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Size distribution of particle-phase sugar and nitrophenol tracers during severe urban haze episodes in Shanghai

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HIGHLIGHTS

- Size-resolved aerosol samples were collected in Shanghai during the haze events.
- Levoglucosan, 4-nitrocatechol, OC, and EC dominated in fine particles.
- Sucrose, fructose and glucose dominated in coarse particles.
- Sugar alcohols and some nitrophenols presented bimodal distribution.
- The major sources were biomass burning, combustion, and biological emission.

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ABSTRACT

In this study, measurements of size-resolved sugar and nitrophenol concentrations and their distributions during Shanghai haze episodes were performed. The primary goal was to track their possible source categories and investigate the contribution of biological and biomass burning aerosols to urban haze events through regional transport. The results showed that levoglucosan had the highest concentration (40–852 ng m^{-3}) followed by 4-nitrophenol (151–768 ng m^{-3}), sucrose (38–380 ng m^{-3}), 4-nitrocatechol (22–154 ng m^{-3}), and mannitol (5–160 ng m^{-3}). Size distributions exhibited over 90% of levoglucosan and 4-nitrocatechol to the total accumulated in the fine-particle size fraction (<2.1 μm), particularly in heavier haze periods. The back trajectories further supported the fact that levoglucosan was linked to biomass-burning particles, with higher values of associated with air masses passing from biomass burning areas (fire spots) before reaching Shanghai. Other primary saccharide and nitrophenol species showed an unusually large peak in the coarse-mode size fraction (>2.1 μm), which can be correlated with emissions from local sources (biological emission). Principal component analysis (PCA) and positive matrix factorization (PMF) revealed four probable sources (biomass burning: 28%, airborne pollen: 25%, fungal spores: 24%, and combustion emission: 23%) responsible for urban haze events. Taken together, these findings provide useful insight into size-resolved source apportionment analysis via molecular markers for urban haze pollution events in Shanghai.

1. Introduction

Atmospheric aerosol particles derived from biomass burning and biological origin have significant local to regional impact on climate, air quality, and human health (Kasischke and Penner, 2004; Keywood et al., 2013; Voulgarakis et al., 2015). Among all properties of the aerosol particles, their size-resolved chemical composition, which can be determined via organic molecular tracers, is essential for accurately estimating their atmospheric trajectory and release sources (Kasischke and Penner, 2004; Keywood et al., 2013; Voulgarakis et al., 2015).

Sugars and nitrophenols are two major compound classes which are often utilized as molecular tracers for atmospheric aerosols

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(Harrison et al., 2005; Scaramboni et al., 2015). In ambient aerosol particles, nitrophenols primarily originate from vehicular exhaust, coal and wood combustion, and the use of herbicides and insecticides in agriculture (Harrison et al., 2005), while sugar compounds are produced by biomass burning and biological origin (Scaramboni et al., 2015). The anhydrosaccharides levoglucosan, mannosan, and galactosan originate from the combustion of cellulose and hemicellulose and are accordingly typically recognized as biomass-burning markers (Fabbri et al., 2009; Hsu et al., 2007; Iinuma et al., 2009; Keywood et al., 2015; Louchouarn et al., 2009). The use of the anhydrosugars as tracers may be limited due to degradation in the atmosphere, which can significantly change their concentration especially with increasing distance and hence processing time after emission (Hennigan et al., 2010; Hoffmann et al., 2010).

Primary saccharides such as fructose, glucose, and sucrose are characteristic of material such as pollen, fruit, and plant fragments (Jia and Fraser, 2011), while sugar alcohols, such as arabitol and mannitol are characteristic of fungal spores (Bauer et al., 2008). By virtue of their ubiquity and abundance, sugars and nitrophenols are useful compounds in elucidating the sources, processes, and pathways of atmospheric aerosol particles (Fraser and Lakshmanan, 2000; Harrison et al., 2005; Medeiros et al., 2006; Scaramboni et al., 2015; Urban et al., 2014). Characterizing them at the particle scale can thus enhance our understanding of the outflow of aerosols from combustion-related emission (Wang et al., 2011). Previous studies have focused on the seasonal and temporal variations of atmospheric sugars or nitrophenols in several areas throughout the world (Fu et al., 2012; Harrison et al., 2005; Yang et al., 2012; Yttri et al., 2007), however, the particle-size-dependent concentrations of sugars and nitrophenols are rarely researched. Research in this area is crucial, though, because it provides useful data regarding the sources and processing of aerosol particles released into the atmosphere from biomass burning, soil dust, and primary biological aerosols such as fungal spores and pollen, all of which have considerable impact on the environment.

