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Trace gas emissions from laboratory biomass fires measured by open-path Fourier transform infrared spectroscopy: Fires in grass and surface fuels

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Abstract. The trace gas emissions from six biomass fires, including three grass fires, were measured using a Fourier transform infrared (FTIR) spectrometer coupled to an open-path, multipass cell (OP-FTIR). The quantified emissions consisted of carbon dioxide, nitric oxide, water vapor, carbon monoxide, methane, ammonia, ethylene, acetylene, isobutene, methanol, acetic acid, formic acid, formaldehyde, and hydroxyacetaldehyde. By including grass fires in this study we have now measured smoke composition from fires in each major vegetation class. The emission ratios of the oxygenated compounds, formaldehyde, methanol, and acetic acid, were 1-2% of CO in the grass fires, similar to our other laboratory and field measurements but significantly higher than in some other studies. These oxygenated compounds are important, as they affect O_3 and HO_x chemistry in both biomass fire plumes and the free troposphere. The OP-FTIR data and the simultaneously collected canister data indicated that the dominant C_4 emission was isobutene (C_4H_8) and not 1-butene. The rate constant for the reaction of isobutene with the OH radical is 60% larger than that of 1-butene. We estimate that $67 \pm 9\%$ of the fuel nitrogen was volatilized with the major nitrogen emissions, ammonia, and nitric oxide, accounting for $22 \pm 8\%$.

1. Introduction

Biomass burning is a major source of trace gases and particles in the global atmosphere [*Crutzen and Andreae*, 1990]. Uncertainty in the initial composition and subsequent transformations of fire emissions limits the accuracy of regional-global chemistry and global climate models [*Chatfield et al.*, 1996; *Kaufman and Nakajima*, 1993; *Olson et al.*, 1997]. In regions such as southern Africa or Brazil, where many different types of fires burn simultaneously, airborne studies have been successful in quantifying some of the important atmospheric impacts [*Andreae et al.*, 1988, 1994; *Lindesay et al.*, 1996]. The work of *Ward et al.* [1992, 1996], along with others, has helped explain how different types of fuels and burning conditions, associated with specific land-use practices, affect the initial emissions of particles and specific compounds (CO_2, CO, and hydrocarbons). Laboratory experiments have also contributed to our overall understanding of the emissions from biomass burning [*Lobert et al.*, 1991; *Yokelson et al.*, 1996b, 1997, 1999a].

The open-path Fourier transform infrared (OP-FTIR) technique and a laboratory setting offer some critical advantages for quantifying fire emissions as discussed previously by *Yokelson et al.* [1996b]. These advantages include the opportunity to sample smoke from an entire fire and the ability to provide continuous, interference-free measurements of a broad variety of reactive and stable gases. We have been exploiting these advantages in a series of studies that now provides comprehensive emissions data from a survey of fires in each major vegetation class.

The series began with a report on the emissions from coniferous and brush fuels that simulated important fire-types (crown fires, slash piles, etc.) [*Yokelson et al.*, 1996b]. A second study quantified the emissions from the smoldering combustion of organic soils, grasses, hardwoods, coniferous fuels, and other fuels [*Yokelson et al.*, 1997]. A third study included an initial probe into the effects of wind, fire retardant, and fuel orientation on the emissions from fires in coniferous, brush, and hardwood fuels [*Yokelson et al.*, 1999a]. A major result of these three studies was the observation of oxygenated organic compounds, such as formaldehyde, methanol, acetic acid, and formic acid, at higher levels than previously reported in nonspectroscopic studies and at an abundance similar to that of the much more heavily studied nonmethane hydrocarbons. Our recent airborne FTIR measurements of the emissions from forest fires (R. J. Yokelson et al., Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy (AFTIR), submitted to *Journal of Geophysical Research*, 1999) (hereinafter referred to as Yokelson et al., submitted manuscript, 1999); J. G. Goode et al., manuscript in preparation, 1999) suggest that our laboratory fires, including those studied here, are quite representative of full-scale fires in the open environment. *Worden et al.* [1997], using an airborne emission spectrometer, have also obtained emission ratios that are in reasonable agreement to those measured by our FTIR system.

To address the possibility that our differences with nonspectroscopic studies resulted from the fact that we had not

yet measured the full range of possible emissions from fires in all the important vegetation classes, we decided to include measurements of the emissions from whole grass fires in our fourth open-path FTIR laboratory study. Although grass fires are believed to account for approximately 50% of biomass burning on a global scale [*Hao and Liu*, 1994], we had previously only measured their emissions during smoldering combustion [*Yokelson et al.*, 1997]. This study would then complete our initial survey of fire emissions from all the important vegetation classes.

We were given the opportunity to collect this data during a collaborative experiment with groups from the Intermountain Fire Sciences Laboratory, NASA Goddard Space Flight Center, and the Jet Propulsion Laboratory. Their objective was to measure the radiative signatures for flaming and smoldering combustion using two modified emission FTIR spectrometers (A. E. Wald et al., Laboratory studies of radiant and gaseous emission from biomass burning for use in remote sensing, submitted to *Journal of Geophysical Research*, 1998). To avoid saturation of the emission FTIR spectrometers, these fires were kept small in size. This meant that our S/N ratio was not maximized. Nevertheless, we obtained important results on grass and surface fires that are presented below.

