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Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy

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Abstract. Biomass burning is an important source of many trace gases in the global troposphere. We have constructed an airborne trace gas measurement system consisting of a Fourier transform infrared spectrometer (FTIR) coupled to a "flow-through" multipass cell (AFTIR) and installed it on a U. S. Department of Agriculture Forest Service King Air B-90. The first measurements with the new system were conducted in North Carolina during April 1997 on large, isolated biomass fire plumes. Simultaneous measurements included Global Positioning System (GPS); airborne sonde; particle light scattering, CO, and CO_2; and integrated filter and canister samples. AFTIR spectra acquired within a few kilometers of the fires yielded excess mixing ratios for 10 of the most common trace gases in the smoke: water, carbon dioxide, carbon monoxide, methane, formaldehyde, acetic acid, formic acid, methanol, ethylene, and ammonia. Emission ratios to carbon monoxide for formaldehyde, acetic acid, and methanol were each 2.5 ± 1%. This is in excellent agreement with (and confirms the relevance of) our results from laboratory fires. However, these ratios are significantly higher than the emission ratios reported for these compounds in some previous studies of "fresh" smoke. We present a simple photochemical model calculation that suggests that oxygenated organic compounds should be included in the assessment of ozone formation in smoke plumes. Our measured emission factors indicate that biomass fires could account for a significant portion of the oxygenated organic compounds and HO_x present in the tropical troposphere during the dry season. Our fire measurements, along with recent measurements of oxygenated biogenic emissions and oxygenated organic compounds in the free troposphere, indicate that these rarely measured compounds play a major, but poorly understood, role in the HO_x, NO_x, and O_3 chemistry of the troposphere.

1. Introduction

Biomass burning can be a useful land management practice [*Wade and Lunsford*, 1989], a natural and beneficial part of the ecology of the world's seasonally dry forests and grasslands [*Mutch*, 1994], a key component of important agricultural systems [*Steinhart and Steinhart*, 1974; *Jordan*, 1985], and an enormous potential source of renewable energy [*Brink et al.*, 1976]. Biomass burning is also a significant source of atmospheric trace gases and particles [*Crutzen and Andreae*, 1990]. Uncertainty in the initial characteristics and the subsequent transformations of these emissions is a major limiting factor in models of atmospheric chemistry, radiative transfer, and global climate change [*Crutzen and Carmichael*, 1993; *Kaufman and Nakajima*, 1993; *Prather et al.*, 1994]. Airborne studies have quantified some of the important

atmospheric impacts that result from individual fires [*Nance et al.*, 1993] or that occur over large regions where many different types of fires burn simultaneously [*Andreae et al.*, 1988, 1994; *Lindesay et al.*, 1996]. The field work of several investigators [*Ward et al.*, 1992, 1996] has helped clarify how the different types of fuels and burning conditions, associated with specific land use practices, affect the initial emissions of particles, CO_2, CO, and hydrocarbons. Laboratory studies of simulated fires have provided measurements of the initial emissions for many compounds, including some containing nitrogen or halogens [*Lobert et al.*, 1991; *Kuhlbusch et al.*, 1991].

We have carried out a series of laboratory studies designed to give an overview of fire emissions that has exploited the high accuracy possible in the laboratory environment and the advantages of open-path Fourier transform infrared spectroscopy (OP-FTIR) [*Yokelson et al.*, 1996b, 1997, 1999; *Goode et al.*, 1999]. The advantages of OP-FTIR included the ability to make continuous, smoke-plume-integrated, low-interference measurements of nearly any reactive or stable gas present at, or above, mixing ratios of a few parts per billion by volume (ppbv). In the laboratory we made OP-FTIR measurements of the major emissions generated by the different combustion processes throughout fires in well-characterized fuels. These emissions included carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), formaldehyde (HCHO), hydroxyacetaldehyde (CH_2OHCHO),

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methanol (CH$_3$OH), phenol (C$_6$H$_5$OH), acetic acid (CH$_3$COOH), formic acid (HCOOH), sulfur dioxide (SO$_2$), carbonyl sulfide (OCS), nitric oxide (NO), nitrogen dioxide (NO$_2$), nitrous oxide (N$_2$O), ammonia (NH$_3$), hydrogen cyanide (HCN), ethylene (C$_2$H$_4$), ethane (C$_2$H$_6$), acetylene (C$_2$H$_2$), propene (C$_3$H$_6$), isobutene (C$_4$H$_8$), and water from laboratory fires in grass, brush, hardwood, coniferous, organic soil, and other fuels [*Yokelson et al.*, 1996a, 1996b, 1997, 1999; *Goode et al.*, 1999]. We compared our OP-FTIR technique with other more established techniques and the results implied good accuracy for our relatively new method [*Yokelson et al.*, 1996a, 1997; *Goode et al.*, 1999]. Our results included confirmation of earlier reports that formaldehyde is a ubiquitous fire product [*Griffith et al.*, 1991] by finding that it was emitted at ~ 2% of CO for a large selection of different fuels. In addition, we found that many other oxygenated organic molecules, such as hydroxyacetaldehyde, acetic acid, formic acid, methanol, and phenol, could be emitted at similar levels, or up to several hundred times the amount previously measured by some other techniques [*Yokelson et al.*, 1996b, 1997]. These compounds are all of atmospheric importance, most frequently as HO$_x$ sources [*Finlayson-Pitts and Pitts*, 1986; *Griffith et al.*, 1991; *Yokelson et al.*, 1996b].

We initiated airborne FTIR studies for two major reasons. First, the convection column above a fire should draw in the fire emissions from all the combustion processes and provide a good comparison to our laboratory data integrated over a whole fire. Thus we can confirm the relevance of our results from laboratory fires. Field confirmation for high levels of oxygenated organic molecules is especially important, as they are considered difficult to measure and would contribute strongly to plume chemistry. Second, most of the species emitted by fires react too quickly to be well mixed in the global troposphere [*Prather et al.*, 1994]. Several different likely, but incompletely understood, local-regional atmospheric processing scenarios could strongly affect the local-global impact. Detailed chemistry-transport models (including smoke dilution rate; temperature effects on reaction rates, thermal decomposition, and absorption cross sections; available UV; and known heterogeneous processes) need to be compared to in situ data sets. This will help determine how well we can understand and predict the atmospheric processing.

In early 1997 we constructed a new airborne Fourier transform infrared spectrometer (AFTIR) coupled to a flow-through multipass cell. We installed AFTIR aboard the Forest Service King Air B-90 and sampled three fires in North Carolina and four fires and the regional haze in Alaska (during April and June 1997, respectively). The goal of these first missions was to acquire airborne measurements of the smoke chemical composition and transport on isolated biomass burning plumes both near the source and downwind. The airborne source measurements should be comparable to our laboratory measurements of initial emissions, and our downwind measurements (which included actual smoke age) could be directly comparable to plume models.

On the fires in North Carolina we were able to perform detailed source characterization. Because the plumes from these fires extended into controlled airspace we were not able to sample them more than a few kilometers downwind. The AFTIR data from these North Carolina fires are reported here along with a description of the prototype AFTIR system, a preliminary assessment of the accuracy of the first AFTIR

results, a comparison with results from other studies, and a brief discussion of some possible influences of oxygenated organic compounds on plume chemistry. On the fires we sampled in Alaska, we were successful in measuring both source composition and downwind O$_3$ formation. These results are being reported separately (J. G. Goode et al., manuscript in preparation).

2. Experimental Methods

2.1. Fire Descriptions

The three fires were located on the coastal plain of eastern North Carolina, near the towns of Goldsboro or Jacksonville, in an area mapped by Kuchler as pine-oak-hickory forest [*Kuchler*, 1975]. Two of the fires were large (several hundred ha) prescribed burns in a hurricane-damaged pine-oak forest on the Camp Lejeune Military Reservation. These fires were ignited in strips by dropping incendiary "balls" from a helicopter. The other fire was a small wildfire in a pine plantation near Goldsboro (further inland). Additional details for each fire are given below, and more complete documentation is available from one of the authors (D. W.). The average fuel loading values are derived from a comprehensive biomass inventory/classification scheme similar to that described by *Shea et al.* [1996]. The values are a prefire estimate of the total biomass in categories likely to be affected by the fire under the prevailing conditions. In a typical case this might be approximately equivalent to biomass less than 25 mm in diameter and 2 m or less above the ground. The treatment areas given below include some internal areas that were not expected to burn (i.e., previously burned or swampy).

2.1.1. Camp Lejeune fire 1 (CL1): April 14, 1997. This fire was prescribed to treat a 464 ha area centered approximately at 34.56°N, 77.31°W. A mature pine forest (15-25 m in height) dominated the site with an oak-brush understory. Estimated prefire fuel loading was 9 t/ha with fuel moistures ranging from 9% to18%. A backfire was started at 1420 local time (EST) and aerial ignition commenced at ~1500 with a 90-150 x 15 m ball spacing. Spread rate and flame length varied considerably and had average values of 2.1 m/min and 3 m, respectively, during the most intense period of the fire. (Individual flames much longer than the maximum average flame length were observed on each fire.) All size classes of fuels ignited and an average of 5.6 t/ha was consumed over the 300 ha that burned. Temperature and relative humidity on the ground ranged from 14°C and 40% at ignition to 15.5°C and 50% at burnout (~1630). The local wind was a sea breeze (~5 m/s) that diminished with altitude and gave way to a NW flow above 1600 m characterized by increasing velocity and temperature with altitude. Cloud cover was about 80% (high cirrus), and the lapse rate was -9°C/km up to 1.6 km. The plume rose first under the influence of the sea breeze and then sheared and drifted horizontally (in the opposite direction) in the NW flow. Samples were taken both in the rising plume and downwind in the horizontally drifting plume. All downwind samples were within a few kilometers of the source because the plume drifted into more restricted airspace.

