 1996).

B. COMBUSTION CHEMISTRY

The generalized representation of biomass (or fuel) does not explain the diversity of compounds produced in smoke as a result of burning the material. Combustion efficiency is a term used to describe the overall conversion of carbon to carbon dioxide (Ward and Hardy, 1991). Byram (1959) illustrated the case for complete combustion of plant fuel with the following chemically balanced oxidation reaction:

$$\begin{aligned}&4C_6H_9O_4 + 25O_2 + [0.322MH_2O + 94.0N_2]\\ &\quad\rightarrow 18H_2O + 24CO_2 + [0.322MH_2O + 94.0N_2] + 11.6 \times 10^9\,\mathrm{J}\end{aligned} \tag{1}$$

Moisture in the fuel and water and nitrogen in the air are shown as bracketed quantities because they do not take part in the combustion reaction. It should be noted that the combustion of plant material releases the moisture contained with the fuel shown in brackets for this case and the water of combustion which is 18 kg moles of water for each 4 kg moles of plant material [(18*18 g)/(4 * 145) = 0.559]. For each kg of plant material (dry weight basis), 0.559 kg of water is released. Therefore, if one considers the moisture content of the fuel, it is readily seen that the rate of release of water is equal to the water of combustion plus the contained moisture (0.559 + 0.01 M). It should further be recognized from Eq. (1) that 4 kg moles of plant material release 11.6×10^9 J of heat energy. If we divide this heat release by the molecular weight and number of kg-mol of fuel, the high heat of combustion can be derived as 20,000 kJ/kg. The high heat of combustion is defined as the heat released from a unit mass of fuel without accounting for the heat required to vaporize the moisture of combustion or moisture content of the fuel (see Byram (1959) for a more complete treatment).

The combustion of plant material from open fires is seldom if ever 100% efficient; hence, products of incomplete combustion are produced that are of a major concern from an air pollution standpoint. Carbon monoxide is the major carbonaceous product of incomplete combustion, whereas carbon dioxide and water are the major products of complete combustion. Carbon dioxide contains as much as 95% of the carbon released in smoke from biomass fires where the combustion efficiency is high (e.g., grassland fires). On the other hand, the sum of carbon in other compounds of incomplete combustion makes up less than 5% (Figure 1). For fires of lower combustion efficiency, the percentage of carbon released as carbon dioxide would be lower and the products of incomplete combustion higher than shown in Figure 1. Minor constituents such as nitrogen, phosphorus, and sulfur affect the mix of pollutants generated by burning plant material. Other factors are important as well and contribute to the diversity of combustion products. For example, most plant material contains classes of compounds known as extractables, consisting of aliphatic and aromatic hydro-

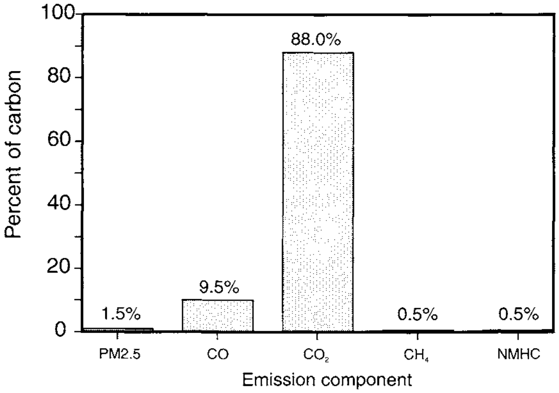

FIGURE 1 The average distribution of carbon between the primary products of combustion for broadcast burns of logging slash in the Pacific Northwest in the United States.

carbons, alcohols, aldehydes, gums, and sugars. These extractables, as a group, have a higher heat value than cellulose, lignin, and hemicellulosic substances. Other extractables from forest fuels contain a complex mixture of terpenes, fats, waxes, and oils. Not all of the extractable substances have low boiling points. For example, some of the extractives were shown by Shafizadeh *et al.* (1977) to evaporate or pyrolyze only at temperatures above 300°C.

C. PYROLYSIS

Pyrolysis is defined as the chemical breakdown of solid fuel under the influence of heat and usually in an oxygen-deficient environment. The pyrolytic decomposition of cellulose is generally believed to follow one of two paths dependent on whether the pyrolysis is occurring under high-temperature or low-temperature conditions. Usually under low-temperature conditions (200–280°C), the cellulose undergoes dehydration with the evolution of char, H_2O, CO_2, CO, and other compounds. Under higher temperature conditions (280–340°C), the pyrolysis proceeds in the production of levoglucosan, a volatile fuel that supports a gas-phase flame (Kilzer and Broido, 1965).

Thermal gravimetric analysis methods have been used by Susott (1980) and Susott *et al.* (1979) to evaluate the evolution of pyrolysis gases from solid fuels as a function of temperature during heating. The evolution of pyrolysis gas using this technique exhibits a spectrum reflecting the thermal stability of the fuel components as shown in Figures 2 and 3. Each component released can have a

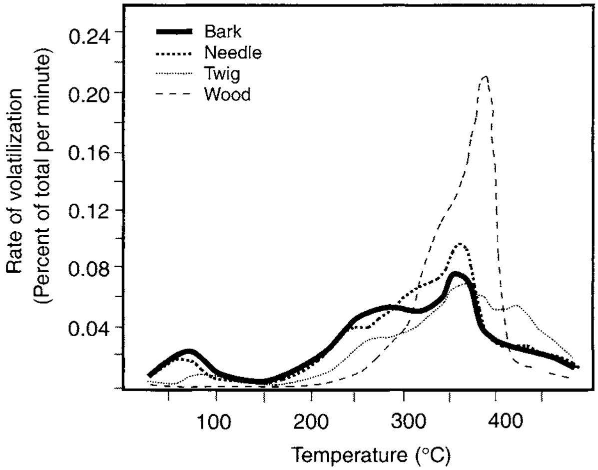

FIGURE 2 Different classes of forest fuels tend to volatilize at different rates as a function of temperature. The rates of volatilization were determined using thermal gravimetric measurement techniques.

