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Recommended Citation

Christian, T. J., B. Kleiss, R. J. Yokelson, R. Holzinger, P. J. Crutzen, W. M. Hao, B. H. Saharjo, and D. E. Ward, Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, *J. Geophys. Res.*, 108(D23), 4719, doi:10.1029/2003JD003704, 2003.

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Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels

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Received 21 April 2003; revised 4 July 2003; accepted 15 August 2003; published 4 December 2003.

[1] Trace gas and particle emissions were measured from 47 laboratory fires burning 16 regionally to globally significant fuel types. Instrumentation included the following: open-path Fourier transform infrared spectroscopy; proton transfer reaction mass spectrometry; filter sampling with subsequent analysis of particles with diameter <2.5 μm for organic and elemental carbon and other elements; and canister sampling with subsequent analysis by gas chromatography (GC)/flame ionization detector, GC/electron capture detector, and GC/mass spectrometry. The emissions of 26 compounds are reported by fuel type. The results include the first detailed measurements of the emissions from Indonesian fuels. Carbon dioxide, CO, CH₄, NH₃, HCN, methanol, and acetic acid were the seven most abundant emissions (in order) from burning Indonesian peat. Acetol (hydroxyacetone) was a major, previously unobserved emission from burning rice straw (21–34 g/kg). The emission factors for our simulated African fires are consistent with field data for African fires for compounds measured in both the laboratory and the field. However, the higher concentrations and more extensive instrumentation in this work allowed quantification of at least 10 species not previously quantified for African field fires (in order of abundance): acetaldehyde, phenol, acetol, glycolaldehyde, methylvinylether, furan, acetone, acetonitrile, propenenitrile, and propanenitrile. Most of these new compounds are oxygenated organic compounds, which further reinforces the importance of these reactive compounds as initial emissions from global biomass burning. A few high-combustion-efficiency fires emitted very high levels of elemental (black) carbon, suggesting that biomass burning may produce more elemental carbon than previously estimated.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 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; *KEYWORDS:* biomass burning, oxygenated organic compounds, Indonesian fires

Citation: Christian, T. J., B. Kleiss, R. J. Yokelson, R. Holzinger, P. J. Crutzen, W. M. Hao, B. H. Saharjo, and D. E. Ward, Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, *J. Geophys. Res.*, 108(D23), 4719, doi:10.1029/2003JD003704, 2003.

1. Introduction

[2] Most of the Earth's ecosystems co-evolved with fire since plants emerged from the sea. Humans later introduced

the use of fire to improve grazing and crop production and for waste disposal, hunting, cooking, heating, and lighting. These uses continue today, on the largest scale in the tropics, where population is rapidly increasing. The gas and particle emissions from biomass burning strongly influence the physical and chemical properties of the atmosphere [Crutzen and Andreae, 1990] through the following: release/redistribution of carbon [Prather *et al.*, 1994], changes in oxidative capacity [Lelieveld *et al.*, 1997; Mason *et al.*, 2001], changes in atmospheric radiative transfer [Hobbs *et al.*, 1997; Kaufman and Fraser, 1997], and human health effects [Sharkey, 1997]. Uncertainty and natural variation, perhaps as large as a factor of 10, still exist in the amount of biomass burned and in the relative abundance of many important initial emissions [Goode *et al.*, 2000].

[3] Most fires occur unscheduled in remote areas of the tropics where a fraction of the smoke, at low concentrations, is occasionally sampled by aircraft that employ a limited

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number of instruments. African fires have been studied the most [Yokelson *et al.*, 2003a], some work has been done on fires in the neotropics [Ferek *et al.*, 1998], and very little is known about Southeast Asian fires. To complement the field measurements, laboratory measurements have been conducted in which all the smoke from simulated fires can be captured and characterized at high concentrations [Lobert *et al.*, 1991; Yokelson *et al.*, 1996, 1997, 1998; Holzinger *et al.*, 1999; Goode *et al.*, 1999; Bertschi *et al.*, 2003a]. These laboratory studies are in good agreement with field measurements in nascent smoke [Yokelson *et al.*, 2003a], and they provide details on compounds that are below detection limits in field studies. However, before this work, none of the laboratory studies had featured a comprehensive suite of instruments.

[4] In this work, using an extensive suite of instrumentation, we quantified the emissions from 47 fires that burned 16 major fuel types from Africa, Indonesia, and elsewhere. The work was carried out at the U.S. Department of Agriculture (USDA) Forest Service Fire Sciences Laboratory (FSL) in Missoula, Montana. The trace gas measurements employed two recently developed methods: proton transfer reaction mass spectrometry (PTR-MS) and Fourier transform infrared spectrometry (FTIR) coupled with canister samples analyzed by gas chromatography (GC)/mass spectrometry (MS) GC/electron capture detector (ECD), and GC/flame ionization detector (FID). PTR-MS quantifies, at parts per trillion levels (ppt, 1 trillion = 10^{12}), many volatile species that have a proton affinity moderately above that of water. However, it provides a single peak for each molecular mass making compound identification challenging under some conditions [Holzinger *et al.*, 2000]. Since all molecules have a unique IR signature, FTIR is well suited for identification and quantification of most trace gases, but only at parts per billion levels (ppb, 1 billion = 10^9) [Goode *et al.*, 1999]. The canister techniques provide analysis at ppt levels, but they are subject to sampling and storage artifacts so they are best suited for trace gases that are not reactive or sticky. Such problematic gases account for $\sim 70\%$ of the organic emissions from fires (on a molar basis) and most of the organic constituents of the remote troposphere [Yokelson *et al.*, 1996, 2003a; Singh *et al.*, 2001]. Open-path FTIR (OP-FTIR) is not subject to sampling artifacts and the PTR-MS technique involves no sample storage. In summary, the combination of these five techniques provides the most comprehensive trace gas analysis applied to fires to date. In addition, since the smoke was well mixed, this study provided the first informal, but rigorous, intercomparison of PTR-MS, OP-FTIR, and canister sampling. The focus of this paper is presenting the emissions from Indonesian and African fuels. A detailed discussion of the intercomparison between the FTIR, the PTR-MS, and canister sampling is given by Christian *et al.* [2003].

2. Experiment

2.1. Combustion Facility

[5] The combustion facility at FSL (described in more detail by Christian *et al.* [2003]) measures $12.5\text{ m} \times 12.5\text{ m} \times 22\text{ m}$ high. A 1.6 m diameter exhaust stack with a 3.6 m,

inverted funnel opening extends from $\sim 2\text{ m}$ above the floor to the ceiling. The room is pressurized with outside air that has been conditioned for temperature and relative humidity (RH), and is then vented through the stack, completely entraining the emissions from fires burning beneath the funnel. A sampling platform surrounds the stack at 17 m elevation where all the temperature, pressure, trace gas, and particle measurement equipment for this experiment was deployed except the instrument for background CO_2 (LICOR 6262). Temperature, flow, and mixing ratios were constant across the width of the stack (at the height of the sampling platform), as determined by moving probes for point measurements to different positions within the stack. The fuel bed was a ($80 \times 210\text{ cm}$) tray covered by an inert heat shield, a layer of sand, and continuously weighed by two electronic balances. During these experiments, chamber temperature and RH were $25^\circ \pm 1^\circ\text{C}$ and $25.6 \pm 5.2\%$. Smoke temperature and RH, at platform level, varied throughout each fire and from fire to fire. The maximum smoke temperature observed was 86.5°C . Flame temperatures were not measured, but typical values are $1000^\circ\text{--}1100^\circ\text{C}$.

2.2. Fuels: Selection, Sampling, Characterization, and Fire Simulations

2.2.1. Selection, Sampling, and Simulations of African Fuels

[6] Key data for all the fuels burned in this study are presented in Table 1. Sixteen of the 47 fires burned grass and/or leaf/twig litter from humid savannas in Zambia (humid savannas include both pure grassland and "open" woodland and have 700–1400 mm/yr seasonal rainfall). There are ~ 7.7 million km^2 of humid, woodland savannas (sometimes termed tropical dry forests) in the world, of which 5.5 million are in the central African plateau. Half of these are miombo forests (~ 2.8 million km^2) [International Geosphere-Biosphere Program (IGBP), 1997], which constitute the largest contiguous dry forest/woodland savanna in the world. Miombo tree species are resistant to low-medium intensity fire, so that grass and leaf litter are the primary fuels [Shea *et al.*, 1996; Hoffa *et al.*, 1999]. The miombo understory burns about every 2 years [Shea *et al.*, 1996; IGBP, 1997], and this likely accounts for more biomass burning than any other single ecosystem on Earth [IGBP, 1997]. The miombo covers most of central Africa ($\sim 80\%$ of Zambia is miombo [Hoffa *et al.*, 1999]) and fires in the miombo account for the great majority of sub-Saharan fires [Justice *et al.*, 1996; IGBP, 1997]. Dambos are seasonally flooded grasslands that are the major enclaves in the miombo. Dambos usually burn annually [Hoffa *et al.*, 1999], and this accounts for a large fraction of African fires.

