

Supplemental Material

1. Estimating the N lost to N₂ and N₂O.

The loss of N to N₂ and N₂O in the stack fires was estimated using the fuels data compiled in the Supplemental Material of Selimovic et al., [2018], and the ash data listed in Table S1 of this Supplemental. The fuels data used in the analysis include: Total Fuel Mass, Total Residual Mass, %N Fuel (by weight), %C Fuel (by weight), and the ash data used in the analysis include: the ratio Ash/Burned Fuel, %N Ash (by weight), %Total C Ash (by weight). The gas phase measurements used for the analysis include: Total Reactive Nitrogen (N_r) reported here, and Total Carbon (CO₂ + CO + CH₄ + ΣNMOC + Particle Carbon), calculated in the manner described by Selimovic et al., [2018]. In the calculations below, we assume the Ash/Burned Fuel, %N Ash and %C Ash are the same for the stack burns as the quantities measured during the room burns. These assumptions add only a modest level of uncertainty since the fuels burned in each set of experiments were subsets of large samples of each fuel type, and the use of Ash/burned fuel removes some of the variability in fire conditions and extent, as it accounts for unburned residual fuel. Another source of uncertainty is the application of fuel moisture measurements. In general, the correction for fuel moisture applies equally to foliage (needles) and woody biomass, but there are occasions where those were not equal or the residual fuel was more heavily represented by woody biomass. Residual masses were often 10% of the initial fuel mass, but sometimes as high as 50% of initial mass. Considering these factors, we estimate an uncertainty in the mass balance calculations to be ±25%.

The mass balance equations for Nitrogen and Carbon are;

$$\begin{aligned} \text{Mass N emitted} &= \text{Mass Total Fuel} \cdot \%N \text{ Fuel} - \text{Mass Ash} \cdot \%N \text{ Ash} - \text{Mass Unburnt residual} \\ \%N \text{ Fuel} &= \text{Mass (N}_r + \text{N}_2 + \text{N}_2\text{O}) \end{aligned} \quad \text{Eq. S1}$$

$$\text{Where: Mass Unburnt residual} = \text{Mass Total Residual} - \text{Mass Ash} \quad \text{Eq. S2.}$$

and

$$\begin{aligned} \text{Mass C emitted} &= \text{Mass Total Fuel} \cdot \%C \text{ Fuel} - \text{Mass Ash} \cdot \%C \text{ Ash} - \text{Mass Unburnt residual} \\ \%C \text{ Fuel} &= \text{Mass (CO}_2 + \text{CO} + \text{CH}_4 + \text{NMOC} + \text{Particle C}) = \text{Mass Total C} \end{aligned} \quad \text{Eq. S3}$$

$$\text{Where: Mass Unburnt residual} = \text{Mass Total Residual} - \text{Mass Ash} \quad \text{Eq. S4.}$$

There are measured concentrations of N_r, and Total C, however there were not accurate measurements of the actual flow rates of air up the stack. The concentrations (mixing ratios) of N and C species are related to mass flow by several constants, e.g. pressure, temperature, Avogadro's number, all of which are the same for both N and C, except for the atom weights. As a consequence, we can use the ratios of concentrations to obtain the following relationships;

$$\frac{(\text{N}_r + \text{N}_2 + \text{N}_2\text{O})}{\text{Total C}} = \frac{(\text{Mass Total Fuel} \cdot \%N \text{ Fuel} - \text{Mass Ash} \cdot \%N \text{ Ash} - \text{Mass Unburnt residual} \cdot \%N \text{ Fuel})/14g}{(\text{Mass Total Fuel} \cdot \%C \text{ Fuel} - \text{Mass Ash} \cdot \%C \text{ Ash} - \text{Mass Unburnt residual} \cdot \%C \text{ Fuel})/12g} \quad \text{Eq.S5}$$

$$\text{Total C} = \frac{(\text{Mass Total Fuel} \cdot \%N \text{ Fuel} - \text{Mass Ash} \cdot \%N \text{ Ash} - \text{Mass Unburnt residual} \cdot \%N \text{ Fuel})/14g}{(\text{Mass Total Fuel} \cdot \%C \text{ Fuel} - \text{Mass Ash} \cdot \%C \text{ Ash} - \text{Mass Unburnt residual} \cdot \%C \text{ Fuel})/12g} \quad \text{Eq.S6}$$

