Laboratory and Ambient Studies of Water Uptake by and Optical Properties of Wildfire Smoke: Role of Fuel Chemistry, Combustion Phase, and Age

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Abstract

Carbonaceous aerosols (CAs) from biomass burning (BB) have increased substantially with the observed warming and drying of the US. While wildfires are projected to intensify in the future missing knowledge of BB CAs hampers assessments. Observations show that warming effects of BB CAs can dominate over cooling effects due to enhanced light absorption by internal mixing. However, if internal mixing reduces the aerosol lifetime it would lower their atmospheric burden. We report observations of BB smoke to help elucidate mechanisms that control this tradeoff.

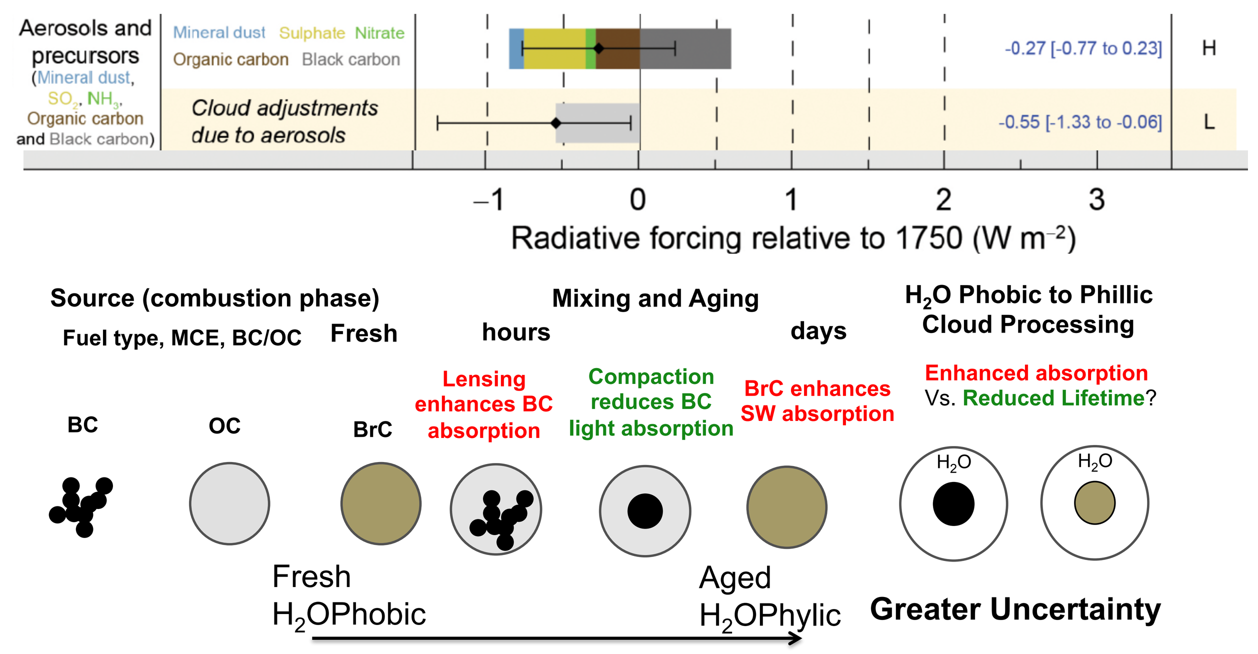


Fig 1. Aerosol Radiative Forcing and Mixing Effects on CA properties

Fresh emissions from ~32 fuels burned under flaming and smoldering conditions were investigated. We measured aerosol size distribution, absorption, scattering and extinction at multiple wavelengths, water uptake at 85% relative humidity ($f^{RH85\%}$) with a humidity controlled dual nephelometer, optical properties with a 3-wavelength photoacoustic (PASS-3), refractory CA mass with a SP2, and composition with a SP-AMS. We find that the observed hygroscopicity was intimately linked to the chemical composition of the fuel. We compare our laboratory results with ambient fire results that spanned aging times of less than an hour and 3 days to evaluate mixing rules and the chemical changes. Our goal is to develop a mechanistic framework to predict water uptake and optical properties of smoke s as a function of fuel, fire intensity and age.

