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Recommended Citation

Bertschi, I. T., R. J. Yokelson, D. E. Ward, T. J. Christian, and W. M. Hao, Trace gas emissions from the production and use of domestic biofuels in Zambia measured by open-path Fourier transform infrared spectroscopy, *J. Geophys. Res.*, 108(D13), 8469, doi:10.1029/2002JD002158, 2003.

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Trace gas emissions from the production and use of domestic biofuels in Zambia measured by open-path Fourier transform infrared spectroscopy

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Received 1 February 2002; revised 10 June 2002; accepted 10 June 2002; published 13 February 2003.

[1] Domestic biomass fuels (biofuels) were recently estimated to be the second largest source of carbon emissions from global biomass burning. Wood and charcoal provide approximately 90% and 10% of domestic energy in tropical Africa. In September 2000, we used open-path Fourier transform infrared (OP-FTIR) spectroscopy to quantify 18 of the most abundant trace gases emitted by wood and charcoal cooking fires and an earthen charcoal-making kiln in Zambia. These are the first in situ measurements of an extensive suite of trace gases emitted by tropical biofuel burning. We report emission ratios (ER) and emission factors (EF) for (in order of abundance) carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), acetic acid (CH₃COOH), methanol (CH₃OH), formaldehyde (HCHO), ethene (C₂H₄), ammonia (NH₃), acetylene (C₂H₂), nitric oxide (NO), ethane (C₂H₆), phenol (C₆H₅OH), propene (C₃H₆), formic acid (HCOOH), nitrogen dioxide (NO₂), hydroxyacetaldehyde (HOCH₂CHO), and furan (C₄H₄O). Compared to previous work, our emissions of organic acids and NH₃ are 3–6.5 times larger. Another significant finding is that reactive oxygenated organic compounds account for 70–80% of the total nonmethane organic compounds (NMOC). For most compounds, the combined emissions from charcoal production and charcoal burning are larger than the emissions from wood fires by factors of 3–10 per unit mass of fuel burned and ~2 per unit energy released. We estimate that Zambian savanna fires produce more annual CO₂, HCOOH, and NO_x than Zambian biofuel use by factors of 2.5, 1.7, and 5, respectively. However, biofuels contribute larger annual emissions of CH₄, CH₃OH, C₂H₂, CH₃COOH, HCHO, and NH₃ by factors of 5.1, 3.9, 2.7, 2.4, 2.2, and 2.0, respectively. Annual CO and C₂H₄ emissions are approximately equal from both sources. Coupling our data with recent estimates of global biofuel consumption implies that global biomass burning emissions for several compounds are significantly larger than previously reported. Biofuel emissions are produced year-round, disperse differently than savanna fire emissions, and could strongly impact the tropical troposphere.

INDEX TERMS: 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; *KEYWORDS:* oxygenated organic compounds, biomass burning, biofuel, fuelwood, charcoal, biomass energy

Citation: Bertschi, I. T., R. J. Yokelson, D. E. Ward, T. J. Christian, and W. M. Hao, Trace gas emissions from the production and use of domestic biofuels in Zambia measured by open-path Fourier transform infrared spectroscopy, *J. Geophys. Res.*, 108(D13), 8469, doi:10.1029/2002JD002158, 2003.

1. Introduction

[2] Biomass burning is a globally important source of gases and particles in the atmosphere [Crutzen and Andreae, 1990]. Approximately 80% of biomass burning occurs in the tropics [Crutzen and Andreae, 1990]. Savanna fires and domestic biofuel use are the two main types of biomass burning consuming about 3160 and 2701 Tg dry mass (dm) yr⁻¹, respectively [Andreae and Merlet, 2001]. Biofuels are the main source of energy in almost all African countries providing 90–98% of residential energy and ~75% of the total primary energy in all of sub-Saharan Africa (excluding

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the Republic of South Africa) [FAO, 1999]. Zambia has the 12th largest annual biofuel consumption rate out of 55 countries in Africa. Wood and charcoal are the major biofuels in tropical Africa and they accounted for ~90% and 10%, respectively, of the Zambian annual biofuel use from 1980 to 1994 [FAO, 1999]. Wood is the major fuel in rural areas and charcoal is used mostly in urban areas [Chidumayo, 1994].

[3] Despite the fact that biofuel fires are the second largest type of global biomass burning, there were very few emissions data for biofuel use [Andreae and Merlet, 2001]. Therefore, as part of SAFARI 2000, we used open-path Fourier transform infrared (OP-FTIR) spectroscopy to measure the trace gases emitted from several wood and charcoal fires and an earthen charcoal-making kiln in Zambia during the second week of September 2000. We quantified 18 of the most abundant emissions. These are the first in situ measurements of an extensive suite of trace gases emitted from the production and use of biofuels in the tropics.

2. Experimental Details

2.1. Description of the OP-FTIR System

[4] The OP-FTIR system was described previously by Yokelson *et al.* [1997] so only a brief description emphasizing updates is given here. The key elements are an FTIR spectrometer (MIDAC 2500) and unenclosed, multipass optics (1.6 m basepath) mounted on Super-Invar, Teflon-coated girders (see Figure 1). The IR beam from the spectrometer is directed into the open-path White cell (Infrared Analysis, Inc.) by in-house transfer optics. The White cell path length was either 38.4 or 51.2 m in the work reported here. The White cell exit beam is focused onto an LN₂-cooled, mercury-cadmium-telluride (MCT) detector (Graseby, FTIR-M16). The system can measure the mid-infrared spectrum (400–4000 cm⁻¹) of the optical path every 0.83 s with a spectral resolution of 0.5 cm⁻¹. The spectra are stored on a laptop computer and later analyzed to yield the mixing ratios for stable and reactive gases as described in section 2.3.

2.2. Sources of Biofuel Emissions and Measurement Configurations

[5] Kaoma, Zambia served as a central base for all the measurements described in this paper. Kaoma is a small city located about 400 km west of Lusaka in the Western Province of Zambia. Subsistence agriculture is practiced by a majority of the inhabitants of the large rural region surrounding Kaoma. Detailed photographs that complement the experimental descriptions below can be viewed at <http://www.umt.edu/chemistry/faculty/yokelson/galleries/s2k/index.htm>.

2.2.1. Wood Cooking Fires

[6] In rural areas of Zambia, open wood fires are the main source of heat for cooking. We measured the emissions from three open wood cooking fires that were built and tended by local residents in both Kaoma (1 fire) and the remote village of Milumbwa (2 fires; location ~50 km west of Kaoma on a one-lane dirt road). The cooking fire in Kaoma was in a sheltered area of the backyard of our rented house and the Milumbwa cooking fires were conducted inside traditional huts (~2 × 2 m floor area). The fires in both locations were

built with the regions most commonly used firewood (the Miombo tree species *Julbernardia* sp. and *Brachystegia* sp.). The fuel was typically 3–5 pieces of small diameter (2.5–7.0 cm) wood branches or logs with their long axes arranged radially. The fires were ignited at the center of the group where they burned gently (to minimize wasted heat or wood). The wood was pushed toward the center as the fire burned and quickly extinguished after cooking. At both locations, the OP-FTIR was supported by shipping crates ~1 m above the fires and weak convection from the fires directed the emissions through the optical path of the open White cell. Spectra were acquired continuously over the course of each fire with each individual spectrum lasting 3–11 s. Background spectra were collected in clean air upwind of the fires before and after each fire. We used a hand-held, chromel-alumel thermocouple and a portable, digital barometer (Cole-Parmer) to measure the temperature and pressure in the OP-FTIR optical path. AC power was available for the FTIR and computer in Kaoma, but they were powered by automotive batteries in Milumbwa and other rural locations.

2.2.2. Charcoal Cooking Fires

[7] Charcoal is used mostly in urban areas and it is normally burned in a rudimentary stove or metal container. We measured the emissions from one charcoal cooking fire in Kaoma. The charcoal was produced locally from the same tree species used for firewood above and it was burned in a simple stove consisting of an open, perforated metal cylinder supported by three legs and underlain by a “floor” to catch ashes. The OP-FTIR deployment was the same as for the wood cooking fires (described above).

