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The tropical forest and fire emissions experiment: Trace gases emitted by smoldering logs and dung from deforestation and pasture fires in Brazil

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Abstract

Earlier work showed that Amazonian biomass burning produces both lofted and initially unlofted emissions in large amounts. A mobile, Fourier transform infrared spectrometer (FTIR) measured the unlofted emissions of 17 trace gases from residual smoldering combustion (RSC) of logs as part of the Tropical Forest and Fire Emissions Experiment (TROFFEE) during the 2004 Amazonian dry season. The RSC emissions were highly variable and the few earlier RSC measurements lay near the high end of combustion efficiency observed in this study. Fuel consumption by RSC was ~5% of total for a planned deforestation fire. Much regional RSC probably occurs in the residual woody debris burned during pasture maintenance fires. RSC could increase estimated total fire emissions for the Amazon region by 20–50% for several important VOC. FTIR emissions measurements of burning dung (in a pasture) showed high emission ratios for acetic acid and ammonia to CO (6.6 ± 3.4% and 8.9 ± 2.1%). Large emissions of nitrogen containing trace gases from burning dung and crop waste could mean that biomass burning in India produces more particle mass than previously assumed. Measurements of late-stage kiln emissions suggested that VOC/CO may increase as carbonization is extended. A cook stove emitted many VOC and NH_3 far outside the range observed for open wood cooking fires. Enclosed/vented cooking stoves may change the chemistry of the smoke that is emitted.

Keywords

tropical, forest, fire, emissions, experiment, Trace, gases, emitted, smoldering, logs, dung, from, deforestation, pasture, fires, Brazil

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[1] Earlier work showed that Amazonian biomass burning produces both lofted and initially unlofted emissions in large amounts. A mobile, Fourier transform infrared spectrometer (FTIR) measured the unlofted emissions of 17 trace gases from residual smoldering combustion (RSC) of logs as part of the Tropical Forest and Fire Emissions Experiment (TROFFEE) during the 2004 Amazonian dry season. The RSC emissions were highly variable and the few earlier RSC measurements lay near the high end of combustion efficiency observed in this study. Fuel consumption by RSC was ~5% of total for a planned deforestation fire. Much regional RSC probably occurs in the residual woody debris burned during pasture maintenance fires. RSC could increase estimated total fire emissions for the Amazon region by 20–50% for several important VOC. FTIR emissions measurements of burning dung (in a pasture) showed high emission ratios for acetic acid and ammonia to CO ($6.6 \pm 3.4\%$ and $8.9 \pm 2.1\%$). Large emissions of nitrogen containing trace gases from burning dung and crop waste could mean that biomass burning in India produces more particle mass than previously assumed. Measurements of late-stage kiln emissions suggested that VOC/CO may increase as carbonization is extended. A cook stove emitted many VOC and NH_3 far outside the range observed for open wood cooking fires. Enclosed/vented cooking stoves may change the chemistry of the smoke that is emitted.

1. Introduction

[2] This paper describes ground-based FTIR measurements of trace gas emissions from residual smoldering combustion (RSC) in Brazil. RSC implies that the initial emissions are not lofted by fire-induced convection and so cannot be measured from the air. These measurements are part of the Tropical Forest and Fire Emissions Experiment (TROFFEE), a combination of airborne, ground-based, and laboratory experiments designed to more fully characterize VOC emissions from tropical forests and tropical deforestation and pasture fires [*Yokelson et al.*, 2007]. The ground-based portion of TROFFEE included detailed prefire and postfire fuels inventory measurements on a 4 ha planned deforestation fire, and trace gas measurements by FTIR on this fire and on fires of opportunity in the surrounding area. The work was carried out in the Amazonian state of Mato Grosso in Brazil from 27 August to 9 September 2004. The timing of these field experiments overlapped the spatial and temporal peak of global deforestation fires for 2004 (http://satelite.cptec.inpe.br/). This paper presents more extensive field measurements of the trace gas emissions from RSC than previously available. Results from the airborne and laboratory measurements are presented in detail elsewhere [*Yokelson et al.*, 2007; *Karl et al.*, 2007a, 2007b; T. J. Christian et al., The tropical forest and fire emissions experiment: Laboratory fire measurements and synthesis of campaign results, manuscript in preparation, 2007].

[3] Brazil has ~4 × 10^6 km^2 of evergreen tropical forest, mostly in the Amazon basin. This represents ~25% of the world's total "rain forest" and is five times the amount in the Democratic Republic of the Congo or Indonesia. The Brazilian space agency (Instituto Nacional de Pesquisas

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Espaciais, INPE) monitors deforestation in the Amazon basin (http://www.obt.inpe.br/prodes/). Deforestation rates since 1977 have ranged from $11-29 \times 10^3$ km^2 y^{-1}. Cumulative deforested area through 2005 is estimated by INPE at 564,585 km^2 with 85% of this occurring in just 19% of the Amazon basin, mainly in the states of Pará, Mato Grosso, Maranhão, and Rondônia. Deforestation fires are characterized by enormous dry weight total above-ground biomass (TAGB) loading: e.g., 292, 265, 349 ± 21 (n = 7), 402, and 288 megagrams per hectare (Mg ha^{-1}) reported by *Ward et al.* [1992], *Fearnside et al.* [1993], *Guild et al.* [1998], and *Carvalho et al.* [1998, 2001], respectively. In these studies the percentage of the TAGB consumed by the fires was 53, 29, 48 (n = 7), 21, and 50, respectively, and large diameter fuels (>10 cm) typically accounted for > 50% of the total fuel consumption. Ground-based measurements of trace gas emissions from deforestation fires are limited (e.g., carbon dioxide (CO$_2$), carbon monoxide (CO), methane (CH$_4$), and selected hydrocarbons [*Greenberg et al.*, 1984; *Ward et al.*, 1992]).

[4] Following initial slash fires of primary forest, lands may be converted directly to cropland or pasture, or they may be used for several cycles of shifting cultivation prior to conversion to pasture. In shifting cultivation the plots are used for 2–3 years, left fallow for 4–6 years while secondary forest grows, then burned and reused. Pastures are burned every 2–3 years and usually have a lifetime of 10–20 years [*Guild et al.*, 1998]. As a result, according to *Barbosa and Fearnside* [1996] and *Kauffman et al.* [1998], pastures in the Amazon occupy the most deforested land, pasture burning is the most common type of fire, and the total emissions from pasture fires are comparable to the emissions from deforestation fires. Unlike Brazilian savannas, in which the majority of the fuel is grass, Brazilian pastures commonly include a substantial amount of residual wood debris (RWD) that persists for many years. Reported TAGB ranges from 119 Mg ha^{-1} (with 87% of TAGB being RWD in a 4 year old pasture) to 53 Mg ha^{-1} (47% RWD, in a 20 year old pasture) [*Barbosa and Fearnside*, 1996; *Guild et al.*, 1998; *Kauffman et al.*, 1998]. Large-diameter RWD is reported to account for 38–49% of the fuel consumption in the above studies. Mechanized agriculture is expanding in the Brazilian Amazon. Direct conversion of forest to cropland in Mato Grosso for the years 2001–2004 averaged 17% of total deforested area [*Morton et al.*, 2006]. The average clearing size for conversion to cropland (333 ha) was twice the average size for conversion to pasture (143 ha). In addition, unlike pastures, virtually all of the vegetation from cropland is removed at once and burned within a few weeks.

[5] Because Brazilian fires consume large quantities of large diameter material, RSC could be important. There is mixed evidence in this respect for fires in Brazil. In two studies *Carvalho et al.* [1998, 2001] found that RSC did not account for a significant fraction of the fuel consumption for primary deforestation fires. In contrast, *Kauffman et al.* [1998] reported that for pasture fires, 10–20 Mg ha^{-1} of grass burned in ~2 hours and 10–20 Mg ha^{-1} of RWD burned by smoldering over the course of ~3 days. *Fearnside* [1990] observed that smoldering of logs persisted for days in a secondary forest fire. The RWD in secondary forests and pastures may be older, drier, more cracked, or

smaller than the fuel at primary deforestation sites. Any of these attributes might promote more complete combustion and more RSC. *Babbitt et al.* [1996] measured ground-based emission factors (EF) for CH$_4$ and CO for pasture and primary forest fires that were about double the EF measured for the same compounds on the same fires from an aircraft. This could be due to large amounts of weakly lofted smoldering emissions. During SCAR-B *Reid and Hobbs* [1998] observed a smoke albedo (550 nm) of 0.35 for flaming grass, 0.79 on average for nascent plumes, 0.9 for smoldering slash, and an average of 0.85 in the regional haze. Thus RSC may contribute a significant amount of the total Amazonian emissions. Our goal was to measure the chemical composition of RSC emissions and explore how RSC might affect regional-global atmospheric chemistry.

