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Chemical characterization and sources of personal exposure to fine particulate matter ($PM_{2.5}$) in the megacity of Guangzhou, China☆

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ABSTRACT

Concurrent ambient and personal measurements of fine particulate matter ($PM_{2.5}$) were conducted in eight districts of Guangzhou during the winter of 2011. Personal-to-ambient (P-C) relationships of $PM_{2.5}$ chemical components were determined and sources of personal $PM_{2.5}$ exposures were evaluated using principal component analysis and a mixed-effects model. Water-soluble inorganic ions (e.g., SO_4^{2-}, NO_3^-, NH_4^+, $C_2O_4^{2-}$) and anhydrosugars (e.g., levoglucosan, mannosan) exhibited median personal-to-ambient (P/C) ratios < 1 accompanied by strong P-C correlations, indicating that these constituents in personal $PM_{2.5}$ were significantly affected by ambient sources. Conversely, elemental carbon (EC) and calcium (Ca^{2+}) showed median P/C ratios greater than unity, illustrating significant impact of local traffic, indoor sources, and/or personal activities on individual's exposure. SO_4^{2-} displayed very low coefficient of divergence (COD) values coupled with strong P-C correlations, implying a uniform distribution of SO_4^{2-} in the urban area of Guangzhou. EC, Ca^{2+}, and levoglucosan were otherwise heterogeneously distributed across individuals in different districts. Regional air pollution (50.4 ± 0.9%), traffic-related particles (8.6 ± 0.7%), dust-related particles (5.8 ± 0.7%), and biomass burning emissions (2.0 ± 0.2%) were moderate to high positive sources of personal $PM_{2.5}$ exposure in Guangzhou. The observed positive and significant contribution of Ca^{2+} to personal $PM_{2.5}$ exposure, highlighting indoor sources and/or personal activities, were driving factors determining personal exposure to dust-related particles. Considerable discrepancies (COD values ranging from 0.42 to 0.50) were shown between ambient concentrations and personal exposures, indicating caution should be taken when using ambient concentrations as proxies for personal exposures in epidemiological studies.

1. Introduction

Fine particulate matter ($PM_{2.5}$, particles with aerodynamic diameter < 2.5 μm) pollution poses vast public health risks globally (Kim et al., 2015; WHO, 2014). Over the past decades, epidemiological studies have reported significant associations between exposure to $PM_{2.5}$ and a variety of adverse health effects including cardiovascular disease, respiratory problems, and lung cancer (Franklin et al., 2006; Laden et al., 2000; Peng et al., 2009). Most particulate matter health effect studies use ambient (outdoor) stationary monitoring data as a surrogate for human exposure (Franklin et al., 2006; Le Tertre et al., 2002). People usually spend the majority (> 85%) of their time indoors, and more than 65% of the time is spent in their residence (Jahn et al., 2013; Klepeis et al., 2001). People can be exposed to indoor sources of $PM_{2.5}$, but also

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to ambient-generated particles while indoors. Several epidemiological studies have demonstrated that exposure to $PM_{2.5}$ of ambient origin is more deleterious compared with exposure to particles emitted indoors (Ebelt et al., 2005; Ji and Zhao, 2015; Koenig et al., 2005). In spite of the various exposure studies performed worldwide to assess personal exposure levels (Jahn et al., 2013; Johannesson et al., 2007; Weisel et al., 2004; Williams et al., 2000), only a few studies have been conducted on personal chemical composition and emission sources in developed countries over the past few years (Noullett et al., 2006; Steinle et al., 2015). Limited studies have been done on the chemical components and emission sources of particulate matter contributing to personal exposure among residents living in China (Wang et al., 2014; Xie et al., 2015; Zhang et al., 2015a), where human exposure and emission sources differ considerably from those in developed countries (Brinkman et al., 2009; Kim et al., 2005; Koistinen et al., 2004). It is important to take into account the variability of the composition and sources of personal exposure to $PM_{2.5}$ since it would provide more comprehensive information regarding an individual's exposure.

Previous studies have addressed that personal exposure to particles can be directly influenced by indoor air pollutants of ambient origin as well as exposure related to indoor sources and individual's activities (Allen et al., 2004; Noullett et al., 2010). These studies focused on the indoor-to-outdoor relationships of particulate matter as well as the variability of their chemical components (Hassanvand et al., 2014; Ho et al., 2004; Long and Sarnat, 2004). Source apportionment techniques, including Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA) have been used to estimate the contribution of specific sources to ambient and indoor $PM_{2.5}$, which have also been applied to multi-subject personal exposure data to determine the contribution of potential sources to personal exposure (mainly in developed countries) (Hopke et al., 2003; Koistinen et al., 2004; Larson et al., 2004; Minguillón et al., 2012). Few studies have been conducted in Chinese cities where elevated air pollution and adverse health impacts are likely (Xie et al., 2015). Source apportionment studies have revealed that vehicle emissions, secondary aerosols, biomass burning emissions, sea-salt, and coal combustion influence the levels and composition of ambient $PM_{2.5}$ in Guangzhou (Lai et al., 2016; Wang et al., 2006). Indoor sources (e.g., cooking, smoking, cleaning) and personal activities (e.g., vehicle emissions during commutes) are significant contributors to personal exposure (Abt et al., 2000; Hassanvand et al., 2014; Larson et al., 2004). Regression analysis has been used to differentiate the contribution of indoor and outdoor sources to particles in residential houses (Hassanvand et al., 2014; Xu et al., 2014).