[7] During the Southern African Regional Science Initiative (SAFARI) 2000, several groups [Sinha *et al.*, 2003; Yokelson *et al.*, 2003a] made the most extensive field measurements to date of the main emissions from African savanna fires. One goal of the work described here was to quantify additional compounds emitted by savanna fires (in the laboratory) by sampling more concentrated smoke and employing more extensive instrumentation. Miombo leaf/twig litter and miombo/dambo grasses were sampled in the western province of Zambia at the end of the dry season,

Table 1. Fires and Fuel Types Sorted by Country of Origin

Fire Name ^a	Number of Fires	Fuel Description	Origin	Percent C	Percent H	Percent N	Percent Ash	FM ^b	Average Fuel Loading, kg/m ²
Dambo (db)	10	Dry land dambo grass	Zambia	46.3	5.90	0.23	3.35	5.8–17.3	0.59
Miombo (mb)	5	Miombo vegetation type (~50:50 mixture of dambo grass and miombo litter)	Zambia	48.9	5.93	0.71	3.65	8.7–10.5	1.00
MiomboLit (ml)	1	Miombo litter (mainly leaves and twigs)	Zambia	51.6	5.96	1.20	3.95	12.6	0.21
Alang-alang (al)	5	Initial, invasive, fire-maintained grass after deforestation	Indonesia	42.1	5.25	0.78	10.3	8.7–41.9	0.62
Indopeat (ip)	1	Peat	Indonesia	54.7	4.90	2.12	6.55	30.5	12.8
IndoSFLit (il)	4	Secondary forest floor litter	Indonesia	47.0	5.50	1.22	7.15	12.8–17.9	3.79
Rice Straw (rs)	3	Rice stalks after grain is removed	Indonesia	35.4	4.73	0.68	22.3	18.8–32.3	2.31
Semak (sk)	4	Successional shrub/brush after deforestation	Indonesia	46.8	5.37	1.33	6.80	12.1–26.9	5.07
German grass (gg)	3	Grass from heavily industrialized region	Germany	45.1	5.73	1.06	5.40	9.2–21.6	1.14
NWTDuff (nw)	1	Soil, litter, duff - Northwest Territories	Canada	56.8	5.09	1.62	2.80	10.7	
Cottonwood (cw)	1	Hardwood log	United States	48.0	5.84	0.04	1.30	14.6	^c
Excelsior (ex)	2	Shredded hardwood (Quaking Aspen)	United States	47.7	5.92	0.055	0.00	6.4	2.45
FirDuff (fd)	3	Douglas Fir forest floor soil, duff, litter	United States	42.4	4.65	1.06	20.9	12.3–19.3	
PPine (pp)	3	Ponderosa Pine needles	United States	51.4	6.26	0.58	3.35	15.0–15.9	2.98
PPineFirDuff (pf)	1	Ponderosa Pine/Douglas Fir forest floor soil, duff, litter	United States	43.0	4.81	0.99	18.8	15.8	47.3

^aTwo-letter fuel type abbreviation in parentheses.

^bFM (fuel moisture) expressed as dry weight %, see text. Ranges are min–max.

^cCottonwood log: radius equals 18 cm, length equals 47 cm, and mass equals 18.5 kg.

shipped directly to Montana, and stored at low temperature until burning. For these fires, a layer of sand covered the fuel bed, which simulated the sandy miombo soils. The grass was arranged vertically in clumps to simulate natural geometry (held in place with a wire mesh with $\sim 10 \times 10$ cm grid). For the miombo simulations, we added a roughly equal mass of leaf/twig litter as a layer on the sand. The fuel loading for grass fires was $0.43\text{--}0.85$ kg/m², which overlaps the range of values measured for grass loading in central Africa ($0.18\text{--}0.57$ kg/m²) [Shea *et al.*, 1996; Hoffa *et al.*, 1999; J. M. C. Pereira *et al.*, personal communication, 2002]. (We did not detect any influence of fuel loading on the relative abundance of the emitted species.) The average miombo total fuel loading was 1.0 ± 0.03 kg/m², which is in excellent agreement with field measurements described in the above studies.

2.2.2. Selection, Sampling, and Simulations of Indonesian Fuels

[8] Extensive biomass burning can occur in Indonesia, especially during El Niño years [Siegert *et al.*, 2001]. However, there have been no classical fuel consumption studies for Indonesian fires to our knowledge and the relative importance of different fuel types is unknown. A few studies observed which ecosystems burned in specific provinces of Indonesia during the fires associated with the 1997/1998 El Niño haze event over southeast Asia. Liew *et al.* [1999] used C-band SAR (synthetic aperture radar) and found that the dominant ecosystem that burned in 1997/1998 in South Kalimantan was peat swamp. The island of Sumatra and the province of West Papua also contain large areas of peatland. On the basis of Landsat thematic mapper

data and some limited post-fire observations of depth of burn for peat, Page *et al.* [2002] calculated that ~ 1.7 Pg of C was emitted by Indonesian peat fires in 1997: $\sim 26\%$ of the annual global carbon emissions from fossil fuels. On the other hand, Siegert *et al.* [2001] used AMI (active microwave instrument) SAR to map area burned in East Kalimantan during 1997/1998. According to that study, 75% of the 5.2 million hectares burned was lowland forest (mostly previously logged), secondary forest, plantations, and farmland. Of the remaining 25%, 6% was grassland, and only 6% was peat swamp forest. Much anecdotal evidence suggests that an invasive fire-maintained grass “alang-alang” (*Imperata cylindrica*) accounts for much of the fuel consumption in Indonesia [Jacobs [1988], Seavoy [1975], Pickford *et al.* [1992], and J. Goldammer, S. Siebert, and R. Yokelson, personal observations, 1997, 1994, 1994 and 1997, respectively). Smoldering piles of rice straw are ubiquitous in much of Indonesia and East Asia where rice is harvested by hand. We decided to measure the emissions from these Indonesian fuels: peat, secondary forest floor litter, semak (brush that colonizes clearings), alang-alang (grass noted above that colonizes clearings), and rice straw.

[9] A block of peat (~ 25 cm on each side) was hand-cut by B. H. Saharjo from an ongoing research plot in an *Acacia* plantation in Teluk Pulai in south Sumatra [Saharjo, 1998]. The intact peat sample was ignited with a torch and it smoldered for ~ 2.5 hr while the emissions were monitored. Secondary forest floor litter, alang-alang, semak, and rice straw were sampled in Curug village, Jasinga subdistrict, Bogor District, West Java. The fuel loading for alang-alang in this study (0.62 kg/m²) was typical for grass loading

worldwide, but only $\sim 1/3$ the loading of alang-alang measured by *Pickford et al.* [1992] on a single plot in Depok, West Java. We burned small piles of rice straw by smoldering combustion that lasted up to one hour to simulate the situation in east Asia where rice straw is burned in small to large piles that burn by smoldering for up to several days.

2.2.3. Other Fuels

[10] We burned several fuels typical of North American forests (large-diameter hardwood log, shredded hardwood, organic soil, duff, and litter) mainly for comparison to previous studies or to provide slowly changing emissions for the intercomparisons [*Yokelson et al.*, 2003b; *Christian et al.*, 2003]. We also burned grass collected by J. Goldammer near an industrial site in Germany to check for resuspension of industrial pollutants.

2.3. Fuel Characterization

[11] Carbon, hydrogen, nitrogen, chlorine, and ash content for each fuel type were measured by independent laboratories on a dry weight basis. Moisture content was determined by measuring the mass loss after holding the sample at 90°C overnight. Fuel moisture (FM) is expressed as dry weight % as follows:

$$FM = \left(\frac{\text{wet} - \text{dry}}{\text{dry}} \right) \times 100. \quad (1)$$

2.4. Trace Gas and Particle Instrumentation

2.4.1. Open-Path FTIR

[12] The open-path Fourier transform infrared spectrometer (OP-FTIR) was positioned on the sampling platform so that the open white cell spanned the stack directly in the rising emissions stream for continuous (0.83 s resolution) scanning. The OP-FTIR system [*Yokelson et al.*, 1997; *Bertschi et al.*, 2003b] includes a MIDAC model 2500 spectrometer; 1.6 m base-path, open multipass cell; and a mercury-cadmium-telluride (MCT), LN₂-cooled detector. The path length was set to 57.7 m and spectral resolution was 0.5 cm⁻¹. All spectra were stored on a computer synchronized with the rest of the data acquisition. Before each fire, we scanned for 2–3 min to obtain a background spectrum, and then made absorbance spectra for each scan during the fire at 0.83 s resolution using the background spectrum. For fires with slowly changing temperature and emissions, we increased signal to noise through spectral averaging of as many as 72 absorbance spectra (~ 1 min resolution). For fires with larger or more rapid temperature fluctuations spectral averaging was limited to 7 scans (~ 6 s resolution).