[6] In addition to emissions measurements of RSC from deforestation and pasture fires, we also obtained a few measurements of the emissions from smoldering dung, a charcoal cooking kiln, and a wood cooking fire. These data are presented in a single section following the RSC results.

2. Experimental Details
2.1. Site Descriptions

[7] Table 1 gives a brief description of the sites and fuels sampled for this study. Of the 27 IR sample spectra acquired from RSC (not including numerous background spectra), about half (14) were from smoldering logs and branches on a planned 4 ha deforestation fire in primary forest on a farm (fazenda Caiabí) ~30 km ESE of Alta Floresta in the state of Mato Grosso (09°58′S, 56°21′W). This fazenda comprises ~7000 ha and produces primarily cattle with some coffee, soy, honey, Brazil nuts, guaraná, etc. During the month of June, vegetation on the 4 ha plot was felled and left to dry until September. There was an unusual amount of regrowth and there may have been higher-than-normal rainfall during the intervening months. It was necessary to work for several days cutting new growth prior to burning. The freshly cut vegetation and the potentially anomalous rainfall might have affected the combustion. However, these conditions were probably widespread and this fire was likely representative of many deforestation fires for the 2004 burning season in northern Mato Grosso, southwestern Pará, and southeastern Amazonas. Measurements in other years would be needed to explore how much regional and interannual variability may occur.

[8] For samples outside the boundaries of the fazenda we ranged (by dirt road) approximately 35 km east and 80 km south and west of the fazenda. Ten of these 13 IR sample spectra of smoldering logs and brush were acquired on small, subsistence farms (sites A, C, and D) where several hectares of secondary forest had been cut, dried, and burned for crop expansion. The other three RSC sample spectra were taken on a pasture maintenance fire on a subsistence farm (site B), where we also sampled smoldering dung and flaming grass.

[9] The charcoal kiln spectra were taken from the exhaust plume of a relatively large, brick, beehive kiln built into the side of a hill. It had a walk-in door that had been closed off by stacking bricks in the opening, and a small vent near the top for the smoke to escape. It was loaded with ~600 kg of logs approximately 20–40 cm in diameter and 1–2 m in

Table 1. Site Descriptions and Locations, Number of Samples, and Basic Fuel Types (in Chronological Order)

Site ID	Number of FTIR Sample Spectra (Number of Logs)	Sample Type	Description	Latitude	Longitude
Fazenda Caiabí	14 (12)	RSC	primary forest clearing fire (4 ha) on ~7000 ha cattle farm, smoldering logs/brush	−9.965	−56.342
Kiln A	3	charcoal production	single brick beehive kiln, built underground in hillside with walk-in door, ~600 kg capacity	−10.074	−56.178
Site A	2 (2)	RSC	secondary forest clearing fire on subsistence farm, smoldering logs	−10.085	−56.199
Site B	7[a] (3)	RSC, dung, grass	pasture maintenance fire on subsistence cattle farm, smoldering logs and dung, some flaming grass	−10.356	−56.354
Site C	2 (2)	RSC	secondary forest clearing fire on subsistence farm, smoldering logs	−10.398	−56.420
Site D	6 (6)	RSC	secondary forest clearing fire on subsistence farm, smoldering logs	−9.925	−56.766
Site E	1	cooking fire	exterior chimney exhaust from cast iron woodstove	−9.925	−56.766

[a]Seven sample spectra as follows: three smoldering logs, three smoldering dung, and one flaming grass.

length. According to the kiln owner, the charcoal making cycle was in its sixth day since ignition and within about 2 days of completion. The cooking fire sample spectrum was collected from the exterior chimney outlet of a cast iron wood cooking stove in a small family home.

2.2. Fuels Inventory and Consumption

[10] The central hectare of the 4 ha Caiabí planned fire site was divided into 100 square plots of 100 m^2 each (10 m × 10 m), of which six were randomly chosen for inventory and consumption estimates (Figure 1). The total mass of logs and larger branches with diameter at breast height (DBH) > 10 cm was estimated according to the allometric equation of *Santos* [1996]:

$$FW = \sum \exp[3.323 + 2.546 \ln(DBH)] \qquad (1)$$

where FW is the fresh weight (10^3 kg) and DBH is in meters. The consumption of these large fuels was estimated using the log-wiring procedure of *Sandberg and Ottmar* [1983]. Small-size material was composed of leaves, small bushes, branches (with DBH < 10 cm), litter, and lianas. Consumption of these smaller fuels was estimated by weighing all the biomass, before and after the fire, in subplots A and B of all six plots (see Figure 1). The subplots were bounded with wires for identification after the fire. Weighing was performed on site with a portable scale with a precision of 0.01 kg. The fire was ignited with drip torches along one edge of the site and took approximately one hour to advance to the opposite border.

2.3. Description of FTIR

[11] We designed and built a mobile, ground-based FTIR system that is easily transported, can be set up and deployed relatively quickly by one person, and can negotiate rough terrain (Figure 2). The optical bench is based on the same spectrometer (MIDAC 2500) and detector (Graseby FTIR-

M16) as our airborne and open path FTIR systems [e.g., *Yokelson et al.*, 2003a] but with a smaller, multipass White cell (Infrared Analysis, Inc. 16-V) and more compact geometry. There are two off-axis parabolic mirrors and a flat mirror (Janos Technology) to transfer the IR signal from the spectrometer through the cell to the detector. Outside air is drawn through a 3 m section of corrugated 0.635 cm Teflon tubing into the cell by a 12V, 40 slpm diaphragm pump (Gast 22D). A pair of Teflon shutoff valves allow trapping the sample in the cell for signal averaging. Temperature and pressure inside the cell are monitored in real time (Minco TT176 RTD, MKS Baratron 722A). The optical bench is isolated from the chassis by helical, wire rope shock absorbers (Aeroflex C1260 Series) sized pri-
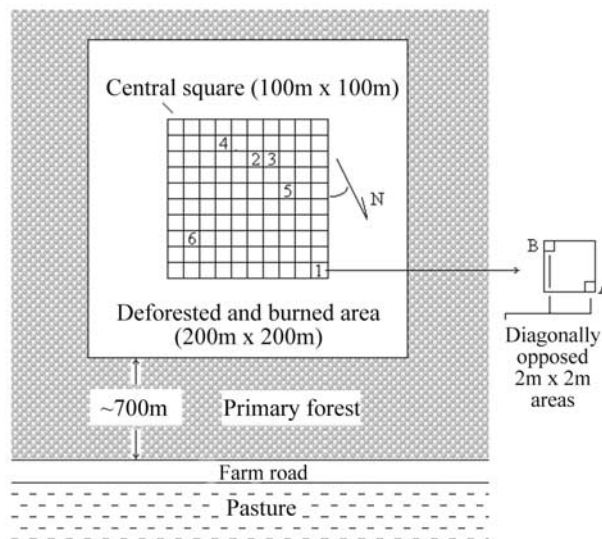
Figure 1. A schematic of the biomass loading and fuel consumption sampling scheme for the Caiabí planned fire. Lines point to subplots A and B.
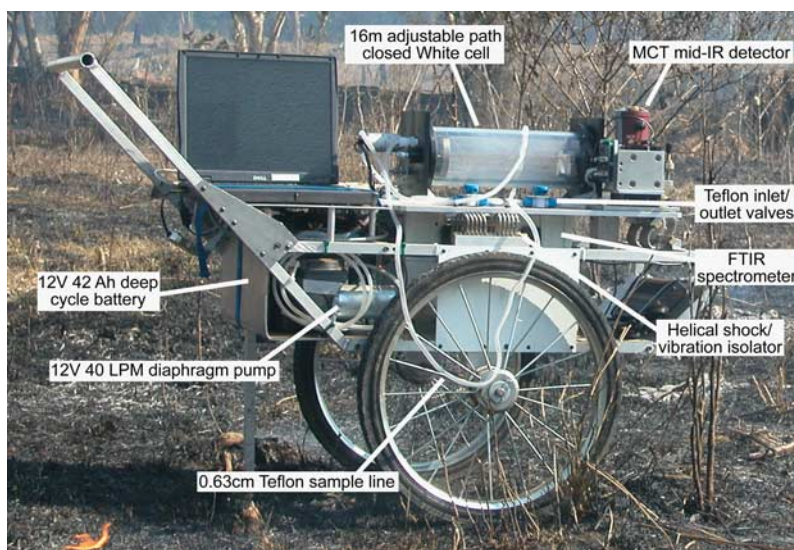
Figure 2. Basic configuration of the custom mobile FTIR system.

marily to absorb large shock loads associated with bouncing and jostling. The rolling chassis is a simple pushcart design that can be dragged and cajoled over logs, roots, and stumps. A marine deep cycle battery (42 AH, 100 min. RC) provides more than enough power to run the system for several hours before recharging. The tubeless semipneumatic tires are removable, provide good traction, especially on off-camber trails, and do not go flat.

