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Understanding aerosol formation mechanisms in a subtropical atmosphere impacted by biomass burning and agroindustry

Michele L. Souza, Andrew G. Allen, Arnaldo A. Cardoso *

Department of Analytical Chemistry, Institute of Chemistry, São Paulo State University (UNESP), Araraquara, SP 14800-060, Brazil

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ABSTRACT

This work provides evidence for the existence of strong seasonality in homogeneous and heterogeneous aerosol formation in a subtropical region affected by agricultural biomass burning. Acquisitions of aerosol size distributions were made in central São Paulo State between August 2011 and November 2012, using a scanning mobility particle sizer (SMPS) system. Aerosols were also collected using a high volume impactor for analysis of major ions in the <0.49 μm size fraction. The SMPS data were grouped into three size fractions: <25 nm, 25–100 nm, and 100–615 nm, which were used to represent the nucleation, Aitken, and lower accumulation mode size ranges, respectively. Different aerosol types and atmospheric conditions were shown to influence the relative contributions of the different aerosol size fractions and their interrelationships. The total number concentrations of particles in the nucleation size range varied between 4.03×10^{-3} and 5.18×10^{4} cm^{-3}, concentrations in the Aitken size range varied between 1.60×10^{1} and 3.17×10^{4} cm^{-3}, and concentrations in the accumulation size range varied between 0.00 and 6.67×10^{3} cm^{-3}. Distinct seasonal differences in particle formation were observed, with evidence for the preferential occurrence of homogeneous nucleation during the wetter summer months and heterogeneous nucleation during the winter when there were strong emissions from biomass burning. Homogeneous nucleation of new particles was inhibited in the winter, due to the greater surface area of existing aerosols available for the uptake of reactive gases. Consequently, the nucleation and Aitken modes were favored in the wet (summer) and dry (winter biomass burning) periods, respectively. The accumulation mode showed peaks in the summer and winter, which could be explained by hygroscopic particle growth and heterogeneous reactions, respectively.

1. Introduction

The relevance and role of atmospheric aerosols in the ambient environment are scientifically well established. Aerosols affect visibility and air quality, and have impacts on human health (Singh and Dey, 2012; Lei and Wuebbles, 2013; Kan et al., 2012). The particles can act as cloud condensation nuclei and also modify the heat transfer properties of the atmosphere, with consequent changes in cloud formation processes and alteration of rainfall patterns (Rosenfeld et al., 2008). The deposition of aerosols onto terrestrial and oceanic surfaces can increase the availability of nutrients and other species, and hence affect the biogeochemical cycles of various elements (Andreae and Crutzen, 1997). It is therefore essential to understand the mechanisms of formation of aerosols, as well as their subsequent behavior in the environment.

In the atmosphere, the formation of ultrafine particles can proceed according to either homogeneous or heterogeneous mechanisms. Homogeneous nucleation occurs when low vapor pressure gas phase molecules condense to form extremely small new particles, and is favored by low concentrations of existing particles. Examples of substances that can undergo homogeneous nucleation processes are sulfuric acid (H_2SO_4) and the oxidation products of hydrocarbons released into the atmosphere from natural and anthropogenic sources. In contrast, heterogeneous nucleation proceeds by condensation of molecules onto existing small particles, so that the latter grow in size. It is generally accepted that nucleation mode particles originate from homogeneous nucleation, while Aitken mode particles originate from the growth of nucleation mode particles by heterogeneous nucleation (Kulmala, 2003).

The aerosols observed in the atmosphere are the result of earlier emissions and/or *in situ* formation and growth, and the particles are eventually removed by deposition (Kulmala et al., 2004; Holmes, 2007; Allen et al., 2010). Secondary aerosols are formed by nucleation through a number of different mechanisms. The formation rates of new particles have been explained using the processes of ion-induced nucleation, binary nucleation (involving water and sulfuric acid), and ternary nucleation (sulfuric acid–ammonia–water) (Kulmala et al., 2000; Hegg et al., 1990; Korhonen et al., 1999; Laakso et al., 2002; Kulmala et al., 2013). Ternary nucleation yields thermodynamically stable clusters 1–3 nm in size. These particles grow due to coagulation with other particles, or by condensation of gas phase species, at a rate that is dependent on factors including particle size, chemical composition, concentration, and temperature (Vuollekoski et al., 2010). Studies of the

* Corresponding author.
E-mail address: acardoso@iq.unesp.br (A.A. Cardoso).

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smallest nucleation mode particles have been restricted to a few regions. For example, Kulmala et al. (2013) observed aerosol nucleation in a remote forest in Finland, using new analytical tools. However, information is lacking concerning the mechanisms of aerosol nucleation in many global regions.

Despite the increasing number of studies, understanding of particle formation and growth is largely limited to modeling exercises, rather than experimental observations (Holmes, 2007). Most of the available instrumentation is only able to detect particles larger than 3 nm, which means that it is difficult to characterize the earlier stages of particle nucleation. It is possible that a reservoir of undetectable particles exists at all times in the atmosphere (Holmes, 2007). Furthermore, for many regions there is little information concerning the chemical composition of the finest atmospheric particles, often related to the fact that chemical methods require a minimum amount of material for analysis. The lack of chemical data is another limitation to understanding nucleation processes and the initial growth of particles.

