

Emissions from smoldering combustion of biomass measured by open-path Fourier transform infrared spectroscopy

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Abstract. Biomass samples from a diverse range of ecosystems were burned in the Intermountain Fire Sciences Laboratory open combustion facility. Midinfrared spectra of the nascent emissions were acquired at several heights above the fires with a Fourier transform infrared spectrometer (FTIR) coupled to an open multipass cell. In this report, the results from smoldering combustion during 24 fires are presented including production of carbon dioxide, carbon monoxide, methane, ethene, ethyne, propene, formaldehyde, 2-hydroxyethanal, methanol, phenol, acetic acid, formic acid, ammonia, hydrogen cyanide, and carbonyl sulfide. These were the dominant products observed, and many have significant influence on atmospheric chemistry at the local, regional, and global scale. Included in these results are the first optical, in situ measurements of smoke composition from fires in grasses, hardwoods, and organic soils. About one half of the detected organic emissions arose from fuel pyrolysis which produces white smoke rich in oxygenated organic compounds. These compounds deserve more attention in the assessment of fire impacts on the atmosphere. The compound 2-hydroxyethanal is a significant component of the smoke, and it is reported here for the first time as a product of fires. Most of the observed alkane and ammonia production accompanied visible glowing combustion. NH_3 is normally the major nitrogen-containing emission detected from smoldering combustion of biomass, but from some smoldering organic soils, HCN was dominant. Tar condensed on cool surfaces below the fires accounting for ~ 1% of the biomass burned, but it was enriched in N by a factor of 6 - 7 over the parent material, and its possible role in postfire nutrient cycling should be further investigated.

Introduction

Biomass burning emissions are well-established as a significant influence on the atmosphere [Crutzen and Andreae, 1990; Crutzen and Carmichael, 1993; Prather *et al.*, 1994; Prather and Logan, 1994]. Flaming combustion of biomass fuels primarily produces highly oxidized compounds such as CO_2 , NO_x , and SO_2 . What is commonly called "smoldering combustion" can be a complex mix of fuel pyrolysis (thermal decomposition of fuel), small flames, and glowing combustion of char. These processes can accompany flaming or occur in varying combination after flaming and produce many less-oxidized gaseous emissions of considerable interest to atmospheric chemists [Lobert *et al.*, 1991; Yokelson *et al.*, 1996a]. Grasses and tropical broadleaved trees are the predominant biomass fuels globally [Crutzen and Andreae, 1990]. Flaming combustion accounts for most of the fuel consumption in grass fires. However, the emissions from smoldering combustion in grass fires also play

an important role in tropical dry season tropospheric chemistry [Connors *et al.*, 1996; Thompson *et al.*, 1996; Chatfield *et al.*, 1996; Crutzen and Carmichael, 1993; Granier *et al.*, 1996]. In fires in tropical and temperate forests, a much larger percentage of the fuel consumption is by smoldering combustion [Ward *et al.*, 1992; Susott *et al.*, 1991], and thus smoldering emissions strongly impact the dry season troposphere in tropical deforestation regions [Connors *et al.*, 1996; Chatfield and Delaney, 1990; Richardson *et al.*, 1991; Keller *et al.*, 1991; Crutzen and Carmichael, 1993; Granier *et al.*, 1996].

In contrast to grass and hardwood fuels, the emissions from combustion of the carbon stored in "belowground biomass" (biomass directly on top of or incorporated into the soil) are still relatively unexplored. Very high carbon loading is possible in some organic soils. For example, Zinke *et al.* [1984] report over 1000 t C per hectare in the top 1 m of North American bogs, a carbon loading about twice the maximum reported due to the aboveground biomass in tropical forests [Brunig, 1977]. Globally, it has been estimated that over two thirds of the carbon in forest ecosystems is contained in soils and associated peat deposits [Dixon *et al.*, 1994] and that the carbon in soils represents an even larger carbon pool than aboveground biomass [Woodwell *et al.*,

1978]. Both wildfires and land-management activities expose belowground biomass to fire, and it may account for a significant fraction of the fuel consumption in fires in the boreal forest [Hungerford, 1995] or in tropical forests such as the kerangas or caatinga [Jacobs, 1988]. It has been projected that much more of this carbon may burn in global warming scenarios [Kasischke et al., 1995; Keane et al., 1997]. Smoldering combustion should account for essentially all fuel consumption in burning organic soils.

In earlier work, we carried out pilot studies of the effectiveness of open-path Fourier transform infrared spectroscopy for measuring biomass fire emissions [Griffith et al., 1991; Yokelson et al., 1996a, b]. Our report on the laboratory pilot study [Yokelson et al., 1996a] quantified the relative fire-integrated production of both reactive and stable emissions from flaming, smoldering, and pyrolysis. We followed Ward and Radke [1993] in using modified combustion efficiency (MCE) defined as $\Delta\text{CO}_2/(\Delta\text{CO}_2+\Delta\text{CO})$ as an index of the relative amount of flaming and smoldering combustion occurring during a fire. We observed a correlation between emissions and MCE which independently verified the earlier work of Lobert et al. [1991], Ward et al. [1992], and others. Another major result of our pilot study [Yokelson et al., 1996a, b] was observation of oxygenated volatile organic compounds (OVOC) at as much as 10 to 100 times the levels previously measured in nonspectroscopic studies. In the work of Yokelson et al. [1996a], we suggested that some differences between studies could be due to the different fire types probed or to the different measurement techniques employed (in particular, other studies had concentrated on hardwoods and grasses, while our measurements had been primarily on coniferous fuels). Oxygenated organic molecules, if emitted in sufficient amounts, could significantly impact plume chemistry [Atkinson, 1990; Singh et al., 1995] and regional chemistry [Crutzen and Andreae, 1990]. Therefore data on the amount and type of OVOC initially produced in biomass fires will be of use in modeling the atmospheric influence of these fires.

In this paper, we address the need for information on both OVOC production and smoldering combustion of biomass by presenting some initial results from a new open-path FTIR apparatus optimized to continue the smoke measurements initiated in our pilot studies. In this work, our experimental approach was determined primarily by the following three objectives: (1) to increase the fundamental understanding of the smoldering combustion process, which may influence global climate and has other ecological effects (process level knowledge is also often useful to rationalize diverse measurement results), (2) to obtain data at several heights above fires to facilitate detecting the most reactive initial emissions and to search for evidence of rapid loss or production of species in the nascent plume, and (3) to determine whether OVOC are likely to be important emissions from most biomass fires.

Experimental Details

Fuel Selection Objectives

We burned fires in a large variety of fuels for three main reasons: (1) to investigate the natural variability in emissions from different fire types and to estimate the "boundary conditions" for initial emissions from biomass fires. (2) to

increase our chance of detecting more of the species emitted from biomass fires, and (3) to enhance our ability to model the emissions from specific types of biomass fires. The fuel for each smoke sample is listed in Table 1, and the rationale for its selection in our study is summarized below.

Grass and hardwood fuels were selected because they account for a large fraction of the global biomass burning [Crutzen and Andreae, 1990; Scholes et al., 1996] and because no in situ, spectroscopic measurements of smoke composition from fires in these fuels had been reported. Grass samples (Table 1) were rough fescue (*Festuca scabrella*, a bunch grass native to Montana) and wire grass from the southeastern United States. Hardwood fuels (Table 1) included poplar wood shavings, gallberry leaves and stems, aspen bark, and brown, partially decomposed maple leaves. The maple leaves are representative of hardwood leaf litter, a significant fuel in (temperate through tropical) seasonal, deciduous forests. We also burned one sample of banana leaves since attached leaves may comprise over one half of the aboveground biomass in some tropical secondary forests [Uhl and Jordan, 1984].

In some tropical pastures and secondary forests, dead wood left over from a preexisting primary forest is reported to account for a large fraction (up to 87 %) of the aboveground biomass [Ewel et al., 1981, p. 820; Uhl and Jordan, 1984, Tables 5 and 6; Kaufmann and Uhl, 1990; Barbosa and Fearnside, 1996]. Dead wood, decomposed by either "white" or "brown" rot (fungi) [Terron et al., 1995] can have percentages of cellulose and lignin very different from the 50 and 25% respectively, typically found in live wood. Brown rot removes cellulose leaving a powdery wood as high as 70 - 80 % lignin. Lignin contributes heavily to charcoal formation [Susott et al., 1975; Shafiqzadeh and DeGroot, 1976] which is important in carbon cycling [Crutzen and Andreae, 1990], and lignin has been reported to comprise up to 48% of some peat deposits [McMahon et al., 1980]. White rot preferentially removes the lignin from wood [Terron et al., 1995]. For initial exploration of the effect of lignin content on biomass fire emissions, we burned one sample of Ponderosa pine wood which had been decomposed by brown rot and had a lignin content of 66.4%. Organic soil and duff samples were removed intact from various ecosystems throughout the United States (Table 1). Other fuels (Table 1) were burned mainly to increase the range of samples such as cattails and palmetto and to overlap with previous work (sagebrush).

