Size-resolved source apportionment of carbonaceous particulate matter in urban and rural sites in central California

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ABSTRACT

Very little is currently known about the relationship between exposure to different sources of ambient ultrafine particles ($PM_{0.1}$) and human health effects. If human health effects are enhanced by $PM_{0.1}$'s ability to cross cell membranes, then more information is needed describing the sources of ultrafine particles that are deposited in the human respiratory system. The current study presents results for the source apportionment of airborne particulate matter in six size fractions smaller than 1.8 μm particle diameter including ultrafine particles ($PM_{0.1}$) in one of the most polluted air basins in the United States. Size-resolved source apportionment results are presented at an urban site and rural site in central California's heavily polluted San Joaquin Valley during the winter and summer months using a molecular marker chemical mass balance (MM–CMB) method. Respiratory deposition calculations for the size-resolved source apportionment results are carried out with the Multiple Path Particle Dosimetry Model (MPPD v 2.0), including calculations for ultrafine ($PM_{0.1}$) source deposition.

Diesel engines accounted for the majority of $PM_{0.1}$ and $PM_{1.8}$ EC at both the urban and rural sampling locations during both summer and winter seasons. Meat cooking accounted for 33–67% and diesel engines accounted for 15–21% of the $PM_{0.1}$ OC at Fresno. Meat cooking accounted for 22–26% of the $PM_{0.1}$ OC at the rural Westside location, while diesel engines accounted for 8–9%. Wood burning contributions to $PM_{0.1}$ OC increased to as much as 12% of $PM_{0.1}$ OC during the wintertime. The modest contribution of wood smoke reflects the success of emissions control programs over the past decade. In contrast to $PM_{0.1}$, $PM_{1.8}$ OC had a higher fraction of unidentified source contributions (68–85%) suggesting that this material is composed of secondary organic aerosol (SOA) or primary organic aerosol (POA) that has been processed by atmospheric chemical reactions. Meat cooking was the largest identified source of $PM_{1.8}$ organic carbon (OC) at the Fresno site (12–13%) while diesel engines were the largest identified $PM_{1.8}$ OC source at the rural site (5–8%). Wood burning contributions to $PM_{1.8}$ OC increased during the wintertime at both sites (6–9%) but were relatively small during the summertime (∼1%).

As expected, diesel engines were the dominant source of $PM_{0.1}$ EC respiratory deposition at both the urban and rural site in both summer and winter (0.01–0.03 μg $PM_{0.1}$ EC deposited per m^3 air inhaled). Meat cooking accounted for 0.01–0.025 μg $PM_{0.1}$ OC deposited per m^3 air inhaled while diesel fuel accounted for 0.005–0.013 μg $PM_{0.1}$ OC deposited per m^3 air inhaled. Minor contributions from wood burning, motor oil, and gasoline fuel were calculated at levels <0.005 μg $PM_{0.1}$ OC deposited per m^3 air inhaled at both urban and rural locations during winter and summer seasons. If the burden of $PM_{0.1}$ deposited in the respiratory system is relevant for human health effects, then future toxicology studies should be carried out at $PM_{0.1}$ concentrations and source mixtures equivalent to those measured in the current study.

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1. Introduction

Exposure to elevated concentrations of fine particulate matter ($PM_{2.5}$, Dp < 2.5 μm) has been associated with adverse health effects in recent epidemiological and toxicological studies (Dominici et al., 2005; Laden et al., 2000; Ostro et al., 2006). Fine particles consist of a complex mixture of chemicals in a wide range of particle diameters that come from a variety of sources (Kleeman et al., 2008c; Phuleria et al., 2006; Riddle et al., 2007; Zielinska et al., 2004). It is known that particle diameter strongly influences deposition patterns in the respiratory system (Asgharian et al., 2004, 1995; Asgharian and Price, 2007; International

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Commission On Radiological, 1994) and the smallest airborne particles ($PM_{0.1}$; $Dp < 0.1$ μm; ultrafine PM) have the ability to cross cell membranes (Li et al., 2003) which may greatly influence their health effects. Carbonaceous particles are of particular interest because they often make up a significant fraction of ultrafine PM and various compounds within the carbonaceous matrix (polycyclic aromatic hydrocarbons, quinones, etc) can directly cause health effects (Goulaouic et al., 2008; Lewtas, 2007). Carbonaceous particles also contain molecular markers which may be used as tracers in source apportionment studies (Chow et al., 2007; Schauer and Cass, 2000; Schauer et al., 1996; Sheesley et al., 2007). Because the deposition efficiency of PM in the respiratory system is dependent upon particle size, determining the size-resolved source origins of ambient PM is a critical step in developing control strategies to mitigate adverse health effects caused by source-specific PM.

Many studies have performed source apportionment of carbonaceous PM for coarse (Dp 10–2.5 μm) and fine PM (see for example refs. (Chow et al., 1992; Chowdhury et al., 2007; Schauer et al., 1996; Stone et al., 2010, 2008; Wang and Shooter, 2005; Watson et al., 2001)) though very few studies have performed source apportionment calculations with more detailed size resolution (Kleeman et al., 2009; Minguillon et al., 2008). This lack of size-resolved source apportionment information limits the ability to test dose-dependent biological end points relating airborne PM to human health effects. Source apportionment results without size resolution cannot predict how source apportioned-PM deposits in the respiratory system. Furthermore, health studies cannot account for the amount of source-oriented ultrafine particle mass ($PM_{0.1}$) that may cross cell membranes in the respiratory system. A need exists to determine if this lack of size-resolved source resolution seriously biases source exposure estimates based on filter-based sampling methods and to demonstrate the ability to identify the dominant sources of $PM_{0.1}$ respiratory deposition in heavily polluted air basins.

