

In-situ measurement of pyrolysis and combustion gases from biomass burning using swept wavelength external cavity quantum cascade lasers

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Abstract: Broadband high-speed absorption spectroscopy using swept-wavelength external cavity quantum cascade lasers (ECQCLs) is applied to measure multiple pyrolysis and combustion gases in biomass burning experiments. Two broadly-tunable swept-ECQCL systems were used, with the first tuned over a range of 2089–2262 cm^{−1} (4.42–4.79 μm) to measure spectra of CO₂, H₂O, and CO. The second was tuned over a range of 920–1150 cm^{−1} (8.70–10.9 μm) to measure spectra of ammonia (NH₃), ethene (C₂H₄), and methanol (MeOH). Absorption spectra were measured continuously at a 100 Hz rate throughout the burn process, including inhomogeneous flame regions, and analyzed to determine time-resolved gas concentrations and temperature. The results provide *in-situ*, dynamic information regarding gas-phase species as they are generated, close to the biomass fuel source.

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1. Introduction

Biomass burning related to agriculture, wildfires, domestic heating, and other purposes is a significant source of pollutants, greenhouse gases, and aerosols [1,2]. Detailed knowledge of the gas composition released from biomass burning, and its dependence on fuel source and burning conditions, is needed to improve models for plume chemistry and atmospheric transport [1,2]. Experiments to study biomass burning have included small-scale laboratory experiments [3,4], larger-scale laboratory burns [5], and prescribed outdoor burns [6–10]. These experiments have detected and identified dozens of trace gases emitted from biomass burning [1,2,9–12].

Biomass burning involves multiple chemical processes occurring over a wide temperature range. Pyrolysis (thermal decomposition) of solid biomass fuel particles produces a large variety of combustible gases, tar and char [13]. Smoldering combustion via surface oxidation or “glowing” (~800–1000 K) produces CO, CH₄, non-methane organic compounds (NMOC), and organic aerosols [2,14]. Flaming combustion (~1400 K) involves rapid oxidation of gases to produce CO₂, H₂O, NO_x, SO₂, and carbon soot. In actual burning environments, these processes evolve continuously in both time and space, and often occur simultaneously [5]. In addition, many gas species produced during the burning are reactive or transient, being consumed at later times in the burn evolution or during plume propagation. There is an important need to characterize biomass burning products close to the fuel source and with high temporal resolution because gas concentrations vary strongly with time and distance [2]. However, such measurements are challenging due to the high temperatures, turbulent environment, and rapid flame dynamics.

Extractive methods are often used to sample gases downwind of a fire or close to the fuel source, typically followed by laboratory or on-site analysis with analytical instruments [9]. Extractive methods used for biomass burning analysis include proton transfer reaction mass spectrometry

(PTR-MS) [12], gas chromatography mass-spectrometry (GC-MS) [11], and gas-phase Fourier-transform infrared spectroscopy (FTIR) [7–10]. Extractive techniques can be extremely sensitive, but even when sampling gases close to the fuel there is a possibility that species may react or adsorb to surfaces before reaching the measurement region, thereby changing the composition or concentrations of gases in the sample. In addition, extractive techniques are fundamentally limited in measurement speed and cannot capture rapid dynamic processes occurring during the burn.

Open-path FTIR (OP-FTIR) has been used extensively to identify and quantify a wide range of trace gases emitted from biomass burning [5,7,8,15]. Use of open-air multi-pass cells to provide measurement path lengths of tens of meters enables detection of gases at ppb-level concentrations at ~ 1 Hz rates. Gas-phase molecular species are identified based on their characteristic absorption spectra arising from ro-vibrational transitions in the infrared spectral regions. Measurement rates of OP-FTIR are usually limited by trade-offs in spectral resolution. For biomass burning studies, high spectral resolution ($\lesssim 0.5 \text{ cm}^{-1}$) is critical for distinguishing broad spectral features of larger NMOCs at low concentrations from the resolved line absorption of more prominent small-molecule species such as CO, CO₂, H₂O, etc. [9] but use of these spectral resolutions limits FTIR measurement speeds to ~ 1 Hz. OP-FTIR experiments typically measure gases at distances > 1 m away from the fuel source, after the emitted gases are entrained in the ambient air, with corresponding dilution and cooling. Transmission/absorption of flame regions using FTIR is usually not possible due to high optical density of the sample region, strong emission of infrared radiation from the flame, and low spectral radiance of the incoherent sources used for transmission. FTIR emission spectroscopy has been used to measure CO, H₂O, and temperature in biomass burning flames [16], yet it is difficult to obtain quantitative results and measure trace species with this method.

Laser absorption spectroscopy is a proven technique for dynamic measurements in extreme environments such as flames. The high spectral radiance of laser sources enables transmission through optically dense regions and the laser signal of interest can be separated from incoherent emission using spectroscopic or modulation techniques. Tunable diode laser absorption spectroscopy (TDLAS) at visible or near-infrared wavelengths has seen widespread use for measurement of combustion products (H₂O, CO, CO₂, etc.) and temperatures in flames [17,18], but is limited to detection of small molecules with resolved ro-vibrational lines due to limitations in laser tuning range. In biomass burning applications, TDLAS has been used to measure molecular species from combustion of wood fuel pellets [4,19] and biomass gasification [20].

Quantum cascade lasers (QCLs) have dramatically increased the potential for infrared laser absorption spectroscopy of molecular compounds, allowing access to strong fundamental ro-vibrational molecular transitions [21,22]. While QCL-based spectroscopy is becoming established for combustion research applications [23–26], it has seen less use in biomass burning applications. Narrowly-tunable distributed feedback (DFB) QCLs were used for measurement of NH₃ and C₂H₄ in biomass steam gasification [27] and were evaluated for suitability in photo-acoustic detection of species in biomass burning [28].

Broadly-tunable external cavity quantum cascade lasers (ECQCLs) [29] provide tuning ranges $> 10\%$ of the center wavelength, which is sufficient to measure multiple gas-phase molecular species including larger NMOCs with unresolved ro-vibrational lines. Development of swept-ECQCL spectroscopy techniques [30,31] has enabled acquisition of infrared absorption spectra over broad spectral ranges ($> 100 \text{ cm}^{-1}$) with high spectral resolution ($< 0.3 \text{ cm}^{-1}$) and at fast spectral acquisition rates (> 100 Hz). Swept-ECQCL spectroscopy has been used to quantify chemical mixtures [32,33] and measure rapid dynamics of chemical plumes in open-path and standoff configurations [34–36]. Recent work using swept-ECQCL spectroscopy measured time-resolved infrared absorption spectra through explosive fireballs to quantify multiple combustion gases and temperature [37].

In this paper, we apply broadband swept-ECQCL absorption spectroscopy to measure dynamics of combustion and pyrolysis gases emitted from biomass burning. Laboratory-scale wind tunnel experiments were conducted in which a bed of plant material was ignited at one end, and beams from swept-ECQCL systems were propagated perpendicular to the flame front direction, directly above the plant bed. Infrared transmission/absorption spectra were measured continuously at 100 Hz as the flame front propagated along the bed, providing dynamic measurement of gases and temperature adjacent to the fuel source. Two swept-ECQCL systems were used, with one measuring combustion gases CO_2 , H_2O , and CO , and the other measuring trace species ammonia (NH_3), ethene (C_2H_4), and methanol (MeOH). Fitting of measured absorption spectra was used to determine time-resolved concentrations of species and temperature. Temperatures >1000 K were measured as the flame front propagated through the ECQCL beam paths and compared with time-resolved infrared emission intensity. Effects of spatial inhomogeneity along the measurement path are observed and found to be important for interpretation of the results. The time-resolved dynamics of multiple species and temperature shows correlation of gases with flaming combustion versus smoldering/pyrolysis processes. The results provide *in-situ*, dynamic information regarding biomass combustion and pyrolysis products as they are generated, in regions close to the fuel source.

2. Experimental

Figure 1 shows schematic diagrams and photographs of the experimental setup and measurement configuration with the swept-ECQCL systems. The wind tunnel contained the biomass material under study and a fan with flow conditioner at one end provided constant wind velocity along the fuel bed and between the walls of the wind tunnel [38]. The 2 m long x 1 m wide fuel bed consisted of 1 kg dead needles from longleaf pine (*Pinus palustris* Mill.) interspersed with a grid of living plants (*Ilex glabra* (L.)). The *Ilex* plants were grouped into 37 ramekins with 2 plants/ramekin, giving a total of 74 plants. Individual plant heights ranged from 12 to 28 cm and crown areas ranged from 108 to 2477 cm^2 . Pine needle moisture content (dry weight basis) was 8% and plant foliar moisture content was 92%. This range of pine needle moisture content is close to the preferred range used by practitioners in the southern United States [39]. The fire was initiated by applying denatured alcohol (95% ethanol, 5% methanol + isopropanol) to the pine needles at the end of the wind tunnel nearest the fan bank and igniting with a flame. The uniformly distributed pine needles were burned as spreading line fires with wind velocity of ~ 1 m/s in a cool/moist atmosphere. The flame front linear spread rate was 0.014 m/s and flame lengths ranged from 0.3 to 0.6 m which are typical for backing fires in southern pine fuel beds [39]. The flame front propagated the length of the wind tunnel in ~ 2.5 minutes. Air temperature in the wind tunnel was 12.8 $^\circ\text{C}$ and relative humidity was 33%.