Description of FTIR and White Cell

The IR radiation from the FTIR (MIDAC model 2500) is directed through a 1.6 m base path open White cell (Infrared Analysis, Inc.) and then refocused on an external "wideband" Mercury Cadmium Telluride (MCT) detector (Graseby FTIR M-16). (See Figure 1.) The White cell allows long path lengths to increase absorption levels (we used 70.1 or 76.5 m in all experiments reported here), and directing the IR beam through the interferometer before the long, open, atmospheric path reduces measurement noise due to emission from the hot gases [Hanst and Hanst, 1994]. The spectrometer was configured for a scan speed (and maximum time resolution) of 3 s at the spectral resolution of 0.5 cm^{-1} used in all measurements reported here. The spectrometer and White cell are mounted on a Super-Invar™ (Carpenter, Inc.) structure, and the mirror substrate has the lowest available thermal

Table 1. Summary of Data With Emissions Reported as 100 X (Moles Compound/Total Moles C Detected) and Moisture and Elemental Analysis Reported as a Mass Percentage of Dry Matter

Fuel (depth, cm) ^a	Location	Fuel Composition				Oxides		Hydrocarbons				Aldehydes		Acids		Alcohols		Nitrogen		Sulfur
		H ₂ O%	C	H	N	CO ₂	CO	CH ₄	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
Bunch grass	Montana	88.4	37.67	5.21	1.83	87.7	9.5	0.33	0.181	0.052	0.060	0.375	0.087	0.117	0.235	0.139	0.083	0.127	0.073	0.004
Bunch grass	Montana	88.4	37.67	5.21	1.83	83.8	11.9	0.54	0.214	0.047	0.079	0.525	0.135	0.211	0.389	0.239	0.148	0.272	0.140	0.006
Wire grass	SE U.S. ^b	5.6	47.47	6.14	0.76	87.7	11.0	0.51	0.056	0.010	0.055	0.059	0.029	0.014	0.046	0.070	0.032	0.299	0.045	0.005
Poplar	SE U.S.	5.3	48.97	7.55	0.12	71.5	22.9	1.57	0.113	0.016	0.082	0.591	0.481	0.393	0.531	0.470	bid ¹²	0.064	bid	0.008
Sedge ^c	Alaska	7.4	40.40	5.32	1.66	80.6	14.7	1.50	0.128	0.005	0.125	0.102	0.035	0.054	0.350	0.228	0.163	1.480	0.360	0.023
Spagnum moss ^d (0-5)	Alaska	11.1	30.02	3.76	1.28	76.9	17.1	1.07	0.180	0.014	0.171	0.307	0.107	0.159	0.630	0.274	0.259	0.312	0.222	0.007
Spagnum moss (10-25)	Alaska	11.1	30.02	3.76	1.28	82.8	13.1	1.55	0.160	0.010	0.181	0.080	0.045	0.008	0.221	0.357	0.057	1.868	0.371	0.008
Peat ^e	Minnesota	9.9	49.37	6.42	3.06	78.5	15.2	1.47	0.141	0.009	0.174	0.053	0.006	0.016	0.196	0.437	0.375	2.265	0.712	0.127
Peat ^f	Alaska	nm	nm	nm	nm	75.6	21.1	0.61	0.096	0.009	0.149	0.269	0.056	0.182	0.394	0.176	0.038	0.298	0.204	0.005
Feather moss ^g top	Alaska	17.3	45.84	6.36	0.84	81.5	15.8	0.64	0.089	0.023	0.141	0.141	0.020	0.057	0.389	0.215	0.008	0.436	0.168	0.003
Feather moss mid	Alaska	17.3	37.15	4.38	0.78	75.7	20.9	1.15	0.143	0.007	0.158	0.198	0.020	0.074	0.285	0.218	0.021	0.442	0.212	0.010
Feather moss bot	Alaska	24.0	41.01	5.34	0.93	81.8	15.7	0.78	0.087	0.012	0.090	0.084	0.016	0.043	0.250	0.224	0.015	0.712	0.228	0.005
Bog soil ^h	N. Carolina	2.6	63.95	7.82	0.70	72.2	23.9	1.50	0.179	0.012	0.155	0.073	0.014	0.063	0.231	0.226	0.068	0.063	0.298	0.021
White spruce ⁱ (0-5)	Alaska	13.1	38.31	4.89	1.18	82.5	13.4	1.92	0.198	0.026	0.143	0.019	0.002	bid	0.111	0.455	0.062	1.444	0.143	0.004
FF; duff ^j ; pine-larch	Montana	8.9	34.25	4.72	0.95	79.5	15.8	1.62	0.165	0.007	0.147	0.111	0.023	0.043	0.343	0.533	0.107	0.900	0.231	0.009
FF; duff; pine-oak	SE U. S.	27.5	52.63	5.98	0.70	78.7	17.8	0.91	0.141	0.024	0.090	0.313	0.040	0.135	0.262	0.375	0.078	0.052	0.092	0.009
FF; duff; longleaf pine	SE U. S.	nm	50.56	6.34	1.02	65.1	26.4	1.85	0.192	0.026	0.170	0.784	0.183	0.316	0.855	1.095	0.219	0.086	0.148	0.011
Decomposed pine	Montana	34.0	52.63	5.76	0.36	76.0	19.6	1.62	0.183	0.032	0.065	0.563	0.032	0.101	0.122	0.391	0.120	0.075	0.040	0.009
Cigarette tobacco	SE U. S.	~5	42.65	4.98	3.29	88.7	6.8	1.48	0.231	0.023	0.306	0.320	0.152	0.023	0.060	0.376	0.063	2.984	0.040	0.006
Banana leaves	Indoors	5.3	41.28	5.52	2.34	79.4	15.3	0.82	0.347	0.032	0.483	0.475	0.182	0.033	0.218	0.477	0.056	2.422	0.170	0.010
Palmetto/gallberry	SE U. S.	4.9	48.50	5.83	0.63	76.6	17.1	1.20	0.104	0.008	0.103	0.161	0.029	0.002	0.850	0.428	0.339	0.476	0.103	0.009
Cottonwood bark	Montana	~5	47.91	5.10	0.45	79.5	15.2	2.21	0.211	0.013	0.128	0.201	0.044	0.035	0.345	0.567	0.108	0.522	0.018	0.009
Cattails	Montana	~5	45.40	6.14	2.58	78.6	14.8	1.69	0.315	0.012	0.336	0.234	0.132	0.159	0.600	0.438	0.146	1.680	0.151	0.020
Brown maple leaves	Montana	~5	43.19	4.47	1.34	74.9	16.9	1.99	0.275	0.040	bid	0.481	0.131	0.166	0.712	0.720	0.404	0.430	0.093	0.003
Sagebrush trunks	Montana	nm	49.53	6.14	0.67	81.0	12.6	2.43	0.151	bid	0.175	0.120	bid	0.041	0.352	0.548	0.285	0.448	bid	bid

Not measured (fuel composition measurements were omitted), nm; below detection limit, bld.

^aThe depth of soil layer sampled is provided if known.

^bFuels were sampled from coastal areas of Florida, Georgia, and South Carolina.

^cSite, Tannana river valley near Tok, Alaska; fuel details, decomposing dead vegetative matter and live roots; vegetation type, subarctic wet sedge meadow.

^dSite, Tannana river valley near Tok, Alaska; fuel details, decomposing dead vegetative matter and live biomass; vegetation type, black spruce woodland.

^eSite, Aggasiz National Wildlife Refuge; soil order, histisol; suborder, saprist; vegetation type, sedge/grass community.

^fSite, Tannana river valley near Tok, Alaska; fuel details, decomposing dead vegetative matter; vegetation type, peat bog.

^gSite, Tannana river valley near Tok, Alaska; soil order, inceptisol; suborder, aquept; vegetation type, open black spruce woodland.

^hSite, Alligator National Wildlife Refuge; soil order, histisol; suborder, saprist; vegetation type, low pocosin.

ⁱSite, Tannana river valley near Tok, Alaska; soil order, entisol; suborder, fluvent; vegetation type, open white spruce forest.

^jFF; duff indicates intact cross section of forest floor with ground fuels (needles; leaves; and twigs) overlaying duff (decomposing organic matter).

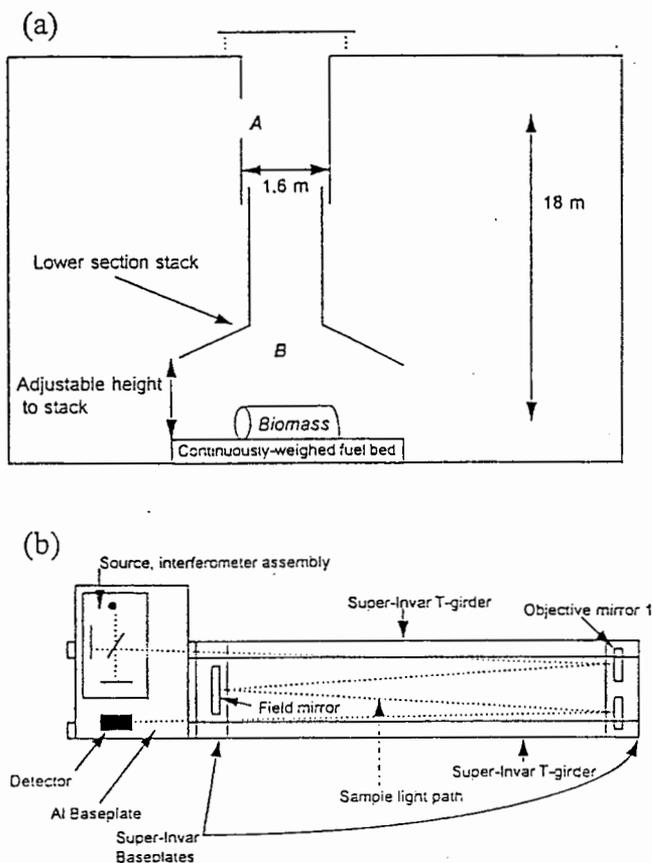


Figure 1. (a) Simplified illustration of the Intermountain Fire Sciences Laboratory combustion lab (not to scale). The Fourier transform infrared spectrometer (FTIR) was located at "A" in the pilot study and at both "A" and "B" in this study. (b) Schematic diagram of the new OP-FTIR system (not to scale).

expansion (ULE™ (ultralow expansion) Corning, Inc.). The optical throughput of the system was not measurably affected when portions of the structure were subjected to substantial, rapid increases in temperature.

Measurement Platforms and Fire Behavior

Direct measurement over low-intensity fires. Samples of organic soils listed in Table 1 (nominal size: 10 X 10 X 5 cm) were placed on Al foil several centimeters below the center of the White cell. A propane torch was used to initiate a slowly expanding "glowing pit" on the sample surfaces similar to those observed in field fires in this material [McMahon *et al.*, 1980; Hungerford *et al.*, 1995]. A very slow burning "steady state" or stable mix of glowing combustion and white smoke production (*vide infra*) was established within minutes. A large hood above the White cell drew the (sometimes barely visible) emissions through the optical path. The fan-induced flow was much greater than the fire-induced flow, so that the total flow was constant. Pressure and smoke temperature were also constant with smoke temperature measured to be the same as room temperature. Spectra were acquired continuously with 3 to 10 min time resolution until the size of the burning pit approached ~ 50% of the size of the sample (to prevent edge effects). The spectra of the emissions were ratioed to

background spectra collected before and after the "fire" to form absorbance spectra which yielded the net concentration, above background for up to 15 compounds.