Recognizing that;

$$\frac{(\text{N}_2 + \text{N}_2\text{O})}{\text{Total C}} = \frac{(\text{Mass Total Fuel} \cdot \%N \text{ Fuel} - \text{Mass Ash} \cdot \%N \text{ Ash} - \text{Mass Unburnt residual} \cdot \%N \text{ Fuel})/14g}{(\text{Mass Total Fuel} \cdot \%C \text{ Fuel} - \text{Mass Ash} \cdot \%C \text{ Ash} - \text{Mass Unburnt residual} \cdot \%C \text{ Fuel})/12g} \quad \text{Eq.S6}$$

$$\text{Total C} = \frac{(\text{Mass Total Fuel} \cdot \%N \text{ Fuel} - \text{Mass Ash} \cdot \%N \text{ Ash} - \text{Mass Unburnt residual} \cdot \%N \text{ Fuel})/14g}{(\text{Mass Total Fuel} \cdot \%C \text{ Fuel} - \text{Mass Ash} \cdot \%C \text{ Ash} - \text{Mass Unburnt residual} \cdot \%C \text{ Fuel})/12g} \quad \text{Total C}$$

The ratio of Eqs. S6 and S5 gives;

$(N_2 + N_2O) / (N_r + N_2 + N_2O) =$ The fraction of N lost as N_2 and N_2O , estimated from fuel and ash composition and the measured quantity N_r /Total Carbon.