2. Experiment

The current series of fires took place in the combustion laboratory at the Intermountain Fire Sciences Laboratory (IFSL). The experimental configuration and FTIR spectrometer have been described in detail by *Yokelson et al.* [1997]. Briefly, the fuel is burned on an ~1 x 2 m continuously weighed fuel bed, and the smoke is captured by a 1.6 m diameter stack with a 3.6 m inverted funnel opening just above the fuel bed. A sampling platform surrounds the stack 18 m above the fuel bed. The open-path FTIR spectrometer consisted of a spectrometer (MIDAC Inc., model 2500), a 1.6 m base, open-path White cell (Infrared Analysis, Inc), and an external, "wideband" Mercury Cadmium Telluride (MCT) detector (Graseby FTIR M-16). For all the measurements reported in this paper, the spectrometer was operated at a spectral resolution of 0.5 cm^{-1} and a temporal resolution of 1.7 s. Subsequently, one to five scans were coadded to increase the S/N, while retaining sufficient temporal resolution. The White cell was used with a total path length of 44.6 m. Spectra recorded prior to the fire were used as background spectra to generate the smoke absorbance spectra and also to determine background levels of CO_2, CO, and CH_4.

The smoke temperature at the sampling platform was measured by a chromel-alumel thermocouple verified to be accurate to within 0.1°C at the freezing and boiling points of water. Pressure (~90.2 kPa) was measured by the built-in pressure sensor in a CO_2/H_2O analyzer (LICOR model 6262) and stack flow was measured by a Kurz (model 455) mass flow meter. Total fuel bed mass was logged every second using either one or two Mettler PM34 digital scales. Smoke samples were also collected in specially manufactured and cleaned stainless-steel canisters during a few of the fires and analyzed using a gas chromatograph (GC) with a flame ionization detector (FID).

Six small fires were burned in 0.4 - 2.1 kg of fuel and OP-FTIR spectra recorded throughout the duration of each fire. The fuels consisted of (1) ponderosa pine needles (PPN), (2) ponderosa pine needles and Douglas fir litter (a mixture of twigs, bark, and needles) and (3) grass (a mixture of smooth brome, intermediate wheat grass, and sheep fescue). These fuel samples

were set up either on a flat fuel bed or on a 40% slope to mimic a backing fire, as indicated in Table 1. Each fuel element was subsampled to obtain the fuel moisture and the carbon/hydrogen/nitrogen content by a Perkin-Elmer Model 2400 CHN analyzer.

2.1. Brief Overview of Smoke Analysis by FTIR Spectroscopy

Here we give a brief summary of our measurement approach. (More detailed background information about spectroscopic measurements in ambient air or smoke are given by *Hanst and Hanst* [1994], *Griffith* [1996], *Yokelson et al.* [1996a, b, 1997].) Every molecular species absorbs IR radiation in a unique pattern of frequencies and in known proportion (normally) to the amount present. If a beam of IR energy (~50 m long) is directed through a smoke plume, an IR spectrum of the smoke can be recorded which contains peaks due to most of the compounds present at a path-average mixing ratio above several ppbv. (Notable exceptions include homonuclear diatomics such as N_2, H_2, O_2, etc.) We have normally been able to assign every peak in our smoke spectra to specific compounds and to determine the mixing ratio for every identified compound. Since significant features are very rare in the residual spectrum, it seems likely that we have quantified the large majority of the compounds present above 10 ppbv in the smoke from the fires we investigated. While other compounds must be present, evidently most of them are less abundant. Many compounds can be analyzed using several groups of peaks ("spectral windows") that are nearly or completely interference free. We perform a multicomponent analysis on each spectral window that retrieves the individual mixing ratios for all the compounds present (including any potential interferant). Agreement between different spectral windows for the same compound is generally excellent and an average value is reported [*Yokelson et al.*, 1996a, b, 1997]. In summary, our open-path FTIR technique has certain advantages and limitations. The advantages include the following: (1) There is no need to take samples and no possibility of sampling- or storage-related artifacts so that reactive gases can be quantified. (2) The measurement is path integrated, averaging over small-scale local variations; thus it is more immune to spatial variation than point sampling. (3) Measurements can be made with high-temporal resolution so that dynamic processes can be followed. (4) Simultaneous measurements can be made of a wide variety of species, with good resistance to interference, over a wide range of concentrations with detection limits in the low parts per billion range. (5) There is high potential to observe and quantify unanticipated species. Thus it is possible to obtain a broad overview of certain complex environments, such as smoke, with OP-FTIR that cannot be obtained by any other single technique. The limitation is generally sensitivity. Sample preconcentration combined with an enclosed optical path can be used to lower FTIR detection limits into the pptv range and thus greatly expand the number of compounds observed [*Hanst et al.*, 1975], but only with the risk of improperly measuring reactive or sticky compounds.