Smoke f(RH), Optical & SP-AMS Measurements

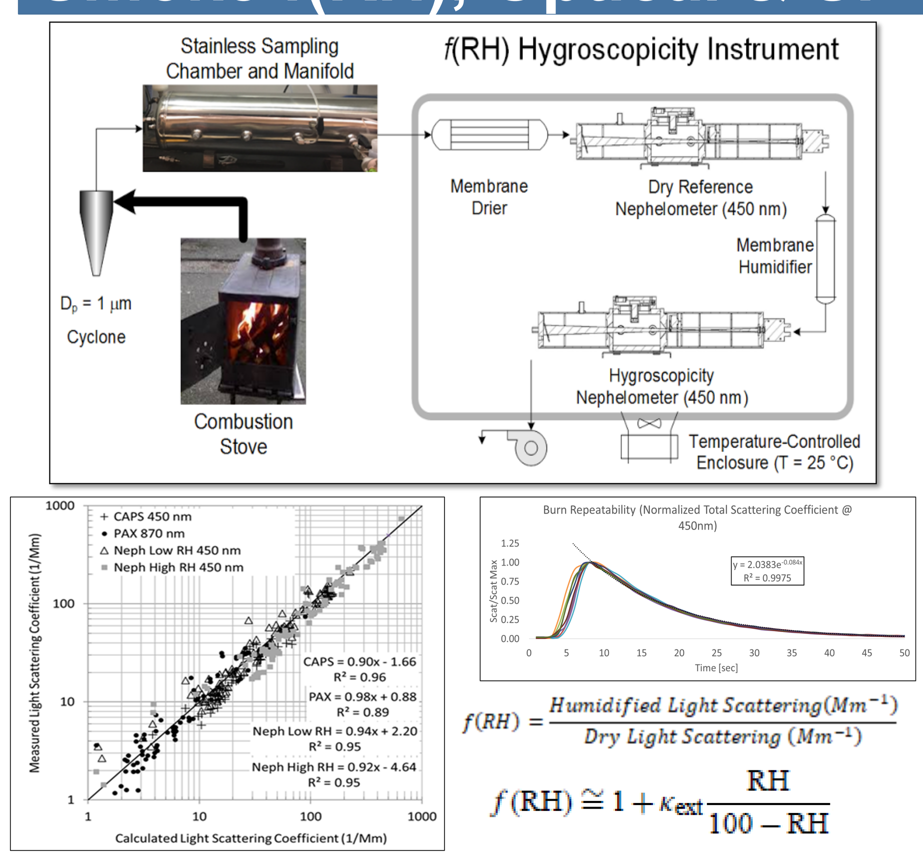
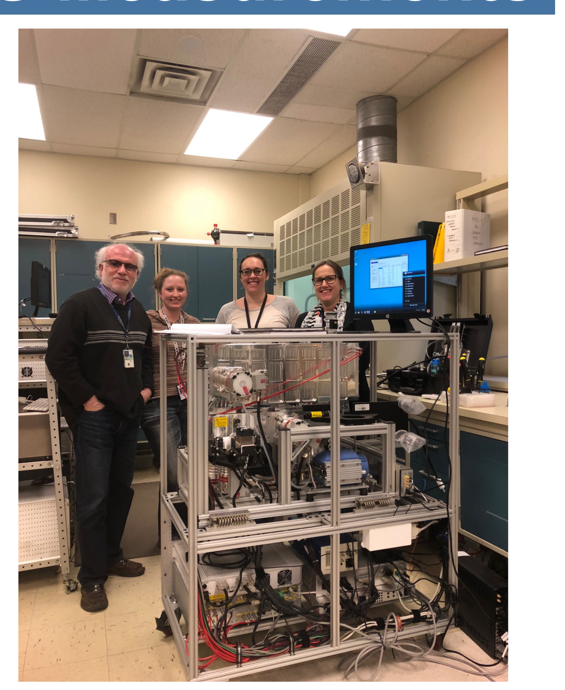


Fig 2. Humidified Nephelometer Calibrations, Repeatability and Optical and Chemical instruments



- Humidity controlled dual nephelometer.
- Photoacoustic absorption & nephelopmeter.
- Size distributions with SMPS and laser sizer.
- Bulk off-line & SP-AMS chemical analysis.