different molecular weight and chemical form which can have significant implications regarding the formation of emissions. These materials pass through the flame structure or are released directly into the atmosphere. Oxidation may or may not occur at the solid fuel interface. For woody biomass, most researchers have studied the decomposition of cellulose and hemicellulose. Little is known about the thermal decomposition of bark, of which suberin—a polymer of long-chain hydroxy fatty acids esterified to phenolic acids—is one substance. The degradation products in the 425°C peak form a sizable fraction, but the chemical content may be different than for the woody carbohydrate products (Figure 2).

D. PHASES OF COMBUSTION

Preheating, flaming, smoldering, and glowing combustion compete for available fuel (Figure 3) and are markedly different phenomena that contribute to the diversity of combustion products. The fuel characteristics (including arrangement, distribution by size class, moisture, and chemistry) dominate in affecting the duration of flaming and smoldering combustion phases and combustion efficiency. Open combustion occurs through a diffusion flame process in which the fuel from the interior of the flame (oxygen-deficient area) diffuses outward, and the oxygen from the free-air diffuses inward. This results in a narrow envelope

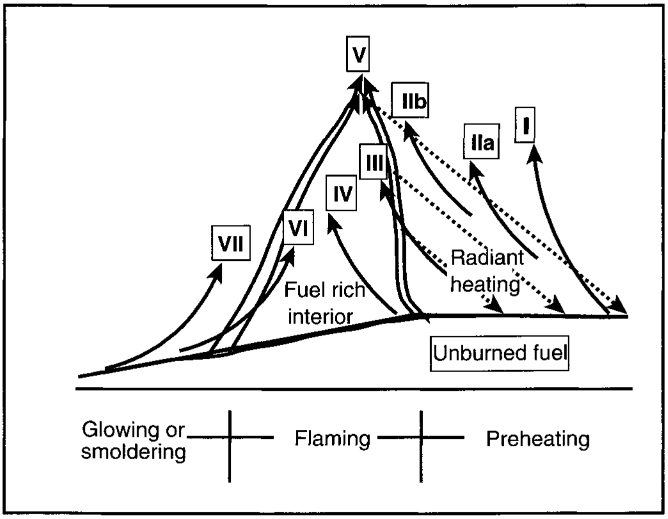

FIGURE 3 Diffusion flame model of pyrolysis and vaporization of volatiles during the preheating, flaming, glowing, and smoldering phases of combustion. The more highly volatile oleoresins are evaporated from the surface fuels in advance of the flame front for an advancing fire moving from left to right. The diagram above is a cross-section through a line of fire with the line of fire extending through the paper. There are several features describing the thermal environment and the effect of changing heat load on the early evaporation and later pyrolysis of fuel:

I. Evaporation of the highly volatile compounds. No condensation or polymerization is expected for the compounds released that are not in close proximity to the flame envelope.
IIa. Evaporation of the highly volatile compounds increases in this zone and the potential for polymers to form increases as bond rupturing takes place for the terpenes.
IIb. Abundant evaporation of oleoresins occurs with partial oxidation due to the intense thermal environment and extreme bond rupturing resulting from the high-intensity radiant energy source.
III. Introduction of evaporated oleoresins into a high-temperature oxygen-deficient environment with considerable oxidation occurring as molecules diffuse through the flame envelope. Those not undergoing complete oxidation may be fragmented into ethylene units and/or free radicals.
IV. Very high-temperature environment with oxygen depletion occurring as the carbon fragments reach the tip of the flame envelope. The amount of compound oxidation is dependent on the depth of the flame envelope and the amount of ventilation (turbulence). As the flames become taller, the heat feedback to the solid fuels becomes less, and the radiant energy loss becomes greater. The result is that particle formation/polymerization reactions may be increased because of the loss of heat within the fuel-rich zone.
V. Recombination takes place with the formation of compounds not found during the evaporation phase or inside the flame envelope due to pyrolysis. Aromatic hydrocarbon molecules are synthesized during this phase of transport.
VI. Products of pyrolysis and glowing combustion are transported across the flame surface.
VII. Transport of products of pyrolysis and glowing combustion completely miss the flame envelope and enter the atmosphere with no additional oxidation.

around the fuel-rich zone where the oxygen and fuel are mixed in stoichiometric proportions to produce rapid oxidation chemical reactions which result in the visible emission of light called a flame. The chemical reactions also cause the rapid liberation of heat which feeds back to the interior of the flame envelope and ahead of the flame envelope (Figure 3). This causes further vaporization of fuels with low vapor pressures and pyrolysis of solid fuels.

