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# Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil

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**Abstract.** Airborne measurements of the emissions of gases and particles from 19 individual forest, cerrado, and pasture fires in Brazil were obtained during the Smoke, Clouds, and Radiation-Brazil (SCAR-B) study in August-September 1995. Emission factors were determined for a number of major and minor gaseous and particulate species, including carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen oxides, methane, nonmethane hydrocarbons, halocarbons, particulate (black and organic) carbon, and particulate ionic species. The magnitude of the emission factors for gaseous species were determined primarily by the relative amounts of flaming and smoldering combustion, rather than differences in vegetation type. Hydrocarbons and halocarbons were well correlated with CO, which is indicative of emissions primarily associated with smoldering combustion. Although there was large variability between fires, higher emission factors for SO<sub>2</sub> and NO<sub>x</sub> were associated with an increased ratio of flaming to smoldering combustion; this could be due to variations in the amounts of sulfur and nitrogen in the fuels. Emission factors for particles were not so clearly associated with smoldering combustion as those for hydrocarbons. The emission factors measured in this study are similar to those measured previously in Brazil and Africa. However, particle emission factors from fires in Brazil appear to be roughly 20 to 40% lower than those from North American boreal forest fires.

## 1. Introduction

Emissions from biomass burning cause significant perturbations in certain trace gas and particle concentrations in the Earth's atmosphere [*Intergovernmental Panel on Climate Change (IPCC)*, 1995]. Although carbon dioxide is the most abundant component of biomass burning emissions, a wide variety of other compounds that are important in global atmospheric chemistry are also emitted. Hydrocarbons, produced during oxygen-poor smoldering combustion, are thought to influence tropospheric ozone concentrations over much of the globe [*Fishman et al.*, 1996; *Roelofs et al.*, 1997]. Halocarbons, such as methyl chloride and methyl bromide, may influence stratospheric ozone concentrations [*Cicerone*, 1994]. Other important trace gases, such as CO, NO<sub>x</sub>, and SO<sub>2</sub>, are also emitted in globally significant quantities by biomass burning [*Andreae*, 1991; *Fearnside*, 1991].

Particles emitted from biomass burning, which are composed primarily of organics and black carbon, play an important role in the Earth's radiation balance through their direct scattering and absorption properties and their effects on the microphysical structures of clouds [*Hobbs and Radke*, 1969; *Kaufman et al.*, 1990; *Christopher et al.*, 1996].

Gas-to-particle conversion of hydrocarbons, NO<sub>x</sub>, and SO<sub>2</sub> may further alter the radiative and cloud-nucleating properties of smoke aerosols.

Although the emissions from biomass burning of many of the aforementioned species have been estimated in a number of previous studies of laboratory controlled and natural fires, relatively few data have been collected from individual fires in South America, which account for roughly one third of worldwide biomass burning emissions [*Andreae*, 1991]. In addition, relatively little is known about the influence of different vegetation types on the mixture of chemical species emitted from biomass fires in Brazil.

In August and September 1995 the University of Washington (UW) Cloud and Aerosol Research group, with its Convair C-131A research aircraft, participated in the Smoke, Clouds, and Radiation-Brazil (SCAR-B) field project. The goal of SCAR-B was to obtain measurements of the physical, chemical, and radiative properties of the palls of smoke that cover millions of square kilometers of the Amazon Basin and the cerrado regions of Brazil during the burning season. This paper focuses on the emission factors of gases and particles for flaming and smoldering combustion of cerrado (brush and scrub forest), grass (or pasture), and rain forests in Brazil.

## 2. Experiment

Gases and particles within 4 min of emission were measured from individual biomass fires aboard the UW research aircraft

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by a variety of airborne techniques during SCAR-B [Hobbs, 1996]. Several of the relevant techniques are described briefly below.

### 2.1. Sampling

Instrumentation was carried aboard the UW research aircraft for both continuous and intermittent grab-bag sampling. Much of the instrumentation for the aerosol measurements, and some of the gas measurements, required sampling times longer than it typically took the aircraft to penetrate individual smoke plumes. Therefore in order to collect smoke from plume samples, we employed a grab-bag technique, in which a 2.5 m<sup>3</sup> electrically conducting plastic (Velostat) bag was rapidly filled by ram air. With a 12 s fill time, the bag sampler could capture a large volume of concentrated smoke from which filter samples were subsequently drawn. Particle size measurements were also made on the bag samples. The grab-bag system had an aerosol 50% cut point diameter of about 4 μm (PM<sub>4</sub>). Larger particles are lost in the inlet and on the walls of the grab bag during filling. The cut point was determined from data collected on many previous field projects in which aerosol mass concentrations derived from filters fed from the grab bag were compared with mass concentrations derived from measurements of the aerosol size spectra.

To minimize losses of particles to the walls of the grab bag, sample volumes were generally not allowed to exceed one-third the volume of the bag. In addition, a valve on the continuous gas analyzer manifold could be briefly switched to the bag to obtain measurements on a bag sample. All of the measurements from the grab bag were correlated with measurements from the continuous sampling instruments by averaging the latter over the time period for which a grab-bag sample was collected.

A slightly different approach was used for obtaining whole air samples in electropolished stainless steel canisters. To avoid hydrocarbon contamination from the plastic bag material, whole air samples were obtained from a stainless steel inlet attached to a metal bellows pump. The canisters were pressurized during the time the aircraft penetrated a plume. Although roughly concurrent with the grab-bag samples, the canisters took about 45 s to fill, and often, two penetrations of a plume were required to obtain sufficient sample. Care was taken to quickly maneuver the aircraft back into the same portion of the plume penetrated in the first pass. Since the time between penetrations was approximately 2 min and the two locations within approximately 100 m of each other, the uncertainties involved in sampling slightly different regions of the smoke plume are probably small. Since the air sampled was not identical to that captured in the bag, hydrocarbon and halocarbon concentrations were ratioed to the above-ambient concentrations of CO<sub>2</sub> measured in the canisters, and normalized to the above-ambient CO<sub>2</sub> concentrations measured in the bag by the continuous analyzers. This provided data that were comparable to the particle species measured in the grab bag. Background samples were obtained just upwind of the fires and subtracted from the concentrations measured in the smoke samples. From these measurements of all the major carbon-containing species in a smoke sample (CO, CO<sub>2</sub>, CH<sub>4</sub>, NMHCs, black carbon, and organic aerosol), emission factors for all of the measured species could be calculated.

### 2.2. Gas Measurement Techniques

Gaseous species routinely measured aboard the UW C-131A aircraft included CO<sub>2</sub>, CO, NO<sub>x</sub>, NO, and SO<sub>2</sub>. Continuous measurements were made of these species using the following methodologies: NO and NO<sub>x</sub> with a modified Monitor Labs model 8840 chemiluminescent analyzer (uncertainly of ±2 ppb), CO with a Teco model 48 infrared analyzer (uncertainly of ±100 ppb), CO<sub>2</sub> with a Teco model 41H infrared analyzer (uncertainly of ±4 ppm at 350 ppm), a Li-Cor model LI-6262 infrared analyzer (uncertainly of ±0.3 ppm at 350 ppm), and SO<sub>2</sub> with a Teco model 43S pulsed-fluorescence analyzer (uncertainly of ±4 ppb). Calibration of the CO and CO<sub>2</sub> instruments was carried out during each flight using a commercial standard mixture (400 ppm CO<sub>2</sub>/15ppm CO, Scott-Marrin, Inc.) and zero air stored in passivated aluminum cylinders. Calibration of the SO<sub>2</sub> and NO<sub>x</sub> instruments was carried out periodically in the field with a commercial standard mixture of SO<sub>2</sub> and NO in ultrapure air (Scott-Marrin, Inc.). The stability of the mixture and calibration of the instruments over a range of concentrations were checked before and after the field program using a combination of permeation tube standards and high concentration cylinder standards (5 ppm SO<sub>2</sub>, NO, and NO<sub>2</sub> in ultrapure N<sub>2</sub>, Scott-Marrin, Inc.) diluted to 10-200 ppb with zero air. While the instruments used to measure CO<sub>2</sub>, NO<sub>x</sub>, and O<sub>3</sub> had short enough response times to permit continuous sampling during a plume penetration, CO and SO<sub>2</sub> concentrations could only be obtained reliably by switching the inlet to the gas monitors over to grab-bag samples. In this study all of the continuous gas instruments had signal-to-noise ratios of the order of 10:1 to 100:1.