[12] Spectra were averaged in real time over a period of 1–2 min and stored for analysis. We used spectral subtraction [*Yokelson et al.*, 1997] to retrieve excess mixing ratios for water (H_2O), formaldehyde (HCHO), acetic acid (HAc), formic acid (HFo), and hydroxyacetone (acetol). The H_2O data are available from the authors, but not reported here. We used classical least squares spectral analysis [*Griffith*, 1996; *Yokelson et al.*, 1996; *Yokelson and Bertschi*, 2002] to retrieve excess mixing ratios for H_2O, ethylene (C_2H_4), acetylene (C_2H_2), methanol (CH_3OH), phenol, furan, NO, NO_2, and hydrogen cyanide (HCN). (NO_2 was near or below the detection limit in all spectra and is not included in the tables.) Because of the high smoke concentrations sampled in this study, the IR throughput dropped to near zero in some spectral regions. Therefore, for H_2O, ammonia (NH_3), CO, CH_4, propylene (C_3H_6), and CO_2 we used a new, nonlinear least squares, synthetic calibration method [*Griffith*, 2002]. This new technique is very robust for spectral regions that contain saturation. The retrieval methods described above were based on line parameters from HITRAN (http://www.cfa.harvard.edu/HITRAN/) and/or reference spectra from Infrared Analysis, Inc. (QASoft, http://www.infraredanalysisinc.com), Pacific Northwest National Laboratory [*Sharpe et al.*, 2004], and our laboratory.

[13] The molecules discussed above account for all the significant, sharp (i.e., full width at half height < ~5 cm^{-1}) features observed from 600 to 3400 cm^{-1} in all the IR spectra. The path length of the mobile FTIR used here was 11.2 m, shorter than typical path lengths used previously with the same spectrometer (60–100 m). This had the effect of raising previously obtained detection limits using the same spectrometer by a factor of ~10. [e.g., *Bertschi et al.*,

2003b; *Yokelson et al.*, 2003a]. Therefore the detection limit for most gases was ~50–200 ppb. Smoke samples in this study were quite concentrated and, except where noted, signals were many times higher than the detection limit. For the first deployment of this new FTIR system, the typical uncertainty in the VOC mixing ratios was ±10% (1σ), and ±50% for acetol. For CO_2, CO, CH_4, and NH_3, the uncertainties were 3–5%.

3. Results and Discussion

3.1. Planned Fire Fuel Measurements

[14] One goal of this work was to obtain more insight into the amount of fuel consumption by RSC in tropical deforestation fires. To accomplish this, detailed biomass fuel consumption measurements were made on the 4 ha planned deforestation fire at fazenda Caiabí. On the basis of the variation between plots (not shown) we estimate that an uncertainty of about 30% is appropriate for the biomass loading and fuel consumption values in Table 2 and the rest of this paragraph. Table 2 summarizes the results of the prefire fuels inventory on the site. Fuels are loosely defined here as biomass exposed to the fire and likely to burn (e.g., small diameter live biomass and all dead biomass). Fuels are divided according to size classes from smallest to largest. We calculated TAGB of 306 Mg ha^{-1} on the site before ignition (238 Mg ha^{-1} trees > 10 cm DBH and 68 Mg ha^{-1} litter, leaves, and small branches, assuming 42% moisture content on a wet weight basis [*Carvalho et al.*, 1995]). This lies between the 288 and 402 Mg ha^{-1} determined by *Carvalho et al.* [1998, 2001] on similar sites near Alta Floresta and Manaus, and corresponds to 153 Mg ha^{-1} of carbon on the ground before burning if we make the common assumption of 50% carbon content on a dry weight basis. If we instead assume 48% carbon as has also been measured on some similar sites [*Carvalho et al.*, 1995] then the carbon loading on the site was 147 Mg ha^{-1}. Either estimate is close to that of *Fearnside et al.* [1993] who estimated the Amazon rain forest carbon content at 151 ± 39 Mg ha^{-1}. In Table 2, the postfire measurement of

Table 2. Distribution and Consumption of Biomass by Size Class for the Caiabí Planned Fire

Size Class (DBH)	Individual Logs	Dry Weight,[a] Mg ha^{-1}	Dist.,[b] %	n_{ind},[c] %	Ctb,[d] %
Litter	n/a[e]	nm[f]	4.8	88.6	4.3
Leaves	n/a[e]	nm[f]	5.2	88.6	4.6
Branches < 10 cm	n/a[e]	nm[f]	6.5	88.6	5.8
All Fuels < 10 cm	n/a[e]	68	16.5	n/a[e]	14.7
Branches > 10 cm	n/a[e]	nm[f]	23.5	16.9	4.0
Logs 10−20 cm	396	nm[f]	nm[f]	nm[f]	nm[f]
Logs 20−30 cm	105	nm[f]	nm[f]	nm[f]	nm[f]
Logs 30−40 cm	34	nm[f]	nm[f]	nm[f]	nm[f]
Logs 40−50 cm	8	nm[f]	nm[f]	nm[f]	nm[f]
Logs 50−60 cm	2	nm[f]	nm[f]	nm[f]	nm[f]
Logs 60−70 cm	0	nm[f]	nm[f]	nm[f]	nm[f]
Logs 70−80 cm	3	nm[f]	nm[f]	nm[f]	nm[f]
Logs > 80 cm	4	nm[f]	nm[f]	nm[f]	nm[f]
All Fuels > 10 cm	nm[f]	238	83.5	n/a[e]	9.2
All Logs 10−30 cm	501	nm[f]	19.1	16.9	3.2
All Logs > 30 cm	51	nm[f]	40.9	4.82	2.0
Total	552	306			23.8 (7)[g]

[a]Measured in this work, assumes 42% moisture on a wet weight basis.

[b]Dist. (%) is the mass distribution among size classes, from *Carvalho et al.* [2001].

[c]n_{ind} (%) is the consumption for each size class measured in this work (see text).

[d]Ctb (%) is the percent of the total prefire biomass that was consumed in the biomass category.

[e]n/a, not applicable.

[f]nm, not measured for this specific classification, but measured for a broader classification, in this work.

[g]Total estimated percentage combustion completeness. Uncertainty estimate in parentheses (see text).

combustion completeness by mass is divided into size classes. Using percent combustion of each class measured on this fire and the distribution of these classes measured by *Carvalho et al.* [2001], we calculate 23.8% as the total combustion completeness for this fire. This corresponds to a total fuel consumption of 73 ± 22 Mg ha^{-1}.

[15] It was not possible to access the site immediately after convection ceased to measure intermediate fuel consumption before the onset of RSC. However, a rough idea of the magnitude of RSC fuel consumption was obtained as follows. The number of smoldering logs on the 4 ha site at noon on 6 September (the day after the fire) was 190 and at noon on 7 September, 39 logs were still smoldering. Extrapolation of a linear fit to these data suggests that the last log on the site finished smoldering at 1800 local time (LT) on 7 September and that at ∼1500 LT on 5 September, when convection from the site ceased, about 322 logs would have been smoldering. Using the average log diameter (measured at 15 cm), the average linear smoldering rate for a log (measured at 4 cm h^{-1}), and an average wood density of 0.5 g cm^{-3}, we estimate that ∼12 megagrams of fuel were consumed on the site by RSC. Thus about 3 Mg ha^{-1} of the total 73 Mg ha^{-1} fuel consumption (or about 4%) was by RSC. This is likely a lower limit since W. M. Hao and R. E. Babbitt (unpublished data, 2007) found that the rate of fuel consumption by RSC actually dropped off in exponential fashion. We would have needed additional counts of smoldering logs, especially some right after flaming had ceased, to support an exponential fit and the higher initial rate and extended smoldering time that it would imply. However, even if our rough estimate of

RSC fuel consumption is doubled it is still a fairly small percentage and in relatively good agreement with what can be gleaned from past fuel consumption measurements on tropical deforestation fires. In addition, the linear smoldering rate measured on this fire was slightly higher than measured on similar fires in similar fuels (0.6−2.4 cm h^{-1} [*Carvalho et al.*, 2001]; 0.7−3.8 cm h^{-1} [*Rabelo et al.*, 2004]).

[16] *Rabelo et al.* [2004] counted 59 smoldering logs greater than 10 cm diameter on a 4 ha planned deforestation fire 1 day after ignition. This constituted 2.9% of the estimated 2028 total logs on the site. They collected samples from 11 of these logs and subjected them to thermogravimetric analysis in the laboratory. Those 11 logs showed an average mass loss of 79.7% (±6.5%) during a controlled temperature change from 30°C to 700°C. Assuming the laboratory experiment was a fair simulation of smoldering on the deforestation site, 2.3% (2.9% × 0.797) of the total mass loss from the fire after 1 day was from smoldering. The authors noted some logs smoldering after several days and a single, large log still smoldering 43 days after the burn.

