Particle emissions from laboratory combustion of wildland fuels: In situ optical and mass measurements

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[1] Time-resolved optical properties of smoke particles from the controlled laboratory combustion of mid-latitude wildland fuels were determined for the first time using advanced techniques, including cavity ring-down/cavity enhanced detection (CRD/CED) for light extinction and two-wavelength photoacoustic detection for light absorption. This experiment clearly resolves the dependence of smoke properties on fuel and combustion phase. Intensive flaming combustion during ponderosa pine wood (PPW) burning produces particles with a low single scattering albedo of 0.32 and a specific mass extinction efficiency of $8.9 \, \text{m}^2 \, \text{g}^{-1}$. Burning white pine needles (WPN) features a prolonged smoldering phase emitting particles that are not light-absorbing and appear much larger in size with an extinction efficiency $\approx 5 \, \text{m}^2 \, \text{g}^{-1}$.


1. Introduction

[2] Biomass burning, ranging from natural forest fires to different types of anthropogenic combustion, is one of the largest sources of accumulation-mode particles on a global scale [Kasischke and Penner, 2004], strongly affecting the atmospheric radiation budget. During the last decade, there have been extensive studies characterizing biomass-burning particles; however, most key parameters related to particle-radiation interactions, such as particle size, black carbon (BC) content, and mass specific absorption/scattering/extinction ($E_{ap}/E_{sp}/E_{pp}$), are quite inconsistent in the literature. A recent review [Reid et al., 2005a] attributes the inconsistency to: 1) the dynamic nature of fires; 2) variations in smoke aging processes; and 3) differences in measurement techniques. Most of the previous measurements were made during wildland fires [see Reid et al., 2005a] and reflect a mixture of fuels and of flaming and smoldering combustion phases. Untangling the influence of individual fuels and combustion phases is essential for estimating emissions and impacts from wildland fires because particle characteristics and emission factors vary strongly with these parameters. This untangling can be achieved through laboratory combustion of individual fuels and the time-resolved characterization of combustion products as function of combustion phase.

[3] This paper demonstrates mass and advanced optical measurements for smoke particles emitted from the controlled laboratory combustion of individual wildland fuels. These measurements not only determine $E_{ap}$, $E_{sp}$, and $E_{pp}$ but also infer particle size and BC fraction that are most useful for modeling aerosol radiative forcing. This experiment is part of an integrated study conducted at the United States Forest Service Fire Science Laboratory (FSL, Missoula, MT) 19–26 November 2003 with the objectives of characterizing smoke/flame properties, quantifying emission factors, and testing innovative measurement techniques. Emphases have been put on fuels commonly burned in mid-latitude forests.

2. Optical Model

[4] Fresh smoke particles can be described as a two-component system: a light-absorbing BC component and a non-absorbing component containing organic matter (OM) as well as other minor constituents. Extensive microscopic examination of smoke particles [see Reid et al., 2005b and references therein; Chakraborty et al., 2006] indicate that they are internally mixed for the most part and have a uniform density irrespective of their sizes.

[5] Figure 1 demonstrates how particle diameter and BC fraction might influence the single scattering albedo ($\omega$) and specific mass extinction efficiency ($E_{ap} = E_{sp} + E_{pp}$). It is based on a standard Mie scattering code [Wiscombe, 1980] with Bruggeman mixing rule [Lesins et al., 2002], recommended for a mixture of insoluble particles where the dry aerosol components (i.e., BC and OM) are interspersed. A refractive index $n_i$ of 1.96–0.66i at 532 nm is assumed for BC due to its proven effectiveness in several optical-closure analyses [e.g., Fuller et al., 1999; Hand and Kreidenweis, 2002]. The rest of the material is modeled with $n_i$ of 1.42–0.001i; resulting in a mixture $n_i$ of 1.45–0.03i if the BC volume fraction is 5%. The BC and OM mass densities are assumed to be 1.7 g cm$^{-3}$ [Haywood et al., 2003] and 1.2 g cm$^{-3}$ [Turpin and Lim, 2001], respectively. A
pure BC sphere of 0.14 μm diameter would have ω, $E_{\text{ep}}$, and $E_{ap}$ of 0.3, 10 m$^2$ g$^{-1}$, and 7 m$^2$ g$^{-1}$, respectively. $E_{ap}$ of 4.2–4.7 m$^2$ g$^{-1}$ and ω of 0.82–0.92 at mid-visible wavelengths have been reported for six types of wildland fires: fresh/aged grass/savanna, tropical, and temperate/boreal with higher values associated with fresh temperate/boreal fires [Reid et al., 2005a]; effective particle diameters ($d_{ep}$) of 0.27 – 0.33 μm can be derived from Figure 1. Small differences between this optical $d_{ep}$ and the measured volume median diameter (VMD, mostly 0.2 – 0.3 μm) [see Reid et al., 2005b] are related to particle size distribution, non-spherical shape of smoke particles, and variability of BC and OM refractive indices and densities. The same ranges of $E_{ap}$ and ω could also yield $d_{ep} = 0.9 – 1.1$ μm (Figure 1) but this size range is seldom observed. From Figure 1, BC may constitute only 5 – 7% of the particulate emission in these fires.