Initial heating of unburned fuel releases the more volatile components by distillation which then leads to pyrolysis and fragmentation of polymers and the release of oxygenated organic compounds (Yokelson *et al.*, 1996). Flaming is initiated when the fuel-to-oxygen mixture reaches flammable proportions and there is a source of ignition. Flaming and smoldering combustion are reasonably distinct combustion processes that involve different chemical reactions and are quite different in appearance (see also Chapters 2 and 13 in this book). Flaming combustion dominates during the startup phase, with the fine fuels and surface materials supplying the volatile fuel required for the rapid oxidation reactions to be sustained in a flaming environment. The heat from the flame structure and the diffusion and turbulent mixing of oxygen at the surface of the solid fuel promote generation of the heat required to sustain the pyrolysis processes. Early in the flaming phase, the more volatile hydrocarbons are vaporized from the fuels. Later the cellulosic and lignin-containing cellular materials decompose through pyrolysis. These processes produce the fuel gases that sustain the visible flame structure (Figure 4).

Once carbon and ash begin to build up on the solid fuel surfaces, the pyrolytic reactions no longer produce sufficient fuel gases to maintain the flame envelope. For combustion to continue, oxygen must diffuse to the surface of the fuel. Diffusion of oxygen and the availability of oxygen at the fuel surface are enhanced through turbulence in the combustion zone and through premixing by oxygen transport at ground level. This allows oxidation to take place at the solid fuel surface and provides for heat evolution and heat feedback to accelerate the pyrolytic reactions and volatilization of the fuel gases from the solid fuel. The process ultimately leads to the production of charcoal for which the only combustion occurring is of the glowing type—a surface reaction of oxygen with carbon.

III. SMOKE PRODUCTION

The smoldering combustion phase produces large amounts of particulate matter and carbon monoxide. Fires of very low intensity (those in which the flaming combustion phase is barely sustained) produce proportionately higher amounts of particulate matter. Heading fires generally are associated with conditions that produce two to three times as many particles (by weight) as backing fires. The

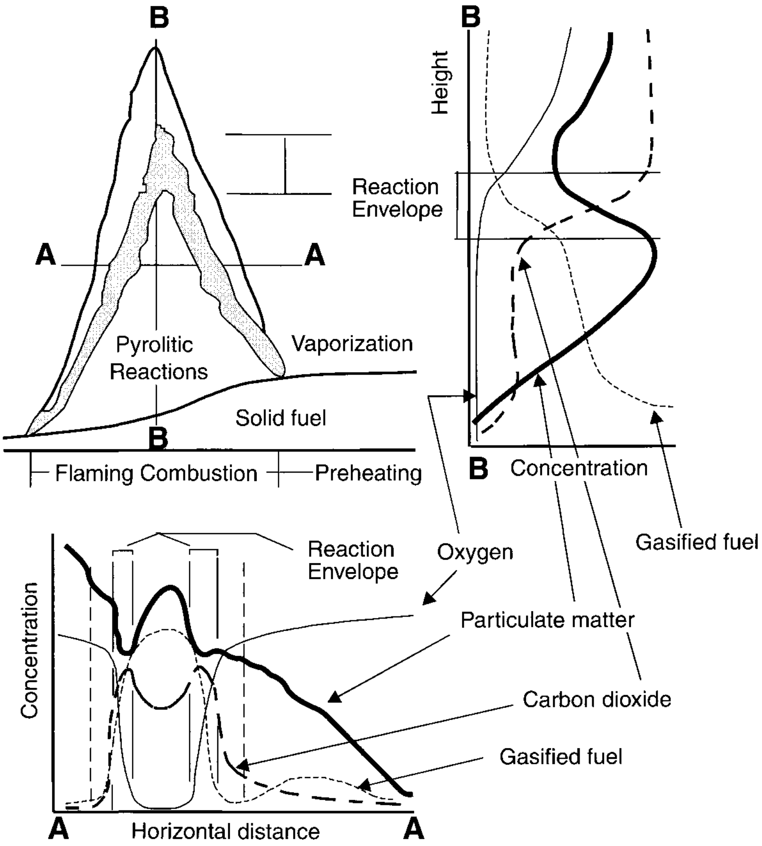

FIGURE 4 Relative concentrations of basic combustion gases with horizontal distance, A–A, and height, B–B, cross-sectioning a typical diffusion flame resulting from the oxidation of pyrolyzed forest fuels.

formation of particles results primarily from two processes: (1) the agglomeration of condensed hydrocarbon and tar materials and (2) mechanical processes which entrain fragments of vegetation and ash.

A. RELEASE OF CARBON

When vegetation is burned, carbon is released in the form of carbon dioxide, carbon monoxide, hydrocarbons, particulate matter, and other substances in decreasing abundance (Figure 1). A carbon mass-balance procedure is often employed by researchers in developing emission factors for different fuel conditions (Ward and Hardy, 1984). An emission factor is defined as the mass of a specific combustion product released per unit dry mass of fuel consumed and usually is expressed in pounds per ton or grams per kilogram. Emission factors are highly variable, but generally a large part of the variance can be explained through using a measurement of combustion efficiency for the independent variable. The combustion efficiency is a measure of the overall oxidation capacity for the combustion of fuel under a given set of weather and fuel conditions. It is a ratio of the mass of carbon released in the form of carbon dioxide to the mass of carbon in the original fuel and ranges from 0.98 for flaming combustion of fully cured grass vegetation with virtually no smoldering combustion to 0.75 for 100% smoldering combustion of deep duff. To simplify the calculation of combustion efficiency, Ward *et al.* (1996) adopted the use of modified combustion efficiency (MCE), or the ratio of the carbon released as carbon dioxide to the sum of the carbon released in the form of carbon dioxide and carbon monoxide. MCE is illustrated in Figure 5 for a number of different fuel types and is often used to predict emission factors for different compounds and particulate matter (Ward and Hardy, 1991; Ward *et al.*, 1996). For example, Ward *et al.* (1996) showed that MCE can be predicted for savanna fuels by using the

