Journal of Aerosol Science 79 (2015) 31–39

Contents lists available at ScienceDirect

Journal of Aerosol Science

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

Oxidative aging and cloud condensation nuclei activation of laboratory combustion soot

A.T. Lambe [a,b,*], A.T. Ahern [a,b,1], J.P. Wright [a], D.R. Croasdale [a], P. Davidovits [a], T.B. Onasch [a,b,**]

[a] *Chemistry Department, Boston College, Chestnut Hill, MA 02467, USA*
[b] *Aerodyne Research, Inc., Billerica, MA 01821, USA*

ARTICLE INFO

Article history:
Received 15 July 2014
Received in revised form
19 September 2014
Accepted 6 October 2014
Available online 18 October 2014

Keywords:
Soot
Oxidative aging
Cloud condensation nuclei
Aerosol mass spectrometer

ABSTRACT

Radiative forcing by aerosol particles containing black carbon (BC) may be positive or negative depending on specific atmospheric conditions. Black carbon itself absorbs solar radiation and thereby heats the surrounding environment. On the other hand, as a result of atmospheric aging, BC-containing particles may become hydrophilic due to oxidation, condensation, and/or coagulation of water-soluble material. The aged particles can act as cloud condensation nuclei (CCN) and contribute to cloud formation that may result either in cooling or heating. In this work, through a series of laboratory experiments, we investigate the transformation of soot particles from hydrophobic to hydrophilic and estimate the atmospheric residence time required for this transformation. Ethylene flame-generated soot particles were size-selected and exposed to OH radicals in a Potential Aerosol Mass flow reactor. Aging was simulated via OH exposures equivalent to atmospheric lifetimes over a range from hours to multiple days. The chemical composition of the organic coatings as a function of OH exposure was monitored with an Aerodyne Aerosol Mass Spectrometer. The CCN activity of the aged soot particles was measured as a function of OH exposure and chemical composition. Experimental measurements indicate that heterogeneous OH oxidation of initially CCN-inactive nascent soot produces CCN-active particles. Critical supersaturations at integrated OH exposures equivalent to 0.4, 2, and 10 days are 2.1%, 0.82%, and 0.40%. Corresponding values for the effective hygroscopicity parameter, κ_{eff}, ranged from $\kappa_{\text{eff}} < 8 \times 10^{-4}$ to $\kappa_{\text{eff}} = 0.09$ as a function of OH exposure. Condensation of hydrophilic organic or inorganic coatings (produced from oxidation of gas-phase precursors introduced to the flow reactor) on soot particles speeds up the CCN activation by a factor of 6–50 depending on the nature and thickness of the coating. The results suggest that CCN activation of atmospheric BC-containing particles is primarily due to secondary coatings.

---

* Corresponding author at: Aerodyne Research, Inc., Billerica, MA 01821, USA.
** Principal corresponding author at: Aerodyne Research, Inc., Billerica, MA 01821, USA.
E-mail addresses: lambe@aerodyne.com (A.T. Lambe), aahern@andrew.cmu.edu (A.T. Ahern), paul.davidovits@bc.edu (P. Davidovits), onasch@aerodyne.com (T.B. Onasch).
[1] Now at: Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, PA 15232, USA.

http://dx.doi.org/10.1016/j.jaerosci.2014.10.001
0021-8502/© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Aerosol particles affect climate through direct and indirect interactions (Mahowald, 2011). Direct interactions consist of scattering or absorption by the particles of solar radiation. Indirect interactions are due to the role of hydrophilic aerosols in cloud formation and cloud lifetime. Clouds may either cool or warm the atmosphere depending on atmospheric conditions.