[17] As mentioned earlier, *Carvalho et al.* [1998, 2001] did not witness significant RSC for six planned deforestation fires, five of which were cut in one year and burned in the same year and one of which was burned the year after it was cut. However, while traveling to and from the sites listed in Table 1 we noted that widespread, thick, ground-level biomass burning haze developed in the early afternoon and persisted late into the evening. This indicates the presence of a significant regional RSC source. This source was most likely the common, concurrent pasture maintenance fires in the area. *Kauffman et al.* [1998] observed significant smoldering of residual wood debris for several days by three pasture fires where the initial burn covered the entire pasture in less than two hours. The biomass consumed on these fires was divided approximately in half between grass and RSC of wood debris. In this work we do not further quantify the regional fuel consumption by RSC. We do explore the effect on estimates of regional fire emissions based on reasonable assumptions about the amount of fuel consumed by RSC using our newly available regional RSC emission factors measured as described next.

3.2. Residual Smoldering Combustion Emission Ratios and Emission Factors

[18] Fourteen emissions measurements were made on RSC of logs on the planned deforestation fire and 10 on RSC of logs on the 3 deforestation fires that we were able to find in the area. One pasture maintenance fire was located in the area and it had smoldering logs from which we obtained 3 emissions measurements. This data set on smoldering logs is more extensive than previously published work on RSC. *Bertschi et al.* [2003a] reported the results for one spot measurement of a smoldering log in Zambia and the average of 11 spot measurements over the course of 34 hours on one cottonwood log that was burned in the Missoula Fire Sciences Laboratory. The spot measurements for the smoldering cottonwood log in that study were generally within ±20% of the fire-integrated emission factor for the whole fire; the emissions were relatively constant throughout the combustion of the whole log. Thus it may be appropriate to

Table 3. Normalized Excess Emission Ratios (ER) and Emission Factors (EF) for All Smoldering Logs in This Study

	Current Study (n = 27)		Zambian Log[a] (n = 1)	Cottonwood Log[a] (n = 11[b])
	Average	stdev		
ER, mol/mol				
MCE	0.788	(0.059)	0.854	0.856
$\Delta CO/\Delta CO_2$	0.275	(0.093)	0.171	0.166
$\Delta CH_4/\Delta CO$	0.143	(0.086)	0.256	0.182
$\Delta C_2H_4/\Delta CO$	0.0071	(0.005)	0.0133	0.0152
$\Delta C_2H_2/\Delta CO$	0.0005	(0.001)		0.0006
$\Delta C_3H_6/\Delta CO$	0.0046	(0.0036)	0.0086	0.0101
$\Delta HFo/\Delta CO$	0.0007	(0.0011)	0.0044	0.0046
$\Delta HAc/\Delta CO$	0.042	(0.028)	0.025	0.020
$\Delta HCHO/\Delta CO$	0.0080	(0.0046)	0.0205	0.0116
$\Delta CH_3OH/\Delta CO$	0.0411	(0.0243)	0.0446	0.061
$\Delta Phenol/\Delta CO$	0.0036	(0.0070)	0.0042	0.0092
$\Delta Acetol/\Delta CO$	0.0164	(0.0139)		
$\Delta Furan/\Delta CO$	0.0038	(0.0015)	0.0053	0.0053
$\Delta NH_3/\Delta CO$	0.0128	(0.0110)	0.0199	0.0056
$\Delta HCN/\Delta CO$	0.0015	(0.0013)		
EF, g kg^{-1} dry fuel				
CO_2	1343	(123)	1454	1469
CO	229	(64.6)	158	155
CH_4	17.1	(10.0)	23.2	16.2
C_2H_4	1.42	(0.79)	2.11	2.36
C_2H_2	0.07	(0.10)		0.08
C_3H_6	1.43	(1.12)	2.04	2.36
HFo	0.26	(0.40)	1.15	1.16
HAc	19.7	(12.9)	8.43	6.73
HCHO	1.88	(1.10)	3.48	1.92
MeOH	10.3	(6.03)	8.09	10.8
Phenol	2.42	(4.49)	2.26	4.78
Acetol	8.89	(7.53)		
Furan	2.08	(0.88)	2.04	2.01
NH_3	1.64	(1.44)	1.92	0.53
HCN	0.35	(0.34)		

[a]Data from *Bertschi et al.* [2003a].
[b]Average of 11 samples of one log from *Bertschi et al.* [2003a]. Current study is 27 samples of 25 different logs.

assume that each spot measurement in the current work is reasonably representative of the total emissions for each log sampled.

[19] The emission ratios (ER) reported here are quotients of excess mixing ratios ($\Delta X/\Delta Y$); the excess amount of compound X above background is divided by the excess amount of compound Y (CO or CO_2) above background. Emission factors (EF) are calculated using the carbon mass balance method [*Ward and Radke*, 1993], which assumes that all of the carbon from burned fuel is volatilized and measured. We assumed a fuel carbon content of 50% by mass on a dry weight basis. This is probably accurate to ±5% (1σ) of the actual value [*Susott et al.*, 1996]. More details of the calculations are given by *Yokelson et al.* [2003a]. The ER and EF for logs are reported in Table 3 along with the previously published values of *Bertschi et al.* [2003a]. The study averages differ to some degree, but such a simple comparison is a bit misleading as explained next.

[20] The modified combustion efficiency (MCE) for a sample is the ER $\Delta CO_2/(\Delta CO + \Delta CO_2)$. The MCE is related to the amount of fuel carbon converted to CO_2 and is useful as an indicator of the relative amount of flaming and smoldering in a fire. Low MCE near 0.8 are typical of smoldering combustion and higher MCE near 0.95 are typical of the more efficient, mostly flaming combustion

occurring in fine fuels such as grasses. Emission factors for fires featuring both flaming and smoldering are usually tightly correlated with MCE [*Yokelson et al.*, 2003a]. In contrast, Figure 3 shows EF versus MCE from this study and they are not tightly correlated. This is in agreement with EF from several smoldering fuels published by *Bertschi et al.* [2003a], who speculated that the scatter was due to fuel differences. However, in this study we find scatter even for nominally similar log fuels. Thus part of the scatter may be caused by varying degrees of log decomposition or differences in log-log spacing and the resulting heat transfer [*Bertschi et al.*, 2003a]. We encountered a broad range of MCE for the measurements of smoldering logs, roughly from 0.69 to 0.92. The average MCE for smoldering logs in the current study (0.788 ± 0.059) is lower than for the Zambian and cottonwood logs (0.855). However, the two MCE reported by *Bertschi et al.* [2003a] fall in the upper third of our range. More importantly, with the exception of formic acid, the previous EF fall within the range of our EF at similar MCE, as seen in Figure 3. Our current observation of lower formic acid in Brazil is consistent with the observation of lower than "normal" formic acid emissions in the concurrent airborne measurements of Brazilian fires by *Yokelson et al.* [2007]. Thus a tendency for burning Brazilian logs to emit less formic acid than burning logs
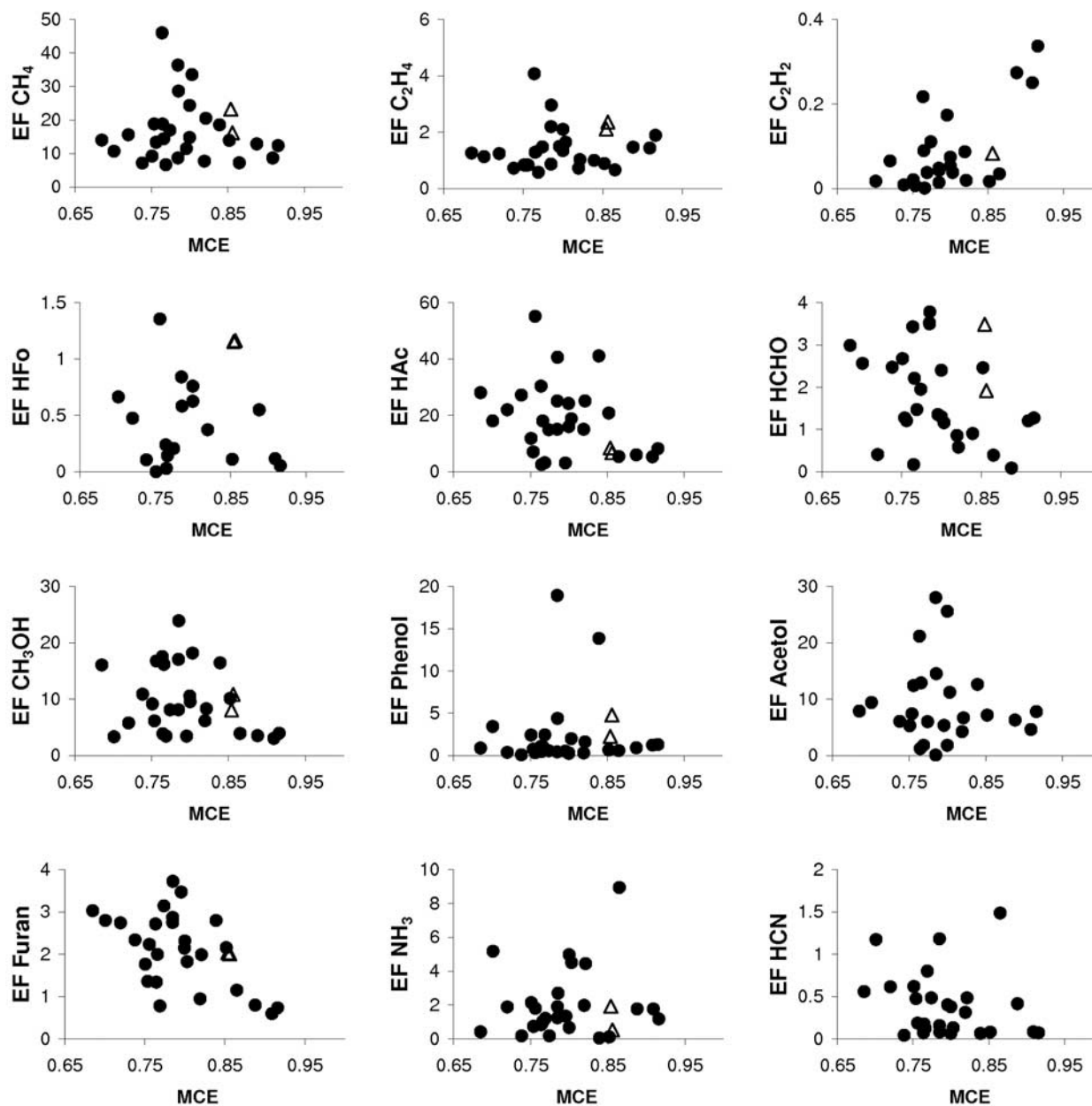
Figure 3. EF (g kg^{-1} dry fuel) versus MCE for 12 trace gases emitted from smoldering logs in the current study (solid circles) and in the study by *Bertschi et al.* [2003a] (open triangles). HFo, formic acid; HAc, acetic acid.

