Atmospheric Environment 120 (2015) 244–252

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Evolution of biomass burning smoke particles in the dark

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HIGHLIGHTS

- Aerosol chamber simulation of agricultural residue burning in the dark.
- Hygroscopicity and effective density measurement using TDMA-APM system.
- RH effect on smoke particle chemical and effective density evolution.
- Density growth with the chemical evolution and morphology changes of smoke particle.

ARTICLE INFO

Article history:
Received 1 July 2015
Received in revised form
29 August 2015
Accepted 1 September 2015
Available online 5 September 2015

Keywords:
Smoke particle
Aerosol chamber
Dark aging
RH effect
Effective density
Hygroscopicity

ABSTRACT

The evolution in the dark of physiochemical properties and chemical composition of smoke particles emitted from wheat straw burning, as well as the effect of relative humidity (RH) on these properties, was investigated in an aerosol chamber. The smoke particles are composed primarily of carbonaceous materials and a considerable amount of inorganic salts (~25 wt.%). During aging, the fraction of inorganic salts in smoke $PM_{1.0}$ increases, mainly due to the formation of more sulfate and nitrate at the expense of chloride; this heterogeneous conversion is facilitated at high RH. The hygroscopicity parameter κ_H of fresh smoke particles is 0.27 and this is estimated to decrease by 0.01 after 4 h dark aging. Both aging and high RH lead to increases of particle size and density. The effective densities of smoke $PM_{2.5}$ and $PM_{1.0}$ deduced from concurrent mass and volume concentration measurements gradually increase from about 1.18 to 1.44 g/m^3 within 4 h aging at 45%–55% RH, in line with the results obtained both from size-resolved particle density analysis using an aerosol particle mass analyzer (APM) and from estimation using composition-weighted bulk densities. The density of smoke particle is size-, RH-, and aging extent-dependent; the size effect becomes less pronounced with aging.

1. Introduction

The emission of carbonaceous aerosols from agricultural waste burning contributes greatly to the deterioration of atmospheric quality in some developing countries (Saikawa et al., 2009; Andreae and Merlet, 2001). In China, it was estimated that field burning consumes over 20% (equivalent to 100–120 Tg) of the total agricultural waste each year, generating large amounts of smoke particles consisting of humic-like substances, polycyclic aromatic hydrocarbons (PAHs), and black carbon, which have a significant impact on human health, climate changes, and atmospheric chemistry (Lin et al., 2010; Cao et al., 2011; Li et al., 2007; Zhang et al., 2011). The large-scale emission of smoke particles during harvest degrades the visibility and threatens public health (Kennedy, 2007; Jung et al., 2009). In addition, suspended smoke particles may act as sites for heterogeneous chemical processes, and influence local and regional climate, though direct and indirect aerosol effects. For these reasons, it is of great interest to understand the physiochemical properties and environmental effects of smoke particles, which may certainly change as the particles are

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http://dx.doi.org/10.1016/j.atmosenv.2015.09.003

"aged" due to atmospheric chemical processes.

Many studies have focused on the physicochemical properties and environmental/health effects of fresh or photo-oxidized biomass burning particles via ambient investigation, chamber-simulation, remote-sensing, model calculation, or epidemiological research (Zha et al., 2014; Bølling et al., 2009; Hays et al., 2005; Mukherjee et al., 2013; Reid and Hobbs, 1998; Sarnat et al., 2008; Zauscher et al., 2013). Reid et al. (2005) and Zauscher et al. (2013) found that the diameter and chemical compositions of wood fire particles changed rapidly during the daytime. Li (2003) observed that KCl in biomass burning aerosol partly transformed to K_2SO_4 and KNO_3 upon photochemical aging. Grieshop et al. (2009) and Hennigan et al. (2011) found that photochemical oxidation increased organic aerosol emissions from wood fires. Giordano and Asa-Awuku, 2014, Giordano et al. (2013) examined the hygroscopicity and surface tension properties as a function of photochemical aging of biomass burning aerosol. Engelhart et al. (2012) measured hygroscopicity of different smoke particles and found the cloud condensation nuclei (CCN) activity was impaired by photo-oxidation.

These studies suggest that there can be significant physicochemical changes associated with the photochemical aging of fresh smoke particles. However, field burning is now happening mostly at night in China to circumvent recent rigorous policy that forbids agricultural fires. Since there is no sunlight during the night and the fluctuation of nighttime relative humidity (RH) is great, it is desirable to study the evolution of smoke particles in the absence of light and as a function of RH. Water vapor may amplify the environmental effects of smoke particles in haze formation and the deterioration of visibility (Shi et al., 2014; Jung et al., 2009), and it may also change the micro-structure and physiochemical properties of aerosol during aging and transport (Rubasinghege and Vicki, 2013; Cocker Iii et al., 2001; Lewis et al., 2009). Nevertheless, the dynamic influence of humidity on the evolution of smoke particles is still undefined in the ambient environment, which limits our overall understanding of the atmospheric process and ultimate impacts of smoke particles.

