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Combustion particles as ice nuclei in an urban environment: Evidence from single-particle mass spectrometry

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ABSTRACT

This paper presents measurements of the single-particle composition of ice nuclei (IN) in downtown Toronto, Canada, made at 239 ± 1 K, 134 ± 2% relative humidity with respect to ice (RH_i). IN were activated within the University of Toronto Continuous-Flow Diffusion Chamber (UT-CFDC), separated from background aerosol using a pumped counterflow virtual impactor (PCVI), and analyzed using a dual-polarity single-particle mass spectrometer (ATOFMS). To account for particles leaked by the PCVI, the ratio of particles observed at high RH_i to low RH_i was calculated. This ratio was greater than unity for EC (elemental carbon), BB (biomass burning) and dust particles, however only the increase in EC was statistically significant (1σ level) due to a low number of detected particles. The remaining particle categories were: metal-rich organic carbon (M/OC), potassium-rich OC (K/OC), OC potentially mixed with EC (OC/EC) and "other", none of which were enhanced in number at high RH_i. To complement the direct PCVI observations and enhance the number of spectra available, a second study was performed where particle composition and IN concentrations (C_{IN}) were measured in parallel. IN concentrations were regressed against the same categories as above, and dust, BB and EC particles were identified as the best predictors of C_{IN}. Consistency between these two methods provides increased confidence in their individual results and encourages additional study of these potential IN.

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1. Introduction

The subset of atmospheric particles that trigger heterogeneous ice nucleation in the atmosphere can strongly influence the ice-crystal concentrations of cirrus and mixed-phase clouds. These particles, termed ice nuclei (IN), may catalyze ice formation under conditions ranging from a few degrees of supercooling down to about 237 K, below which a rapid increase in the rate of homogeneous ice nucleation renders heterogeneous nucleation less significant (Pruppacher and Klett, 1996). Heterogeneous ice nucleation may occur via the liquid phase, for example by an insoluble IN immersed within an aqueous droplet, or via deposition and crystallization of water vapour onto an IN surface (Pruppacher and Klett, 1996). The former scenario is termed immersion freezing, unless contact is made between the IN and the air–water interface, in which case contact freezing can occur under relatively milder supercooling (Durant and Shaw, 2005). The latter scenario is deposition freezing. The number concentration of particles capable of initiating freezing by each of these mechanisms affects subsequent cloud crystal size, number and shape (Hallett and Mason, 1958; Lohmann et al., 2004), thereby influencing cloud precipitation and lifetime (e.g. Lohmann et al., 2007). The global significance of IN in climate systems remains uncertain (IPCC, 2007).

Atmospheric IN particles may consist of mineral dust (e.g. DeMott et al., 2003a), soot (Cozic et al., 2008; Pratt et al., 2009; Pratt et al., 2010), fragments of biological material (Pratt et al., 2009; Prenni et al., 2009), or effloresced salts (Abbatt et al., 2006; Wise et al., 2011). Furthermore, there is evidence that glassy organic particles may nucleate ice in the upper troposphere (Froyd et al., 2010; Murray et al., 2010) and that fragments of marine diatoms are important IN (Knopf et al., 2011). Anthropogenic emissions may affect the global concentrations of some of these IN both directly and indirectly: direct emission of the IN mentioned above will enhance IN concentrations (C_{IN}), while secondary aerosol precursors such as SO_2 or volatile organic compounds may be oxidized (to sulphuric acid or secondary organics, respectively) and deposited upon pre-existing IN to inhibit their deposition nucleation activity (Cziczo et al., 2009; Eastwood et al., 2009; Möhler et al., 2008, 2005).

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The relative importance of anthropogenic IN is uncertain, as most recent field studies of IN have reported on relatively pristine environments such as isolated mountain sites (Chou et al., 2011; DeMott et al., 2003a; Richardson et al., 2007), the Amazon rainforest (Prenni et al., 2009), or, from aircraft, the upper troposphere (DeMott et al., 2003b; Froyd et al., 2010; Pratt et al., 2009). Of particular interest are direct measurements of the chemical composition of individual IN (DeMott et al., 2003a; Prenni et al., 2009; Richardson et al., 2007), which can been attained by activating IN to form ice crystals, using a counterflow virtual impactor (CVI) to separate the ice crystals from the background aerosol (Cziczo et al., 2003), and subsequently passing the evaporated crystals into a single-particle mass spectrometer (SPMS). This CVI–SPMS technique provides valuable information on both the internal composition of ice-nucleating particles and their external mixing state.

While the CVI–SPMS approach has not previously been pursued in an urban environment, Knopf et al. (2010) recently used a different technique, X-ray microscopy, to characterize the ice-nucleation ability of Mexico City aerosol. Particles consisted mostly of organic carbon, with some elemental carbon and inorganic material, and contained IN active at 200–230 K and 10–40% relative humidity with respect to ice (RH_i) below homogeneous freezing for the deposition mode, and at 235–253 K for the immersion mode. These values indicate that IN within an urban outflow may be active enough to influence future cloud formation; however, it is not clear which components of the aerosol acted as IN. Earlier field studies of urban IN (Szyrmer and Zawadzki, 1997 and references therein) did not chemically characterize the aerosol.

