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Online single particle measurement of fireworks pollution during Chinese New Year in Nanning

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ABSTRACT

Time-resolved single-particle measurements were conducted during Chinese New Year in Nanning, China. Firework displays resulted in a burst of SO_2, coarse mode, and accumulation mode (100–500 nm) particles. Through single particle mass spectrometry analysis, five different types of particles (fireworks-metal, ash, dust, organic carbon-sulfate (OC-sulfate), biomass burning) with different size distributions were identified as primary emissions from firework displays. The fireworks-related particles accounted for more than 70% of the total analyzed particles during severe firework detonations. The formation of secondary particulate sulfate and nitrate during firework events was investigated on single particle level. An increase of sulfite peak ($80SO_3^-$) followed by an increase of sulfate peaks ($97HSO_4^-$+$96SO_4^-$) in the mass spectra during firework displays indicated the aqueous uptake and oxidation of SO_2 on particles. High concentration of gaseous SO_2, high relative humidity and high particle loading likely promoted SO_2 oxidation. Secondary nitrate formed through gas-phase oxidation of NO_2 to nitric acid, followed by the condensation into particles as ammonium nitrate. This study shows that under worm, humid conditions, both primary and secondary aerosols contribute to the particulate air pollution during firework displays.

Introduction

Fireworks or crackers, which are commonly set off during celebrations and vacations, are unique anthropogenic sources that generate massive quantities of air pollutants within a short span of time. In general, fireworks consist of three main components: oxidants, flammable materials and flame agents. Potassium compounds in the form of nitrates, perchlorates, and chlorate (much less common) usually act as main oxidizers in commercial fireworks. Charcoal and sulfur are burnt as fuel when setting off fireworks. Elements, metal chlorides, metal nitrates or metal carbonates are usually added to produce different flame colors. Burning of fireworks can release great amount of gaseous pollutants (SO_2, NOx, CO, *etc.*) and suspended particles in short span of time (Barman et al., 2008; Beig et al., 2013). In general, the aerosols emitted by fireworks are composed of metals (e.g., K, Mg, Sr, Ba, Cu, Mg and Al), elemental carbon, organic carbon and inorganic anions such as SO_4^{2-}, Cl^- and NO_3^- in both coarse and fine mode (Moreno et al., 2007; Croteau et al., 2010; Sarkar

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et al., 2010; Zhang et al., 2010; Crespo et al., 2012; Do et al., 2012). Firework displays are associated with serious health hazards (Lemieux et al., 2004; Shi et al., 2011), ecological impacts (Sijimol and Mohan, 2014) and may result in serious accidents and lethal injuries (Puri et al., 2009).

Chinese New Year (CNY), which is also called Spring Festival, is an important Chinese festival celebrated with intensive firework displays all over the China both in megacities and in rural areas. CNY celebrations traditionally start from Chinese New Year's Eve (NYE) and last for 7 or 15 days. Chinese government reported that more than 1500 tons of fireworks debris could be generated during a NYE in a middle scale city. Although fireworks activities usually take a relatively short time, the high concentrations of gaseous and particulate pollutants can have huge impacts on air quality (Yerramsetti et al., 2013). Due to the formation of atmospheric inversion in winter season, pollutants may be trapped close to ground level, resulting in long-term haze and visibility reduction. As firework displays generate massive amounts of particulate matter precursors such as SO_2, NOx, and organic compounds, secondary processes between gas-phase and particle-phase compounds may lead to production of secondary air pollutants after firework displays. Since other forms of anthropogenic emissions usually decrease during holidays, CNY also provides scientists with an opportunity to study short-term degradation of air quality and its possible human health impacts under reduced emission conditions.

Previous research on CNY events examined total particle mass, composition and aging processes based on conventional filter measurements, which provide average properties of particles. Morphology and chemical composition of individual long-range transported fireworks aerosols and lab-generated samples were investigated by transmission electron microscopy, revealing that firework emissions during the CNY significantly changed the atmospheric transformation pathway of SO_2 to sulfate (Li et al., 2013). However, information on the properties of individual fireworks aerosol particles is still limited.

