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A Combined Experimental and Theoretical Study of the Combustion of Live vs. Dead Leaves

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The behavior of live fuels is clearly different from that of dead fuels in wildfire conditions. Fire spread is sustainable at higher fuel moisture contents in live fuels than in dead fuels, but the fundamental reasons for this difference are not understood. Studies have examined the ignition times, rates of fire spread, moistures of extinction, and the fuel temperature histories of both dead and live fuels in a variety of conditions. However, a study of the temperature distribution and mass history of single live and dead leaves of the same moisture content in a wildfire condition has not previously been performed. Live and dead manzanita leaves (*Arctostaphylos glandulosa*) were conditioned to roughly 30% moisture content (dry basis) and burned over a flat flame burner. A base case of manzanita leaves at 4% moisture content was also burned. Each leaf had its mass logged by a cantilever balance and its face temperature recorded by an infrared camera. The temperature distribution of each leaf was tracked from the start of preheating to burnout and was analyzed as a whole leaf and in sections. Live leaves had a strong temperature plateau indicative of evaporation although it occurred well above the normal boiling point of water. In contrast, the conditioned and unconditioned dead leaves showed little if any temperature plateau.

Using the dry, dead set, the average temperature of each section was used as the temperature input for a devolatilization model to predict the mass release of the leaf over time. This was compared to the measured mass release, showing good agreement. A theory to describe water release in moist leaves was developed to account for the difference in temperature distributions and histories of the dead and live leaves, especially with regards to the temperature plateau observed for live leaves. While the liquid in a dead leaf quickly diffuses out of a leaf as it locally reaches its boiling point, plant cells have been documented to hold pressures of between 30 atm and 100 atm (based on 50% bursting), depending on the species. These pressures correspond to water boiling temperatures of 235°C and 312°C which is similar to the temperature range of the live leaf temperature plateaus. This explanation was used to develop evaporation models which differentiate live and dead fuels and were coupled with a devolatilization model to predict a mass release curve which was compared to the measured history.

1. Introduction

A fundamental understanding of how live and dead fuels burn (and their differences) is necessary to appropriately model fire spread, but is lacked. Finney et al (2012) summarized several ways that fire spread in live vegetation is unexplained by current modeling and theory, including: (a) the ability of live fuels to sustain fire spread at much higher moisture contents than is possible in dead fuels and

(b) that upon preheating, water is released in live fuels due to structural failure rather than diffusively as in dead fuels. Although the moisture of extinction (moisture content at which a fire will not spread continuously) is usually between 15% and 40% (dry basis) for dead fuels, Dimitrakopoulos and Papaioannou (2001) have measured extinction as high as 140% moisture content in live foliage. Moisture content (MC) is defined in terms of the sample mass (m_0) and its oven-dry mass (m_{dry}):

$$MC = \frac{m_0 - m_{dry}}{m_{dry}} \tag{1}$$

While burning live fuels, Pickett (2008) observed temperature plateaus, indicative of evaporation, at mean leaf temperatures of 140°C and 200°C and suggested that the elevated boiling point of water solutions was a possible explanation for temperature plateau at 140°C. This is supported by a measured elevated boiling point of 140°C for 95% concentrated sucrose-water solutions at 100 kPa (Ozdemir and Pehlivan, 2008). An explanation for the temperature plateaus in live leaves above 140°C may be related to the tensile strength of cell walls. Carpita (1985) used a gas decompression technique to pressurize cells and then measured the fractions of intact cells for varying pressures, demonstrating that plant cells burst when internal pressures are in the range of 10 atm to 150 atm, depending on the species. Water release from live leaves (in fire conditions) should be considered for a high-pressure scenario. Structural failure and the resulting water release from cell lumens in live leaves may occur at elevated temperatures resulting from of combination of cell weakening (from thermal decomposition) and internal pressure (from high pressure steam).

Water in dead fuels is bound to cell walls (especially cellulose and hemicellulose) up to the fiber saturation point (usually about 30% MC) and responds to relative humidity; higher moisture contents occur when liquid water on the leaf surface is absorbed into cell cavities (Viney, 1991; Laboratory, 2010). Lignocellulosic materials have been described as a composite having a transient microcapillary network in which water can occur as monolayer water (closely associated with OH groups) or polylayer water (more loosely associated) (Hill et al., 2009). Hill et al (2012) concluded that the water sorption rate in thin wood samples is "limited by the ability of the cell wall matrix to deform." Water desorption had an activation energy of 10 – 30 kJ mol^{-1}, consistent with the energy required to break hydrogen bonds (Hill et al., 2012).

2. Objectives

The first objective of this work is to determine if live and dead leaves at similar moisture contents heat differently under wildfire conditions. The second objective is to infer the temperature ranges of moisture release for live and dead leaves by comparing models of mass release to experimental results.