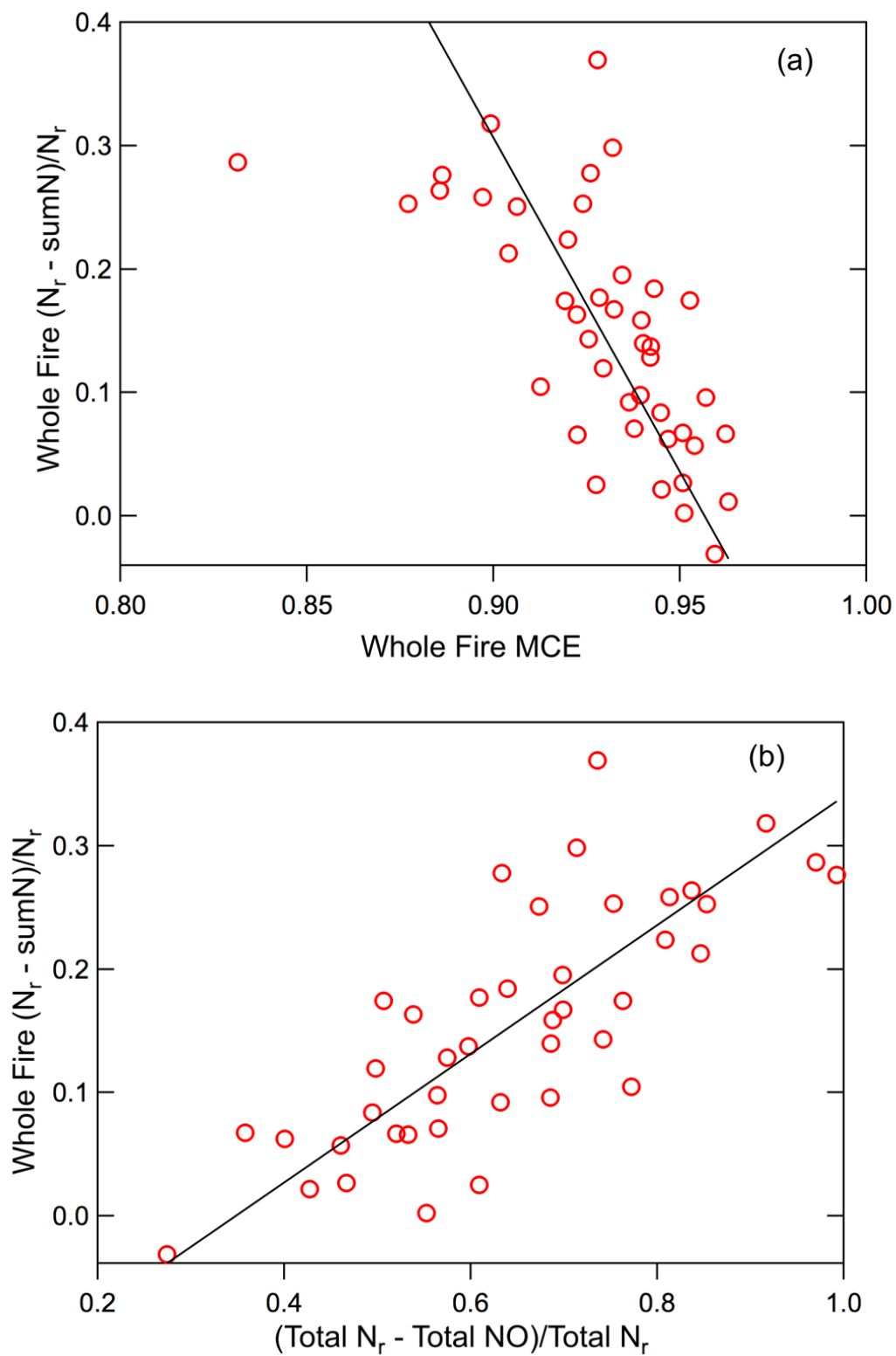


Figure S1. The relative amounts of residual N_r vs MCE (a) and vs $(N_r - \text{sum}N)/N_r$ (b) for whole fires. The lines are orthogonal-distance-regression fits that assume uncertainty in each variable.