Two swept-ECQCL systems were used for the measurements. Both were custom-built systems similar to ones described previously [30–37]. We denote the systems by the wavelength band of operation. The first system operated in the mid-wave infrared (MWIR) and was swept over a tuning range of 2089–2262 cm^{-1} (4.42–4.79 μm) using a sinusoidal modulation with 100 Hz frequency. The second system operated in the long-wave infrared (LWIR) and was swept over a tuning range of 920–1150 cm^{-1} (8.70–10.9 μm) using a sinusoidal modulation with 250 Hz frequency.

The beam from each ECQCL was directed through access holes cut into the wind tunnel sides, propagated across the wind tunnel to a mirror, and reflected along a path at a slight angle in the horizontal plane. After propagation back through the wind tunnel, a fraction of each return beam was reflected from a BaF_2 wedged window and focused onto an infrared photodetector (DET) using a ZnSe lens with 25 mm focal length. The beams were located at a height 36 cm above the base of the plant bed. The MWIR beam was located closer to the start of the plant bed and experienced the flame front first. The LWIR beam was located 30 cm away from the

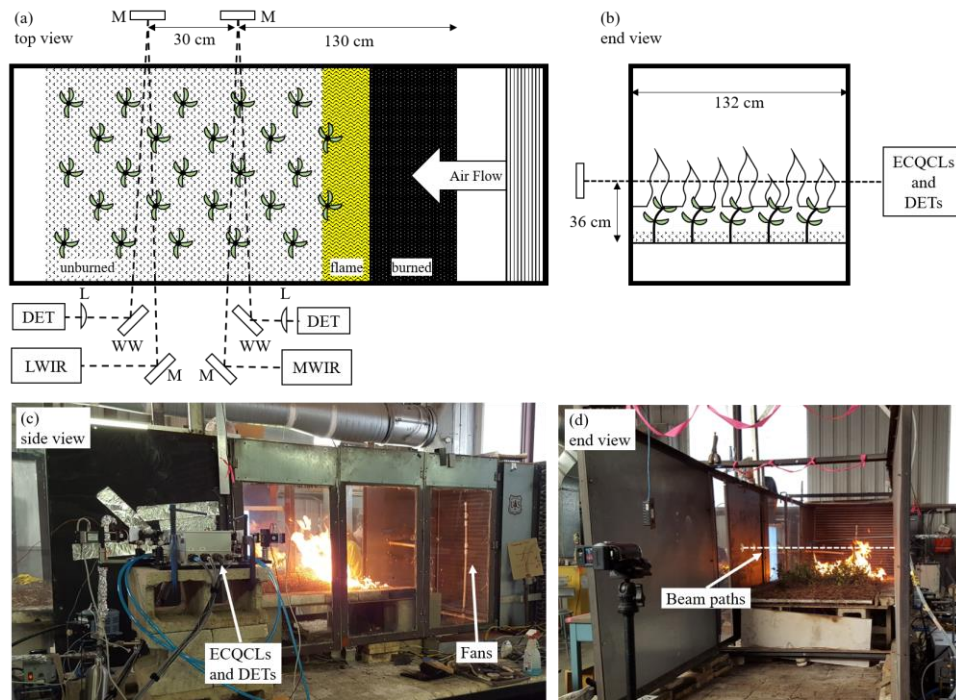


Fig. 1. Experimental setup and photographs of wind tunnel for biomass burning experiments. (a) Schematic top view, (b) schematic end view, (c) photograph side view, and (d) photograph end view. Ilex plants interspersed with dry pine needles (not drawn to scale) were ignited at one end of the wind tunnel and the flame front propagated the length of the wind tunnel. Beams from the two ECQCL systems were directed across the wind tunnel at a height 36 cm above the plant base to mirrors (M). The mirrors directed the ECQCL beams back to BaF₂ wedged windows (WW) which reflected a portion of the beam to a lens (L) and infrared detector (DET). The ECQCL beam paths were separated horizontally by 30 cm and the flame front reached the MWIR beam path before reaching the LWIR beam.

MWIR beam and experienced the flame front second. The total path length accounting for the double-pass configuration inside the wind tunnel for each ECQCL system was 2.64 m, with a 2 m path length directly above the plant bed. The regions of the beam outside the wind tunnel were not included in the measurement path length, as it was assumed the conditions in these regions did not change during the burn.

Both ECQCL systems were operated using a full-depth 500 kHz square wave current modulation to produce a corresponding amplitude modulation (AM) of the output intensity. Use of modulated current in these ECQCLs provides two benefits. It has been previously shown that the modulated current reduces spectral scan noise due to mode-hops [31]. Second, the AM signal on the detector allows separation of the ECQCL light from any background infrared light on the detector using lock-in detection. For operation in ambient conditions, the demodulation eliminates drifts in the detector signal due to undesired background fluctuations. In the measurements performed here, the detector offset was used to measure the emission from the high-temperature flame regions. Similar techniques for simultaneous measurement of laser transmission and optical emission have been used with diode lasers for measuring soot in flames [40] and more recently with a swept-ECQCL for characterization of explosive fireballs [37].

The signals from the photo-detectors were digitized at a 2 MHz rate. The amplitude of the modulated signals over each 500 kHz cycle provided a signal proportional to the detected ECQCL intensity. The DC offset of the modulated signal provided a signal proportional to the broadband infrared emission within the detector field-of-view. Thus, the measurements provided both the ECQCL transmission and the spectrally-integrated infrared emission at a sampling rate of 500 kHz. The detector used with the MWIR ECQCL (VIGO PVI-4TE-6) has a spectral responsivity from 3-7 μm but atmospheric attenuation limits the range to 3-5 μm . The detector used with the LWIR ECQCL (VIGO PVI-4TE-10.6) has a spectral responsivity from 3-12 μm which spans both the MWIR and LWIR spectral regions.

Each ECQCL system was swept repeatedly over its tuning range using a sinusoidal modulation and measurements were performed continuously throughout the entire burn process. After detection and demodulation, the ECQCL wavelength scans were subdivided into blocks separated by half the scan period (the same wavelength region is covered twice during each sinusoidal scan period), yielding scans at 200 Hz (MWIR ECQCL) and 500 Hz (LWIR ECQCL). Relative wavelength calibration was performed using data acquired before the burn by measuring transmission through a solid silicon etalon with 0.416 mm length, inserted temporarily into each beam path. The absolute wavelength calibration was determined by comparing a measured gas spectrum to a known reference absorption spectrum. For the MWIR ECQCL, a measured spectrum of CO + CO₂ acquired during the burn was used, and for the LWIR ECQCL a measured spectrum of Freon-152a (1,1-difluoroethane) from an air duster sprayed into the beam path was used.

After wavelength calibration, the ECQCL scans were further averaged to a common measurement rate of 100 Hz, corresponding to a 10 ms interval between scans. This averaging time was selected based on a balance between tracking the fluctuations in spectra during the turbulent flame region and reducing the number of spectra for fitting. The ECQCL intensity for each scan was converted to absorbance units by normalizing to a background portion of the data recorded before ignition of the fire: $A_i(\tilde{\nu}) = -\ln[I_i(\tilde{\nu})/I_0(\tilde{\nu})]$. Here, $A_i(\tilde{\nu})$ is the base-e absorbance of the i -th scan, $I_i(\tilde{\nu})$ is the measured ECQCL intensity for the i -th scan, and $I_0(\tilde{\nu})$ is the intensity of the background scan. The background $I_0(\tilde{\nu})$ was taken as the average of 100 scans (1s total duration) from the beginning of the measurement run and is shown in Fig. 2(a) for the MWIR ECQCL and in Fig. 2(b) for the LWIR ECQCL. The absorbance spectra calculated in this manner show the changes in absorbance relative to the ambient conditions during the background. Thus, the species concentrations determined from the absorbance spectra reflect the difference relative to the starting ambient conditions, directly providing the excess mixing ratio (EMR) for each analyzed species [2].