2.2. Open-Path FTIR Spectrum Analysis

Several different methods were used to retrieve concentrations from the spectra. In general, to accomplish the bulk of the analysis and provide efficient processing of congested smoke spectra acquired at many different temperatures, we have coupled the techniques of synthetic calibration [*Griffith*, 1996] and classical least squares (CLS) fitting [*Haaland*, 1990]. The

computer program MALT (Multiple Atmospheric Layer Transmission) [*Griffith*, 1996] computes ideal spectra from HITRAN [*Rothman et al.*, 1992] absorption line parameters. These spectra are then convolved with the instrument function. In this way the calculated spectra closely match real experimental spectra, and a set of calibration spectra over a range of gas concentrations are generated for multicomponent quantitative analysis using CLS methods. This eliminates the need to acquire reference spectra for a large number of compounds at many temperatures, rigorously deconvolves the multicomponent spectra, and is readily automated to decrease analysis time. In summary, MALT/CLS allows rapid, accurate analysis of any of the 35 molecules in the HITRAN database, at arbitrary concentration, temperature, and pressure. The MALT/CLS analysis has a typical 1σ standard error of ± 5%. For species for which spectral line parameters are not available, MALT/CLS cannot be used, and the more traditional method of spectral subtraction is employed which has an estimated 1σ error of < 10% as discussed by *Yokelson et al.* [1997]. The accuracy at low mixing ratios is limited by the signal to noise which, at high temporal resolution, varies from scan to scan and from compound to compound. However, typical detection limits (for a S/N=1) are 10-20 ppbv for a 10 s measuring time and a few ppbv for several minutes measuring time.

A limited test of our accuracy estimates was possible since earlier tests had shown that the smoke is well mixed at the level of the sampling platform. Canister samples were collected over a period of ~ 75 s, adjacent to the OP-FTIR path and at constant fill rates during two of the fires. These were analyzed for CO_2, CO and hydrocarbons by the established laboratory technique of GC/FID. The OP-FTIR spectra acquired while the canisters were being filled were averaged together and analyzed for the same compounds, as discussed above. The canister results provide a benchmark to investigate our FTIR analysis methods, which are also used for quantifying many reactive compounds that are difficult to measure with other techniques. The results for each can are shown in Figure 1, plotted as a ratio between the OP-

FTIR absolute mixing ratio and the can absolute mixing ratio for carbon dioxide, carbon monoxide, and the hydrocarbons methane, ethylene, acetylene, and isobutene. The error bars for each ratio are the sum of the estimated 1σ accuracy of the OP-FTIR data and the precision of duplicate analysis for the GC data (± 2% for CO_2, CO, and CH_4, ± 5% for C_2 compounds, and ± 20% for C_4 compounds). In 8 out of the 10 spot comparisons, the agreement between the canisters and the OP-FTIR is within 1σ. For both CH_4 and CO, one canister was found to be outside the 1σ range but still well within the 2σ limit. Thus this limited test appears to confirm our earlier accuracy estimates given above. Further, our accuracy estimates are probably also valid for the more reactive compounds (such as methanol and formaldehyde) which are quantified by the same methods used in this test.

3. Results and Discussion

The open-path FTIR spectra and associated analysis techniques allow us to determine the mixing ratios of a large number of chemical species throughout the course of each fire, despite the small size of these fires. The molecular species measured were carbon dioxide, carbon monoxide, methane, ethylene (C_2H_4), acetylene (C_2H_2), isobutene (C_4H_8), formaldehyde (H_2CO), hydroxyacetaldehyde ($CHOCH_2OH$), methanol (CH_3OH), formic acid ($HCOOH$), acetic acid (CH_3COOH), water, nitric oxide (NO), and ammonia (NH_3). The fire-integrated mass emission factors (grams of compound emitted per kilogram of fuel burned (dry weight)) and 1σ errors for each fire are given in Table 1. The fire-integrated modified combustion efficiency (MCE) for each fire (calculated by taking the ratio of the excess CO_2 to the sum of the excess CO_2 and CO) is also given in Table 1. In this case the MCEs fall in a fairly narrow range (95-98%), typical of fires burning in fine fuels. The fuel type and fuel moisture for each fire is also listed in Table 1. Detailed calculations for the emission results given in Table 1 were described by *Yokelson et al.* [1996b]. The mass emission factors can be converted to molar emission ratios using
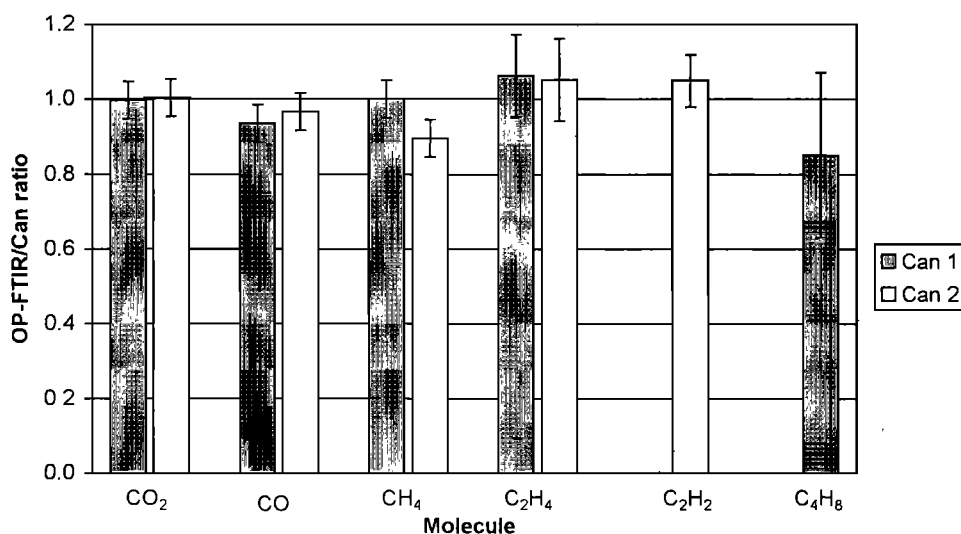