The whole air samples collected in the stainless steel canisters were sent to the University of California, Irvine, and analyzed by gas chromatography using a flame ionization detector (FID) [Blake *et al.*, 1996]. For each sample, concentrations of CO<sub>2</sub>, CO, CH<sub>4</sub>, and hydrocarbons (C<11) were measured. Typically, about 21 NMHC species were identified which accounted for more than 70% of the total mass of volatile organic carbon (VOC) measured in a sample. An additional 30-50 small unidentified peaks (probably mostly NMHC but also containing some oxygenated species and other short-lived organic compounds) were also usually measured. To derive an accurate total organic carbon vapor concentration for inclusion in the carbon budget, the total carbon in VOC was determined by integrating the area of all peaks between the C-2 and the C-11 region and dividing this area by the methane response factor. Measurement precisions for alkanes, alkenes, alkynes was 2% or 8 ppt, whichever was larger.

Concentrations of five halocarbons were determined from the canister samples using gas chromatography with an electron capture detector. These were CH<sub>3</sub>Cl, CHCl<sub>3</sub>, CH<sub>3</sub>I, CH<sub>3</sub>Br, and CHBr<sub>3</sub>, which were measured at precisions of 1.2, 12, 12, 8, and 12%, respectively.

### 2.3. Particle Measurement Techniques

Particles were collected on both quartz and Teflon filters. The Teflon filters were gravimetrically analyzed in a humidity controlled chamber (RH = 35%) to determine the ambient aerosol dry mass concentration. From control and field blank filters, we estimate that the uncertainty in the mass concentrations measured with these filters was less than ±6

$\mu\text{g}$ . By comparison, the typical filter loading for smoke samples was always greater than 100  $\mu\text{g}$ .

After gravimetric analysis the Teflon filters were extracted in deionized water and analyzed by standard ion chromatography (IC) techniques. This analysis yielded the following ions:  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^-$ ,  $\text{SO}_4^-$ , and  $\text{C}_2\text{O}_4^-$  (oxalate).  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^-$ , and  $\text{C}_2\text{O}_4^-$  were determined to have an uncertainty of  $\pm 3\%$  or better and were always more than five standard deviations above the detectable limits. All other species were measured to have an uncertainty  $\pm 10\%$  or better.

Aerosol samples collected on the quartz filters were used to determine the atmospheric particulate carbon concentration by thermal analysis [Cachier *et al.*, 1989]. Filters were subjected to HCl vapors for 24 hours to remove any carbonate. The total carbon (TC) content of the sample was determined through coulometric titration. The black carbon (BC) content of the aerosol was determined through coulometric titration after the sample was thermally pretreated at  $340^\circ\text{C}$  for 2 hours to remove any organic carbon (OC). The OC content of the aerosol was assumed to be the difference between the TC and the BC. Because of negative artifacts that develop when using this technique on biomass burning aerosols, all BC values were adjusted upward by 25%. This correction was necessary because BC can be combusted at lower than expected temperatures due to catalytic reactions with Na and K [Novakov and Corrigan, 1995]. A complete discussion on the error analysis of the BC measurements performed in SCAR-B is given by Reid *et al.* [this issue (b)].

#### 2.4. Calculations of Emission Factors and Combustion Efficiencies

Smoke samples from individual plumes were obtained for a variety of vegetation types in different regions of Brazil. In each case, visual observations and photographs of the fuel type and fire phase (flaming or smoldering) were made. Fire fuels were divided into three categories: grass (or pasture), cerrado, and forest.

Emission factors for gases and particles were calculated from the carbon balance method [Ward *et al.*, 1982; Radke *et al.*, 1988]. The underlying premise of this method is that all of the carbon combusted in a fire and released to the atmosphere is emitted into the smoke plume in five forms of carbon ( $\text{CO}_2$ , CO,  $\text{CH}_4$ , nonmethane hydrocarbons (NMHCs), and particulate carbon (PC)). The emission factor of a species  $X$  is calculated from the ratio of the mass concentration of that species to the total carbon concentration emitted in the plume:

$$\text{EF}(X) = \frac{[X]}{[\text{C}]_{\text{CO}_2} + [\text{C}]_{\text{CO}} + [\text{C}]_{\text{CH}_4} + [\text{C}]_{\text{NMHC}} + [\text{C}]_{\text{PC}}} \quad (1)$$

Thus the emission factor is expressed in units of grams of  $X$  emitted per gram of carbon burned. To convert this emission factor to units of grams of  $X$  emitted per gram of fuel burned, the EF is multiplied by the mass fraction of carbon in the fuel, if it is known. Typically, the carbon content of woody fuels varies from 45 to 50% [Susott *et al.*, 1997]. Because we did not have data on the actual carbon content of the various fuels that produced the smoke we studied, in this paper, emission factors are expressed either in units of grams of  $X$  emitted per kilogram of carbon burned ( $\text{g}/\text{kgC}$ ) or in units of grams of

carbon in  $X$  emitted per kilogram of carbon burned ( $\text{g}(\text{C})/\text{kg}(\text{C})$ ).

Ward and Hardy [1991] define the combustion efficiency (CE) as the ratio of carbon (C) emitted as  $\text{CO}_2$  to the total carbon emitted:

$$\text{CE} = \frac{[\text{C}]_{\text{CO}_2}}{[\text{C}]_{\text{CO}_2} + [\text{C}]_{\text{CO}} + [\text{C}]_{\text{HC}} + [\text{C}]_{\text{PC}}} \quad (2)$$

where the subscript HC indicates the total unburned hydrocarbons (methane and NMHC). Thus CE is the fraction of fuel carbon emitted which is completely oxidized to  $\text{CO}_2$ . Combustion efficiency is a useful way to quantify the relative amounts of flaming and smoldering combustion. When  $\text{CE} \geq 90\%$ , a fire is generally in the flaming phase, and when  $\text{CE} \leq 90\%$ , it is in the smoldering phase [Ward and Hardy, 1991]. The smoke emitted from most of the fires we studied derived from both flaming and smoldering combustion, which we refer to as "mixed phase" smoke.

Although the CE is a useful quantity for fire models, in experimental studies it is often difficult to measure all the individual carbon species in the emissions. As will be shown below, the emission of CO is closely linked to the emission of HC and PC. Therefore in this study we have chosen to use the modified combustion efficiency (MCE) as the principal quantity to describe the relative amounts of flaming and smoldering combustion [Ward and Hao, 1992]. The modified combustion efficiency is defined as

$$\text{MCE} = \frac{[\text{C}]_{\text{CO}_2}}{[\text{C}]_{\text{CO}_2} + [\text{C}]_{\text{CO}}} \quad (3)$$

Since NMHC and particulate carbon are emitted in relatively small quantities relative to  $\text{CO}_2$  and CO, the difference between CE and MCE is typically only a few percent. For the SCAR-B data set, combustion efficiency and modified combustion efficiency are related by

$$\text{CE} = \frac{\text{MCE} - 0.18}{0.82} \quad (r^2 = 0.99) \quad (4)$$

### 3. Results

Sampling of smoke from individual fires for the purpose of determining emission factors was generally done at an altitude of about 500 m above the fires. Since visibility was usually poor ( $< 4$  km) in the boundary layer, we were able to detect and obtain measurements only on the larger fires that had a visible plume extending above the low-level haze layer. The measurements obtained yielded emission factors on 24 samples from 19 individual forest, cerrado, and grass fires. For some of the forest fires, we were able to sample both the flaming and the smoldering phases of the same fire.