2.1.2. Wildfire 1 (WF1): April 19, 1997. This fire burned in a 12 year old, loblolly pine plantation, located approximately at 35.41°N, 78.05°W. The stand was dense and

~8-11 m in height. The dead biomass was very dry for this region (5-9% moisture), which accounts for the high estimated fuel loading of 18 t/ha. The sky was clear, and temperature and relative humidity were 19.5°C and 38%, respectively. The wind was generally from the west and less than 8 m/s. The fire started before 1400 EST and spread intermittently at average rates up to ~ 3 m/min (occasionally torching individual trees). The maximum, average flame length was ~3 m and about 80% of the estimated fuel consumption of 11 t/ha occurred in the flame front. The fire burned about 24 ha by 1815. We obtained one AFTIR sample from this fire, which coincided with a less active period when only a faint column of (mainly) smoldering emissions was present.

2.1.3. Camp Lejeune fire 2 (CL2): April 26, 1997.

The treatment area was 564 ha containing 281 ha of 50+ year old pine (20-23 m height), 121 ha of hardwood, and 162 ha of annually burned military range. The approximate location was 34.60°N, 77.24°W. The average fuel load estimated before the fire was 11 t/ha. The conditions were the wettest of the three fires with fuel moistures ranging from 8% to 28%. Cloud cover ranged from 0 in the morning to 75% by midafternoon. The temperature and relative humidity ranged from 19°C and 40% (~1000) to 21°C and 37% (1300). The wind speed was 1-4 m/s and varied widely in direction throughout the day. The backfire was started at 0940, and aerial ignition commenced within the next hour using a 23 x 23 m ball spacing. The fire skimmed off the top layer of ground fuels at average spread rates of 0.6 to 2.1 m/min and with average flame lengths up to 2 m. About 182 ha burned with the most active flaming combustion ending by 1300, but pockets of flaming combustion and a convection column persisted until ~1600. The lapse rate was -8.8°C/km in the morning, decreasing to -8.5°C/km in the afternoon, up to an inversion at 2 km. All the samples were taken close to the fire (again due to airspace restrictions) and below 1.7 km.

2.2. Measurement Strategy

Many configurations can be used to perform airborne FTIR. Solar, atmospheric, or terrestrial radiation that has passed through a long atmospheric path can be collected and analyzed [*Mankin*, 1978; *Toon et al.*, 1989; *Traub et al.*, 1994; *Worden et al.*, 1997]. This approach is very powerful, but not ideal for measuring excess combustion emissions that are also present in large quantities in background air, such as CO_2, and methane. Local, external, optical in situ measurements can be made by employing a source (or retroreflector) attached to the aircraft [*Webster and May*, 1987; *Haschberger and Lindermeir*, 1996], but this would limit us to a short path length. In this work we coupled an FTIR to a multipass cell inside the aircraft. The system performs in situ measurements by admitting external air into the cell through a sampling line connected to a port on the aircraft exterior. An analogous arrangement has been used for diode laser measurements of ambient atmospheric trace gases [*Hastie and Miller*, 1985; *Sachse et al.*, 1987; *Schiff et al.*, 1990; *Podolske and Loewenstein*, 1993; *Webster et al.*, 1994] and by *McGee and Gerlach* [1998] for FTIR measurements of SO_2 in a volcanic plume. Use of this configuration incurs a small risk of sampling artifacts, which we reduced by coating the intake surfaces with nonreactive halocarbon wax [*Webster et al.*, 1994].

2.3. Optical System Design

The Forest Service King Air can support a scientific payload, including passengers, of approximately 800 kg for a 3 hour flight. To accommodate the largest possible selection of instrumentation for smoke plume characterization, a primary design consideration for AFTIR was minimizing size and weight while maximizing the optical path length (proportional to sensitivity). Figure 1 shows a schematic of the AFTIR system. The system is described in detail, as it was configured for the North Carolina flights, below. (Photographs of the system can be found on the World Wide Web (http://www.cas.umt.edu/chem/yokelson/).)

The IR beam exiting the spectrometer (MIDAC, Inc.) is steered by transfer optics to a "tripled" white cell (IR Analysis, Inc.) featuring MgF_2-coated silver mirrors and two retroreflectors mounted inside a 15 (i.d.) X 91 cm Pyrex tube. The variable path cell has a base path of 0.81 m and was passed 120 times for a total path of 97.5 m. Viton O-rings seal the ends of the tube to nickel-plated aluminum endplates. Temperature inside the white cell was measured by a thermocouple at each end, and cell pressure was measured by a capacitive transducer (Kavlico, Inc.). All metal surfaces inside the cell were coated with halocarbon wax to reduce surface reactivity (Halocarbon, Inc.). Mirrors directed the exit beam from the cell through a 25 mm focal length ZnSe lens onto the LN_2-cooled, "wideband" MCT detector (Graseby, Inc., model FTIR M-16). The MIDAC spectrometer was operated at its maximum spectral resolution of 0.5 cm^{-1}. The optical elements of the AFTIR system were mounted on a 28 x 175 x 11 cm, honeycomb core, optical table (Newport, Inc.) that was shock mounted (Aeroflex, Inc.) to the floor of the aircraft. Total system weight including a protective sheet metal shield was approximately 64 kg.

2.4. Sample/Flow System

An aluminum plate was built to temporarily replace the copilot's vent window upon which forward facing aluminum elbows were mounted to serve as sample inlets. The AFTIR inlet was 25 mm i.d. and was wax coated as described above. Approximately 1.5 m of 17 mm i.d. (wax-coated) Teflon tubing connected the aircraft sample inlet to the multipass cell inlet located near the top of the front endplate. A deflector attached to the inside of the front endplate served to deflect the incoming gas stream into a circular pattern behind the field mirror. The gas then flowed slowly through large notches in the field mirror and through the cell to an outlet near the bottom of the back endplate. Manual 15 mm i.d. ball valves (wax-coated) provided flow control for the inlet and outlet lines. Use of the valves allowed us to perform in situ measurements of the cell exchange time by opening the valves in clean air after "grabbing" a sample in a smoke plume. The 1/e exchange time was typically 7-8 s (considerably longer than the 1.7 s spectrometer scan speed) and limited our spatial accuracy to ~700 m at the King Air sampling speed of 90 m/s.

The optical throughput of the AFTIR system and the spectrum of background air were constantly monitored throughout the experiment to check for a variety of potential problems, including cell contamination. The throughput (when measured at a pressure of ~ 1 atm) did not vary significantly throughout the study. The background spectra did not show any noticeable features indicating a buildup of
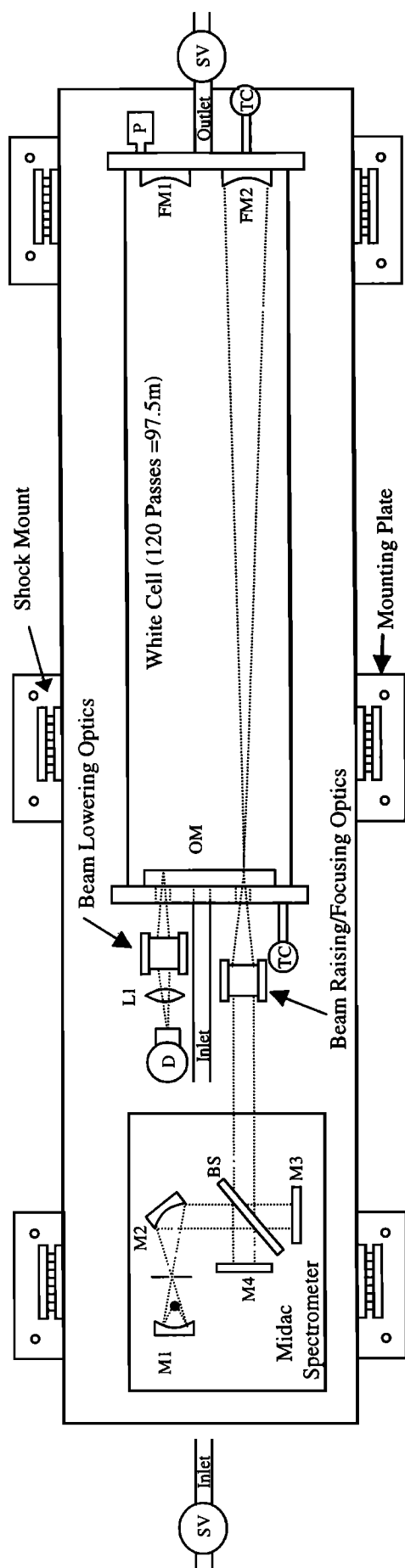
Figure 1. A top view diagram (not to scale) of the AFTIR system as it was configured in the initial deployment described in the text. Key to abbreviations: SV, shutoff valve; D, detector; TC, thermocouple gauge; P, baratron; FM, field mirror; OM, objective mirror; M1, collect and direct infrared source through aperture; M2, collimate infrared beam; M3, stationary mirror; M4, moving mirror; BS, beamsplitter; (M3, M4, and BS are part of Michelson interferometer); L1, lens. Note that the inlet depiction is discontinuous and the retroreflectors are not shown.

smoke constituents. These results suggest that the cell was not measurably contaminated by exposure to smoke (and that the system had good optomechanical stability). The lack of contamination could be due to the fact that the system was flushed with background air during approximately 11 of the 12 flight hours and that the smoke concentrations were much lower than encountered in laboratory or ground-based experiments.