3. Methods

Manzanita (*Arctostaphylos glandulosa*) shrubs are prevalent in California shrublands and their leaves were selected to investigate pyrolysis and moisture release. Samples were collected in the mountains near Riverside California and shipped to Brigham Young University where they were measured (height, width, thickness, mass and moisture content) and individually burned in a well-controlled apparatus. Different treatments were applied to three groups of leaves prior to experiments. The first group, representing dead, dry fuel, was allowed to dry at room temperature to a moisture content of 4%. The second group, representing dead wet fuel, was allowed to dry at room

temperature for over a month and then was submerged in water and soaked overnight prior to testing and had a pre-burn moisture content of 26%. The third group, representing live but severely dehydrated fuels, was allowed to dry (leaves still on branches) for two to three weeks and had a moisture content of 31%. The final two groups were compared as dead and live leaves with similar moisture contents. Moisture contents of each group were determined by analyzing a 2-4 gm sample in an Arizona Instruments Computrac Max 1000.

Each leaf was individually suspended in the center of a glass cage from cantilever mass balance which was synchronized and time stamped along with video images. A porous 7.5 x 10 inch flat flame burner producing a 10 mol% O_2, 1000°C post-flame gas from hydrogen and methane fuel was quickly rolled into position directly under the leaf and glass cage (see Figure 1). The setup shown in Figure 1 was slightly modified by moving the mass balance to the back side and recording infrared (IR) images through the view port in the glass panel located on the right side. Video images, temperature data, and mass data are collected and time-stamped in order to synchronize the data (see Figure 2). IR thermal images were manually synchronized.

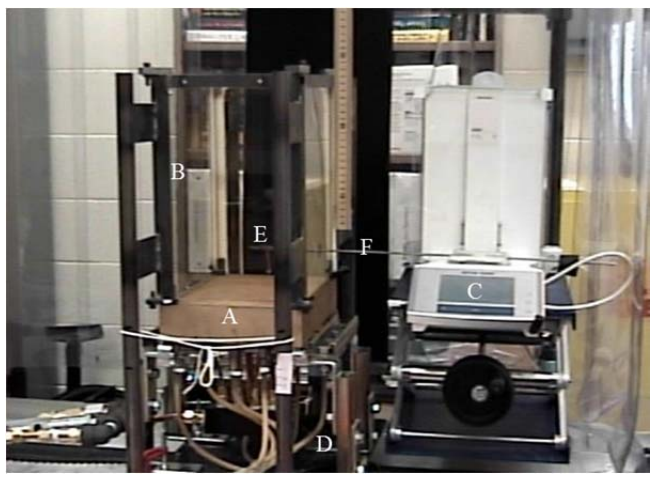


Figure 1. Experimental apparatus including large, flat flame burner (A), glass duct (B) and mass balance (C). The burner is on a movable cart (D) below the duct, and the sample clip (E) is positioned above the center of the burner, supported by a rod extending from the mass balance (F).

A histogram of the leaf surface temperatures was analyzed for each of the runs, 20 per group, to determine general trends and differences. Since there is a high degree of temperature variation while leaves heat and burn (see Figure 2) and devolatilization is an exponential function of temperature, averaging out the temperature variation distorts mass release calculations. To overcome this in the calculations, leaves were divided into sections which were recalculated with each new time frame, roughly keeping each section associated with the same part of the burning leaf. The temperature of each section was used locally to predict devolatilization and water release (see Figure 3). The bulk calculated mass release was determined from the contributions of the local sections.

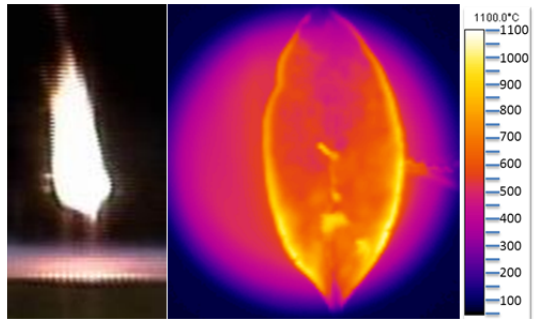


Figure 2. Synchronized video (from front view) and IR (from side view port) images of live leaf at 4 s of heating.

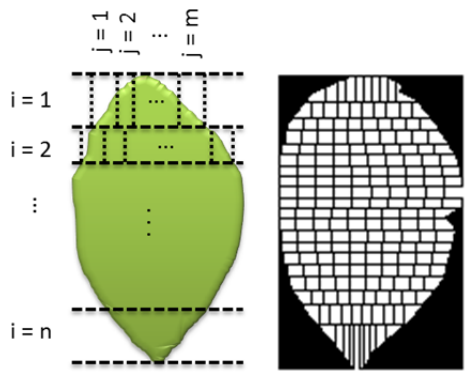


Figure 3. (Left) schematic of leaf subdivisions, first into equal leaf-area rows, then into equal leaf-area sections on each row; (right) example of a subdivided leaf (n = 20, m = 10).

A one-step devolatilization model was used to predict local volatiles release from the average temperature of each section:

$$\frac{dV}{dt} = A \cdot e^{-E/RT}(V_\infty - V) \tag{2}$$

where V is the fraction of volatiles released, t is time, A is frequency factor, E is activation energy, R is the universal gas constant, T is the absolute temperature and V_∞ is the maximum volatile release fraction.