The other biomass fuels were more flammable. 15 - 900 g of sample, in a "loose" approximately "natural" configuration, were ignited with a match ~ 0.5 m below the White cell. Spectra were acquired continuously with the appropriate time resolution (3 - 120 s) throughout the period of the fire dominated by smoldering combustion. These spectra were also ratioed to background spectra collected before and after the fire. As with the soils, temperature, pressure, and flow were constant during smoldering combustion.

Single-temperature thermal analysis with enclosure. Fuels can be gently heated and produce emissions due to proximity to a fire or (in the case of soils) to increased insolation after a fire. To investigate these types of emissions, we placed samples of biomass on a hot plate (at ~ 58°C) directly below the White cell which was then enclosed on the sides and top with a sheet metal structure to slow the transport of the thermally generated substances out of the optical path. The spectra thus acquired were ratioed to background spectra acquired just before with clean air in the path.

Multitemperature thermal analysis. Biomass fuel samples were subjected to heating rates of 30° to 50°C per minute so that order of appearance for each observed product could be noted. An upper limit to the (inhomogeneous) biomass sample temperature was continuously measured at the hot plate surface. The fuel was heated just below the objective mirror end of the White cell, while the other end of the White cell was inserted about 30 cm through a window in the combustion laboratory stack. With the stack vertical flow nominally 4 m s⁻¹, the emissions (visible or otherwise) from the heated fuel were drawn horizontally through a long portion of the optical path and then up the stack within a few seconds. This optimized S:N while ensuring sufficient temporal resolution. Each fuel sample was fastened to the hot plate surface with steel wire, FTIR scanning was initiated, the hot plate was then turned to its highest setting to achieve rapid heating, and scanning continued until ignition.

Measurements 18 m above large-scale fires. A series of fires was conducted similar to those described in detail in our pilot study papers [Yokelson *et al.*, 1996a, b]. The major change was to use the new FTIR apparatus described above to acquire the spectra. In this paper, we report only results from time-averaged data acquired near the end of these fires when slow, "steady state" smoldering and little or no change in flow or temperature was observed. During one of these fires, the prefire CO₂ was measured independently by a Licor (model 6262) calibrated with National Institute of Standards and Technology traceable standards to check on the accuracy of our FTIR retrievals. (Results from the large fires have been reported elsewhere [Yokelson *et al.*, 1997].)

Auxiliary Measurements

Smoke/room temperature was measured by chromel-alumel thermocouples verified to be accurate within 0.1°C at the freezing and boiling temperature of water. Pressure (~ 90.2 kPa) was measured by the built-in pressure sensor in the Licor (model 6262). Stack flow was measured by a Kurz (model 455) mass flowmeter. Total fuel bed mass was logged every second using either one or two Mettler PM34 digital scales. Each fuel or fuel component was subsampled for

measurement of the fuel moisture and replicate measurements of the C:H:N content by a Perkin-Elmer Model 2400 CHN analyzer.

Spectrum Analysis

Two different methods were used to retrieve concentrations from spectra: (1) synthetic calibration coupled with classical least squares (CLS) fitting based on the program Multiple Atmospheric Layer Transmission (MALT) [Griffith, 1996] and (2) spectral integration and subtraction using commercially available software (QASOFT, Infrared Analysis, Inc. and GRAMS/386, Galactic, Inc.). In both cases, the instrument resolution is approximately equal to 3 times the width of isolated peaks due to single molecular rovibrational transitions. Under these conditions, a linear relation between concentration and absorbance holds if the analysis is restricted to features exhibiting less than ~ 0.05 peak absorbance₁₀ [Anderson and Griffiths, 1975; Hanst and Hanst, 1994]. This restriction can be relaxed somewhat for broadened composite features such as an entire Q branch.

MALT-CLS-based retrievals. The computer program MALT [Griffith, 1996] computes ideal spectra from HITRAN absorption line parameters [Rothman et al., 1992], convolves these spectra with the instrument function to generate calculated spectra which closely match real experimental spectra, and generates a set of calibration spectra over a range of gas concentrations for quantitative analysis using CLS methods [Haaland, 1990]. MALT-CLS allows accurate analysis of any of the 32 molecules in the HITRAN database, at arbitrary temperature, without the need for acquiring reference spectra. Our usage of this method was described in

detail earlier [Yokelson et al., 1996a, b], and only minor changes were necessary. Because of Beer's law limitations, it was sometimes necessary to analyze spectra in newly identified regions with weaker peaks meeting the criteria noted above. In a very few cases, strong peaks of an absorber were unavoidable, and they were successfully modeled by including a "pseudocomponent" in the CLS basis set for which absorbance was proportional to the square of the concentration of the absorber [Haaland, 1987]. In most cases, the analysis for a compound was possible in at least two independent spectral regions. Table 2 lists all the spectral regions used to derive concentrations reported here. The concentrations in Table 1 are the weighted average of all the regions used.

Spectral-subtraction-based retrievals. For molecules for which spectral line parameters are not available, MALT-CLS cannot be used, and other methods are required. The FTIR software allows development of "custom" spectral integration/subtraction sequences using both the supplied spectral library of room-temperature reference spectra and "user" reference spectra [Hanst et al., 1996]. The molecules analyzed in our sequence are listed in order in Table 2. For each molecule, an isolated feature in the smoke spectrum and integration limits, which include that peak but preclude features due to other compounds, are selected. Comparison of the integration result from the smoke spectrum and appropriate reference spectrum yields the smoke concentration for that molecule. The reference spectrum is then scaled, and its features are subtracted from the smoke spectrum to improve the analysis of the "residual" spectrum for other compounds. In a few cases, significant, unassigned residual

Table 2. Spectral Regions Used to Retrieve Concentrations Reported in This Work

Compound	MALT-CLS	Spectral Integration/Subtraction		
	Spectral Region, cm ⁻¹	Compound	Integration Limits, cm ⁻¹	Peak, cm ⁻¹
CO	2225.5 - 2217.2	H ₂ O	1136.2 - 1135.1	1135.7
CO	2223.4 - 2211.0	NH ₃	970.0 - 960.0	967.2
CO	2056.2 - 2048.4	CH ₃ OH	1034.8 - 1030.0	1033.4
CO ₂	2236.6 - 2223.5	HCO ₂ H	1106.0 - 1104.5	1105
CO ₂	758.2 - 746.2	CH ₃ CO ₂ H	1185.0 - 1182.0	1183.8
HCO ₂ H	1108.9 - 1100.9	C ₂ H ₄	951.0 - 948.5	949.5
HCN	737.0 - 724.7	C ₃ H ₆	912.9 - 911.8	912.4
HCN	734.4 - 722.8	C ₂ H ₄ O ₂	1115.4 - 1113.5	1114.6
HCN	717.1 - 708.8	C ₂ H ₄ O ₂	861.4 - 857.0	860.4
HCN	3352.6 - 3338.7			
HCN	3324.3 - 3316.1			
HCN	3253.2 - 3246.9			
NH ₃	818.4 - 801.3			
NH ₃	837.0 - 829.6			
NH ₃	969.8 - 956.8			
CH ₄	1309.9 - 1291.5			
CH ₄	3020.5 - 3006.5			
H ₂ CO	2771.1 - 2763.2			
H ₂ CO	2783.8 - 2776.3			
H ₂ CO	2888.5 - 2879.3			
H ₂ CO	2901.2 - 2890.0			
C ₂ H ₂	737.0 - 724.7			
C ₂ H ₂	734.4 - 722.8			
OCS	2092.7 - 2028.8			

Unknowns remain at 2848, 853, and 805 cm⁻¹.

absorption remained after the subtractions of the sequence were performed. The peak wavelengths of features which are still unassigned are listed in Table 2.

With the exception of 2-hydroxyethanal, the reference spectra used in our sequence were derived by reducing the resolution of the supplied high-resolution (0.125 cm^{-1}) spectra in the Fourier domain to match the resolution of our experimental data. We obtained a relative 2-hydroxyethanal cross section by warming crystals on a hot plate below the multipass cell and put this relative cross section on an absolute scale by comparison to a resolution independent part of the absolute 2-hydroxyethanal spectrum published by *Niki et al.* [1981].

Accuracy and Detection Limits

The nominal accuracy of both the molecular line parameters in HITRAN and the commercially supplied reference spectra is 5% or better [Rothman *et al.*, 1992; Hanst and Hanst, 1994]. The precision and accuracy of our MALT-CLS data are indicated by plotting against each other the concentrations retrieved for the same molecule in the same spectrum but from different spectral regions. Typical comparisons (see Figure 2) yield a slope and r -squared value of 0.985 and 0.98 for CH_4 and 1.007 and 0.99 for CO_2 . NH_3 and formic acid were analyzed by both methods. We plotted the results from the MALT-CLS approach versus the results from the spectral subtraction protocol and obtained agreement at the 10% level which we deemed sufficient at this time. Finally, we compared the concentration of CO_2 derived from MALT-CLS analysis of a single-beam spectrum of background air to that obtained by simultaneous measurement with a nondispersive infrared CO_2 analyzer (Licor Model 6262). The MALT-CLS retrievals from the two independent spectral regions used had a weighted average of 378 ppm. The Licor simultaneously indicated a concentration of 384 ppm which is about 1.5% higher. On the basis of the above results, the uncertainty in the individual concentration measurements is $\leq 10\%$ (1σ) or the detection limit, whichever is greater. The detection limits are different for each species and for each spectrum but are normally in the low "tens" part per billion (ppb) when $> 70\text{ m}$ path lengths are used.