2.5. Data Acquisition Protocols

Two data acquisition modes were utilized. During the first fire (Camp Lejeune 1), spectra were collected continuously during flight using ram pressure to drive air (or smoke) through the cell. We found that many of the plume penetrations were on a time scale (~15 s) similar to the cell exchange rate and that the single-scan noise level in the important 900-1100 cm^{-1} region was enormously reduced when the inlet and outlet valves were both closed. Thus the continuous measurements were superseded by an intermittent grab-sampling protocol described next.

For near-source plume samples, both valves were initially open and then both were simultaneously closed just before exiting the plume when the cell should have been well-flushed with smoke. The valves remained closed for 1 to 10 minutes while ~30-350 spectra of the smoke sample were acquired. (These spectra were later averaged together (coadded) to improve the signal-to-noise ratio (SNR).) Next, both valves were opened and the cell was flushed with background air for at least 60 s. Then, both valves were closed again, and spectra were acquired for another smoke or background sample.

2.6. Other Simultaneous Measurements

Other measurements made on each King Air flight included CO_2 and H_2O (Licor model Li6262), CO (TECO model 48), NO (TECO model 42), O_3 (TECO model 560), Global Positioning System (GPS) (Magnavox, then Garmin 12XL), smoke absorption (Radiance Research), and particle light scattering (Radiance Research nephelometer M903). Data from each of these instruments were recorded every second. In addition, each flight carried 30-50 stainless steel canisters and a 0.3 m^3 Tedlar bag that could be filled within ~ 10 s. Teflon filter samples were drawn from the bag or ambient air. A sonde (Avtech, Inc.) for air temperature, dew point, pressure, wind speed, wind direction, latitude, longitude, and altitude was mounted on a Cessna 172 that flew vertical profiles nearby while the King Air measurements were in progress. The sonde readings were recorded every second.

2.7. Data Analysis Protocol and Accuracy

A typical flight produced almost 7000 "raw" AFTIR spectra (obtained every 1.7 s) and 18 channels of ancillary data with a 1 s time base. A program was written to estimate the CO mixing ratio in each of the "raw" spectra, and these spectra were then coadded as appropriate to form "sample" spectra of background air and smoke. Mixing ratios for H_2O, CO_2, CO, CH_4, and HCHO were obtained by fitting sections of the single-beam transmission "sample" spectra with synthetic calibration, classical least squares (CLS) methods described fully elsewhere [Griffith, 1996; Yokelson et al., 1996a, b, 1997]. Absorption sample spectra of smoke were
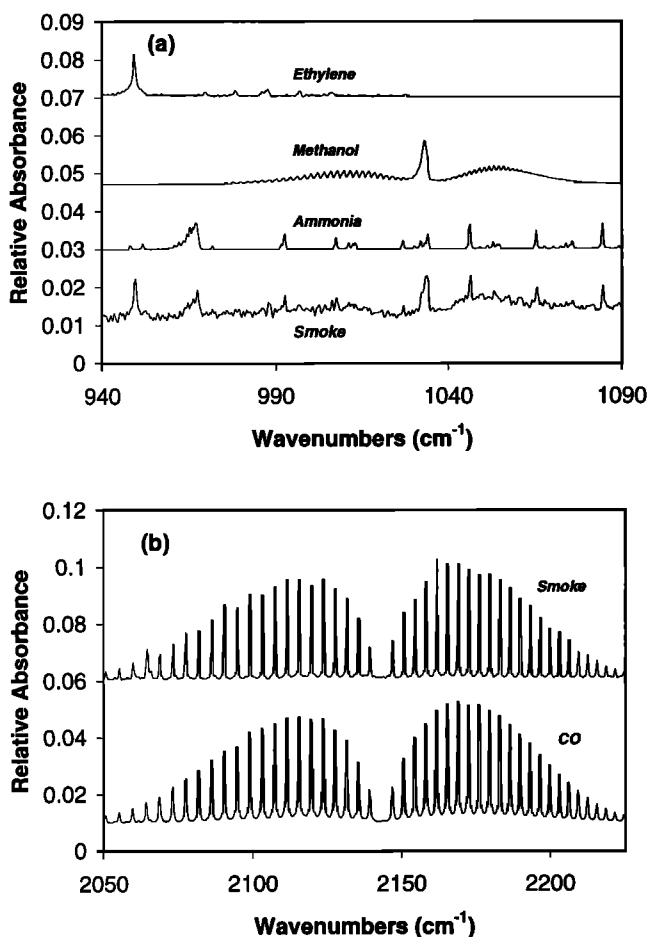
Figure 2. Two regions of an AFTIR absorbance spectrum. (a) The spectral region used to quantify ethylene, methanol, and ammonia, along with the reference spectra for these compounds. Water is also included in the spectral subtraction protocol for this region. (b) The spectral region around 2100 cm,$^{-1}$ along with a reference spectrum of CO to illustrate the excellent SNR for this compound. (Actual quantification is done with the transmission spectrum as explained in the text. The effects of water lines, which are fit simultaneously in the CLS analysis, explain the "extra" or distorted features in the smoke spectrum.)

made by using background sample spectra obtained at nearly the same altitude, and these were analyzed by spectral subtraction [*Yokelson et al.*, 1997] to yield mixing ratios for H$_2$O, HCOOH, CH$_3$COOH, NH$_3$, C$_2$H$_4$, and CH$_3$OH. Figure 2a shows part of an AFTIR smoke absorption spectrum along with reference spectra for the three latter compounds. Figure 2b shows another portion of the same smoke absorption spectrum, along with a CO reference spectrum, to illustrate the high SNR for this important combustion tracer. For this application we developed programs to efficiently perform these mixing ratio retrievals for large numbers of spectra acquired at many different temperatures and pressures.

For ammonia only, a modified data analysis protocol was followed as discussed next. Several smoke storage tests conducted in the cell (in our laboratory) showed ammonia and all the other species to be sufficiently stable to justify signal averaging for the 1-10 min time periods that samples were stored in the field. (Species 1/e lifetimes were typically > 10

hours.) However, at the lower smoke concentrations actually encountered in the field, ammonia, and ammonia only, showed evidence of a decay during the time grab samples were held. The decay had a 1/e lifetime of about 35 s. We investigated this decay as follows. We used detailed formulas given by *Perry et al.*, [1963] to calculate the diffusion coefficient for ammonia in air and obtained 0.282 cm^2/s. We then used this value of D(NH$_3$/air) in a formula given by *McDaniel* [1964] to calculate the diffusion-limited, first-order wall-loss lifetime for a species in a cylinder of known dimensions. The theoretical ammonia lifetime due to wall loss limited by radial diffusion, in our cell, was 35 s. Thus we conclude that the observed decay seems consistent with a first-order wall loss. Accordingly, for the ammonia analysis, the smoke sample scans were analyzed at higher time resolution, and the mixing ratios were then back-corrected to "time zero" assuming a first-order decay. We ignored NH$_3$ values below 20 ppb because of the extra error introduced by the back-correction and the reduced SNR at higher time resolution. A plot of NH$_3$ versus CO for the CL2 fire is shown in Figure 3. The plot indicates that our approach is yielding fairly consistent results.

In this type of airborne plume sampling, the mixing ratio in a measurement is not always the absolute mixing ratio at a known point in the plume. We compute the difference between similarly collected samples of the plume and background air to obtain and report "excess mixing ratios." However, it is the arithmetic ratios between the excess mixing ratios that are the most meaningful quantity (especially ratios to excess CO, which is the best short-term smoke tracer).