For dead leaves at wildfire heating rates, several water release scenarios were considered: (1) water behaves as bulk water and primarily evaporates at some temperature between 100°C – 140°C, depending on the solute concentration; (2) water release is (Fickian) diffusion limited and occurs at some temperature range above 100°C but below major structural breakdown begins (200°C – 250°C); (3) major water release requires or accompanies structural breakdown (lignocellulosic pyrolysis) and is lost somewhere between (200°C – 350°C). Water was modeled as being released within each of these temperature ranges, as a linear function of temperature, to examine the relative likelihood of each scenario. Water release was also be modeled using the one-step Arrhenius devolatilization model, adapted for water. The sorption of water (on wood) has an activation energy of 10 – 30 kJ mol^{-1} (Hill et al., 2012) which was considered for dead leaves. The presence of water within cell lumens was not modeled for dead fuels.

Live foliar moisture doesn't respond directly to relative humidity but is controlled by the plant and therefore depends on plant resources. While water occurs in cell walls, as with dead fuels, a live cell also maintains water solution in its plasma membrane and included organelles. This water solution vaporizes at the normal boiling point of the solution or at some elevated temperature if the plasma membrane and cell wall (or cell layers) contain and pressurize the steam, thereby raising the boiling point. While cells have been observed at room temperature to withstand pressures between 30 atm and 100 atm with 50% of the cells remaining intact, this has not been demonstrated at elevated temperature (Carpita, 1985). When the internal cell water cannot be dissipated diffusively before water temperatures and their corresponding steam pressures exceed the tensile strength of the cell and leaf structure (possibly weakened by thermal degradation) cell bursting may occur. Surface bubbles and bursting has been documented by Pickett (2008) and occurred during the temperature plateau (usually about 200°C) of leaves at high moisture (90 – 130% MC). This behavior was modeled by releasing live moisture within the high temperature range (200°C – 350°C). Even when bursting does not occur, water release may be accelerated by high temperatures and pressures.

4. Results and Discussion

Temperature histograms (Figures 4-6) show the temperature distribution of leaf pixels from the IR video images at 1 second intervals. The temperature distribution had a steady progression to higher temperatures for dead, dry samples (i.e. Figure 4), as noted by a shift in the temperature distribution curve to higher temperatures at each time in Figure 4a. The temperature distribution had a nearly as steady progression to higher temperatures for dead, wet leaves (i.e. Figure 5). The temperature distribution did not progress as steadily for live leaves (i.e. Figure 6) but stalled with the major portion of the leaf with a temperature centered between 200°C and 300°C for 3 to 7 seconds. Figures 4-6 show a detailed temperature development for one run from each treatment group.

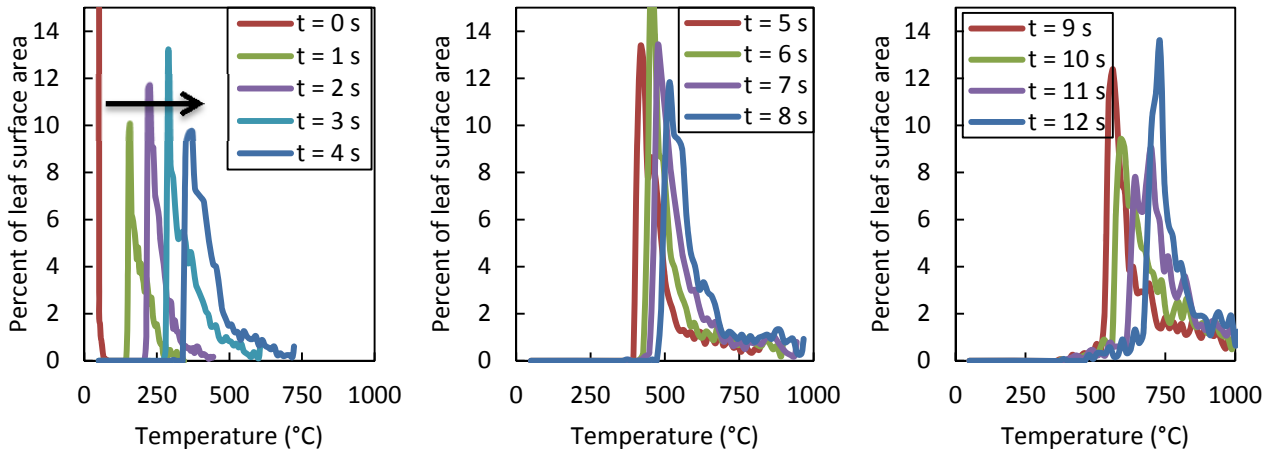


Figure 4. Histograms of IR leaf pixel temperatures for each second during leaf heating and combustion for a dead, dry leaf.