[13] We used classical least squares (CLS) spectral analysis [*Griffith*, 1996; *Yokelson and Bertschi*, 2002] to retrieve excess mixing ratios ($\Delta X = X_{\text{smoke}} - X_{\text{background}}$) for methane (CH₄), methanol (CH₃OH), ethylene (C₂H₄), phenol (C₆H₅OH), acetone (CH₃C(O)CH₃), acetol (CH₂(OH)-C(O)CH₃), isoprene (C₅H₈), hydrogen cyanide (HCN), acetylene (C₂H₂), furan (C₄H₄O), nitric oxide (NO), and formaldehyde (HCHO). We used spectral subtraction [*Yokelson et al.*, 1997] to retrieve excess mixing ratios for ammonia (NH₃), formic acid (HCOOH), acetic acid (CH₃COOH), glycolaldehyde (GA, CH₂(OH)CHO), propyl-

ene (C₃H₆), and methylvinylether (MVE, CH₃OCHCH₂). While CO₂ and CO are readily measured accurately by our OP-FTIR [*Goode et al.*, 1999], because of the large volume of data we opted to use the convenient, synchronized data for these molecules from the real-time instruments (see below). The above list of molecules, along with H₂O, accounted for all the significant features in the IR spectra, except for an occasional peak at 2848 cm⁻¹, which is still unassigned. Higher-resolution FTIR has been used to quantify SO₂ in smoke [*Yokelson et al.*, 1996], but SO₂ was not detected in this study. The detection limit for most molecules was 5–20 ppb for a 1-min measurement time (72 scans) and ~ 10 –50 ppb at the highest time resolution used (6 s or 7 s scans). The typical uncertainty in an FTIR mixing ratio is $\pm 5\%$ (1σ) because of calibration or the detection limit (2σ), whichever is greater. The less favorable detection limits at high temporal resolution (compared to FTIR field measurements) were more than offset by the factor of ~ 15 increase in trace gas mixing ratios sampled in the laboratory. The advantages and disadvantages of FTIR are discussed by *Christian et al.* [2003].

2.4.2. PTR-MS

[14] The PTR-MS sampled continuously from the emissions stream through ~ 2 m of 6 mm inside diameter (i.d.) Teflon tubing that opened directly above the center of the OP-FTIR optical path. The sample line was short to minimize losses of reactive and sticky compounds and to assure a fast response time (around 5 s). The PTR-MS employs chemical ionization to measure volatile organic compounds (VOC) in real time [*Hansel et al.*, 1995; *Lindinger et al.*, 1998]. Briefly, the instrument features a hollow cathode ion source that produces H₃O⁺ reactant ions from water vapor in the sample. The sample air then passes through a drift tube where VOC with proton affinities greater than that of water are ionized by proton transfer reactions with the H₃O⁺. The product ions are analyzed by a quadrupole mass spectrometer. Under favorable operating conditions less than 5% of the H₃O⁺ ions react with VOC in the sample and the concentration of product ions in the sample can be calculated using equation (2),

$$[\text{VOC} - \text{H}^+] \cong [\text{H}_3\text{O}^+]_0 [\text{VOC}] k_{\text{VOC}t}, \quad (2)$$

where $[\text{H}_3\text{O}^+]_0$ is the density of H₃O⁺ ions in the absence of neutral reactants, k_{VOC} is the respective reaction rate constant for the proton transfer from H₃O⁺ to the VOC and t is the reaction time, which depends on length, pressure, and voltage of the drift tube. The reaction rate of most exothermic proton transfer reactions is nearly equal to the collision rate, and when specific reaction rates are unknown they can be calculated [*Su and Chesnavich*, 1982]. An average reaction rate constant of 2×10^{-9} cm³ s⁻¹ is used in this study for the quantification of unidentified ions.

[15] During these experiments, the PTR-MS operated in either of two modes. In full mass scan mode the instrument was configured to scan incrementally from 17 to 142 atomic mass units, with a sample time of 20 ms per mass. In selected mass scan mode the instrument was configured to scan a selection of 30–36 masses, with a sample time of 0.1 to 0.2 s. Overall time resolution for either mode was about 4–8 s. The PTR-MS computer was synchronized with the rest of the data acquisition and the results were splined to match the

time resolution of the OP-FTIR data. For methanol, acetonitrile, acetone, and acetaldehyde the rate constants are known and the estimated accuracy of the mixing ratios is $\pm 15\text{--}20\%$ (2σ). For species with unknown rate constants, the overall accuracy should be better than $\pm 50\%$ with the estimate of the reaction rate constant ($\pm 30\%$) being the main source of error. The strengths and limitations of PTR-MS are discussed in more detail by *Christian et al.* [2003].

2.4.3. Canister Sampling

[16] Up to three evacuated stainless steel canisters could be simultaneously filled in ~ 10 s to ambient pressure via a “cross” manifold and a 4 mm i.d. stainless steel sampling tube that opened next to the PTR-MS inlet. The sample line pressure was logged on the data system so that the filling time of these “quick cans” with respect to other instruments was precisely known. “Integrated” cans were filled at a preselected linear rate, over a precisely known period, through another collocated inlet. Forty integrated cans and 28 quick cans taken before or during most fires were analyzed by GC-FID for CO_2 , CO, and $\text{C}_1\text{--C}_4$ hydrocarbons by the USDA Forest Service. Seven quick cans taken during the fires were analyzed at University of California, Irvine, by GC/FID, MS, and ECD for ethylene, propylene, acetylene, isoprene, benzene, toluene, and *p*-xylene. More details about the canister measurements are found elsewhere [*Hao et al.*, 1996; *Colman et al.*, 2001]. The canister data were used mostly to independently verify the accuracy of the CO_2 and CO measurements and for the intercomparisons.

Table 2. Emission Factors for Total $\text{PM}_{2.5}$, and EC, OC, Chlorine, Potassium, and Sulfur in $\text{PM}_{2.5}$ ^a

Fuel Type	$\text{PM}_{2.5}$	EC	OC	Cl in Fuel	Cl in $\text{PM}_{2.5}$	K in $\text{PM}_{2.5}$	S in $\text{PM}_{2.5}$
<i>Fire Average</i> ^b							
Alang - T	6.6			4.710	1.82	1.29	0.11
Alang - Q		c	c				
Dambo - T	2.9			0.248	0.013	0.044	0.006
Dambo - Q		1.39	0.99				
Excelsior - Q		0.53	3.20	0.032			
German grass - T	3.2			0.218	0.027	0.031	0.012
German grass - Q		0.38	2.74				
Indopeat - Q		0.04	6.02	0.962			
IndoSFLit - T	61.6			0.119	0.042	0.022	0.064
IndoSFLit - Q		0.54	15.7				
Miombo - T	3.6			0.246	0.028	0.065	0.009
Miombo - Q		1.52	2.58				
MiomboLit - T	9.8			0.235	0.044	0.076	0.024
PPine - T	36.0			0.141	0.032	0.040	0.031
PPine - Q		0.53	3.37				
Semak - T	39.2			4.350	1.06	0.58	0.14
<i>Spot Measurement (Probably Not Representative of Fire Average)</i> ^d							
Cottonwood - T	20.9			0.052	0.005	0.049	0.008
Cottonwood - Q		0.68	23.8				
Fir duff - T	40.8			0.134	0.019	0.007	0.052
Fir duff - Q		4.99	122.4				
NWT duff - T	84.3			0.727	0.560	0	0.097
Pine-Fir duff - T	51.3			0.073	0.016	0	0.025
Rice straw - T	4.2			3.310			
Semak - Q		0.63	32.8	4.350			

^aEmission factors are given in g kg^{-1} fuel. Fuel chlorine content (g kg^{-1}) is also given. T indicates Teflon filter, and Q indicates quartz filter obtained on a different fire.

^bFilter duration \approx fire duration.

^cTotal carbon equals 1.69 g kg^{-1} fuel.

^dFilter duration \ll fire duration.

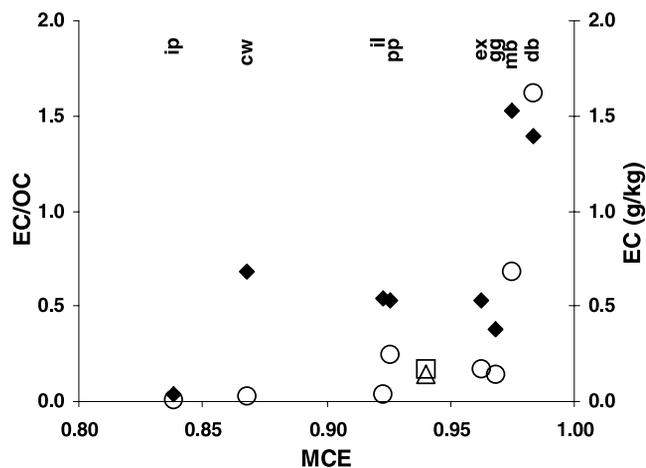


Figure 1. Particle EC/OC ratio and EC emission factors measured in this study plotted against MCE. Open circles represent EC/OC measured in this study. Also shown are global averages for savanna fires: open box, *Sinha et al.* [2003]; open triangle, *Andreae and Merlet* [2001]. Solid diamonds represent our EC values. (Two-letter fuel type abbreviations are shown at the top of the plot.) Field fires that burn at high MCE may be contributing more EC than previously thought.