Figure 1. Results of an instrumental comparison carried out in well-mixed smoke. Two canisters of smoke were collected, adjacent to the OP-FTIR optical path, at a constant rate during a known set of FTIR scans. The ratio obtained by dividing the OP-FTIR absolute mixing ratio by the absolute mixing ratio from the GC/FID analysis is shown for each compound. The error bars for each ratio are calculated from the sum of the estimated 1σ accuracy of the OP-FTIR data and the precision of duplicate analysis for the GC/FID data as discussed in the text.

Table 1. Mass Emission Factors for Each Fire Expressed as Grams of Compound Emitted per Kilogram of Dry Fuel Burned

Fire Number	Fuel[a]	Fuel Composition				MCE[b]	Flaming Compounds		Smoldering Compounds						Pyrolysis Compounds				
		$H_2O\%$	C%	H%	N%		CO_2	NO	CO	CH_4	NH_3	C_2H_2	C_2H_4	C_4H_8	CH_2O	CH_3OH	CH_3COOH	HCOOH	$C_2H_4O_2$
1	Ponderosa pine needles (PPN)	10.3	54.2	7.0	0.39	97.2%	1918.8 (96)[c]	1.95 (0.44)	35.7 (1.8)	1.939 (0.097)	0.430 (0.065)	0.096 (0.010)	0.649 (0.097)	bdl[d]	bdl	0.590 (0.097)	1.375 (0.268)	bdl	bdl
2	Grass	13.5	44.9	6.0	0.66	96.4%	1572.6 (79)	1.92 (0.53)	37.6 (1.9)	2.492 (0.125)	0.366 (0.037)	bdl	0.548 (0.066)	bdl	0.790 (0.170)	0.565 (0.068)	1.262 (0.120)	bdl	0.270 (0.070)
3	Douglas Fir litter on PPN starter	11.6	51.1	6.2	0.41	95.0%	1764.9 (88)	1.65 (1.62)	58.8 (2.9)	2.664 (0.160)	0.282 (0.141)	bdl	1.105 (0.282)	bdl	bdl	0.824 (0.272)	2.197 (1.099)	0.895 (0.899)	bdl
4	PPN backing Fire - 40% slope	7.8	54.2	7.0	0.39	97.9%	1932.8 (97)	1.57 (0.34)	26.8 (1.3)	1.197 (0.060)	0.195 (0.040)	0.152 (0.015)	1.284 (0.064)	0.174 (0.042)	bdl	bdl	0.548 (0.274)	bdl	bdl
11	Grass	12.2	44.9	6.0	0.66	96.9%	1586.7 (79)	1.71 (0.29)	32.0 (1.6)	1.129 (0.068)	0.207 (0.033)	0.142 (0.014)	0.298 (0.052)	bdl	0.757 (0.193)	0.316 (0.085)	0.648 (0.220)	0.245 (0.168)	bdl
12	Grass	19.3	44.9	6.0	0.66	96.0%	1567.0 (78)	1.41 (0.23)	42.0 (2.1)	1.281 (0.064)	0.314 (0.025)	0.104 (0.010)	0.386 (0.042)	0.644 (0.119)	0.547 (0.118)	0.572 (0.057)	1.641 (0.181)	bdl	0.608 (0.143)

[a] Unless otherwise indicated the fuel bed orientation was flat.
[b] Modified combustion efficiency (MCE) *100
[c] 1σ error in the mass emission factor.
[d] bdl, below detection limit.

equation (1) where EF is the mass emission factor and MM is the molecular mass.

$$\text{molar emission ratio}\left(\frac{i}{j}\right) = \frac{EF(i)}{MM(i)} \bigg/ \frac{EF(j)}{MM(j)} \qquad (1)$$

Many of the compounds identified in Table 1 are attributed to flaming or smoldering combustion based on their temporal correlation with CO_2 or CO, respectively. However, we also measured significant amounts of compounds that do not correlate temporally with either CO_2 or CO. These compounds are known biomass pyrolysis products contained in the white smoke produced by heating of the primary fuel [Shafizadeh et al., 1976; DeGroot et al., 1988; Yokelson et al., 1997]. Pyrolysis products quantified in this study include acetic acid, formic acid, methanol, formaldehyde, hydroxyacetaldehyde, and light unsaturated hydrocarbons. Examples of normalized temporal profiles for selected flaming, smoldering, and pyrolysis compounds for a PPN burn (Fire 1) are shown in Figure 2. Figure 2 shows a pattern of fire behavior and emissions production that is typical of a small fire in fine fuels. The combustion processes and emissions shown are discussed in more detail by Yokelson et al. [1996b, 1997].