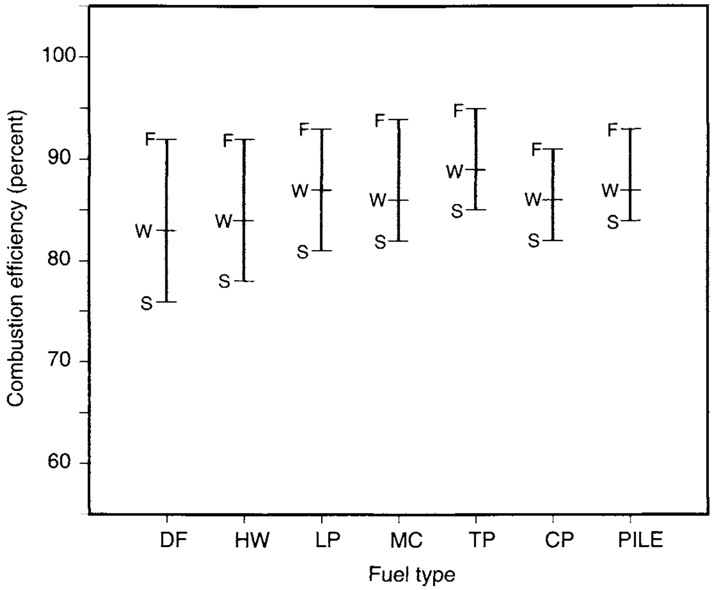

FIGURE 5 Range in combustion efficiency (the ratio of carbon released as CO_2 to the sum of carbon released as CO_2 and CO) for fires burning in seven different fuel types as follows: DF, Douglas Fir; HW, Hardwood; LP, ponderosa pine and lodgepole pine (long-needled conifers); MC, Mixed Conifer; TP, Tractor Piles; CP, Crane Piles; PILE, Combined TP and CP.

ratio of the mass of standing grass to the total mass of standing grass and litter using:

$$\text{MCE} = 0.85 + 0.111\ \text{Grass}/(\text{Litter} + \text{Grass})^{0.34} \qquad R^2 = 0.68 \qquad (2)$$

The model was developed for African savanna conditions of completely cured grass (no green grass). When the grass is lying flat (i.e., grass = 0) the predicted MCE is 0.85. When the grass is standing and there is no litter, the MCE is predicted to be 0.96. A summary of algorithms for predicting emission factors for several vegetation types, including the African savanna ecosystem, will be provided.

B. FORMATION OF PARTICLES

Wildland fires are a complex form of the diffusion flame process where pyrolysis of solid fuels produce vapors that interdiffuse with oxygen from the atmosphere. Turbulent mixing of fuel and oxygen is important, and as the turbulence increases, the flame characteristics and the chemical processes occurring in the flame zone change. Although this has never been completely substantiated, it is believed that there is a level of fire intensity where MCE reaches its highest level (perhaps 0.96 to 0.98 for many fuel types) (Ward, 1983) and particulate matter production is lowest (Nelson and Ward, 1980). For very high-intensity fires, some of the pyrolyzed fuel may no longer pass through an active oxidation zone. At times, even in lower intensity fires, pockets of unburned, partially oxidized gaseous fuels escape the combustion zone or undergo delayed ignition. The influence of flame turbulence on combustion efficiency is not fully understood; however, as the intensity of the fire increases and the zone of complete mixing of gaseous fuel and oxygen moves farther from the solid fuel, combustion efficiency is believed to decrease and the production of pollutants to increase. Because of the increased depth and height of the flame zone, heading fires and area fires create an extended reducing environment in which continued pyrolysis and synthesis of hydrocarbon gases and fragmented particles can occur under conditions of reduced oxygen content. In addition, heat reradiated from the particles to the atmosphere can slow down the reactions as the unburned gases and particles are convected away from the active combustion zone. Combustion of the particles requires prolonged exposure at high temperatures (>800°C) in a zone with near ambient concentrations of oxygen (Glassman, 1977). Greater premixing seems to reduce the production of fine particles ($< 2.5\ \mu\text{m}$ diameter).

Fuel chemistry plays an important role in the formation and release of particles to the atmosphere. For example, it is well known that fuels high in oleoresins smoke profusely when burned. The pitch has a high terpene content; the terpenes are similar to aromatic compounds in structure (five carbon atom building blocks instead of six carbon atoms such as occurs in benzene and some other highly aromatic compounds). These highly volatile compounds have a low oxygen content and during pyrolysis produce ethylene units which tend to polymerize and form long-chain compounds which, in turn, condense into tar-like substances that coat most particles from fires. Ward (1979) found that emission factors for particulate matter are inversely related to the oxygen content of the fuel molecules and suggested that cellulose and hemicellulose may produce less particulate matter when burned (due to their high oxygen content) than the very low oxygen content oleoresins.

Smoke particles have been measured using sophisticated instruments ranging from Differential Mobility Particle Sizer (DMPS) to methods for sizing particles based on their aerodynamic properties. These instruments have been used onboard aircraft to cover the broad range of particle sizes from 0.01 to over 43 μm (Radke *et al.*, 1991; Reid and Hobbs, 1998). The results suggest a very pronounced number concentration peak at a diameter of 0.15 μm. The volume distribution, when one assumes a unit mass density for smoke particles, represents the mass distribution and exhibits a bimodal distribution with peaks at about 0.3 μm and greater than 43 μm (Figure 6).