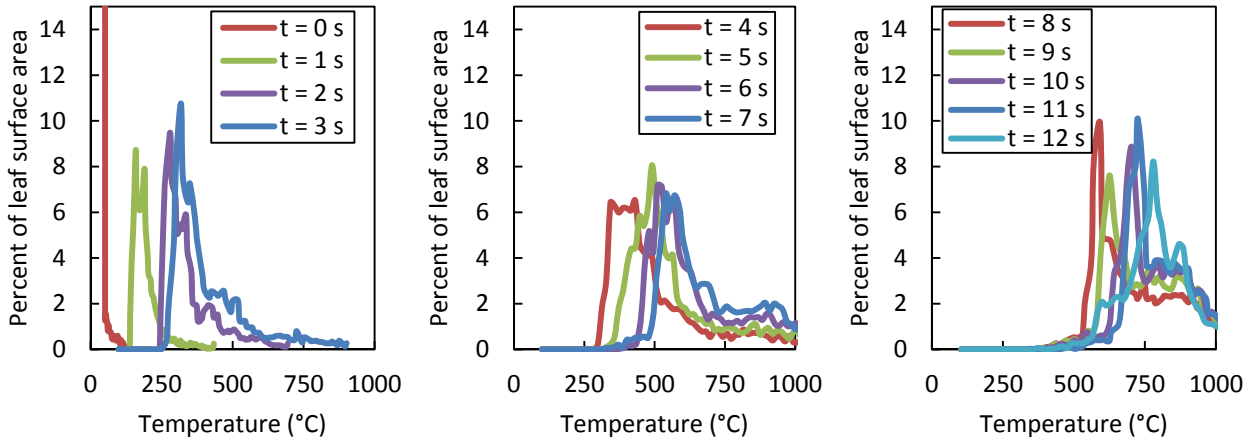


Figure 5. Histograms of IR leaf pixel temperatures for each second during leaf heating and combustion for a dead, wet leaf.

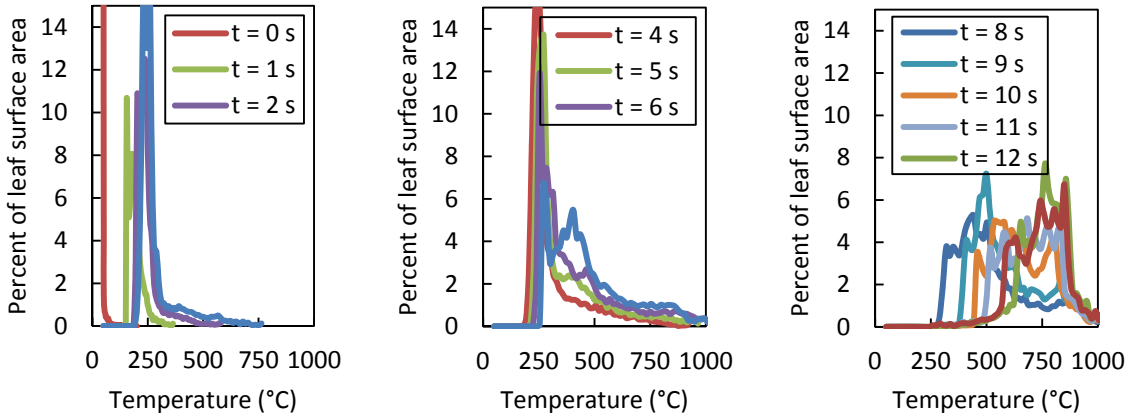
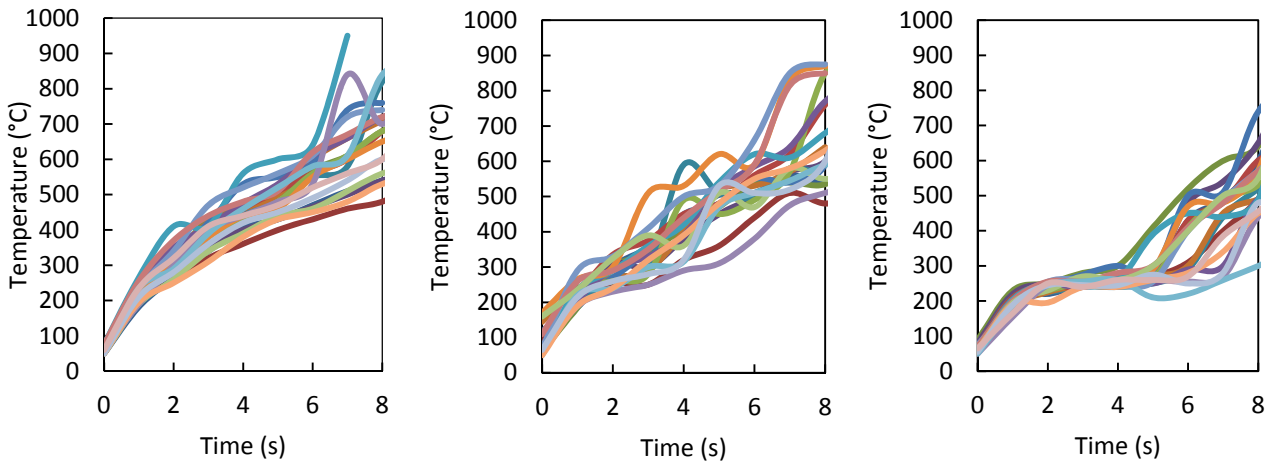


Figure 6. Histograms of IR leaf pixel temperatures for each second during leaf heating and combustion for a live leaf.