Laboratory Results: Hygroscopicity

The mean hygroscopicity of BB CAs from various fuels ranged from nearly hydrophobic ($f^{RH85\%} = 1$) to very hydrophilic ($f^{RH85\%} = 2.1$) values typical of pure deliquescent salts. We also measured some $f^{RH85\%}$ values <1 indicative of particle collapse at high RH. The κ values varied from 0.004 to 0.18 and correlated well with fuel and smoke inorganic content. Invasive halophytes with high salt content exhibit greater water uptake than native coniferous species with low inorganic content. Combustion temperature and phase play a secondary role. High temperature ignition methods create flaming conditions that enhance hygroscopicity while lower temperature smoldering conditions diminish hygroscopicity. We correlate the measured smoke or wood inorganic content with κ to construct an empirical relation.

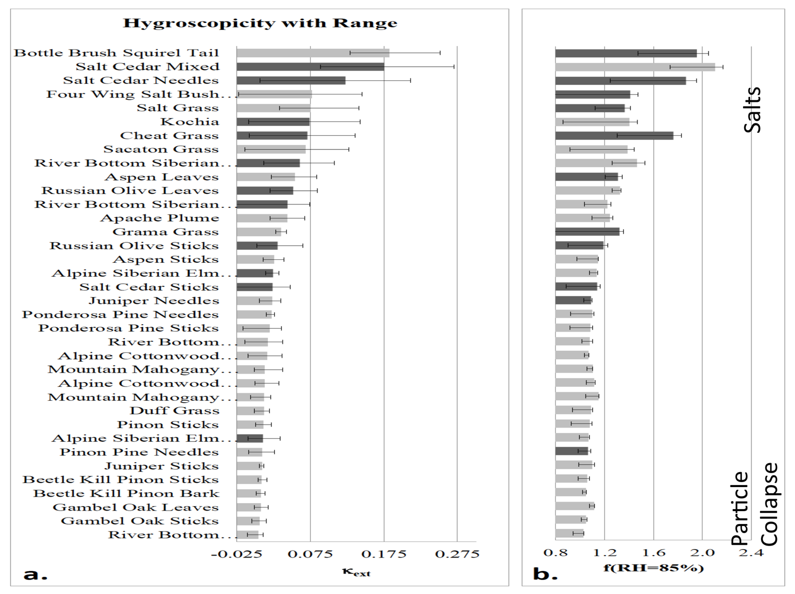


Fig 3. $f^{RH85\%}$ and κ_{ext} versus fuel type

Fuel Type	Lower Combustion Temperatures	Higher Combustion Temperatures
Evergreen Needles and Woods	Low Hygroscopicity $Kappa_{avg}$: 0.008 $Kappa_{nin}$: 0.003 $Kappa_{max}$: 0.012	Low Hygroscopicity $Kappa_{avg}$: 0.014 $Kappa_{nin}$: -0.008 $Kappa_{max}$: 0.040
Deciduous Woods	Low Hygroscopicity $Kappa_{avg}$: 0.008 $Kappa_{nin}$: -0.002 $Kappa_{max}$: 0.017	Low Hygroscopicity $Kappa_{avg}$: 0.014 $Kappa_{nin}$: -0.005 $Kappa_{max}$: 0.041
Deciduous Leaves	Low Hygroscopicity $Kappa_{avg}$: 0.007 $Kappa_{nin}$: -0.007 $Kappa_{max}$: 0.027	Moderate Hygroscopicity $Kappa_{avg}$: 0.032 $Kappa_{nin}$: -0.011 $Kappa_{max}$: 0.086
Grasses (Native and Invasive)	Moderate Hygroscopicity $Kappa_{avg}$: 0.025 $Kappa_{nin}$: 0.006 $Kappa_{max}$: 0.100	High Hygroscopicity $Kappa_{avg}$: 0.098 $Kappa_{nin}$: 0.004 $Kappa_{max}$: 0.234
Halophytic and Salt Tolerant	Moderate Hygroscopicity $Kappa_{avg}$: 0.036 $Kappa_{nin}$: -0.013 $Kappa_{max}$: 0.179	High Hygroscopicity $Kappa_{avg}$: 0.056 $Kappa_{nin}$: -0.004 $Kappa_{max}$: 0.266