from elsewhere could underlie the observation of lower formic acid emissions in both the ground-based and airborne work in Brazil. However, with the exception of formic acid, the differences in study averages shown in Table 3 might not represent real differences between Brazil and Africa or temperate regions. It might be that the means of the current, larger data set give a better view of the average emissions for RSC of smoldering logs globally. In turn, the estimate of the effect of RSC on fire-integrated savanna fire EF by *Bertschi et al.* [2003a] could be reevaluated using our newer EF for RSC of logs. We have not done this, but note that the largest increases in a new analysis would be about 10% and 40% in the fire-integrated

EF respectively for CO and acetic acid. The largest decreases would occur for formic acid and formaldehyde.

[21] Acetol was not measured previously in the field for smoldering logs and is high relative to other gases (~1.6% of CO). This is comparable to laboratory measurements of acetol emissions from smoldering Indonesian biomass [*Christian et al.*, 2003]. During that study we compared our acetol determinations by FTIR to the mass 75 signal on a proton transfer reaction mass spectrometer (PTR-MS) and found good agreement for high signal to noise (S/N) samples but higher than expected FTIR retrievals for low S/N samples [*Christian et al.*, 2004]. The current study acetol determinations by FTIR were complicated by lower

Table 4. Calculated Effect of RSC on Emission Factors[a] for Deforestation and Pasture Fires[b]

	CO_2	CO	NH_3	CH_4	C_2H_4	C_2H_2	C_3H_6	CH_3OH	Phenol	Acetol	HCHO	HFo	HAc	Furan	HCN
							Deforestation[c]								
EF_{RSC}	1360	218	2.51	17.6	1.60	0.09	1.75	10.4	1.33	9.53	1.90	0.16	19.1	2.10	0.36
EF_{conv}	1683	60.0	1.24	3.36	0.64	0.92	0.09	2.26			1.74	0.98	3.59		2.10
EF_{tot}	1667	67.9	1.30	4.07	0.69	0.88	0.17	2.66			1.75	0.94	4.36		2.02
EF_{tot}/EF_{conv}	0.99	1.13	1.05	1.21	1.07	0.95	1.91	1.18			1.00	0.96	1.22		0.96
							Pasture[d]								
EF_{RSC}	1386	233	1.53	15.7	1.33	0.14	0.91	4.36	0.56	1.98	0.22	0.35	10.1	1.62	0.40
EF_{conv}	1596	112	1.37	6.93	1.24		0.73	2.88			1.92	0.52	4.18		0.54
EF_{tot}	1512	161	1.43	10.4	1.28		0.80	3.47			1.24	0.45	6.55		0.48
EF_{tot}/EF_{conv}	0.95	1.43	1.05	1.50	1.03		1.10	1.21			0.64	0.87	1.57		0.90

[a] g kg^{-1} dry fuel.
[b] Assumes 5% of the emissions from deforestation and 40% from pasture fires are from RSC.
[c] RSC and convected emissions data from the planned fire on fazenda Caiabí [see also *Yokelson et al.*, 2007].
[d] RSC data from site B, convected emissions data from a fire of opportunity in Mato Grosso [*Yokelson et al.*, 2007].

S/N in general. Acetol also has a relatively small absorption cross section and relatively broad spectral features that are overlain by, e.g., H_2O, NH_3, and molecules with C-O stretching vibrations.

[22] In general, Brazilian biomass fire and biofuel emissions (section 3.4) showed higher acetic acid than previously reported values. Acetic acid has relatively weak reactivity in the atmosphere [*Chebbi and Carlier*, 1996] with a low rate constant for reaction with OH [*Dagaut et al.*, 1988], can contribute to rainwater acidity [*Chebbi and Carlier*, 1996] with high solubility (k$°_H$ ≅ 5500 mol/kg bar, http://webbook.nist.gov/), and has been observed to increase in aging biomass burning plumes [*Goode et al.*, 2000; *Hobbs et al.*, 2003; *Yokelson et al.*, 2003a].

3.3. Impact of RSC on Regional Emissions

[23] We can estimate the total fire emissions for a trace gas using RSC EF for unlofted emissions from the current study; EF for lofted emissions from the concurrent, airborne study of *Yokelson et al.* [2007]; a realistic range of estimates for the relative amount of biomass consumed by RSC; and the equation of *Bertschi et al.* [2003a]:

$$EF_{i,tot} = f \times EF_{i,RSC} + (1 - f) \times EF_{i,conv} \qquad (2)$$

[24] $EF_{i,RSC}$ and $EF_{i,conv}$ are the emission factors measured for compound i during RSC and in the lofted (convected) plume, and f is the fraction of the fuel consumed by RSC. Although the pasture logs, or RWD, could have been considerably more aged than the logs on the deforestation fire, the average MCE for these two fuels were within 1% of each other (Table 4). The emissions results for these sites are explicitly incorporated in the analysis that follows. Figure 4 depicts the calculated effect of RSC on some selected emission factors. Each bar represents the range of $EF_{i,tot}$ expected for that compound for an assumed range of% RSC contribution. The deforestation data are airborne EF and ground-based EF (measured the next day) at the Caiabí planned fire. The airborne EF for pasture maintenance fires were acquired at a pasture fire SE of Alta Floresta on 29 August. The ground-based EF for pasture fires were made at site B (SW of Alta Floresta) on 2 September. Both sites are in the same, but diverse, vegetation classification. On the basis of limited published

data and our own observations we assumed ranges of 1–20% contribution of RSC to deforestation fires, and 10–50% for pasture fires. The dark bars are for deforestation fires and the light bars are for pasture maintenance fires. The arrows above each bar in Figure 4 indicate whether total EF increased (upward arrow) or decreased (downward arrow) with increasing % RSC. Note that CO_2, CO, CH_4, and acetic acid have been scaled to fit on the chart and their actual EF were 3, 2, 1, and 1 orders of magnitude greater than depicted, respectively. Also, we do not have acetylene or NO data for the convected plume from a pasture fire.

[25] One might anticipate that the difference between the EF determined in the lofted plume and the "true" EF that considers RSC as well would be small for deforestation fires since the lofted plume contains emissions from burning logs and the % RSC is small. In fact, there are fairly large increases in the improved fire-average estimate of the EF for CH_4, acetic acid, methanol, and propylene if 20% RSC is assumed (Figure 4). However, assuming a "typical" RSC of 5% (Table 4) leads to changes of no more than 22%, except for propylene. The propylene effect is large because the RSC EF for propylene at Caiabí was ~19 times larger than that measured in the lofted plume at Caiabí and ~4 times larger than the airborne study average EFC_3H_6. Overall, the effect of RSC on the fire-averaged EF for deforestation fires is not major and mostly a "fine-tuning." On the other hand, a realistic assumption of 40% RSC for pasture fires (see introduction) leads to adjustments on the order of 50% for 4 of 12 compounds considered (CO, CH_4, HCHO, and CH_3COOH). Thus RSC is of more concern when measuring or estimating emissions from this common type of Amazonian fire.