To demonstrate the repeatability of these trends for all runs, the temperature of the maximum histogram peak for each second was plotted over time for all runs in each treatment group, giving approximately 20 heating curves for each group (see Figure 7). Both the dead-dry group and the dead-wet group showed a continual rise in peak temperatures in the first 6 seconds. However, the live group (Figure 7c) shows a plateau in peak temperatures in the 2-4 second range, indicating that a different mechanism is occurring in this time-temperature range.



(a) dead, dry **(b) dead, wet** **(c) live**

Figure 7. Summary of all runs showing the temperature of the largest area of leaf at each time step for every run; from left to right: dead and dry group, dead and wet group, live group

Calculations were performed based on the IR temperature images to model the mass release based on surface temperature alone. The devolatilization and evaporation calculations were performed individually for 20 sections on each of 30 rows, or a total of 600 sections. Simple kinetic parameters that fit the mass release data well for this heating rate (but are not likely to adapt well to other heating rates) are given in Table 1. Using the volatile release parameters given in Table 1, water release for dead leaves based on the lower temperature ranges (100°C to 140°C and 100°C to 200°C) was far too aggressive. An empirical model to release water linearly across the range 266°C to 315°C gave a much better total mass release fit. For live leaves, an empirical model to release water across the range (250°C to 315°C) gave in good agreement with experimental mass release data.

Table 1. Devolatilization kinetic parameters for general leaf mass.

	Dead dry	Dead wet	Live
V_∞ (devol.)	0.87	0.83	0.84
A (devol.)	$1x10^{2}$ s^{-1}	$1x10^{2}$ s^{-1}	$1x10^{2}$ s^{-1}
E/R (devol.)	4300 K	4300 K	4000 K

The values of A and E/R values given in Table 1 are much lower than expected for lignocellulosic pyrolysis. Therefore, a more sophisticated model was implemented. Kinetic parameters for the thermal bond breaking of side chains and aromatic clusters of each species (cellulose, hemicellulose and lignin) were reported by Fletcher (2012) and were considered equivalent to first-order devolatilization parameters. Relative amounts of side chain and aromatic cluster mass were also estimated (Fletcher et al., 2012) and were used to partition species mass into kinetic groups for the devolatilization model, as shown in Table 2. Heterogeneous char combustion was modeled based on the work of Porterie et al (2000). Parameters for char combustion rates are given in Table 2. The value for V_∞ (0.769) was obtained from Pickett (2008). A single water release model was used for all runs using an activation energy of 166 kJ/mol and a frequency factor of $3x10^{13}$ s^{-1}. Results of the calculations are given in Figures 8-10. The sudden drop in measured mass that occurs at the start of each run is likely due to the buoyant plume from the flat flame burner that contacts the leaf.

Table 2. Summary of kinetic rate constants adapted from Fletcher (2012) and Porterie et al (2000). *A and E/R values for char and water are for a single reaction rate with no distinction between mechanisms.

	Lignin	Cellulose	Hemicellulose	Char	Water
Mass	$0.35 \cdot m_{dry}$	$0.33 \cdot m_{dry}$	$0.32 \cdot m_{dry}$	$0.5 \cdot (1-V_{\infty}) \cdot m_{dry}$	$m_0 - m_{dry}$
$Fraction_{side}$	0.39	0.46	0.47	(single rate)	(single rate)
A_{side}*	$7x10^{16}\ s^{-1}$	$2x10^{16}\ s^{-1}$	$5x10^{19}\ s^{-1}$	$1.6x10^{3}\ s^{-1}$	$3x10^{13}\ s^{-1}$
$(E/R)_{side}$*	27,898 K	27,898 K	25,934 K	9,000 K	20,000 K
$A_{cluster}$	$2.3x10^{19}\ s^{-1}$	$3x10^{15}\ s^{-1}$	$3x10^{13}\ s^{-1}$		
$(E/R)_{cluster}$	34747 K	30819 K	19237 K		