This paper presents a CVI–SPMS study of urban IN performed Toronto (Canada) during the winter of 2011. Ice nuclei were activated within the University of Toronto Continuous Flow Diffusion Chamber (UT-CFDC, Kanji and Abbatt, 2009) before being selected and analyzed by the CVI–SPMS system. The CFDC was operated at 239 ± 1 K, $134 \pm 2\%$ RH_i ($96 \pm 2\%$ relative humidity with respect to water, RH_w). Under these conditions, the chamber remains just below the conditions required for both homogeneous freezing and droplet activation, thus activating a maximal number of deposition-mode IN while avoiding experimental ambiguity. These conditions are considered deposition-mode, although some degree of water was likely adsorbed to particle surfaces.

Single-particle mass spectra from the CVI–SPMS system were sorted into 7 categories and relative concentrations per category were compared at high and low humidities to identify IN-active species. Because low particle concentrations observed during this experiment limited the statistical confidence in the results, a second, separate study is also presented where IN concentrations and ambient-particle mass spectra were measured in parallel. Multiple regression of the IN concentration against compositionally-resolved surface area (estimated by combining mass spectral and particle number concentration measurements) identified the same potential urban IN as the CVI–SPMS approach.

2. Methods

2.1. Sampling location

Experiments were performed in a roadside building in downtown Toronto (43.66°N, 79.40°W), where a nearby major intersection sees ~33 000 vehicles/weekday (Jeong et al., 2011a). Two semi-continuous winter sampling campaigns were performed: IN concentrations were measured over 22 days starting January 19th 2010, while CVI-SPMS experiments were performed over 16 days starting from March 2nd 2011. Simultaneous measurement in both configurations was not possible due to long sampling times required for statistically useful CVI–SPMS data, as discussed below. These experiments were part of the long-term Seasonal Particulate Observation in Regional Toronto (SPORT) study, and are referred to as SPORT 2010 and SPORT 2011.

Typical ambient conditions at this site have been extensively characterized by both direct measurement and receptor modelling (Godri et al., 2009; Jeong et al., 2011b; Owega et al., 2004; Rehbein et al., 2012; Slowik et al., 2010). Aerosol chemistry at the site is generally impacted by coal-fired power plant emissions from the south/southwest, rural air from the north/northwest, or local emissions during periods of stagnation. During the winter, airborne salt particle concentrations are enhanced due to municipal salting of the nearby road in response to snowfall.

The two different experimental configurations used in this study are shown in Fig. 1. For the first experiment (solid lines), all instruments were operated in parallel. Outdoor air samples were split between an Aerodynamic Particle Sizer (APS), Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) and Continuous-Flow Diffusion Chamber (CFDC). These instruments are described below. In the second configuration, the CFDC, Pumped Counterflow Virtual Impactor (PCVI) and ATOFMS were connected in series, similarly to Slowik et al. (2011). In both cases, air was sampled through a 3 m long, heat-insulated primary inlet (10 cm i.d.) at 50 L min^{-1} before being diverted towards the sampling equipment. The primary sampling inlet was approximately 15 m from a four-lane road, and 6 m above ground.

2.2. Instrument description and data processing

2.2.1. Aerodynamic Particle Sizer

During SPORT 2010, an Aerodynamic Particle Sizer (APS, TSI Model 3321) sized particles 0.52–20 μm in aerodynamic diameter, with a resolution of 1 min in 51 size bins.

2.2.2. University of Toronto Continuous-Flow Diffusion Chamber

The design and validation of the University of Toronto Continuous-Flow Diffusion Chamber (CFDC) is detailed in Kanji and Abbatt (2009); only a brief description is given here. A movable injector introduces sample aerosol to the centre of a parallel-plate diffusion chamber, where a humidified nitrogen sheath flow (ten times larger than the sample flow, at ~2.5 L min^{-1}) isolates the sample from the walls. The sheath flow is dynamically humidified by layers of ice on the upper and lower walls of the chamber. The upper wall is kept at a higher temperature than the lower, resulting in a linear vapour pressure gradient across the height of the chamber. The vapour pressure and corresponding temperature gradients result in a region of supersaturation near the centre of the chamber, due to the non-linear relationship between saturation pressure and temperature (Murphy and Koop, 2005). The residence

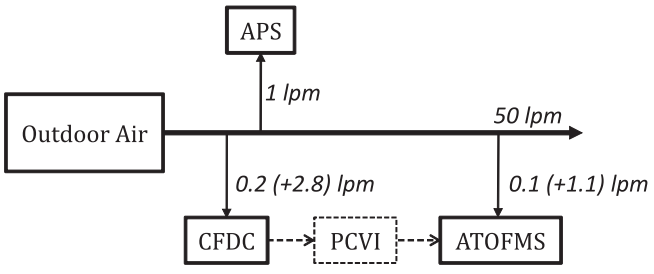

Fig. 1. Schematic of the instrumental configuration for the PCVI (dashed lines) and IN concentration (solid lines) measurements. The flows to each instrument, shown in L min^{-1}, were increased during both experiments by the number shown in parentheses. PCVI flow rates are discussed in the text.

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