2.2.3. Earthen Charcoal-Making Kiln

[8] Charcoal is produced in rural areas for use mainly in urban areas. Our kiln study site was in a remote clearing in the Miombo woodland ~20 km SE of Kaoma (14.86°S, 24.82°E). Local residents experienced in charcoal making constructed the kiln and tended it throughout the experiment. The wood used for making the charcoal (*Julbernardia* sp. and *Brachystegia* sp.) was felled nearby and cut into logs 1–2 m in length. After drying, the logs were stacked ~1.5 m high. Soil clumps (~40 × 40 × 20 cm) that were held together by dry grass roots were excavated next to the wood stack and used to encase the wood in an earthen layer 20–40 cm thick. This was a small kiln designed to produce five bags of charcoal weighing ~40 kg each. The wood was ignited through a small opening at one end of the kiln on the morning of 10 September. A few minutes after ignition, the opening was sealed with more soil clumps to reduce airflow into the kiln and promote carbonization of the wood charge. On the morning of 14 September, the kiln was broken to retrieve the charcoal.

[9] The kiln emissions emanated from numerous small holes in the walls and they were conveniently directed horizontally by a strong easterly wind through the optical path of the OP-FTIR system, which was operated as described above. Background spectra were collected in a smoke-free area upwind of the kiln before and after each smoke measurement. Because of the need to sample both cooking fires and kiln emissions within 1 week and at different locations, we could not measure the kiln emissions continuously. Instead, we collected three extended measurements of the emissions lasting ~1–2 hours each on 10, 11,

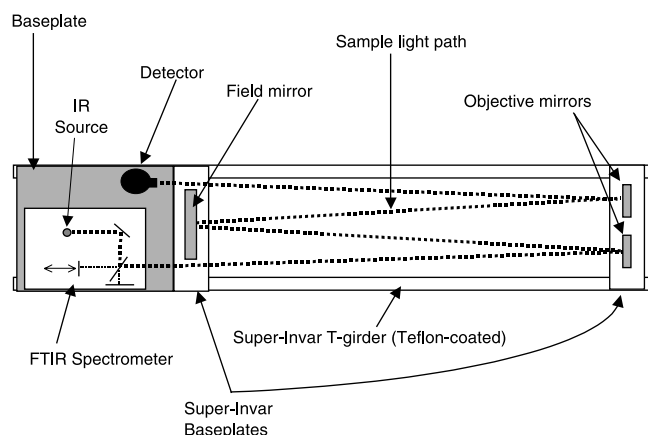


Figure 1. A simplified, top view schematic (not to scale) of the OP-FTIR we deployed in Zambia to measure the trace gas emissions from the production and use of biofuels.

and 13 September, which spanned the 4-day lifetime of the kiln. We estimate the charcoal yield (charcoal produced dry mass (dm)/wood used dm) and the charcoal carbon content based on previous work [Chidumayo, 1994; Lacaux *et al.*, 1994; Ishengoma *et al.*, 1997; Smith *et al.*, 1999; Pennise *et al.*, 2001].

2.3. Analysis of the OP-FTIR Spectra

[10] We obtained absolute mixing ratios for H₂O, nitrous oxide (N₂O), carbon dioxide (CO₂), carbon monoxide (CO), and methane (CH₄) by fitting regions of the transmission, or “single-beam,” spectra with synthetic calibration classical least squares (CLS) methods described in detail elsewhere [Griffith, 1996; Yokelson *et al.*, 1996, 1997; Yokelson and Bertschi, 2002]. The excess mixing ratios in the smoke (ΔX for a species “X”) are the absolute mixing ratios in the smoke spectra minus the absolute mixing ratios in the appropriate background spectra. We also generated absorbance spectra of the smoke using background spectra obtained between the smoke measurements. We analyzed these absorbance spectra by synthetic calibration CLS to directly yield excess mixing ratios in smoke for formaldehyde (HCHO), ethane (C₂H₆), acetylene (C₂H₂), nitric oxide (NO), nitrogen dioxide (NO₂), and ammonia (NH₃). Analysis of these absorbance spectra by spectral subtraction [Yokelson *et al.*, 1997] directly yielded excess mixing ratios in the smoke for H₂O, ethene (C₂H₄), propene (C₃H₆), acetic acid (CH₃COOH), methanol (CH₃OH), formic acid (HCOOH), phenol (C₆H₅OH), furan (C₄H₄O), hydroxyacetaldehyde (HOCH₂CHO), and NH₃. The above compounds accounted for all of the significant features in the spectra collected during this study. The detection limit for each species depended on the amount of signal averaging and the analysis method, but was usually in the range 5–20 ppbv. For most of the spectra, the excess mixing ratios retrieved for all of the reported species were 20–1000 times higher than the detection limit and the uncertainty for a typical excess mixing ratio was $\sim\pm 5\%$ (1 σ). However, the excess mixing ratios for N₂O were near our detection limit so we do not present results for this compound. We did not find features in the spectra from this study (or in the spectra from a separate study of smoldering logs in Zambia [Bertschi *et*

al., 2003]) that were due to a number of compounds sometimes reported in smoke such as acetonitrile, OCS, and HCN. HCN was a major emission from savanna fires [Yokelson *et al.*, 2003].

3. Results and Discussion

[11] As noted above, we were able to quantify 18 of the 19 trace gases identified as emissions during the combustion of biofuels. Since IR spectroscopy can measure most gases present above 5–20 ppb [Goode *et al.*, 1999] and these species accounted for all of the major features in our smoke spectra, they are then 18 of the most abundant emissions. The main trace gases that were probably emitted, but not detected here are H₂ [Cofer *et al.*, 1996] and N₂ [Kuhlbusch *et al.*, 1991], which are weak absorbers of IR.

3.1. Calculation of Emission Ratios (ER)

[12] The excess mixing ratios (ΔX , the mixing ratio of species “X” in the smoke minus the mixing ratio of “X” in the background air) that are observed in biomass burning studies reflect the degree of dilution of the smoke at the point of measurement. Thus, a more widely used, derived quantity is the normalized excess mixing ratio where ΔX is compared to a simultaneously measured smoke tracer such as ΔCO or ΔCO_2 . A measurement of $\Delta X/\Delta CO$ or $\Delta X/\Delta CO_2$ made in nascent smoke ($< \sim 5$ min old) is an ER. We used the fire-integrated excess mixing ratios to calculate fire-average ERs. The fire-average ER for each wood cooking fire and the study-average ER for all the wood cooking fires are shown in Table 1. The fire-average ER for the charcoal cooking fire is shown in Table 2. For the charcoal kiln, we calculated an ER for each day and averaged them together to obtain the kiln-average ER. These ER are reported in Table 3. We include in Tables 1, 2, and 3 the previously measured ER for biofuel use to facilitate comparisons (next).

3.2. Comparison of ERs With Previous Work

3.2.1. Wood Cooking

[13] Four previous studies measured some of the emissions from open wood cooking fires. Kituyi *et al.* [2001] measured trace gas emissions from wood burned in both open fires and different types of stoves. They found that the use of various stoves strongly influenced the mix of trace gases emitted. Therefore, we limit this discussion to open wood cooking fires, which are what we sampled and the most common type of cooking fire in Africa.