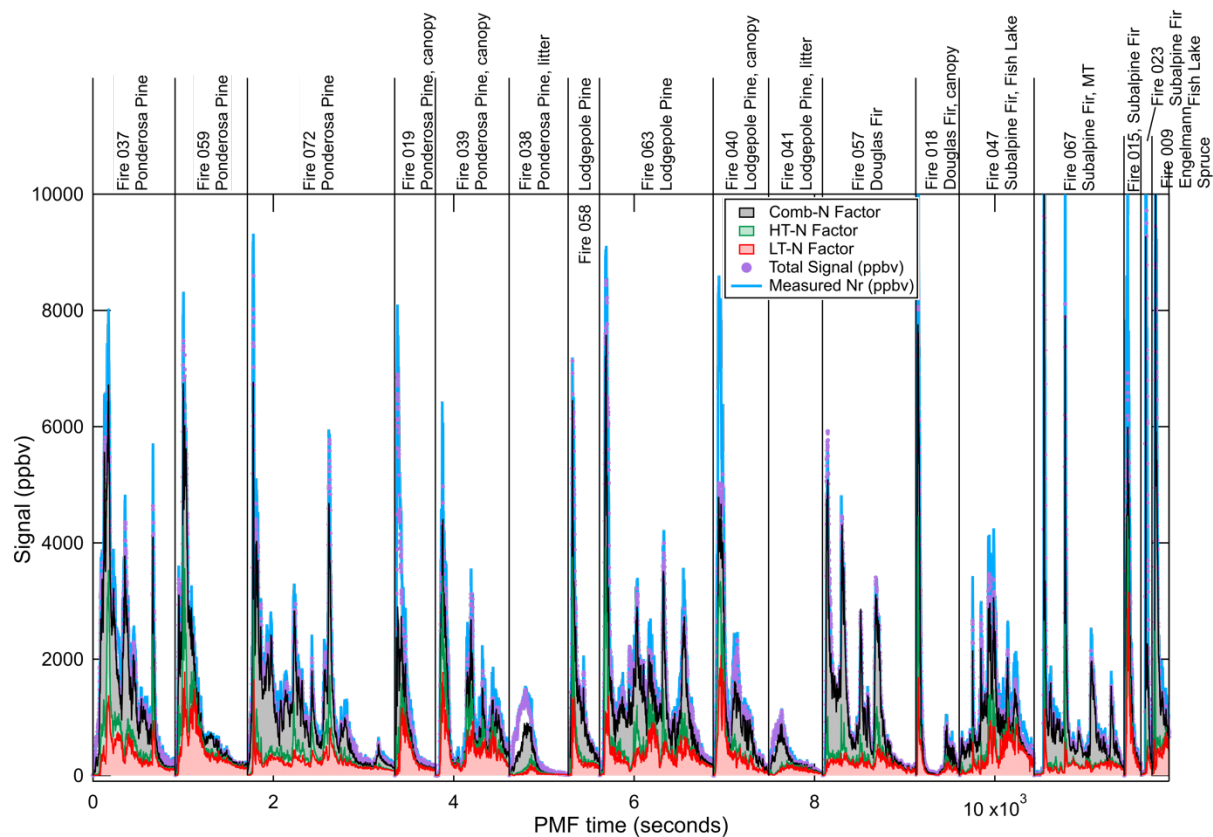


Figure S2. Combined PMF timeline for the fires that involved coniferous fuels. The measured N_r is shown as a blue line, the total of N_r compounds used in the PMF is shown as purple points, and Comb-N (grey), HT-N (green), and LT-N (red) factors plotted stacked on top of one another. The vertical lines show where individual fires start and stop.

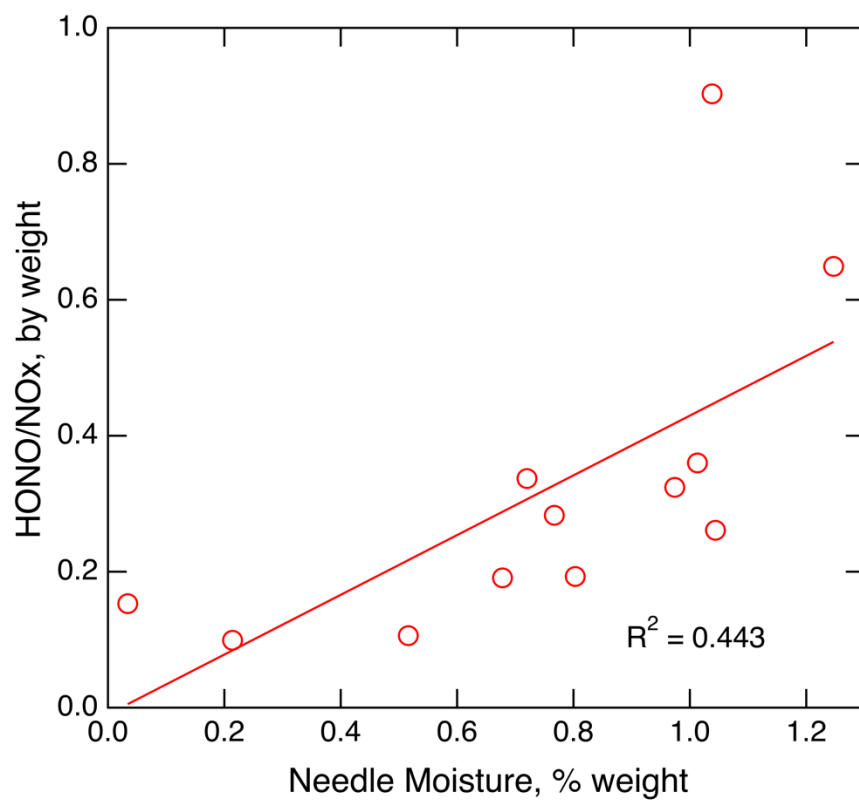


Figure S3. The correlation of HONO/NO_x (by mass) with needle moisture for fires that were canopy fuels only (Fires 015, 017, 018, 019, 020, 023, 025, 039, 040, 044, 045, and 064).