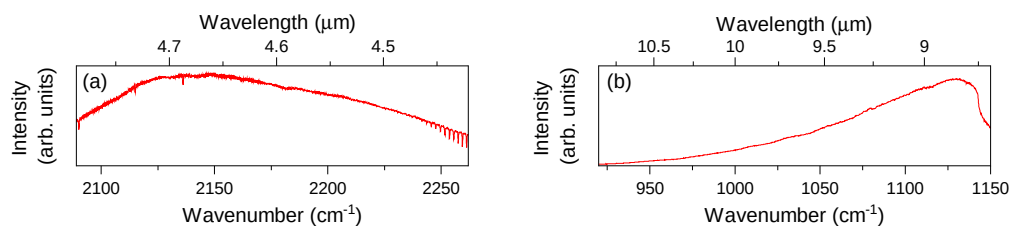


Fig. 2. Intensity versus wavelength/wavenumber for (a) MWIR ECQCL and (b) LWIR ECQCL, recorded before ignition of flame.

3. Spectral analysis

After averaging of scans, the data sets consisted of 36,000 absorbance spectra for the MWIR ECQCL and 38,000 absorbance spectra for the LWIR ECQCL, corresponding to a measurement

time of ~6 minutes with a time interval of 10 ms between spectra. Large temporal variations in temperature were present during the measurement period, especially as the flame front propagated through the measurement paths, and the effects of temperature on the absorbance spectra must be accounted for in the spectral fitting to obtain meaningful results. More critically, the measured absorbance spectra are path-integrated and may contain contributions from spatial regions with highly variable temperature and species concentrations along the measurement path, especially when localized flame fronts intersect the beam path. Inverse modeling of measured spectra to determine spatial variations of parameters along the measurement path presents a considerable challenge and often requires additional measurement data (e.g. high-speed imaging or point measurements) along with radiative transport considerations [23], and is beyond the scope of the efforts presented here. Instead, the spectral fitting model used here assumes uniform conditions along the measurement path. Despite the limitations inherent to fitting path-integrated spectra in this manner, the spectra may still be analyzed to identify species, estimate chemical concentrations, estimate temperatures, and especially to study the temporal dynamics of these parameters. For the results presented in this manuscript, it is to be understood that the reported concentrations and temperatures do not imply uniform conditions along the measurement path. Furthermore, results from analysis of the path-integrated spectra will have a high uncertainty in absolute concentrations and temperatures for times at which large spatial gradients exist.

The absorbance spectra from each ECQCL system were analyzed in two stages. The first stage used a weighted nonlinear least squares (WNLS) fit on a spectral subset to estimate the temperature based on strong variations with temperature for the relative absorption line areas of combustion gases (CO_2 , CO , H_2O). In contrast to traditional TDLAS analysis where it is common to use ratios between two lines to determine temperature [25], the ECQCL spectra were analyzed using broadband fits to multiple lines (10-100's). In this case, variations in peak areas and band profiles provide an estimate of temperature averaged over many transitions [37]. The second stage used a linear weighted least squares (WLS) fit to determine the concentrations of various species, using the estimated temperature as a parameter. Breaking the analysis into two stages was found to give better spectral fits (lower residuals) than attempting a single WNLS fit to the entire spectrum and significantly decreased the computation time for analysis. In addition, the WLS fits provided better convergence in regions with low concentrations where the WNLS fit parameters were indeterminate. In both cases, the fits were weighted by $I_0(\tilde{\nu})^2$ to account for variations in detected intensity [41] and points with absorbance >5 were excluded from the fits.

For the MWIR region, the temperature was estimated by performing a WNLS fit on the absorbance spectra from $2150\text{--}2262\text{ cm}^{-1}$, which contains CO and CO_2 lines/bands sensitive to temperature. A detailed description of the WNLS procedure in the MWIR was provided in [37]. A 2nd order polynomial fit to the baseline was subtracted before fitting. Line parameters for CO and CO_2 were obtained from HITEMP [42] and standard isotopic abundances listed in HITRAN [43] were used. To reduce computation time, lines with peak areas $<0.001 \times$ the maximum peak area in the spectral region of interest were excluded from the simulation, with the peak areas calculated at 1000 K. Absorbance peaks were modeled using Lorentzian lineshapes to approximate the instrumental linewidth of the ECQCL measurement. All peaks of each species were modeled using the same linewidth and all species were assumed to be present at the same temperature. For spectra with low CO/CO_2 concentrations the temperature could not be determined with confidence. Therefore, a threshold was set whereby only temperatures determined from spectra with CO_2 column density $> 2 \sigma_{\text{CO}_2}$ were retained, where σ_{CO_2} is the standard deviation of CO_2 concentrations before ignition of the flame (reflecting the measurement noise). The temperature was set to a default value of 298 K for spectra failing to meet this condition. After thresholding, the temperatures were smoothed using an adjacent averaging filter with 1 s width to use in the subsequent WLS fitting routine.

The WNLS fitting to estimate temperature for the LWIR data was similar to the MWIR data, but used the spectral region $1090\text{--}1150\text{ cm}^{-1}$, which contains multiple H_2O lines sensitive to temperature. A 7th order polynomial fit to the baseline was subtracted before fitting. The H_2O spectrum was modeled using line parameters from HITRAN [43] with standard isotopic abundances and all lines were kept (no significant difference was found versus using HITEMP parameters). The threshold for determining temperature was computed similarly to the MWIR data but using the H_2O concentration. The low absorption cross-section of the H_2O lines in the LWIR spectral region resulted in more spectra falling below the threshold, and the uncertainty in temperature is thus higher for the LWIR data than for the MWIR data. Figure 3 shows three examples of WNLS fits to H_2O in the LWIR spectra, from which the strong temperature dependence of the H_2O lines is apparent.

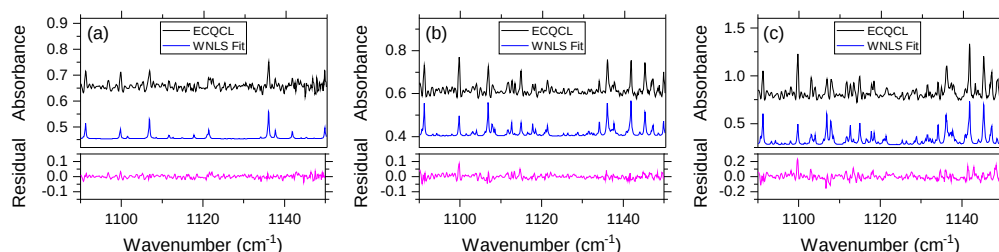


Fig. 3. Examples of WNLS fits to estimate temperature from the LWIR spectra, with (a) $\tilde{T}_{fit}=530\text{ K}$, (b) $\tilde{T}_{fit}=860\text{ K}$, and (c) $\tilde{T}_{fit}=1010\text{ K}$. The top panel shows the experimental absorbance (black) and the WNLS fit (blue). The bottom panel shows the fit residuals.

After the temperatures were estimated from the WNLS fits, a subsequent WLS fitting was performed on the absorbance spectra over the full spectral range. For the MWIR spectra, the fitting library consisted of CO , CO_2 , and H_2O . For each experimental absorbance spectrum, a library absorption spectrum for each species was modeled using HITEMP parameters at the temperature determined previously from the WNLS fit. For the WLS fits, the modeled spectra used Lorentzian peak shapes with 0.2 cm^{-1} full width at half-maximum (FWHM), determined from the average best-fit widths found during the WNLS fit routine; this represents the effective instrumental linewidth of the absorbance spectra measured with the MWIR ECQCL.

For the LWIR spectra, the fitting library consisted of CO_2 , H_2O , NH_3 , C_2H_4 , MeOH , and EtOH . Library absorption spectra for CO_2 , H_2O , and NH_3 were modeled using HITRAN parameters at the temperature estimated previously from the WNLS fit. The modeled spectra used Lorentzian peak shapes with 0.25 cm^{-1} FWHM, the effective instrumental linewidth of the absorbance spectra measured with the LWIR ECQCL. Absorbance spectra for C_2H_4 , MeOH , and EtOH were taken from the Northwest Infrared (NWIR) spectral library [44]. For consistency throughout the full burn, NWIR library spectra at a temperature of 298 K were used and increased uncertainty in the absolute concentrations is thus expected for fitting spectra at higher temperatures. However, by examining the fit residuals it was found that the NWIR library spectra provided good fits to most measured experimental spectra, even for temperatures above 298 K . Attempts to model C_2H_4 and MeOH spectra using HITRAN parameters resulted in higher fit residuals with significantly longer computation times due to the high number of spectral lines; therefore, the NWIR library spectra were used instead.

For the WLS analysis of the MWIR (LWIR) spectra, the spectral baseline was fit as follows. Principal component analysis (PCA) was performed on a set of 60(80) absorbance spectra acquired before the fire was ignited, and the first 4(8) principal component vectors were included in the fitting library to account for systematic drifts in the absorbance baseline due to variations in the MWIR (LWIR) ECQCL scans, respectively [31]. In addition, a 7th order polynomial was

used to account for random fluctuations in absorbance occurring over time scales shorter than the scan time, which were most prevalent during high turbulence when measuring through the flame region.