[14] The ER $\Delta CO/\Delta CO_2$ and the modified combustion efficiency (MCE) ($\Delta CO_2/(\Delta CO_2 + \Delta CO)$) indicate both the relative amount of the two main emissions and the relative amount of flaming and smoldering combustion during a fire. Higher $\Delta CO/\Delta CO_2$ or lower MCE indicates more smoldering [Ward and Radke, 1993]. Kituyi *et al.* [2001, Table 1] reported an average ER $\Delta CO/\Delta CO_2$ of 0.072 ± 0.03 for 20 open wood cooking fires in Kenya. Brocard *et al.* [1996] sampled 43 open wood cooking fires in the Ivory Coast. They described these fires as having four “phases” and estimated that $\sim 80\%$ of the wood was consumed in the “cooking phase,” which had an ER $\Delta CO/\Delta CO_2$ of 0.057 ± 0.011 . The other phases consumed less fuel and had ER $\Delta CO/\Delta CO_2$ from 0.15 to 0.26. They

Table 1. ERs and EFs for Open Wood Cooking Fires

	ERs										Average EFs (g kg ⁻¹ dm)						
	This Work					Brocard <i>et al.</i> [1996]		Smith <i>et al.</i> [2000]		Kituyi <i>et al.</i> [2001]		Ludwig <i>et al.</i> [2003]		Trace Gas	This Work ^a	Brocard <i>et al.</i> [1996]	Smith <i>et al.</i> [2000]
	Fire 1	Fire 2	Fire 3	Average	SD	Average	SD	Average	SD	Average	SD	Average	SD				
MCE	0.933	0.906	0.892	0.910	0.021	0.927	0.021	0.966	0.933	0.913	0.022	0.933	0.022	CO ₂	1525	1467	1455
ΔCO/ΔCO ₂	0.0716	0.1035	0.1217	0.0989	0.0254	0.079	0.015	0.035	0.072	0.095	0.022	0.072	0.022	CO	96	70	62
ΔCH ₄ /ΔCO	0.1957	0.1491	0.2334	0.1930	0.0420	0.048	0.0014	0.369	0.072	0.03	0.022	0.072	0.022	CH ₄	10.6	2.0	6.1
ΔC ₂ H ₆ /ΔCO	0.0142	0.0116	0.0178	0.0145	0.0031	0.048	0.0014	0.369	0.072	0.03	0.022	0.072	0.022	C ₂ H ₆	1.50		
ΔC ₂ H ₄ /ΔCO	0.0380	0.0141	0.0213	0.0245	0.0123	0.048	0.0014	0.369	0.072	0.03	0.022	0.072	0.022	C ₂ H ₄	2.35		
ΔC ₂ H ₂ /ΔCO	0.0267		0.0107	0.0187	0.0024	0.048	0.0014	0.369	0.072	0.03	0.022	0.072	0.022	C ₂ H ₂	1.67		
ΔC ₃ H ₄ /ΔCO	0.0038	0.0082	0.0079	0.0066	0.0024	0.048	0.0014	0.369	0.072	0.03	0.022	0.072	0.022	C ₃ H ₄	0.95		
ΔHAc ^b /ΔCO	0.0634	0.0202	0.0348	0.0394	0.0219	0.008	0.004	0.005	0.072	0.03	0.022	0.072	0.022	HAc	8.12	1.27	
ΔHFo ^c /ΔCO	0.0090	0.0018	0.0022	0.0043	0.0040	0.001	0.0005	0.005	0.072	0.03	0.022	0.072	0.022	HFo	0.68	0.12	
ΔCH ₂ O/ΔCO	0.0464	0.0270	0.0291	0.0342	0.0106	0.001	0.0005	0.005	0.072	0.03	0.022	0.072	0.022	CH ₂ O	3.52		
ΔGA ^d /ΔCO			0.0027	0.0027	0.0027	0.001	0.0005	0.005	0.072	0.03	0.022	0.072	0.022	GA	0.66		
ΔCH ₃ OH/ΔCO	0.0492	0.0172	0.0390	0.0351	0.0164	0.001	0.0005	0.005	0.072	0.03	0.022	0.072	0.022	CH ₃ OH	3.61		
ΔC ₄ H ₂ OH/ΔCO		0.0103		0.0103		0.001	0.0005	0.005	0.072	0.03	0.022	0.072	0.022	C ₄ H ₂ OH	3.32		
ΔC ₄ H ₄ O/ΔCO		0.0017		0.0017		0.001	0.0005	0.005	0.072	0.03	0.022	0.072	0.022	C ₄ H ₄ O	0.40		
ΔNMOC ^e /ΔCO	0.2506	0.1121	0.1654	0.1760	0.0699	0.081	0.03	0.465	0.083	0.0019	0.0006	0.0010	0.0004	gC(NMOC)	26.78	3.04	5.89
ΔNO/ΔCO ₂	0.0021	0.0020	0.0009	0.0016	0.0007	0.001	0.0005	0.005	0.083	0.0019	0.0006	0.0010	0.0004	NO	1.72		
ΔNO ₂ /ΔCO ₂	0.0005	0.0003	0.0002	0.0003	0.0002	0.001	0.0005	0.005	0.083	0.0019	0.0006	0.0010	0.0004	NO ₂	0.49		
ΔNO _x /ΔCO ₂	0.0026	0.0022	0.0011	0.0020	0.0008	0.0015	0.0004	0.004	0.0015	0.0004	0.0004	0.0004	0.0004	NO _x as NO	2.04	1.48	
ΔNH ₃ /ΔCO	0.0192	0.0204	0.0266	0.0221	0.0040	0.0015	0.0004	0.004	0.0015	0.0004	0.0004	0.0004	0.0004	NH ₃	1.29		

^aComputed from average ERs.^bHAc = acetic acid.^cHFo = formic acid.^dGA = glycolaldehyde, Other names include hydroxyacetaldehyde and hydroxyethanal.^eFor Brocard *et al.*, we calculated NMOC by adding their organic acid values to their ΣNMHC.

Table 2. ERs and EFs for Charcoal Cooking Fires

	ERs								EFs (g kg ⁻¹ Dry Charcoal Burned)				
	This Work	<i>Kaoma and Kasali</i> [1994]		<i>Brocard et al.</i> [1996]		<i>Smith et al.</i> [2000]		<i>Kituyi et al.</i> [2001]		Compound	This Work ^a	<i>Brocard et al.</i> [1996]	<i>Smith et al.</i> [2000]
		Average	Average	SD	Average	SD	Average	SD	Average				
MCE	0.919	0.914		0.867		0.847		0.927		CO ₂	2402	2226	2411
$\Delta\text{CO}/\Delta\text{CO}_2$	0.0878	0.094	0.046	0.155	0.003	0.180	0.032	0.0785	0.015	CO	134	208	275
$\Delta\text{CH}_4/\Delta\text{CO}$	0.0735			0.016	0.012	0.051	0.016			CH ₄	6.88	2.4	7.9
$\Delta\text{C}_2\text{H}_6/\Delta\text{CO}$	0.0043									C ₂ H ₆	0.747		
$\Delta\text{C}_2\text{H}_4/\Delta\text{CO}$	0.0044									C ₂ H ₄	0.720		
$\Delta\text{C}_2\text{H}_2/\Delta\text{CO}$	0.0034									C ₂ H ₂	0.514		
$\Delta\text{HAc}^b/\Delta\text{CO}$	0.0091									HAc	3.20		
$\Delta\text{HFo}^c/\Delta\text{CO}$	0.0006									HFo	0.159		
$\Delta\text{CH}_2\text{O}/\Delta\text{CO}$	0.0042									CH ₂ O	0.733		
$\Delta\text{CH}_3\text{OH}/\Delta\text{CO}$	0.0066									CH ₃ OH	1.24		
$\Delta\text{NMOC}^d/\Delta\text{CO}$	0.0326			0.0039	0.0004	0.0597	0.0105			NMOC	7.31		
										gC(NMOC)	3.77	0.36	7.0
$\Delta\text{NO}/\Delta\text{CO}_2$	0.0007							0.0020	0.0003	NO	1.16		
$\Delta\text{NO}_2/\Delta\text{CO}_2$	0.0002									NO ₂	0.384		
$\Delta\text{NO}_x/\Delta\text{CO}_2$	0.0009									NO _x as NO	1.41		
$\Delta\text{NH}_3/\Delta\text{CO}$	0.0097									NH ₃	0.97		

^aComputed from average ERs.

^bHAc = acetic acid.

^cHFo = formic acid.