Increasing Hygroscopic Response

Fig 4. κ_{ext} variation with plant phenotypes

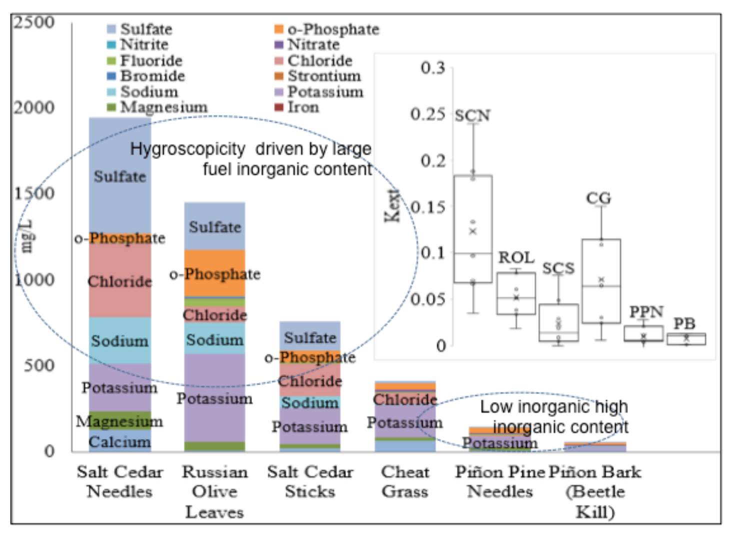


Fig 5. Fuel ion content dependence of κ_{ext}

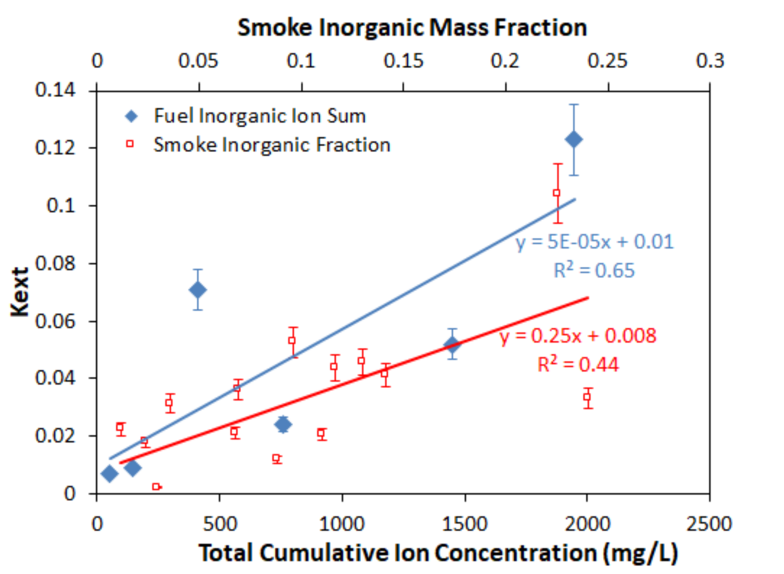


Fig 6. κ_{ext} vs. inorganic fraction or fuel ion content

Laboratory Results: Optical Properties

We measured light scattering and absorption at 405, 532 and 780nm with a photoacoustic extinctiometer (PASS-3) and size distributions with a SMPS. To understand the absorbing aerosols optical properties we plot the single scatter albedo (SSA) at 405 nm against the Absorption Angstrom Exponent (AAE) (405/780nm) for 27 burns. While there is large variability between fuels and burns distinct patterns emerge that we interpret using Mie theory constrained by particle size and refractive indices for organic, red-brown and black carbon. Regimes are identified by Mie theory, and used to bin these. At ignition we see large brown carbon particles (high SSA, AAE) that transition to low AAE abruptly (constant SSA) or gradually (decreasing SSA) to a black, brown carbon or organic carbon state at the end.