2.4.4. Other Measurements

[17] The co-located 19 mm inlet used for filling canisters at a linear rate also provided sample air for continuous CO_2 (LICOR 6262) and CO (TECO 48C) measurements. The TECO and both LICORs (including the background air monitor) were calibrated daily with National Institute of Standards and Technology traceable standards. Stack air was drawn at 30 l min^{-1} through dielectric tubing to a cyclone to remove particles larger than $2.5 \mu\text{m}$ effective diameter, then onto Teflon or quartz filters. Teflon filters were analyzed gravimetrically by the USDA Forest Service [*Trent et al.*, 2000] and then by XRF, which provided halogens, potassium and sulfur. Quartz filters were analyzed for organic and elemental (“black”) carbon by independent laboratories. Only one filter collection apparatus was available so quartz and Teflon filters for the same fuel type were acquired during different fires. We continuously monitored fuel mass and stack temperature, pressure, and flow with 2 s resolution. The mass flowmeter (Kurz model 455) calibration was checked frequently by burning ethanol fires. Pure ethanol has a known % C, which is efficiently converted to CO_2 ; thus comparison of the CO_2 and mass-loss data allows a check on the flow.

3. Results

3.1. Particle Emissions for All Fuels

[18] Table 2 presents particle emissions data for each fuel type. The emission factors (EF, g kg^{-1} dry fuel) for particles with diameter $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) were determined from gravimetric analysis of Teflon filters, which were collected over the entire course of the fire for all but cottonwood, fir duff, NWT duff, pine-fir duff, and rice straw. Cottonwood and duff fires can burn for hours to days and the fires of this type in this study were truncated. The $\text{PM}_{2.5}$ data collected

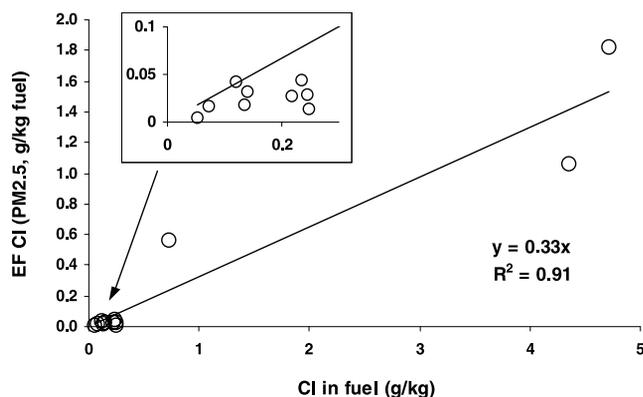


Figure 2. Regression of particle chlorine content against fuel chlorine content, suggesting that about one third of the fuel chlorine is transferred to the particles. However, the inset shows that the regression does not fit the many low values well.

over the limited initial period very likely reflect higher emissions than are typical of the whole fire [Bertschi *et al.*, 2003a]. The rice straw fire was shorter and not truncated, but the filters were taken during periods of heavy smoke and likely return values above the average for the whole fire. Spot measurements are listed separately in the table to indicate that no filter representative of the fire-average was collected for that fuel type. The values in Table 2 are based on only one or two filters per fuel type. The EF_{PM2.5} obtained for savanna-type fuels are similar to literature average values [Andreae and Merlet, 2001; Sinha *et al.*, 2003].

[19] Emission factors for elemental and organic carbon (EC and OC, respectively) are also listed in Table 2. Since emission factors can depend heavily on the relative amount of flaming and smoldering combustion, we continue our discussion using an index of this known as “modified combustion efficiency” (MCE, $\Delta\text{CO}_2/(\Delta\text{CO} + \Delta\text{CO}_2)$) [Ward and Radke, 1993]. Our dambo and miombo fires burned with MCE (0.97–0.98) near the upper end of MCE observed for individual fires in the field [Ferek *et al.*, 1998; Sinha *et al.*, 2003; Yokelson *et al.*, 2003a] (indicating nearly pure flaming). This probably contributes to our emission factor for elemental carbon (EF_{EC}) being substantially larger (~ 1.5 g/kg) than the literature average for savanna fires (0.48 g/kg, at MCE ~ 0.94) reported by Andreae and Merlet [2001] (Figure 1). Our EF_{EC} for the other fuels, which burned at lower MCE, are close to the literature averages [Andreae and Merlet, 2001]. Similarly, our EF_{OC} are lower than the literature average for African fuels, but close to previously reported values for the other fuels. In fact, the EC/OC ratio for the broad mix of fuels investigated here is weakly dependent on MCE for MCE $< \sim 0.97$ (Figure 1), but above that it is positively correlated. The study-average EC/OC for African savanna fires recently measured by Sinha *et al.* [2003] and the literature-average value derived by Andreae and Merlet [2001] are in good agreement with our current study data at the same MCE (Figure 1). However, Figure 1 and Table 2 suggest that some naturally occurring high-MCE savanna fires may be emitting much more elemental carbon (and less OC) than is currently thought.

[20] Gras *et al.* [1999] characterized smoke particles during the 1997 fires in South Kalimantan, Indonesia that burned mainly peat. They observed a very high single-scattering albedo for the smoke (ω up to 0.98) and very high hygroscopic growth (the average relative increase in light scattering as RH was ramped from 20–80% was 1.65). Since EC is the main light-absorbing component of aerosol, and OC can be polar, their observations are consistent with our observation of very low EC (0.04 g/kg) and EC/OC for peat smoke particles. Conversely, the high OC/EC ratio (~ 150) may enhance the particles action as cloud condensation nuclei and contribute to the dense cloud cover that was observed over the 1997 Kalimantan fires by two authors (D. Ward and R. Yokelson). It would be important if peat-fire smoke promotes cloud formation since cloud-processing can cause large changes in gas-phase smoke chemistry [Yokelson *et al.*, 2003a].

[21] The emission factor for chlorine in PM_{2.5} was loosely correlated to the widely ranging fuel chlorine content (Table 2 and Figure 2). The high r^2 for this plot is deceiving, as shown in the inset, since the regression line does not accurately represent the many lower values. The percentage of the fuel chlorine recovered in the PM_{2.5} was only weakly dependent on MCE ($r^2 = 0.36$), suggesting that incorporation of chlorine into the fine particles may not depend strongly on the ratio of flaming to smoldering combustion. The chlorine in the PM_{2.5} only accounted for about one third of the chlorine in the fuel. HCl is a possible combustion product that is readily detected by FTIR (detection limit ~ 10 ppb). Alang-alang was the fuel with the highest chlorine content and it burned mostly by flaming combustion; rice straw had the third highest chlorine content and burned mostly by smoldering combustion. We did not locate HCl features

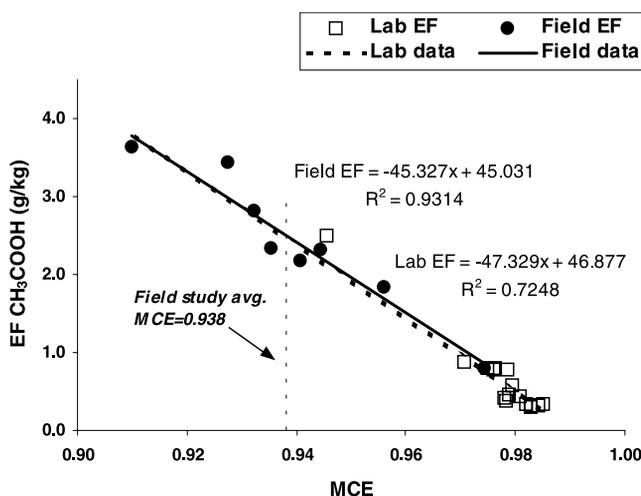


Figure 3. Emission factor (EF) for acetic acid versus MCE for African fuels (field data, solid circles; laboratory data, open squares). The data sets overlap, but the laboratory data were obtained at higher MCE on average. Independent regressions of EF versus MCE for the individual data sets predict similar EF at the field study average MCE. (The laboratory fire at MCE ~ 0.94 was omitted from the laboratory regressions, which slightly improved the agreement between predictions.)

Table 3. Comparison of Emission Factors (for Six Compounds) Calculated From EF Versus MCE on the Basis of Either Field Data Only or Laboratory Data Only^a

	Field				Laboratory				Percent Difference
	Slope	Intercept	r^2	EF	Slope	Intercept	r^2	EF	
CH ₄	-48.52	47.80	0.87	2.29	-32.40	31.92	0.86	1.53	-33.2
CH ₃ OH	-21.28	21.17	0.80	1.21	-32.98	32.45	0.68	1.51	25.3
CH ₃ COOH	-45.33	45.03	0.93	2.51	-47.33	46.88	0.72	2.48	-1.0
C ₂ H ₄	-15.91	16.11	0.76	1.19	-22.30	22.02	0.84	1.10	-7.1
Benzene	-2.87	2.87	0.81	0.18	-3.70	3.66	0.49	0.20	5.5
Toluene	-2.13	2.11	0.32	0.12	-2.04	2.01	0.70	0.10	-15.4
Average absolute difference									14.6 ± 12.5

^aThe field data are from *Yokelson et al.* [2003a], except benzene and toluene from *Sinha et al.* [2003]. MCE for all calculations is 0.938, the field study average.

in the smoke spectra from either of these fuels even when CO was as high as 60 ppm. This indicates that the EF_{HCl} for these fires was <0.05 g/kg and 0.05 g/kg is a typical, literature emission factor for chloromethane [*Andreae and*

Merlet, 2001]. Thus these gases each account for ≤~1% of the fuel chlorine. It is likely that most of the fuel chlorine remains in the ash or is emitted in unidentified trace gases.