The Shanghai metropolitan area in eastern China has garnered the attention of the scientific community due to its very large emission of aerosols and gases to the atmosphere (Cheng et al., 2014; Ci et al., 2011; He et al., 2015; Lin et al., 2014; F. Wang et al., 2015a; Xiao et al., 2015). Shanghai is one of the world's largest metropolitan areas with a population of over 24 million people. The city is located in a transitional zone of the northern subtropical monsoon system, where the northwesterly winter monsoon enters from Mainland China, while the southeasterly summer monsoon enters from the Western Pacific oceans (Shi and Cui, 2012). The boom in industrialization and urbanization in and around Shanghai has resulted in consistent and excessive release of pollutants into the surrounding atmosphere (Lin et al., 2014). Atmospheric particulate matter and particle-bound compounds levels have continually increased due to the increase in number of motor vehicles, as well as expanded urban construction, heating installation, and the illegal, open burning of biomass in nearby rural areas during the post-harvest season (Lin et al., 2014; Peng et al., 2013; Wang et al., 2014; Zhao et al., 2015). Shanghai and its surrounding region is also subject to frequent temperature inversions due to its proximity to rivers and the Pacific, so air pollutants tend to accumulate in the lower atmosphere. Atmospheric haze is quite common in the region as a result, especially in the colder months (He et al., 2015; Lin et al., 2014).

To elucidate the sources, loadings, and trajectories of air pollutant components in and near Shanghai, it is essential to accurately measure sugar and nitrophenol species in haze particles as a function of particle size and to compare the size distribution of different component groups. To this effect, we conducted a sampling campaign for haze events in Shanghai and analyzed the results as discussed below. The main objectives of the study were: 1) to collect size-segregated aerosol particle samples during Shanghai haze episodes, 2) to quantify the size-resolved concentrations of sugars and nitrophenols, and 3) to use these compounds as molecular markers to reveal additional, size-resolved information about emission sources that directly caused or contributed to haze and pollution over Shanghai.

2. Experiment

2.1. Chemicals and standards

Sugar chemicals, including levoglucosan (>98%), D-(+)-arabitol (>99%), D-mannitol (>99%), D-(+)-glucose (99%), D-(+)-sucrose (>99%), and D-(−)-fructose (99%) were obtained from Fluka (St. Louis, MO, USA). Mannosan (>98%) and meso-erythritol (>99%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). The nitrophenol chemicals, including 4-nitrophenol (≥99%), 4-nitrocatechol (97%), 2,6-dimethyl-4-nitrophenol (98%), 2-methyl-5-nitrophenol (98%), 4-nitroguaiacol (97%) and 2,6-dinitrophenol (95%) were purchased from Sigma-Aldrich (Munich, Germany). Methanol, acetonitrile, dichloromethane, and other solvents were all HPLC grade. Milli-Q grade water (Millipore, Eschborn, Germany) was used throughout the study.

A stock solution containing eight standard sugar compounds was prepared in ultrapure (UP) water (100 mg L^{-1}), then the stock solution was diluted further with UP water to form a series of standard solutions at 0.16, 0.31, 0.63, 1.25, 2.5, 5.0, and 10 mg L^{-1}. Another stock solution containing six nitrophenol standard compounds was prepared in acetonitrile (1000 mg L^{-1}), then diluted further with 1:1 (v/v) mixture of acetonitrile and Milli-Q water to make a series of standard solutions at 0.1, 0.5, 1.0, 2.0, 4.0, 8.0, and 10 mg L^{-1}. The stock solution was kept at −28 °C until use; the standard solutions were freshly prepared at the start of each analytical week and stored at 4 °C.

Calibration was performed for each analytical sequence. There was no degradation of standard compounds observed over the course of the analysis process.

2.2. Aerosol sampling

The measurement campaign was conducted during Shanghai haze episodes from 2013 to 2015. The criterion of haze occurrences set in this work was based on the criterion of WMO, i.e., visibility <10 km for 6 h and relative humidity (RH) < 85%. Under such conditions, the concentrations of aerosol particles, especially fine particles, were generally high (Deng et al., 2008). In order to emphasize high fine particle pollution during haze episodes, we further defined heavy haze associated with $PM_{2.1}$ mass data, e.g., $PM_{2.1}$ >100 μg m^{-3}, visibility <5 km, and RH <85%. Hourly meteorological data including wind speed, temperature, relative humidity, dew point, pressure, and visibility were collected via automatic meteorological stations. The sampler was situated on the rooftop of the No.4 Teaching Building (20 m a.g.l.) at Fudan University (121.49E, 31.30N). Due to its distance from heavy industries or large emission sources, this site can be considered representative of Shanghai in terms of effectively measuring its air quality. More details regarding this sampling site can be found in the literature (P. F. Li et al., 2011; X. Li et al., 2011). We used an Anderson 8-stage air sampler (Thermo Electron Corporation, USA) to collect size-resolved aerosol samples into 10 size bins: <0.4, 0.4–0.7, 0.7–1.1, 1.1–2.1, 2.1–3.3, 3.3–4.7, 4.7–5.8, 5.8–9.0, and 9.0–10.0 μm (inlet). The sampler was controlled at a constant flow rate of 28.3 L min^{-1}. Twenty haze episodes occurred in Shanghai on the days 2013-12-