Formation of Refractory Black Carbon by SP2-Induced Charring of Organic Aerosol

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Introduction

Black carbon (BC) in the atmosphere continues to be a focus of research because its light-absorptive properties put it second only to CO2 as a warming agent of Earth's climate. Towards this end, the measurement of ambient BC has been aided greatly by the development of the Single Particle Soot Photometer (SP2) – an instrument that detects refractory black carbon (rBC) through laser-induced incandescence (Schwarz et al., 2006). Potential interference from other substances that can incandesce under 1064 nm illumination (e.g., some metals and minerals) is mitigated through the use of spectral bandpass filters (color temperature) to ensure that the SP2 remains highly selective to rBC. Here, we report on the detection of rBC that is produced through SP2 laser-induced charring (i.e., carbonization) of organic aerosols. Nigrosin – a non-BC-containing material – was used as a surrogate for light absorbing organic aerosols. The color temperature of the detected particles originating from charred nigrosin is near that of carbon black, fullerene soot, and ethylene soot, indicating that it is rBC. Failure to properly account for this heretofore unidentified source of rBC will lead to an overestimate of rBC loadings, which could, in turn, impact aerosol radiative forcing model predictions.

Methods

Aerosols were generated from deionized water-based stock solutions of nigrosin (Aldrich, 198285; NKbg74932; 4 mg/g) and carbon black (CAB-O-JET® 200 pigment; Cabot Corp; 110 mg/g) using a constant output atomizer (TSI; model 3076) and dried inline in a diffusion drier (Topas; model DDU 570/H). Nigrosin, a water-soluble, polyaniline-based black dye is often used as a surrogate for black-carbon in studies of atmospheric aerosol absorption as it possesses a
broad, featureless absorption spectrum in the visible and near-IR (Bluvshtein et al., 2017; Hung et al., 2015) and dries to make spherical particles (Lack et al., 2006). Carbon black was used as BC reference material for comparison with nigrosin. Additional experiments were carried out using fullerene soot, a calibration standard for the SP2 instrument (Gysel et al., 2011), and ethylene flame-generated soot.

Particles used in these experiments were selected by their mobility diameter (DMA, TSI model 3081) or the combination of mobility diameter and mass using a Centrifugal Particle Mass Analyzer (CPMA, Cambustion Ltd.). A mixing condensation particle counter (MCPC, BMI model 1710) was used to monitor particle number concentration. The Single Particle Soot Photometer (SP2; Droplet Measurement Technologies; revision D) was used to detect rBC. To minimize the effects of particle size on SP2 detection efficiency (Schwarz et al., 2010), 400 nm mobility diameter particles (30 fg nigrosin; 19 fg carbon black) were studied exclusively, and the particle number concentrations were kept low (<1000 cm\(^{-3}\)) to minimize particle coincidence in the instrument.

**Results and Discussion**

Time series of SP2-detected incandescent (i.e., rBC-containing) particles, non-incandescent (i.e., pure scattering) particles, and their sum as a function of SP2 laser power (parameterized by the internal power meter voltage) for nigrosin and carbon black are shown in Figure 1. Over the time period shown, the total number concentrations of nigrosin and carbon black remained constant at 350 cm\(^{-3}\) (± 10 cm\(^{-3}\)). We draw attention to two striking features in this plot. First, incandescent particles are detected for the nigrosin aerosol. Second, the number concentrations of incandescent and non-incandescent nigrosin particles are strongly dependent on laser power, with more scattering particles being detected at lower laser powers, and more incandescent particles being detected at higher laser powers (although the sum was constant). In contrast, carbon black particles were almost entirely detected as incandescent particles, independent of laser power; this behavior is expected once the SP2 laser power fluence exceeds the ability of an individual particle to dissipate the absorbed energy. The carbon black data indicate that the lowest laser power used in this experiment is sufficient to detect rBC with high efficiency. Examination of the color temperature derived from the two spectral bandpass filters used by the
SP2 to discriminate against other species that can incandesce (e.g., metals and minerals) indicates that both the charred nigrosin and the carbon black particles incandesce at a temperature characteristic of rBC (near 4000 K), similar to the fullerene and ethylene soot samples. It is important at this point to recall that nigrosin is a polyaniline-based black dye that does not contain rBC.