Particle size and BC fraction referred to hereafter are all retrieved from Figure 1. Chand et al. [2005] observe a larger $E_{ap}$ of 6.5–8.2 m$^2$ g$^{-1}$ and ω of 0.98–0.99 during smoldering combustion of Indonesian peat; these are consistent with smoke particles of 0.5–0.7 μm diameter and nearly BC free.

3. Experiment

The combustion facilities at the FSL contain a continuously weighed fuel bed (80 × 210 cm) where the burning occurs, and a 1.6 m diameter exhaust stack with a 3.6 m diameter inverted funnel opening 2 m above the fuel bed [Christian et al., 2004]. The stack extends to the ceiling (≈17 m high) where the sampling platform is located. The fuels were selected to be representative of mid-latitude forest burning [Chakrabarty et al., 2006]. Most fires burned ≈ 250 g fuel and typically lasted 5–10 minutes, evolving through ignition, flaming, and smoldering phases. Carbon dioxide (CO$_2$), carbon monoxide (CO), and nitrogen dioxide (NO$_2$) were monitored by commercial instruments on the sampling platform. The modified combustion efficiency (MCE = CO$_2$/[CO$_2$ + CO]) [e.g., Yokelson et al., 1996] is used to quantify combustion efficiency.

Total suspended smoke particles were sampled with two photoacoustic instruments (PA) at 532 nm and 1047 nm [Arnott et al., 2000], a hybrid cavity ring-down/enhanced detector (CRD/CED) at 532 nm [Moosmüller et al., 2005], and a tapered element oscillating microbalance (R&P TEOM, Series 1105). A PA measures the light absorption coefficient ($\sigma_{ap}$) in the smoke directly at 10-s time resolution with a minimum detection limit (MDL) of 1–2 Mm$^{-1}$. The response of PA to light scattering and relative humidity is negligible [Arnott et al., 2003], but NO$_2$ produced during combustion may interfere with the absorption at 532 nm (≈0.306 Mm$^{-1}$ ppb NO$_2$) [e.g., Arnott et al., 2000]. Spectral dependence of particle light absorption is derived from NO$_2$-corrected absorption at the two wavelengths (i.e., $\alpha_{ap} = -\ln [\sigma_{ap,\lambda}/\sigma_{ap,\lambda_0}]/\ln[\lambda/\lambda_0]$). The TEOM is designed specifically for source sampling of particle mass; 10-s averages were used with a MDL ≈50 μg m$^{-3}$ and uncertainty <10% for mass concentration >500 μg m$^{-3}$. The TEOM was calibrated with gravimetric analysis of time-integrated Teflon-filter samples. Combining PA and TEOM has been demonstrated for characterizing diesel exhaust [Moosmüller et al., 2001a, 2001b]. In that study BC and OM masses agree best with those determined by the thermal method when an $E_{ap}$ of 7.36 m$^2$ g$^{-1}$ is assumed for BC.