Emission factors have been measured for a number of different combinations of forest fuel and weather influences (Lobert *et al.*, 1991; Ward and Hardy, 1991; Nance *et al.*, 1993; Andreae *et al.*, 1996; Ward *et al.*, 1996; Ferek *et al.*, 1998;

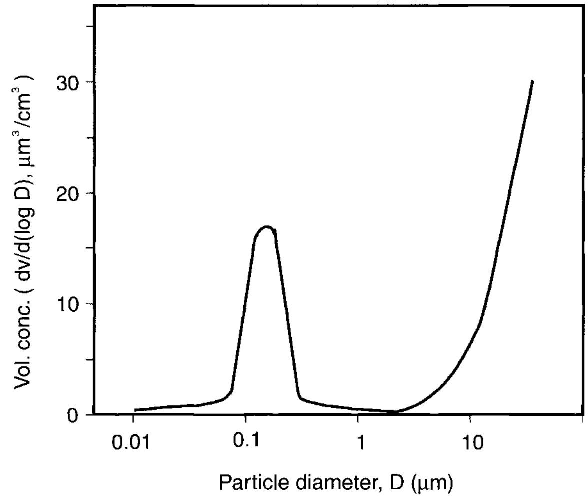

FIGURE 6 Bimodal distribution of particles on a volume basis. The percentage of particles larger than 10 μm typically increases for the flaming phase of combustion due to the turbulence generated in the combustion zone and the lofting of ash and partially burned biomass fragments.

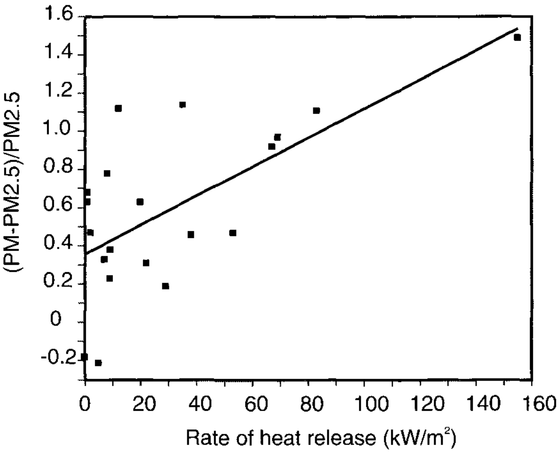

FIGURE 7 Higher intensity fires entrain additional large particles relative to fine particles.

Hoffa *et al.*, 1999; Yokelson *et al.*, 1999). Empirical data suggest that emission factors for particulate matter range from 4 to more than 40 g/kg for particles less than 10 μm in diameter (EFPM10); for particles without regard to size (EFPM), the range may be 20% larger, and emission factors for particles less than 2.5 μm diameter (EFPM2.5) are typically 10% smaller than EFPM10. However, the difference between EFPM and EFPM2.5 is highly dependent on fire intensity as illustrated by Figure 7. For savanna grassland ecosystems, Ward *et al.* (1996) found that EFPM2.5 can be predicted from the following equation:

$$\text{EFPM2.5} = 87.65 - 88.51\ \text{MCE} \qquad R^2 = 0.56 \tag{3}$$

The content of particulate matter varies between flaming and smoldering combustion. Between 1 and 10% of a particle's mass may consist of trace elements of potassium, chlorine, sulfur, phosphorus, and sodium. On a percentage basis, the mass of trace elements contained in particles from smoldering combustion is 10–20% of that from the flaming phase. Figure 8 for logging slash fires in the Pacific Northwest illustrates this dramatic difference between flaming and smoldering combustion (Ward and Hardy, 1989).

Emissions of graphitic and organic carbon are especially important because of the increased absorption of light by smoke particles that are high in graphitic carbon content. Absorption of light is due primarily to the black carbon content of the particles (Patterson *et al.*, 1986). For logging slash fires of the Pacific Northwest, emission factors for graphitic carbon ranged from 0.46 to 1.18 g/kg of fuel consumed. For fuel beds burned under laboratory conditions, the emission factors ranged to 5.4 g/kg of fuel consumed. Though graphitic or black carbon is produced proportional to the intensity of the fire, it is generally true

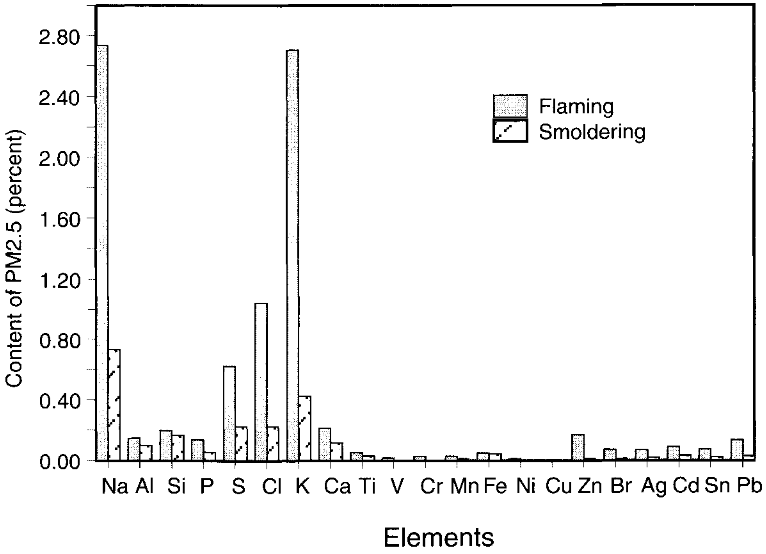

FIGURE 8 Difference in percent composition of particles for flaming and smoldering combustion reflecting the difference in ash content of the fine particles.

that emission factors for PM2.5 are inversely proportional to higher intensity burns. The organic fraction of the particles smaller than 2.5 μm is as much as 50–70% of the mass of the particulate matter for the smoldering phase, but can be lower for the flaming phase emissions.

