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Absorption of chemically aged biomass burning carbonaceous aerosol

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ABSTRACT

Smog chamber experiments were conducted to study the changes of the physical properties and chemical composition of biomass burning particles as they evolve in the atmosphere. A Soot Particle Aerosol Mass Spectrometer (SP-AMS) and a Single Particle Soot Photometer (SP2) were used for the chemical characterization of the particles. An Aethalometer and a green and a blue photoacoustic extinctiometer (PAX) were used for the study of the aerosol optical properties. As smoke aged, exposed to UV light, ozone or OH radicals, organic material condensed on the preexisting particles. This coating led to an increase of the absorption of the black carbon-containing particles by as much as a factor of two. The absorption enhancement of biomass burning particles due to their coating with aromatic secondary organic aerosol (SOA) was also studied. The resulting absorption enhancement was determined mainly by the changes in the SOA mass concentration and not the changes of its oxygen to carbon ratio. The measured absorption enhancements were consistent with the predictions of Mie theory assuming core-shell morphology for the aged particles.

1. Introduction

Biomass burning particles consist of organic compounds, black carbon (BC), and inorganic salts. On a global scale biomass burning is the major source of both primary organic aerosol (POA) and black carbon (Bond et al., 2004, 2013). The composition of biomass burning particles depends on the fuel type, moisture content, and combustion conditions. Oxygen-rich flaming combustion generally releases more BC, while lower-temperature smoldering fires emit more total particulate matter and CO (Lobert et al., 1991).

One of the major components of biomass burning emissions is BC which is unique in its properties compared to other aerosol components. BC strongly absorbs visible light (Bond et al., 2006), is refractory with vaporization temperature near 4000 K (Schwarz et al., 2006), has an aggregate morphology (Medalia & Heckman, 1969), and is insoluble in water and common organic solvents (Fung, 1990). Its refractive index is constant across the visible spectrum (Marley et al., 2001).

The emitted organic particulate matter and surrounding vapors can undergo subsequent reactions in the gas and particulate phases leading to changes in the organic compound volatility and thus phase partitioning. This series of processes is called chemical aging and can be a significant source of SOA in the atmosphere (Donahue et al., 2012). As smoke ages, organic material condenses or evaporates from the particle phase, but there is no additional BC production.

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The presence of a scattering shell around an absorbing core can increase its absorption efficiency by focusing more photons onto the core (Fuller, Malm, & Kreidenweis, 1999). Light absorption by the BC core can be enhanced due to mixing of BC with OA and inorganic salts such as sulfate, a process called lensing (Jacobson, 2001; Lack & Cappa, 2010). Lensing has been shown theoretically and in laboratory experiments to increase the absorption of the BC core up to a factor of two for atmospherically relevant core and shell sizes (Jacobson, 2001; Schnaiter et al., 2005; Bond et al., 2006; Saliba et al., 2016).

Understanding the photochemical evolution of biomass burning OA (bbOA) and the corresponding volatile organic compound (VOC) emissions which can undergo atmospheric aging is crucial in the effort to obtain a complete picture of the role of biomass burning in the atmosphere including its effect on climate.

A number of previous studies have examined the chemical aging of bbOA. Grieshop, Logue, Donahue, and Robinson (2009) exposed biomass burning emissions from three different sources (mixed hardwoods, laurel oak and yellow pine) to UV-light. The experiments were performed under high NO_x conditions. They found that the fresh emissions from burning yellow pine under flaming conditions with embers had an O:C of 0.13–0.22, while under smoldering conditions the O:C was 0.2. The photochemical aging of the emissions resulted in an OA/BC increase ranging from 20–170%. Similarly, the photochemical aging led to the increase of the O:C up to 0.4 for the flaming and up to 0.5 for the smoldering experiments. Hennigan et al. (2011) performed chemical aging experiments of emissions coming from the combustion of 12 types of wood fuel. They initiated chemical aging using UV lights, sunlight or a combination of both. In other experiments they produced hydroxyl (OH) radicals under high NO_x conditions by the photolysis of nitrous acid (HONO). In all the experiments in which ponderosa pine was used as a fuel the chemical aging of the emissions resulted in a 10% decrease of the OA/BC. In the lodgepole pine burning experiments exposure to UV led to 130% increase of the OA/BC. When the chemical aging was initiated by the photolysis of HONO the OA/BC increased 40%. Ortega et al. (2013) used a potential aerosol mass (PAM) flow reactor to study the chemical aging of different fuel types. They found that the OA change during the chemical aging varies with the fuel type and the OH exposure. As exposure to OH radicals increased, the OA increased until it reached a maximum. Aging of smoke from most fuels resulted in a net OA increase. Negligible increase or net decrease was observed for ponderosa and lodgepole pine. During the chemical aging of the ponderosa pine emissions the OA remained almost stable (3% increase) or decreased as much as 38%. For the lodgepole pine the OA decreased 10–14%. Their results indicate that the photochemical aging of the emissions of fuels with higher emissions resulted in a lower relative OA enhancement. Tiitta et al. (2016) performed aging experiments of biomass burning emissions under dark conditions (ozone injection), photooxidation, or a combination of both. They used three different kinds of wood as fuel (birch, beech and spruce). For the experiment in which birch logs were used as fuel the OA/BC was 0.2, the O:C was 0.35 and the H:C was 1.5. The exposure of the emissions to ozone led to 77% OA mass increase. The O:C increased to 0.75 and the H:C decreased to 1.29.