The output from the WLS fitting routine is a set of column densities versus time for each analyzed species. To facilitate comparison with other biomass burning studies, we report the results as concentration mixing ratios (ppm_v) relative to air at 298 K by dividing the column densities by the 2.64 m measurement path. For times at which conditions are uniform along the measurement path, the reported concentrations represent average values. However, for times with variations in temperature or concentrations along the measurement path, the reported concentrations and temperatures should not be considered as average values and have a high uncertainty due to the fitting of path-integrated spectra. Nevertheless, the reported values do provide valuable information on relative changes in temperature and concentrations, as shown below. To indicate that reported concentrations and temperatures result from fitting of path-integrated spectra, we denote the reported parameters with a tilde – e.g. $\tilde{C}_{fit}$ or $\tilde{T}_{fit}$. Additional details on the WNLS fitting routine can be found in Phillips et al. [37] and additional details on the use of PCA in the WLS fitting routine can be found in Phillips et al. [31]. Details on the methods used to reduce effects of turbulence on broadband absorption spectra as measured with the swept-ECQCL, which include scanning at rates above the dominant turbulence time scales and inclusion of the PCA to fit the baseline, are reported in [36].

4. Results

Figure 4 provides an overview of the entire burn process by plotting the time-dependence of various parameters measured with the MWIR and LWIR ECQCLs. Figure 4(a) shows the infrared emission intensity (I_e) detected in the MWIR and LWIR channels. The flame was ignited at 10:40:00. The detected emission is zero until the flame front reaches the field-of-view of each detector. The flame front reaches the MWIR channel first, and the emission peaks near 10:41:30. The flame front then reaches the LWIR detector and the emission signal peaks near 10:42:00. After the flame front propagates through the beam paths, the emission signals return to near-zero values.

Figure 4(b) shows the temperatures estimated from the WNLS fits to the MWIR and LWIR absorption spectra. As expected, the temperature profiles versus time show a strong correlation with the measured infrared emission. The temperatures show a more gradual rise and fall and a broader profile in time than the emission signals, likely due to heated gases propagating into the beam paths before/after observing the strong infrared emission from the flame front itself. The fit temperatures (averaged to 1 s) range from ~ 300 – 1100 K, which are reasonable values observed for biomass burning [2], although local temperatures within flames will be higher. In addition, the temperature ranges estimated from the absorption spectra are similar for the MWIR and LWIR channels.

Figure 4(c) shows the fit concentration of H_2O , and Fig. 4(d) shows the fit concentration of CO_2 determined from the WLS fit for both MWIR and LWIR channels. The H_2O and CO_2 fit concentrations for both channels are highest during the flame front region, but both are detected throughout the burn. The exact shapes of the temporal profiles compared between MWIR and LWIR channels are different due to the different spatial positions of the beam and different local conditions of the burn; however, the ranges of CO_2 and H_2O fit concentrations determined from the analysis are similar for both.

The data can be divided into three general regions depending on timing relative to the flame front passing the ECQCL beams. The first region consists of times before the flame front reaches the beam paths. During this time period, infrared emission signals are low, and the temperatures are near ambient levels. Gases emitted by the burning material propagates downwind and into the ECQCL beam paths. The second region consists of the time period when the flame front

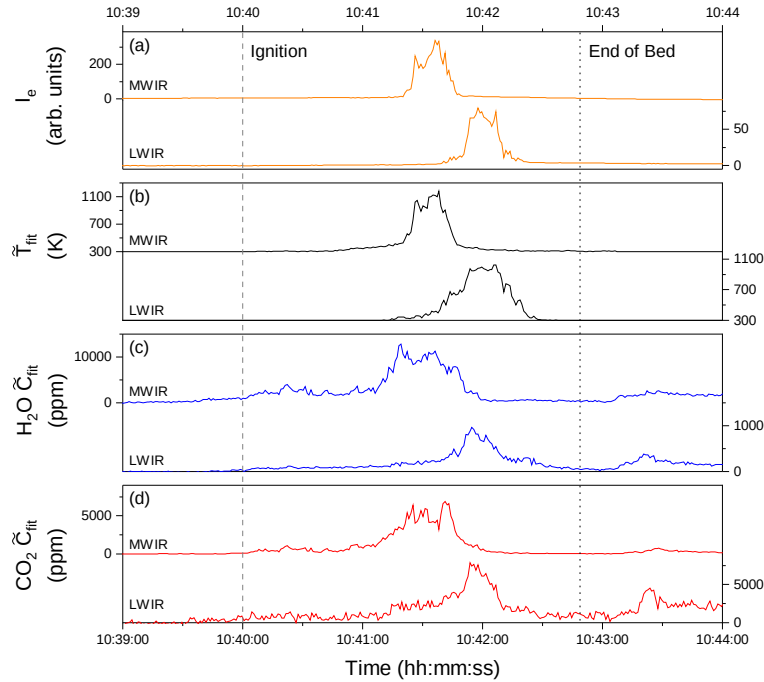


Fig. 4. Time-dependence of (a) emission intensity, (b) fit temperature, and fit concentrations of (c) H_2O , and (d) CO_2 measured throughout the burn using the MWIR ECQCL (top traces) and LWIR ECQCL (bottom traces). Signals have been averaged to 1 s. The dashed line marks the time of ignition and the dotted line marks the time at which the flame reached the end of the plant bed. The MWIR measurement was 30 cm closer to the start of the bed than the LWIR measurement.

passes through the ECQCL beam path and strong emission signals are detected, along with gases present at elevated temperatures. The high thermal and spatial gradients from the flames cause large signal fluctuations and increased noise via beam steering and turbulence. There may also be gases emitted upwind from previously burned regions which are detected during this time period. The third region consists of times after the flame front has passed the ECQCL beam path, resulting in low infrared emission signals with temperatures slightly above ambient. Gases are emitted from previously burned regions, which continue smoldering after the flame passes. We present the results of each region in turn below.

We first consider the initial time period before the flame front reaches the ECQCL beam paths. Figure 5(a) shows the concentrations versus time for H_2O , CO_2 , and CO determined from fits to the MWIR spectrum, during these initial stages of the burn. Before ignition at 10:40:00, the fit concentrations of the H_2O , CO_2 , and CO are low with fluctuations due to measurement noise. A small rise in all gases is seen before ignition, likely due to increased human activity in the wind tunnel during this time. After ignition, the fit concentrations of H_2O , CO_2 , and CO all increase above the noise levels, and exhibit correlated fluctuations between the species. The results show detection of the plume of gaseous combustion products generated from the burning plants at the start of the bed, which propagate downwind through the tunnel and intercept the MWIR beam path.

The modified combustion efficiency (MCE) is defined as:

$$MCE = \frac{[CO_2]}{[CO] + [CO_2]}$$

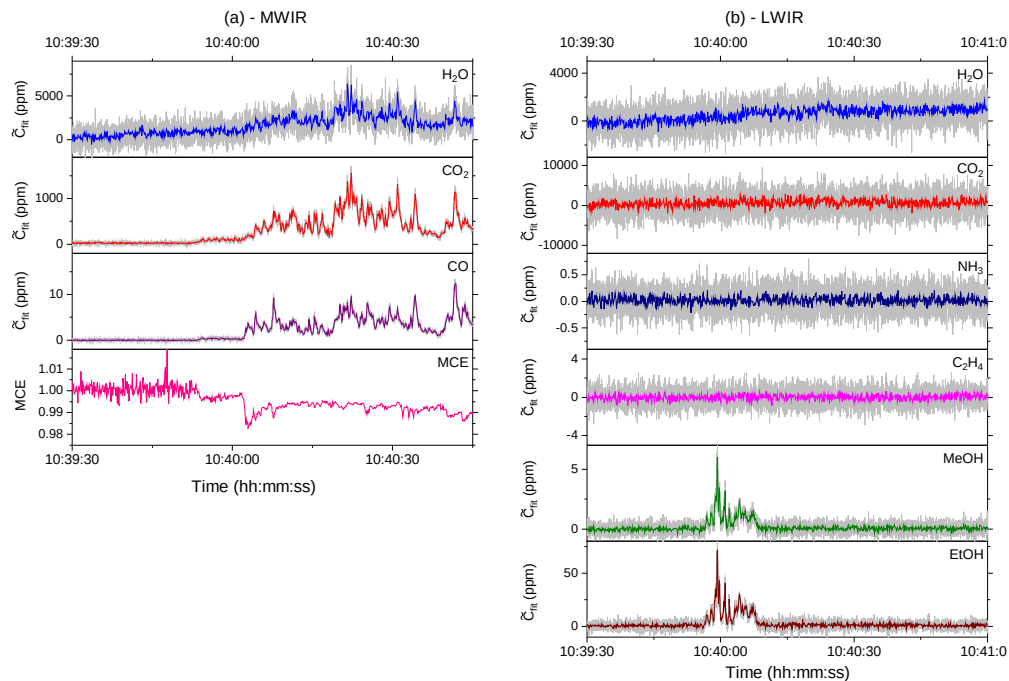


Fig. 5. Fit concentrations versus time before flame front reaches measurement region for (a) MWIR and (b) LWIR ECQCLs. Results are shown for 100 Hz measurements (light traces) and averaged to 10 Hz (dark traces). Species are noted in the figure. The modified combustion efficiency (MCE) is calculated from CO₂ and CO and is averaged to 10 Hz.

where $[CO]$ and $[CO_2]$ are the detected EMRs of the gases [45]. The MCE provides a measure of the combustion process from flaming (high MCE) versus smoldering (low MCE). The lower panel in Fig. 5(a) shows the MCE during the times shortly after ignition. The initial burning of the plant material is dominated by flaming combustion and the gases detected downwind reflect this behavior with a high MCE > 0.98 .