The accuracy of the excess mixing ratios measured in this experiment is mainly determined by the SNR of the spectra and by uncertainty in the spectroscopic cross sections and sample density measurements. The last type of error should tend to cancel when measuring ratios between compounds, the quantity of most interest here. The rms noise level in the spectra acquired in North Carolina is < 0.001 absorbance units for a 1 min signal-averaging period. Thus the detection limits (which vary by compound and spectrum) were typically from 5 to 20 ppbv (SNR=1). The spectroscopic cross sections are estimated to be accurate to ± 5% [*Rothman et al.*, 1992; *Hanst and Hanst*, 1994]. The relative density of the background and smoke samples was resolved to about ± 5%. The residual from the CLS fit or subtraction routine is < 5%. Thus the
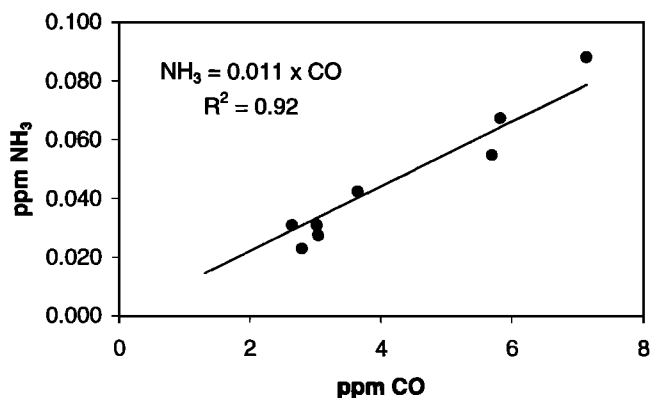

Figure 3. Excess ammonia mixing ratios for the CL2 fire, obtained by the method described in the text, plotted against the simultaneously measured excess mixing ratios for CO.

Table 1. Excess Mixing Ratios Determined by AFTIR and Sample Time and Location Data for the CL1 Fire on April 14, 1997

Sample	Altitude, m	Time, EST	CO_2, Δppmv	CO, Δppmv	CH_4, Δppmv	HCHO, Δppmv
s01	331	14:28	16.9	1.26	0.031	0.045
s02	197	14:30	18.8	1.55	0.144	
s03	510	14:35	9.9	0.51	0.091	
s05	492	14:39	17.7	0.85	0.090	0.041
s06	413	14:45	68.0	4.21	0.324	0.076
s07	416	14:52	12.1	0.66	0.107	
s08	360	14:53	16.1	1.40	0.207	0.036
s09	473	14:55	37.2	2.65	0.270	0.077
s11	902	14:58	50.5	2.86	0.214	0.087
s12	1009	15:01	42.2	2.88	0.307	0.121
s13	1025	15:04	38.5	3.41	0.116	0.105
s14	1347	15:07	38.7	3.44	0.233	0.125
s15	1415	15:09	20.8	1.07	0.007	0.007
s16	1421	15:11	52.3	4.67	0.382	0.062
s17	1537	15:14	43.6	4.70	0.372	0.050
s18	1875	15:18	29.2	3.48	0.413	0.126
s19	1832	15:25	11.8	2.24	0.149	
s20	1656	15:27	42.0	4.72	0.317	0.117
s21	1577	15:29	11.4	1.70	0.011	
s22	1446	15:33	12.3	1.49	0.150	
s23	1586	15:39	34.1	3.29	0.211	0.076
s28	1610	15:45	42.7	2.91	0.117	0.096
s30	315	15:55	42.1	4.32	0.479	0.083
s31	487	16:00	32.6	2.99	0.232	0.022
s32	493	16:06	76.3	5.86	0.349	0.146

	Intercompound Ratios		
	CO/CO_2	CH_4/CO	HCHO/CO
Values based on slope	0.082	0.076	0.024
R^2	0.74	0.64	0.30

	CO_2	CO	CH_4	HCHO
Emission factors, g/kg	1682	87.8	3.73	2.18
Combustion efficiency	0.917			
Modified combustion efficiency	0.925			

typical uncertainty of the individual excess mixing ratios determined in this work is estimated to be ± 8% 1σ or the detection limit, whichever is larger. Owing to additional uncertainties introduced by the back-correction procedure we estimate that the detection limit for NH_3 is at least 20 ppb. The 1σ error for the NH_3 excess mixing ratios is probably closer to ± 15%, and they should be considered a lower limit until we can complete planned tests to further characterize cell and inlet performance. Gases abundant in background air are treated separately. For CO and CH_4 the estimated 1σ uncertainty in an excess mixing ratio is 20-30 ppbv and for CO_2 the 1σ uncertainty is 2-3 ppmv.

3. Results and Discussion

Analysis of smoke and background sample-spectra acquired with the flow control valves continuously open (above the Camp Lejeune 1 fire) yielded excess mixing ratios

for CO_2, CO, CH_4, and HCHO. Table 1 presents these excess mixing ratios, determined by AFTIR, for the 25 smoke samples from the CL1 fire along with the time and altitude of each measurement. Analysis of smoke and background sample-spectra acquired with the flow control valves closed (above the other two fires) yielded excess mixing ratios for CO_2, CO, CH_4, HCHO, CH_3COOH, HCOOH, CH_3OH, C_2H_4, and NH_3. Table 2 presents these AFTIR data (and time and altitude) for the 15 samples at the CL2 fire and the single sample at the WF1 fire. For the WF1 fire only, the CO_2 and CH_4 excess mixing ratios are not reported as the AFTIR measurements for these compounds were unreliable due to low enhancements above background.

We calculated fire-average emission ratios for the two Camp Lejeune fires by four different methods to test the sensitivity of the result to the calculation method as discussed next. Since the fire emissions may be changing or poorly mixed, the average of all the near-source samples, weighted

Table 2. Excess Mixing Ratios Determined by AFTIR and Sample Time and Location for the CL2 fire on April 26, 1997, and the Single Sample for the Wildfire on April 19, 1997

Sample	Altitude, m	Time, EST	CO_2, Δppmv	CO, Δppmv	CH_4, Δppmv	HCHO, Δppmv	NH_3, Δppmv	CH_3OH, Δppmv	HCOOH, Δppmv	CH_3COOH, Δppmv	C_2H_4, Δppmv
s01	84	10:24	45.8	2.79	0.494	0.059	0.023	0.048	0.021	0.059	0.044
s02	133	10:38	100.8	7.15	0.643	0.203	0.088	0.158	0.059	0.109	0.136
s03	208	10:46	44.6	3.05	0.427	0.077	0.027	0.072	0.026	0.058	0.054
s04	327	10:48	39.7	3.03	0.448	0.076	0.031	0.066	0.011	0.086	0.049
s05	457	10:50	18.6	1.54	0.291	0.058		0.038		0.035	0.019
s06	598	10:52	29.4	2.65	0.420	0.097	0.031	0.057	0.036	0.075	0.052
s07	692	10:54	21.0	1.59	0.343	0.042		0.035	0.033	0.030	0.022
s08	796	10:57	11.0	1.31	0.215	0.039		0.031	0.020	0.026	0.019
s09	1031	10:59	19.4	2.48	0.201	0.065		0.062	0.009	0.060	0.024
s10	995	11:11	13.3	1.81	0.209	0.045		0.041	0.028	0.016	0.026
s11	215	11:40	59.8	5.83	0.589	0.144	0.068	0.128	0.050	0.140	0.102
s12	154	11:51	42.0	3.65	0.407	0.107	0.042	0.074	0.032	0.062	0.049
s14	120	14:40	74.6	5.71	0.520	0.131	0.055	0.135		0.060	0.054
s16	268	15:37	57.0	5.06	0.413	0.114		0.084		0.046	0.054
s17	122	15:53	35.8	2.66	0.382	0.056		0.022	0.014	0.063	0.055

Intercompound Ratios

	CO/CO_2	CH_4/CO	HCHO/CO	NH_3/CO	CH_3OH/CO	HCOOH/CO	CH_3CO_2H/CO	C_2H_4/CO
Value based on slope	0.079	0.108	0.0258	0.0110	0.0211	0.0085	0.0173	0.0150
R^2	0.89	0.24	0.91	0.92	0.90	0.50	0.45	0.79

	CO_2	CO	CH_4	HCHO	NH_3	CH_3OH	HCOOH	CH_3COOH	C_2H_4
Emission factors, g/kg	1671	84.0	5.18	2.32	0.56	2.03	1.17	3.11	1.26
Combustion efficiency	0.907								
Modified combustion efficiency	0.927								

	CO	HCHO	NH_3	CH_3OH	HCOOH	CH_3COOH	C_2H_4
Sample from wildfire 1, Δppmv	2.93	0.096	0.077	0.071	0.035	0.050	0.040
Ratio to CO		0.033	0.026	0.024	0.012	0.017	0.014

