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Physiochemical properties of carbonaceous aerosol from agricultural residue burning: Density, volatility, and hygroscopicity

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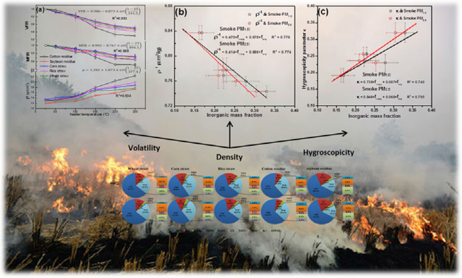
HIGHLIGHTS

- Effective densities, volatility, and hygroscopicity of smoke particle were measured using V/H-TDMA-APM system.
- Smoke particles were produced from filed burning simulation of crop straws with aerosol chamber system.
- Density, volatility, and hygroscopicity of smoke particles were measured using V/H-TDMA-APM system.
- Integrated density and hygroscopicity of smoke particles scale with the inorganic mass fraction.
- More volatile organic materials have less density and lower OM/OC ratios in the external mixed smoke particles.

GRAPHICAL ABSTRACT



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ABSTRACT

Size-resolved effective density, mixing state, and hygroscopicity of smoke particles from five kinds of agricultural residues burning were characterized using an aerosol chamber system, including a volatility/hygroscopic tandem differential mobility analyzer (V/H-TDMA) combined with an aerosol particle mass analyzer (APM). To profile relationship between the thermodynamic properties and chemical compositions, smoke $PM_{1.0}$ and $PM_{2.5}$ were also measured for the water soluble inorganics, mineral elements, and carbonaceous materials like organic carbon (OC) and elemental carbon (EC). Smoke particle has a density of 1.1–1.4 g cm^{-3}, and hygroscopicity parameter (κ) derived from hygroscopic growth factor (GF) of the particles ranges from 0.20 to 0.35. Size- and fuel type-dependence of density and κ are obvious. The integrated effective densities (ρ) and hygroscopicity parameters (κ) both scale with alkali species, which could be parameterized as a function of organic and inorganic mass fraction (f_{org} & f_{inorg}) in smoke $PM_{1.0}$ and $PM_{2.5}$: $\rho^{-1} = f_{inorg} \cdot \rho_{inorg}^{-1} + f_{org} \cdot \rho_{org}^{-1}$ and $\kappa = f_{inorg} \cdot \kappa_{inorg} + f_{org} \cdot \kappa_{org}$. The extrapolated values of ρ_{inorg} and ρ_{org} are 2.13 and 1.14 g cm^{-3} in smoke $PM_{1.0}$, while the characteristic κ values of organic and inorganic components are about 0.087 and 0.734, which are similar to the bulk density and κ calculated from predefined chemical species and also consistent with those values observed in ambient air. Volatility of smoke particle was quantified as volume fraction remaining (VFR) and mass fraction remaining

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(MFR). The gradient temperature of V-TDMA was set to be consistent with the splitting temperature in the OC-EC measurement (OC1 and OC2 separated at 150 and 250 °C). Combing the thermogram data and chemical composition of smoke $PM_{1.0}$, the densities of organic matter (OM1 and OM2 correspond to OC1 and OC2) are estimated as 0.61–0.90 and 0.86–1.13 g cm^{-3}, and the ratios of OM1/OC1 and OM2/OC2 are 1.07 and 1.29 on average, indicating more volatile organic materials have less density and lower OM/OC ratios in the external mixed smoke particles.

1. Introduction

Combustion of biomass has caught extensive concern among the scientific community as a major source of carbonaceous aerosol regionally and globally (Ram et al., 2011; Saikawa et al., 2009; Tian et al., 2008). These smoke aerosols have potential CCN (cloud condensation nuclei) activity, chemical reactivity, and inhalation toxicity that present great effect on the climate changes and public health (Bølling et al., 2009; Huang et al., 2014; Janssen et al., 2011; Rosenfeld, 2006; Shindell et al., 2012).

Biomass burning is an important global source of CCN, which eventually influence the hydrologic cycle, precipitation, and forcing balance (Ramanathan et al., 2001; Spracklen et al., 2011). However, highly variable CCN activity of source-dependent smoke particles challenges the climate modelling. And it was believed the CCN activity of smoke particles was response to the organic contents and also SOA (secondary organic aerosol) production upon photochemical aging, while organic compositions tightly relate to the source, burning condition, size, and extent of oxidation, which make the predication of CCN activity even complicated (Novakov et al., 1996; Engelhart et al., 2012; Giordano et al., 2013). Based on field investigation using aerosol mass spectrometer (AMS) and CCN counter, Gunthe et al. simplified the influence factors and established a parameterized function that linearly related the hygroscopicity parameter and integrated inorganic and organic fractions of certain sized ambient aerosol (Gunthe et al., 2011; Rose et al., 2011), but the derived characteristic hygroscopicity parameter values of inorganic and organic fractions still need to be proved by detailed chemical compositions.