The LWIR results are shown in Fig. 5(b) for the initial time period before the flame front reaches the beam path. The H₂O and CO₂ signals do not show a strong increase, due to low absorption cross-sections in the LWIR (especially at temperatures near ambient). NH₃ and C₂H₄ are not detected above the noise levels. A plume of MeOH and EtOH vapor is detected starting just before the flame is ignited, originating from the denatured alcohol used to start the flame. The strong temporal correlation between MeOH and EtOH serves as a benchmark of the ability of the swept-ECQCL to measure chemical mixtures and distinguish actual fluctuations from measurement noise.

Figure 6(a) shows an absorption spectrum measured by the MWIR ECQCL before arrival of the flame front. Measured and best-fit spectra are overlaid to show their quantitative agreement, and differences are shown by the residual spectrum in the lower panel. Sharp spikes in the fit residuals near strong absorption peaks result from small offsets in line position or linewidth between the measured and modeled spectra as are commonly observed when detecting narrow spectral lines with the swept-ECQCL [30,35,37]. The CO₂ absorption cross-sections within this spectral window are relatively weak, arising from the P branch of the minor isotopologue ¹³CO₂, and higher energy rotational lines from the P branch of ¹²CO₂. Figure 6(b) shows a LWIR absorption spectrum of the MeOH and EtOH vapor plume resulting from the denatured alcohol used to start the flame.

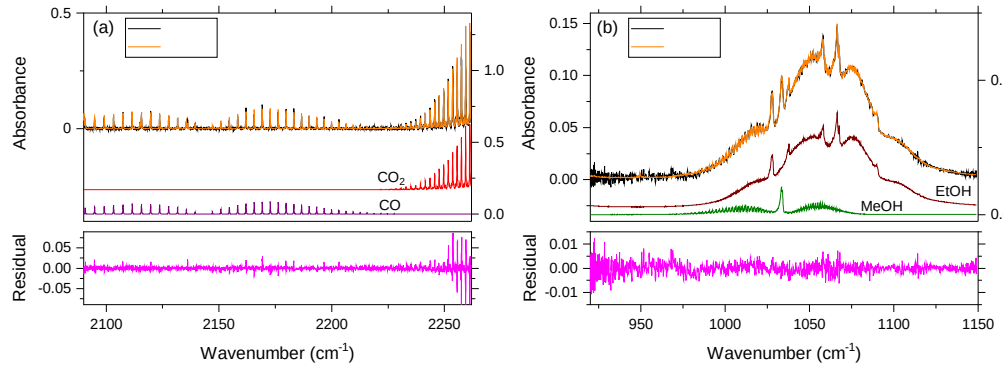


Fig. 6. (a) MWIR absorption spectrum shortly after ignition (10:40:41.9 - 0.1 s average). Concentrations from the fit are 893 ppm CO₂, 10 ppm CO, 2690 ppm H₂O, and $\bar{T}_{fit}$ =314 K. (b) LWIR absorption spectrum (10:39:59.3 - 0.1 s average) showing plume from denatured alcohol used to ignite the flame. Concentrations from the fit are 6 ppm MeOH and 72 ppm EtOH, and T = 298 K (fixed). For both (a) and (b), the top panel (left axis) shows the experimental absorbance (black) and the best fit (orange). The top panel (right axis) shows selected library spectra, offset for clarity. The bottom panel shows the fit residuals.

Figure 7(a) shows the time-dependence of fit concentrations for H₂O, CO₂, CO, fit temperature, and MCE in the time period when the flame front crosses the MWIR beam path. The MCE

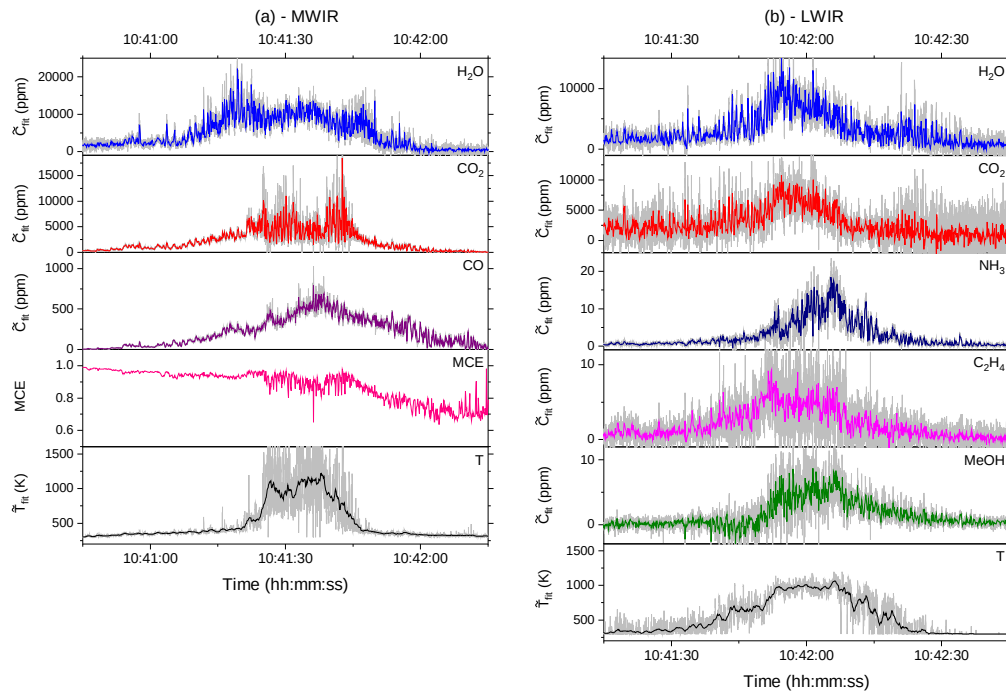


Fig. 7. Fit concentrations and fit temperatures versus time as the flame front passes through the measurement region for (a) MWIR and (b) LWIR ECQCLs. Results are shown for 100 Hz measurements (light traces) and averaged to 10 Hz (dark traces). Species are noted in the figure.

shows a steady decrease as the flame front approaches the MWIR beam path and decreases at a faster rate after the flame front passes. Large fluctuations in the fit parameters are observed as the beam passes through the highly dynamic and spatially inhomogeneous flame region, with corresponding large uncertainty in absolute concentrations and temperature. Increased turbulence is expected due to large refractive index gradients present in and near the flames. The high spectral acquisition rate of the swept-ECQCL helps to mitigate the effects of turbulence on the measured absorption spectra and reduces random noise in the spectral fit parameters, as has been previously shown [34]. The remaining fluctuations in the fit parameters thus largely reflect actual changing conditions in time and not solely noise from turbulence, as will be addressed in the Discussion section.

Figure 7(b) shows the time dependence of fit concentrations for species detected as the flame front passes the LWIR ECQCL beam. Elevated levels of H_2O and CO_2 are detected, with similar magnitudes to those detected by the MWIR ECQCL. An increase in NH_3 is detected, which peaks later in time than H_2O and CO_2 . This observation suggests that the NH_3 is emitted more strongly from smoldering sections, including the previously burned material upwind of the beam path [7,10]. Elevated levels of C_2H_4 and MeOH are also detected as the flame front propagates through the beam path. The fit temperatures estimated from the LWIR spectra are of similar magnitude to the MWIR spectra when averaged to 10 Hz, peaking at values near 1000 K. The short-term extremes in temperature at 100 Hz are higher for the MWIR than the LWIR measurements, which may reflect the use of spectra from different species to estimate the temperature, but are still within expected ranges for biomass burning flames [2].