Six samples for emission factor determinations were obtained from four cerrado fires (one outside Brasília and three near Cuiabá). Because of the nature of the fuels (small and dry), modified combustion efficiencies were above 90%, with an average of 0.94. Aerosol mass concentrations ( $\text{PM}_{10}$ ) in the plumes at the level of our measurements varied from 60 to 450

$\mu\text{g m}^{-3}$  above ambient (background concentrations ranged from 20 to 50  $\mu\text{g m}^{-3}$ ).

Six samples for emission factor determinations were obtained from five grass (pasture) fires (two near Brasília, one near Porto Velho, and two near Marabá). Like the cerrado, grass fires consume small and dry fuel and thus have high combustion efficiencies (average MCE = 0.94). Excess particle mass concentrations ( $\text{PM}_{10}$ ) in these smoke plumes ranged from 130 to 500  $\mu\text{g m}^{-3}$  (background concentrations ranged from 30 to 80  $\mu\text{g m}^{-3}$ ).

Twelve samples (six flaming and six smoldering) for emission factor determinations were obtained in ten forest fires (three near Porto Velho and seven near Marabá). Modified combustion efficiencies for these samples varied from 0.84 to 0.98, with an average of 0.89. The forest fires was divided into forest flaming (MCE>0.90) and forest smoldering (MCE<0.90). The average MCE for flaming and smoldering samples was 0.94 and 0.87, respectively. Fuel for the forest fires varied from slash to standing forest. Smoke aerosol concentrations ( $\text{PM}_{10}$ ) ranged from 200 to 3400  $\mu\text{g m}^{-3}$  (background concentrations ranged from 30 to 80  $\mu\text{g m}^{-3}$ ). In all cases when the MCE was less than 90%, the smoke was from mixed phase combustion.

A summary of the derived emission factors is given in Table 1 for cerrado, grass, and forest-flaming and forest-smoldering fuels. For flaming combustion,  $\text{CO}_2$  accounted for 90% of the carbon released to the atmosphere, followed by 5% in the form of CO. The remaining 5% was roughly equally partitioned between hydrocarbon and particulate carbon species. There is a statistically significant increase in the emission factors of methane from the flaming combustion of forest fires compared to cerrado and grass fires. As the forest fires evolved from flaming to smoldering combustion, there was a very large shift in the carbon budget into incomplete products of combustion (such as CO, NMHC, and particulate carbon).

### 3.1. Gas Emission Factors

In general, the emission of hydrocarbons is associated with smoldering combustion (i.e., oxygen-starved, inefficient consumption of the fuel). Typically, the concentration of total NMHC was better correlated with CO (Figure 1b) than with  $\text{CO}_2$  (Figure 1a) regardless of the type of vegetation. Similar behavior was true for most individual hydrocarbon species. In addition, individual hydrocarbon species were typically very well correlated with each other (Figure 2).

Table 2 shows a list of regression relations for the above-background concentrations of various individual hydrocarbon species versus the above-background concentration of  $\text{CO}_2$ , CO, and NMHC. The individual HC species were emitted in relatively constant ratios regardless of vegetation type. Thus if the emissions of CO are measured from a biomass fire in Brazil, the emission of hydrocarbons, methyl bromide, and particulate species can be deduced rather accurately.

Figure 3 shows the variation of the emission factor of total NMHC with combustion efficiency. Almost a tenfold variation of emissions occurred across the range of combustion efficiencies measured during SCAR-B. This behavior has a significant impact on our ability to predict emissions of trace hydrocarbon species from estimates of biomass burned. Although techniques for estimating the global amounts of biomass burned have improved in recent years [Levine *et al.*, 1995], better global and regional estimates of trace species emitted will require a quantitative understanding of combustion efficiency and fire behavior as it varies across biomass types and regions.

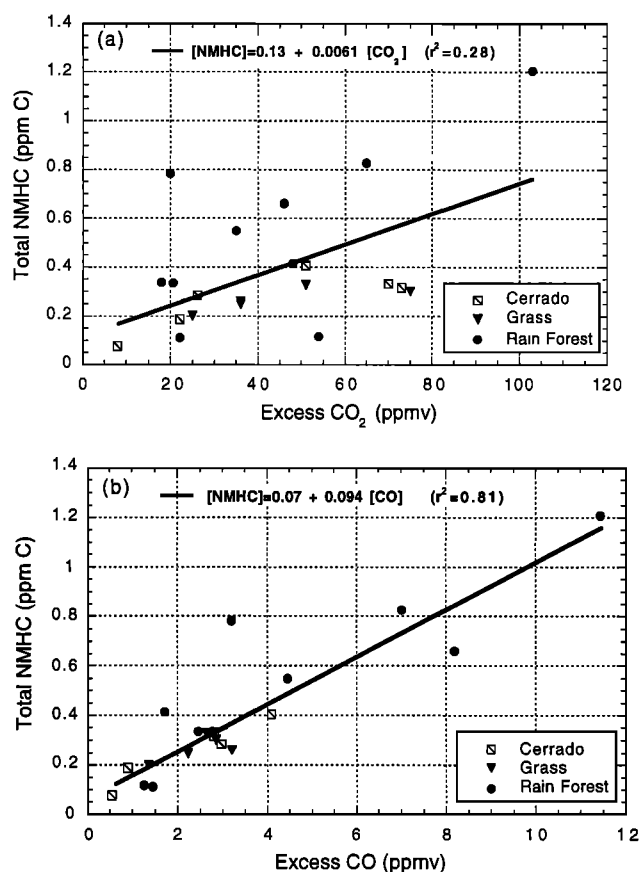
The halocarbons exhibited a somewhat more complicated emission pattern than the NMHC. Of the five species measured, only  $\text{CH}_3\text{Br}$  was fairly well correlated with combustion efficiency (Figure 4) and appeared to have an unambiguous biomass burning source. In addition, it exhibited a behavior similar to the other hydrocarbons (i.e., a clear association with smoldering combustion). This is contrary to the results reported by Mano and Andreae [1994], who associated the emission of methyl bromide with the flaming phase of combustion for African savannah grasses burned in a laboratory. In a subsequent study of savannah fires in Africa, Andreae *et al.* [1996] found methyl halide emissions well correlated with CO, indicating an unambiguous association with smoldering combustion.

For the SCAR-B results,  $\text{CH}_3\text{Cl}$ ,  $\text{CHCl}_3$ , and  $\text{CH}_3\text{I}$  also appeared to have a biomass burning source but were less well correlated with combustion efficiency. These species all had a large group of data points that were well correlated with CO. However, there were a few extraneous data points that significantly reduced the regression coefficient ( $r^2$ ) to under 0.1. It is unclear whether these outliers were a result of measurement error or are due to variations in the chloride and iodide content of the fuel.  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  appeared not to have a significant biomass source.