Smoke particle density as a function of individual compound density affect the estimation of bulk hygroscopicity parameter and refractive index of OC and EC content (Petters et al., 2007; Schmid et al., 2009; Schkolnik et al., 2007). Besides, density bonds the aerodynamic diameter and mobility diameter, and it also plays a vital role in the mass concentration conversion and mass closure calculation (Beddows et al., 2010; Khlystov et al., 2004). Thus, value of density applied in the research will influence the result of online instruments like aerosol time-of-flight mass spectrometer (ATOFMS), AMS, and aerodynamic particle sizer (APS) in particle mass spectra analysis and size distribution measurements. However, few study ever reported the densities of smoke particles, and the limited densities of associated aerosol from APM measurement, from size conversion extrapolation based on APS-SMPS (scanning mobility particle sizer) data, and from bulk density calculation according to chemical composition all vary widely. And most study applied hypotheses-driven density values range from 1.0 to 1.7 g cm^{-3} without considering size difference or atmospheric aging effect (Engelhart et al., 2012; Gunthe et al., 2011; Reid et al., 2005; Schmid et al., 2007; Rissler et al., 2006).

Hygroscopicity and density are both result of chemical composition and mixing state of particles. Volatility or thermostability analysis helps get insight into the mixing sate and aging degree of carbonaceous aerosol (Pratt et al., 2009). Besides, volatility is a key property in the phase partition and secondary organic aerosol formation of the organic components (Grieshop et al., 2009; Tritscher et al., 2011). Volatility of aerosol has been commonly applied in thermo-optical method based OC-EC measurement and organic chemical compound analysis with thermal-denuder mass spectrometer (Pratt et al., 2009; Seinfeld et al., 2012). However, seldom research ever conducted to investigate the volatility of fresh smoke particles (Grieshop et al., 2009; Pratt et al., 2009), and it is fundamental to study the photochemical oxidation and atmospheric aging of biomass burning aerosol.

Herein, V/H-TDMA-APM system was coupled to an aerosol chamber to provide size- and fuel type-resolved hygroscopicity, effective density, and volatility of fresh smoke particles. The relationship among hygroscopicity, density, and chemical compositions of smoke particles were elaborated using Köhler theory analysis. Combining V-TDMA-APM data and OC-EC fractions of smoke particles, density of OM and OM/OC factors were estimated.

2. Experiment and method

2.1. Smoke particle production and aerosol chamber system

Physical and chemical properties of fresh smoke particles were characterized by injecting the emissions from crop residues burning into the dark aerosol chamber system (Fig. 1). The chamber is capsule-like stainless tank of 4.5 m^3 with 0.3 mm Teflon coating at the inner face, details can be found elsewhere (Zhang et al., 2008,

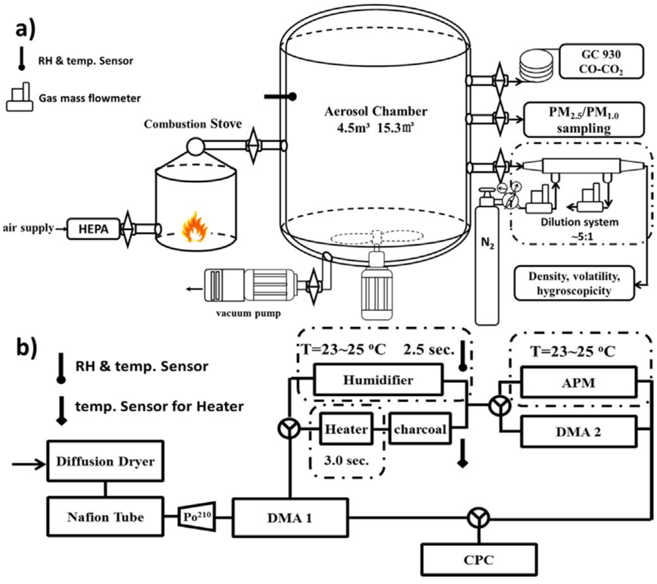

Fig. 1. Schematic graph of experimental setup. a) Flow chart of experiment, b) Detailed setup of thermodynamic properties measurement of aerosol including hygroscopicity, volatility, and density.