The sample for wildfire 1 was at an altitude of 267 m and was taken at 1640 EST.
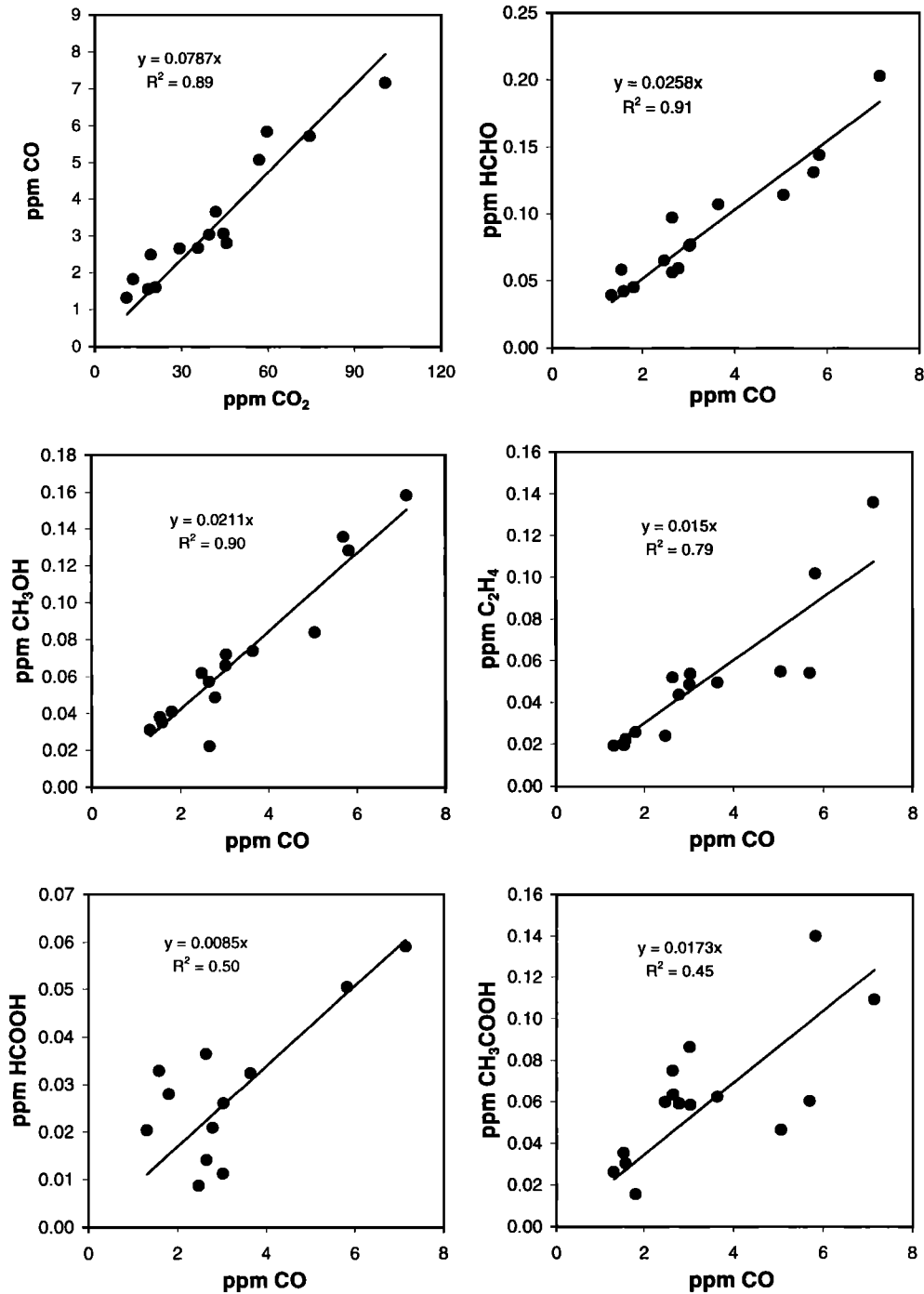
Figure 4. Excess mixing ratios measured in the smoke plume above the CL2 fire are plotted versus each other to illustrate the preferred method of obtaining fire-average emission ratios.

by their signal to noise, may best estimate the source characteristics. The SNR-weighted, fire-average emission ratios (ER) can be estimated by plotting one compound versus the other, by computing the intercompound ratios from the average of all the mixing ratio observations for each compound, or from the SNR-weighted average of the emission ratios in each sample. In this work, all three approaches give the same result within experimental uncertainty (when both compounds were measured in all the samples from a fire). For example, Figure 4 includes the plot

of methanol versus CO from the CL2 fire. The slope of the plot is 0.0211. In Table 2 the average of the methanol observations divided by the average of the CO observations gives the ratio 0.0209, which is also the result from using the third method described above. It is worth noting one other procedure that we tested for computing fire-averaged emission ratios. In the CL1 fire only, we sampled continuously, and the smoke sample times ranged from 15 to 177 s. Therefore we computed fire-average ERs by weighting individual ERs with their sample time. In all cases the

resulting values were within a few percent of those obtained using the other methods described above. *Little and Rubin* [1987] discussed estimating ratios between measured quantities when a data set has some missing values, as is the case in a few instances in this study. They concluded that the best estimate of the ratio is the slope of the least squares line, with the intercept forced to zero, in a plot of one set of measurements versus the other. The fire-average emission ratios shown in Tables 1 and 2 are computed in this way, though, as we showed above, essentially the same result is obtained by the three other methods.

For the CL1 and CL2 fires we measured a suite of the major carbon-containing fire emissions. Thus we can calculate an approximate emission factor for any species "i" using

$$EF_i(g/kg) = F_c \times 1000(g/kg) \times \frac{MM_i(g)}{12(g)} \times \frac{C_i}{C_T} . \qquad (1)$$

In equation (1), EF_i is the mass (g) of compound i emitted per kg of fuel burned, F_c is the mass fraction of carbon in the fuel, and MM_i is the molecular mass of species i. C_i/C_T is the number of moles emitted of species i divided by the total number of moles of carbon emitted. C_i/C_T can be calculated from an individual, a fire-averaged, or a study-averaged suite of measurements. In this case we wanted the best estimate of fire-average C_i/C_T, so we calculated this value from fire-average emission ratios using

$$\frac{C_i}{C_T} = \frac{\dfrac{\Delta C_i}{\Delta CO_2}}{\displaystyle\sum_{j=1}^{n}\left(NC_j \times \dfrac{\Delta C_j}{\Delta CO_2}\right)} . \qquad (2)$$

In equation (2), $\Delta C_i/\Delta CO_2$ is the fire-average emission ratio of compound i to CO_2, NC_j is the number of carbon atoms in compound j, and the sum is over all the species (including CO_2). The use of equations (1) and (2) to estimate fire-average emission factors is most accurate when all the burnt carbon is volatilized and detected, the fraction of fuel carbon is precisely known, and the measurements probe all the smoke produced by the fire. In this study we probably underestimate the total carbon 1-2% by ignoring particulate and another 1-2% due to unmeasured gases. We also assume that the fuel is 0.5 carbon by mass [*Susott et al.*, 1996], which is probably accurate to ± 10% (2σ).

Our fire-averaged quantities could also differ from the actual source characteristics if our sampling was unrepresentative. This condition might occur if the plume was changing in composition, poorly mixed, or, for any other reason, not characteristic of the products of the whole fire. These issues are addressed next. In previous ground-based experiments we have learned that as long as flames persist on the site, emissions from the various combustion processes can be drawn into the plume (including smoldering combustion emissions originating some distance from the moving flame fronts) [*Ward et al.*, 1992]. If large amounts of fuel were consumed after convection from the site ceased, then airborne measurements could be in error (if the smoke composition also changed). On the two Camp Lejeune fires for which we report emission factors the amount of postconvection residual smoldering combustion was minimal because the proportion

of large dead fuels was small and any organic soils were too wet to ignite. This was confirmed by direct observation of the burn interior during and after the fire. We have also taken some precautions against poor mixing or changing composition. We acquired a fairly large number of samples (15 or 25), the samples were from many different locations in the plume, the samples integrated over transects through the plume, and they were taken during a large portion of the time that fuel consumption occurred.

For fires CL1 and CL2 the estimates of the fire-average emission factors, the fire-average modified combustion efficiency (MCE), and the fire-average combustion efficiency are shown in Tables 1 and 2. Combustion efficiency (CE) is defined as the fraction of burned carbon that is released as CO_2. Modified combustion efficiency is defined as $\Delta CO_2/(\Delta CO_2+\Delta CO)$; where the "$\Delta$" indicates an excess mixing ratio [*Ward and Radke*, 1993]. MCE is also equal to $1/((\Delta CO/\Delta CO_2)+1)$. CE and MCE are useful as indexes of the relative amount of flaming and smoldering combustion throughout (or during) a fire, and these terms are used to compare studies below. The concept of MCE is also important because if our measurements oversampled either flaming or smoldering combustion, the relation obtained between MCE and the emission factors should still be valid.

A full discussion of the emissions of CO_2, CO, particles, NO, and hydrocarbons from these fires, and earlier fires in Florida and Georgia (where the AFTIR was not deployed), will be presented separately. We limit further discussion in this paper to the AFTIR measurements of oxygenated organic compounds (for which much less literature information is available).

3.1. Production of Oxygenated Organic Compounds From Biomass Fires

Comparison of measurements of biomass fire emissions between different studies is complicated by the fact that natural fires burn in a wide variety of fuels and environmental conditions and with different relative amounts of flaming and smoldering combustion. Some consideration of the differences between fires can be incorporated into a comparison by plotting emission factors versus modified combustion efficiency (MCE) [*Ward and Radke*, 1993]. These plots give a two-dimensional (2-D) comparison, which is more informative than a simple one-dimensional comparison of emission ratios from potentially very different fires. It is of special interest to use this 2-D plot to compare our current field data for the three main oxygenated organic compounds (HCHO, CH_3COOH, and CH_3OH) with our previous laboratory data for these compounds. This helps determine how similar the emissions from our laboratory fires are to the emissions from full-scale field fires and could confirm the relevance of our extensive, laboratory fire emissions data for these, and other, compounds.