3.1. Grass Fires and Oxygenated Organic Compounds

The average molar emission ratios for methanol, formaldehyde, and acetic acid to CO in the three grass fires in this study were 1.1%, 1.8% and 1.4%, respectively (calculated from Table 1 using equation (1)). These values are generally consistent with the emission ratios observed in our previous laboratory work [Yokelson et al., 1996b; 1997; 1999a], with the emission ratios observed in fires in the other fuels in this study, and with the emission ratios observed in our fieldwork [Yokelson et al., submitted manuscript, 1999; J. G. Goode et al., manuscript in preparation, 1999]. This result suggests that the large interstudy differences for these compounds discussed earlier do not seem to be directly related to differences between the major vegetation-types.

The largest single source of biomass burning emissions is believed to be savanna fires [Hao and Liu, 1994]. These fires occur predominantly in the tropics where grass is the major fuel. If the mass emission factors for the oxygenated organic compounds measured in our current grass fire study are representative of savanna fire emissions, these oxygenated organic compounds could have a significant influence on plume HO_x and O_3 chemistry. Oxygenated organic compounds are also being increasingly recognized as important biogenic emissions [Konig et al., 1995; Kirstine et al., 1998]. Although these compounds are miscible with water, their Henry's Law solubility coefficients [Betterton, 1992] are small enough that removal by washout/rainout processes will not compete favorably with removal by OH reaction and photolysis in most situations. The main removal processes, oxidation, and photolysis, are therefore a net source of HO_2 [Madronich and Calvert, 1989; Atkinson, 1994; Singh et al., 1995; Lee et al., 1998] which would be expected to rapidly initiate O_3 producing photochemistry in the early plume by converting NO to NO_2 [Altshuller et al., 1967; Seinfeld, 1986; Lelieveld et al., 1997]. The increased, initial, modeled O_3 formation rate seems to agree with our field observations of O_3 formation on single biomass fire plumes in Alaska (J. G. Goode et al., manuscript in preparation, 1999).
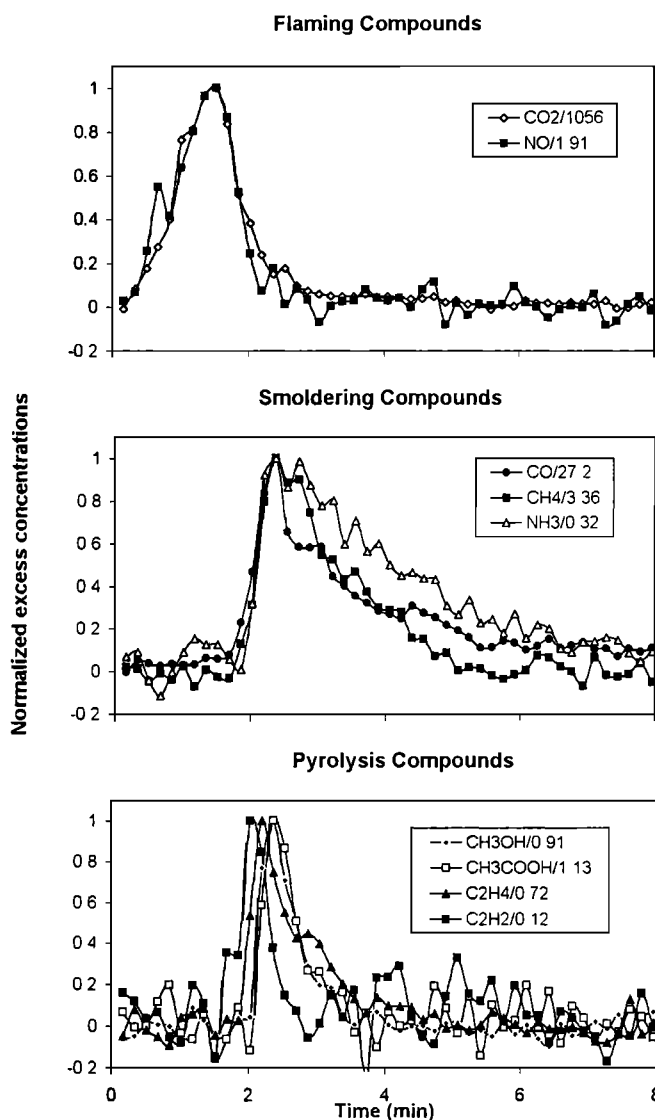
Given the importance of these oxygenated compounds in the

Figure 2. Temporal profiles for pyrogenic compounds emitted from a small ponderosa pine needle fire (Fire 1) separated by flaming, smoldering, and pyrolysis/distillation combustion processes. Each compound has been normalized to its maximum mixing ratio, which is indicated in the legend.