A few studies have focused on the absorption of black carbon and the absorption enhancement (E_{Abs}) after the BC particles were coated with aged OA. Lack et al. (2012) investigated the optical properties of particles from a large ponderosa pine forest smoldering fire. During two biomass burning events, the absorption Angström exponent (AAE) was 2.3, indicating more absorption by the POA at 404 nm than at 532 nm. The absorption enhancement (E_{Abs}) was also larger at 404 nm than at 532 nm. The difference in the E_{Abs} at different wavelengths and the high values of the AAE suggested the existence of internally or externally mixed absorbing POA. Cappa et al. (2012) reported that during the CalNex study and the Carbonaceous Aerosol and Radiative Effects Study (CARES) studies, photochemical aging of the OA did not cause a substantial absorption enhancement, especially compared to Mie theory calculations. They reported as average E_{Abs} at 532 nm equal to 1.06, and at 404 nm equal to 1.13.

In this study we want to close the scientific gap between the two sets of studies that have explored the chemical aging of the biomass burning emissions and the ones that have focused on the absorption enhancement after the BC particles were coated with aged OA. More specifically, we investigate how the changes of the properties of the bbOA during chemical aging affect the absorption enhancement of the BC particles.

2. Experimental methods

Experiments were carried out in the smog chamber of Carnegie Mellon University at the Center for Atmospheric Particle Studies (CAPS). The smog chamber contained a 12 m^3 Teflon reactor (Welch Fluorocarbons) suspended inside of a temperature-controlled room. The walls of the smog chamber room are lined with UV lights (General Electric model 10526 black). Prior to an experiment, the chamber was flushed with purified air for 12–48 h. Air was purified by passing through HEPA and carbon filters to remove particles and gas-phase organics respectively and silica gel to reduce relative humidity to $< 10\%$. All the experiments were carried out at a constant temperature of 20 ± 2 °C and at RH $< 10\%$.

Two different kinds of wood were used as fuels: longleaf pine wood and white birch bark. An environmentally efficient cook stove (G3 Rocketstove, Envirofit) was used for the burning. The emissions were injected in the smog chamber using two Dekati diluters (DI-1000) in a parallel configuration. Each of the diluters had a dilution ratio of 1:10. The emissions were injected during the flaming phase of the combustion for 5 min resulting in approximately 10,000 particle cm^{-3} in the smog chamber. The sampling flow rate was approximately 40 L min^{-1}.

Ozone or OH radicals were introduced in the system after the injection of the biomass burning emissions. Ozone was added to the chamber using an electrical discharge generator (AZCO, model HTU-500ACPS). For the production of OH radicals, HONO or H_2O_2 (Sigma-Aldrich, 50–50% solution) photolysis was used. A fresh solution of HONO was produced and used in each experiment by mixing a 4.9 g L^{-1} sulfuric acid solution with a 6.9 g L^{-1} sodium nitrite solution with a volumetric ratio of 2:1. HONO or H_2O_2 were injected into the chamber using a bubbler. After the injection, the UV light was turned on to initiate the production of OH radicals. We tested the injection method by measuring the concentration of the OH radicals using 2-butanol as a tracer and a GC/FID