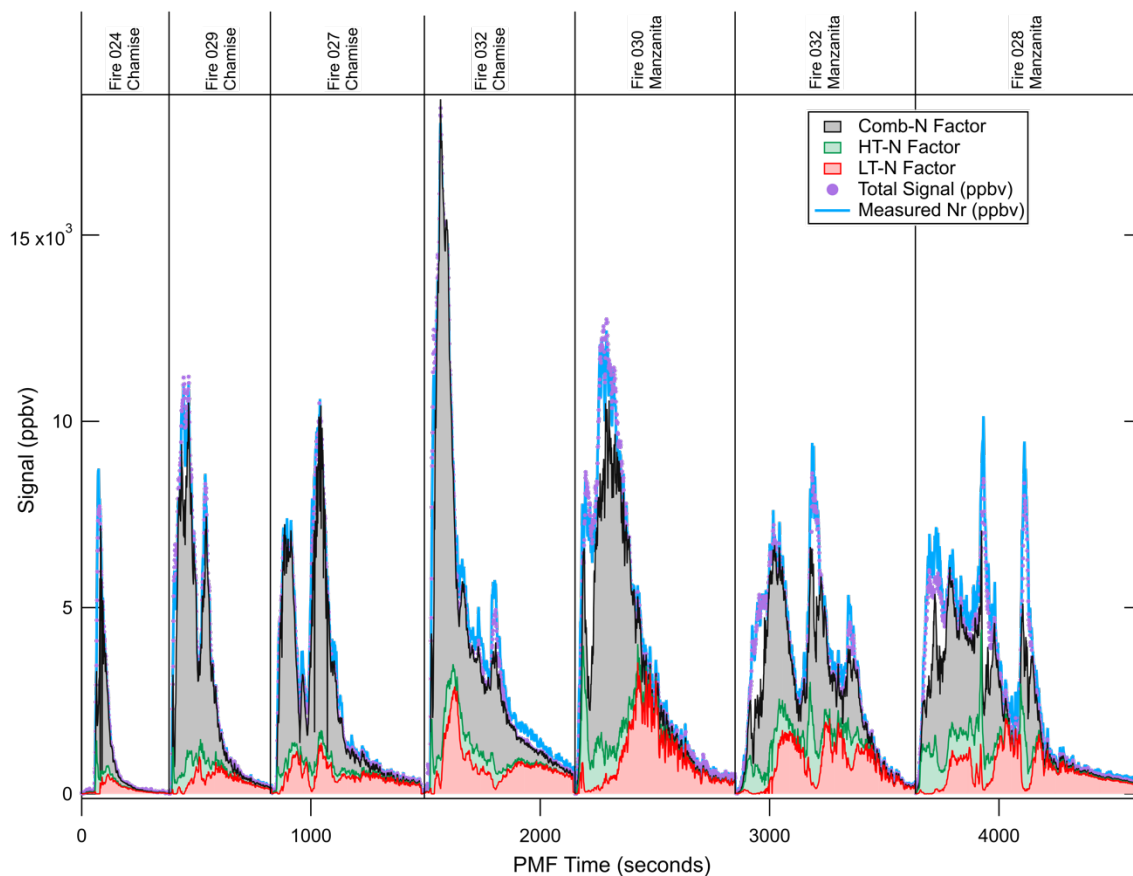


Figure S4. The timeline for the combined PMF analysis of chaparral fuels. The measured N_r is shown as a blue line, the total of N compounds used in the PMF is shown as purple points, and Comb-N (grey), HT-N (green), and LT-N (red) factors plotted stacked on top of one another. The vertical lines show where individual fires start and stop.