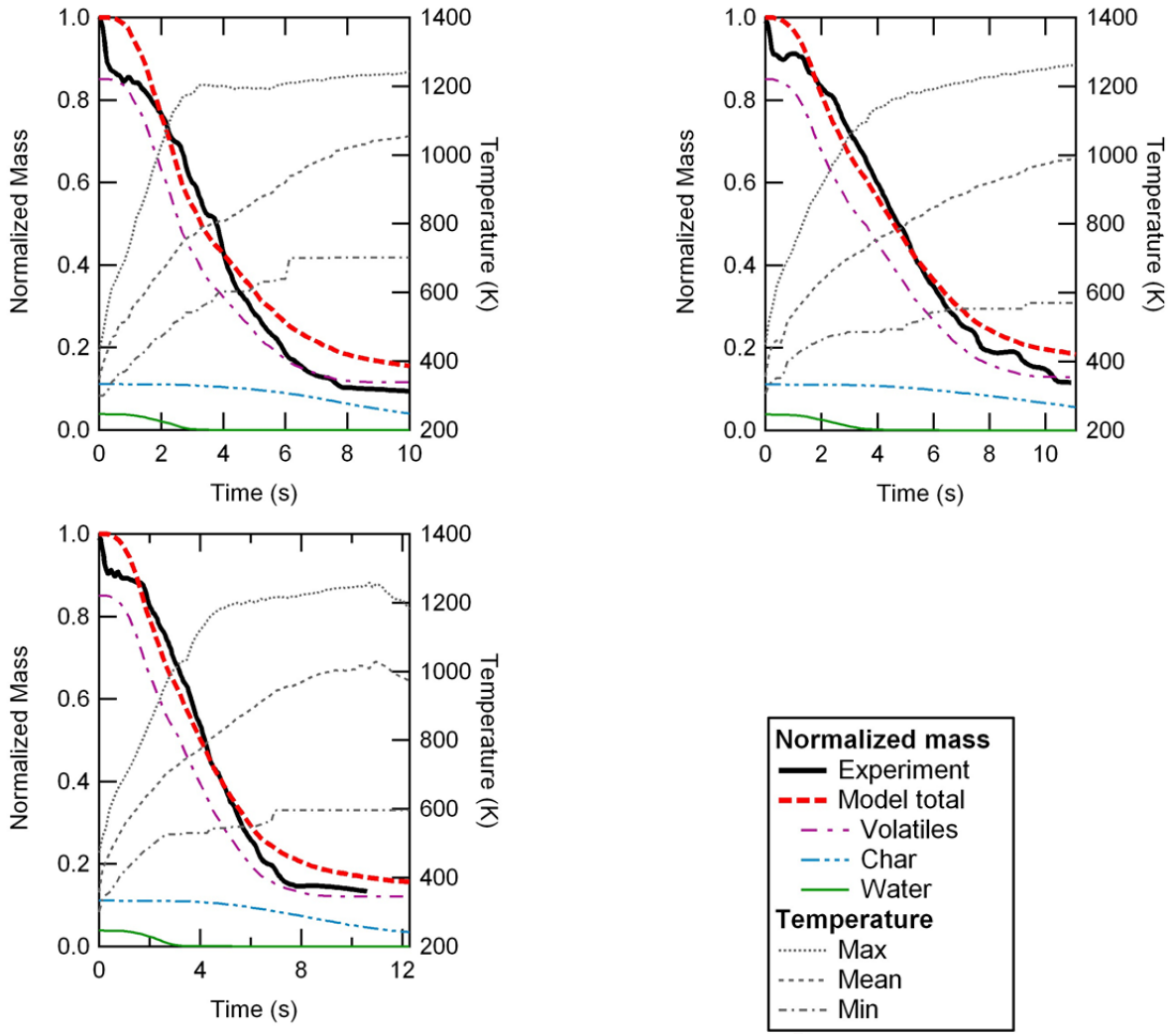


Figure 8. Comparison of experimental and modeled mass release for dead, dry leaves with leaf temperatures.