Results and Discussion

Scope of Results

We have investigated 24 small fires and, in the process, collected over 1000 individual real-time spectra. Since temperature, pressure, and flow were all constant during smoldering in these fires, the mixing ratios from the spectra acquired during the time dominated by smoldering combustion have been averaged together for each of the 24 fires in Table 1. For each fire listed in Table 1, the fuel, fuel sample location, fuel moisture, and fuel C:H:N content are indicated as well as the emissions detected. (The C:H:N analysis is listed for the bulk material, and the soils contained from 2 - 60% inorganic material.) Fifteen molecules were normally present in the smoke at concentrations well above the detection limits including carbon dioxide, carbon monoxide, methane, ethene (C_2H_4), ethyne (C_2H_2), propene (C_3H_6), formaldehyde (H_2CO), 2-hydroxyethanal (CHOCH_2OH), methanol (CH_3OH), phenol ($\text{C}_6\text{H}_5\text{OH}$), acetic

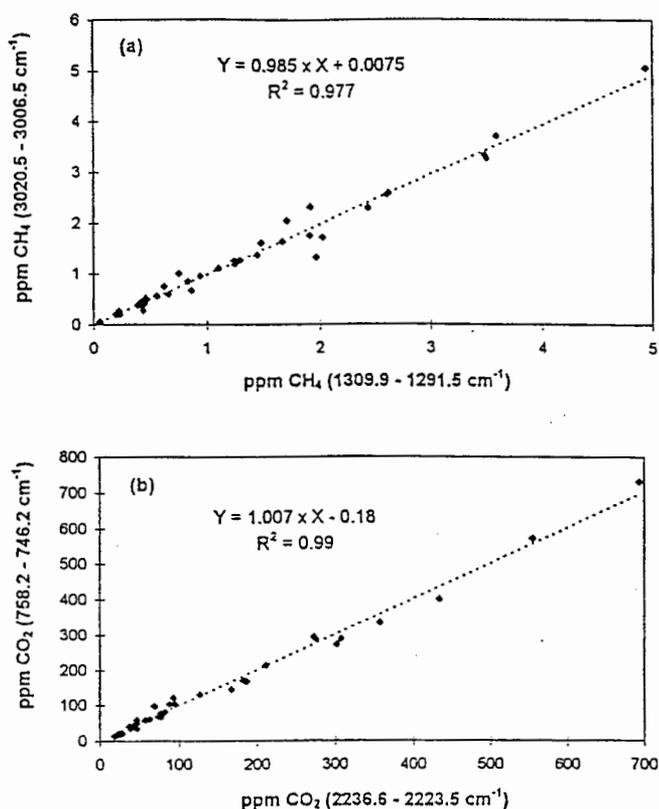


Figure 2. In each plot the concentrations derived from Multiple Atmospheric Layer Transmission-classical least squares analysis of two independent regions of the same spectra are plotted versus each other (see text). (a) Concentrations from ν_3 versus ν_4 for CH_4 . (b) Results from ν_2 versus ν_3 for CO_2 .

acid (CH_3COOH), formic acid (HCOOH), ammonia, hydrogen cyanide (HCN), and carbonyl sulfide (OCS). This list excludes water and four other molecules which were measured in our pilot study [Yokelson *et al.*, 1996a]. Three of these molecules (NO , NO_2 , and SO_2) are readily detectable with our apparatus but are formed primarily by flaming combustion [Yokelson *et al.*, 1996a]. A number of spectra were checked for evidence of these compounds. None showed evidence of NO and only one contained evidence of NO_2 and SO_2 (near the current detection limits of about 20 ppb). Ethane (C_2H_6) was readily detected in the current spectra of emissions from "pure" glowing combustion at an average molar ratio to methane of 7.4% in excellent agreement with average values of this ratio reported by *Lobert et al.* [1991] (7.5%) and *Hao et al.* [1996] (7.4%). However, since C_2H_6 was near, or below, our detection limits in the majority of the spectra, the data are not included in Table 1.

Fire Behavior and Emissions-Producing Combustion Processes

Visual observation of an initial series of fires provided a framework for our subsequent spectroscopic observations. The fuel for these fires was ($\sim 30 \times 30 \times 10\text{ cm}$, average mass $\sim 1\text{ kg}$) pine needles, wooden sticks, or hardwood shavings and was ignited with a match. Black smoke was generated just above the flame tips. White smoke was generated (initially) by

heating of the fresh fuel adjacent to the flame front. Glowing combustion began on the fuel elements before flaming ceased. After flames ceased, glowing combustion continued and generated white smoke by heating that part of the fuel element which was not yet glowing. For thin fuels ($\leq \sim 1$ mm), glowing soon covered the whole fuel element and then continued for some time alone, producing emissions but not visible smoke. Thus, in thin fuels, white smoke appeared as an accompaniment to flaming and as an interlude after flaming. For larger fuel elements (such as plant branches or organic soils), glowing and white smoke production coexisted long after any flaming. Placing fresh biomass on top of glowing combustion or a hot plate caused production of white smoke which could be readily ignited to initiate flaming. Alternatively, continued heating of the fresh biomass also often culminates in ignition of the white smoke.

Spectra of Emissions From Specific Thermal and Combustion Processes

The black smoke, white smoke, and glowing emissions were found to contain very different products. Figure 3 shows the same spectral region (the "fingerprint" region) from two different spectra acquired at different times during the same fire in thin hardwood fuel. The top spectrum is of the fire products when white smoke and glowing combustion coexist just after the cessation of flames. The bottom trace was acquired ~ 50 s later, when only glowing combustion, with no visible smoke production, was observed. As indicated in figure 3, the top ("white smoke plus glowing") trace is dominated by the features of acetic acid, formic acid, methanol, ethene, and 2-hydroxyethanal but also includes smaller features due to NH_3 and CH_4 . In contrast, the "fingerprint" spectrum of the glowing emissions is remarkably simple and consists almost entirely of NH_3 and CH_4 features. Similarly, in the "C-H stretch" region (2700 -

3100 cm^{-1}), H_2CO and heavy NMHC's were observed only in the "white smoke plus glowing" spectrum. In the "smokeless glowing" spectrum, the C-H stretch region only shows strong features due to CH_4 and weak features due to C_2H_6 .

We conducted "temperature ramp" experiments (as described in the experimental section) to isolate the pyrolysis process and determine whether "pure white smoke" contains NH_3 and CH_4 . For both pine needles and hardwood shavings, white smoke generation preceded the onset of glowing as the fuel temperature was increased. In the spectrum of white smoke acquired before glowing combustion was present, the sharp features were due only to H_2O , H_2CO , CH_3OH , CH_3COOH , and HCOOH . Methanol had the lowest "appearance temperature" from pine needles, perhaps because (in addition to being a pyrolysis product) it is a significant biogenic emission [MacDonald and Fall, 1993; König *et al.*, 1995]. Ammonia and methane were observed only in the spectra acquired at higher temperatures when visible glowing combustion had begun. In a related, fixed-temperature experiment, heating green pine needles (at 58°C) produced high levels of β -pinene. In all the "white smoke plus glowing" spectra, or the spectra acquired early during temperature ramps, the shape of the "C-H stretch region" also resembles monoterpene spectra. The thermal order in which these compounds are observed is in good agreement with numerous other works [Lephardt and Fenner, 1980; Evans *et al.*, 1986; DeGroot *et al.*, 1988; Jakab *et al.*, 1993]. In summary, initial heating of fresh fuel produces a flammable mixture of oxygenated compounds and unsaturated hydrocarbons, subsequently, alkanes and NH_3 are produced at higher temperatures, apparently in conjunction with visible glowing combustion.

Summary of Emission Production Chemistry

The black smoke associated with flaming consists primarily of CO_2 and other highly oxidized compounds

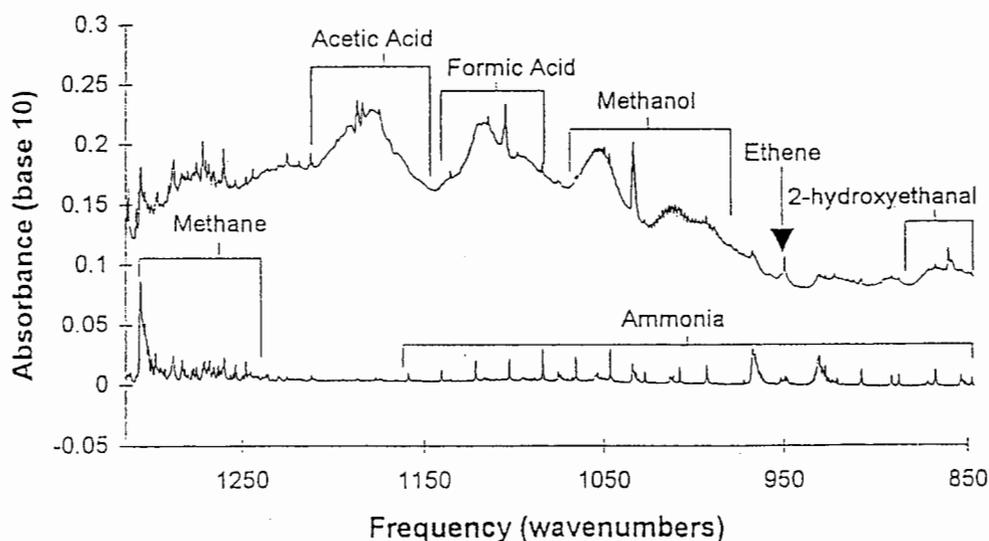
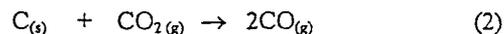
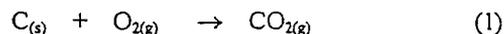
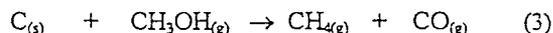


Figure 3. The top trace shows the "fingerprint region" of a smoke spectrum from a fire in thin hardwood fuel elements that is producing white smoke at the same time that glowing combustion is observed. The bottom trace is the same spectral region for the same fire ~ 1 min later when white smoke production has ceased and only glowing combustion is observed. The top (white smoke plus glowing) trace is dominated by strong features due to the indicated oxygenated organic compounds. The lower (glowing only) trace shows features due to CH_4 and NH_3 only. (CO_2 and CO features are present in both traces in a spectral region not shown here.)