Furthermore, CNY firework event is a short-time air pollution episode, and the off-line methods may not have enough time resolution to capture its chemical evolution. In order to establish a better understanding on the rapid formation and composition evolution of firework displays, time-resolved measurements are required. Only a few real-time measurements of particle composition were conducted during CNY events. An aerosol chemical speciation monitor (ACSM) was used to achieve the first real-time measurements during a CNY event, however the information on metal constituents of particles was not acquired due to the limitations of the ACSM instrument (Jiang et al., 2015). Aerosol time-of-flight mass spectrometer (ATOFMS) has been proven to successfully detect heavy metals emitted from firework displays (Liu et al., 1997). Positive matrix factorization was applied to identify firework-family particles detected by ATOFMS in U.S. (McGuire et al., 2011). Previous single-particle mass spectrometry measurements mainly aimed at distinguishing unique firework particles, especially those containing metals, from particles found in the ambient environment. However, different types of particles could be co-emitted from a single source. In this study, we focus both on the identification of different types of particles emitted by fireworks and on the real-time analysis of the chemical processes that occurred on particles after the firework displays.

Several field measurements based on filter samples collected during CNY events have been reported in Beijing (Wang et al., 2007; Huang et al., 2012), Jinan (Li et al., 2013; Yang et al., 2014), Tianjin (Tian et al., 2014), Shanghai (Zhang et al., 2010; Feng et al., 2012), Nanjing (Kong et al., 2014) and Lanzhou (Shi et al., 2011; Zhao et al., 2014). It is the first time to investigate firework displays in Nanning, which is quite different in terms of environmental conditions from the previously examined sites. Specifically, the higher temperature and relative humidity in Nanning might favor secondary chemical processes that are unique to this geographic location.

1. Experiment and methods

1.1. *Ambient individual particle observation by SPAMS*

The design and operation of the single particle aerosol mass spectrometer (SPAMS, Hexin Analytical Instrument Co., China) used in this study is described in detail elsewhere (Li et al., 2011). In brief, after passing through a 0.1 mm orifice at a flow of 0.08 L/min, the air is drawn into a series of aerodynamic lens of SPAMS, where the particles are focused and accelerated to their terminal velocity. The particles then pass through two continuous neodymium-doped yttrium aluminum garnet (Nd:YAG) laser beams (532 nm). The time difference between the two scattering signals is used to calculate the velocity and vacuum aerodynamic diameter (D_{va}) of individual particles. The scattering signals also trigger the firing of a Nd:YAG laser (266 nm), operating at 0.5 mJ, for the desorption and ionization of each sized particle. Dual polarity time-of-flight mass spectra are acquired after each laser pulse. Polystyrene latex spheres (PSL, 0.2–2.0 μm) and standard metal solutions were used to calibrate particle size and mass before sampling. In general, the SPAMS instrument used in this work shares the similar aerosol sampling methods, sizing and desorption/ionization modules as better known ATOFMS (Li et al., 2014), and it has been proven to achieve comparable single-particle sensitivity and time resolution.

A total of approximately 350,000 particles, with both positive and negative ion spectra, were analyzed (34% of total sized particle). Particles' sizes and individual mass spectra were imported into MATLAB and further analyzed with YAADA (Yet Another ATOFMS Data Analyzer, www.yaada.org), a software toolkit for processing single-particle mass spectra. Individual particle clustering was performed with Art-2a (adaptive resonance theory based neural network algorithm) (Song et al., 1999), based on the presence and intensities of ion peaks in individual mass spectra. The parameters applied in the algorithm were set as: vigilance factor: 0.85; learning rate: 0.05; and number of iterations: 20. Nearly 5000 particle clusters were gained and then re-grouped again using the same Art-2a parameters to reduce the number of particle types. The resulting particle clusters were further manually merged into 14 particle sub-types, and then grouped to 7 main groups, based on the similar mass pattern, time variation and size distribution. All the grouped particles accounted for ~95% of all analyzed particles, implying the result can be representative

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