**Table 1.** Average Emission Factors, With Mean Standard Error in Parentheses, in g C/kg C Burned for Various Types of Individual Fires in Brazil

Fuel Type (No. of samples)	$\text{CO}_2$	CO	NMHC	$\text{CH}_4$	$\text{PM}_{10}$	Total Particulate Carbon	Black Carbon
Grass ( $n=6$ )	927 (56)	56 (15)	6 (1.3)	3.1 (2.4)	16 (7.4)	11.5 (4.4)	1.3 (0.9)
Cerrado ( $n=6$ )	928 (30)	57 (28)	7 (2.4)	3.7 (2.7)	9.6 (4)	6.6 (2.8)	1.0 (0.4)
Forest-flaming ( $n=6$ )	913 (34)	60 (28)	7 (3.3)	7.9 (3.9)	16 (7.5)	10.2 (5.7)	1.1 (0.4)
Forest-smoldering ( $n=6$ )	831 (22)	120 (13)	17 (8.1)	12.5 (6.1)	26.6 (11)	19.4 (7.8)	1.5 (0.9)

Value of  $n$  is the number of individual samples.



**Figure 1.** (a) Total excess (i.e., above background) nonmethane hydrocarbon (NMHC) concentration versus excess  $\text{CO}_2$  in smoke from 21 individual fires in Brazil. (b) As for Figure 1a but NMHC versus excess CO.

$\text{SO}_2$  and  $\text{NO}_x$  exhibited behaviors opposite to that of the hydrocarbons, in that their emission factors increased with combustion efficiency (Figure 5). Their production was associated weakly with the flaming phase of combustion, perhaps due to more complete burning of the fuel and a higher burning temperature.

### 3.2. Particle Emission Factors

Particle emission factors were not so clearly associated with smoldering combustion as the hydrocarbons. Figure 6 shows the particle mass emission factor as a function of combustion efficiency; although there is a weak correlation, it seems that the production of particulate matter in smoke is a complex process not readily predicted by knowledge of the phase of the fire. Black carbon (Figure 7) was essentially independent of the combustion efficiency and varied in what appears to be a random manner from fire to fire. Overall, BC comprised about 5–9% of the emitted particle mass.

A summary of the particle emission factors and elemental compositions is given in Table 3. Cerrado fires had the lowest particle emission factors of any fuel type or combustion efficiency (10 g/kg C burned). Grass and flaming forest fires had similar particle emission factors (16 g/kg C burned). Smoldering forest fires had the highest particle emission factor (27 g/kg C burned).

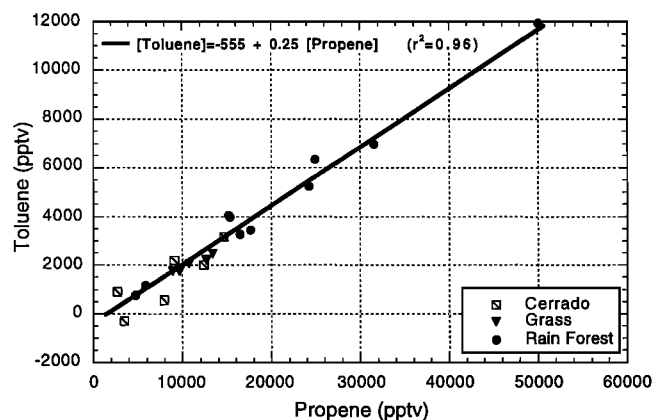
Particle emission factors for forest fires varied widely, as is evident in the large standard deviations associated with the

data (Table 3). A regression of particle emission factors for forest fires against the MCE shows that unlike hydrocarbons, particle production is not strictly associated with smoldering combustion (Figure 6). While the particle emission factor shows a statistically significant (at the 95% confidence level) increase with decreasing MCE, the correlation is low ( $r^2 = 0.18$ ) and is strongly dependent on one data point (at MCE = 0.98).

As discussed by *Reid and Hobbs* [this issue], particle properties are influenced by two principle processes: condensation and coagulation of high temperature products in the flame zone during flaming combustion and condensation of low-volatility organics during low temperature, smoldering combustion. Thus the particle formation mechanisms for purely flaming and purely smoldering combustion are quite different. This difference is illustrated in Figure 8, where the emission ratio of particles to CO is plotted as a function of the MCE for smoke from forest fires. Here we find that the emission ratio increases with increasing MCE. This trend is identical to that found by *Ward et al.* [1991] for North American forest fires, where it was shown that during flaming combustion particles are formed by a mechanism distinctly different from that which produces CO. In view of the small range of values of the MCE observed in this study, it is not surprising that the correlation between the particle emission factor and the MCE is poor.

Even though the correlation between the particle emission factor and the MCE is poor, the correlation between the particulate mass concentration and the CO is fairly good (Figure 9). In this case, we have plotted the particle concentration versus CO for all our data. Two possible regression lines can be drawn depending on whether or not the outlying data point (at a CO concentration of 17 ppm) is included. For all the data, the regression yields a slope of  $156 \mu\text{g ppm}^{-1}$ . However, if the outlying data point is discarded, the regression slope drops to  $80 \mu\text{g ppm}^{-1}$ .

It is likely that the  $80 \mu\text{g ppm}^{-1}$  slope is a more representative emission ratio for typical fires in Brazil. This is similar to the value of  $82 \mu\text{g ppm}^{-1}$  found by *Anderson et al.* [1996]. The fire for which the outlying data point was obtained was atypical in comparison to the other fires sampled during SCAR-B. Not only was this the largest fire we encountered (with smoke concentrations greater by a factor of 2 than the next largest fire), but conditions at the surface



**Figure 2.** As for Figure 1 but for excess toluene versus excess propene.

**Table 2.** Regression Slopes and Correlation Coefficients for the Concentrations of Individual Hydrocarbons, Halocarbons, Trace Gases and Particulate Species Versus the Concentrations of CO<sub>2</sub>, CO, and Total NMHCs