[Lobert *et al.*, 1991; Ward and Radke, 1993; Yokelson *et al.*, 1996a] as well as carbonaceous aerosol [Radke *et al.*, 1991]. In contrast, the white smoke produced by heating fresh fuel is rich in pyrolysis or "distillation" products (such as formaldehyde, 2-hydroxyethanal, methanol, phenol, and organic acids) and (probably) "heavy hydrocarbons." Glowing combustion, in the absence of visible flames or smoke, did not produce oxygenated compounds or "heavy hydrocarbons" but did produce a good deal of excess CO₂, CO, CH₄, and NH₃. The CO₂ and CO (the major emissions of "smoldering combustion") probably arise predominantly from gassification of char which includes the following reactions [Hshieh and Richards, 1989; Kannan and Richards, 1990].



CH₄ and NH₃ may arise from simultaneously occurring aromatization of low temperature char [Yokelson *et al.*, 1996a, Figure 7]. Another possible source of CH₄ and CO could be the following reaction which is more thermodynamically favored than the well known "water-gas reaction."



The model fire emissions were due to a combination of at least three very different, temporally overlapped combustion processes. Each process produces its own mix of emissions (including some reactive gases), and the relative weighting of these processes can sometimes change rapidly leading to a rapid change in smoke composition. These observations are consistent with at least one airborne fire observation where the albedo of smoke was determined to be higher for smoldering combustion [Radke *et al.*, 1991]. The dynamics observed in the model fires should be considered in the design of field emissions-measurement programs and microscale plume models. The process-level knowledge developed here may have some predictive power for assessing field fire impacts on the atmosphere. For instance, deforestation fires which feature large fuel elements and a high percentage of fuel consumption by "smoldering" [Susott *et al.*, 1991; Ward *et al.*, 1992] might be predicted to inject especially large quantities of oxygenated organics into the atmosphere. It is also possible that photographs of field fires may assist in qualitatively estimating their emissions.

Production of Oxygenated Compounds

Open-path FTIR measurements of smoke composition from hardwood, grasses, and other fuels. In Yokelson *et al.* [1996a], we thoroughly compared our open-path FTIR measurements of OVOC with other published measurements for which there were sufficient auxiliary data to compute a modified combustion efficiency (MCE). We noted that, compared to other nonspectroscopic studies, our study showed much higher production levels and a strong correlation with MCE which was absent from other work. We speculated that a possible cause of this inconsistency was a difference in the fuels burned. In particular, most of the other studies featured hardwood or grass fuels as opposed to the mainly coniferous fuels used in our pilot study. In part, that hypothesis was supported by the fact that acetic acid and methanol were below our detection limit when sagebrush was burned in the pilot study. However, both these compounds are clearly

produced in the sagebrush fire in this work which featured white smoke production and glowing combustion coexisting on the trunks for a prolonged period after the cessation of flaming. The ratio of methanol or acetic acid to CO produced in our current sagebrush fire would have been observable in the pilot study sagebrush fire had it occurred.

Figure 4 shows the data for acetic acid, methanol, and formaldehyde from mostly coniferous fuels, which were compared with other work by Yokelson *et al.* [1996a], coplotted with data for the same molecules from the grass fires in our current work. The data from the pilot study are fire-integrated and from fires featuring both flaming and smoldering, while the data from the current work represent a series of "snapshots" of smoldering combustion only. The linear response function for OVOC production versus MCE is different for the two fuel/fire types, but a single line can be fit reasonably well to the combined data sets, and that is shown here to indicate the qualitative consistency between our two measurement sets separately obtained from grass and coniferous fuels which is in contrast to the very large differences between studies shown by Yokelson *et al.* [1996a].

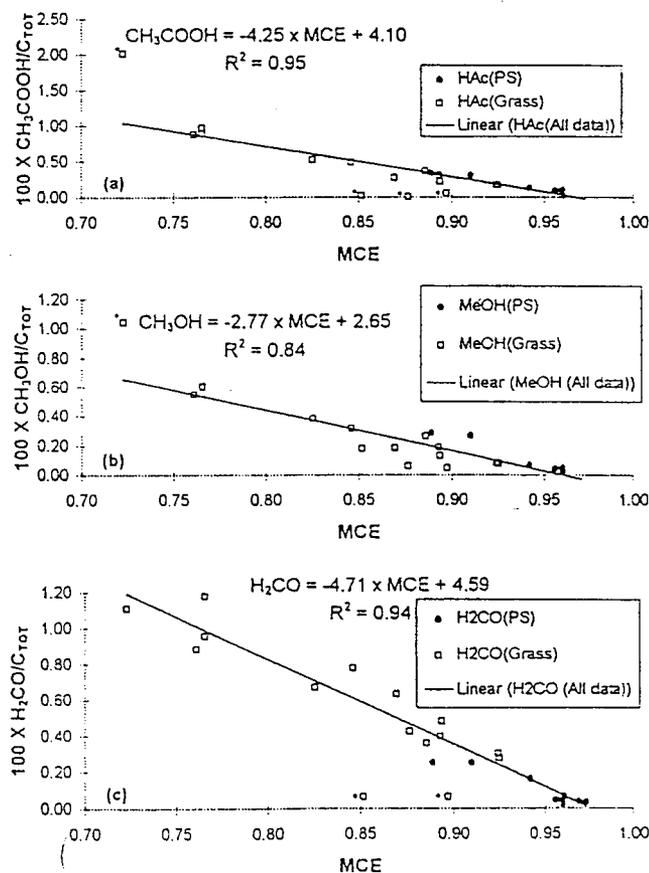


Figure 4. The real-time production for (a) formaldehyde, (b) acetic acid, and (c) methanol, versus modified combustion efficiency from grass fires in this work, is coplotted with the fire-integrated measurements for the same compounds, but in mostly coniferous fuels, reported by Yokelson *et al.* [1996a]. The y axis quantity is the mole percent of compound relative to total carbon emitted and detected. Points treated as outliers and not included in the indicated fit are marked with an asterisk.

The above observations suggest that the large differences between studies discussed by Yokelson *et al.* [1996a] are mainly due to differences in fire behavior or measurement technique [Cofer *et al.*, 1985; McKenzie *et al.*, 1995] rather than a difference in fuels. In particular, there are differences in experimental design between our work and that of McKenzie *et al.* [1995] which may limit the validity of detailed comparison.

Real-time OVOC production was both substantial and well correlated with real-time MCE for the "duff" fuels burned in this work. Real-time data for OVOC production from hardwood fuel was less correlated with real-time MCE, but (Table 1) OVOC accounted for more than 2.5 % of the carbon produced. Only a few correlations stand out in the data from the diverse organic soils burned in this work, but OVOC do account for ~ 0.5 to 2.0 % of the carbon production which is qualitatively similar to the amount observed for methane. Taken together, these observations suggest that OVOC production in most real fires is likely to be significant.

Observation of 2-hydroxyethanal. Prominent narrow absorption features due to 2-hydroxyethanal (hydroxyacetaldehyde and glycolaldehyde) appear in all the spectra of white smoke. Table 1 shows that this compound, previously unreported in smoke, is a significant emission from biomass fires accounting for up to ~ 1% of the carbon detected in the emissions. Figure 5 shows that 2-hydroxyethanal production is about one third of formaldehyde production during smoldering combustion in our bunch grass fires. The 2-hydroxyethanal features also account for the largest (formerly) unassigned peaks in the pilot study spectra, some of which were reanalyzed to yield 2-hydroxyethanal at ~ one fourth the formaldehyde production, in reasonable agreement with the present data set. Observation of this compound is not surprising as 2-hydroxyethanal is usually the dominant product that arises from fast pyrolysis of untreated cellulose [Richards, 1987; Radlien *et al.*, 1991].

Little is known about the atmospheric chemistry of 2-hydroxyethanal. The Henry's law constant [Betterson, 1992] limits its atmospheric lifetime to 3 - 5 days. However, aldehydes are expected to react with HO₂, OH, and tropospheric solar radiation on the timescale of hours [Finlayson-Pitts and Pitts 1986, Figure 3.45 and page 507].

Secondary production of this compound in smoke plumes is also likely to be significant. Niki *et al.* [1981] measured a 20% yield of 2-hydroxyethanal from the reaction of OH and C₂H₄ in the presence of NO_x, and the atmospheric modeling studies of Calvert and Madronich [1987] found α-hydroxy-carbonyls to be a significant product channel in the oxidation of alkenes. Our data indicate that 2-hydroxyethanal and C₂H₄ are initially emitted in comparable amounts, and thus the direct emission of 2-hydroxyethanal may dominate the secondary production in the early plume. In modeling air pollution due to fossil fuel combustion, OVOC are important as secondary photochemical products; however, in the combustion of biomass (~ 45 % oxygen), OVOC are also important as initial products.

Lignin content and OVOC production. Lignin is a polymer composed of phenol-like subunits and has lower oxygen content than cellulose [Evans *et al.*, 1986]. High lignin content would be expected to correlate with lower OVOC production and higher emissions of phenol-like compounds. Lignin content was only measured for the decomposed pine (66.4 %). The only phenol-like compound we detected was phenol itself. A preliminary, qualitative comparison can be made between the undecomposed poplar sample (which is high in cellulose content) and the decomposed pine. Table 1 shows that poplar smoke contains about twice the ratio of (total OVOC)/(total C) as smoke from the decomposed pine. The 2-hydroxyethanal and organic acids are clearly lower from the "rotted" wood, and phenol is clearly lower from the poplar. Methanol and formaldehyde are prominent in both samples. Phenol is also produced in large amounts from decomposed maple leaves and other samples. This could be due to lignin and/or the presence of other phenolic compounds which can occur in significant quantities in leaves, litter, or soils [Jacobs, 1988; Flaig, 1971]. More study is needed to determine if lignin content is a useful predictor of emissions. Phenol was also reported, but as a comparatively minor product, in the study of McKenzie *et al.* [1995].