In three previous laboratory studies [*Yokelson et al.*, 1996b, 1999; *Goode et al.*, 1999] our work included measurements of the fire-integrated emission factors for formaldehyde, methanol, and acetic acid from fires burning in different fuels and at different MCEs. In one previous laboratory study [*Yokelson et al.*, 1997] we measured emission factors and MCEs for smoldering combustion only. In Figure 5 we compare our current field measurements of emission factors (for the dominant oxygenated organic
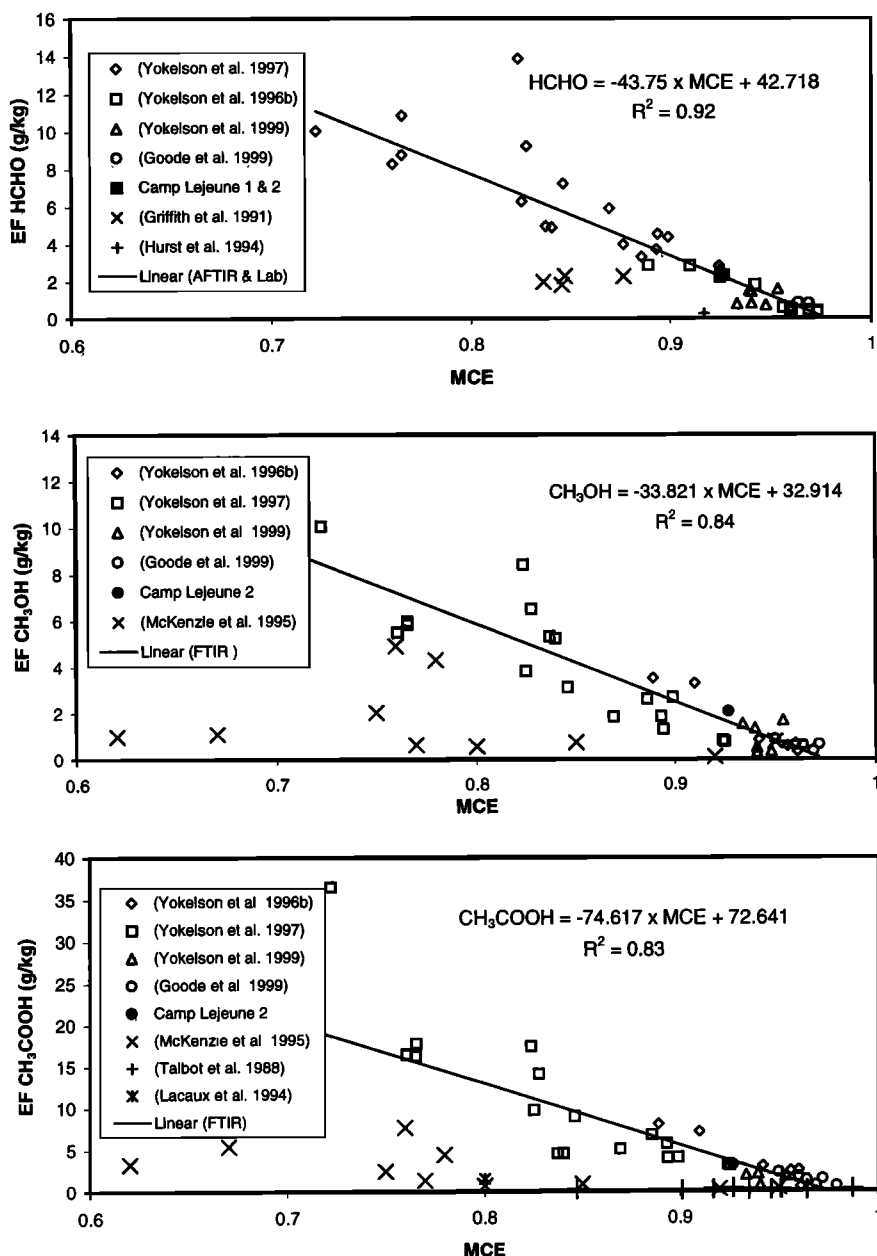
Figure 5. For the three major oxygenated organic compounds emitted from fires, we compare published emission factors as a function of modified combustion efficiency. The FTIR data from the laboratory (closed, unfilled symbols) and the field (closed, filled symbols) are in good agreement with each other, highly linearly correlated, and show generally larger values than the other studies shown (which also show lower or no linear correlation).

compounds) versus MCE with all our fire-integrated laboratory data and all our laboratory data for smoldering combustion of aboveground biomass. It is clear that for each of these three compounds, a single highly correlated linear model fits the data from all our studies. It is also clear that our current field data lie very close to the line established primarily by our laboratory data. Thus the model based on our laboratory fires can predict the emission factors we measure on full-scale field fires. Other intriguing results are evident from these plots. One is the wide range in possible emission factors. (In fact, our highest emission factor for acetic acid (at a low MCE) is ~600 times higher than the lowest emission

factor for acetic acid of *Talbot et al.* [1988] (at high MCE).) Second, the data for these compounds from the other studies included in Figure 5 show little or no linear correlation with MCE and significantly lower absolute values. This suggests that the amount of the difficult to measure oxygenated organic compounds emitted from fires may have been previously underestimated. In any case, the levels we report here indicate that fires can be significant sources for these compounds, as shown next.

Using standard methods to estimate 95% confidence [*Wonnacott and Wonnacott*, 1977], the uncertainty in the slope and intercept for the plots in Figure 5 is less than 5%

and 1%, respectively. Further, plotting the data versus $\Delta CO/\Delta CO_2$ gives essentially the same correlation and only a small (~ 1%) shift in the intercept toward the equivalent of higher MCE fires. Thus the plots appear to be fairly robust models for predicting fire emissions in a wide variety of circumstances with the following caveats. We have no data at an MCE above 0.98 and no points from in situ measurements in tropical fuels. Therefore we plan such measurements in the near future to enable more confident prediction for these scenarios. Meanwhile, the plots can be employed for predicting emissions from temperate zone fires and for preliminary estimates of the emissions from tropical fires. For instance, *Andreae et al.* [1996] reported a global average MCE for tropical savanna fires of 0.94. Employing Figure 5, we obtain average savanna fire emission factors for formaldehyde, methanol, and acetic acid of 1.6, 1.1, and 2.5 g/kg respectively (±50%). *Ward et al.* [1992] reported an average MCE for tropical deforestation fires of 0.89. Employing Figure 5 (a little more confidently in this case), the analogous emission factors for tropical forest fires are considerably higher at 3.8, 2.8, and 6.2 g/kg respectively (±30%). Combining these emission factors with estimates of the amount of biomass burned in savanna and forest fires in the tropics [*Crutzen and Andreae*, 1990] yields emissions of 14 ±8, 10 ±6, and 22 ±13 Tg/yr. It should be recalled that these emissions are concentrated spatially and temporally to a few months during the tropical dry season and that the compounds are too reactive to become well mixed in the global troposphere.

The estimates derived above can be compared on a very limited basis with other estimates. *Singh et al.* [1995] suggested that total global methanol production is ~45 Tg/yr based on their methanol measurements in the remote troposphere and they estimated that ~6 Tg/yr of this production is due to total global biomass burning. Our calculation suggests a larger fire source of methanol since we obtain 10 ±6 Tg/yr without including burning of fuel wood and agricultural waste (which may be 10-20% of global biomass burning). Evidently, fires may contribute some 10-30% of global atmospheric methanol. The major source of this compound is probably biogenic emissions [*Konig et al.*, 1995; *Singh et al.*, 1995; *Kirstine et al.*, 1998].

A plot of emission factor versus MCE does not imply that the emission ratio to CO for a compound is constant. In fact, for most smoldering compounds the emission ratio to CO increases as MCE decreases. Thus comparison of emission ratios from two fires with different MCE can be misleading. However, in many studies, and in our measurements of WF1, there is insufficient data to calculate MCE. Therefore examination of emission ratios allows us to compare/integrate data from a larger number of studies, with the limitations just noted. Additionally, comparison of emission ratios is more meaningful if the two compounds in the ratio are from the same type of combustion. Thus comparison of smoldering or pyrolysis compounds to CO is quite useful, especially since CO is a smoldering compound and also the best gas phase tracer for smoke in the field.

In Table 3 we compare our field measurements of the fire-average emission ratios for oxygenated organic compounds to CO with our laboratory study-average emission ratios and to other work. All the measurements were made on different fires, so only a summary comparison of this data is justified. *Talbot et al.* [1988] sampled laboratory fires for

emissions of formic and acetic acid with a mist chamber technique. Their study-average emission ratios to CO for these compounds are about 100 and 20 times lower than ours, respectively. The tendency for their values to be lower than ours holds for a wide range of MCEs, as was seen in Figure 5. *Griffith et al.* [1991] reported that HCHO was a ubiquitous fire product emitted on average at ~1.3% of CO. (*Lobert et al.* [1991] did not attempt to quantify oxygenated organic compounds in their benchmark study.) *Hurst et al* [1994] sampled savanna fire smoke in glass bulbs and later analyzed the contents with matrix isolation-FTIR. They reported an average HCHO/CO value of 0.25 that is ~7 times lower than our typical value. However, they also reported total aldehyde emissions up to 1.7% of CO. *McKenzie et al.* [1995] packed finely ground biomass into ceramic crucibles and heated it from above. Smoke generated in this manner was cryotrapped and analyzed by gas chromatography-mass spectrometry (GC-MS) for a variety of oxygenated compounds, of which four are also measured in our FTIR work. Their values of HCOOH/CO, CH_3COOH/CO, and CH_3OH/CO are 1/4 to 1/2 of our typical values. Their data are not correlated with MCE (see Figure 5), perhaps partly due to the highly stratified biomass they burned [*Yokelson et al.* 1997].