[26] Regional, bottom-up, emissions estimates are usually the product of an amount of biomass burned times an emission factor. By the early 1990s enough land had been converted to pasture in the Amazon basin to cause several authors to estimate that roughly equal amounts of biomass were consumed annually in pasture maintenance and primary deforestation fires [*Guild et al.*, 1998; *Kauffman et al.*, 1998]. If this is the case, then our EF for RSC could increase estimates of the annual regional fire emissions for several important VOC within the range of 10–50%. Photochemical box models indicate that an important effect of increased VOC would be to speed up the initial smoke
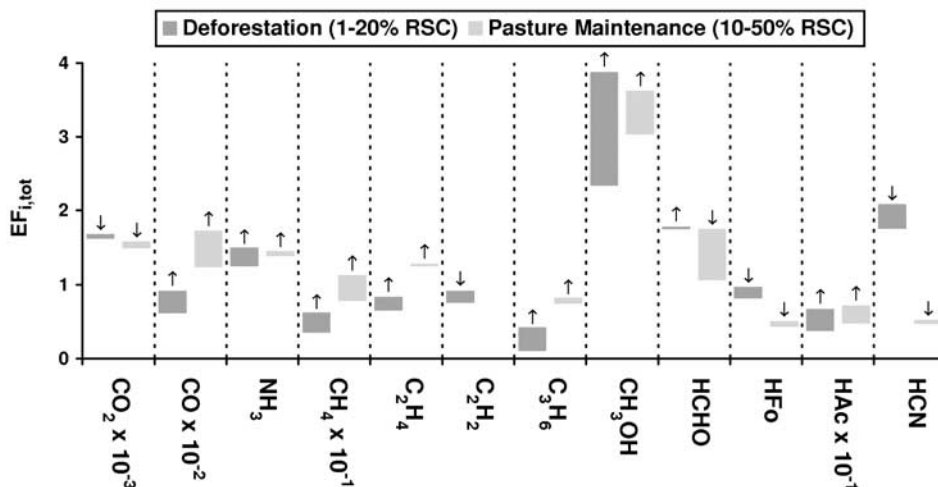
Figure 4. Varying effect of RSC on overall emission factor ($EF_{i,tot}$) for 12 trace gases emitted from smoldering logs measured during the planned deforestation fire (dark bars) and a pasture maintenance fire of opportunity (light bars). The length of each bar represents a range of calculated $EF_{i,tot}$ based on an assumed fractional contribution of RSC to the total mass of emissions (1–20% RSC contribution for deforestation, 10–50% for pasture maintenance). Each arrow depicts whether increasing the RSC contribution caused the level of that trace gas to increase (upward arrow) or decrease (downward arrow). Note that CO_2, CO, CH_4, and acetic acid (HAc) have been scaled to fit. HFo, formic acid.

photochemistry [*Mason et al.*, 2001, 2006; *Trentmann et al.*, 2005].

3.4. Emissions From Burning Dung, Late Stages of a Charcoal Kiln, and a Wood Cooking Fire in a Stove

3.4.1. Emissions From Burning Dung

[27] We measured the emissions from three separate burning cattle dung piles at the site B pasture fire. Table 5 gives the average ER and EF for these samples, with a comparison to data from laboratory fires burning dung collected in India [*Keene et al.*, 2006]. That study reported an average of 22 g carbon per kg dry fuel emitted in particles and 32.6% fuel carbon content on a dry weight basis for three dung samples. Our EF calculations incorporate those values. Without also making measurements in India and China, we cannot be sure how well our measurements represent burning dung in those areas. However, we can compare to the limited emissions data available for those regions. The samples of *Keene et al.* [2006] were from India and burned with nearly identical average MCE as the dung in the Brazil pasture. The MCE of ~0.84 is the same as the average for glowing combustion measured by *Yokelson et al.* [1997] and may indicate that this is an important burning mode for dung. (Glowing combustion produces about half the heat in a typical western fireplace.) On the other hand, *Smith et al.* [2000] sampled dung from India, burned it in a laboratory simulation of a rural kitchen, and observed a range of MCE from 0.88 to 0.97. Thus the MCE observed by *Keene et al.* [2006] and us might be lower than the average value in real Indian kitchens. If that were the case, the relevant EF for smoldering compounds could be lower than we report. However, *Smith et al.* [2000] report EF for one smoldering compound (CH_4) and they observed a range for $EFCH_4$ of 3–18 g/kg. The midpoint of their range, 10.5 g/kg is not much different from our

average $EFCH_4$ of 11 g/kg. On the basis of the reasonable agreement shown above and the expanded amount of trace gases we measured (see below) we believe our data is of value in understanding global dung fuel use, at least until more detailed measurements from Asia become available.

[28] Only 3 and 5 of the 13 compounds we report were measured by *Smith et al.* [2000] and *Keene et al.* [2006], respectively. Thus this work considerably expands our knowledge of the nature of these emissions. In comparison to *Keene et al.* [2006], our ER are ~1.5 times higher and our EF ~1.7 times higher, on average, for formic acid, acetic acid, and NH_3. Ammonia is a particle precursor and it influences particle inorganic composition and the gas/particle conversion of inorganic and organic anionic species [*Trebs et al.*, 2005, and references therein]. Organic acids are also of interest as particle precursors. Since the direct emission of particles is already quite large, direct emission and secondary formation of particles from burning dung could be quite significant in both India and sections of China where dung is a major biofuel. This is discussed in more detail in section 3.4.2.

[29] *Yevich and Logan* [2003] estimated global use of dung as a biofuel in 1985 at 136 (±50%) Tg DM (dry matter), of which India and China were responsible for the majority (93 and 20 Tg, respectively). *Habib et al.* [2004], using the novel approach of basing biofuel use calculations on food consumption statistics, estimated 35–108 Tg yr^{-1} dung burned in India for the year 2000. *Yevich and Logan* [2003] also predicted a 17% increase in total biofuel use from 1985 to 1995. If we assume an equal relative increase for all biofuel types then the 1995 global estimate for dung use is 159 Tg. (There is no direct indication in that study of whether dung use was expected to increase at the same rate as other biofuels. Also, declining fuelwood supply and increased use of mechanization will have had some effect

Table 5. Normalized Excess Emission Ratios (ER) and Emission Factors (EF) for Cattle Dung

	Current Study (n = 3)		Keene et al. [2006] (n = 2), Average
	Average	stdev	
ER, mol/mol			
MCE	0.837	(0.013)	0.836
$\Delta CO/\Delta CO_2$	0.195	(0.019)	0.196
$\Delta CH_4/\Delta CO$	0.19	(0.059)	
$\Delta C_2H_4/\Delta CO$	0.011	(0.002)	
$\Delta C_3H_6/\Delta CO$	0.012	(0.003)	
$\Delta HFo/\Delta CO$	0.0056	(0.004)	0.0037
$\Delta HAc/\Delta CO$	0.066	(0.034)	0.043
$\Delta CH_3OH/\Delta CO$	0.036	(0.011)	
$\Delta Phenol/\Delta CO$	0.0063	(0.001)	
$\Delta Acetol/\Delta CO$	0.036	(0.012)	
$\Delta Furan/\Delta CO$	0.0038	(0.001)	
$\Delta NH_3/\Delta CO$	0.089	(0.021)	0.068
$\Delta HCN/\Delta CO$	0.0053	(0.003)	
EF, [a]g kg^{-1} dry fuel			
CO_2	832	(15)	899
CO	104	(10)	106
CH_4	11.0	(3.3)	
C_2H_4	1.12	(0.23)	
C_3H_6	1.89	(0.42)	
HFo	0.91	(0.61)	0.50
HAc	14.3	(6.2)	7.85
MeOH	4.14	(0.88)	
Phenol	2.16	(0.36)	
Acetol	9.60	(2.38)	
Furan	0.95	(0.22)	
NH_3	5.55	(1.17)	3.54
HCN	0.53	(0.30)	

[a]EF calculations for current study include 22 g carbon per kg dry fuel emitted in particles and 32.6% fuel carbon content on a dry weight basis measured by *Keene et al.* [2006].

on the relative use of various biofuel types.) Combining this estimate with the EF for formic acid, acetic acid, and NH_3 from *Keene et al.* [2006] and our work (Table 5) leads us to estimated ranges of 0.08–0.14 Tg formic acid, 1.25–2.27 Tg acetic acid, and 0.56–0.88 Tg NH_3 emitted per year from dung in the mid 1990s. These represent ∼2, 14, and 7% of the total annual emissions of these compounds from biomass burning in the late 1990s as estimated by *Andreae and Merlet* [2001]. By comparison, *Christian et al.* [2003] combined their laboratory $EFNH_3$ measurements for Indonesian peat with the estimate of *Page et al.* [2002] for peat consumption during the anomalous 1997/1998 Indonesian fire events to calculate an estimated 28 Tg NH_3 emitted in that single fire season. This is nearly three times the *Andreae and Merlet* [2001] annual estimate of 10.3 Tg for NH_3 from biomass burning.