According to Atkinson [1990], phenol is produced in the atmosphere by oxidation of benzene. Our average phenol/CO is 0.69 % which is about 3 times the benzene/CO ratio of 0.21 % reported by Lobert *et al.* [1991]. Again, this illustrates the

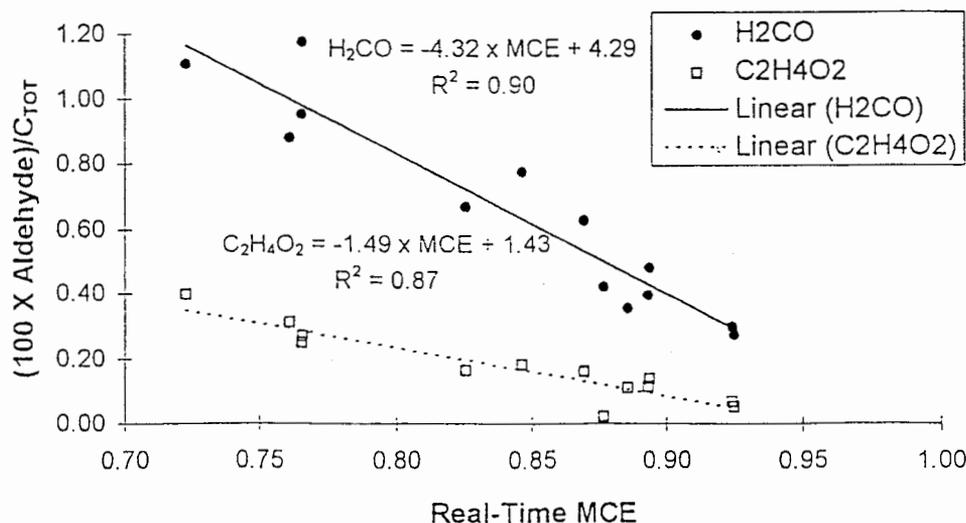


Figure 5. Real-time formaldehyde and 2-hydroxyethanal production from bunch grass fires is plotted versus real-time modified combustion efficiency.

high relative importance of initial emissions of oxygenated compounds from biomass combustion. Phenol would react quickly with NO_3 at night to yield nitric acid while reaction with OH during the day evidently yields pyruvic acid, then acetaldehyde [Atkinson, 1990], and eventually (primarily) methyl radicals through reaction with OH [Finalyson-Pitts and Pitts, 1986]. In a related note, phenolic compounds, attributed to lignin pyrolysis and extracted from particulate, have been investigated extensively as tracers for biomass combustion [Simoneit *et al.*, 1993, and references therein].

Production of Nitrogen and Sulfur Compounds

In the work of Yokelson *et al.* [1996a], we noted that the bulk of available evidence indicated that HCN was relatively unimportant in accounting for fate of fuel nitrogen and that NH_3 was the dominant, detected, nitrogen-containing product of smoldering combustion. Most of our current results with aboveground biomass (Table 1) also support that conclusion. However, with organic soils included, the HCN/ NH_3 ratio varies about 2 orders of magnitude. For the fire in the sample of North Carolina bog soil, HCN production actually dominated ammonia production by a factor of 5. The chemical makeup of organic soils has been reviewed by Flaig [1971]. In most cases, over half of the nitrogen is contained in amino acids [Flaig, 1971; Sowden *et al.*, 1978; Gonzalez-Prieto and Carballas, 1991] which are "artifacts" formed during analysis by acid hydrolysis of plant or microbe proteins. The high-temperature pyrolysis of some amino acids has been shown to yield NH_3 [Djilas *et al.*, 1994], but others may preferentially pyrolyze to yield HCN. Alternately, steam distillation of soil nitrates is a source of NH_3 [Stevenson, 1982], and consistent with this, there was a tendency for the drier soils to produce a higher HCN/ NH_3 ratio. A systematic study of this second effect is both feasible and warranted. In summary, the high N content of the organic soils, combined with the lack of flaming combustion, caused very large emissions of NH_3 (as much as 16% of CO and 3 % of CO_2), considerable HCN emissions, and insignificant NO_x emissions. The spectra of smoke from the soil sample highest in N did not yield evidence of any of the 32 other nitrogen-containing compounds for which we have reference spectra (including HNO_3). These facts should be considered in assessing the impact of fires in the boreal forest. Tropical vegetation has a higher tendency than temperate vegetation to store nutrients in the leaves [Jordan, 1985], and levels of NH_3 , as high as in soil fire emissions, were also produced from the smoldering banana leaves. However, unlike the organic soils, the banana leaves were primarily consumed by flaming combustion.

The N:C ratio (defined as $(\text{NH}_3 + \text{HCN})/C_{10}$) detected in the emissions from smoldering soils was about one half the N:C ratio in the biomass. This reflects our inability to detect N_2 [Kuhlbusch *et al.*, 1991; Yokelson *et al.*, 1996a] and the presence of inorganic nitrogen which would "inflate" the biomass N:C ratio. The N balance is also affected by tar formation. The tar yield was measured twice at slightly over 1% by mass; however, the tar was enriched in N by a factor of 6 to 7 over the parent material. (Gentle heating of the tar produced NH_3 as well as acetic acid and heavy hydrocarbons.)

The only sulfur compound we report is carbonyl sulfide, and biomass sulfur content was not measured. OCS emissions correlated with soil nitrogen contents ($r^2 = 0.87$)

suggesting that sulfur and nitrogen content are correlated in our soil samples. There was evidence of small amounts of SO_2 from the peat sample with the highest nitrogen content, but we did not quantify SO_2 as we have shown earlier that it is primarily produced by flaming combustion [Yokelson *et al.*, 1996a].

Estimates of Initial Emissions for Atmospheric Models

The results presented here and by Yokelson *et al.* [1996a] show clearly that different fire types may emit compounds in quite different relative proportions. In addition, the initial emissions will vary throughout a single fire [Lobert *et al.*, 1991; Yokelson *et al.*, 1996a, Figures 4 - 6], and (except for CO_2 and CH_4) most of the dominant biomass fire emissions are too reactive to be well mixed in the global troposphere [Prather *et al.*, 1994]. Therefore the influence of individual fires could vary strongly depending on the fire type and the state of the atmosphere. We plan detailed, microscale modeling of fire plumes to investigate these and other effects. Regional models (including transport) have demonstrated important links between fire emissions and regional tropospheric chemistry as noted earlier. These studies model the transformation of the emissions resulting from many fires burning simultaneously in a source region, and therefore a reasonable estimate of the initial emissions from an "average" fire in the source region is of use. The initial fire emissions for a number of atmospherically significant compounds have now been measured by OP-FTIR, and these data are presented in Table 3 with each species reported simply as a ratio to CO or CO_2 (for reasons discussed below). (In Table 3 an "average" appropriate for the more commonly modeled tropical scenarios is derived from the current data by weighting the average of the three grass fires equal to the hardwood fire and the average of all the other fires.) The spectroscopic data in Table 3 should be combined with data from other sources such as gas chromatography (GC)/flame ionization detection data for hydrocarbons, GC/electron capture detection data for halogenated organics, the H_2 data of Cofer *et al.* [1988, 1990], and field data for CO and CO_2 from fire types of interest for a more complete characterization of the initial emissions.

We use several different emissions reporting methods in this work for reasons explained next. Plotting emission factors versus MCE can represent well how emissions vary with fuel type or fire combustion characteristics and facilitate the intercomparison of data sets. The plot of emission factors versus MCE for smoldering and pyrolysis compounds is often well fit by a line which has a negative slope and passes nearly through the x intercept of 1. This is approximately algebraically equivalent to the assumption that the compound is emitted in a constant ratio to CO, independent of MCE. Thus we use the compact "ratio" format in Table 3 with reasonable accuracy for estimating the initial emissions of an "average" regional fire. However, it is important that pyrolysis compounds do not track temporally with CO which implies serious limitations in the representativeness of grab sampling [Yokelson *et al.*, 1996a]. Fire-integrated emissions of pyrolysis compounds do scale reasonably well with fire-integrated CO. In the work of Yokelson *et al.* [1996a], the ratios of pyrolysis compounds to CO measured during smoldering were only (on average) 60% of the same ratio determined over the whole fire. With this in mind, the entries in Table 3 from this work for pyrolysis compounds may be a

Table 3. A Summary of in Situ, Spectroscopic, Biomass Fire Emission Measurements Expressed as Percentages of CO₂ and CO

Study	Emissions as Percent of CO ₂			Emissions as Percent of CO												
	NO	SO ₂	NO _x	Hydrocarbons					Aldehydes		Acids		Alcohols		Nitrogen ^a	
	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 <i>et al.</i> [1991]	0.095	nm	0.050			1.27	nm	nm	nm	nm	nm	3.24	0.12	nm		
Yokelson <i>et al.</i> [1996a]	0.178	0.063	0.050			1.60	nm	0.73	2.32	1.61	nm	1.91	0.44	nm		
This work	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		
Average all	8.34	0.94	1.35	0.57	0.65	1.73	1.08	0.91	2.26	1.80	0.84	2.60	0.40	0.04		

Not measured, nm.

^aIf fuel N data are available, Figure 12 and text of Yokelson *et al.* [1996a] can be consulted to partition NH₃ and NO_x.

lower limit. In summary, the data presented in this paper and Yokelson *et al.* [1996a, b; 1997] suggest that it is desirable to include OVOC as important initial constituents in regional atmospheric chemistry models of biomass burning plumes. All spectroscopic work is consistent with the following summary of fire-integrated emissions. CO₂, CO, and CH₄ are the three dominant emissions and a fourth "tier" (just below methane) includes methanol, acetic acid, formaldehyde, ethene, ammonia and nitric oxide.