Another airborne FTIR smoke study [*Worden et al.*, 1997] reported values for two spot measurements of HCOOH/CO, CH_3OH/CO, and NH_3/CO obtained during smoldering combustion that are well within the range we observed in a study of smoldering combustion [*Yokelson et al.* 1997]. Recently, *Holzinger et al.* [1999] used a chemical ionization mass spectrometer for on-line emissions measurements of six trace gases from laboratory fires. Their average value for HCHO/CO (2.2%) is essentially the same as ours. Their average value for CH_3OH/CO (0.64%) is about 1/3 of our typical FTIR value. Finally, *Koppmann et al.* [1997] used absorption tube/GC-MS to measure many high-molecular-mass organic emissions from savanna fires in southern Africa. They reported that the oxygenated compounds were approximately equal to the straight hydrocarbons in abundance. This is consistent with our findings for the lighter C_1 and C_2 hydrocarbons as indicated in the footnote to Table 3. In summary, consideration of the published measurements of the ratio of oxygenated organic compounds to CO supports our earlier conclusion that fires are a major source of these compounds.

3.2. Influence of Oxygenated Organic Compounds on Initial Plume Chemistry

In this section we briefly summarize some of the published results relevant to "smoke chemistry" and then, in the context of this previous work, we demonstrate that oxygenated compounds may play an important, but poorly understood, role in early plume chemistry. Trace gas emissions from biomass fires have many important influences on the atmosphere. This includes emission of 10-30% of global CO and significant amounts of greenhouse gases [*Crutzen and Andreae*, 1990]. Another important topic is the influence of fires on tropospheric O_3 formation [*Chatfield and Delaney*, 1990; *Fishman et al.*, 1991; *Richardson et al.*, 1991; *Keller et al.*, 1991; *Jacob et al.*, 1992; *Crutzen and Carmichael*, 1993; *Chatfield et al.*, 1996; *Thompson et al.*, 1996; *Jacob et al.*, 1996; *Koppmann et al.*, 1997; *Lelieveld et al.*, 1997; *Olson et al.*, 1997; *Mauzerall et al.*, 1998; *Lee et al.*, 1998]. About 80-90% of the global biomass burning is estimated to occur in

Table 3. Selected Data From Studies That Include Measurements of the Initial Emissions of Oxygenated Organic Compounds From Biomass Fires.

| | | | Emissions as percent of CO | | | | | | | | | | | | |
| | | | Hydrocarbons | | | | | Aldehydes | | Acids | | Alcohols | | Nitrogen[a] | | Sulfur |
Study	Method	L/F[b]	CH$_4$	C$_2$H$_6$	C$_2$H$_4$	C$_2$H$_2$	C$_3$H$_6$	HCHO	Glycol-	Formic	Acetic	CH$_3$OH	C$_6$H$_6$O	NH$_3$	HCN	OCS
Griffith et al. [1991]	OP-FTIR[c]	F	7.61	...	...	...	...	1.27	...	...	...	...	...	3.24	0.12	...
Yokelson et al. [1996b]	OP-FTIR	L	10.9	1.42	1.71	0.98	...	1.60	...	0.73	2.32	1.61	...	1.91	0.44	...
Yokelson et al. [1997]	OP-FTIR	L	6.55	0.45	0.98	0.17	0.65	2.33	1.08	1.09	2.20	1.98	0.84	2.66	0.65	0.04
Yokelson et al. [1999]	OP-FTIR	L	6.43	...	1.49	...	...	1.55	...	0.58	1.12	1.21	...	1.42	...	...
Goode et al. [1999]	OP-FTIR	L	8.06	...	1.97	0.37	1.14	1.80	0.51	1.12	1.47	1.21	...	1.31	...	...
Camp Lejeune 1	AFTIR	F	7.70	...	...	...	...	2.6	...	...	...	...	...	...	...	...
Wildfire 1	AFTIR	F	...	...	1.4	...	...	3.3	...	1.2	1.6	2.4	...	2.6	...	...
Camp Lejeune 2	AFTIR	F	11.4	...	1.5	...	...	2.6	...	0.85	1.8	2.1	...	1.1	...	...
Talbot et al. [1988]	MIST[d]	L	...	...	...	...	...	...	...	0.009	0.09	...	...	...	...	...
McKenzie et al. [1995]	GC-MS[e]	L	2.9	0.25	1.2	...	...	...	...	0.15	0.74	1.1	0.03	...	...	...
Worden et al. [1997]	AES[f]	F	...	...	...	...	...	...	...	1.55	...	3.10	...	4.3	...	...
Hurst et al. [1994]	MI-FTIR[g]	F	4.5	...	...	0.07	...	0.25	...	...	...	...	...	2.6	0.03	...
Holzinger et al. [1999]	CIMS[h]	L	...	...	...	...	...	2.21	...	...	...	0.64	...	...	0.12	...
Average of above	all		7.33	0.71	1.46	0.40	0.90	1.95	0.79	0.81	1.41	1.71	0.43	2.35	0.27	0.04

The study means are reported expressed as molar percentages of CO. The value of one standard deviation is typically from 1/3 to 2/3 of the mean. Three dots indicate that the compound was below the detection limit or it was not measured. The sum of C$_1$ and C$_2$ hydrocarbons (average values) is 9.90. The sum of selected C1 and C2 oxygenates is 6.67.

[a] Highly dependent on fuel nitrogen content.

[b] Fire location: L, laboratory; F, field.

[c] Open path Fourier transform infrared spectroscopy.

[d] Mist chamber (see reference).

[e] Gas chromatography-mass spectrometry.

[f] Airborne emission spectrometer (operates in the infrared region).

[g] Matrix isolation FTIR.

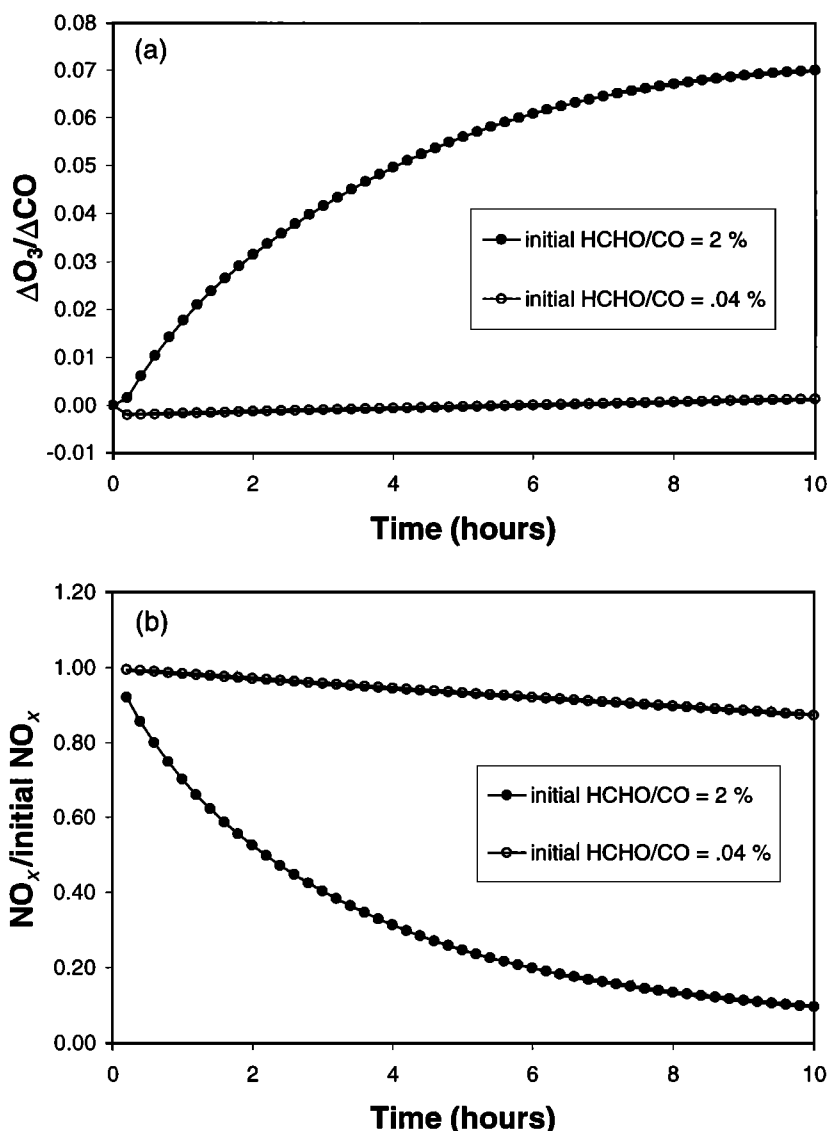[h] Chemical ionization mass spectrometer.