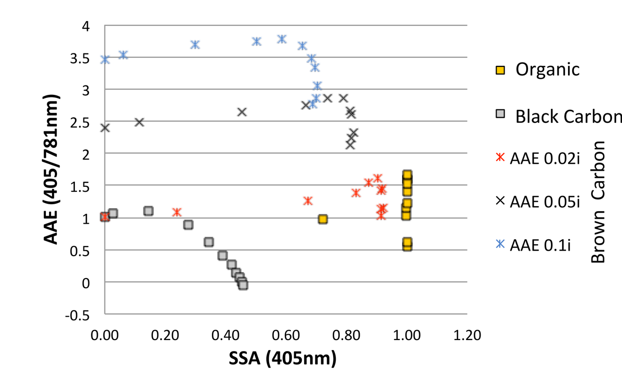


Fig 7. AAE vs. SSA. Mie results for OC, BrC and BC as a function of size highlighted

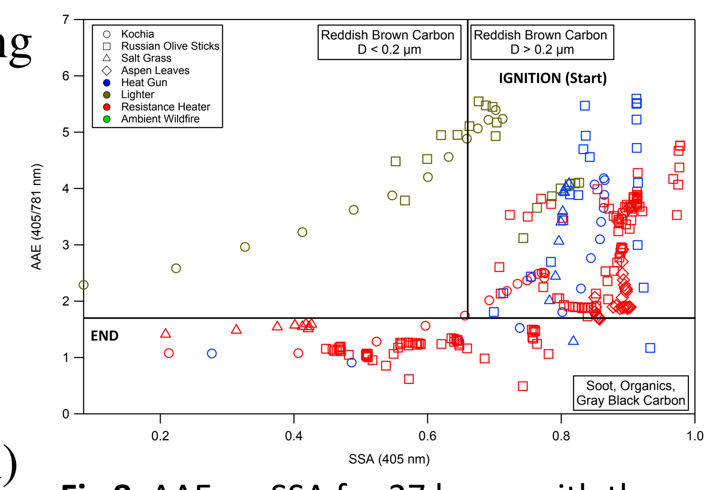


Fig 8. AAE vs. SSA for 27 burns with the distinct CA optical regimes highlighted.

Ambient Fire Observations

We sampled smoke from 5 wildfire plumes that included fresh plumes from 4 small to moderate sized fires and control burns near Los Alamos, NM and an aged plume (>3 days) from the large labor day Pacific NW fires in 2017. The Los Alamos fires burned coniferous and mixed-coniferous species including ponderosa, pinion, juniper, and deciduous aspen. Ambient light scattering measured during the larger smoke impacted events, occurring on June 27th, was determined to have a $\kappa_{ext} = 0.024 \pm 0.005$ ($f^{RH85\%}) = 1.15$). Using laboratory calculated hygroscopicity for the aforementioned fuels, a linear combination of water uptake was calculated as $\kappa_{ext} = 0.022 \pm 0.01$($f^{RH85\%}) = 1.15$). This good agreement is promising for the use of mixing rules to predict water uptake by biomass burning from fuel composition data. The effects of aging the long-range Pacific NW fire smoke that burned similar fuel was small. However, we do see variability in κ_{ext} for local fires, particularly prescribed burns could that result from differences in fuel type and combustion phase that we are investigating.