Figure 8 shows MWIR absorption spectra measured in the flame region. A wide range of physical conditions are spanned during the flame front region, and example spectra are plotted for two times at which the instantaneous fit temperature was low [Fig. 8(a), $\tilde{T}_{fit}=656$ K] and high [Fig. 8(b), $\tilde{T}_{fit}=1170$ K]. The most notable feature compared to Fig. 6(a) is the increase in strength and spectral density of the hot lines of $^{12}\text{CO}_2$ due to the elevated temperatures. Additional higher energy lines from CO are also observed due to the increased temperatures. The fit residuals increase in the flame front region, partly due to increased measurement noise from turbulence but more notably from deficiencies in the spectral fitting model. In particular, the fit residuals in Fig. 8(b) suggest additional CO present at a temperature lower than the best-fit temperature

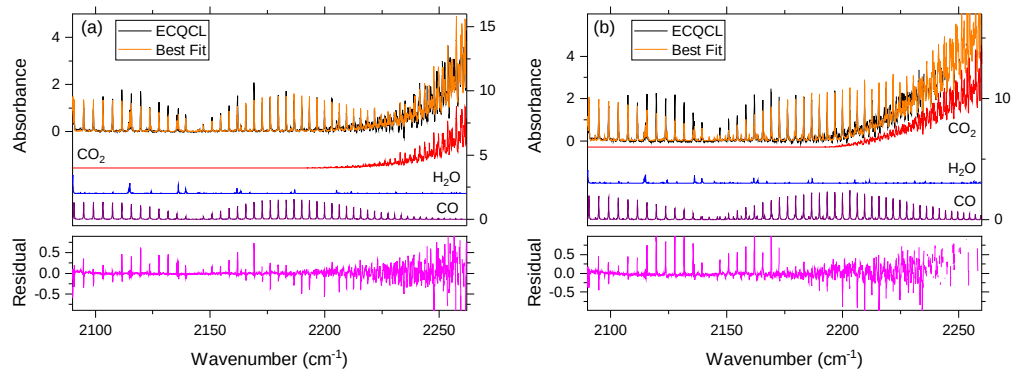


Fig. 8. Example MWIR absorption spectra from flame region at two temperatures. (a) 10:41:24.6 - 0.1 s average. Concentrations from the fit are 6610 ppm CO_2 , 266 ppm CO, 9810 ppm H_2O , and $\tilde{T}_{fit}=656$ K. (b) 10:41:38.6 - 0.1 s average. Concentrations from the fit are 12,510 ppm CO_2 , 2722 ppm CO, 34,860 ppm H_2O , and $\tilde{T}_{fit}=1170$ K. For both (a) and (b), the top panel (left axis) shows the experimental absorbance (black) and the best fit (orange). The top panel (right axis) shows library spectra, offset for clarity. The bottom panel shows the fit residuals.

of 1170 K (which is determined primarily by the fit to the CO₂ spectrum). As addressed in the Discussion section, this observation is consistent with spatial inhomogeneity in temperature and species along the measurement path, which is not accounted for in the spectral fit.

Figure 9(a) shows an example LWIR spectrum measured as the flame front enters the beam path, showing increased fit concentrations of H₂O and CO₂ at elevated temperature. Figure 9(b) shows a spectrum obtained later in the flame region, detailing the presence of NH₃ lines and H₂O lines, also at elevated temperature. For both spectra, the fit residuals are significantly higher than in the pre-flame region due to increased turbulence at the elevated temperatures. But it is also apparent that not all the spectral lines are fit accurately, partly due to limitations of the fitting model. In particular, Fig. 9(b) shows a number of spectral lines not accounted for in the fitting model which could be due to additional species or variations in line-strengths due to deviations from the average (best-fit) temperature. Nevertheless, it is clear visually from the agreement between line positions and band shapes that the identified species (H₂O, CO₂, NH₃) are present in the spectra shown in Fig. 9.

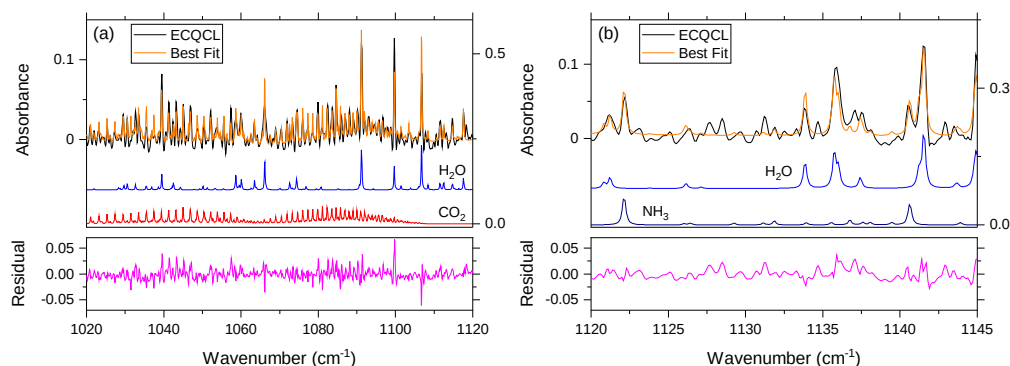


Fig. 9. Example LWIR absorption spectra from flame region (a) 10:41:49.8 - 0.1 s average. The concentrations from the fit are 7800 ppm H₂O, 6400 ppm CO₂, and $\bar{T}_{fit}$ = 650 K. (b) 10:42:05.4 - 0.1 s average. Concentrations from the fit are 12,900 ppm H₂O, 40.2 ppm NH₃, and $\bar{T}_{fit}$ = 985 K. For both (a) and (b), the top panel (left axis) shows the experimental absorbance (black) and the best fit (orange). The top panel (right axis) shows selected library spectra, offset for clarity. The bottom panel shows the fit residuals.

Figure 10(a) shows fit concentrations versus time for species measured with the MWIR ECQCL after the flame front has passed the beam. The H₂O, CO₂, and CO fit concentrations were observed to decrease initially after the flame front passed the beam, but then increased again from 10:43-10:44. The MCE is poorly determined when the CO₂ fit concentration is near zero, but after the rise in concentration the MCE remains nearly constant at ~0.7 which indicates smoldering. Figure 10(b) shows fit concentrations versus time for species measured with the LWIR ECQCL. The fit concentrations for H₂O and CO₂ show a peak near 10:43:30 similar to the MWIR measurements. The gases NH₃, C₂H₄, and MeOH also show increased fit concentrations during this time, consistent with emission from smoldering regions.

Figure 11(a) shows an example MWIR absorption spectrum from the time period after the flame front has passed with the relative heights of the CO and CO₂ absorption features reversed from the pre-flame region, and also indicative of smoldering. Figure 11(b) shows a LWIR spectrum obtained during this post-flame smoldering region in which spectral features of NH₃, C₂H₄, and MeOH are clearly identified.

The results show detection of multiple species, all of which change in time during the burn process. The presence of each chemical species was confirmed by visual examination of measured absorption spectra and comparison with identifying features in the modeled spectra, and examples

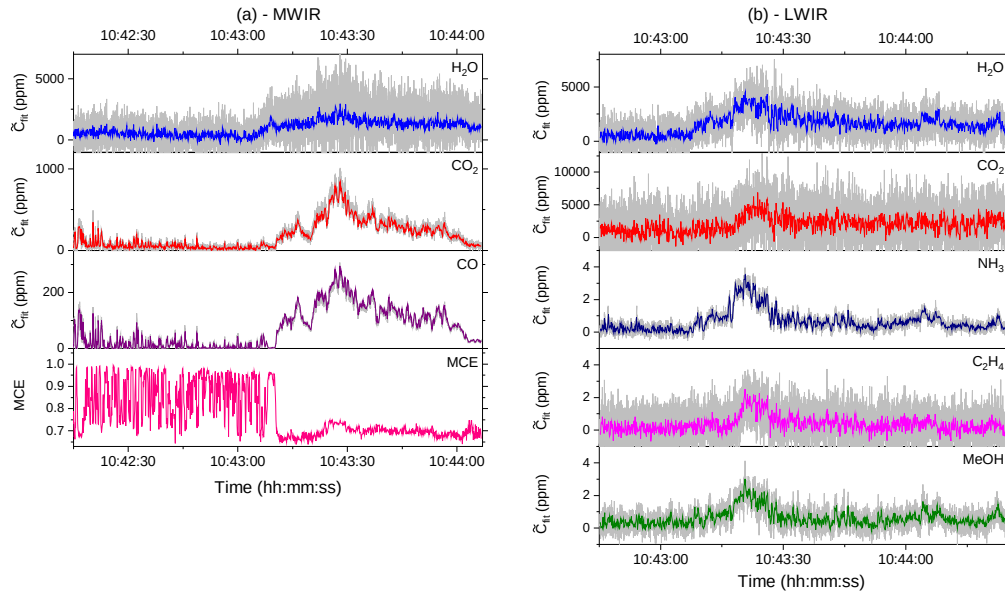


Fig. 10. Fit concentrations versus time after flame front passes the measurement region for (a) MWIR and (b) LWIR ECQCLs. Results are shown for 100 Hz measurements (light traces) and averaged to 10 Hz (dark traces). Species are noted in the figure.