The current study presents size-resolved source contribution estimates (SCE) of $PM_{0.1}$ and $PM_{1.8}$ at an urban site (Fresno, CA) and rural site (Westside, CA) in California's heavily polluted San Joaquin Valley (SJV) during the winter and summer months. Size-resolved PM source apportionment calculations are combined with a particle dosimetry model to estimate the respiratory deposition of the size-resolved source apportioned PM at different sites and seasons. These source apportionment deposition results should provide useful insights for ongoing health studies that utilize only filter-based methods for source apportionment information. Furthermore, these deposition results should aid in the design of new toxicology experiments seeking to study realistic ambient mixtures.

2. Methods

Ambient PM samples were collected in Fresno, CA (urban site) during the summer of 2006 and winter of 2007 and at Westside, CA (rural site) during the summer of 2007 and winter of 2008. The urban sampling site was bounded by a commercial development 100 m to the south, residential neighborhood 10 m to the north, and a busy regional highway 400 m west. All sample collection occurred between 9am and 3pm in a 2-week pattern (5 days on, 2 days off, and 5 days on) alongside health effects studies with results reported elsewhere (Ngo et al., 2010; Plummer et al., in preparation; Wilson et al., 2010). Six Micro-Orifice Uniform Deposit Impactors (MOUDI model 110, MSP Corp.) were used to collect ambient $PM_{1.8}$ in six size fractions to determine size distributions of organic carbon (OC), elemental carbon (EC), metals, and a number of trace organic compounds including PAHs, levoglucosan, cholesterol,

hopanes, steranes, and alkanes. Three MOUDIs were operated with Teflon (R2PJ047, Pall Corp.) substrates for gravimetric and metals analyses while the remaining three MOUDIs were loaded with aluminum foil and quartz fiber filter substrates for gravimetric and detailed organics speciation analysis. Bulk $PM_{1.8}$ Teflon and quartz filter samples were collected with co-located Reference Ambient Air Samplers (RAAS, RAAS2.5–400, Andersen) operating alongside MOUDI samplers to provide quality assurance and quality control. Each RAAS was configured to have multiple quartz behind quartz (QBQ) channels to quantify the effect of gas-phase artifacts. Aluminum and quartz filter media were pre-baked at 550 °C for 48 h prior to collection to remove background carbon.

Teflon and aluminum foil substrates underwent gravimetric analysis before and after PM collection using a Cahn-28 microbalance. Teflon filters were extracted with 75% acetone (Fisher Optima grade) and 25% 1N HNO3 (Fisher Trace Metal Grade diluted with MilliQ ultra-pure water) and evaporated under 99.9995% pure nitrogen prior to being analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500i). Detailed information regarding extraction processes and method inter-comparisons have been described previously (Herner et al., 2006a). A thermo-optical method (NIOSH 5040) was used to quantify OC and EC concentrations on foil and quartz substrates. Foil and quartz filters were composited based on PM size and analyzed by the Wisconsin State Laboratory of Hygiene. Samples were extracted with organic solvents (dichloromethane and methanol), evaporated under nitrogen, and analyzed with Gas Chromatography and Mass Spectrometry (GC–MS) using methods described previously (Schauer et al., 1996; Sheesley et al., 2004). Isotopically labeled molecular standards were added to sample extracts and served as internal standards for quantification. All Teflon and aluminum foil sample composite concentrations were field blank subtracted and all quartz sample composites were QBQ-backup subtracted.

CMB modeling (EPA CMB8.2) using trace organic molecular markers was performed on a total of 72 size-resolved filter samples. The profiles utilized in this study include wood burning, meat cooking, road dust, vegetative detritus, gasoline exhaust, diesel exhaust, and motor oil. Table S1 summarizes the $PM_{1.8}$ OC-normalized source profiles used in the current study. Composite size-resolved gasoline, diesel, and motor oil source profiles based on dynamometer testing were used as described in previous source apportionment studies (Kleeman et al., 2009; Robert, 2008). Of the molecular markers measured in the current study, benzo[ghi]perlyene and coronene were used as unique molecular markers for gasoline–fuel PM while 17α(H)-21β(H)-29-norhopane, 17α(H)-21β(H)-hopane, and αβ β20R-C29-ethylcholestane were used as unique molecular markers for motor oil PM as discussed previously be Kleeman et al. (Kleeman et al., 2008b). Levoglucosan was used as a unique tracer for wood smoke and cholesterol was used as a tracer for meat cooking. These profiles were calculated with unique ratios of tracers/OC on MOUDI stages as described by Kleeman et al. (Kleeman et al., 2008c). A paved road dust profile, based on resuspended road dust samples from Fresno was selected from the U.S. EPA's SPECIATE database (Houck et al., 1989). Finally, a vegetative detritus profile was adapted from Rogge et al. (Rogge et al., 1993b) for this study. CMB results were evaluated based on several performance measures including R^2 (0.7–1.0), χ^2 (0–4.0), degree of freedom (DF > 5.0) and an acceptance criteria ratio of 0.8–1.2 (calculated/measured) for molecular markers with high specificity to individual sources (e.g. levoglucosan for wood burning). Representative CMB fit statistics may be found in the supplemental information in Table S3.

The Multiple Path Particle Dosimetry Model (MPPD v 2.0, (MPPD)) was used to estimate deposition fractions of PM with