Reid *et al.* (1998) conducted a very intensive study of "young" smoke (less than 2 hours old) in comparison to "aged" smoke (from 2 to 4 days old) from biomass fires in the very humid Brazilian Amazon region. Among other findings, they hypothesized that hydrocarbons of fewer than 11 carbon atoms were depleted over time and converted to CO_2, CO, and reactive molecular species and likely removed through dry deposition and/or by conversion to particulate matter. Although somewhat contradictory, the argument concludes that individual particle mass increased over time, and it was estimated that 20–45% of the mass concentration of the particles was due to the condensation of organics. It is interesting to note that most of the active "new" fires are lit between 1:00 and 3:00 P.M. local time and active flaming is nearly complete in 3 to 4 hours with smoldering combustion then dominating. Smoldering combustion continues for several hours to several days (Ward *et al.*, 1992). The organic content of particles produced during smoldering combustion of biomass is approximately 20% higher than the organic content of particles produced during the flaming combustion phase (Ward and Hardy, 1988) (likely dominating the emissions for the "young" fire plumes of Reid *et al.*, 1998). There are still many issues to be resolved before it can be conclusively demonstrated that condensation of hydrocarbons occurs at a higher rate than volatilization in contributing to the mass of particulate matter once the smoke is more than a few minutes old.

C. EMISSION OF TRACE GASES

In this section, fuel chemistry and combustion efficiency effects are discussed as they affect the production of trace gases from combustion sources. In particular, studies are reviewed that have examined the production of gases containing nitrogen, sulfur, and chlorine. Other gases produced, such as methane, nonmethane hydrocarbons (NMHC) and oxygenated hydrocarbons, also are discussed in this section.

1. Nitrogen Gases

Generally, temperatures within flame structures of vegetation fires do not exceed 1000°C, which suggests that molecular nitrogen gas (N_2) from the atmosphere is not dissociated to combine with free radicals within the combustion zone to form oxides of nitrogen (NO_x). Several studies have reported the production of NO_x from the burning of biomass.

Evans *et al.* (1977) measured NO_x in forest fire plumes in Australia. Their findings showed NO_x concentrations as high as 0.024 ppm. The conclusion was that NO_x is produced proportional to fire intensity. The same relationship has not been found for fires in the United States.

Results of Clements and McMahon (1980) suggest that the production of NO_x strongly increases with the nitrogen content of the fuel burned. Conversion of fuel-bound nitrogen to NO_x can occur readily in oxygen-depleted air. Simple linear regression equations were developed with coefficients of determination greater than 0.70 for predicting the production of NO, NO_x, NO_2, as functions of the nitrogen content of the fuel. The quantity of fuel nitrogen converted to NO_x was found to range from 6.1 to 41.7% for wood and organic soil, respectively.

Proximate analysis for the nitrogen content is an important measurement to make in interpreting differences between NO_x emissions for different ecosystems. The emissions of N_2O from combustion of forest fuels showed a small variance for two extreme fuel types—the boreal forest of Canada and the chaparral fuels of California. However, for some measurements of NO_x the difference between boreal and chaparral NO_x emissions was quite large (Hegg *et al.*, 1989).

Hegg *et al.* (1989) measured emission factors for NH_3 of 0.1 to 2.0, for NO_x of 0.81 to 8.9, and for N_2O of 0.16 to 0.41 g/kg of fuel consumed. Nitrogen loss from the biological site was significant. In addition, a fraction of the nitrogen is contained within the particulate matter. NH_4 is contained within the particles and may contribute as much as 0.05 g/kg of fuel consumed.

Volatilization and release of nitrogen to the atmosphere can be significant on a total mass basis per unit area burned. Yokelson *et al.* (1996) demonstrated a relationship between the NH_3/NO_x ratio and MCE where NO_x dominates the emissions during flaming combustion and NH_3 dominates during smoldering combustion as follows:

$$NH_3/NO_x = 14(1 - MCE) \qquad R^2 = 0.96 \tag{4}$$

The total of NH_3 and NO_x accounts for approximately 50% of the fuel nitrogen. Therefore, if the nitrogen content of the fuel is known and the MCE for the combustion is known, then the emissions of NH_3 and NO_x can be estimated.

Crutzen *et al.* (1985) found an average ratio of N_2O to CO_2 of 1.5×10^{-4} for tropical biomass burning. If one sums the carbon released as CO, CO_2, CH_4, and NMHC and assumes an emission rate of 1% for particulate matter (Ward and Hardy, 1991), the conversion of biomass to CO_2 is 77.8% efficient. This compares favorably with average rates of combustion efficiency for logging slash fires of 82.8% in the western United States (Ward and Hardy, 1984). The emission factor for N_2O was computed from Crutzen *et al.* (1985), and the result is 0.22 to 0.44 g N_2O per kilogram of fuel consumed. The emission factor for burning of tropical biomass is quite similar to that for boreal, chaparral, and coniferous biomass in North America as measured by Hegg *et al.* (1989). Ozone is not a byproduct of biomass combustion but forms as a product of secondary chemical reactions once the combustion products enter the atmosphere.