In many regions worldwide, biomass burning is a major contributor to the atmospheric aerosol (Ichoku et al., 2012; Zhao et al., 2015; Zhu et al., 2016). The atmosphere of the region studied here is affected by widespread emissions from the burning of sugar cane, the most important agricultural crop, which for many years has had a dominant influence on aerosol chemistry during the winter dry (burning) season (Allen et al., 2004; Allen et al., 2010; Da Rocha et al., 2005; Urban et al., 2016).

In the present work, continuous measurements of aerosol number size distributions was used together with determinations of the chemical composition of the particles and meteorological parameters in order to understand the main factors affecting aerosol formation in a subtropical region affected by emissions from biomass burning and industrialized agriculture.

2. Experimental

2.1. Ground-based measurements

Measurements were made between August 2011 and November 2012 on the campus of São Paulo State University, in a rural location ~4 km southwest of the town of Araraquara (site coordinates: 21° 48′ 50.3″ S; 48° 12′ 07.2″ W; 658 m above sea level). Equipment was installed on the roof of a building at ~5 m above the ground (Fig. 1). To the south of the site there was a clear fetch of >30 km over sugar cane plantations. To the northeast were the UNESP campus and the Araraquara urban area.

The aerosol instrumentation comprised an electrostatic aerosol classifier (TSI Model 3080L) connected to a condensation particle counter (TSI Model 3775), operated in scanning mobility particle sizer (SMPS) configuration. Ambient aerosols were conveyed directly to the SMPS inlet through a short (60 cm) length of 8 mm i.d. copper tubing. Particle number concentrations in the size range 14.6–615.3 nm (selected using an impactor attached to the inlet of the instrument) were continuously recorded as 2-minute averages (acquired every 10 min). In the following discussion, the terms "nucleation", "Aitken", and "accumulation" refer to particles with diameters <25 nm, 25–100 nm, and 100–615.3 nm, respectively.

Seasonal differences in particle number concentrations were determined for the period starting in the winter of 2011 (dry period) and ending in the spring of 2012 (at the start of the rainy period). The seasons considered were: winter 2011 (August 11 to September 23); spring 2011 (September 23 to December 22); summer 2011/2012 (December 22, 2011 to March 20, 2012); autumn 2012 (March 20 to June 20); winter 2012 (June 20 to September 22); spring 2012 (September 22 to November 31).

2.2. Bulk aerosol sampling

Bulk aerosols were collected on a fortnightly basis using a high-volume sampler (Model TE-5000, Tisch Environmental), operated at a flow rate of 1140 L min^{-1}, onto glass fiber filters (Whatman, 25.2 × 20.2 cm). The filters were used as received, without any pretreatment. Size-resolved samples for chemical analysis were collected using a six-stage (including backup filter) cascade impactor, with aerodynamic cutoffs for the individual stages of 7.2, 3.0, 1.5, 0.95, and 0.49 μm. The exposed filters were folded in half, wrapped in aluminum foil, and stored in plastic bags at 22 °C for no longer than three months, until analyzed. In this work, only the fraction corresponding to particles in the size range < 0.49 μm was used.

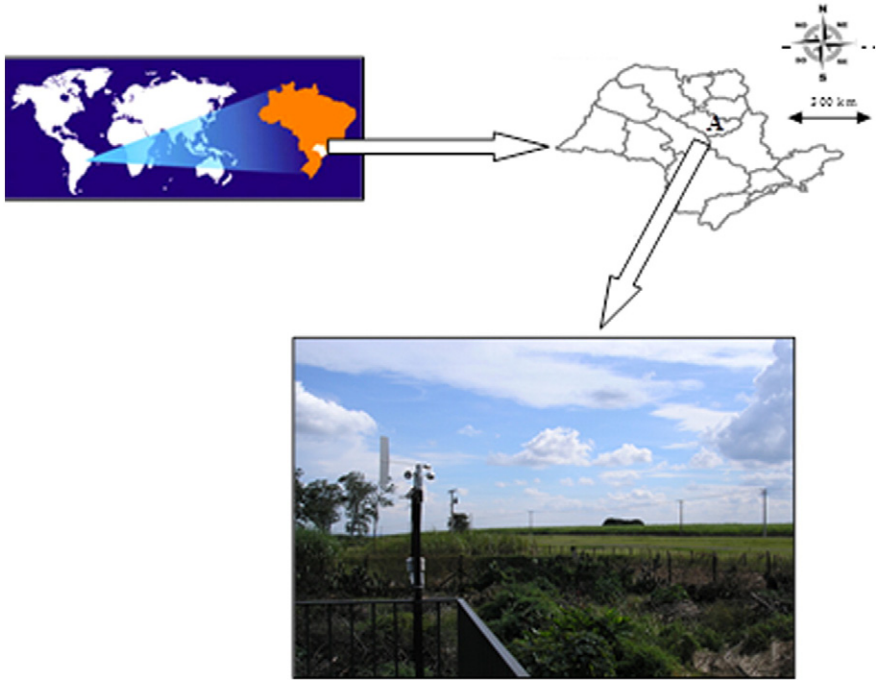

Fig. 1. Location of the measurement site (A) in São Paulo State.