^dThe value for Brocard et al. is their ΣNMHC .

estimated the fuel consumption weighted, average ER $\Delta\text{CO}/\Delta\text{CO}_2$ for the overall wood cooking process as 0.079. *Smith et al.* [2000] sampled six open wood cooking fires built with native wood in a laboratory in India and they reported an average ER $\Delta\text{CO}/\Delta\text{CO}_2$ of 0.035 indicating that relatively more of the fuel was consumed by flaming combustion in their fires. *Ludwig et al.* [2003] reported an average, fire-integrated ER $\Delta\text{CO}/\Delta\text{CO}_2$ of 0.095 ± 0.022 for 94 open wood cooking fires in Zimbabwe and also for 17 open wood cooking fires in Nigeria. They proposed that 0.095 should be adopted as the global average ER $\Delta\text{CO}/\Delta\text{CO}_2$ for biofuel use. For the three wood fires we measured, the fire-average ER $\Delta\text{CO}/\Delta\text{CO}_2$ ranged from 0.07 to 0.12 with a study average of 0.0989 (Table 1). Our study-average ER $\Delta\text{CO}/\Delta\text{CO}_2$ is within 4% of the value obtained in the most extensive study [*Ludwig et al.*, 2003]. Thus, our fires may have had an average flaming to smoldering ratio (F/S) that was similar to the average F/S for the fires in the largest study. This observation and some of the ER comparisons below suggest that our fires may be reasonably representative of African biofuel use.

[15] Our average ER for both $\Delta\text{CH}_4/\Delta\text{CO}$ and excess nonmethane organic compounds/ ΔCO ($\Delta\text{NMOC}/\Delta\text{CO}$) are in the middle of the very different values reported by *Brocard et al.* [1996] and *Smith et al.* [2000]. We do not have an explanation for the wide range in the CH₄ results, but the large range in the results for NMOC could be due partly to the different measurement methods employed. *Brocard et al.* actually measured individual, “light” non-methane hydrocarbons and reported the sum as NMHC. The sum of the individual light $\Delta\text{NMHC}/\Delta\text{CO}$ we measured is very close to their total $\Delta\text{NMHC}/\Delta\text{CO}$ value. To derive the ER $\Delta\text{NMOC}/\Delta\text{CO}$ for *Brocard et al.* in Table 1, we add their organic acid ER to their $\Delta\text{NMHC}/\Delta\text{CO}$. However, our value for $\Delta\text{NMOC}/\Delta\text{CO}$ includes oxygenated organic compounds not measured by *Brocard et al.* Therefore, it is not surprising that our $\Delta\text{NMOC}/\Delta\text{CO}$ is considerably larger than their $\Delta\text{NMOC}/\Delta\text{CO}$. In contrast, *Smith et al.*

measured total organic compounds by flame ionization and then subtracted their CH₄ value to estimate total NMOC. Their approach should be sensitive to higher molecular weight compounds not measured in the other studies and they report the highest $\Delta\text{NMOC}/\Delta\text{CO}$ value. However, it is surprising that *Smith et al.* report both the lowest $\Delta\text{CO}/\Delta\text{CO}_2$ (which indicates flaming combustion) and the highest ER to CO for smoldering compounds.

[16] Our $\Delta\text{NO}/\Delta\text{CO}_2$ ER is 16% smaller than reported by *Kituyi et al.* [2001] and our $\Delta\text{NO}_x/\Delta\text{CO}_2$ ER is 33% larger than reported by *Brocard et al.* [1996]. These small differences probably arise from variation in the fuel nitrogen content [*Kituyi et al.*, 2001], which was not measured in most of the studies. Other differences with previous studies may be partially related to the measurement techniques used. For instance, we report study-average ERs for CH₃COOH and HCOOH to CO that are 5 and 4 times larger, respectively, than *Brocard et al.* measured using a mist chamber [*Cofer et al.*, 1985]. This may be partly due to differences in the emissions since our ratios vary significantly from fire to fire. However, our much larger study-average ratios might also reflect some of the advantages of open-path spectroscopic methods for measuring sticky or reactive compounds. In particular, production or loss of species on sample lines, in containers, or within instruments cannot occur and our broadband, spectroscopic technique is also very resistant to interference [*Yokelson and Bertschi*, 2002]. A direct comparison of the mist chamber and OP-FTIR on the same smoke (and standards) would help quantify the possible causes for the observed interstudy variation.

[17] This study triples the number of ER reported for tropical, open wood cooking fires from 6 to 18. Perhaps the most important new finding is that many of the most abundant compounds emitted by open wood cooking fires are oxygenated volatile organic compounds (OVOC): they account for ~70% of the NMOC. Because OVOC were previously found to be major emissions from large-scale biomass fires in boreal, temperate, and tropical ecosystems

Table 3. ERs and EFs for Earthen Charcoal-Making Kilns

	ERS										Average EFs						
	This Work					Smith et al. [1999]					Lacaux et al. [1994]		Smith et al. [1999]		Pennise et al. [2001]		
	Date (2000)					Average					Average		g kg ⁻¹ Charcoal		g kg ⁻¹ Charcoal		
	10 September	11 September	13 September	Average	SD	Average	SD	Average	SD	Average	SD	Compound	g kg ⁻¹ Wood	g kg ⁻¹ Charcoal	g kg ⁻¹ Charcoal	g kg ⁻¹ Charcoal	
MCE	0.820	0.792	0.737	0.783	0.042	0.806	0.042	0.768	0.042	0.831	0.042	CO ₂	542	1935	1571	1140	1802
Δ CO/ Δ CO ₂	0.220	0.263	0.358	0.280	0.071	0.24	0.071	0.302	0.071	0.204	0.04	CO	96.8	346	250	226	223
Δ CH ₄ / Δ CO	0.160	0.264	0.301	0.242	0.073	0.28	0.073	0.217	0.03	0.418	0.12	CH ₄	13.4	47.7	38.0	27.7	44.6
Δ C ₂ H ₆ / Δ CO	0.015	0.023	0.060	0.033	0.024							C ₂ H ₆	3.40	12.2			
Δ C ₂ H ₄ / Δ CO	0.013	0.012	0.015	0.013	0.002							C ₂ H ₄	1.31	4.66			
Δ C ₃ H ₆ / Δ CO	0.010	0.006	0.015	0.010	0.005							C ₃ H ₆	1.50	5.35			
Δ HAc ^b / Δ CO	0.020	0.031	0.078	0.043	0.031	0.0067	0.031	0.0067	0.031	0.0067	0.0004	HAc	8.92	31.9	3.43		
Δ HFo ^c / Δ CO	0.002	0.002	0.004	0.003	0.001	0.0004	0.001	0.0004	0.001	0.0004		HFo	0.45	1.62	0.16		
Δ CH ₃ O/ Δ CO	0.014	0.007	0.007	0.011	0.011							CH ₃ O	1.06	3.80			
Δ CH ₃ OH/ Δ CO	0.059	0.083	0.191	0.111	0.070							CH ₃ OH	12.3	43.8			
Δ C ₆ H ₅ OH/ Δ CO	0.007	0.003	0.016	0.009	0.007							C ₆ H ₅ OH	2.75	9.83			
Δ C ₄ H ₄ O/ Δ CO	0.004	0.003	0.008	0.005	0.003							C ₄ H ₄ O	1.15	4.11			
Δ NMOC ^d / Δ CO	0.144	0.170	0.387	0.234	0.133	0.061	0.133	0.740	0.700	0.692	0.190	NMOC	32.8	117	8.55	81.7	62
												gC(NMOC)	16.7	59.9			0.057
Δ NO/ Δ CO ₂	0.0003			0.0003						0.000035		NO	0.12	0.45			
Δ NO ₂ / Δ CO ₂												NO ₂					
Δ NO _x / Δ CO ₂	0.0003			0.0003		0.0002				0.000036		NO _x as NO	0.12	0.45	0.15		0.063
Δ NH ₃ / Δ CO	0.0070	0.0080	0.0040	0.006	0.002	0.002	0.002	0.002	0.002			NH ₃	0.37	1.32	0.30		

^aComputed from average ERs.^bHAc = acetic acid.^cHFo = formic acid.^dFor Lacaux et al., we calculate NMOC by adding their organic acid values to their Σ NMHC.