2. Sulfur Emissions (Carbonyl Sulfide)

Along with nitrogen, sulfur is one of the essential nutrients required in the synthesis of plant amino acids and other physiologically important substances (Grier, 1975; Tiedemann, 1987). Hence, the volatilization and loss of these important nutrients is of extreme interest in sustaining the productivity of ecosystems. Nitrogen can be replaced through symbiotic N-fixation, whereas sulfur is replenished mainly through atmospheric deposition. Very little work has been done in identifying the form of the sulfur- or nitrogen-containing emissions released during the combustion of biomass fuels.

Crutzen *et al.* (1985) measured carbonyl sulfide (COS) emission ratios to CO_2 of approximately 4 to 8×10^{-6} (5.71 to 11.42 mg/kg of fuel consumed). Ward *et al.* (1982) measured emission factors for COS of 0.18 to 2.36 mg/kg of fuel consumed from controlled experiments in a combustion laboratory-burning hood facility. The experiments were for fuels of varying sulfur content ranging from 0.55% (by weight) for organic soil to a low of 0.065% for pine needles. Ward *et al.* (1982) calculated emission factors from Crutzen *et al.* (1979) of 16.2 and 35.3 mg/kg of fuel consumed for fires in the Rocky Mountain area of the United States. The results of Ward *et al.* (1982) can be used to predict emission factors for COS as a function of the rate of heat release per unit area (I_R, kW/m^2) as follows: $EF_{COS} = 0.732 - 0.0065\ I_R$ where the coefficient of determination is 0.99. This would suggest that the production of COS is independent of the sulfur content of the fuel—a result that probably is not valid. However, it may be concluded that COS production is extremely sensitive to the thermal environment reflected through the apparent dependence on I_R. Other sulfur-containing compounds were measured as well including H_2S, $(CH_3)_2S$, CS_2, CH_3SSCH_3, and other unknown mercaptan compounds. The sulfur quantified made up less than 0.25% of the total sulfur released during the combustion experiments. The balance of the sulfur may be partially explained by measurements of Yokelson *et al.* (1996) who estimate the molar ratio of SO_2 emitted to that of CO_2 as $(7.3\ !\ 3.0) \times 10^{-4}$. As with nitrogen compounds, the sulfur content of the fuel is highly variable and becomes the dominant characteristic in estimating the release of sulfur compounds.

3. Methyl Chloride

Methyl chloride has been suggested as a natural tracer unique to the combustion of biomass fuels (Khalil *et al.*, 1985) and seems to work well for apportioning the impact of residential wood combustion. For open burning, Ward (1986) found that methyl chloride is produced in much greater quantities in the smoldering combustion phase than in the flaming phase. Thus, unless the actual ratio of flaming to smoldering is known for smoke impacting a site, the apportionment may be in error.

Ward (1986) found an inverse relation between chlorine content of fine particles and the amount of methyl chloride released and that emission factors for methyl chloride are inversely proportional to the rate of heat release. For chaparral fuels, methyl chloride emission factors ranged from 16 to 47 mg/kg of fuel consumed (Ward and Hardy, 1989). Reinhardt and Ward (1995) found that most, if not all, of the methyl chloride is produced from the smoldering combustion process.

4. Carbon Monoxide

Carbon monoxide is the second most abundant carbon-containing gas released during the combustion of biomass (Figure 1). Combustion efficiency and MCE are nearly perfectly correlated with the ratio of the production of carbon monoxide relative to carbon dioxide. Ward and Hardy (1991) found particulate matter concentration to be strongly correlated with carbon monoxide concentration ($r = 0.89$). Reinhardt and Ward (1995) found the concentration of formaldehyde to be correlated with the concentration of carbon monoxide ($r = 0.93$). Generally, emission factors for carbon monoxide on a mass basis are ten times greater than for the fine particle fraction. Emission factors for carbon monoxide range from 40 to over 300 g/kg of fuel consumed. Ward *et al.* (1996) found for fires in savanna grassland ecosystems that the following relationship can be used for computing emission factors for carbon monoxide (EFCO):

$$\text{EFCO} = 1834(1 - \text{MCE}) * 0.64 \tag{5}$$

5. Methane and Nonmethane Hydrocarbons

Methane is produced in much larger quantities during the smoldering combustion phase than in the flaming phase (Ward and Hardy, 1991). Emission factors are about two to three times greater for the smoldering phase than for the flaming phase. For one study, however, they ranged from 5.7 to 19.4 g/kg of fuel consumed for smoldering combustion and the flaming phase emission factors ranged from 1 to 4.2 g/kg. The volatile hydrocarbons are well correlated with methane, and emission factors for the hydrocarbons are well correlated with MCE. Ward *et al.* (1992) and Hao and Ward (1993) demonstrated that linear relationships between CH_4 emission factors and MCE are quite different for forest and savanna fires. In addition to the different slopes of the linear regression models, typical MCE values were found to be 0.84 for slash fires in primary forests of Brazil, 0.90 for second-growth deforestation burns in the same area, and 0.94 for cerrado savanna ecosystems of Brazil. Ward *et al.* (1996) found for fires in savanna ecosystems that the following equations can be used for calculating emission factors for CH_4 and NMHC:

$$\text{EFCH}_4 = 60.76 - 62.41\ \text{MCE} \qquad R^2 = 0.84 \tag{6}$$

$$\text{EFNMHC} = 45.5 - 45.8\ \text{MCE} \qquad R^2 = 0.96 \tag{7}$$

IV. MINIMIZING SMOKE PRODUCTION

One way to reduce the amount of air pollutants released to the atmosphere is to adjust the fire return interval to minimize the total smoke production. Here, an example is presented using information for a pure grassland ecosystem in Africa (Ward *et al.*, 1996). The decision to be made is whether it should be burned annually or biennially or a fire return interval of 3 or more years should be used to minimize the release of pollutants to the atmosphere. To assist in making this decision, we can apply the equations presented in the previous sections to first of all estimate the MCE using Eq. (2) which in turn can be used to estimate the emission factors needed for evaluating the emissions of PM2.5, CO, CH_4, and NMHC. We first need to know something about the rate of litter accumulation. For our Africa example, Ward *et al.* (1996) assumed that the area would be burned biennially and that half of the first year's standing grass decomposes naturally and the other half becomes incorporated into the litter layer during the 2-year period (i.e., $L = 0.5G$ in the second year). The ratio under this set of circumstances for the standing grass to the sum of standing grass plus the litter would be 0.67. Even though the total amount of fuel consumed is less, the MCE declines as a result of the increase in litter so that the emission factors are larger. The total products of incomplete combustion are shown in Table 1 to be more than the amount that would be produced were the area burned annually. The amount of nonmethane hydrocarbons and PM2.5 is 8 and 12% greater and the CH_4 released is 60% greater than would occur with annual burning. Other examples could be developed based on higher or lower decomposition rates for the litter and longer periods between burns.

TABLE 1 Example of Application of Algorithms for Assessing the Optimal Burning Interval for Minimizing the Release of Pollutants to the Atmosphere from the Use of Prescribed Fire in a Pure Grassland Ecosystem

	1 year	2 years
Available fuel	1.000	1.500
$G/(G + L)$	1.000	0.667
MCE	0.961	0.947
$EFCO_2$	1762	1736
EFCO	45.8	62.6
$EFCH_4$	0.8	1.7
EFNMHC	1.5	2.1
EFPM2.5	2.6	3.9
Emissions		
CO_2	1762	2604
CO	45.8	93.8
CH_4	0.78	2.51
NMHC	1.49	3.21
PM2.5	2.59	5.79
Ratios to one year		
CO_2	1.00	1.48
CO	1.00	2.05
CH_4	1.00	3.21
NMHC	1.00	2.16
PM2.5	1.00	2.23
The total emissions relative to burning every year		
CO_2		0.74
CO		1.02
CH_4		1.60
NMHC		1.08
PM2.5		1.12

After Ward *et al.*, 1996.

TABLE 2 Algorithms and Ratios Developed for Logging Slash of the Pacific Northwest in the United States and Used for Computing Emission Factors (g of emission per kg of dry fuel consumed)

	Algorithm	Ratio model	Flaming	Smoldering	Units
MCE			0.92	0.75	
Carbon dioxide		MCE * 1834	1687	1376	g/kg
Carbon monoxide		(1 − MCE) * 1834 * 0.64	94	293	g/kg
Methane	42.7 − MCE * 43.2		3.0	10.3	g/kg
Nonmethane hydrocarbons	0.760 + $EFCH_4$ * 0.616		2.6	7.1	g/kg
PM2.5	67.4 − MCE * 66.8		5.9	17.3	g/kg
PM10		1.18 * EFPM2.5	7.0	20.4	g/kg
PM	93.3 − MCE * 90.5		10	25	g/kg
Benzene		0.00592 * EFCO	0.56	1.74	g/kg
Benzo[a]pyrene		13 * EFPM	131	331	μg/kg

After Ward *et al.*, 1993.

Ward *et al.* (1993) used similar algorithms developed for vegetation types in the United States to estimate the total criteria pollutant and air toxic emissions released from the prescribed use of fire nationally for the year 1989. The system they employed identified the fuel consumed by National Fire Danger Rating Fuel Model types and assigned a ratio of flaming to smoldering for each type. Then emission factors were computed for flaming and smoldering based on using an MCE of 0.92 for flaming and 0.75 for smoldering. Table 2 lists the algorithms and the emission factors for flaming and smoldering combustion used in this study. It immediately follows that a weighted emission factor can be computed by knowing the amount of fuel consumed during flaming versus smoldering combustion. For example, for 100% flaming a valid emission factor for particulate matter for particles less than 2.5 μm diameter would be 5.9 g of PM2.5/kg of fuel consumed on an oven dry weight basis. On the other hand, for a fuel complex where we expect about 30% of the fuel to be consumed during flaming and 70% during smoldering, we would weight the emission factor by multiplying the flaming emission factor by 30% and the smoldering emission factor by 70%, add the two together, and derive a weighted emission factor of 13.9 g of PM2.5/kg of fuel consumed.

V. CONCLUSIONS

The combustion of biomass in the open environment is a source of pollution and greenhouse gases to the atmosphere. Incomplete combustion, primarily from the smoldering phase, results in a very complex mixture of gaseous and particulate matter called smoke. The mixture is somewhat dependent on the elemental composition, size distribution, and moisture content of the fuel particles at the time of burning. The environmental conditions prevailing at the time of the fire and the type of fire (whether heading, backing, flanking, or an area fire) are important as well. Combustion efficiency can be calculated and/or estimated for determining the magnitude of emission factors for different compounds and particulate matter for different combinations of fuel and fire. The outcome of these calculations can be used for assessing management strategies in developing environmental impact assessments. By knowing fuel loading, available fuel, and ratio of fuel consumed by phase of combustion, the amount and rate of release of smoke can be estimated.

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