Title
Investigation of Particle Effective Density, Size Distribution and Dose Metric of Ambient Aerosol

Permalink
https://escholarship.org/uc/item/1mj9x7ns

Author
Lin, Yue

Publication Date
2018

Peer reviewed|Thesis/dissertation
Investigation of Particle Effective Density, Size Distribution and Dose Metric of Ambient Aerosol

A Dissertation submitted in partial satisfaction of the requirements for the degree of

Doctor of Philosophy

in

Mechanical Engineering

by

Yue Lin

December 2018

Dissertation Committee:
  Dr. Heejung Jung, Chairperson
  Dr. Kambiz Vafai
  Dr. Roya Bahreini
The Dissertation of Yue Lin is approved:

Committee Chairperson

University of California, Riverside
Acknowledgments

I would like to dedicate this part of my dissertation to thank all the agencies and individuals who helped make this dissertation possible. I would like to thank the University of California, Riverside for providing me this opportunity to study in the Department of Mechanical Engineering and supporting me financially to complete this program. I also would like to thank the Center of Environmental Research and Technology (CE-CERT) for providing me an interdisciplinary and positive learning environment as well as the necessary resources to conduct my research.

I would like to show appreciation to the University of California Transportation Center (UCTC) and National Center for Sustainable Transportation (NCST) for the fellowship I received. I acknowledge the National Science Foundation (Grant #: 1233038) for supporting this research. I acknowledge TSI, Magee Scientific and MSP for allowing us to use their equipment and vehicles for the cabin air project. I want to thank Maynard Havlicek and Ryan Han from TSI for their professional technical support all the way in troubleshooting the instruments and facilitating the data analysis. I would like to thank Dr. Roya Bahreini from the Department of Environment Science, UC Riverside for letting me use their lab for particle sampling, providing mAMS data support on my study and providing valuable insight and review opinions on my publications. I would like to thank Dr. Akua Asa-Awuku, and Dr. Emmanuel A. Fofie for providing Black Carbon data collection and analysis for my research. I would like to thank Dr. Kent Johnson and Dr. Tom Durbin’s lab for the support in our collaboration of Black Carbon study funded by ICCT. I would like to thank Michael Kleinman’s lab at UC Irvine for their support in our
The technical projects I worked on there is directly beneficial to my thesis. I also would like to thank my previous colleagues during my internship at Cummins: Sam Cao, Yusuf Khan, Chet Mun Liew, and my supervisor Shirish Shimpi. They provided professional support and guidance and led me grow on my research field.

Without the tremendous support from my colleagues and mentors at CE-CERT and the Mechanical Engineering Department, this dissertation would not be possible. I want to thank my labmates whom are Dr. Jian Xue, Yang Li, Liem Pham, Desireé Smith, and Dr. Chengguo Li for their insights and support. I also want to thank other colleagues from other groups, Dr. Ji (Jill) Luo, Dr. Peng Hao, Jiacheng (Joey) Yang, Yu (Jade) Jiang, Xinze (Eric) Peng, Weihan Peng. I want to thank Dr. Roya Bahreini’s group members Kennedy Vu, Justin Dingle, and Stephan Ziemmerman for the kind helping during my research work in their lab space.

I would like to give a special gratitude to my advisor, Dr. Heejung Jung, who had been there to guide me through this journey for the last five years. He provided guidance, knowledge, and financial support for me to thrive in this research area. On the other hand, he respected me and cared about me like a friend. Lastly, I would like to thank my family for their understanding, unconditional support and encouragement for which I am forever grateful. Without them, this would not be possible. Thank you all.
To my parents,

Zhu Lin and Shaohua Cai
ABSTRACT OF THE DISSERTATION

Investigation of Particle Effective Density, Size Distribution and Dose Metric of Ambient Aerosol

by

Yue Lin

Doctor of Philosophy, Graduate Program in Mechanical Engineering
University of California, Riverside, December 2018
Dr. Heejung Jung, Chairperson

The exposure to particulate matter (PM) has strong adverse health effects, such as aggravated asthma, decrease in lung function, and increase respiratory symptoms. PM is complex and dynamic in its chemical composition and physical mixing state. The properties of PM have not been thoroughly characterized, and the mechanism of PM causing adverse effect has not been well understood. This study focuses on characterizing physical properties of urban background air particles by analyzing the particle spectra, particle effective density, black carbon, and active surface area along with chemical characterization using AMS. The effective density profiles were used to estimate the respiratory system-deposited ambient particle mass according to lung deposition fraction curve reported by ICRP (1994).