global troposphere, it is of interest to estimate global emission factors for these compounds from savanna fires. We assume 950 $\pm$ 650 Tg yr^{-1} (1 Tg = 10^{12} g) of carbon are released by savanna fires [Crutzen and Andreae, 1990]. Using the average mass emission factors for the oxygenated organics for the three grass fires reported in Table 1, we estimate a lower limit (due to the high MCE) of 1 $\pm$ 0.7 Tg yr^{-1} methanol, 1.5 $\pm$ 1 Tg yr^{-1} formaldehyde, and 2.5 $\pm$ 1.7 Tg yr^{-1} acetic acid. Given that the estimated global source of methanol is 45 Tg yr^{-1} [Singh et al., 1995] and biogenic grassland methanol emissions may account for approximately 13 Tg yr^{-1} or 15% of the VOCs emitted from grasslands, [Kirstine et al., 1998], it is apparent that methanol emissions from biomass burning in tropical savannas are small compared to the global total. However, since these emissions are concentrated temporally and spatially to a few months during the tropical dry season, they can impact a globally important process, as noted earlier. In contrast to savanna fires, permanent

deforestation and shifting agriculture fires may produce considerably higher amounts of these oxygenates due to their lower MCEs [Yokelson et al., submitted manuscript, 1999] and could have a much larger impact both locally and regionally.

One of the long-term objectives of our laboratory OP-FTIR study was to investigate fire emissions in at least one example of each major vegetation class. This was necessary to determine the probable boundary conditions for the initial emissions from the many types of fires. Our previous work toward this goal had included fires in several major vegetation classes with the exception of grass. This study, by acquiring data from three grass fires, completes our initial fire emissions survey.

Consideration of our fire-integrated initial emission measurements and other literature reports allows us to "rank" the major individual constituents of fresh smoke. CO_2 and CO are the first and second most common emissions (after water), typically accounting for 80-95% and 5-15%, respectively, of the total carbon emissions. The fire-integrated emissions of CH_4, H_2 [Cofer et al., 1996], and particulate matter [Ward et al., 1996] are each typically about 0.2-2% of the total carbon emissions (or 2-20% of CO). The dependence of the above emissions on combustion processes has now been well documented [Ward et al., 1992; Cofer et al., 1996; Ward and Yokelson, 1997; Yokelson et al., 1999a]. A fourth "tier" of emissions (just below methane, H_2, and particulate) consists of methanol, acetic acid, formaldehyde, ethylene, diatomic nitrogen, ammonia, and nitric oxide. The fire-integrated emission of each of these compounds is usually 2 ± 1% of CO. Detailed models for estimating N_2 [Kuhlsbuch et al., 1991] and the other fourth "tier" compounds [Yokelson et al., 1996b, 1997] have been presented previously. Many other compounds are typically emitted at 1% or less of CO. The emissions of these latter compounds appear to be much more variable and are seemingly more heavily dependent on fuel chemistry and fire behavior [Yokelson et al., 1997]. We have not included potentially significant emissions of individual monoterpenes in this summary as our analysis is still in development [Yokelson et al., 1996a].

There now exists sufficient understanding of how flaming and smoldering combustion affect fire emissions to enable atmospheric modelers and authors of national greenhouse gas inventories [Houghton et al., 1997] to choose a set of initial fire emissions appropriate for the combustion characteristics (for example MCE) of regional fuels and fires. This is discussed by Yokelson et al. [1999b] and could help to improve model accuracy.

3.2. C_4 Hydrocarbons

An important earlier study of biomass burning emissions by Lobert et al. [1991] identified a peak due to C_4H_8 compounds by GC/FID analysis. Using a general purpose column, they were able to assign the peak to a combination of isobutene and 1-butene. The OP-FTIR smoke spectra from both Fire 4 (surface fuels) and Fire 12 (grass fuel) contain a strong feature at approximately 890 cm^{-1}. Figure 3 shows the OP-FTIR smoke spectrum from Fire 12 between 770 cm^{-1} and 1050 cm^{-1} after subtracting features due to ammonia, ethylene, and methanol. Also shown are the FTIR reference spectra for both isobutene and 1-butene. From Figure 3 it is clear that the smoke feature at 890 cm^{-1} is associated with isobutene rather than 1-butene. In addition, no feature due to 1-butene is observed in the smoke spectrum.