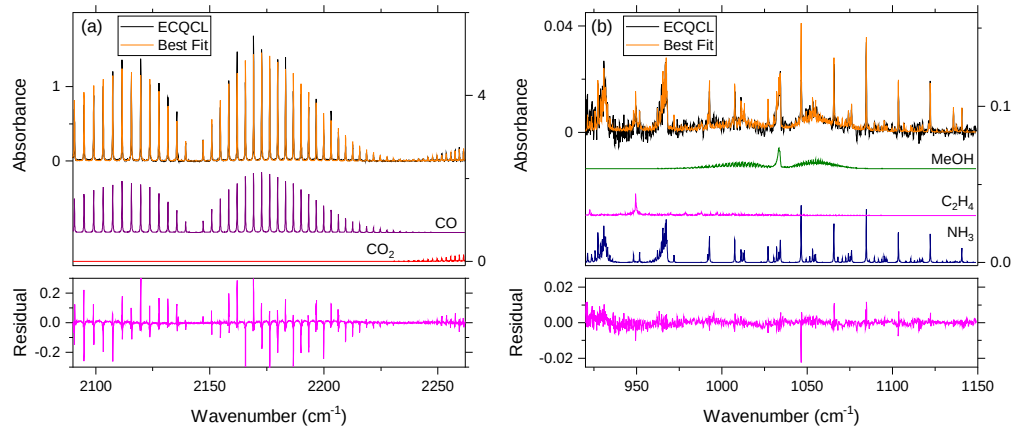


Fig. 11. (a) MWIR absorption spectrum after the flame front passes measurement region (10:43:16.2 - 0.1 s average). Concentrations from the fit are 327 ppm CO_2 , 170 ppm CO , 1156 ppm H_2O , and $\tilde{T}_{fit}=341$ K. (b) LWIR absorption spectrum (10:43:19.2 - 1 s average) showing NH_3 , C_2H_4 , and $MeOH$. Concentrations from the fit are 3100 ppm H_2O , 2700 ppm CO_2 , 2.6 ppm NH_3 , 1.1 ppm C_2H_4 , 2.0 ppm $MeOH$, and $T = 298$ K (fixed). For both (a) and (b), the top panel (left axis) shows the experimental absorbance (black) and the best fit (orange). The top panel (right axis) shows selected library spectra, offset for clarity. The bottom panel shows the fit residuals.

were shown for each species. However, spectra were also identified which exhibited poor spectral fits arising from a source other than random noise. As discussed in the next section, we attribute these poor fits to a limitation of the spectral fitting model, which does not account for spatial

inhomogeneity along the measurement path. We also show that spatial and temporal variations must be considered when interpreting the measurement results.

5. Discussion

The swept-ECQCL measurements provide dynamic information on physical and chemical conditions over both fast and slow time scales at locations close to the fuel source. To provide detail on the fast temporal fluctuations, Fig. 12(a)-MWIR and Fig. 12(b)-LWIR show the high-speed temporal variations in fit concentrations, fit temperature, and emission intensity for 5 s time periods in the flame period, plotted at 10 ms temporal resolution. Figure 12 shows that the fit concentrations of CO_2 and H_2O vary by orders of magnitude, and fit temperatures vary by 100's of K over sub-second time scales when measuring through the flames, and the 100 Hz spectral rate used for the ECQCL measurement and analysis tracks these variations without discontinuities. For both the MWIR and LWIR measurements, the strong temporal correlation between H_2O , CO_2 , emission intensity, and fit temperature indicates the H_2O and CO_2 are measured in the high-temperature flame conditions. The correlated behavior provides additional evidence that the fluctuations are due to actual source variations in space and time and not solely due to measurement noise or turbulence.

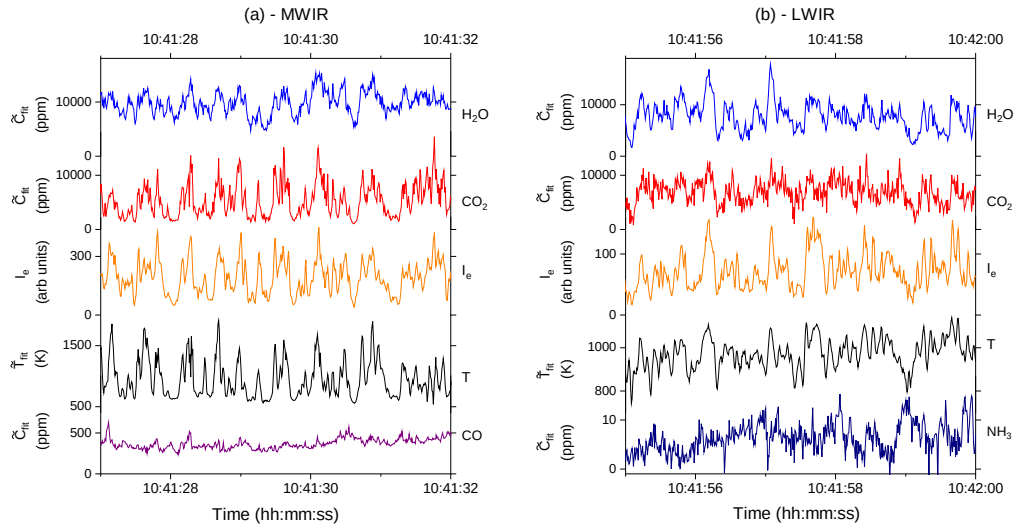


Fig. 12. Time-dependence of fit parameters plotted at 100 Hz measurement rate over 5 s of flame region for (a) MWIR, and (b) LWIR ECQCL. Fit concentrations of H_2O and CO_2 , emission intensity I_e , and fit temperature show high temporal correlations. Fit concentrations of CO and NH_3 show reduced temporal correlation with the other parameters.

The results in Fig. 7 and Fig. 9 appear to indicate the presence of NH_3 , C_2H_4 , and MeOH at temperatures well above their flash points or autoignition temperatures. The temperature was determined from spectral fits primarily to H_2O and CO_2 , which are produced from combustion in the flaming regions and thus exist initially at high temperatures. While the spectral fit assumes a set of species at a uniform temperature, in reality each species is present over a distribution of temperatures along the path-integrated measurement. Thus, the high temperature determined from fits to the H_2O and CO_2 spectra does not preclude the existence of localized cooler regions along the beam path, in which flammable gases may exist. Since the flame front is inhomogeneous and does not cross the beam path all at once, localized pockets of gases from flaming, unburned, and smoldering material may all exist simultaneously along the measurement path. It is also

possible that pyrolysis species are released near the burning flame region, or that they are emitted upwind of the measurement from smoldering regions and propagate downwind into the beam path.

The effect of spatial inhomogeneity can also explain the fit residuals in Fig. 8(b), which strongly suggest the presence of CO at multiple temperatures. This observation is consistent with CO being emitted from cooler smoldering regions, while CO₂ is emitted from higher temperature flaming regions. Figure 12(a) shows that the CO fit concentration exhibits lower fluctuations and less correlation with CO₂, H₂O, and temperature, providing additional evidence that the CO may be measured in lower temperature regions along the beam path. These observations are consistent with the CO being emitted from smoldering regions upwind of the flame front and propagating downwind into the measurement path. Figure 12(b) shows similar uncorrelated behavior of NH₃ with the other species, indicating the NH₃ may be measured in a different spatial location, and likely at a lower temperature, than the H₂O and CO₂.

Spatial inhomogeneity along the measurement path also helps interpret the MCE results. Despite measurement through a strongly flaming region, the MCE in Fig. 7(a) is significantly lower than would be expected for these conditions. Due to the wind tunnel configuration, the measurement may detect gases from all points upwind of the beam path. Therefore, even when the beam is passing through the flame front region, there may be contributions to the detected gas composition from upwind smoldering regions which the flame front has already passed. In particular, the detected CO likely originates largely from smoldering regions upwind of the beam path. The steady decrease in MCE during the burn process is consistent with this mechanism, as the fraction of smoldering material upwind of the measurement path increases during the flame front propagation. The measured MCE in the post-flame region of ~0.7 is also lower than the value ~0.8 typically observed from smoldering in biomass burning studies [5,10,15]. In addition to the mechanism discussed above, the lower observed MCE may result from the *in-situ* measurement at close proximity to the smoldering fuel source which reduces the likelihood of reactive CO decreasing in concentration during propagation to a remote measurement or through sampling effects.