The behavior exhibited by nigrosin under varying laser power suggests that nigrosin is charring, thereby producing rBC detected by the SP2. Nigrosin possesses a broad absorption spectrum that spans into the near-IR, with an imaginary component of refractive index at 1064 nm estimated to be 0.07 based on Bluvshtein et al. (2017) and Hung et al. (2015). The proposed explanation for this behavior is that nigrosin molecules absorb 1064 nm laser light, heating the particle sufficiently that chemical reactions result in charring of a fraction of the nigrosin, with the formed rBC material continuing to heat in the SP2 laser until incandescence.

Figure 1. Time series of SP2-detected rBC particles and non-rBC particles (e.g., pure scatterers) as a function of SP2 laser power (red trace) for nigrosin (peach shaded region) and carbon black (blue shaded region). Upper portion of plot displays the total number concentration of particles detected by the SP2 (sum of rBC and pure scatterers) and particle number concentration reported by the MCPC (denoted CN Conc). Dips observed in total particle concentration reported by SP2 is due to interruption of data acquisition when changing laser power.

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The efficiency of charring of the nigrosin particles by the SP2 laser, characterized by the ratio of rBC particle mass as derived from the SP2 to the original particle mass selected by the CPMA (Fig. 2) is near unity for carbon black, as expected, but is 25 – 45% (depending on laser power) for nigrosin. The reason for the decrease of the mass-based, per particle nigrosin charring efficiency with increasing laser power is not known. Similarly, the number concentration ratio is near unity for carbon black, but depends on laser power for nigrosin.

The rBC size distribution of the charred nigrosin also displays a strong dependence on SP2 laser power, whereas that for carbon black exhibits virtually none (Fig. 3). The absence of mass ratio (Fig. 2) and size-distribution (Fig. 3) at the lowest laser power for nigrosin reflects the fact that negligible rBC was generated at this laser power. The complex sensitivities of the nigrosin-derived rBC mass ratios (i.e., efficiencies) and size distributions to the laser power suggests a competition between nigrosin vaporization and charring as a function of particle heating rates, warranting further study.
The class of light-absorbing organic aerosols, commonly referred to as brown carbon (BrC) for its tendency to absorb predominantly in the mid- to shortwave spectrum, is recognized as another important direct radiative forcing agent (Andreae and Gelencsér 2006; Chen and Bond 2010; Feng et al., 2013). However, there is at least one class of atmospherically-relevant BrC that absorbs at longer wavelengths: Tar Balls (TBs), a type of carbonaceous particle that appears to be the near exclusive byproduct of some types of biofuel combustion/pyrolysis and wildfires (Pósfai et al., 2004; Adachi and Buseck 2011). Hoffer et al. (2017) reported that TBs exhibit longwave absorption. More recently, Sedlacek et al. (2018) reported that the TB mass fraction in the emission plume in some wildfires in the northwestern United States was 30-40%. In light of the Hoffer and Sedlacek findings on TBs, and given the propensity of the near-IR light-absorbing nigrosin to char under SP2 laser illumination, it is possible that TBs also exhibit some degree of charring in the SP2 that could bias the rBC loading reported by this instrument when sampling air containing TBs.
In a series of experiments to examine the refractory character of TB particles, we pyrolyzed pine needles and twigs using the TB synthesis procedure described by Tóth et al. (2014) and sampled these laboratory-generated particles with the SP2. Microscopy confirmed the production of TBs via this method, and incandescence and color temperature signals observed by the SP2 indicate the presence of rBC. While quantification of the charring efficiency of TBs (~9% mass loading ratio) needs to be examined more fully, this preliminary finding is consistent with observations on nigrosin and suggests that use of the SP2 in wildfire plumes containing TBs could result in overestimation of the rBC loadings.

Finally, it is also interesting to consider the potential impact of these findings for those measurement schemes that employ thermal denuders as a method of removing semi-volatile organic aerosols or coatings on rBC. As has been documented elsewhere (Swanson and Kittelson 2010; Yu et al., 2002), charring of organic aerosol can readily occur during the thermal denuding process. While the efficiency of charring via this method depends upon temperature, composition, and amount of material, overestimation of rBC could occur if the charring efficiency was non-negligible.

In summary, we have demonstrated that production of rBC can occur by charring of light-absorbing organic particles that did not originally contain rBC. This behavior results in an overestimate of rBC, and thus misapportionment of BC and BrC, with implications for models attempting to simulate radiative forcing from biomass burning. The production of rBC from BrC could have been a factor in the BC/BrC correlation reported by Saleh et al. (2014).

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