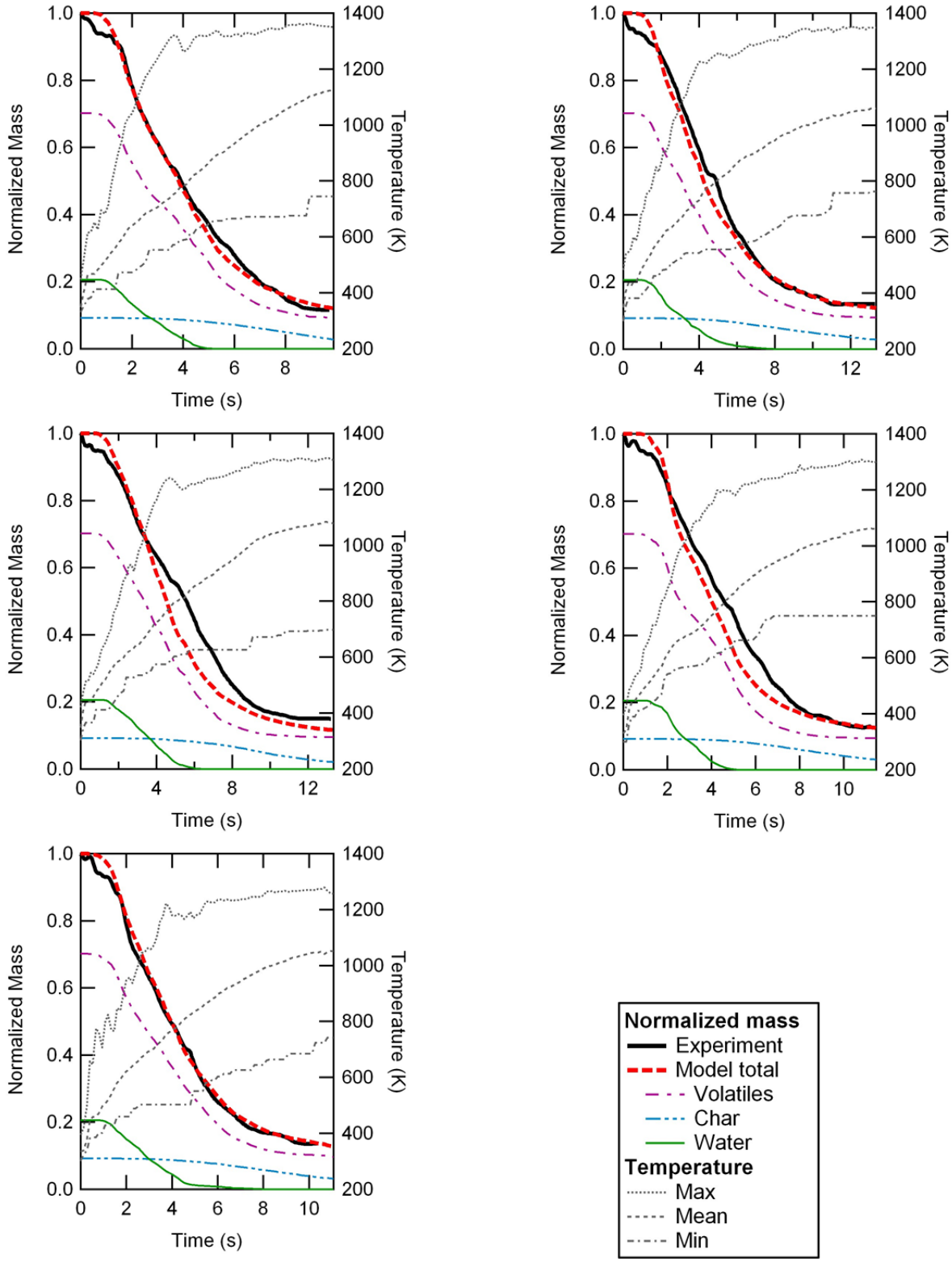


Figure 9. Comparison of experimental and modeled mass release for dead, wet leaves with leaf temperatures.