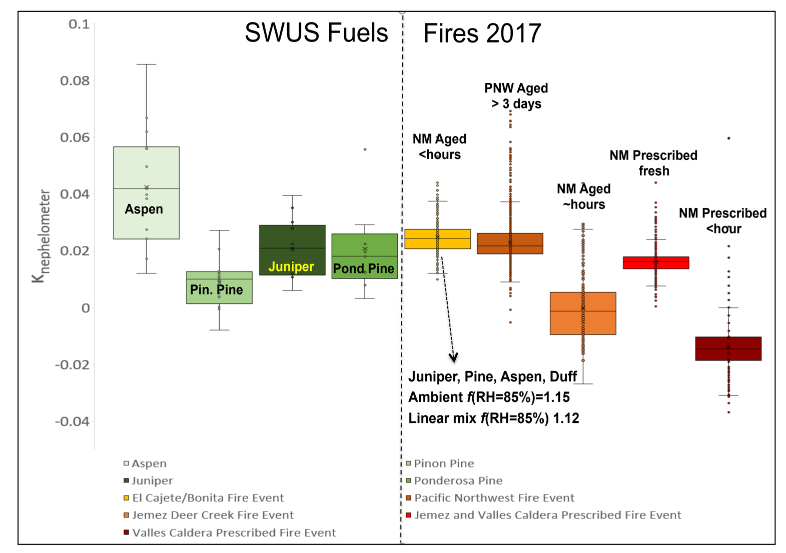


Fig 9. Comparison of lab. and ambient fire κ_{ex} to evaluate mixing rules and aging effects

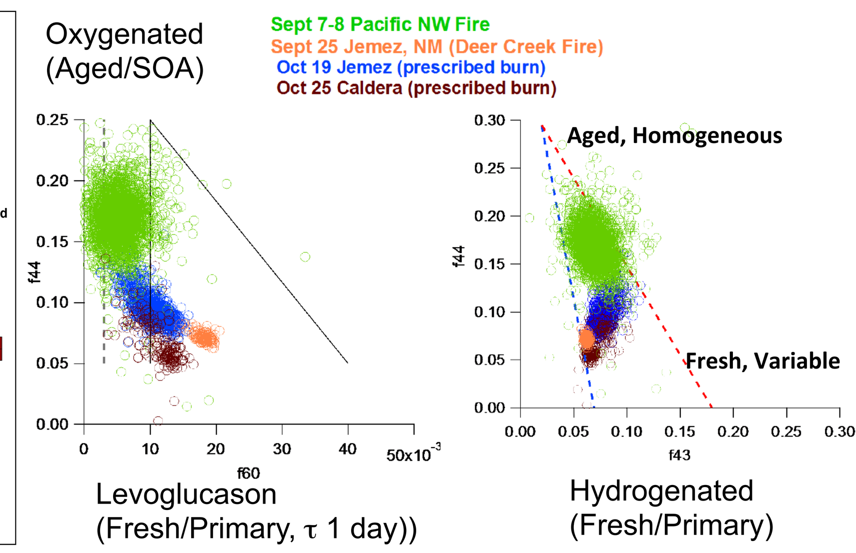


Fig 10. Analysis of the SP-AMS data to discriminate aged and fresh BB smoke.

We also sampled the chemical composition of the ambient fire aerosols with a new Soot Particle Aerosol Mass Spectrometer (SP-AMS) run in the thermal ionization mode. We clearly resolve the chemical differences between the aged 3 day old smoke from the Pacific NW fires and the fresh smoke from the local Jemez fires. We use the mass f_{44}, f_{43}, and f_{60} fractions as a measures of secondary oxygenated, primary hydrocarbons, and primary levoglucosan components in smoke. The aged Pacific NW smoke is highly oxidized (large f_{44}), contains no primary levoglucosan (f_{60}) that has a lifetime of about a day, and low primary hydrogenated (f_{44}) compounds. The fresh smoke has high f_{60} and low f_{44} values. The triangle summarize the behavior from published laboratory and field studies that our data follows.

Conclusions

- We demonstare that fuel *inorganics* drives smoke hygroscopicity to 1st order and report an empirical relation between them for use in models.
- *Flaming* fire smoke exhibits *higher hygroscopicity* than smoldering *fires* with other detectable 2nd order effects: Large Inorganic Fraction >> Little Inorganic, Flaming > Smoldering, Leaves > Woods and Barks Deciduous > Evergreen, and Invasive > Natives.
- Mixing rules can predict κ_{ex} for fresh ambient wild-fire smoke. Prescribed burns smoke κ_{ex} differs from wildfires and aging can also effect it.
- Optical properties of our burn experiments can be interpreted using Mie theory. For grasses, we observe large brown carbon aerosols at ignition that transition to mixed organics and finally black carbon at the end.
- Our new SP-AMS quantifies aging effects on chemistry of BB CAs.
- ***Publications***: Carrico et al. *Atm. Env.* 2018, Gomez et al. *JGR-Atm*. 2018.

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