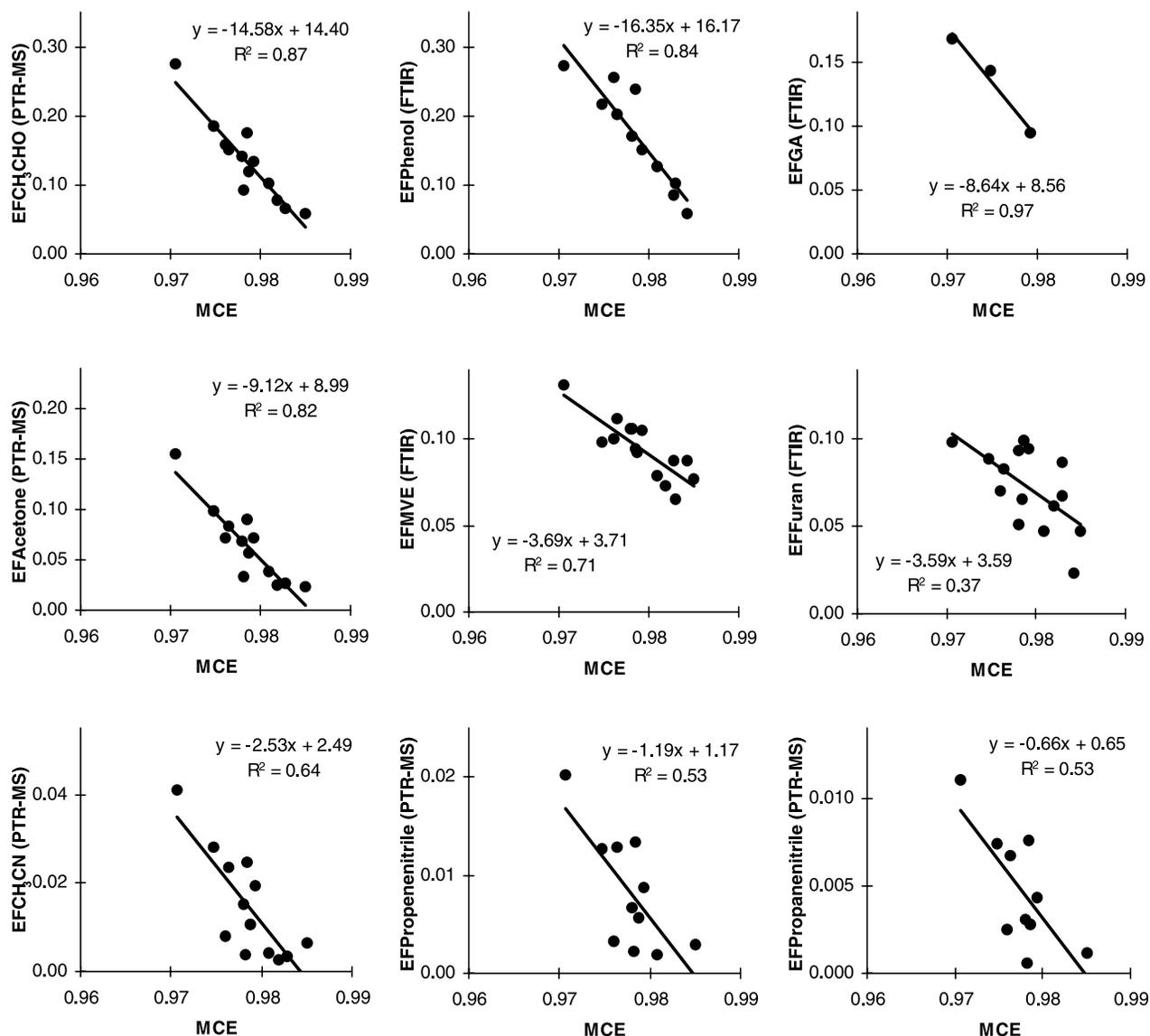


Figure 4. EF versus MCE for nine fire emissions that were below FTIR detection limits in an African field study but successfully quantified in this work. The regression equations were used as described in the text to derive values for Table 4.

[22] Total potassium and sulfur in PM_{2.5} were not dependent on MCE ($r^2 = 0.071$ and 0.11). However, an actual dependence was probably masked by variation in fuel K and S (which we did not measure), since *Ward and Hardy* [1989] observed a large dependence of EFK on MCE.

3.2. African Fuels

[23] In this study, both the high smoke concentrations and the use of PTR-MS contributed to the quantification of at least 10 gases that were not observed by FTIR or GC/FID in a recent field study of African savanna fires [*Sinha et al.*, 2003; *Yokelson et al.*, 2003a]: acetaldehyde (CH₃CHO), phenol, acetol, glycolaldehyde (GA), acetone, methylvinylether (MVE), furan, acetonitrile (CH₃CN), propenenitrile (C₃H₃N), and propanenitrile (C₃H₅N). Seven of these 10 are oxygenated volatile organic compounds (OVOC), which have large effects on modeled smoke plume chemistry and acetonitrile is important as an indicator of biomass burning that is reliably measured by PTR-MS [*Holzinger et al.*, 1999; *Mason et al.*, 2001; *Jost et al.*, 2003; *Christian et al.*, 2003]. It is important to use the new laboratory data to estimate the EF and emission ratios (ER, the relative, molar production of two species by a fire) for these compounds from typical fires in African savannas where massive biomass burning occurs. However, we do not directly use the laboratory-average emissions data for this purpose because the laboratory fires we burned with African fuels had a higher average MCE than the average MCE observed in the field in Africa. For example, recent airborne measurements in Africa [*Yokelson et al.*, 2003a] yielded an MCE of 0.941 for a miombo fire, 0.975 for a dambo fire, and ~ 0.94 as the average for 10 savanna fires. In the current study, the average MCE was 0.976 for five miombo fires and 0.980 for 10 dambo fires. Since EF and ER (relative to CO or CO₂) decrease with increasing MCE for smoldering compounds [*Yokelson et al.*, 1997], our laboratory-average EF and ER are lower than the field-average EF and ER for smoldering compounds from real fires.

[24] A preferred method to estimate the previously undetected emissions from real fires is based on the fact that our laboratory fire emission factors for African fuels have a dependence on MCE that is very similar to that of the field-fire emission factors, for compounds measured in both experiments. Figure 3 shows the laboratory and field EF for acetic acid versus MCE (as measured by FTIR). There is overlap in the MCE values from the two studies, the laboratory EF near the field average MCE is reasonable, and similar regression equations are suggested by both data sets. Table 3 compares EF calculated (at the field-average MCE) from regression equations based on either laboratory or field data for six compounds that were common to both studies. The laboratory regression equations shown in Table 3 do not include the laboratory point at MCE 0.94, because omitting it improved the average agreement for the predictions with the field observations from $\pm 23\%$ to $\pm 15\%$. The difference between the field and laboratory results is small for acetic acid, ethylene, and benzene, and not overly large for methane, methanol, and toluene. This good agreement supports the use of laboratory-based regression equations (at the field-average MCE) to calculate average African EF for compounds that were not quantified by GC, or were below FTIR detection limits, in the field.

Table 4. Emission Ratios Relative to CO₂ (mmol/mol), in Order of Abundance, for the Top Trace Gas Emissions (Excluding H₂O) Reported in the Initial Smoke From Fires in African Savanna Fuels^a