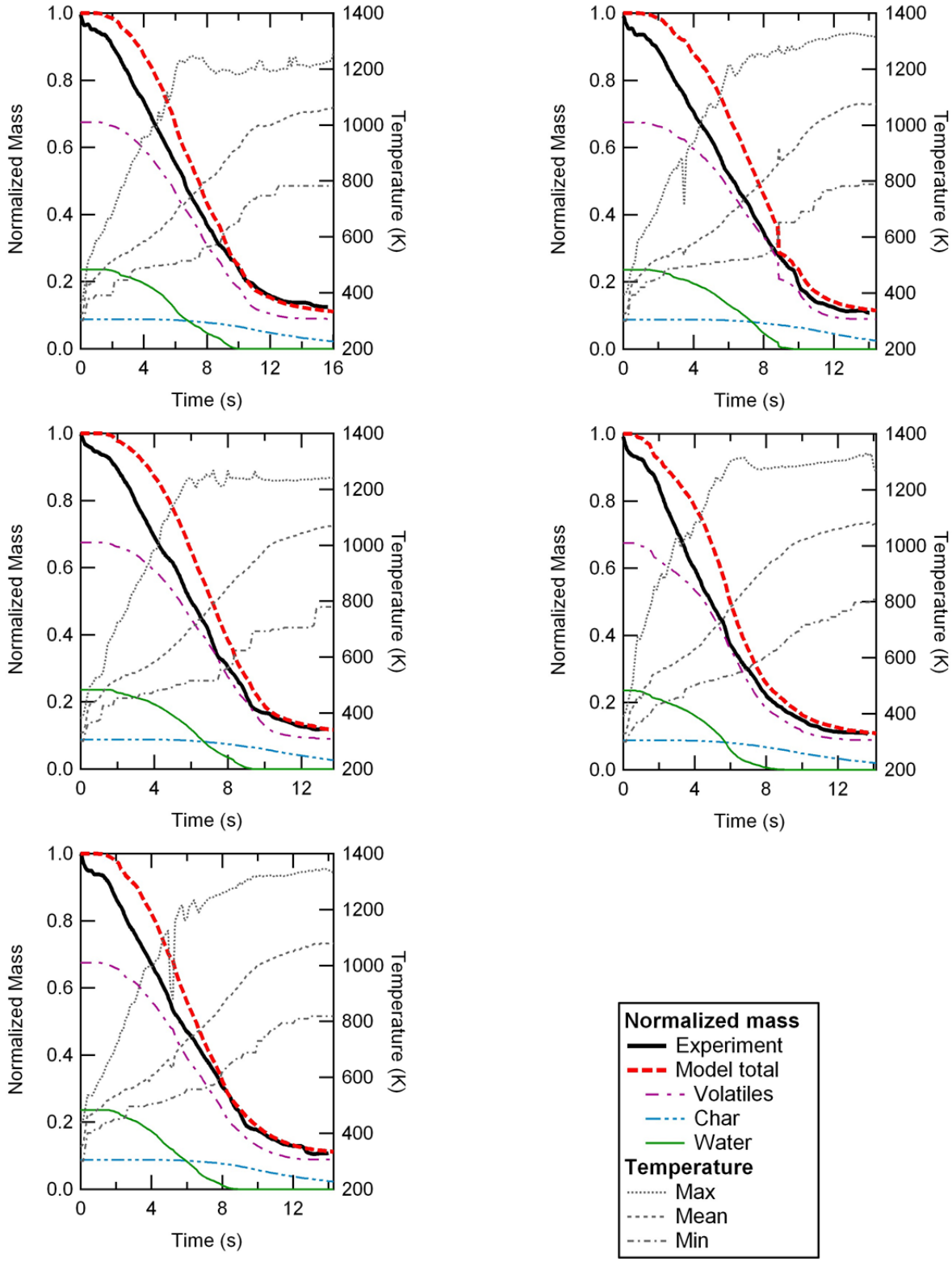


Figure 10. Comparison of experimental and modeled mass release for live leaves with leaf temperatures.

The modeled total mass release (bold red dashed line, Figure 10) lagged the experimental mass release (bold solid black line) for live leaves during the first part of each run. For dead leaves (Figures 8-9) this was not usually the case. This marks a key difference between live and dead leaves which can probably be traced to either differences in their lignocellulosic properties or differences in the state of their water content. Treating 5% of the water as "bound" water (see Table 2), the remainder was considered pressurized liquid water and was evaporated as a linear function with temperature from 240°C to 300°C based on the observed range of the temperature plateau (presented in Figure 7). This resulted in a better mass fit, as shown for the first two live cases (Figure 11, compare Figure 10). In Figure 10, water release (modeled as "bound" water) is completed after 8 to 10 seconds; in Figure 11, water release (modeled mostly as "bulk" water) is completed after about 7 seconds. In Figure 10, most water is released after 5 seconds while in Figure 11, most water is released before 4 seconds. This distinction in water behavior supports the concept that live water is held differently in a leaf than dead leaf moisture, and that live moisture, due to that difference, is a more effective coolant for burning leaves than adsorbed water as held by dead leaves.

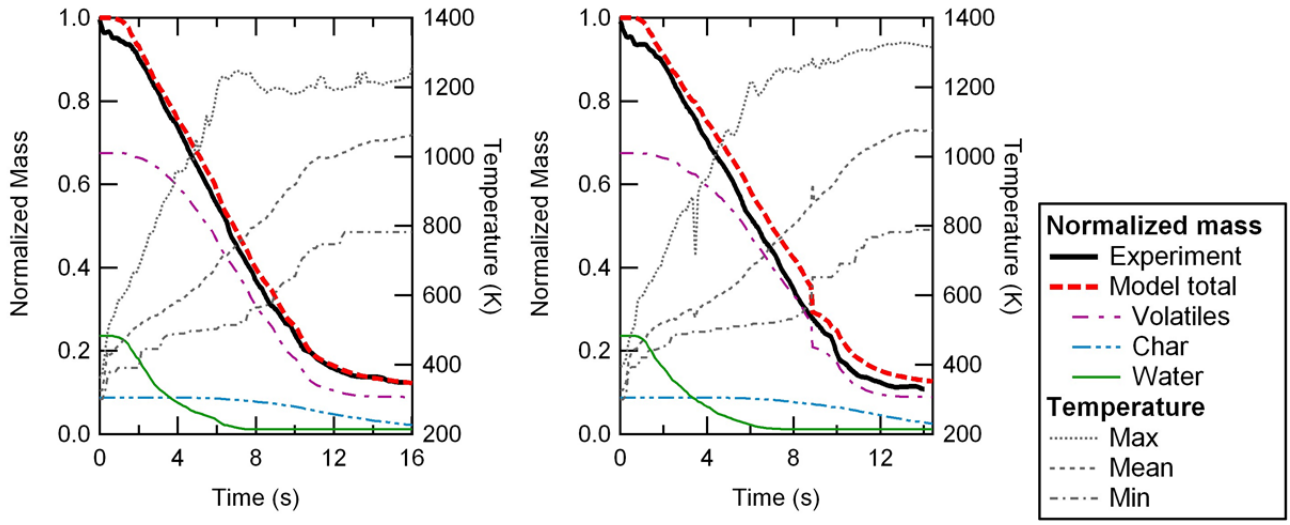


Figure 11. Comparison of experimental and modeled mass release for live leaves using linear evaporation function from 240°C to 300°C (compare to the first two runs in Figure 10).

5. Conclusions

Dead and live leaves have a different thermal response to heating at wildfire conditions. Live leaves maintain much of the leaf between 200°C and 300°C for several seconds while dead leaves have a more regular temperature increase. This difference as well as mass release modeling marks a difference between live and dead moisture, with live moisture being pooled as bulk water and providing cooling to the leaf while dead moisture is bound nearly exclusively within the cell wall polymer matrix and behaving very differently from bulk water. Differences in lignocellulosic composition or quality between live and dead leaves may also play a role in these differences, but this was not investigated. More research is needed to better understand these differences and to understand how water state might affect the bulk combustion behavior of live and dead foliage, for instance, by changing the flame composition and heat release due to the manner and timing of water release.

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