In this study, $PM_{2.5}$ chemical components extracted from ambient and personal samples collected in eight districts of Guangzhou, China were measured. The objectives of this study were to 1) characterize the variability of carbonaceous components (organic carbon and elemental carbon), water-soluble ions, and anhydrosugars (e.g., levoglucosan, mannosan) in $PM_{2.5}$ across Guangzhou; 2) investigate the personal/ambient relationships of $PM_{2.5}$ chemical components; 3) identify the major sources for the personal $PM_{2.5}$ by PCA and quantify the contribution of each source to personal $PM_{2.5}$ exposure using a mixed-effects model.

2. Materials and methods

2.1. Sample collection and analysis

Personal $PM_{2.5}$ samples were collected (near the breathing zone of the subjects) over a range of nine to twelve days from eleven healthy adults (non-smokers, 5 males and 6 females, aged 18–30 years at recruitment) residing in eight districts of Guangzhou during the winter of 2011. Simultaneous stationary ambient $PM_{2.5}$ sampling (on building roofs) was performed during the same sampling period. The eight observation sites (Table 1), including three urban sites (i.e., Haizhu, Yuexiu, Tianhe), four suburban locations (i.e., Baiyun, Luogang, Panyu, Nansha), and one background site (Conghua), covering most regions of the megacity Guangzhou. Campaign design, as well as the data regarding study subjects' activity patterns, have been described in detail by Jahn et al. (2013) and Chen et al. (2016). Briefly, personal exposure to $PM_{2.5}$ was directly measured using a Personal Environmental Monitor (PEM, Model 200, MSP Corp., Shoreview, MN, USA) loaded with one quartz fiber filter (37 mm, 2 μm pore size), and connected to a portable Leland Legacy pump (SKC Inc., Eighty Four, PA, USA) at a flow rate of 10 L/min. Ambient $PM_{2.5}$ sample collection was conducted with filter based Mini-vol TAS $PM_{2.5}$ samplers (Airmetrics, Eugene, OR, USA) at a flow rate of 5 L/min. Concurrent ambient and personal exposure to $PM_{2.5}$ was measured over twenty-four hour (24 h) (from noon to noon the next day).

General information about fire counts and three-day backward trajectories at the background site, urban sites (e.g., Tianhe), and suburban sites (e.g., Nansha) during the study period is given in Fig. S1 (Supplementary material).

Collected filters were transported to the laboratory for equilibration (20 ± 5 °C, 30–40% RH) followed by gravimetric $PM_{2.5}$ mass determination. All filters were stored in a refrigerator (−20 °C) until chemical analysis. Blank samples were collected and analyzed along with the filter samples.

A 2.26 cm^2 punch was taken from each quartz filter for the analysis of organic carbon (OC) and elemental carbon (EC) concentrations by thermal-optical transmittance (TOT) with a Sunset OC/EC analyzer following the NIOSH protocol (Birch, 2002).

A portion (1.33 cm^2) of each filter sample was extracted with 3 mL ultra-pure deionized water (18.2 MΩ cm^{-1}) in pre-baked brown glass bottles under ultrasonic agitation for 60 min without heating. The extracted solution was filtered through a syringe filter (0.45 μm, Pall Corporation, NY, USA) to remove insoluble materials, and the filtrate was stored in glass bottles at 4 °C until chemical analysis. Major water-soluble anions (e.g., chloride [Cl^-], nitrate [NO_3^-], sulfate [SO_4^{2-}], oxalate [$C_2O_4^{2-}$]) and cations (e.g., sodium [Na^+], ammonium [NH_4^+], potassium [K^+], magnesium [Mg^{2+}], calcium [Ca^{2+}]) were determined using an ion chromatography (IC, ICS-3000, Dionex Corporation, Sunnyvale, CA, USA) system. Concentrations of these ionic species were corrected by subtracting the field blank values.

The solutions obtained from the same water extracts as those prepared for water-soluble inorganic ion determination were analyzed for anhydrosugars as well. Anhydrosugars (e.g., levoglucosan, mannosan) were separated, identified, and quantified by high-performance anion exchange chromatography coupled with pulsed amperometric detection (HPAEC-PAD). A Dionex ICS-3000 system was employed in this study, consisting of a dual pump module, electrochemical detector/chromatography compartment, and auto-sampler. The separation of the carbohydrate species was carried out on a Dionex Carbopac MA1 analytical column (250 × 4 mm) equipped with a guard column. An aqueous sodium hydroxide solution (NaOH, 480 mM) was used as eluent at a flow rate of 0.4 mL min^{-1}. None of the carbohydrate species were detectable in the blank samples. The detailed description of the analytical method can be found in Engling et al. (2006) and Zhang et al. (2013).

2.2. Statistical analysis

The analytical results were statistically processed by the SPSS