[Yokelson et al., 1996, 1997, 1999, 2003; Worden et al., 1997; Holzinger et al., 1999; Goode et al., 1999, 2000], Mason et al. [2001] explored their influence on modeled smoke plume chemistry. They found that OVOC have a large impact on HO_x, O₃, and nitrogen chemistry. Since we measure ER to CO for all the OVOC (except HCOOH) that are larger than what we obtained for African savanna fires [Yokelson et al., 2003], it would be of interest to explore the influence of these reactive biofuel emissions on the tropical troposphere. In contrast to the other types of biomass burning, biofuel emissions are produced year-round and they have different dispersion characteristics. The implications of our measurements are discussed further in sections 3.5 and 3.6.

3.2.2. Charcoal Cooking

[18] At least four previous studies quantified some trace gas emissions for charcoal cooking fires. Our average ER $\Delta\text{CO}/\Delta\text{CO}_2$ (0.0878 ± 0.051) is lower than the values of Brocard et al. [1996] (0.155 ± 0.003) and Smith et al. [2000] (0.18 ± 0.03) but close to the reports of Kituyi et al. [2001] (0.0785 ± 0.015) and Kaoma and Kasali [1994] (0.094 ± 0.046). The variation in this ER could be caused partly by the different types of stoves used. Our average $\Delta\text{CH}_4/\Delta\text{CO}$ is larger than the other two reports. Our average $\Delta\text{NMOC}/\Delta\text{CO}$ lies between those of the other two reports, as was the case for wood cooking fires. All the studies that measured $\Delta\text{NMOC}/\Delta\text{CO}$ concluded that this ratio is much lower for charcoal cooking than for wood cooking. We report a much lower ER $\Delta\text{NO}/\Delta\text{CO}_2$ than the value of Kituyi et al. [2001], but, as discussed above, this may be due to differences in fuel nitrogen content. Again, our study greatly expands the number of compounds quantified and OVOC again account for $\sim 70\%$ of the NMOC.

3.2.3. Earthen Charcoal-Making Kiln

[19] ERs for earthen charcoal-making kilns were reported in three previously published studies. The $\Delta\text{CO}/\Delta\text{CO}_2$ ER for all four studies is between 0.2 and 0.3 reflecting the importance of pyrolysis in the carbonization process. Three of the four $\Delta\text{CH}_4/\Delta\text{CO}$ ER are in good agreement, but that of Pennise et al. [2001] is much larger than the others. Our $\Delta\text{NMOC}/\Delta\text{CO}$ is between that of Lacaux et al. [1994] and the other studies. We observe much lower NO_x emissions from charcoal than from wood yet we report a $\Delta\text{NO}_x/\Delta\text{CO}_2$ ER that is ~ 8 times larger than that of Pennise et al. [2001]. Again, this variation may be mainly due to differences in fuel nitrogen content.

[20] Large differences occur between our measurements of organic acids and those made by Lacaux et al. [1994] using a mist chamber; as reported in more detail by Brocard et al. [1996]. Our ER for total excess organic acids/ ΔCO is about 6.5 times higher. We also observe an ER $\Delta\text{NH}_3/\Delta\text{CO}$ that is ~ 3 times higher than Lacaux et al. measured by chemiluminescence. Our larger values could arise from differences in the kilns and/or the measurement approach. Unlike the kiln sampled by Lacaux et al. [1994], our kiln had no chimney or branch bed and this may have led to different combustion characteristics. In addition, our kiln probably had higher nitrogen content in the initial wood charge since our $\Delta\text{NO}_x/\Delta\text{CO}_2$ ER is 50% larger than Lacaux et al. observed. This probably accounts for some of our higher NH₃ emissions. Our smoke measurements

probed $\sim 0.05 \text{ m}^3$ of the plume emitted by the kiln, whereas, Lacaux et al. used a metal tube to draw samples from a point inside the kiln. The trace gases could change between these locations or the concentrations of reactive species (e.g., CH₃COOH or NH₃) could be altered on the walls of the metal tube. In studies of other types of biomass burning, FTIR returned higher values for organic acids than had been observed using mist chambers (see section 3.2.1 or the studies of Yokelson et al. [1996] and Goode et al. [2000]). Finally, Lacaux et al. probably sampled for a greater fraction of the time that emissions were produced and both studies sampled only one kiln, which means that the kiln–kiln variation is not well known. In summary, more measurements are needed, but our study approximately doubles the amount of ER reported for earthen kilns and almost 80% of the NMOC are oxygenated organic compounds. Thus, OVOC are a major component of the emissions from both the production and use of biofuels.

3.3. Calculation of Emission Factors (EF)

3.3.1. Cooking Fires

[21] We calculated EF (g compound emitted per kg dm fuel burned) for each trace gas emitted from the wood cooking fires using the carbon mass balance method, which is described in full by Ward and Radke [1993]. In brief, we assume that all the burned carbon is volatilized, partitioned according to our ER, and that the fuel carbon content is known. By ignoring unmeasured gases, particles, and other condensed-phase carbon products, we are probably inflating the EFs by a few percent. To estimate the fuel carbon content for the wood cooking fires, we use previously reported values for Miombo tree species. Chidumayo [1994] reported a carbon content (by mass) of $47.4 \pm 1.8\%$ for 21 Miombo tree species. Similarly, Susott et al. [1996] reported a carbon content of $48.4 \pm 1.3\%$ in the wood of tree species found in the Zambian Miombo. We use the average of the values from these two studies, $48 \pm 2\%$ (2σ), to estimate the carbon content of the wood consumed in this study. We calculated the EF for the charcoal cooking fires in the same way as for the wood cooking fires except that the charcoal is enriched in carbon. Chidumayo [1994] reported an average carbon content of 72% for 103 charcoal samples collected from 65 separate earthen kilns and this is close to the values reported by Ishengoma et al. [1997] (70%), Lacaux et al. [1994] (74.5%), and Smith et al. [1999] (74.8%). Therefore, we assume a carbon content of $72 \pm 3\%$ (2σ) for the charcoal burned in this study. The EFs for the wood and charcoal cooking fires are reported in Tables 1 and 2, respectively.

3.3.2. Charcoal Kilns

[22] We cannot use the carbon mass balance method to calculate kiln EF in the same way that we did to calculate cooking fire EF because the carbon content changes during the kiln lifetime and a lot of the burned carbon is not volatilized. Also, kiln EFs can be expressed as g compound emitted per kg wood used or as g compound emitted per kg charcoal produced; with each form having its advantages. Attempts have been made by previous authors to estimate kiln EF and the methods seem to conflict though each method may have been accurate for the particular circumstances. We describe the various methods and justify our estimate next.

[23] The first estimate of earthen kiln EFs was by *Lacaux et al.* [1994]. These authors formulated the carbon balance for charcoal making as in (1).

$$C_w = C_s + C_l + C_g \quad (1)$$

where C_w , C_s , C_l , and C_g represent the carbon (on a dry matter basis) in the wood charge, charcoal, pyrolyginous liquid (tar), and gases, respectively. In their kiln, the initial wood was 46% C (by mass) and 27.6% of the wood was converted to charcoal that was 74.5% C. Thus, they directly measured C_w and C_s and found that ~44.8% of the carbon in the wood remained in the charcoal. *Lacaux et al.* [1994] assumed that 20.6% of the carbon in the wood was converted to pyrolyginous liquid based on a separate laboratory study of wood pyrolysis by *Dumont and Gelus* [1982]. They then calculated C_g as 34.6% by difference and their EF are based on partitioning C_g according to their ERs. Their assumption of a high liquid yield may not be appropriate for our kiln as discussed in more detail later.

[24] In a study of three Thai earthen kilns, *Smith et al.* [1999] reported wood and charcoal carbon contents of 44% and 74.8% and a charcoal yield (charcoal mass/wood dm) of $29.8 \pm 2.5\%$ similar to values obtained above. (Smith et al. did not measure the moisture content of the charcoal.) In contrast to the study of *Lacaux et al.* [1994], *Smith et al.* [1999] found that the sum of the carbon condensed on the inner walls of the kiln and inside a hood they placed over the kiln accounted for only 0.24% of the carbon in the wood. Even with a cooled apparatus to process the emitted gases, they could only condense a small fraction of the emissions, indicating that ~3% of the wood carbon became condensable gases. Of course, most earthen kilns are not fitted with any condensing device. In another difference with *Lacaux et al.*, *Smith et al.* [1999] found that 15% of the initial carbon ended up in the “brands” (partially carbonized wood pieces). The data of *Smith et al.* suggests to us that (on average) charcoal, brands, and trace gas emissions (by difference) accounted for ~48%, 15%, and 37% of the carbon in the initial wood charge, respectively.