While the climate impact of inorganic components of aerosol particles (e.g. sulfates, nitrates, and mineral dust) is reasonably well understood, aerosol particles containing organic and BC components are not adequately characterized for reliable assessment of their climate effects. The interaction of particles containing absorbing material such as black carbon (BC) is especially complex. Black carbon absorbs solar radiation and thereby heats the surrounding environment, leading to atmospheric warming and surface dimming (Andreae & Ramanathan, 2013; Ramanathan & Carmichael, 2008; Reddy & Boucher, 2007). On the other hand, as a result of atmospheric aging processes, hydrophobic BC-containing particles may become hydrophilic due to oxidation of initially present hydrophobic coatings (Chughtai et al., 1996, 1999; Zuberi, 2005), condensation of hydrophilic material (Hings et al., 2008; Khalizov et al., 2009, 2013; Qiu et al., 2012; Tritscher et al., 2011), or through coagulation with hydrophilic particles (Fierce et al., 2013; Hagen et al., 1991; Podzimek et al., 1991). In this way, BC-containing particles can become cloud condensation nuclei (CCN). In the absence of aging processes, fresh BC particles containing hydrophilic coatings (e.g. produced from combustion of fuels with sufficient sulfur content; Gysel, 2003) may also contribute to CCN formation. The CCN-activated soot particles contribute to cloud formation resulting in cooling or warming depending on atmospheric conditions and soot content. CCN activation may also affect particle atmospheric lifetime via wet deposition.

The deliquescence of soot particles coated with hydrophilic organics approaches the hygroscopicity of the pure organics at large coating thickness (Hings et al., 2008; Wittbom et al., 2014). However, these previous studies have not directly connected changes in soot chemical composition and photochemical age to changes in CCN activity. Thus, the available data are not readily implemented in climate models. To date, models typically simulate aging of soot using highly simplified parameterizations because the dependence of BC hygroscopicity on physicochemical properties is highly uncertain. For example, Cooke et al. (1999) assumed conversion of hydrophobic BC to hydrophilic BC takes 1.15 days, a timescale that has been widely used in modeling BC aging processes (Chin et al., 2002). However, recent field studies suggest that this conversion can occur over significantly faster timescales (Cheng et al., 2012; Moffet and Prather, 2009; Schwarz et al., 2010).

The present work is focused on quantitatively relating oxidative and condensational aging to CCN activity of soot particles. Laboratory generated ethylene flame soot particles were exposed to OH radicals in a flow reactor. Aging was simulated via OH exposures equivalent to atmospheric lifetimes over a range from hours to multiple days. The chemical composition of the organic coatings as a function of OH exposure was measured with an aerosol mass spectrometer. The CCN activity of the aged soot particles was measured as a function of OH exposure and chemical composition. Experiments were performed with both nascent soot and soot particles coated by secondary organic aerosol (SOA) representative of biogenic and anthropogenic compounds found in the atmosphere and by sulfuric acid. The coatings were produced from oxidation of gas-phase precursors added to the flow reactor along with the soot. The measurements were used to estimate, under a range of atmospherically relevant conditions, residence times required for BC containing particles to become CCN-active and to formulate values for the effective hygroscopicity parameter κ_{eff}.

2. Materials and methods

Figure 1 is a schematic of the experimental setup showing soot generation, oxidation, monitoring and characterization.

2.1. Soot generation

Soot particles were generated using a premixed flat burner flame as described in detail elsewhere (Cross et al., 2010; Slowik et al., 2007). Briefly, premixed flows of ethylene, oxygen, and nitrogen gases are delivered through a McKenna flat burner at a total flow of 9 L/min, with a fuel-to-air ratio $\phi = 2.00 \pm 0.05$. A mini-eductor (Fox Valves) extracts a flow of polydisperse soot particles from the tip of the flame into the differential mobility analyzer (DMA, TSI 3081) to select monodisperse soot particles. The flow passes into a charcoal denuder to remove gas-phase organics.

2.2. Particle processing

Soot particles were exposed to OH radicals in a Potential Aerosol Mass (PAM) flow reactor (Kang et al., 2007; Lambe et al., 2011a). The average residence time was approximately 100 s, and the level of processing (i.e., exposure time) was controlled by the OH concentration in the reactor. OH radicals were produced via the reaction $O(^1D) + H_2O \rightarrow 2OH$, with $O(^1D)$ radicals produced via the photodissociation $O_3 + h\nu \rightarrow O_2 + O(^1D)$. The UV light was produced by four mercury lamps (BHK Inc.) inside the PAM reactor with peak emission intensity at $\lambda = 254$ nm. These lamps were mounted in teflon-coated quartz cylindrical sleeves and were continually purged with N_2. O_3 was generated outside the PAM reactor by irradiating O_2 with a mercury lamp ($\lambda = 185$ nm). Water vapor was introduced using a heated Nafion membrane humidifier (Perma Pure LLC). The humidifier temperature was set to provide a controlled relative humidity (RH) in the range of 24–30%.