Compound	Emission Ratio,	Emission	Reference
	mmol/mol CO ₂	Factor, ^b g kg ⁻¹	
Carbon dioxide (CO ₂)	1000	1689	<i>Yokelson et al.</i> [2003a]
Carbon monoxide (CO)	66.4	71.4	<i>Yokelson et al.</i> [2003a]
Hydrogen (H ₂)	12.6	0.97	<i>Cofer et al.</i> [1996]
Methane (CH ₄)	3.53	2.17	<i>Yokelson et al.</i> [2003a]
Nitrogen oxides (NO _x as NO)	3.04	3.50	<i>Yokelson et al.</i> [2003a]
Nitrogen (N ₂)	2.87	3.08	<i>Kuhlbusch et al.</i> [1991]
Ethylene (C ₂ H ₄)	1.14	1.23	<i>Yokelson et al.</i> [2003a]
Acetic acid (CH ₃ COOH)	1.06	2.44	<i>Yokelson et al.</i> [2003a]
Formaldehyde (HCHO)	0.97	1.12	<i>Yokelson et al.</i> [2003a]
Methanol (CH ₃ OH)	0.96	1.18	<i>Yokelson et al.</i> [2003a]
Sulfur dioxide (SO ₂)	0.85	2.09	<i>Sinha et al.</i> [2003]
Hydrogen cyanide (HCN)	0.57	0.59	<i>Yokelson et al.</i> [2003a]
Ammonia (NH ₃)	0.46	0.30	<i>Yokelson et al.</i> [2003a]
Acetaldehyde (CH ₃ CHO)	0.45	0.76	this work (PTR-MS)
Formic acid (HCOOH)	0.39	0.69	<i>Yokelson et al.</i> [2003a]
Acetylene (C ₂ H ₂)	0.29	0.29	<i>Yokelson et al.</i> [2003a]
Phenol (C ₆ H ₅ OH)	0.23	0.83	this work (OP-FTIR)
Acetol (C ₃ H ₆ O ₂)	0.22	0.62	this work (PTR-MS)
Glycolaldehyde (C ₂ H ₄ O ₂)	0.21	0.48	this work (OP-FTIR)
Propylene (C ₃ H ₆)	0.20	0.32	<i>Sinha et al.</i> [2003]
Ethane (C ₂ H ₆)	0.19	0.22	<i>Sinha et al.</i> [2003]
Methylvinylether (C ₃ H ₆ O)	0.11	0.24	this work (OP-FTIR)
Furan (C ₄ H ₄ O)	0.085	0.21	this work (OP-FTIR)
Acetone (C ₃ H ₆ O)	0.085	0.19	this work (PTR-MS) ^c
Acetonitrile (CH ₃ CN)	0.082	0.13	this work (PTR-MS)
Benzene (C ₆ H ₆)	0.069	0.21	<i>Sinha et al.</i> [2003] ^d
Toluene (C ₆ H ₅ CH ₃)	0.052	0.18	<i>Sinha et al.</i> [2003] ^e
Chloromethane (CH ₃ Cl)	0.037	0.072	<i>Sinha et al.</i> [2003]
Propane (C ₃ H ₈)	0.035	0.059	<i>Sinha et al.</i> [2003]
1, 3 Butadiene (C ₄ H ₆)	0.035	0.073	<i>Sinha et al.</i> [2003]
1-butene (C ₄ H ₈)	0.030	0.064	<i>Sinha et al.</i> [2003]
Propenenitrile (C ₃ H ₃ N)	0.030	0.061	this work (PTR-MS)
Propanenitrile (C ₃ H ₅ N)	0.020	0.042	this work (PTR-MS)

^aField measurements are given precedence over laboratory measurements when both are available, but the field and laboratory measurements agree well. Below an emission ratio of ~ 0.08 , the list is mostly incomplete because of a lack of OVOC measurements.

^bConsistent with this set of emission ratios and derived as discussed in section 3.2.

^cCalculated as PTR-MS mass 59 minus FTIR methylvinylether (FTIR acetone below detection limit).

^dThis work PTR-MS benzene equals 0.07 (mmol/mol CO₂).

^eThis work PTR-MS toluene equals 0.03 (mmol/mol CO₂).

[25] The required regression equations are derived next. Figure 4 shows the EF versus MCE plots from this study for acetaldehyde, acetone, acetonitrile, propanenitrile, and propenenitrile as measured by PTR-MS; and for phenol, glycolaldehyde, methylvinylether, and furan as measured by OP-FTIR. (The reasons for choosing data for a compound from a particular instrument are discussed by *Christian et al.* [2003]). The regression equations shown were used to calculate recommended field average EF for these compounds. Recommended ER between compounds (at the field average MCE) can be calculated from these EF with a correction for molecular mass.

[26] We present recommended average values for the main initial emissions from African savanna fires in Table 4 based on integrating field and laboratory results.

Table 5. Average MCE and Emission Ratios for Indonesian Fuels^a

	Alang-Alang (4) ^b		Peat (1)		Secondary Forest Litter (4)		Rice Straw (3)		Semak (4)	
	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS
MCE	0.953 (0.008)		0.838		0.901 (0.030)		0.811 (0.046)		0.891 (0.012)	
$\Delta\text{CO}/\Delta\text{CO}_2$	49.9 (8.8)		194.0		110.7 (36.7)		236.1 (69.0)		122.6 (15.0)	
$\Delta\text{CH}_4/\Delta\text{CO}$	29.0 (12.5)		178.0		81.7 (14.9)		94.5 (14.9)		92.3 (11.0)	
$\Delta\text{C}_2\text{H}_4/\Delta\text{CO}$	8.59 (3.6)		12.6		11.8 (3.4)		15.9 (3.3)		19.0 (3.7)	
$\Delta\text{C}_2\text{H}_2/\Delta\text{CO}$	2.71 (0.48)		0.31		2.15 (0.44)		2.79 (0.21)		4.30 (2.1)	
$\Delta\text{C}_3\text{H}_6/\Delta\text{CO}$	2.83 (2.3)	3.13 (1.1)	10.0	12.8	4.89 (2.3)	15.1 (4.1)	5.89 (3.5)	23.5 (3.2)	8.82 (0.44)	22.9 (5.2)
$\Delta\text{Benzene}/\Delta\text{CO}$		0.70 (0.21)		5.91		1.51 (0.60)		2.12 (0.58)		2.20 (0.21)
$\Delta\text{Toluene}/\Delta\text{CO}$		0.26 (0.12)		2.44		1.51 (0.59)		2.22 (0.81)		2.20 (1.3)
$\Delta\text{HfO}/\Delta\text{CO}$	1.77 (0.79)	0.51 (0.17)	2.36	0.93	3.40 (0.73)	2.24 (1.1)	7.33 (1.1)	3.21 (0.37)	4.51 (1.3)	2.04 (0.70)
$\Delta\text{HAc}/\Delta\text{CO}$	6.38 (2.0)		20.5		40.4 (17.2)		27.8 (2.5)		42.2 (21.5)	
$\Delta\text{GA}/\Delta\text{CO}$	2.71 (1.2)		3.62		4.30 (0.87)		14.2 (3.7)		7.40 (1.6)	
Mass 61 ^c		8.61 (2.8)		26.6		54.9 (16.8)		83.9 (22.5)		57.5 (48.0)
$\Delta\text{HCHO}/\Delta\text{CO}$	9.88 (3.6)		6.40		13.1 (3.3)		16.6 (3.4)		18.9 (4.6)	
$\Delta\text{CH}_3\text{CHO}/\Delta\text{CO}$		4.46 (2.2)		10.7		11.3 (2.9)		29.8 (5.7)		15.6 (2.8)
$\Delta\text{MeOH}/\Delta\text{CO}$	6.30 (3.8)	5.61 (3.1)	37.2	37.2	21.4 (10.4)	22.8 (9.4)	30.3 (4.7)	34.6 (6.1)	25.7 (8.8)	25.7 (10.9)
$\Delta\text{Phenol}/\Delta\text{CO}$	1.19 (0.94)	0.79 (0.31)	5.27	5.17	6.50 (2.5)	2.76 (1.1)	4.94 (1.1)	8.82 (3.2)	4.88 (2.6)	4.60 (3.4)
$\Delta\text{Acetol}/\Delta\text{CO}$	8.09 (3.0)	1.97 (1.0)	7.91	4.31	19.5 (6.7)	8.12 (4.8)	73.6 (12.0)	55.6 (20.8)	27.0 (9.7)	14.4 (14.4)
$\Delta\text{Acetone}/\Delta\text{CO}^d$		1.11 (1.0)	2.96	4.47	3.80 (1.8)	3.79 (1.0)	6.86 (0.49)	15.2 (3.9)	3.83 (0.59)	7.09 (3.1)
$\Delta\text{MVE}/\Delta\text{CO}$	0.78 (0.17)		2.01		2.50 (0.22)		1.17 (0.19)		2.32 (0.44)	
$\Delta\text{Furan}/\Delta\text{CO}$	1.13 (0.20)		3.85		2.17 (0.68)		1.40 (0.34)		2.44 (0.82)	
$\Delta\text{Isoprene}/\Delta\text{CO}$	0.43 (0.39)		0.80		1.68 (0.84)		4.91 (1.5)		4.29 (1.7)	
Mass 69 ^e		0.88 (0.39)		2.23		4.11 (0.59)		10.2 (3.6)		6.33 (4.6)
$\Delta\text{NH}_3/\Delta\text{CO}$	20.4 (18.2)		160.5		42.8 (1.7)		37.0 (4.0)		68.3 (32.3)	
$\Delta\text{HCN}/\Delta\text{CO}$	3.18 (0.44)		41.1		5.41 (1.2)		5.12 (1.0)		6.68 (0.75)	
$\Delta\text{NO}/\Delta\text{CO}_2$	1.02 (0.17)		0.89		1.55 (0.13)		0.74 (0.47)		1.51 (0.40)	
$\Delta\text{CH}_3\text{CN}/\Delta\text{CO}$		1.21 (0.62)		17.3		3.57 (0.43)		5.36 (1.2)		5.23 (2.1)
$\Delta\text{C}_3\text{H}_5\text{N}/\Delta\text{CO}$		0.17 (0.06)				0.71 (0.12)		1.25 (0.28)		1.16 (0.72)
$\Delta\text{C}_3\text{H}_3\text{N}/\Delta\text{CO}$		0.36 (0.11)				0.61 (0.12)		0.70 (0.14)		1.12 (0.35)

^aEmission ratios are given in mmol/mol. The standard deviation is in parentheses. HfO, formic acid; HAc, acetic acid; GA, glycolaldehyde; MVE, methylvinylether.

^bNumber in parentheses following fuel type denotes maximum number of fires sampled.