[25] *Pennise et al.* [2001] measured a charcoal yield of $27.5 \pm 5.4\%$ for five earthen kilns in Kenya. Based in large part on the measurements and assumptions of *Smith et al.* [1999], they estimated that $47 \pm 9\%$ of the wood carbon was converted to charcoal. In an intriguing contrast with *Smith et al.*, they found that in four out of the five kilns, the brands accounted for less than 4% of the wood carbon. Finally, we note that one of us (Darold Ward) has completed detailed measurements of the carbon mass balance for Zambian earthen kilns. A preliminary analysis of that data does not appear to directly support a large yield of brands or liquid.

[26] We need to estimate the carbon content of the wood charge and the fraction of that carbon that is emitted as gases to use our ER to calculate EF as g compound emitted per kg dry wood used. We take the carbon content of the wood to be $48 \pm 2\%$ (2σ) as justified in section 3.3.1. To estimate the fraction of that carbon emitted as gases, we first note that *Lacaux et al.* [1994], *Pennise et al.* [2001], and *Smith et al.* [1999] found that (on average) 45%, 47%, and 48% of the wood carbon ended up in the charcoal, respectively. Thus, 50% seems like an upper limit for an average yield of gases. On the other hand, the assumption of large yields of liquid or

brands is consistent with a gas yield approaching 40%. Since we are not convinced that a large yield of liquid or brands is typical, we estimate that 45% of the wood carbon is emitted as gases. Our earthen kiln EF for g compound per kg wood used are based on this assumption and are therefore, somewhat higher than previous estimates (see Table 3).

[27] We can derive EF (g per kg charcoal produced) from the EF (g per kg wood used) with an estimate of the average charcoal yield. We note that *Chidumayo* [1994] found an average charcoal yield of $23.4 \pm 7.2\%$ (i.e., 1 kg of wood (dm) produces ~234 g of charcoal) for Zambian, earthen kilns. This is lower than the charcoal yields reported by *Pennise et al.* [2001], *Lacaux et al.* [1994], and *Smith et al.* [1999] of $27.5 \pm 10\%$, 27.6%, and $29.8 \pm 2.5\%$, respectively. Therefore, we assume a charcoal yield of 28% (and a conversion factor of 1000/280) to calculate EF per kg charcoal produced. We note that coupling the assumptions we have made above does not account for some 10% of the wood carbon and thus these assumptions are consistent with modest yields of brands or liquid. In summary, we assume a higher gas yield than previous workers and that will contribute to higher EF.

3.4. Comparison of EFs With Previous Measurements

3.4.1. Wood and Charcoal Cooking Fires

[28] Since the calculation of EF for cooking fires is straightforward, the comparison of EF yields conclusions similar to the comparison of ERs given in sections 3.2.1 and 3.2.2 (e.g., we obtained significantly higher EF for organic acids). We note one interesting anomaly. *Smith et al.* [2000] report a considerably higher ER $\Delta\text{NMOC}/\Delta\text{CO}$ than us for wood fires, but a considerably lower g C emitted as NMOC.

3.4.2. Earthen Charcoal-Making Kilns

[29] We have already made the most direct comparisons between kiln studies in section 3.2.3. As noted above, in comparison to other studies our kiln EF are increased across the board by 25–30% because of our assumption of a higher yield of gaseous emissions. Equivalently, if *Lacaux et al.* [1994] and *Smith et al.* [1999] had assumed a negligible yield of both liquid and uncarbonized wood, their reported EF would increase by approximately 60% and 50%, respectively. However, the large differences between our EF and previous reports for reactive and sticky trace gases (i.e., OVOC, NH_3 , etc.) are due mostly to our much larger ERs discussed earlier. In summary, this work has expanded our knowledge of kiln emissions, but more work is needed to improve the understanding of the carbon balance and the variation in emissions for earthen (and other) kilns. When this information becomes available, our ERs could be incorporated into refined EF estimates.

3.5. Comparison of Wood and Charcoal Use: Emissions Per Unit Energy

[30] According to a recent estimate, African fuelwood use is increasing at $\sim 1\% \text{ yr}^{-1}$ and African charcoal use is increasing at $\sim 3\% \text{ yr}^{-1}$ [FAO, 1999]. The main advantage of charcoal over wood is the greater quantity of energy released per unit mass of fuel burned ($\sim 31 \text{ MJ kg}^{-1}$ for charcoal compared to $\sim 16 \text{ MJ kg}^{-1}$ for wood) [FAO, 1985]. However, it is also important to compare these fuels based on the amount of emissions produced per unit energy released.

Table 4. EFs and “Energy-Normalized EFs” From Charcoal Production/Consumption and Wood Burning

Species	EFs				Energy-Normalized EFs ^a	
	Charcoal ^b Production (g kg ⁻¹ Charcoal Made)	Charcoal ^c Fires (g kg ⁻¹ Charcoal Used)	Total ^d Charcoal (g kg ⁻¹ Charcoal Made and Used)	Wood ^e Fires (g kg ⁻¹ Wood Used)	Wood ^f Fires (g MJ ⁻¹)	Total ^g Charcoal (g MJ ⁻¹)
CO ₂	1935	2402	4337	1525	95	140
CO	346	134	480	96.0	6.0	15
CH ₄	47.7	6.9	55	10.6	0.66	1.8
C ₂ H ₆	12.2	0.75	13	1.50	0.09	0.42
C ₂ H ₄	4.66	0.72	5.4	2.35	0.15	0.17
C ₂ H ₂		0.51	0.51	1.67	0.10	0.02
C ₃ H ₆	5.35		5.4	0.95	0.06	0.17
HAc ^h	31.9	3.20	35	8.12	0.51	1.13
HFo ⁱ	1.62	0.16	1.8	0.68	0.04	0.06
CH ₂ O	3.80	0.73	4.5	3.52	0.22	0.15
CH ₃ OH	43.8	1.24	45	3.61	0.23	1.45
C ₆ H ₄ OH	9.83		9.83	3.32	0.21	0.32
C ₄ H ₄ O	4.11		4.1	0.40	0.03	0.13
NO	0.45	1.16	1.6	1.72	0.11	0.05
NO ₂		0.38	0.38	0.49	0.03	0.01
NH ₃	1.32	0.97	2.3	1.29	0.08	0.07

^aUnits in g of species emitted per MJ of energy released.

^bEFs from average EFs reported in Table 3 [this work].

^cEFs from average EFs reported in Table 2 [this work].

^dSum of EFs from charcoal burning and making [this work].

^eEFs from average EFs reported in Table 1 [this work].

^fBased on 16 MJ kg⁻¹ wood consumed.

^gBased on 31 MJ kg⁻¹ charcoal consumed.

^hHAc = acetic acid.

ⁱHFo = formic acid.

[31] The emissions per unit energy are compared for wood and charcoal in Table 4. First, we sum the charcoal production EF (g compound emitted per kg charcoal produced) and the charcoal burning EF (g per kg charcoal burned) to obtain a “total charcoal EF” (g per kg charcoal produced and burned). Then we tabulate the study-average, wood fire EF (g per kg burned) to directly compare the g of emissions per kg of fuel used (including production if applicable). On a per mass basis the total charcoal EF are 3–10 times larger than the wood fire EF for most compounds. Next, we divide the total charcoal EF by 31 MJ kg⁻¹ and the wood EF by 16 MJ kg⁻¹ to yield the “EFs per unit energy” (g compound emitted per MJ energy released) shown in the right-hand columns of Table 4. After normalizing for energy release, the wood fires emit more C₂H₂, HCHO, and nitrogen compounds than the combined production and use of charcoal (the higher nitrogen emissions from wood burning could have been due to higher fuel N content, which we did not measure). However, for all the other trace gases the combined production and use of charcoal releases about twice the amount of emissions as wood burning does per unit energy yielded (see Table 4 and Figure 2).