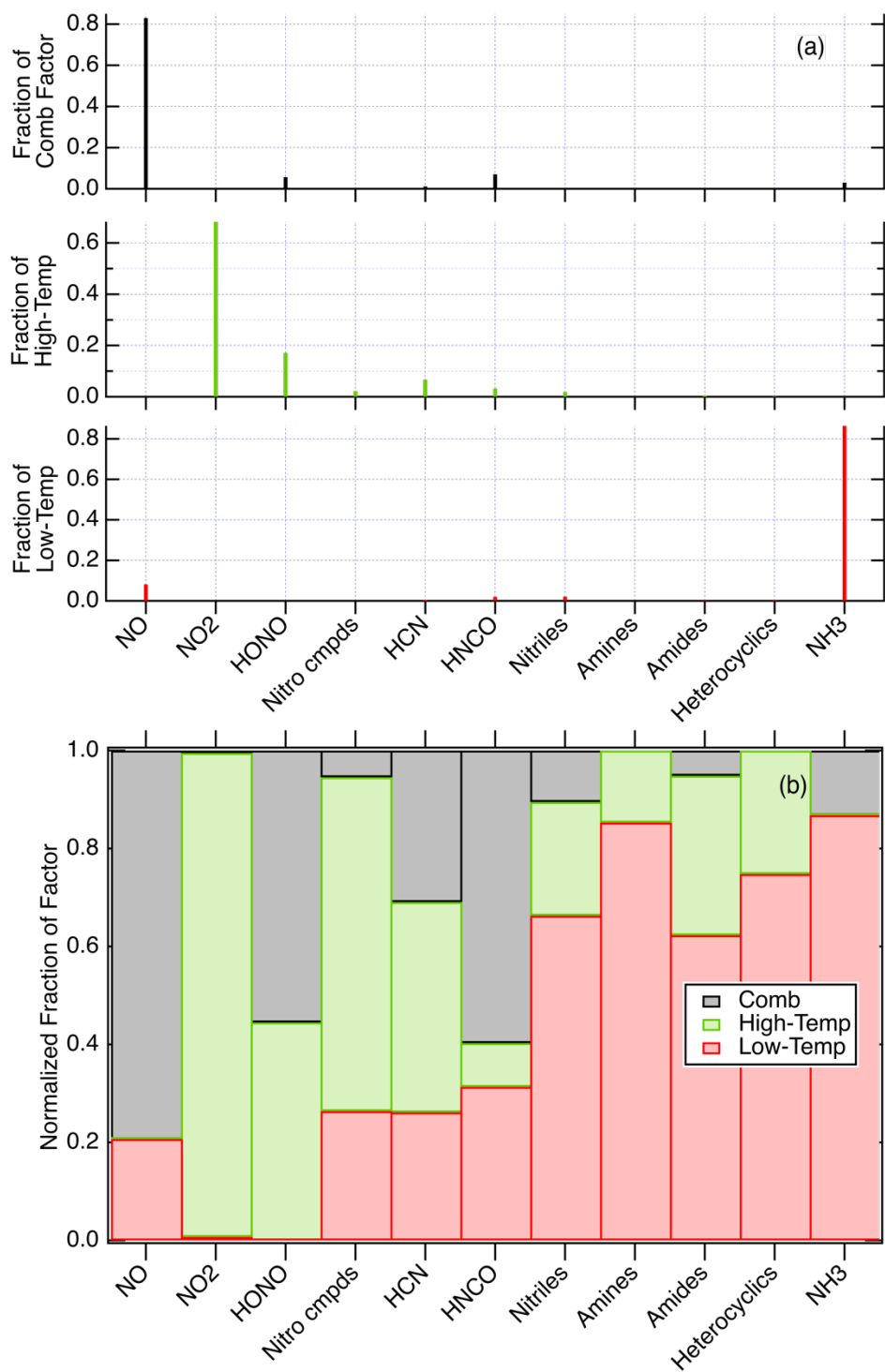


Figure S5. The contributions of nitrogen species to the factors that simulate the emissions from chaparral fuels shown in Figure S3 (panel a), and the fraction of each compound or class found in each factor (panel b).