The emission ratio (ER) was calculated as the ratio of time-integrated EMRs between a given species and CO. Table 1 shows calculated ERs when the time-integral was performed over the entire burn duration (excluding the initial plume of denatured alcohol vapor), and also when the integral was performed over a subset of data after the flame front passes. For NH₃, C₂H₄, and MeOH, the ERs calculated from the ECQCL are in excellent agreement with prior published results [11,12].

Table 1. Emission ratio (ER) relative to CO for entire burn duration 10:40:30-10:44:25, and for subset corresponding to post-flame region 10:42:30-10:44:25.

Species	ER for entire burn (ppb/ppm)	ER for post-flame region $t > 10:42:30$ (ppb/ppm)
NH ₃	12	10
C ₂ H ₄	8	5
MeOH	7	9

Species detected using the LWIR ECQCL with high confidence were H₂O, CO₂, NH₃, C₂H₄, and MeOH, verified by visual examination of the absorbance spectra and identification of distinctive spectral features. For these species, the absorption cross-section in the LWIR ECQCL tuning range multiplied by the concentration is relatively high, resulting in peak absorbance values $\geq 10\times$ the absorbance spectrum baseline noise. Other potential pyrolysis species (EtOH, formaldehyde, SO₂, furan, acetic acid, formic acid, propene, acetaldehyde, acrolein, methyl vinyl ketone, and 2,3-butadione) were considered by adding them to the WLS analysis library; however, these species all have predicted peak absorbances approximately equal to the absorbance

spectrum noise, based on the product of infrared absorption cross-section [44] and the ranges of concentrations expected to be present in biomass burning experiments [11]. The output results from the WLS algorithm indicated possible increases in EtOH, propene, acetic acid, and formic acid in the post-flame region, but the results were ultimately inconclusive because no distinctive spectral features could be reliably and consistently identified in the experimental spectra.

6. Measurement sensitivity and accuracy

Measurement sensitivity expressed as noise-equivalent concentration (NEC) was determined via a standard Allan-Werle analysis [46]. A set of 7,000 spectra acquired over a 70 s time period before the flame was ignited was analyzed to determine the chemical concentrations, which are expected to be zero (relative to background levels). Figure 13 shows the results of the Allan-Werle analysis. All species show excellent averaging behavior indicating good instrument stability and lack of measurement drift over time scales up to 10 s. The Allan deviation results were obtained for stable conditions with low turbulence and near ambient temperatures, and sensitivity will be degraded when measuring through the flame region due to increased turbulence. It is important to note that the rapid fluctuations in species concentrations and temperatures limit the ability to improve the signal-to-noise ratio (SNR) via averaging, since in these cases averaging will reduce the signal levels as well as the noise. In practice, acquiring spectra at a faster rate than the time scales of turbulence and source fluctuations provides the most flexibility for averaging to best match the time scales of the physical system [34,36,37].

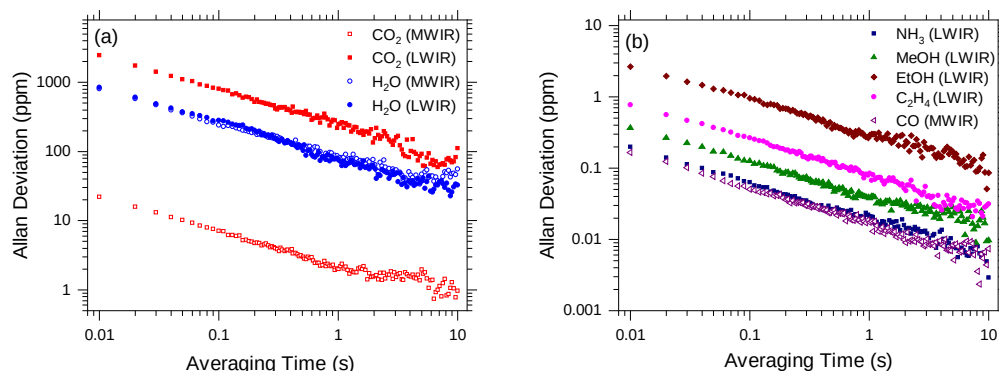


Fig. 13. Allan-Werle analysis for (a) CO₂, H₂O and (b) other trace species at 298 K. The Allan deviation was determined from a dataset of 7000 points (70 s duration) acquired in the period before the flame was ignited.

Measurement accuracy is difficult to quantify without additional reference measurements under known and stable conditions. At temperatures near ambient levels, corresponding to regions before or after the flame front, the agreement of measured spectra with reference data (NWIR or HITRAN) is high and accuracy is primarily limited by uncertainty in species distribution along the measured path. For measurements through the flame front regions, the accuracy is degraded as evidenced by the increased spectral fit residuals. The increased measurement noise due to turbulence partly explains the increased residuals; however, there are also clearly identifiable and systematic discrepancies between the modeled spectra and experimental data. These discrepancies may be due to limited applicability of database spectra at elevated temperature, additional absorbing species in the measurement not included in the selected fitting library, or spatial inhomogeneity along the measurement path. Additional work is needed to validate the measurement and spectral analysis in controlled high-temperature conditions, and to quantify the accuracy and precision of the results.

The path-integrated measurement also limits the accuracy due to the assumption of uniform conditions along the beam path for the modeled spectrum. For higher accuracy, the absorption spectrum should be modeled as a composite mixture of species with varying temperatures and concentrations along the measured beam path using additional spatially-resolved experimental data or assumptions about the distributions of species and temperatures. For example, the spectral fits shown in Fig. 8(b) could be improved by assuming different temperatures for CO and CO₂, or by adding spectra from multiple populations of CO, with each at a different temperature.

The measurements performed here involved a relatively short path length of 2.64 m and a high measurement speed to capture the rapid changes in species concentrations during the burn. Sensitivity could be increased by using a multi-pass configuration across the flame region or by sampling gases generated from the burn followed by offline analysis [9]. In the latter case, by measuring the gases at lower temperatures and in less turbulent conditions it will be possible to detect species at much lower concentrations. For example, using a 50-100 m path length multi-pass cell [31] with 10 s averaging would provide predicted detection limits for many species at low- to sub-ppb concentrations. However, using an extractive or sampling method would reduce the ability to measure transient or reactive species existing only near the flame or smoldering regions. In practice, *in-situ* and extractive measurements provide complementary information for understanding the burn process and both are useful measurement configurations.

7. Summary and conclusions

The measurements reported here used swept-ECQCL spectroscopy to measure gases close to the fuel and flame source in laboratory large-scale biomass burning experiments. A combination of two swept-ECQCL systems provided sensitive detection of CO₂, H₂O, and CO in the MWIR spectral region, and NH₃, C₂H₄, MeOH in the LWIR spectral region. Species were measured throughout a dynamic burn experiment and showed the evolution of temperature and gas concentrations over fast and slow time scales. The 100 Hz measurement speed was able to track the rapid and large variations in gas concentrations and temperatures, especially when measuring through turbulent flame regions. Temporal correlations between gas species, temperature, and emission intensity on sub-second time scales indicate the presence of localized high temperature regions dominated by combustion gases CO₂ and H₂O. Uncorrelated variations in CO and NH₃ indicate that they exist in cooler localized regions along the measurement path and may be generated from upwind regions of previously burned material. The results are consistent with observed variations in MCE during the burn process.

The swept-ECQCL measurements demonstrate a new tool for studying biomass burning dynamics *in-situ* and on faster time scales than have been previously studied. The high spectral radiance of the ECQCL permits measurement through high-temperature flame regions, which is needed to access spatial regions close to the fuel source where transient species may be present. However, path-integrated measurements through inhomogeneous flame fronts leads to high uncertainty in determining absolute concentrations and temperature at these times, and spatial inhomogeneity must be considered when interpreting the results of the measurement and analysis. Modifying spectral analysis algorithms to account for non-uniform temperatures and species distributions is expected to improve accuracy. The preliminary results presented here focused primarily on gases with highest concentrations and infrared cross-sections, with NH₃, C₂H₄, and MeOH being identified unambiguously. The broad tuning range of each swept-ECQCL provides the ability for multi-species detection, and the experiments show an example of using multiple ECQCL systems simultaneously to access different wavelength regions. Although the tuning range of each swept-ECQCL is not as large as FTIR-based instruments, the combination of high measurement speed, high spectral resolution, and high spectral radiance in the swept-ECQCL provides a valuable and complementary capability for infrared absorption spectroscopy. With increased measurement path lengths, the sensitivity of the ECQCL measurements is expected to

improve, enabling time-resolved *in-situ* measurement of a wider range of trace gases emitted from biomass burning.

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Disclosures

MCP: Opticslah, LLC (E).

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