[32] Wood is generally a cleaner energy source from the standpoint of trace gas emissions because traditional charcoal making releases both trace gases and unused energy. There are other related issues such as the efficiency of heat transfer in cooking, potentially lower particle emissions from charcoal use, or emissions associated with fuel transport. Nonetheless, this preliminary analysis is relevant to energy and environmental policies wherever biofuels are a major energy source. Strategies to reduce wasted energy could involve high-yield kilns [Antal et al., 2000], energy

plantations near urban areas [Shafizadeh et al., 1976] or other approaches.

3.6. The Contribution of Biofuel Use to Regional and Global Trace Gas Emissions

[33] The local–global impacts of biofuel emissions are poorly understood. Much of the uncertainty stems from the previous lack of emissions data [Andreae and Merlet, 2001] and the difficulty of estimating the amount of biofuels burned. For instance, we measure ERs for some compounds that are 5–8 times higher than previously reported and estimates of the global, biofuel consumption range from 310 to 1085 Tg C yr⁻¹, which is a factor of 3 [Hao and Liu, 1994; Andreae and Merlet, 2001]. In contrast to the large uncertainty surrounding biofuels, savanna fires are well known to have a large impact on the regional–global atmosphere [Delany et al., 1985; Crutzen and Andreae, 1990; Fishman et al., 1991; Yokelson et al., 2003]. Since the above estimates suggest that global carbon consumption due to biofuel burning is ~10–85% of that due to savanna fires, it is of some interest to further explore the relative magnitude of these sources.

[34] Brocard and Lacaux [1998] estimated that biofuel use produced a significant fraction of the annual pyrogenic emissions for West Africa. In this section, we couple our EFs with estimates of biomass consumption to compare the amount of emissions from biofuel burning and savanna fires in Zambia (see Table 5). Chidumayo [1994] estimated Zambian charcoal use at 0.905 Tg for the year 2000. The Zambian charcoal use for 1996 was estimated at 0.586 Tg by the FAO [1999]. The average of these two recent estimates is 0.75 Tg and that is used in Table 5. If we again assume a 28% charcoal yield, then 2.7 Tg of wood were

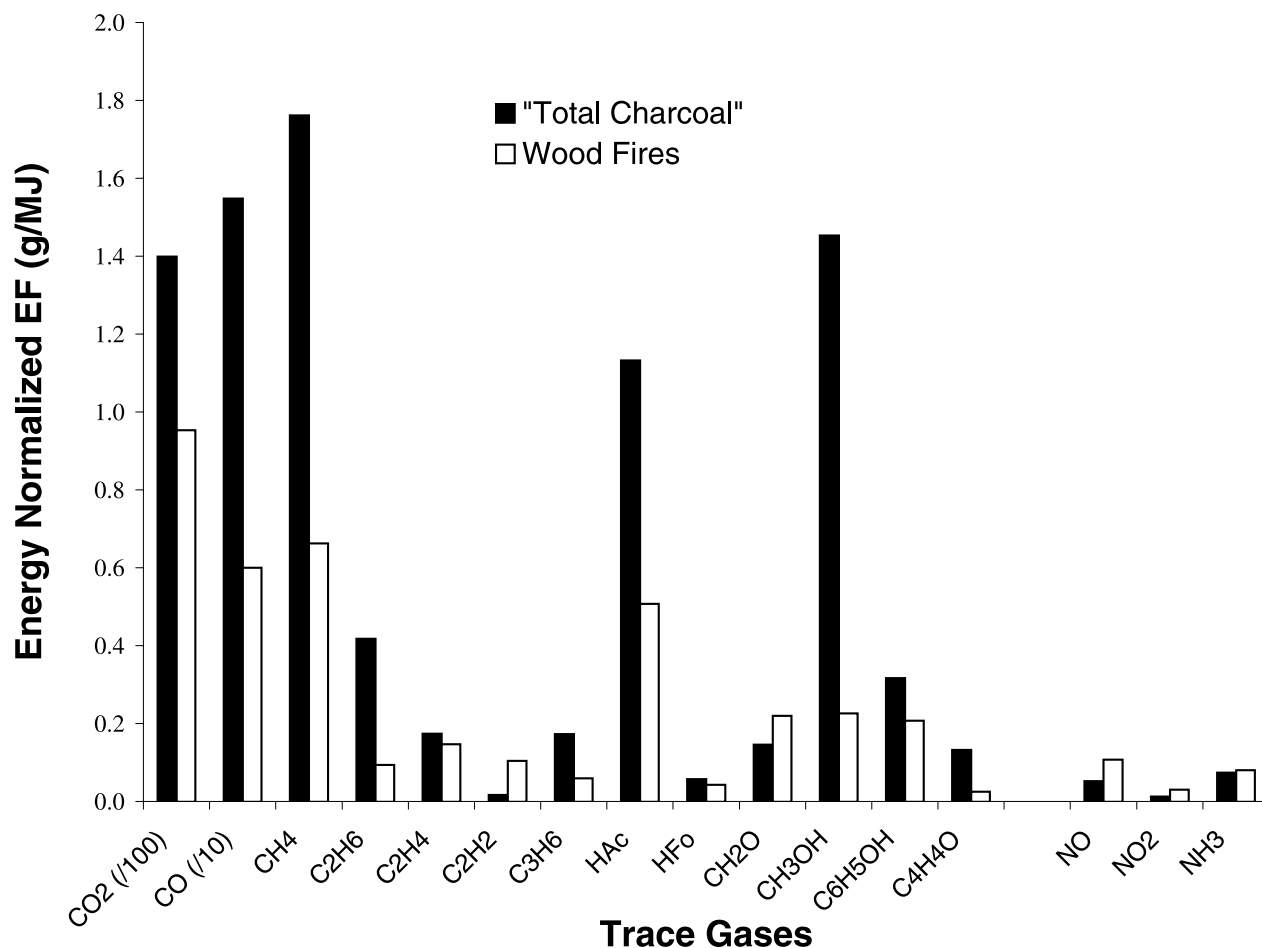


Figure 2. The energy-normalized EFs (g compound emitted per MJ energy released) are compared for wood burning and the combined production and use of charcoal. The values are computed in Table 4 as outlined in section 3.5. Note the scaling factors for CO₂ and CO.

used to make that charcoal. *Zhu et al.* [1998] estimated that 5.6 Tg of wood were consumed directly for domestic cooking during 2000 in Zambia. The Zambian fuelwood use for 1996 was estimated at 7.1 Tg by the *FAO* [1999]. The average of these two estimates is 6.4 Tg (Table 5). *Ludwig et al.* [2003] argued that FAO estimates are based on marketed wood and are therefore conservative. Their measurements supported the use of a formula quoted from the study of *Hall et al.* [1994] for biofuel use in Africa: 1000 kg cap⁻¹ yr⁻¹ (rural) and 500 kg cap⁻¹ yr⁻¹ (urban). Applying this formula to Zambia with a population of ~10 million [*The World Factbook*, 2001] that is 40% urban and 60% rural [*United Nations Statistics Division*, 2000] gives a total biofuel use of 8.0 Tg. This is 23% less than the sum of our species consumption terms derived above. Thus, in light of the difficulty of measuring biofuel consumption and the tendency for recent estimates to be larger, our estimates seem reasonable. *Hao and Liu* [1994] presented a figure based on satellite data from the late 1970s that suggests that ~18.6 Tg dm of biomass are consumed annually by savanna burning in Zambia.

[35] In Table 5, we multiply these biomass consumption estimates by our appropriate EFs to estimate species,

annual, emissions for Zambia from charcoal production and use, firewood use, and savanna fires. (For savanna fire emissions, we use the savanna fire EFs recently measured in Zambia by *Yokelson et al.* [2003].) We complete the comparison by showing estimated ratios of biofuel emissions to savanna fire emissions (by species) in the right-hand columns of Table 5. We find that savanna fires account for most of the annual pyrogenic CO₂ (71%), HCOOH (63%), and NO_x (83%), while biofuel use accounts for most of the CH₄ (84%), CH₃OH (80%), C₂H₂ (73%), CH₃COOH (71%), HCHO (69%), and NH₃ (67%). The annual CO and C₂H₄ production is about equal from both sources. For West Africa, *Brocard and Lacaux* [1998] found that a similar fraction of the total pyrogenic emissions were due to biofuels (approximately one third), but they attributed a smaller fraction of the pyrogenic CO, CH₄, and NMOC to biofuel use than we did. Both estimates suggest that biofuel burning produces an annual amount of reactive compounds comparable to savanna fires; and that indicates a potential to strongly influence the tropical troposphere.