The fire-averaged molar emission ratio for isobutene relative to CO, from the OP-FTIR data, was calculated to be 0.33% and 0.77% for Fires 4 and 12, respectively. The average of these values is 0.55%, almost 3 times larger than the fire averaged value of 0.19% from the study by Lobert et al. [1991]. However, it should be noted that isobutene was below our detection limits in four of the six fires in this study and in many of the canisters collected throughout the joint study and analyzed using a GC/FID preconcentration technique and an alumina column. In addition, those canisters containing isobutene showed an isobutene to 1-butene ratio ranging from 8:1 to 1:1. There are no readily apparent factors, such as fuel moisture, controlling the production of these compounds (see Table 1) and the emissions of C_4 compounds are noted to vary widely from fire to fire. We also note that the rate constant for the reaction of isobutene with the OH radical is over 60% larger than that of 1-butene [Finlayson-Pitts and Pitts, 1986]. These facts may deserve consideration when including C_4 hydrocarbons in smoke and atmospheric models.
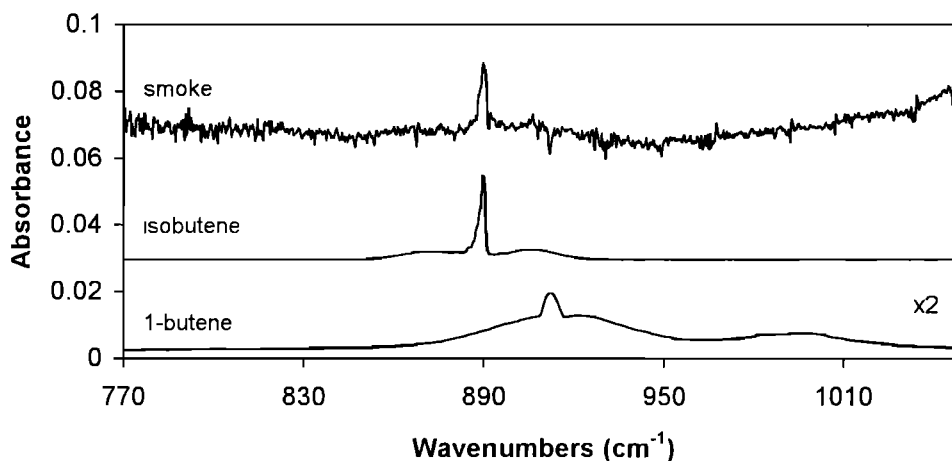

Figure 3. An open-path FTIR smoke spectrum from Fire 12, recorded during a period of peak C_4H_8 emission, is shown between 770-1050 cm^{-1} (after subtracting reference spectra for ammonia, methanol, and ethylene). Reference spectra for isobutene and 1-butene are also shown having been scaled to the same mixing ratio (700 ppbv) as the isobutene peak in the smoke spectrum. Note the expansion factor for the 1-butene reference spectrum. The remaining feature in the smoke spectrum can clearly be assigned to isobutene.

3.3. Nitrogen Compounds

Biomass burning is an important source of reactive nitrogen compounds in the atmosphere. *Yokelson et al.* [1996b] reported that the sum of the NH_3 and NO_x emissions from the large-scale laboratory fires accounted for 55% of the fuel nitrogen. By accepting literature values for the other fates of fuel N, 36 ± 13% for N_2 [*Kuhlbusch et al.*, 1991], and 10% for ash [*Lobert et al.*, 1991; *Hurst et al.*, 1994], they accounted for all the fuel nitrogen within experimental error. The *Yokelson et al.* [1996b] value for NH_3 + NO_x was close to the finding of *Hurst et al.* [1994] who found that these compounds accounted for 44 ± 15% of the fuel nitrogen from Australian savanna fires. In these two studies, 50% was the average amount of fuel N released as NH_3 and NO_x. Finally, they showed that all the published data on NH_3 and NO_x emissions from fires was well fit by the equation NH_3/NO_x = (-14.0 x MCE)+13.8 (see also Figure 4 of this work).

The nitrogen containing emissions measured in this study consisted of NO from flaming combustion and NH_3 from smoldering combustion. Other nitrogen containing compounds such as NO_2, N_2O, and HCN were below our detection limits due to the small size of these fires combined with the relatively low fuel N content (see Table 1). Figure 4 shows the fire-integrated NH_3/NO_x ratio from several smoke investigations as a function of MCE. The study-average ratio from this work is very close to the "best fit" line. The consistency of this result confirms that NO_x (primarily NO) is the dominant reactive nitrogen emission from flaming combustion, whereas NH_3 is the dominant reactive nitrogen emission during smoldering combustion.

In contrast to our earlier result, the average amount of available biomass nitrogen detected in our nitrogen containing emissions (NH_3 and NO) in this study was only 22 ± 8%. This is approximately one half the percentage found in the earlier work discussed above and closer to the report of *Lobert et al.* [1991] who obtained 17.7 ± 8% for NH_3 + NO_x (note that their NH_3/NO_x ratio also falls close to the line in Figure 4). Although we did not

measure the ash N content or the N_2 emissions in this study, we still feel that attempting a nitrogen mass balance is useful. The molecular nitrogen emission can be estimated from the work of *Kuhlbusch et al.* [1991] who reported N_2 emissions as a function of combustion efficiency. Their work suggests an N_2 emission of 36 ± 13% for a fire with a MCE of ~91% (used for the N balance in our earlier study) and a value nearer 45 ± 5% for the MCEs (95-98%) in our current study. If, in addition, we again make the assumption that 10% of the fuel nitrogen remains in the ash as described above and reported elsewhere [*Hurst et al.*, 1994; *Crutzen and Andreae*, 1990], then we are only able to account for 77 ± 9% of the available fuel nitrogen.