Here we report the results of an aerosol chamber simulation that aimed to characterize the evolution of some physiochemical properties and chemical composition of agricultural fire smoke particles exposed to different humidities in the dark, and the relationship between the chemical evolution and thermodynamic property changes were also explored. Wheat straw, accounting for about 25% of total agricultural waste yield in China, was chosen as representative of crop residues. This work adds to the knowledge base regarding atmospheric chemistry and climate change effects related to biomass burning.

2. Experimental section

2.1. Setup and general procedures

The effects of relative humidity on smoke particle aging in the dark were investigated by injecting emissions from wheat straw burnings into an aerosol chamber. The experimental system is located in a temperature/RH-controlled room, and includes a specially designed combustion stove, a stainless-steel aerosol chamber (4.504 m^3 in volume and 0.3 mm Teflon inner coat), and sampling instruments (Fig. S1 in the Supporting Information: SI). Detailed descriptions can be found elsewhere (Zhang et al., 2011). Before each test, the chamber was scrubbed using aqueous ethanol (50%v/v), flushed with HEPA-filtrated air, and subjected to oxidation by high-concentration ozone (~3 ppm) for 12 h. After cleaning, the chamber was humidified and evacuated to a predefined RH (25%–95% RH) and pressure (90 kPa). Smoke particles formed from the burning of 2.0 g wheat straw (dehydrated at 100 °C for 24 h) in the sealed combustion stove were introduced to the chamber using a particle-free air supply; this introduction took less than 5 min until the chamber reached ambient pressure, at which time the chamber was sealed and the experiment began. Magnetic fans fixed at the bottom of the chamber ensured mixing of the chamber contents. The evolution of the smoke particles' properties was monitored for 4 h, during which time the chamber temperature and RH were also tracked using a hygroclip monitor (model IM-4, Rotronic). During each test, the chamber RH fluctuated within 5%, and the temperature was around 20 °C. Experiments were conducted at different humidities, classified into 4 humidity groups (25%–35%, 45%–55%, 65%–75%, 85%–95% RH). At least 4 tests were repeated in each group.

2.2. Modified combustion efficiency (MCE)

To distinguish between flaming and smoldering combustion conditions and to ensure repeatability of agri-fire simulations, the modified combustion efficiency (MCE) of the burning processes was deduced by measuring CO and CO_2 concentrations using GC (Model 930, Shanghai Hai Xin Gas Chromatograph Co., LTD) (Reid et al., 2005). More details are given in SI. The MCE was 0.91 ± 0.03 for all tests, indicating that the flaming phase dominated in these experiments, comparable to the result from field burning campaigns (Li et al., 2007).

2.3. Particle concentrations measurement

Particle concentrations were continuously monitored during the 4 h aging. The particle size, number, and volume were directly measured using a combination of wide-range particle spectrometer (WPS, Model 1000XP, TSI Inc., USA) and aerodynamic particle sizer (APS, Model 3321, TSI, Inc., USA). The WPS was operated in a scanning mobility spectrometer (SMS) mode ($PM_{0.5}$ cutoff – short DMA – CPC, 0.3 L/min, 3 min/loop, 48 channels) covering electrical mobility diameters from 10 to 500 nm; The APS detects particles possessing aerodynamic diameters from 0.5 to 20 μm (1.0 L/min, 3 min/loop, 51 channels). These size distributions were merged by assuming an effective density of spherical smoke particle to be 1.30 g/cm^3 (see SI). $PM_{2.5}$ and $PM_{1.0}$ volume concentrations were transformed from particle number concentrations. The WPS and APS were calibrated with polystyrene latex sphere particles (PSLs, 0.04, 0.08, 0.22, 0.70, and 1.50 μm, 1.05 g/cm^3, Duke Scientific, USA) generated from an atomizer (Model 3076, TSI Inc., USA) before the test.

Real-time smoke particle dry mass concentrations of $PM_{2.5}$ and $PM_{1.0}$ were measured using two aerosol monitors (AM510, Sidepak™ Personal Aerosol Monitor, Model 510, TSI, Inc., USA, 1.6 L/min, resolution of 1 μg/m^3) with 2.5 and 1.0 μm impact cutoff kits. A dilutor system (dilution ratio 5:1) was applied in front of AM510 to ensure the real mass concentration fell into the detection range (0–20 mg/m^3). Zero calibration was conducted before each test, and a humidity effect calibration was made prior to the experiments (Figs. S2–S3, SI).

2.4. Effective particle density measurement

Effective density of smoke particle in dry mobility diameter of 100–400 nm is characterized using a home-fabricated TDMA-APM system which has been described in detail previously (Hu et al., 2011; Zhang et al., 2011). An aerosol mass analyzer (APM, Model 3601, Kanomax Inc.) is combined to classify aerosol particles according to the mass-to-charge ratio. Briefly, smoke particles from the chamber are charged using radiation from a ^{210}Po source, and