The extinction ($\sigma_{ap}$) measurement based on light attenuation has long been limited by its poor sensitivity. The CRD technique has recently achieved a sensitivity better than 1 Mm$^{-1}$ by implementing a multiple-kilometer optical path in a compact cell with highly reflective mirrors and detecting the energy loss in the cell as a function of time due to aerosol extinction [Moosmüller et al., 2005 and references therein]. The complementary CED technique enhances its dynamic range up to 10$^6$. Scattering coefficients ($\sigma_{sp}$) were then determined from the difference between CRD/CED and PA measurements. 10-s averaged $\sigma_{ap}$, $\sigma_{sp}$, and $\sigma_{ap}$ were divided by 10-s particle mass from TEOM to calculate $E_{ap}$, $E_{sp}$, and $E_{ap}$, respectively. Total and back-hemispheric scattering are usually quantified by integrating nephelometry, but forward scattering detection limited by the truncation angle of a nephelometer [Anderson et al., 1999; Moosmüller and Arnott, 2003] requires empirical corrections based on the scattering Angstrom exponent ($\alpha_{sp}$). FSL also operated a 3-wavelength nephelometer (TSI 3563) side by side with the PAs and CRD/CED to determine $\sigma_{sp}$ (i.e., $\sigma_{sp} = -\ln [\sigma_{sp,\lambda}/\sigma_{sp,\lambda_0}]/\ln[\lambda/\lambda_0]$), which is a qualitative measure of the mean particle size. All these data are baseline subtracted to remove contributions from the ambient air.

Reference soot particles were generated by a standard kerosene lamp. At the sampling platform, a mean soot concentration of 51.6 ± 1.7 μg m$^{-3}$ was measured by TEOM during a 55.7-min period where MCE > 0.98. Average particle ω, $E_{ap}$, $E_{sp}$, and $E_{ap}$ (532 nm) are 0.43, 6.3 m$^2$ g$^{-1}$, 4.8 m$^2$ g$^{-1}$, and 11.1 m$^2$ g$^{-1}$, respectively. These values are comparable with those by Sheridan et al. [2005] and consistent with a $d_{ep}$ of 0.22 μm. The BC mass fraction ($f_{BC}$) is more uncertain since both ω and $E_{ap}$ are insensitive to $x_{BC}$ for 0.85 < $x_{BC}$ < 1. $E_{ap}$ of BC should vary inversely with λ (i.e., $\alpha_{ap} = 1$) for a constant n [e.g.,...
A measured $\alpha_{ap}$ of $0.90 \pm 0.14$ is not significantly different from 1.

Even after the truncation correction, the nephelometer determines a lower scattering efficiency and therefore a lower albedo ($E_{sp} = 2.2 \text{ m}^2 \text{ g}^{-1}$ at 550 nm; $\omega = 0.26$), based on which a $d_{eff}$ of only 0.14 $\mu$m would be predicted for the kerosene soot. Mie theory indicates that $\alpha_{sp}$ is more sensitive to particle size for darker (higher $x_{BC}$) particles; $\alpha_{sp}$ (450/700 nm) changes from 3.5 to 1.4 for pure BC with $d_{eff}$ from 0.14 to 0.22 $\mu$m, while the measured value for kerosene soot is $1.8 \pm 0.1$. Moosmüller and Arnott [2003] demonstrate that highly-absorbing particles are more affected by nephelometer truncation than mostly scattering particles. This truncation loss might not be accurately corrected for.

4. Results and Discussions

Dried ponderosa pine wood (PPW) is a common wildland fuel burned in temperate/boreal forest fires. Burning PPW emits highly refractory smoke from a dominant flaming phase. Figure 2a shows the in situ optical (NO$_2$-corrected)/mass/gas measurements during a typical PPW burning cycle. Following the simplest definition of smoldering combustion as MCE of $<0.9$ [e.g., Yokelson et al., 1996], the PPW combustion does not enter the smoldering phase until the very end of the burning cycle. Pure flaming combustion (MCE > 0.98) during the first 3 minutes contributes $\approx$80% of the total particulate mass emission. The decrease of MCE after this period is associated with a lower combustion temperature after most of the volatile components have been expelled from the PPW and smoldering combustion continues as surface reaction.