3.4.2. New Information Relevant to INDOEX

[30] The Indian Ocean Experiment (INDOEX) focused on pollutants transported from the Indian subcontinent over the Indian Ocean [*Ramanathan et al.*, 2001]. The acetonitrile/CO ratio observed was similar to that measured from burning savanna and woodland fuels and this suggested that most of the CO was due to biomass burning [*de Gouw et al.*, 2001; *Reiner et al.*, 2001]. On the other hand, the SO_y (SO_2 + particle sulfate) ratio to CO was 3–10 times higher than previously observed for biomass burning. This along with other particle chemistry results suggested that fossil fuel

burning produced most of the observed particles [*Novakov et al.*, 2000; *Lelieveld et al.*, 2001; *Reiner et al.*, 2001]. We briefly discuss the unusual energy use situation in India and propose preliminary evidence for a slightly modified interpretation.

[31] *Habib et al.* [2004] recently estimated biofuel use in India and reviewed earlier literature on this topic. *Venkataraman et al.* [2006] recently estimated open burning of crop waste, forest, and grasslands in India. *Dickerson et al.* [2002] reviewed fossil fuel burning in India. If we take the average of all the measurements both obtained and cited in the above papers, the following energy/burning picture emerges for India: all open forest and savanna burning, 32 Tg y^{-1}; open burning of crop waste, 148 Tg y^{-1}; total biofuel, 444 Tg y^{-1}; wood biofuel, 261 Tg y^{-1}; dung biofuel, 98 Tg y^{-1}; crop waste biofuel, 85 Tg y^{-1}; fossil fuel, 96 Tg y^{-1}. Some things to note are that total biomass burning is more than 6 times fossil fuel use and ∼70% of biomass burning is biofuel use. The biomass burning and fossil fuel use are not segregated between urban and rural areas and mixing of the emissions can occur before significant transport from the source region. The chemistry of Indian fuel or emissions is also noteworthy. For instance, *Dickerson et al.* [2002] note that two thirds of vehicles in India have 2-stroke engines to which they ascribe an enormous EFCO (∼800 g/kg). Thus burning a unit amount of fossil fuel in representative fashion likely produces far more CO in India than in developed countries. In addition, according to the energy data given above, about 40% of biofuel use and >50% of total biomass burning involve crop waste or dung. Both of these fuels are much higher in N and S than forest or grassland fuels [*Smith et al.*, 2000; *Keene et al.*, 2006], which indicates potential for much higher emissions of N- and S-containing trace gases. In fact, *Christian et al.* [2003] report an acetonitrile/CO emission ratio for burning rice straw that is about 12.5 times greater than that for savanna fuels. Thus observation of an acetonitrile/CO ratio in INDOEX that is "normal" for savanna burning does not imply that all the CO was produced by biomass burning. It would also not be surprising if the aerosol from Indian biomass burning was higher in sulfate than the global average. Finally, the mix of biomass burning that is common in India could produce far more particles than the mix of biomass burning that is common elsewhere. To support this we note the large EF for particles from burning dung measured by *Keene et al.* [2006] and also make another relevant point. Our $EFNH_3$ for dung is 5.6 ± 1.2 g/kg and *Christian et al.* [2003] report an $EFNH_3$ of 4.1 g/kg for burning rice straw and 0.3 g/kg for savanna fuels. According to *Brasseur et al.* [1999], about 93% of emitted NH_3 is sequestered in particles and the average particle in INDOEX was about 8% ammonium by mass [*Chowdhury et al.*, 2001; *Lelieveld et al.*, 2001]. The NH_3 emitted by Indian biomass burning will combine with particles, SO_2, and other gases from both biofuel and fossil fuel burning to generate additional particle mass downwind from the source region. If most of the NH_3 participated in new particle formation, then on the order of 50 g/kg of secondary aerosol would be generated. If most of the emitted NH_3 condenses on existing particles then this still generates an additional 5 g/kg of particle mass. Even this lower limit is significant since it is comparable to a typical,

Table 6. Normalized Excess Emission Ratios (ER, mol/mol) for Spot Measurements of Charcoal-Making Kilns

	Current Study (n = 3) (Day 6)		Bertschi et al. [2003b] (n = 3) (Days 1–4)	
	Average	SD	Average	SD
MCE	0.826	(0.014)	0.783	(0.042)
$\Delta CO/\Delta CO_2$	0.212	(0.020)	0.280	(0.071)
$\Delta CH_4/\Delta CO$	1.27	(0.050)	0.242	(0.073)
$\Delta C_2H_4/\Delta CO$	0.028	(0.002)	0.013	(0.002)
$\Delta C_2H_2/\Delta CO$	0.003	(0.0001)		
$\Delta C_3H_6/\Delta CO$	0.007	(0.003)	0.010	(0.005)
$\Delta HFo/\Delta CO$			0.003	(0.001)
$\Delta HAc/\Delta CO$	0.497	(0.272)	0.043	(0.031)
$\Delta HCHO/\Delta CO$	0.003	(0.002)	0.011	
$\Delta CH^3OH/\Delta CO$	0.067	(0.014)	0.111	(0.070)
$\Delta Phenol/\Delta CO$	0.021	(0.007)	0.009	(0.007)
$\Delta Acetol/\Delta CO$	0.038	(0.062)		
$\Delta Furan/\Delta CO$	0.002	(0.001)	0.005	(0.003)
$\Delta NH_3/\Delta CO$	0.257	(0.295)	0.006	(0.002)
$\Delta HCN/\Delta CO$	0.001	(0.0008)		

total savanna fire EFPM2.5 of ~5 g/kg. A complete analysis of Indian sources is beyond the scope of this paper, but the mostly new information discussed above suggests that fossil fuels and biomass burning contribute more evenly than previously believed to both the trace gas and particulate pollutants observed in the INDOEX haze.

3.4.3. Late Stage Charcoal Kiln Emissions

[32] Our spot measurements of emissions from a charcoal-making kiln are given in Table 6. Here we compare our results with the only other detailed trace gas emissions measurements from a kiln, which were obtained in Africa [Bertschi et al., 2003b]. We present ER only since EF calculations rely on carbon content, which changes constantly during the charcoal making process. We do not know the carbon content at the time of our spot measurements and we were only able to make one set of measurements on a single day. There are some glaring differences between the two sets of data. For example, $\Delta X/\Delta CO$ for CH_4, acetic acid, and NH_3 were ~5, 12, and 43 times higher from the Brazilian kiln than from the African kiln, while the Brazilian kiln means for HCHO and furan were ~60–70% lower. A number of factors might have contributed to these results. For example, the measurements in Africa were taken for 1–2 hours per day over the course of 4 days, which spanned the time from ignition to completion. These data were likely representative of the overall emissions from that particular kiln. The Brazilian kiln measurements were taken for 1–2 hours on a single day approximately 6 days into the carbonization process, and represent only a snapshot with respect to overall emissions.

[33] Interestingly enough, the Brazilian kiln measurements may partially reflect the continuation of patterns exhibited in the multiday record from the African kiln. For instance, CH_4 and acetic acid emissions increased from the African kiln from day 1 to day 4 and were very large in the day 6 measurements from the Brazilian kiln. Figure 5 shows steadily increasing total VOC to CO emission ratios over the course of 6 days after combining the African and Brazilian kiln measurements. Despite the agreement with a possible trend in total VOC, the CH_4 and acetic acid

emissions from the Brazilian kiln were huge in comparison to other work and likely do not represent a defensible average situation for any overall charcoal-making process. We also note that not all species were consistent with increased emissions with time. For instance, HCHO emissions decreased in Africa and were "low" from the day 6 sample of the Brazilian kiln while methanol increased strongly with time from the African kiln but was also low from the Brazilian kiln. We do not know the uncertainties in the daily values for the African kiln and some of the patterns discussed may not be statistically significant. However, the possibility that VOC/CO increases with time is intriguing and may help interpret this and other work. The much higher average NH_3 emissions from the Brazilian kiln (factor of ~43) almost certainly indicate a much higher N content for the kiln charge in Brazil. In general, the measured, average MCE were within ~5% of each other and the similar MCE with some widely varying ER suggests that some real differences could occur in the chemistry or geometry of the kiln charge and/or the combustion chemistry versus time. More work would be needed to determine the relative importance of the fuel chemistry and geometry as opposed to any trends in the combustion chemistry that may occur as the carbonization process is extended in time.