It is unclear why the NH_3+NO_x is lower and why we are unable to account for all the fuel nitrogen in these fires. Independent analysis techniques (MALT and spectral subtraction) for ammonia in the OP-FTIR spectra generated virtually identical concentrations, and the agreement with the previous data sets for the NH_3/NO_x ratio versus MCE indicate that it is unlikely that we have underestimated either of these compounds. The fires probed by *Yokelson et al.* [1996b] and *Hurst et al.* [1994], however, were larger than those probed both here and in the study by *Lobert et al.* [1991]. The larger fire size may help promote conversion of fuel N to NH_3 or NO_x. It is also possible that in the current work, we did not detect some significant nitrogen containing emissions with weak IR spectral features. *Lobert et al.* [1991] report high levels of acetonitrile, which unfortunately has weak IR features. Perhaps the most significant possibility is that > 10% of the N remained in the ash. *Kuhlbusch et al.* [1996] report a highly variable degree of nitrogen volatilization, 74 ± 11% (instead of the 90% above), in the SAFARI-92 study. Thus our reported NH_3 and NO_x, the assumed N_2, and small amounts of NO_2, N_2O, and HCN may well account for all volatilized N. To overcome these uncertainties, measurements of NH_3, NO_x, N_2, and nitrogen in the residual material should be part of any rigorous "N balance."
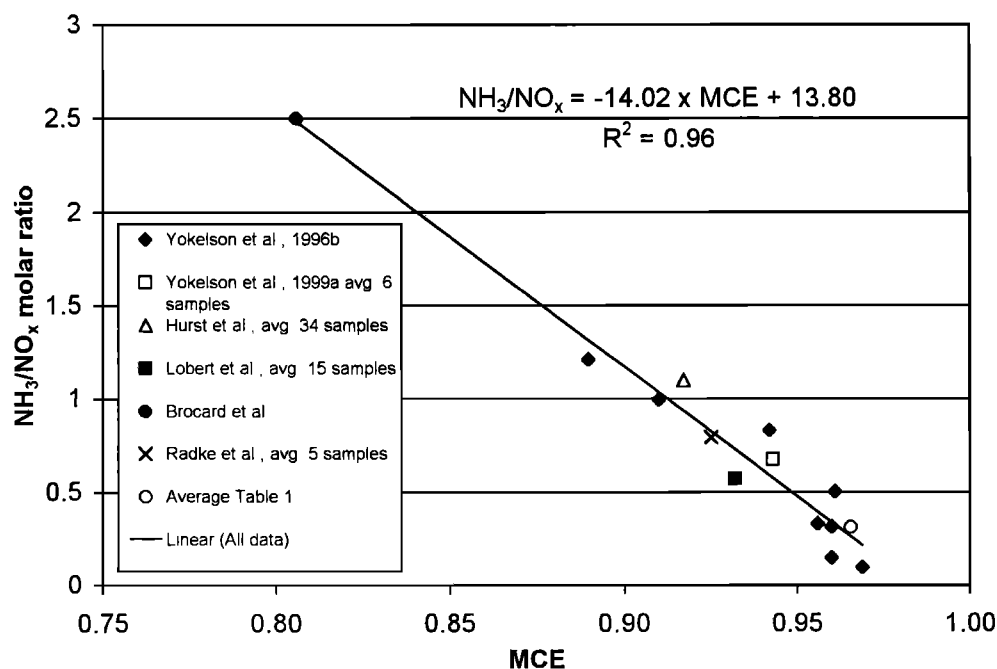

Figure 4. The fire-integrated NH_3/NO_x molar ratio plotted versus the fire-integrated modified combustion efficiency. The study average (the average of the six fire-integrated values) is plotted with the results from a number of other studies. The linear regression fit is also shown.

4. Conclusions

This study includes emission data from three grass fires and therefore completes our initial spectroscopic survey of trace gas emissions from laboratory biomass fires in each major vegetation class. Formaldehyde, methanol, and acetic acid were emitted from the grass fires at approximately 1-2% of CO. Other oxygenates were emitted at ~1% of CO. These emission ratios are consistent with our other work and other spectroscopic work but up to several hundred times higher than reported in some previous studies. These results, combined with our previous three investigations, suggest that some large interstudy differences are probably not accounted for by differences in vegetation burned or combustion efficiency.

If the mass emission factors we have obtained for oxygenated compounds in our grass fires are also characteristic of savanna burning in the tropics, then there may be a significant, previously overlooked effect on the local HO_x and O_3 chemistry in the biomass smoke plume. Given that these oxygenated organic emissions are concentrated temporally and spatially to a few months during the tropical dry season, they could impact a globally important process. Simple calculations suggest that savanna burning is not a major source of methanol to the global troposphere.

Simultaneous measurements by OP-FTIR and canister GC/FID clearly indicate that the dominant 4-carbon-atom emission from these fires was isobutene (C_4H_8) and not 1-butene. The emissions of this compound vary widely from fire to fire. The rate constant for the reaction of isobutene with the OH radical is 60% larger than that of 1-butene. These facts should be considered when C_4 compounds are included in smoke/atmospheric models.

We estimate that $67 \pm 9\%$ of the fuel nitrogen was emitted as trace gases in this study with $22 \pm 8\%$ comprising NH_3 and NO_x. This contrasts with our earlier study where we estimated that 90% of the fuel N was volatilized and 55% was measured as NH_3 and NO_x. The reason for the lower yield of NH_3 and NO_x in this study is not clear. One possibility is that a larger percentage of the fuel nitrogen remained in the ash. The results from all studies are consistent with the equation $NH_3/NO_x = (-14.0 \times MCE) + 13.8$.

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