^cPTR-MS mass 61 can be compared to FTIR $(\Delta\text{HAc} + \Delta\text{GA})/\Delta\text{CO}$.

^dPTR-MS acetone values are PTR mass 59 minus FTIR MVE.

^ePTR-MS mass 69 can be compared to FTIR $(\Delta\text{Furan} + \Delta\text{Isoprene})/\Delta\text{CO}$.

The core of these recommendations is the extensive field measurements of ER in nascent smoke from African savanna fires made during SAFARI 2000 [Yokelson *et al.*, 2003a; Sinha *et al.*, 2003]. On the basis of field measurements in nascent smoke (except for N_2), Yokelson *et al.* [2003a] presented a “reasonably complete” list of the top 15 savanna fire emissions in order of molar abundance. We have augmented that list with ER for the new compounds measured in this study (computed as described above). The extended ER list is presented in columns 1 and 2 of Table 4 in order of their ER to the main C-containing emission CO_2 so that their average relative abundance is highlighted. When both laboratory and field measurements of the ER to CO_2 were available for initial smoke, we used the field data; although, as discussed above, the agreement between laboratory and field data was good for African fuels when MCE is taken into account. For applications requiring EF, we present recommended EF in column 3 for each species that are consistent with our recommended ER. The table is designed to illustrate the relative importance of the different biomass burning emissions and to serve as a starting point for models, emissions inventories, etc. The uncertainty in the entries is governed by numerous complex factors such as natural variation, representativeness of the sampling and the fires sampled, instrumental error, etc. [Yokelson *et al.*, 2003a]. The actual average ER or EF for African savanna fires might deviate from the value in Table 4 by at least $\pm 50\%$ for some nonmethane organic compounds (NMOC).

[27] While the previous list of the top 15 compounds was complete (except for acetaldehyde), this extended list is missing most of the entries below an emission ratio of ~ 0.08 because of the lack of positive identification for OVOC. In fact, we note that some of the major emissions detected by PTR-MS are not in Table 4. For instance, a number of (protonated) masses have study-average emission factors of $\sim 0.4\text{--}0.7$ g/kg, which would place them in the middle of Table 4 on a mass basis. Some of these are listed with tentative identifications in parentheses: mass 73 (methylethylketone), mass 97 (furfural, dimethylfuran), mass 99 (C7 alkenes), mass 109 (benzyl alcohol), mass 111 (trimethylfuran), and mass 113 (C8 alkenes). We estimate that we were able to positively identify, on a molar basis, about 90% of the NMOC, which accounted for $\sim 70\%$ of the carbon emitted as NMOC. The process of compound identification, which led to gases being included in the tables in this paper, is discussed in detail elsewhere [Christian *et al.*, 2003].

[28] An important feature of the earlier version of the list was that OVOC accounted for $\sim 70\%$ of the NMOC emitted by savanna fires on a molar basis. With the increased sensitivity of this study, OVOC still account for $\sim 70\%$ of the NMOC. Unfortunately, below the level of abundance for acetone in Table 4 (below the 24th most abundant compound), we cannot positively identify OVOC even though they dominate. More work is needed to extend reliable speciation of OVOC in mixtures to lower levels since even

Table 6. Average Emission Factors for Indonesian Fuels^a

	Alang-Alang (4) ^b		Peat (1)		Secondary Forest Litter (4)		Rice Straw (3)		Semak (4)	
	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS	OP-FTIR	PTR-MS
CO ₂	1629 (19)		1703		1618 (83)		1216 (97)		1567 (35)	
CO	51.6 (8.6)		210.3		112.5 (31.6)		179.9 (39.8)		122.0 (12.8)	
CH ₄	0.90 (0.50)		20.80		5.26 (1.95)		9.59 (2.01)		6.41 (0.86)	
C ₂ H ₄	0.47 (0.26)		2.57		1.31 (0.55)		2.84 (0.86)		2.33 (0.59)	
C ₂ H ₂	0.13 (0.05)		0.06		0.22 (0.08)		0.47 (0.13)		0.50 (0.26)	
C ₃ H ₆	0.24 (0.22)	0.25 (0.12)	3.05	3.71	0.89 (0.61)	2.58 (1.32)	1.52 (0.86)	5.35 (1.21)	1.61 (0.18)	3.92 (0.66)
Benzene		0.10 (0.03)		3.19		0.43 (0.07)		0.87 (0.20)		0.71 (0.09)
Toluene		0.04 (0.02)		1.55		0.51 (0.12)		1.08 (0.35)		0.80 (0.37)
HCOOH	0.15 (0.07)	0.04 (0.01)	0.79	0.30	0.65 (0.30)	0.44 (0.29)	2.12 (0.26)	0.80 (0.20)	0.92 (0.34)	0.39 (0.14)
CH ₃ COOH	0.73 (0.32)		8.97		10.56 (6.96)		10.61 (1.91)		10.87 (5.45)	
Glycolaldehyde	0.27 (0.15)		1.59		1.06 (0.48)		5.31 (1.01)		1.95 (0.55)	
Mass 61 ^c		0.99 (0.46)		11.04		13.66 (7.43)		26.39 (2.75)		13.51 (10.96)
HCHO	0.54 (0.26)		1.40		1.64 (0.84)		3.17 (0.88)		2.49 (0.72)	
CH ₃ CHO		0.38 (0.24)		3.27		2.03 (1.04)		7.05 (1.59)		2.79 (0.32)
Methanol	0.40 (0.28)	0.35 (0.24)	8.69	8.23	3.02 (2.13)	3.10 (1.98)	6.32 (2.19)	6.07 (1.77)	3.55 (1.17)	3.30 (1.19)
Phenol	0.22 (0.20)	0.14 (0.07)	3.62	3.37	2.65 (1.60)	0.95 (0.25)	2.94 (0.78)	4.34 (1.27)	1.97 (1.00)	1.68 (1.16)
Acetol	0.92–1.59	0.28 (0.18)	4.28	2.21	6.12 (3.63)	2.32 (1.69)	34.48 (6.74)	21.34 (5.15)	8.69 (3.35)	4.15 (4.15)
Acetone ^d		0.13 (0.14)	1.25	1.75	0.95 (0.70)	0.80 (0.55)	2.53 (0.40)	4.60 (0.85)	0.95 (0.19)	1.64 (0.59)
MVE ^e	0.08 (0.01)		0.85		0.64 (0.16)		0.43 (0.07)		0.58 (0.13)	
Furan	0.14 (0.04)		1.91		0.63 (0.33)		0.62 (0.24)		0.71 (0.21)	
Isoprene	0.06 (0.06)		1.38		0.49 (0.36)		2.14 (0.88)		1.23 (0.37)	
Mass 69 ^f		0.11 (0.06)		1.05		1.09 (0.34)		3.63 (1.08)		1.67 (1.07)
NH ₃	0.70 (0.68)		19.92		2.91 (0.78)		4.10 (1.24)		4.95 (2.19)	
HCN	0.16 (0.04)		8.11		0.60 (0.27)		0.87 (0.19)		0.78 (0.10)	
NO	1.13 (0.20)		1.00		1.71 (0.18)		0.62 (0.40)		1.62 (0.44)	
CH ₃ CN		0.09 (0.06)		4.91		0.58 (0.22)		1.19 (0.35)		0.86 (0.27)
C ₃ H ₃ N		0.02 (0.01)				0.15 (0.05)		0.35 (0.01)		0.25 (0.12)
C ₃ H ₃ N		0.04 (0.02)				0.12 (0.02)		0.19 (0.01)		0.24 (0.07)

^aValues are given in g kg⁻¹ dry fuel (ash free), CO and CO₂ by TECO and LICOR. The standard deviation is in parentheses.

^bNumber in parentheses following fuel type denotes maximum number of fires sampled.

^cPTR-MS mass 61 can be compared to FTIR CH₃COOH + glycolaldehyde.

^dPTR-MS acetone values are PTR-MS mass 59 minus FTIR MVE.

^eMVE, methylvinylether.

^fPTR-MS mass 69 can be compared to FTIR furan + isoprene.

relatively less abundant gases can have important effects on atmospheric chemistry.

3.3. Indonesian Fuels

[29] There are no field measurements of MCE or emission factors for “real” Indonesian fires to compare to our simulated fires. A few indirect comparisons can be made that suggest that our laboratory fires may be representative. The MCE for our Indonesian peat fire (0.838) was identical to the MCE for peat from Minnesota and a little above the MCE for peat from Alaska that were burned at FSL several years ago [Yokelson *et al.*, 1997]. The Indonesian grass and forest fuels burned with lower MCE than our African fuels and with MCE that were well within the range observed for grass and forest fuels in Brazil as shown in Figures 3–8 of Ferek *et al.* [1998] and Figures 7 and 8 of Ward *et al.* [1992].

[30] Fire-integrated ER and EF for the Indonesian fuels are presented in Tables 5 and 6, respectively. The $\Delta X/\Delta Y$ notation in Table 5 indicates the measured, fire-integrated ER $(X_{\text{smoke}} - X_{\text{background}})/(Y_{\text{smoke}} - Y_{\text{background}})$, where Y is CO or CO₂. We show the ER for CO and flaming compounds versus CO₂ and the ER for smoldering compounds versus CO [Lobert *et al.*, 1991]. The ER and EF are listed by fuel type for both FTIR and PTR-MS. The standard deviation (in parentheses) is an indicator of the variation among separate burns of the same fuel type. The discussion in section 3.2 about the completeness of Table 4 also applies

to Tables 5 and 6. Some major features of these data are discussed below.