Preliminary Search for Evidence of Chemical Reactions in the Smoke Plume

A careful search of our spectra reveals no features due to a number of reported smoke compounds such as nitric acid [Lobert *et al.*, 1991] or acetone [Singh *et al.*, 1994] which should have been well above our detection limits if initially produced at the levels reported by other workers. One possible explanation for this is rapid secondary generation of chemicals in the plume. For instance, the reaction of OH with NO₂ or the reaction of NO₃ with C₆H₆O could form HNO₃. It has been suggested that acetone could form from oxidation of fire-volatilized terpenes [Singh *et al.*, 1994; Arnts and Gay, 1979; Gu *et al.*, 1984]. In principle, comparison of our data from several centimeters and 18 m above fires could yield some evidence of the earliest 3 - 5 s of chemical transformations. However, initial inspection of our data shows no gross differences between data collected at the different elevations (i.e., there are no compounds which appear only at one elevation). Laboratory determination of these effects will require additional experiments and a light source capable of driving photochemistry.

Conclusions

The high temporal resolution and broad sensitivity of open-path FTIR has contributed to better understanding of combustion-process effects on biomass fire emissions. For example, we demonstrate that white smoke generated by fuel pyrolysis is the major source of oxygenated organic molecules. The production levels of oxygenated organic compounds observed in our earlier work [Yokelson *et al.*, 1996a] were high compared to other work at the time, but these levels have been verified by the current measurements, directly above a

wide variety of biomass fires. The compound 2-hydroxyethanal was discovered to be a significant fire emission. On the basis of its role as an initial biomass fire emission and probable secondary gas-phase product, we suggest that the atmospheric chemistry of 2-hydroxyethanal warrants further investigation. Suggestions for incorporating oxygenated organic compounds into plume models are given. We have verified the well-recognized dependence of fire emissions on combustion efficiency [Ward and Radke, 1993] and on fuel which should be factored (as possible) into assessments of fire impacts on the atmosphere. For instance, the ratio of NH₃/HCN can range from greater than 10 to as little as one fifth depending on the fuel and combustion conditions.

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References

- Anderson, R. J., and P. R. Griffiths, Error in absorbance measurements in Fourier Transform Spectrometry because of limited instrumental resolution, *Anal. Chem.*, **47**, 2339 - 2347, 1975.
- Arnts, R. R., and B. W. Gay Jr., Photochemistry of some naturally emitted hydrocarbons, Rep. EPA-600/1-79-081, Environ. Prot. Agency, Washington, D. C., 1979.
- Atkinson, R., Gas-phase tropospheric chemistry of organic compounds: A review, *Atmos. Environ. Part A*, **24**, 1 - 41, 1990.
- Barbosa, R. I., and P. M. Fearnside, Pasture burning in Amazonia: Dynamics of residual biomass and the storage and release of aboveground carbon, *J. Geophys. Res.*, **101**, 25847 - 25857, 1996.
- Betterton, E. A., Henry's law constants of soluble and moderately soluble organic gases: Effects on aqueous phase chemistry, in *Gaseous Pollutants: Characterization and Cycling*, edited by J. O. Nriagu, pp. 1 - 50, John Wiley, New York, 1992.
- Brunig, E. F., The tropical rain forest - A wasted asset or an essential biospheric resource?, *Ambio*, **6**, 187 - 191, 1977.
- Calvert, J. G., and S. Madronich, Theoretical study of the initial products of the atmospheric oxidation of hydrocarbons, *J. Geophys. Res.*, **92**, 2211 - 2220, 1987.
- Chatfield, R. B., and A. C. Delaney, Convection links biomass burning to increased tropical ozone: However, models will tend to overpredict O₃, *J. Geophys. Res.*, **95**, 18,473 - 18,488, 1990.

- Chatfield, R. B., J. A. Vastano, H. B. Singh, and G. Sachse, A general model of how fire emissions and chemistry produce African/oceanic plumes (O₃, CO, PAN, smoke) seen in TRACE A, *J. Geophys. Res.*, **101**, 24279 - 24306, 1996.
- Cofer, W. R., III, V. G. Collins, and R. W. Talbot, Improved aqueous scrubber for collection of soluble atmospheric trace gases, *Environ. Sci. Technol.*, **19**, 557-560, 1985.
- Cofer, W. R., III, J. S. Levine, P. I. Riggan, D. I. Sebacher, E. I. Winstead, E. F. Shaw Jr., J. A. Brass, and V. G. Ambrosia, Trace gas emissions from a mid latitude prescribed chaparral fire, *J. Geophys. Res.*, **93**, 1653-1658, 1988.
- Cofer, W. R., III, J. S. Levine, E. I. Winstead, P. J. LeBel, A. M. Koller Jr., and C. R. Hinkle, Trace gas emissions from burning Florida wetlands, *J. Geophys. Res.*, **95**, 1865-1870, 1990.
- Connors, V., P. Novelli, and H. Reichle Jr., Space shuttle views changing CO in the lower atmosphere, *Eos Trans. AGU*, **77**, 466 - 467, 1996.
- Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, **250**, 1669 - 1678, 1990.
- Crutzen, P. J., and G. R. Carmichael, Modeling the influence of fires on atmospheric chemistry, in *Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*, edited by P. J. Crutzen and J. G. Goldammer, pp. 89 - 105, John Wiley, New York, 1993.
- DeGroot, W. F., W. Pan, M. D. Rahman, and G. N. Richards, First chemical events in pyrolysis of wood, *J. Anal. Appl. Pyrolysis*, **13**, 221-231, 1988.
- Dixon, R. K., S. Brown, R. A. Houghton, A. M. Solomon, M. C. Trexler, and J. Wisniewski, Carbon pools and flux of global forest ecosystems, *Science*, **263**, 185 - 189, 1994.
- Djilas, S. M., B. L. Milic, and P. I. Premovic, Pyrolysis-evolved gas-Fourier transform-infrared spectroscopy analysis of aminobutanoic acid isomers, *J. Anal. Appl. Pyrolysis*, **29**, 103 - 110, 1994.
- Evans, R. J., T. A. Milne, and M. N. Soltys, Direct mass-spectrometric studies of the pyrolysis of carbonaceous fuels, III, Primary pyrolysis of lignin, *J. Anal. Appl. Pyrolysis*, **9**, 207-236, 1986.
- Ewel, J., C. Berish, B. Brown, N. Price, and J. Raich, Slash and burn impacts on a Costa Rican wet forest site, *Ecology*, **62**, 816 - 829, 1981.
- Finlayson-Pitts, B. J., and J. N. Pitts Jr., *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, John Wiley, New York, 1986.
- Flaig, W., Organic compounds in soil, *Soil Sci.*, **111**, 19 - 25, 1971.
- Gonzalez-Prieto, S. J., and T. Carballas, Composition of organic N in temperate humid region soils (NW Spain), *Soil Biol. Biochem.*, **23**, 887 - 895, 1991.
- Granier, C., W. M. Hao, G. Brasseur, and J. F. Muller, Land use practices and biomass burning: Impact on the chemical composition of the atmosphere, in *Biomass Burning and Global Change*, edited by J. S. Levine, MIT Press, Cambridge, Mass., 1996.
- Griffith, D. W. T., Synthetic calibration and quantitative analysis of gas-phase FTIR spectra, *Appl. Spectrosc.*, **50**, 59 - 70, 1996.
- Griffith, D. W. T., W. G. Mankin, M. T. Coffey, D. E. Ward, and A. Riebau, FTIR remote sensing of biomass burning emissions of CO₂, CO, CH₄, CH₂O, NO, NO₂, NH₃ and N₂O, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, MIT Press, Cambridge, Mass., 1991.
- Gu, C., C. M. Rynard, D. G. Hendry, and T. Mill, OH radical oxidation of α -pinene, *EPA Grant R8081-10010*, SRI Int., Menlo Park, Calif., 1984.
- Haaland, D. M., Methods to include Beer's Law non-linearities in quantitative spectral analysis, in *Computerized quantitative infrared analysis*, edited by G. L. McClure, *Rep. ASTM-STP-954*, Amer. Soc. for Test. and Mater., Philadelphia, Pa., pp. 78 - 94, 1987.
- Haaland, D. M., Multivariate calibration methods applied to quantitative FT-IR analyses, in *Practical Fourier Transform Infrared Spectroscopy, Industrial and Laboratory Chemical Analysis*, edited by J. R. Ferraro and K. Krishnan, pp. 395 - 468, San Diego: Academic Press, 1990.
- Hanst, P. L., and S. T. Hanst, Gas measurement in the fundamental infrared region, in *Air Monitoring by Spectroscopic Techniques*, edited by M.W. Sigrist, pp. 335 - 470, John Wiley, New York, 1994.
- Hanst, P. L., S. T. Hanst, and G. M. Williams, Mouse-controlled air analysis using Grams-386, in *Optical Remote Sensing for Environmental and Process Monitoring*, pp. 640 - 652, Air Waste and Manage. Assoc., Pittsburgh, PA, 1996.
- Hao, W. M., D. E. Ward, G. Olbu, and S. P. Baker, Emissions of CO₂, CO, and hydrocarbons from fires in diverse African savanna ecosystems, *J. Geophys. Res.*, **101**, 23577 - 23584, 1996.
- Hshieh, F. Y., and G. N. Richards, Factors influencing chemisorption and ignition of wood chars, *Combust. Flame*, **76**, 37 - 47, 1989.
- Hungerford, R. D., W. H. Frandsen, and K. C. Ryan, Ignition and burning characteristics of organic soils, in *Fire in wetlands: A management perspective. Proceedings of the Tall Timbers Fire Ecology Conference, No. 19*, edited by S. I. Cerulean and R. T. Engstrom, pp. 78 - 91, Tall Timbers Res. Stat., Tallahassee, Fla., 1995.
- Jacobs, M., *The Tropical Rain Forest: A First Encounter*, Springer-Verlag, New York, 1988.
- Jakab, E., O. Faix, F. Till, and T. Szekely, The effect of cations on the thermal decomposition of lignins, *J. Anal. Appl. Pyrolysis*, **25**, 185 - 194, 1993.
- Jordan, C. F., *Nutrient Cycling in Tropical Forest Ecosystems*, John Wiley, New York, 1985.
- Kannan, M. P., and G. N. Richards, Gasification of biomass chars in carbon dioxide: Dependence of gasification rate on the indigenous metal content, *Fuel*, **69**, 747 - 753, 1990.
- Kasischke, E. S., N. L. Christensen Jr., and B. J. Stocks, Fire, global warming, and the carbon balance of boreal forests, *Ecol. Appl.*, **5**, 437 - 451, 1995.
- Kauffman, J. B., and C. Uhl, Interactions of anthropogenic activities, fire, and rain forests in the Amazon basin, in *Fire in the Tropical Biota: Ecosystem Processes and Global Challenges*, edited by J. G. Goldammer, pp. 117 - 134, Springer-Verlag, New York, 1990.
- Keane, R. E., C. C. Hardy, K. C. Ryan, and M. A. Finney, Simulating effects of fire on gaseous emissions from future landscapes of Glacier National Park, in press, *World Res. Rev.*, 1997.
- Keller, M., D. J. Jacob, S. C. Wofsy, and R. C. Harriss, Effects of tropical deforestation on global and regional atmospheric chemistry, *Clim. Change*, **19**, 139 - 158, 1991.
- Konig, G., M. Brunda, H. Puxbaum, C. N. Hewitt, S. C. Duckham, and J. Rudolph, Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected Mid-European agricultural and natural plant species, *Atmos. Environ.*, **29**, 861 - 874, 1995.
- Kuhlbusch, T. A., J. M. Lobert, P. J. Crutzen, and P. Warneck, Molecular nitrogen emissions from denitrification during biomass burning, *Nature*, **351**, 135 - 137, 1991.
- Lephardt, J. O., and R. A. Fenner, Characterization of pyrolysis and combustion of complex systems using Fourier transform infrared spectroscopy, *Appl. Spectrosc.*, **34**, 174 - 185, 1980.
- Lobert, J. M., D. H. Scharffe, W. M. Hao, T. A. Kuhlbusch, R. Seuwen, P. Warneck, and P. J. Crutzen, Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 289 - 304, MIT Press, Cambridge, Mass., 1991.
- MacDonald, R. C., and R. Fall, Detection of substantial emissions of methanol from plants to the atmosphere, *Atmos. Environ. Part A*, **27**, 1709 - 1713, 1993.
- McKenzie, L. M., W. M. Hao, G. N. Richards, and D. E. Ward, Measurement and modeling of air toxins from smoldering combustion of biomass, *Environ. Sci. Technol.*, **29**, 2047 - 2054, 1995.
- McMahon, C. K., D. D. Wade, and S. N. Tsoukalas, Combustion characteristics and emissions from burning organic soils, paper presented at 73rd Annual Meeting, Air Pollut. Control Assoc., Montreal, Quebec, Canada, June 22 - 27, 1980.
- Niki, H., P. D. Maker, C. M. Savage, and L. P. Breitenbach, An FTIR study of mechanisms for the HO radical initiated oxidation of C₂H₄ in the presence of NO: Detection of glycolaldehyde, *Chem. Phys. Lett.*, **80**, 499 - 503, 1981.
- Prather, M., and J. A. Logan, Combustion's impact on the global atmosphere, in *Twenty-Fifth Symposium (International) on Combustion*, pp. 1513 - 1527, The Combust. Inst., Pittsburgh, Pa., 1994.
- Prather, M., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou, Other trace gases and atmospheric chemistry, in *Climate*