Species	Versus CO <sub>2</sub> , ppmv		Versus CO, ppmv		Versus NMHC, ppmv C	
	Slope	r <sup>2</sup>	Slope	r <sup>2</sup>	Slope	r <sup>2</sup>
CO <sub>2</sub> , pptv	—	—	6.32 × 10 <sup>6</sup>	0.43	5.0 × 10 <sup>7</sup>	0.33
CO, pptv	68500	0.43	—	—	8.3 × 10 <sup>6</sup>	0.81
NMHC, ppt C	6100	0.28	94000	0.81	—	—
Methane, pptv	6900	0.25	124000	0.90	1.09	0.82
Ethane, pptv	318	0.27	5158	0.85	47242	0.78
Ethene, pptv	821	0.42	10521	0.83	104590	0.90
Ethyne, pptv	243	0.53	2436	0.63	24847	0.72
Propane, pptv	87.3	0.36	1028	0.82	11240	0.78
Propene, pptv	241	0.29	3863	0.87	37342	0.89
Isobutane, pptv	3.84	0.19	74.3	0.82	690	0.78
<i>n</i> -Butane, pptv	9.50	0.14	209	0.79	1973	0.78
Propadiene, pptv	8.07	0.49	96.4	0.82	943	0.87
<i>i</i> -2-Butene, pptv	15.5	0.26	262	0.89	2446	0.86
1-Butene, pptv	44.2	0.34	661	0.90	6258	0.89
Isobutene, pptv	31.1	0.21	577	0.87	5347	0.82
<i>c</i> -2-Butene, pptv	13.1	0.27	221	0.89	2049	0.84
<i>i</i> -Pentane, pptv	1.14	0.09	30.6	0.73	270	0.63
<i>n</i> -Pentane, pptv	3.58	0.25	58.6	0.81	553	0.79
Isoprene, pptv	5.93	0.45	69.1	0.73	723	0.88
Benzene, pptv	121	0.34	1492	0.89	17499	0.92
Toluene, pptv	54.4	0.23	941	0.81	9030	0.82
<i>p</i> -Xylene, pptv	3.27	0.19	57.9	0.72	566	0.75
<i>m</i> -Xylene, pptv	5.99	0.19	108	0.72	1053	0.76
Ethylbenzene, pptv	5.67	0.20	96.6	0.70	973	0.79
<i>o</i> -Xylene, pptv	2.51	0.14	48.8	0.62	489	0.69
CH <sub>3</sub> Cl, pptv	-0.404	0.00	116	0.05	1656	0.12
CHCl <sub>3</sub> , pptv	1.48	0.09	-1.06	0.00	-15.5	0.00
CH <sub>2</sub> Br, pptv	1.30	0.24	16.6	0.46	136	0.34
CH <sub>2</sub> I, pptv	5.07	0.03	14.2	0.31	85.5	0.12
CH <sub>2</sub> Br <sub>2</sub> , pptv	-0.021	0.01	0.505	0.08	4.158	0.06
CHBr <sub>3</sub> , pptv	-0.090	0.22	-0.258	0.02	-3.23	0.04
Black carbon, µg m <sup>-3</sup>	0.339	0.38	3.49	0.49	30.6	0.41
TPC, µg m <sup>-3</sup>	3.31	0.24	41.1	0.46	334	0.35
Cl <sup>-</sup> , µg m <sup>-3</sup>	0.148	0.33	0.585	0.06	6.16	0.07
NO <sub>3</sub> <sup>-</sup> , µg m <sup>-3</sup>	0.039	0.26	0.496	0.47	4.206	0.37
SO <sub>4</sub> <sup>2-</sup> , µg m <sup>-3</sup>	0.125	0.33	1.19	0.32	10.3	0.28
Na <sup>+</sup> , µg m <sup>-3</sup>	-0.013	0.55	0.499	0.10	0.623	0.20
K <sup>+</sup> , µg m <sup>-3</sup>	0.284	0.67	2.02	0.37	18.1	0.36
Mg <sup>+2</sup> , µg m <sup>-3</sup>	0.0675	0.42	0.719	0.52	6.49	0.48
Ca <sup>+2</sup> , µg m <sup>-3</sup>	0.957	0.33	1.26	0.61	9.89	0.43
NH <sub>4</sub> <sup>+</sup> , µg m <sup>-3</sup>	0.0016	0.02	0.0354	0.10	0.147	0.02

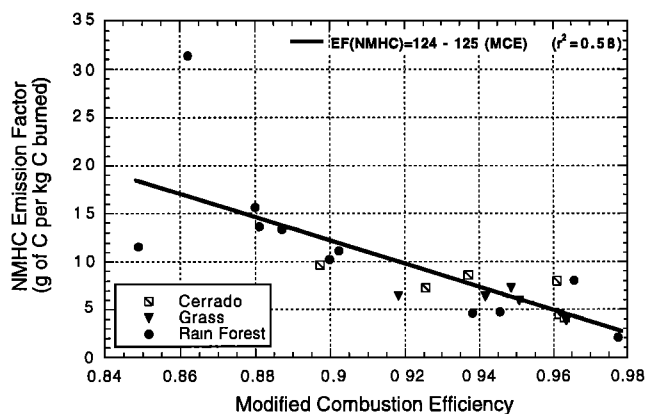
A total of 24 samples were taken for all species, except for the methyl halides where 22 samples were taken.

resembled a full fire storm with very vigorous flaming and strong surface winds. Under such circumstances, particles would have been produced entirely by the high temperature condensation process, and any CO was probably produced by oxygen deprivation in the interior of the fire rather than by low-temperature smoldering processes.

### 3.3. Particle Composition

Carbon species accounted for 60 to 70% of the mass of all particle emissions. Despite wide variations in the emission factors of OC and BC by fuel type and combustion efficiency, their mass fraction in the aerosol was remarkably stable. For all flaming fires (cerrado, grass, and forest), the black carbon content of the emitted aerosols was roughly constant at 7.8%. Similarly, their organic carbon content was roughly constant at 59%. This yields an organic to black carbon ratio of 8:1.

Aerosols from smoldering fires had higher organic carbon (and lower black carbon) contents, resulting in an



**Figure 3.** Emission factors of NMHC versus the modified combustion efficiency (MCE).

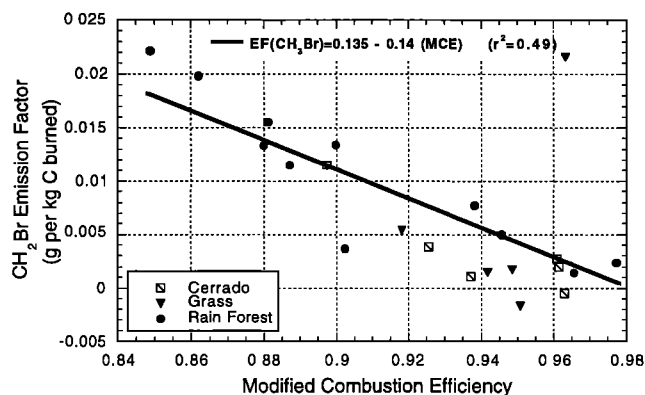


Figure 4. As for Figure 3 but for methyl bromide.

organic-to-black carbon ratio for smoldering combustion of 12 to 1. As discussed above, particle production in smoldering combustion occurs at lower temperatures than flaming combustion, and it is dominated by low-temperature condensation processes. Thus the mass fraction of organic carbon should go up with decreasing MCE.

The ion chromatography analysis was able to speciate only another 6 to 8% of the total aerosol mass. This mass was mostly composed of potassium (3-5%), chloride (1-3%), and sulfate (1-3%). Thus we were unable to speciate about 20% of the aerosol mass; this remainder is classified as "residue" in Table 3. It is likely that this residue mass was composed primarily of hydrogen, oxygen, and nitrogen, which are associated with organic carbon. Thus the ratio of the mass of organic species to organic carbon is likely in the range of 1.2 to 1.5.

#### 4. Discussion

All of the emission factors we measured are shown in Figure 10. They are discussed below under the sub-headings "gases" and "particles".

##### 4.1. Gases

Hydrocarbon emissions were found to have a clear association with smoldering combustion, as evidenced by

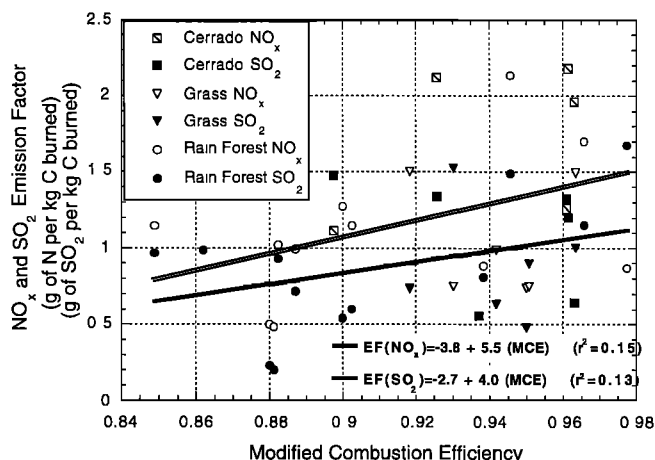


Figure 5. As for Figure 3 but for NO<sub>x</sub> (open symbols) and SO<sub>2</sub> (solid symbols).