[31] Acetol (hydroxyacetone), previously unreported in smoke, was emitted in very large quantities from burning rice straw (~6.5% of CO). This is a level comparable to methane, but it represents more than twice as much carbon! The acetol emissions were large for semak and litter (~2% of CO) and substantial (~0.6% of CO) for the other Indonesian fuels (peat and grass). The acetol emissions from African fuels were much lower (~0.1–0.2% of CO). In previous studies, acetic acid, methanol, and formaldehyde were consistently the three most abundant OVOC emitted by fires [Goode *et al.*, 2000; Yokelson *et al.*, 2003a]. On average, for the Indonesian fuels, acetol is the third most abundant OVOC, acetaldehyde is fourth, and formaldehyde is displaced to fifth (Table 7). Acetol has a UV cross-section similar to that of acetone and reacts quickly with OH [Orlando *et al.*, 1999]. We also report small emissions of methylvinylether for the first time, mostly from peat and litter.

[32] The NH₃ emissions from the single Indonesian peat sample were very large (16% of CO). This is consistent with very large NH₃ emissions noted for Minnesota peat (15% of CO) [Yokelson *et al.*, 1997]. The NH₃ emissions were in the range of 2–6.8% of CO for the other Indonesian fuels, suggesting that Indonesian fires may produce a lot of particle ammonium nitrate. The HCN and acetonitrile emissions were large for peat (4.1 and 1.7% of CO,

Table 7. Emission Ratios Relative to CO₂ for the Top Trace Gas Emissions (Excluding H₂O and SO₂) From Fires in Indonesian Fuels, in Order of Abundance^a

Compound	Emission Ratio, mmol/mol CO ₂	Emission Factor, ^b g kg ⁻¹
Carbon dioxide (CO ₂)	1000	1509
Carbon monoxide (CO)	142.7	137
Hydrogen (H ₂) ^c	49.7	3.41
Methane (CH ₄)	13.6	7.46
Ammonia (NH ₃)	9.39	5.47
Acetic acid (CH ₃ COOH)	3.91	8.05
Methanol (CH ₃ OH)	3.45	3.79
Acetol (C ₃ H ₆ O ₂) ^d	3.15	7.99
Nitrogen (N ₂) ^e	2.87	2.76
Acetaldehyde (CH ₃ CHO)	2.05	3.09
Ethylene (C ₂ H ₄)	1.90	1.82
Formaldehyde (HCHO)	1.85	1.90
Hydrogen cyanide (HCN)	1.75	1.62
Nitric oxide (NO)	1.14	1.17
Acetonitrile (CH ₃ CN)	0.93	1.31
Propylene (C ₃ H ₆)	0.92	1.33
Glycolaldehyde (C ₂ H ₄ O ₂)	0.92	1.89
Acetone (C ₃ H ₆ O) ^f	0.65	1.29
Phenol (C ₆ H ₅ OH)	0.65	2.10
Formic acid (HCOOH)	0.55	0.87
Benzene (C ₆ H ₆)	0.35	0.94
Acetylene (C ₂ H ₂)	0.35	0.31
Isoprene (C ₅ H ₈)	0.35	0.82
Furan (C ₄ H ₄ O)	0.31	0.72
Methylvinylether (C ₃ H ₆ O)	0.25	0.50
Toluene (C ₆ H ₅ CH ₃)	0.25	0.79
Propanenitrile (C ₃ H ₅ N)	0.12	0.23
Propenenitrile (C ₃ H ₃ N)	0.10	0.18

^aEmission ratios are given in mmol/mol. Criteria for inclusion in the table are discussed in text and by *Christian et al.* [2003].

^bCalculated from this set of emission ratios at the average, ash-free fuel carbon content of 50%.

^cEstimated from data for Brazil [*Ward et al.*, 1992].

^dAverage of PTR-MS and FTIR result.

^eEstimated from data of *Kuhlbusch et al.* [1991].

^fPTR-MS mass 59 minus FTIR methylvinylether. FTIR acetone ER equals 0.62.

respectively), but much smaller for the other Indonesian fuels (0.12–0.67% of CO), which is similar to the African fuels.

[33] The emission factors for all Indonesian fuels for NO_x (as NO) were in the range of 0.6–1.7 g/kg, which is low compared to African fuels (~3.5–4.5 g/kg) [*Andreae and Merlet*, 2001; *Yokelson et al.*, 2003a] and may limit O₃ formation in Indonesian biomass burning plumes [*Tsutsumi et al.*, 1999]. *Sawa et al.* [1999] reported low ΔNO_x/ΔCO ratios (~0.0002–0.0005) in smoke of unknown age over South Kalimantan in 1997 where peat was a major fuel component. This ratio is lower than our measurement of the ΔNO/ΔCO ratio for nascent smoke from burning Indonesian peat of ~0.0046. Our measured ratio is identical to the ΔNO_x/ΔCO ratio of 0.0046 assumed by *Levine* [1999] for Indonesian peat on the basis of earlier work [*Yokelson et al.*, 1997], but more than a factor of 6 below the ΔNO_x/ΔCO ratio of ~0.03 assumed by *Hauglustaine et al.* [1999], suggesting that they may have greatly overestimated O₃ production from the 1997/1998 fires.

[34] The estimate of total carbon emissions for peat fires by *Page et al.* [2002] can be combined with our emission ratios to CO₂ for peat fires (derived from Table 5) to roughly estimate the emissions of other compounds from these fires. As an example, this approach suggests that

328 Tg of CO and 28 Tg of NH₃ were emitted by the 1997/1998 Indonesian fires. These amounts are approximately one and 22 times the total annual emissions of these compounds from biomass burning as estimated by *Crutzen and Andreae* [1990]. The large interannual variability in biomass burning is illustrated. During 1997/1998, *Rinsland et al.* [1999] observed an enhancement in column HCN/CO above Mauna Loa, which they attributed to biomass burning in Southeast Asia. They determined a ΔHCN/ΔCO of 1%. Our ΔHCN/ΔCO ER for peat fires was ~4%. The difference could be due to variable ER from burning peat [*Yokelson et al.*, 1997], contribution of other fire types in Asia, and/or transport of emissions from fossil fuel burning and fires in other areas [*Chatfield et al.*, 2002].

[35] As stated earlier, we don't know the relative amount of the different fuels that burn on average in Indonesia. However, we can construct a plausible, and fairly comprehensive, table of the main Indonesian fire emissions (except for SO₂) by weighting the results for all the fuel types in Table 5 equally. The compounds we measured are shown in order of abundance in Table 7. (We have incorporated laboratory data for N₂ from *Kuhlbusch et al.* [1991] and field data for H₂ obtained by *Ward et al.* [1992] in Brazil since the range of ecosystems they probed probably represents Indonesia better than the African savanna fire measurements of *Cofer et al.* [1996]. SO₂ data for Brazil is not "imported" because of the potential for high S content in peat.) The format and the limits on completeness and confidence for Table 4 apply for Table 7. We also note that neither Table 7 nor Table 4 include the fact that very large quantities of biomass are burned as domestic fuel in Indonesia and Africa [*Yevich and Logan*, 2003]. (The emissions from African biofuel use were recently found to rival or exceed the emissions from African savanna fires [*Bertschi et al.*, 2003b].) Table 7 implies that on a molar basis, OVOC account for ~77% of the NMOC emitted by nondomestic Indonesian fires. In addition, the NH₃ emissions are comparable to the CH₄ emissions.

4. Conclusions

[36] These experiments demonstrate the importance of OVOC emissions from biomass burning and that our capacity to sensitively speciate OVOC in complex mixtures limits our understanding of gas-phase atmospheric chemistry. For example, 7 of the 10 "new" compounds that we measured for African fuels in the laboratory, because of increased concentrations, are OVOC. OVOC accounted for 70% of NMOC emitted by African savanna fires and 77% of the NMOC from Indonesian fires (on a molar basis). Indonesian rice straw emitted high levels of acetol (hydroxyacetone), a compound that influences HO_x chemistry. We present the most complete table available of the main emissions from African savanna fires. This study also provides the best available speciation of trace gas and particle emissions from biomass burning in Southeast Asian fuels.

[37] **Acknowledgments.** This research was supported by the National Science Foundation under grants ATM-9900494 and ATM-0228003; the Interagency Joint Fire Science Program; the Rocky Mountain Research Station, Forest Service, U.S. Department of Agriculture (RMRS-99508-RJVA and 03-JV-11222049-046); and the Max Planck Society. Betina

Kleiss thanks the Foundation Gran Mariscal de Ayacucho (Fundayacucho) and the German Academic Exchange Service (DAAD) for financial support. Rupert Holzinger thanks the Austrian Fonds zur Förderung der wissenschaftlichen Forschung (project J1743-PHY) for financial support. We thank Mike Chandler, who helped carry out the fires.

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