An average $\alpha_{ap}$ of $0.89 \pm 0.07$ during the PPW flaming phase is consistent with that for kerosene soot as well as diesel exhaust particles [Kirchstetter et al., 2004]. The relatively lower $\omega$ (on average 0.32) in the PPW smoke can be explained by a smaller particle size ($d_{eff}$ = 0.15 – 0.17 $\mu$m), $E_{sp}$ and $E_{ap}$ decrease as the combustion process proceeds, and this mostly reflects the reduced BC mass fraction, especially after the flaming phase. By the time MCE drops to 0.92 ($\approx$5 min since ignition), $\omega$ reaches 0.6. An $E_{sp}$ of 4.5 m$^2$ g$^{-1}$ then corresponds to a $d_{eff}$ $\approx$ 0.22 $\mu$m and $\approx$14% BC. For ambient aerosols $\alpha_{sp}$ seldom increases with particle size, but $\alpha_{sp}$ increases from 1.9 to nearly 2.5 on the transition from the flaming to the smoldering PPW combustion. This occurs as a result of drastic reductions in BC fraction and imaginary refractive index, on the condition of a minor particle size change.

The combustion of white pine needles (WPN; see Figure 2b) contains a short flaming phase followed by an extended smoldering phase ($\approx$3 min). Though the same amount of WPN and PPW was burned (250 g), the total particulate mass emission from burning WPN is three times higher. Overall WPN burn much less efficiently than PPW. The ignition of WPN emits relatively white particles ($\omega$ = 0.75; $E_{sp}$ = 2 m$^2$ g$^{-1}$) that can be modeled with 5% BC and $d_{eff}$ = 0.17 $\mu$m. As the combustion proceeds, the BC fraction increases along with the combustion temperature and $\omega$ drops to as low as 0.2 implying very small BC particles. The flaming combustion contributes to $\approx$15% of the total particulate emission. $E_{sp}$ is stabilized at $\approx$5 m$^2$ g$^{-1}$ by the time the burning becomes pure smoldering (MCE = 0.85 – 0.88) and the smoke is totally white ($\omega$ > 0.99). The particle $d_{eff}$ appears to increase to $\approx$ 0.36 $\mu$m, which is consistent with a lower $\alpha_{sp}$ of $\approx$1.2. Prior studies [e.g., Reid...
et al., 2005a; Chand et al., 2005) have suggested that smoldering combustion may produce larger particles than flaming combustion due to more OM available for condensation on nuclei particles. An \( E_p \) of 5 m² g⁻¹ is at the higher end of estimates by Reid et al. (2005a) but significantly lower than those in tropical forest smoke [Chand et al., 2005]. \( \alpha_{ap} \) tends to increase with the OM content, averaging at 0.96 and 2.2 for the flaming and smoldering phases, respectively. This has been attributed to significant light absorption by OM in the UV and visible regions (<700 nm wavelength [Kirchstetter et al., 2004]).

Time-averaged \( \alpha_{ap} \), \( \sigma_{ap} \), and mass measurements for the WPB burning indicate an overall \( E_p \) and \( \omega \) of 5.6 m² g⁻¹ and 0.81, respectively. From this, a BC fraction of 7% would be predicted. However, integrating 10-s BC content over the entire combustion yields an overall BC fraction of 12%. BC absorbs light more efficiently as its fraction in the particles decreases [Martins et al., 1998], and this non-uniformity may cause substantial biases for BC retrieval using time-averaged optical measurements. The BC fraction does not vary as much during the PPW burning, and this effect becomes minor. Time-averaged and resolved measurements from the PPW burning yield a BC fraction of 62% and 66%, respectively.

5. Conclusions

[16] Specific mass absorption, scattering, and extinction efficiencies of smoke particles from burning mid-latitude forest fuels are determined with 10-s resolution without some common artifacts, such as the matrix effects of filter-based absorption measurement and truncation losses of scattering measurement by nephelometry. A simple optical model is used to estimate the effective particle size and BC fraction. The dependence of smoke properties on fuel and combustion phase has been clearly resolved. PPW burns more efficiently than WPB, overall generating less and smaller particles. The prolonged smoldering phase during WPB combustion emits larger particles with a higher scattering efficiency. Incorporating these findings into the biomass burning emission inventory may refine aerosol radiative forcing estimates. Absorption varies approximately as \( \lambda^{-0.9} \cdot \lambda^{-1} \) for keroseen soot and smoke from flaming combustions; a larger exponent is found for smoke from smoldering combustion with low BC, consistent with a significant absorption by OM in the visible region.

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