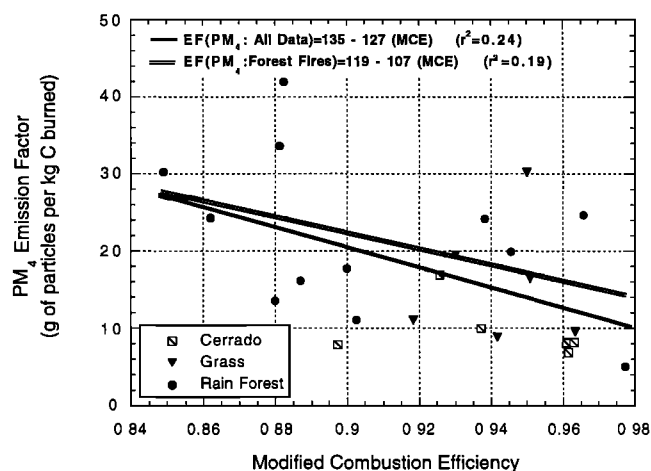


Figure 6. As for Figure 3 but for particulate matter less than 4 μm in diameter (PM<sub>4</sub>). Two regression lines are drawn: for all of the data (solid line) and for forest fires only (double line).

their high degree of correlation with CO and combustion efficiency. This result is consistent with a number of previous studies of emissions from biomass burning [Greenberg *et al.*, 1984; Hurst *et al.*, 1994; Bonsang *et al.*, 1991; Ward *et al.*, 1992, 1996; Blake *et al.*, 1996]. The emission factors for hydrocarbons are closely predicted by the combustion efficiency. For the fires studied during SCAR-B, there were no clear differences in the amounts or relative proportions of hydrocarbons emitted which could be attributed to the different fuel types studied (grass, cerrado, and forest). What did differ between fuel types was the combustion efficiency, with grass and cerrado having relatively high combustion efficiencies (mostly flaming combustion) and forest fires having a relatively larger amount of smoldering combustion. In addition, the distinctions between fuel types were somewhat obscured in that cerrado and grass fires typically had some amount of woody fuels within them, either from young trees or from the remnants of incomplete combustion of the woody fuels (stumps and trunks) when the forest was originally cleared for pasture [Barbosa and Fearnside, 1996]. In addition, forest fires, especially during their flaming phase, probably consumed a large amount of underbrush and grass as well as leaves and branches, further blurring the distinction

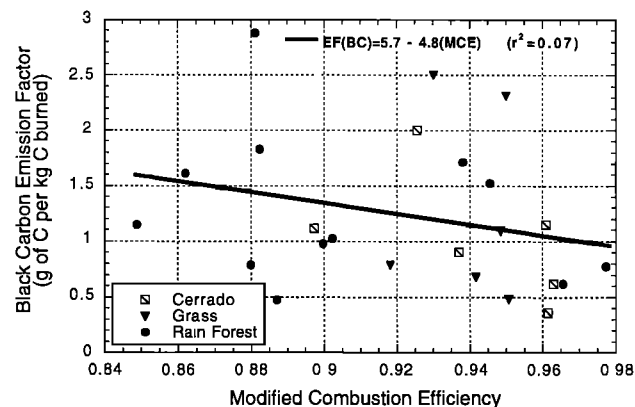


Figure 7. As for Figure 3 but for black carbon.



**Table 3.** Particle Emission Factors and Compositions for Various Types of Individual Fires in Brazil

	Cerrado	Grass	Forest Flaming	Forest Smoldering
<i>Emission Factors, g/kg C Burned</i>				
PM <sub>4</sub>	9.6 ± 4.0	16.0 ± 7.4	17.0 ± 7.5	26.6 ± 11.0
Total carbon	6.6 ± 2.8	11.5 ± 4.4	10.2 ± 5.7	19.4 ± 7.8
Organic carbon	5.9 ± 2.8	10.2 ± 4.5	9.1 ± 5.7	17.9 ± 7.6
Black carbon	0.7 ± 0.4	1.3 ± 0.9	1.1 ± 0.4	1.5 ± 0.9
<i>Mass Speciation, %</i>				
OC	61 ± 20	66 ± 11	53 ± 20	67 ± 11
BC	7.5 ± 4.0	7.5 ± 3.1	7.9 ± 4	5.3 ± 2.0
Ca <sup>+</sup>	0.9 ± 0.5	0.7 ± 0.73	0.9 ± 0.8	0.64 ± 0.7
Cl <sup>-</sup>	3.3 ± 2.8	1.7 ± 1	1.1 ± 1.1	1.0 ± 1.34
K <sup>+</sup>	4.5 ± 2.1	2.9 ± 1.5	4.8 ± 4.5	2.5 ± 2.0
Mg <sup>2+</sup>	0.5 ± 0.3	0.3 ± 0.26	0.6 ± 0.4	0.3 ± 0.3
Na <sup>+</sup>	0.07 ± 0.05	0.1 ± 0.26	0.04 ± 0.08	0.2 ± 0.1
NH <sub>4</sub> <sup>+</sup>	0.05 ± 0.05	0.02 ± 0.04	0.2 ± 0.5	0.1 ± 0.08
NO <sub>3</sub> <sup>-</sup>	1.43 ± 1.1	0.9 ± 0.4	0.8 ± 0.3	0.7 ± 0.2
C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	0.4 ± 0.3	0.3 ± 0.3	0.5 ± 0.3	0.6 ± 0.2
PO <sub>4</sub> <sup>-</sup>	0.07 ± 0.05	0.02 ± 0.02	0.03 ± 0.04	0.03 ± 0.04
SO <sub>4</sub> <sup>-</sup>	1.0 ± 0.5	1.7 ± 1	3.0 ± 2.8	2.1 ± 0.9
Residue	19 ± 21	18 ± 12	27 ± 21	19 ± 12

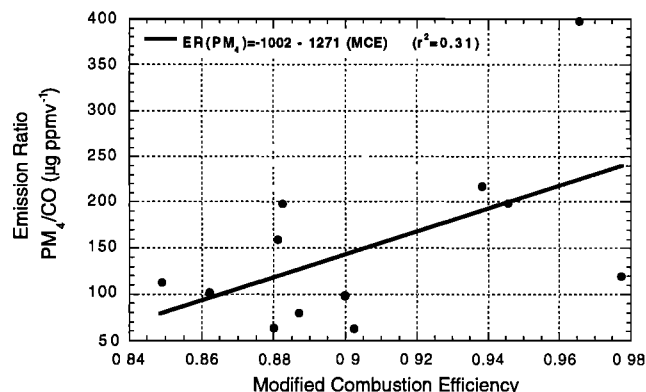
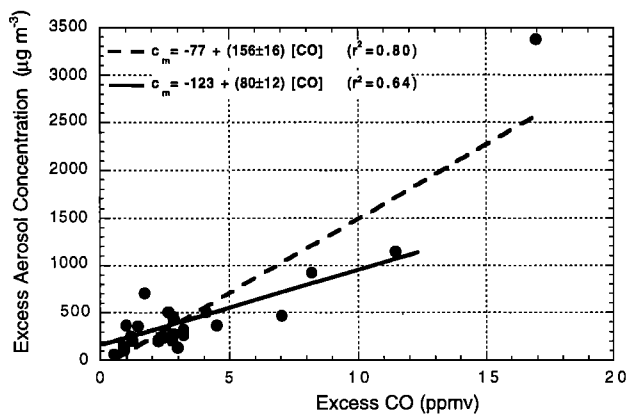
among the three categories of fuels. These fuels, as well as the likely presence of biomass litter in many of the fields, contributed to a significant amount of smoldering combustion observed even from what appeared to be mostly grass fuels. Thus for tropical biomass fires the relative amounts of flaming and smoldering combustion is the key variable for determining the emission rates of these species, at least as far as hydrocarbon emissions are concerned. Therefore a rather accurate estimate of the hydrocarbons emitted from such fires can be obtained from measurements of CO and CO<sub>2</sub> alone.

