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Single particle mass spectral signatures from vehicle exhaust particles and the source apportionment of on-line $PM_{2.5}$ by single particle aerosol mass spectrometry

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HIGHLIGHTS

- Single particle signatures from vehicle exhaust in a tunnel were performed and evaluated in ambient $PM_{2.5}$.
- The detection of PAHs in individual vehicle exhaust particles could be used for future source profiling experiments.
- The major sources of ambient single particles was coal combustion, vehicle exhaust, and secondary ion.

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ABSTRACT

In order to accurately apportion the many distinct types of individual particles observed, it is necessary to characterize fingerprints of individual particles emitted directly from known sources. In this study, single particle mass spectral signatures from vehicle exhaust particles in a tunnel were performed. These data were used to evaluate particle signatures in a real-world $PM_{2.5}$ apportionment study. The dominant chemical type originating from average positive and negative mass spectra for vehicle exhaust particles are EC species. Four distinct particle types describe the majority of particles emitted by vehicle exhaust particles in this tunnel. Each particle class is labeled according to the most significant chemical features in both average positive and negative mass spectral signatures, including ECOC, NaK, Metal and PAHs species. A single particle aerosol mass spectrometry (SPAMS) was also employed during the winter of 2013 in Guangzhou to determine both the size and chemical composition of individual atmospheric particles, with vacuum aerodynamic diameter (d_{va}) in the size range of 0.2–2 μm. A total of 487,570 particles were chemically analyzed with positive and negative ion mass spectra and a large set of single particle mass spectra was collected and analyzed in order to identify the speciation. According to the typical tracer ions from different source types and classification by the ART-2a algorithm which uses source fingerprints for apportioning ambient particles, the major sources of single particles were simulated. Coal combustion, vehicle exhaust, and secondary ion were the most abundant particle sources, contributing 28.5%, 17.8%, and 18.2%, respectively. The fraction with vehicle exhaust species particles decreased slightly with particle size in the condensation mode particles.

1. Introduction

Atmospheric aerosol particles are of considerable importance due to their impacts on global climate, regional air pollution, and human health (Pöschl, 2005; Dockery et al., 1993; Pope et al., 2004). Exposure to particulate matter, particularly those with diameters less than 2.5

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μm ($PM_{2.5}$), is linked to negative health effects, including cardiopulmonary morbidity and mortality (Pope and Dockery, 2006). Primary aerosol particles originate from a variety of both natural and anthropogenic sources, such as biomass burning, incomplete fossil fuel combustion, and the wind-driven suspension of soil, sea spray, and biological materials (plant fragments, microorganisms, etc.) (Pöschl, 2005).

Single aerosol particles are complex mixtures containing on the order of ~10^2 to 10^{15} molecules per particle with masses on the order of ~10^{-20} to 10^{-6} g per particle. Single particle mass spectrometry is one of the few analytical techniques capable of spanning such a broad mass range. Real-time mass spectrometry has been shown recently to provide information of the chemical composition of ambient individual particles in different diameters to further understanding of how particles are formed through nucleation in the atmosphere (Bi et al., 2011; Zhang et al., 2013, 2015; Li et al., 2014). A single particle mass spectrometer can provide information on most species in the particles, as well as size-resolved chemical composition and mixing state of a single particle in real time (Cai et al., 2015; Moffet and Prather, 2009; Spencer et al., 2008; Sullivan et al., 2007). Single particle studies have shown that there are many particle types with complex mixing states in urban areas (e.g., Moffet et al., 2008; Zhang et al., 2013). The physical and chemical properties (including density, shape, hygroscopicity, and refractive index) of these particle types are distinctly different from each other, influenced by various factors such as meteorological conditions and emission sources (e.g., Moffet and Prather, 2009; Zelenyuk et al., 2008; Li et al., 2014).

Source apportionment is a major goal in the field of single particle aerosol mass spectrometry (SPAMS). In order to accurately apportion the many distinct types of individual particles observed in the urban troposphere, it is necessary to characterize particles emitted directly from known sources and measure their chemical "fingerprints". Obtaining size and chemical information of single particles coupled with high temporal resolution provides unique information on source emissions, which can be applied in apportioning ambient particles.

A significant anthropogenic source of atmospheric aerosols arises from the combustion of gasoline or diesel in vehicles and a number of studies have been performed to analyze the chemical composition of particles from automobile emissions (Bhave et al., 2001; Gross et al., 2000a; Shields et al., 2007; Silva and Prather, 1997; Sodeman et al., 2005; Suess and Prather, 2002; Toner et al., 2008). For this to be possible, single particle source profilesŽfrom the major aerosol sources must be obtained. In China, on-line single particle mass spectrometry has recently been applied in the studies on physicochemical properties of individual particles and their potential influence on air quality (Chen et al., 2014; Yang et al., 2012), and mixing state of carbonaceous particles in the atmosphere of the Pearl River Delta (PRD) region (Bi et al., 2011; Zhang et al., 2013; Zhang et al., 2015). However, comprehensive SPAMS source characterization studies of the major anthropogenic sources in China has not yet been completed.