[36] Most of the biofuel emissions are too reactive to become globally mixed, but our measurements do impact

Table 5. Comparison of Estimated Annual Emissions From Biofuel Production and Use to Savanna Fires in Zambia

Species	EFs		EFs		EFs		Ratio: Biofuel/Savanna	
	Wood Fires ^a (g kg ⁻¹ Wood Used)	Annual Emissions ^b Wood Fires (Tg yr ⁻¹)	Total Charcoal ^c (g kg ⁻¹ Charcoal Made and Used)	Annual Emissions ^d Total Charcoal (Tg yr ⁻¹)	Savanna Fires ^e (g kg ⁻¹ Biomass Burned)	Annual Emissions ^f Savanna Fires (Tg yr ⁻¹)	This work Zambia	Brocard and Lacaux [1998] ^g West Africa
CO ₂	1525	9.8	4337	3.3	1734	32.3	0.40	0.32
CO	96	0.61	480	0.36	55.7	1.0	0.9	0.42
CH ₄	10.6	0.068	55	0.041	1.16	0.022	5.1	0.46
C ₂ H ₆	1.50	0.010	13	0.010	—	—	—	—
C ₂ H ₄	2.35	0.015	5.4	0.004	0.77	0.014	1.3	—
C ₂ H ₂	1.67	0.011	0.51	0.0004	0.22	0.004	2.7	—
C ₃ H ₆	0.95	0.006	5.4	0.004	—	—	—	—
HAc ^h	8.12	0.052	35	0.026	1.72	0.032	2.4	—
HFo ⁱ	0.68	0.004	1.8	0.001	0.53	0.010	0.6	—
CH ₂ O	3.52	0.023	4.5	0.003	0.63	0.012	2.2	—
CH ₃ OH	3.61	0.023	45	0.034	0.79	0.015	3.9	—
C ₆ H ₅ OH	3.32	0.021	9.83	0.007	—	—	—	—
C ₄ H ₄ O	0.40	0.003	4.1	0.003	—	—	—	—
NMOC	26.1	0.167	124.5	0.093	4.7	0.087	3.0	0.44
NO _x	2.04	0.013	2.0	0.001	3.14	0.058	0.2	—
NH ₃	1.29	0.008	2.3	0.002	0.27	0.005	2.0	—

^aEFs from the average “wood cooking” EFs reported in Table 1 [this work].

^bBased on 6.4 Tg annual fuelwood use (see section 3.4).

^cEFs from “Total Charcoal” EFs reported in Table 4 [this work].

^dBased on 0.75 Tg annual charcoal use (see section 3.4).

^eEFs for Zambian savanna burning reported by Yokelson *et al.* [2003].

^fBased on 18.6 Tg biomass burned in savanna fires annual from the study of Hao and Liu [1994] (see section 3.4).

^gThe estimates of Brocard *et al.* [1996] for West Africa are assumed to supersede those from 1996.

^hHAc = acetic acid.

ⁱHFo = formic acid.

global budgets. For instance, Singh *et al.* [1995] estimated a global source of ~ 45 Tg yr⁻¹ for CH₃OH based on its abundance in the remote troposphere and its reaction rate with OH. They estimated that global biomass burning produced ~ 6 Tg yr⁻¹ of CH₃OH. If we couple our EFCH₃OH for wood cooking fires (3.61 g kg⁻¹) with the Yevich and Logan (YL) estimate of global biofuel burning (2701 Tg dm yr⁻¹) (quoted in the study of Andreae and Merlet [2001]), the result is 9.75 Tg yr⁻¹. Coupling our EFCH₃OH for savanna fires (1.17 g kg⁻¹) [Yokelson *et al.*, 2003] with the YL estimate of global savanna fire burning (3160 Tg dm yr⁻¹) results in 3.7 Tg yr⁻¹. Combining the YL estimate for total forest fires (1970 Tg dm yr⁻¹) with a EFCH₃OH for forest fires from the study of Yokelson *et al.* [1999] produces an estimate of 5.5 Tg yr⁻¹. Thus, biofuel use is significant compared to the other types of biomass burning on a global scale. In addition, we obtain a CH₃OH source from these three types of biomass burning (19 Tg yr⁻¹) that is 3 times larger than the estimate of Singh *et al.* for total biomass burning. This larger source is partially counteracted by the discovery of Yokelson *et al.* [2003] that CH₃OH is readily scavenged in smoke-impacted clouds.

[37] CH₄ is more stable than CH₃OH. Our EFCH₄ of 10.6 g kg⁻¹ for fuelwood is 40% larger than the EF in an earlier study (7.6 g kg⁻¹) [Hao and Ward, 1993]. Coupling our EF with the YL biofuel estimate yields 28.6 Tg yr⁻¹. This is 4 times larger than the fuelwood contribution estimated by Hao and Ward, and almost as large as their estimate for CH₄ from global biomass burning (30.5 Tg yr⁻¹). Using the YL estimates for each biomass burning category with our most recent EFCH₄ [Yokelson *et al.*, 1999, 2003; Bertschi *et al.*, 2003; T. Christian, personal

communication, 2003] implies a global biomass burning source for CH₄ of ~ 59 Tg yr⁻¹. Source estimates similar to those in the above examples can be made for each trace gas measured in this study. We also plan measurements of the trace gas emissions from biofuel use in other regions of the tropics to further probe the representativeness of our data. Finally, the impact of biofuel burning in atmospheric chemistry models should be reexamined, now that the initial emissions are better characterized.

4. Conclusions

[38] We used OP-FTIR spectroscopy to quantify 18 of the most abundant trace gases emitted by wood and charcoal cooking fires and an earthen, charcoal-making kiln in Zambia. These are the first, in situ measurements of an extensive suite of trace gases emitted by tropical biofuel burning. We report ERs and EFs for (in order of abundance) CO₂, CO, CH₄, CH₃COOH, CH₃OH, HCHO, C₂H₄, NH₃, C₂H₂, NO, C₂H₆, C₆H₅OH, C₃H₆, HCOOH, NO₂, HOCH₂CHO, and C₄H₄O. Compared to previous work, our emissions of organic acids and ammonia are much larger. Another significant finding is that reactive oxygenated organic compounds account for 70–80% of the total NMOCs. Our data suggest that (for most compounds) the combined emissions from charcoal production and charcoal burning are 3–10 times higher than the emissions from wood fires per unit mass of fuel burned. In addition, the combined emissions from the production and use of charcoal exceed the emissions from wood burning per unit energy released. We compare the annual emissions from biofuel use and savanna fires in Zambia. For many compounds (e.g., CH₄, C₂H₂, CH₃COOH,

CH₃OH, HCHO, and NH₃), the biofuel production significantly exceeds that due to savanna fires. In summary, biofuel emissions are an important and growing influence on the tropical troposphere that should be studied further in atmospheric models.

[39] **Acknowledgments.** This research was supported by funds provided by the National Science Foundation under grant ATM-9900494, the Interagency Joint Fire Science Program, and the Rocky Mountain Research Station, Forest Service, U.S. Department of Agriculture (INT-97082-RJVA and RMRS-99508-RJVA). The authors thank Rachel Mayers (deceased), Sidney Ilukena, Freddy Mubita, Alick Rabanda, and the chief and residents of Milumbwa who provided assistance in our measurements and useful information about traditional cooking and charcoal-making methods. We thank Mike King, Bob Swap, Harold Annegarn, Tim Suttles, NASA, and SAFARI 2000 for planning and logistical support. We thank J. Ludwig et al. for an advance copy of their manuscript.

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