Figure 6. Results are shown for O_3 production and NO_x depletion from paired runs of a simple smoke chemistry model. For each plot, one run sets the initial HCHO at background levels and the other run sets the initial HCHO at 2% of the initial CO (see Table 3). (a) The excess O_3 mixing ratio divided by the excess CO mixing ratio (a common measure of ozone production). (b) The NO_x mixing ratio divided by its initial value of 80 ppbv. The differences between the runs are examples of how increased, modeled rates of initial (near source) O_3 formation and NO_x depletion can result from including oxygenated organic compounds in a simple chemical system. Initial mixing ratios for the model runs were: CO, 7.7 ppm (total including 0.2 ppm background); CH_4, 2.3 ppm (total including 1.7 ppm background); NO, 60 ppb (total); NO_2, 20 ppb (total); and O_3, 30 ppb (total). HCHO was varied as indicated above.

the tropics [*Hao and Liu*, 1994]. Further, since the tropical troposphere is where most of the oxidation in the atmosphere occurs, tropical tropospheric ozone has a major influence on the oxidizing capacity of the global atmosphere [*Crutzen and Carmichael*, 1993]. O_3 is also the third most important greenhouse gas (after CO_2 and methane) [*Prather et al.*, 1994], with tropical upper tropospheric O_3 being especially effective in this respect [*Fishman et al.*, 1979]. Using a global three-dimensional chemistry-transport model, *Lelieveld et al.* [1997] estimated that fires cause a 15% increase in tropical O_3 (lower limit) and concluded that most of this O_3 increase appears to be due to regional-scale production from dispersed biomass burning emissions. High regional production is

inferred partly because of the great increase in modeled O_3 formation rates that follows convective transport of "fresh" biomass burning emissions (still containing ample NO_x) to the upper troposphere [*Chatfield and Delaney*, 1990; *Pickering et al.*, 1992; *Thompson et al.*, 1996; *Jacob et al.*, 1996; *Lelieveld et al.*, 1997]. Thus the rate of the chemistry and the transport of the smoke can interact in ways that greatly affect the amount of ozone produced.

Many modeling studies have examined ozone formation in biomass burning plumes, but to our knowledge, none have incorporated a suite of low-molecular-weight oxygenated organic compounds in the initial emissions as our (and other's) work clearly suggests is appropriate. In light of this

fact, we now briefly examine the chemistry of the dominant oxygenated organic emissions from fires. The main removal processes for acetic acid, formaldehyde, and methanol are reaction with OH and photolysis (formaldehyde only). In each case this is a net source of HO_2 [Madronich and Calvert, 1989; Atkinson, 1994]. Phenol and formic acid will also contribute to the early HO_2 [Madronich and Calvert, 1989; Atkinson, 1994]. Hydroxyacetaldehyde is another significant oxygenated fire product that we have quantified in other studies [Yokelson et al., 1997]. We have recently confirmed that hydroxyacetaldehyde absorbs tropospheric radiation and according to G. Tyndall (work in progress) the photolysis products include HCHO, so this product will probably also contribute to the early HO_2. The additional HO_2 from the oxygenated organic compounds would be expected to enhance the importance of reactions such as

$$HO_2 \ + \ HO_2 \ \rightarrow \ H_2O_2 \ + \ O_2 \qquad (3)$$

$$HO_2 \ + \ NO \ \rightarrow \ NO_2 \ + \ OH \qquad (4)$$

$$HO_2 \ + \ O_3 \ \rightarrow \ 2O_2 \ + \ OH. \qquad (5)$$

Reaction (3) could be a secondary source of peroxide, and reaction (4) could promote O_3-producing photochemistry in the early plume by converting NO to NO_2. Lee et al. [1998] noted high levels of peroxide in "biomass burning impacted air." Experimental and modeling evidence also exists for increased importance of reaction (4) due to the presence of aldehydes. Altshuller et al. [1967] found that measured ozone formation in irradiated hydrocarbon/NO_x mixtures was hastened by the addition of aldehydes [Seinfeld, 1986]. The modeling study of Lelieveld et al. [1997, p. 221] demonstrated that the nighttime reaction of O_3 and C_2H_4 in a fire plume would produce HCHO that in the morning would provide "a readily available source of HO_2 and OH radicals, which can rapidly initiate ozone producing photochemistry." We add that since HCHO is already an abundant initial fire product, its effects can occur immediately and possibly affect the time available for convection of "fresh emissions."

To explore the potential importance of the early HO_x in a semiquantitative, preliminary manner, we employed a one-dimensional box model [Braun et al., 1988] and photochemically processed simple, smokelike mixtures under midday conditions without dilution. The model photolysis rates and background concentrations were taken from Richardson et al. [1991] and Finlayson-Pitts and Pitts [1986]. The kinetic rate constants are from DeMore et al. [1997]. The model was initialized with ΔCO scaled to 7.5 ppmv (approximately our maximum field observation) and other key compounds scaled as seen in Figure 6. For each plot in Figure 6, the two traces compare two model runs. In case 1, CO, NO_x, and CH_4 (at 8% of CO) are included as O_3 precursors and HCHO is started at background levels (i.e., assuming that it is not an important initial smoke component). In case 2, we start formaldehyde at 2% of CO (an initial ratio that may be more representative of smoke (Table 3)). The additional formaldehyde is used here as a preliminary probe into the influence of the oxygenated compounds in a simplified depiction of the early plume. One effect of the additional formaldehyde (in Figure 6) is to significantly hasten the early NO_x depletion/O_3 formation chemistry with a resulting NO_x depletion lifetime of a few hours [Seinfeld, 1986; Lelieveld et al., 1997]. We do not yet know if the

effects seen in Figure 6 will occur in more sophisticated models or real plumes. However, this exercise demonstrates that the potential for this class of compounds to have important effects in the early plume should be thoroughly examined. For instance, in this simplified exercise, high initial levels of HCHO significantly reduce the time period during which emissions containing high NO_x could be uplifted to the free troposphere. In addition, more O_3 is made "early" and is thus subject to cloud scavenging during a deep convection event [Chatfield and Delaney, 1990; Richardson et al., 1991; Lelieveld et al., 1997]. If these turn out to be general effects of oxygenated compounds in real plumes, then the amount of O_3 produced could be greatly reduced. Thus assessments of O_3 production from fires should ultimately use as detailed models as possible. For example, more comprehensive simulations should include particle effects, continuous dilution, extensive chemistry (including peroxyacetyl nitrate etc.), and diurnal variation in light intensity. Also, a suite of low-molecular-weight oxygenated organic compounds should be included since they may influence early O_3 production and, depending on the fate of the NO_x, they may also have other effects on regional O_3 production.

The preceding discussion is relevant to the recent observations by Wennberg et al. [1998] of "higher than expected" HO_x levels in the upper troposphere. Wennberg et al. [1998] concluded that HO_x precursors other than O_3 and water [Levy, 1971; Talukdar et al., 1998], such as oxygenated organic compounds, were needed to explain the observed HO_x levels. They also concluded that their report of "high" HO_x meant that NO sources for the upper troposphere, such as biomass fires or aviation, could lead to more O_3 production than previously thought. We suggest that fires will add NO_x and also considerably more HO_x precursors than previously thought to the upper troposphere [Griffith et al., 1991; Yokelson et al., 1996b]. While the more reactive oxygenated organic compounds emitted from fires may be important HO_x precursors in fresh biomass burning plumes, the longer-lived oxygenates (such as methanol) will probably contribute regionally to the ambient upper tropospheric HO_x, at least during the tropical dry season.

Some recent research suggests that oxygenated organic compounds emitted from fires could also be important in several heterogeneous processes. In particular, Iraci and Tolbert [1997] found that a model aerosol readily took up formaldehyde. Cruz and Pandis [1998] reported that a coating of glutaric acid increased the cloud condensation nuclei (CCN) activation of inorganic aerosol. Hobbs and Radke [1969], Desalmund et al. [1985], Andreae et al. [1988], and Hudson et al. [1991] all found that a very high percentage (25-100%) of biomass fire aerosol particles can be active as CCN. However, our ratios of oxygenates to CO are independent of altitude during the first few moments in the plume when surface area density is at its highest. Thus any gas-to-particle conversion that occurs probably involves higher-molecular-mass compounds, lower temperatures, or longer timescales than we probe here.

4. Conclusions

We have used our prototype airborne FTIR system (AFTIR) for field measurements of the chemical composition of fresh, biomass fire smoke. Emission factors were determined for the major combustion products (carbon dioxide and carbon monoxide), a few hydrocarbons (methane

and ethylene), the rarely quantified oxygenated organic compounds (formaldehyde, methanol, acetic acid, and formic acid), and ammonia. The results confirm the importance of biomass fires as a source of oxygenated organic compounds, and a simple model suggests that these compounds will affect the rate of O_3 formation in biomass burning plumes. The results also suggest that fires will contribute to the ambient levels of HO_x and oxygenated organic compounds in the upper troposphere. The agreement between our field results and our previous laboratory results confirms the relevance of our extensive work characterizing emissions from modeled laboratory fires.

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