The goal of this study is to determine the source profile of vehicle exhaust particles by single particle aerosol mass spectrometry in a tunnel that can be applied to $PM_{2.5}$ source apportionment efforts. The results presented are single particle mass spectral signatures from vehicle exhaust particles and an evaluate of these dynamometer particle signatures in a real-world $PM_{2.5}$ apportionment study. A SPAMS was also employed during the winter of 2013 in Guangzhou to determine both the size and chemical composition of individual atmospheric particles, with vacuum aerodynamic diameter (d_{va}) in the size range of 0.2–2 μm. A large set of single particle mass spectra was collected and analyzed in order to identify the speciation and simulation the major sources of the single particles. According to the typical tracer ions for different source types and classification by the ART-2a algorithm based on source fingerprints for apportioning ambient particles, a source appointment of the fine particle matter as determined by a single particle mass spectrometer was performed.

2. Experimental

2.1. Sampling

A single particle mass spectrometry provides real-time size and chemical composition data for single aerosol particles. The details on the specific instrument operation and the validation of single particle mass spectrometry have been described in other studies (Ma et al., 2015; Su et al., 2004). In this research, ambient single particle measurements were carried out from November 18, 2013 to February 8, 2014, with occasional maintenance and recalibration, using an SPAMS made by Hexin Analytical Instrument Co., Ltd (Ma et al., 2015). The ambient temperature varied between 4 and 25 °C (average 15 °C) with relative humidity varying more widely between 22 and 100%. The sampled air was introduced from a platform about 15 m above ground on a four-story building at Guangzhou Hai Qin Tian Cheng Technical Testing Services Co., Ltd. The air was sampled through an 8 mm copper tube connected to the SPAMS instrument, which was installed in an air-conditioned room located on the third floor of the building. Due to the relatively long inlet tubing (approx. 15 m) and low sampling flow rate, an additional pump (operating at a flow rate of 5 L min^{-1}) was used to shorten the residence time of the air in the tube.

The tunnel sampling was conducted in the Zhujiang Tunnel in the western urban area of Guangzhou (113.25°E, 23.13°N). Details of the Zhujiang Tunnel have been described in other studies (He et al., 2008). Traffic flow reached approximately 6000 motor vehicles (cars, buses and trucks) per hour during the rush hours. For this site, about 15% of the motor vehicles were diesel-fueled buses and trucks and others were gasoline-fueled cars. The source sampling events were carried out in December 2013 using 10 L glass sampling containers. The glass container need to be cleaned or pre-baked before collecting a sample. Within 15–30 min sampling, the container was immediately connected to the inlet of the single particle aerosol mass spectrometer using a Teflon transfer line.10–15 samples were collected and analyzed with different glass container. Zero air samples were collected as background samples and data corrected.

2.2. Single particle aerosol mass spectrometry

Sampling particles by a SPAMS has been described elsewhere (Ma et al., 2015; Bi et al., 2011). Briefly, particles are introduced into a vacuum pumped SPAMS through a 0.1 mm critical orifice at a flow of 80 mL min^{-1} with the pressure dropped from ~760 to ~2.2 Torr. They are then focused and accelerated to specific velocities according to their vacuum aerodynamic diameters while passing through the aerodynamic lens. In the sizing region, velocities of individual particles are determined by two continuous diode Nd:YAG laser beams operated at 532 nm and located 6 cm apart. Desorption/ionization is applied subsequently by a 266 nm Nd:YAG laser which is turned on when a particle arrives and the timing is determined exactly by the velocity of the specific particle as measured in the sizing chamber. The positive and negative fragments are detected by a dual-polarity time-of-flight mass spectrometer. In this study, the energy of the desorption/ionization laser was set at about 0.6 mJ. The power density of the desorption/ionization laser was kept relatively low, at about $1.06E^{+08}$ W cm^{-2}. Polystyrene latex spheres (Nanosphere Size Standards, Duke Scientific Corp., Palo Alto) of 0.2–2 mm in diameter were used to calibrate the sizes of the detected particles.

2.3. Analysis of single particle data

Particles size and mass spectra information was used to create peak lists, using TSI MS-Analyze software. The peak lists were then imported into MatLab 7.1 software (The Mathworks Inc.). Peak thresholds were set to record only those peaks with height greater than 10 units and area greater than 20 units to distinguish peaks from the background