- Change 1994: Radiative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenarios*, Edited by J. T. Houghton, L. G. Meira Filho, J. Bruce, H. Lee, B. A. Callader, E. Haites, N. Harris, and K. Maskell, Cambridge Univ. Press, New York, pp 73 - 126, 1994.
- Radke, L. F., D. A. Hegg, P. V. Hobbs, J. D. Nance, J. H. Lyons, K. K. Laursen, R. E. Weiss, P. J. Riggan, and D. E. Ward, Particulate and trace gas emissions from large biomass fires in North America, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 209 - 224, MIT Press, Cambridge, Mass., 1991.
- Radlein, D., J. Piskorz, and D. S. Scott, Fast pyrolysis of natural polysaccharides as a potential industrial process, *J. Anal. Appl. Pyrolysis*, 19, 41 - 63, 1991.
- Richards, G. N., Glycolaldehyde from pyrolysis of cellulose, *J. Anal. Appl. Pyrolysis*, 10, 251 - 255, 1987.
- Richardson, J. L., J. Fishman, and G. L. Gregory, Ozone budget over the Amazon: Regional effects from biomass burning emissions, *J. Geophys. Res.*, 96, 13073 - 13087, 1991.
- Rothman, L. S., et al., The HITRAN molecular database: Editions of 1991 and 1992, *J. Quant. Spectrosc. Radiat. Transfer*, 48, 469 - 507, 1992.
- Scholes, R. J., J. Kendall, and C. O. Justice, The quantity of biomass burned in southern Africa, *J. Geophys. Res.*, 101, 23667 - 23676, 1996.
- Shafizadeh, F., and W. F. DeGroot, Combustion characteristics of cellulosic fuels, in *Thermal Uses and Properties of Carbohydrates and Lignins*, edited by F. Shafizadeh, K. V. Sarkanen, and D. A. Tillman, pp. 1 - 18, Academic, San Diego, Calif., 1976.
- Simoneit, B. R. T., W. F. Rogge, M. A. Mazurek, L. J. Standley, L. M. Hildemann, and G. R. Cass, Lignin pyrolysis products, lignans, and resin acids as specific tracers of plant classes in emissions from biomass combustion, *Environ. Sci. Technol.*, 27, 2533 - 2541, 1993.
- Singh, H. B., M. Kanakidou, P. J. Crutzen, and D. J. Jacob, High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, *Nature*, 378, 50 - 54, 1995.
- Singh, H. B., D. O'Hara, D. Herlth, W. Sachse, D. R. Blake, J. D. Bradshaw, M. Kanakidou, and P. J. Crutzen, Acetone in the atmosphere: Distribution sources and sinks, *J. Geophys. Res.*, 99, 1805 - 1819, 1994.
- Sowden, F. J., H. Morita, and M. Levesque, Organic nitrogen in selected peats and peat fractions, *Can. J. Soil Sci.*, 58, 237 - 249, 1978.
- Stevenson, F. J., Nitrogen-organic forms, in *Methods of Soil Analysis*, edited by A. L. Page, Soil Sci. Soc. of Am., Madison, Wisc., 1982.
- Susott, R. A., W. F. DeGroot, and F. Shafizadeh, Heat content of natural fuels, *J. Fire Flammability*, 6, 311 - 325, 1975.
- Susott, R. A., D. E. Ward, R. E. Babbitt, and D. J. Latham, The measurement of trace gas emissions and combustion characteristics for a mass fire, in *Global Biomass Burning: Atmospheric, Climatic, and Biospheric Implications*, edited by J. S. Levine, pp. 245 - 257, MIT Press, Cambridge, Mass., 1991.
- Terron, M. C., M. L. Fidalgo, G. C. Galletti, and A. E. Gonzalez, Pyrolysis-gas chromatography/mass spectrometry of milled wood lignin of two Chilean woods naturally decayed by *Ganoderma australe*, *Phlebia chrysocrea*, and a brown-rot fungus, *J. Anal. Appl. Pyrolysis*, 33, 61 - 75, 1995.
- Thompson, A. M., K. E. Pickering, D. P. McNamara, M. R. Schoeberl, R. D. Hudson, J. H. Kim, E. V. Browell, V. W. J. H. Kirchhoff, and D. Ngagna, Where did tropospheric ozone over southern Africa and the tropical Atlantic come from in October 1992? Insights from TOMS, GTE, TRACE A, and SAFARI 1992, *J. Geophys. Res.*, 101, 24251 - 24278, 1996.
- Uhl, C., and C. F. Jordan, Succession and nutrient dynamics following forest cutting and burning in Amazonia, *Ecology*, 65, 1476 - 1490, 1984.
- Ward, D. E., and L. F. Radke, Emissions measurements from vegetation fires: A comparative evaluation of methods and results, in *Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires*, edited by P. J. Crutzen and J. G. Goldammer, pp. 53 - 76, John Wiley, New York, 1993.
- Ward, D. E., R. A. Susott, J. B. Kauffman, R. E. Babbitt, D. L. Cummings, B. Dias, B. N. Holben, Y. J. Kaufman, R. A. Rasmussen, and A. W. Setzer, Smoke and fire characteristics for cerrado and deforestation burns in Brazil: BASE-B experiment, *J. Geophys. Res.*, 97, 14,601-14,619, 1992.
- Woodwell, G. H., R. H. Whittaker, W. A. Reiners, G. E. Likens, C. C. Deiwiche, and D. B. Botkin, The biota and the world carbon budget, *Science*, 199, 141 - 146, 1978.
- Yokelson, R. J., D. W. T. Griffith, and D. E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, *J. Geophys. Res.*, 101, 21067 - 21080, 1996a.
- Yokelson, R. J., D. W. T. Griffith, J. B. Burkholder, and D. E. Ward, Accuracy and advantages of synthetic calibration of smoke spectra, in *Optical Remote Sensing for Environmental and Process Monitoring*, pp. 365 - 376, Air Waste and Manage. Assoc., Pittsburgh, Pa., 1996b.
- Yokelson, R. J., D. W. T. Griffith, R. A. Susott, and D. E. Ward, Spectroscopic studies of biomass fire emissions, in *13th Conference on Fire and Meteorology: International Perspectives on Landscape Fires*, edited by J. Greenlee, in press, Int. Assoc. of Wildland Fire, Fairfield, Wash., 1997.
- Zinke, P. J., A. G. Stangenberger, W. M. Post, W. R. Emanuel, and J. S. Olson, Worldwide organic soil carbon and nitrogen data, *Rep. ORNL/TM-8857*, Oak Ridge Natl. Lab., Oak Ridge, Tenn., 1984.

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