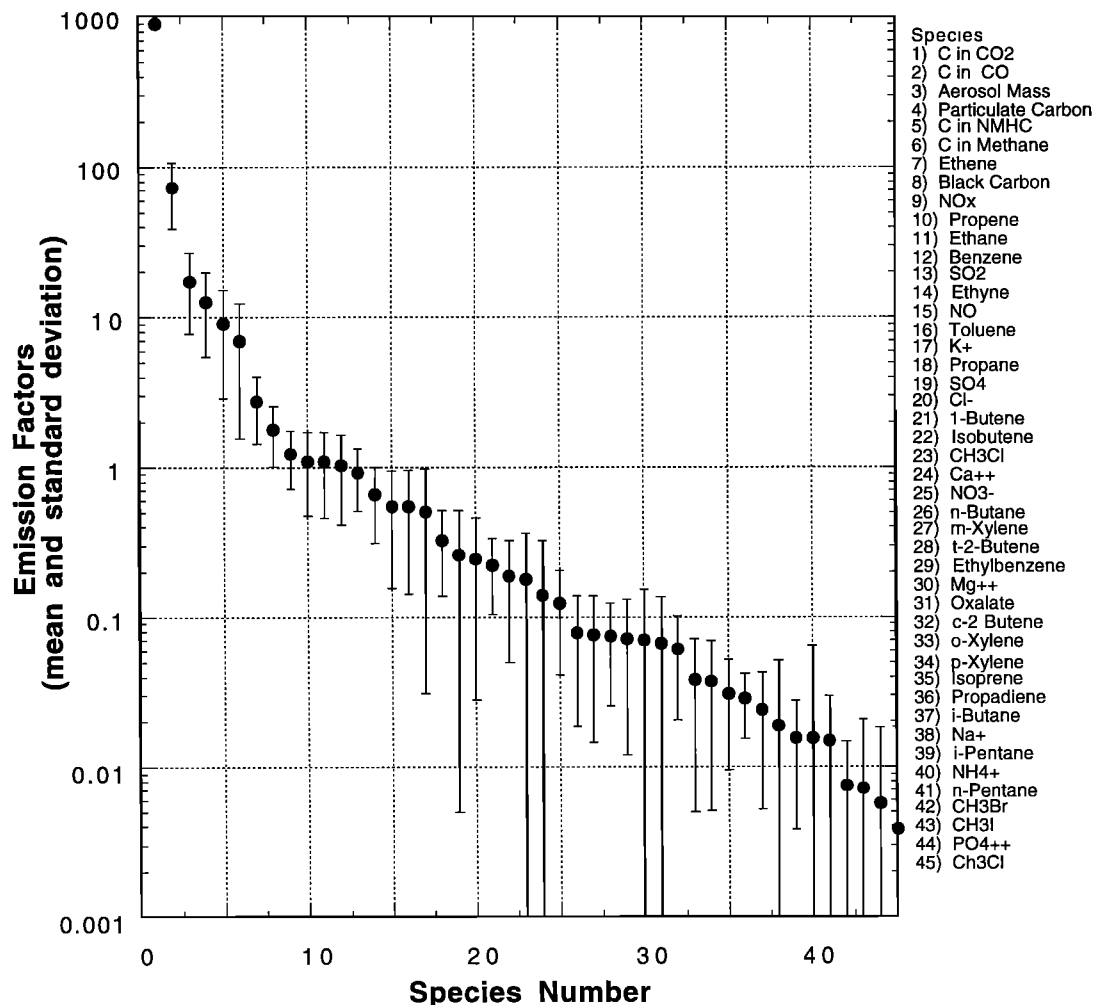
The emission factors for the methyl halides were less well correlated with combustion efficiency than hydrocarbons but clearly showed an association with smoldering combustion. *Andreae et al.* [1996] attributed variations in emission factors of halogenated species to variations in the halogen content of the fuels, with tropical savanna fuels showing considerably higher halogen contents than most forest fuels.

The ratio of the concentrations of hydrocarbons and halocarbons to CO reported here are very similar to those reported previously for Brazilian fires. A comparison of our results with those of the Brazilian Fire Assessment (BFA)

program [*Blake et al.*, 1997] and the Transport and Atmospheric Chemistry near the Equator (TRACE A) studies [*Blake et al.*, 1996] is given in Table 4. As in the case of the SCAR-B results presented here, the ratios from the BFA study are for very young smoke, whereas the TRACE-A ratios are for aged smoke in regional hazes. Our results for CH<sub>4</sub> lie between the BFA and the TRACE-A values. Similarly, our ratios for low reactivity hydrocarbons, such as ethane and benzene, are in good agreement with these two studies. However, there is some difference in the ratios for more reactive species such as propene and toluene. For these species the emission ratios for young smoke (i.e., our study and BFA) are significantly higher than those measured in aged smoke in TRACE A. As discussed by *Reid et al.* [this issue (a)], these reactive species have short photochemical lifetimes.

The CH<sub>3</sub>Cl/CO ratios measured in SCAR-B lie between the values measured in BFA and TRACE A. The SCAR-B CH<sub>3</sub>I/CO

**Figure 8.** PM<sub>4</sub>-to-CO emission ratio versus modified combustion efficiency for forest fires.**Figure 9.** Total excess (i.e., above background) concentration of particulate matter less than 4 µm in diameter (PM<sub>4</sub>) versus excess CO in smoke for 21 in individual fires in Brazil. Two regression lines are shown: for all of the data points (dashed line) and when one data point (at 17 ppmv and 34,000 µg m<sup>-3</sup>) is omitted (solid line).



**Figure 10.** Mean and standard deviations of emission factors plotted in order of decreasing magnitude for 45 gaseous and particulate species from individual fires in Brazil. For CO<sub>2</sub>, CO, BC, particulate carbon, C in NMHC, and C in methane, the units are g C/kg C burned; for NO<sub>x</sub> the units are g N/kg C burned; and for all other species, the units are g/kg C burned.

ratios are similar to those found in BFA but much higher than measured in regional hazes in TRACE A. *McKenzie et al.* [1997] has shown that the halogen content of biomass is highly variable. Thus since the data from SCAR-B, BFA, and TRACE A were collected in different regions in Brazil, differences in the halocarbon to CO ratio are to be expected.

The emission factors of NO<sub>x</sub> and SO<sub>2</sub> exhibited behaviors opposite to that of hydrocarbons, in that their emission factors increased with combustion efficiency, although their correlations with MCE were poor ( $r^2 = 0.15$  and  $0.13$ , respectively). The productions of NO<sub>x</sub> and SO<sub>2</sub> were associated more with flaming combustion, perhaps due to more complete burning of the fuel and a higher burning temperature, but their dependence on combustion efficiency was not so strong as for hydrocarbons. The variability of the emission factors between fires may be attributable to different nitrogen and sulfur contents of the fuels [*Lobert et al.*, 1991; *Turn et al.*, 1997]. Similarly, *Lacaux et al.* [1996] found a clear relationship between the fuel nitrogen content and the NO<sub>x</sub>/CO<sub>2</sub> ratio in emissions from African savannah fires, which burned relatively efficiently (average CE of approximately 0.95). For the SCAR-B data, which spanned a

wider range of combustion efficiencies but for which we do not have information on the fuel nitrogen and sulfur contents, the variability of the results are likely due to variations in fuel composition and, to a lesser degree perhaps, to differences in the relative amounts of flaming and smoldering combustion.