3.4.4. Wood Cooking Fire in a Stove

[34] The single cooking fire measurement during this study was taken from the home of the family-owned site E (Table 1). A small fire was burning, mostly by glowing combustion, in the firebox of a cast iron wood stove/oven. Smoke from the stove rose through a metal chimney to exit through the roof, where the FTIR sample was taken. The emissions from this fire were quite different from those reported by Bertschi et al. [2003b], who measured the emissions from three open, indoor, wood cooking fires in rural Zambia. Table 7 gives ER and EF for both these studies. The EFNH$_3$ for the Brazilian, enclosed cooking fire was 221 times lower than for the open cooking fire in Zambia. Since our Brazilian kiln, which also used local wood, had an EFNH$_3$ that was 43 times higher than a Zambian kiln, the extremely low Brazilian stove values suggest that adsorption and/or reaction of NH_3 on the walls
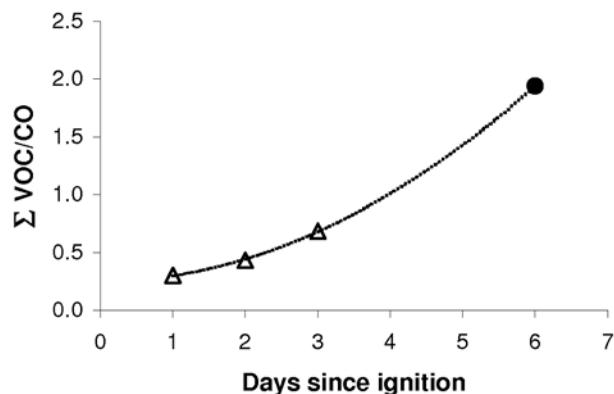
Figure 5. Increasing total $\Delta VOC/\Delta CO$ over the course of several days for charcoal making kilns. The open triangles represent data of Bertschi et al. [2003b]; the solid circle is from the current study. The dashed line visually indicates the trend.

Table 7. Normalized Excess Emission Ratios (ER) and Emission Factors (EF) for Wood Cooking Fires

	Current Study (Stove Exhaust) (n = 1)	Zambia[a] (Open Fire) (n = 3) Average	Current/ Zambia
ER, mol/mol			
MCE	0.856	0.910	
$\Delta CO/\Delta CO_2$	0.168	0.0989	
$\Delta CH_4/\Delta CO$	0.051	0.19	
$\Delta C_2H_4/\Delta CO$	0.0030	0.0245	
$\Delta C_2H_2/\Delta CO$	0.0002	0.019	
$\Delta C_3H_6/\Delta CO$	0.0010	0.0066	
$\Delta HFo/\Delta CO$	0.0019	0.0043	
$\Delta HAc/\Delta CO$	0.138	0.039	
$\Delta HCHO/\Delta CO$	0.0163	0.0342	
$\Delta CH_3OH/\Delta CO$	0.0665	0.0351	
$\Delta Phenol/\Delta CO$	0.0002	0.0103	
$\Delta Acetol/\Delta CO$	0.0468		
$\Delta Furan/\Delta CO$	0.0023	0.0017	
$\Delta NH_3/\Delta CO$	0.0001	0.0221	
$\Delta HCN/\Delta CO$	0.0005		
$\Delta NO/\Delta CO_2$		0.0016	
$\Delta NO_2/\Delta CO_2$		0.0003	
EF, g kg^{-1} dry fuel			
CO_2	1449	1525	0.95
CO	155	96	1.62
CH_4	4.5	10.6	0.43
C_2H_4	0.47	2.35	0.20
C_2H_2	0.03	1.67	0.02
C_3H_6	0.22	0.95	0.24
HFo	0.48	0.68	0.70
HAc	45.9	8.12	5.66
HCHO	2.71	3.52	0.77
MeOH	11.8	3.61	3.27
Phenol	0.08	3.32	0.02
Acetol	19.2		
Furan	0.88	0.4	2.19
NH_3	0.005	1.29	0.004
HCN	0.07		
NO	0.24	1.72	0.14
NO_2		0.49	

[a]From *Bertschi et al.* [2003b].

of the chimney made a major contribution to the very low NH_3 emissions from the stove [*Yokelson et al.*, 2003b]. Phenol, which is also known as a "sticky" compound had an EF from the Brazilian stove that was ~50 times lower than from the open cooking fires. However, acetic acid, which is also subject to some surface losses [*Yokelson et al.*, 2003b] was ~3.5 times higher from the Brazilian stove. The higher acetic acid emissions could be rooted in fuel chemistry since all fuels investigated in both Brazil and Africa showed 2–10 times higher acetic acid in Brazil (Tables 3, 6, and 7). We also note that hydrocarbon emissions were lower from the Brazilian stove than the open cooking fires in Africa. Acetylene was about 90 times lower and the other hydrocarbons were ~4–8 times lower; even though MCE was lower for the Brazil stove. This is not easily rationalized and more work would be needed to determine the natural variability and the relative impacts of fuel, combustion, and surface chemistry on the emissions.

[35] Cooking fires are a major global public health issue. The latest WHO/UNICEF estimates give total global annual mortality for children under 5 as 10–11 million [*Wardlaw et al.*, 2006; http://www.who.int/mdg/goals/goal4/en/]. About 1 million of those deaths are attributed by WHO to acute respiratory infections that resulted from exposure to smoke from indoor cooking fires [*Murray and Lopez*, 1996; Table in annex 11 on web at http://www.who.int/whr/2002/annex/en/index.html; K. Smith, personal communication, 2007]. Stoves with chimneys could be an important public health measure since they vent the emissions outside the home [*Naeher et al.*, 2001]. However, the chimney will still add pollutants to the ambient air and surfaces in the chimney may modify the emissions. Detailed measurements of both open and closed cooking fire emissions are still very limited. Our initial data suggest that changes in both indoor smoke concentration and outdoor smoke chemistry might impact the health of rural inhabitants switching to stoves with chimneys.

4. Conclusions

[36] Earlier work showed that both lofted, and initially unlofted emissions from residual smoldering combustion (RSC), are emitted in significant amounts by fires associated with tropical deforestation in the Brazilian Amazon. In this work, fuel consumption measurements on a planned deforestation fire during the 2004 dry season were consistent with earlier estimates that RSC accounts for about 5% of fuel consumption on deforestation burns and that Amazonian RSC occurs mostly in the residual woody debris that is a major fuel component for pasture maintenance fires.

[37] We used a cart-based FTIR to measure the RSC emissions from 25 smoldering Brazilian logs of H_2O, CO_2, CO, CH_4, three hydrocarbons, seven oxygenated volatile organic compounds, NH_3, HCN, and NO. This probably represented 17 of the ~25 most abundant trace gas emissions. The RSC emissions from Brazilian logs were highly variable and the few, earlier RSC emissions measurements for logs in Zambia and in the Missoula combustion facility were found to lie near the high end of combustion efficiency observed in this study. Thus this study suggests that both lower combustion efficiency and higher emissions for several VOC could be widely appropriate for RSC compared to the findings of the earlier, less extensive measurements. However, more work would be needed to explore variation that might occur in RSC emissions globally or interannually. When the RSC EF are compared to EF measured on the same or nearby fires in lofted plumes they are 2–3 times higher for most smoldering compounds such as VOC [*Yokelson et al.*, 2007] and EFCH$_3$OH and EFCH$_3$COOH were 4 and 5.7 times higher, respectively.

[38] We estimated the effect that RSC emissions could have on the total fire emissions for the Amazon region. For deforestation fires, we derive increases on the order of 20% for methanol, propylene, and acetic acid. For pasture fires, which may be the most common fire-type in the Amazon, increases of 20–50% were derived for 4 VOC. Overall, RSC could increase regional emissions of several reactive VOC by 20–50% and lead to faster regional photochemistry.

[39] We obtained the most chemically comprehensive measurements to date of the emissions from burning dung in a pasture. The emission ratios for acetic acid and NH_3 to CO for burning dung were very high (~7–9%). The large EFNH$_3$ of ~5.6 g/kg represents potential for a large post-

emission increase in particle mass. Dung is an important household fuel in south Asia. The extrapolation of our Brazilian EF to Asia, along with other recent information, suggests that biomass burning and fossil fuel use may have contributed more evenly than previously believed to the particles and trace gases found in the dry season haze over the Indian Ocean.

[40] One spot measurement of the emissions from a charcoal kiln was made later in the charcoal-making process than in earlier studies and the results suggested that the VOC/CO emission ratio may increase as the carbonization period is extended.

[41] One spot measurement of the chimney exhaust from a cast iron wood cooking stove showed many compounds in amounts that were far below the range observed for indoor, open, wood cooking fires in Zambia. Stoves with chimneys improve indoor air quality and public health, but enclosed/vented combustion devices may also impact outdoor air quality. For instance, the stove exhaust contained extremely low NH_3, possibly because of adsorption on chimney walls.

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