#### 4.2. Particles

The particle emission factors and compositions reported here compare fairly well to measurements from previous studies. Previously, the most comprehensive study of particle emissions from fires in Brazil was the BASE-B experiment [*Ward et al.*, 1992]. Assuming the wood fuel was 50% carbon by mass, the average emission factors for cerrado and smoldering forest from Ward et al. is 9 g/kg C burned. This is nearly identical to the value determined in this study. The chemical composition of the particles measured by Ward et al. is also similar to that found in this study. They reported potassium, calcium, and chloride mass fraction which are within the standard deviations of our values. Furthermore, the mass fractions of sulfur in the aerosol, reported by Ward et al., and in the present study are similar.

**Table 4.** Regression Slopes for Concentrations of Various Chemical Species Versus CO Concentrations for Young Smoke Measured in SCAR-B and BFA and in Regional Hazes in Brazil in TRACE A

	This Paper (SCAR-B), pptv ppb <sup>-1</sup>	<i>r</i> <sup>2</sup>	BFA [Blake <i>et al.</i> , 1997], pptv ppb <sup>-1</sup>	<i>r</i> <sup>2</sup>	TRACE A [Blake <i>et al.</i> , 1996], pptv ppb <sup>-1</sup>	<i>r</i> <sup>2</sup>
CH <sub>4</sub>	98 ± 10	0.72	107 ± 4	0.91	94 ± 13	0.70
C in NMHCs (C<11)	95 ± 10	0.80	na	na	na	na
Ethane	5.2 ± 0.7	0.85	8.5 ± 0.3	0.84	8.3 ± 0.3	0.97
Ethene	11 ± 1	0.83	17.1 ± 0.4	0.95	6.1 ± 0.4	0.87
Ethyne	2.4 ± 0.4	0.63	4.6 ± 0.2	0.90	3.3 ± 0.1	0.97
Propane	1.0 ± 0.1	0.82	1.6 ± 0.1	0.79	1.6 ± 0.1	0.95
Propene	3.9 ± 0.3	0.87	4.9 ± 0.1	0.98	0.4 ± 0.1	0.62
Propadiene	0.1 ± 0.09	0.82	na	na	na	na
<i>i</i> -Butane	0.07 ± 0.01	0.82	0.47 ± 0.02	0.87	0.055 ± 0.02	0.55
<i>n</i> -Butane	0.21 ± 0.02	0.79	0.21 ± 0.02	0.70	0.21 ± 0.01	0.21
1-Butene	0.66 ± 0.06	0.90	0.75 ± 0.02	0.75	na	na
<i>t</i> -2-Butene	0.26 ± 0.02	0.89	0.26 ± 0.01	0.88	na	na
<i>c</i> -2-Butene	0.22 ± 0.02	0.89	0.20 ± 0.01	0.87	na	na
<i>i</i> -Pentane	0.03 ± 0.004	0.73	0.020 ± 0.002	0.57	na	na
<i>n</i> -Pentane	0.06 ± 0.006	0.81	0.043 ± 0.002	0.84	0.05 ± 0.01	0.80
Benzene	1.5 ± 0.2	0.89	1.7 ± 0.03	0.97	1.29 ± 0.05	0.97
Toluene	0.9 ± 0.1	0.81	0.72 ± 0.02	0.72	0.57 ± 0.03	0.93
Ethylbenzene	0.10 ± 0.01	0.70	na	na	na	na
<i>o</i> -Xylene	0.05 ± 0.005	0.62	na	na	0.03 ± 0.002	0.87
<i>m</i> -Xylene	0.11 ± 0.01	0.72	na	na	0.04 ± 0.004	0.83
<i>p</i> -Xylene	0.06 ± 0.005	0.72	na	na	0.02 ± 0.003	0.93
Isoprene	0.07 ± 0.01	0.73	na	na	na	na
CH <sub>2</sub> Cl	0.52 ± 0.17	0.56	0.31 ± 0.03	0.90	0.85 ± 0.06	0.88
CHCl <sub>3</sub>	0.001 ± 1e-4	0.63	na	na	na	na
CH <sub>2</sub> I	0.005 ± 0.002	0.30	0.004 ± 0.0003	na	0.001 ± 0.0002	0.57
CH <sub>2</sub> Br	0.01 ± 0.003	0.42	0.007 ± 0.0009	0.49	0.011 ± 0.001	0.88
CHBr <sub>3</sub>	-0.9e-5 ± 1e-4	0.07	na	na	na	na

Units are in change of species concentration (in pptv) per change in CO (in ppbv); *r*<sup>2</sup> is the regression coefficient; na, not available.

The particle emission factors from grass fires in Brazil reported here are similar to those measured in grass fires in Africa. Using the "best guess" emission factor from *Andreae et al.* [1997] for particles from African savannah fires, and assuming a carbon content of the fuel of 50%, we calculate an average PM<sub>2.5</sub> emission factor for African grass fires of 11 g/kg C burned. Thus after adjusting for differences in the size of the particles sampled (PM<sub>4</sub> from our measurements, based on the particle size distribution for the SCAR-B fires reported by *Reid and Hobbs* [this issue], and PM<sub>2.5</sub> for *Andreae et al.*), the emission factors for particles from grass fires in the two regions agree to within 25%.

During the BASE-B study, *Ward et al.* [1992] measured emission factors and the chemical composition of particles emitted from forest fires. The chemical compositions of the aerosols from these fires are similar to those given in this paper. Also, as for the SCAR-B measurements, the correlation between the particle emission factor and the MCE was poor in the BASE-B study. However, the emission factor for particles produced by smoldering combustion reported by *Ward et al.* is only 17 g/kg C burned, compared to our value of 27 g/kg C burned. This large difference cannot be accounted for by differences in the measured particle cut points. The difference could be a result of the process and the temperature at which high molecular weight organic vapors released from smoldering combustion condense onto particles. *Ward et al.* [1992] performed their particle and gas sampling on 10 m towers placed in the center of burning plots. However, *Reid et*

*al.* [this issue (a)] present evidence that in smoke from forest fires, condensation of organic vapors onto particles occurs in the first minutes to hours after emission. In this case, the condensation rate in the smoke must be very high during the first few hundred meters of travel and as the smoke is cooled by entrainment and radiation. Thus it is unlikely that the vapor-particle phase partition was at equilibrium in *Ward et al.*'s [1992] measurements. This would result in an underestimate of the particle emission factor for mixed-phase forest fires. Their reported emission factor for smoldering combustion is significantly lower than our value of 27 g/kg C burned.

Particle emission factors measured for forest fires in Brazil are considerably less than those found in North America. *Radke et al.* [1991] found that boreal fires in the Pacific Northwest have average PM<sub>3.5</sub> emission factors of the order of 30 and 40 g/kg C burned, for flaming and smoldering combustion, respectively. Similarly, *Hobbs et al.* [1997] measured PM<sub>3.5</sub> emission factors of the order of 50 g/kg C burned for very intense flaming combustion from prescribed fires. The reason for these differences are likely due to fuel and fire size. In the North American studies the fires were typically large, fuels were dry, and the fires were ignited rapidly by helitorch, resulting in smoke particle mass concentrations typically in excess of 600 µg m<sup>-3</sup>. In contrast, most of the fires studied in Brazil were small, burned slowly, and produced smoke concentrations near the fire, which were typically less than 400 µg m<sup>-3</sup>. In very large prescribed fires

there is a likelihood that during the most intense phase of flaming combustion, oxygen deprivation can occur at the center of the fire. This would increase the concentration of products of incomplete combustion and produce larger quantities of smoke than slower burning fires of the type encountered in Brazil.

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