The first study was to determine size-resolved effective densities of ambient aerosols in Riverside, CA for four 7-day periods during 2015 – 2016. The mass of size selected particles (50, 70, 101 and 152 nm) were measured to determine the effective density for particles. A catalytic
stripper (CS) in alternating mode was used to remove volatile compounds on the aerosol before density measurements. Aerosol non-refractory composition measurement was conducted in June 2016 campaign to understand the effect of chemical composition on particle density. The average particle densities for all measurement campaigns with CS bypassing mode (BP) were 1.17 g/cm³ at 50 nm and 1.25 – 1.28 g/cm³ at 70, 101 and 152 nm. The average density after CS conditioning (CS mode) showed a decreasing trend from 1.22 g/cm³ to 1.04 g/cm³ withincreasing selected size, and a mass fractal dimension (D_f) of 2.85. Both the BP and CS mode particles showed the lowest effective density from 6:00 AM to 9:00 AM and highest density from 11:00 AM to 3:00 PM. The diurnal variation of density became more profound as particle size increases for both sampling modes. The variation was found to be more intense for the CS mode compared than the BP mode. To confirm this observation, organic aerosol and ammonium nitrate mass in the similar size range were tested simultaneously with BP mode. The results showed effective density measurements correlated well with positively (R²=0.78) and negatively (R²=0.62). This study provided an update to the aerosol density profiles of a well-known receptor site (Riverside, CA) and investigated the transformation of particles in different seasons. The obtained effective density profiles were used in the proceeding study in order to effectively estimate the respiratory-deposited ambient aerosol mass.

In the second study, the size distributions and effective densities of ambient particles measured in September 2015 and June 2016 were used to calculate time-dependent lung deposited particulate matter (PM) mass using lung deposition fraction curve reported by ICRP (1994). The particle active surface area, black carbon (BC) mass, particle number (PN), solid particle number (SPN), and suspended PM mass (from particle size distributions and effective densities) were also obtained to investigate correlations with PM dose. Non-refractory organic and inorganic mass measured by an aerosol mass
spectrometer (mAMS) provided additional information in relation to dose versus chemical nature of particles.

Ambient particle size distributions showed strong diurnal variations during the sampling period. While the lung deposited PM mass fraction (0.32-0.36) did not vary much with time, lung deposited and suspended PM mass in the ambient air showed similar trend. Deposition in the alveolar region was the highest (0.3-1.0 μg/m³), which was followed by the nasal region (0.16 – 0.83 μg/m³) and tracheobronchial region (0.05 – 0.27 μg/m³). All three regions peaked at 12:00 PM – 6:00 PM and reached the lowest value near midnight.

One of the goals of this study was to consider the most prominent ambient PM measurement method in consideration to health and lung deposition. Suspended PM mass had the highest correlation with respiratory doses, which was followed by organics measured using mAMS, active surface area, and BC mass. It is also found that particle hygroscopicity did not affect correlations between metrics and lung deposited PM mass. By taking into account the accessibility and cost of these measurements, we propose the particle active surface area and BC mass to be considered when evaluating/monitoring the health effects caused by PM.
Table of Contents

Table of Contents ............................................................................................................. x
List of Figures .................................................................................................................. xi
List of Tables .................................................................................................................... xiii
Definitions/Abbreviations ................................................................................................. xiv
1 Background ..................................................................................................................... 1
2 Investigation of ambient aerosol effective density with and without using a catalytic stripper .................................................................................................................. 11
   2.1 Introduction .............................................................................................................. 11
   2.2 Experimental .......................................................................................................... 12
      2.2.1 Measurement location and period .................................................................. 12
      2.2.2 Instrumentation .............................................................................................. 13
   2.3 Results and Discussions ....................................................................................... 16
      2.3.1 Overview of meteorological conditions ....................................................... 16
      2.3.2 Size-resolved effective density and fractal dimension ......................... 18
   2.4 Conclusion .............................................................................................................. 30
3 In search of a particle dose metric using estimated lung-deposited PM mass from particle size distributions and effective densities .................................................. 31
   3.1 Introduction .............................................................................................................. 31
   3.2 Experimental .......................................................................................................... 32
   3.3 Results and Discussions ....................................................................................... 34
      3.3.1 Particle size spectra with and without using CS ..................................... 34
      3.3.2 Calculation of the PM dose to three different areas in the human respiratory system 41
      3.3.3 Dose vs PM metric ...................................................................................... 43
      3.3.4 Effect of hygroscopic growth ..................................................................... 51
   3.4 Conclusion .............................................................................................................. 52
References ....................................................................................................................... 54
List of Figures

Figure 2-1: Map of the sampling site and its distance from the closest highway. .......... 12
Figure 2-2 Schematic of the experimental setup................................................................. 14
Figure 2-3 Wind rose in during the four measurement periods.............................................. 17
Figure 2-4 Average effective densities over all the measurement periods for BP and CS modes. Data from previous studies are also included for comparison. ......................... 19
Figure 2-5 Mass fraction of dominant non-refractory species measured by mAMS during June 2016. ...................................................................................................................... 20
Figure 2-6 Effective densities in different measurement periods for particles in BP and CS modes. The whiskers represent the 5th and 95th percentile, the two borders of box display the 25th and 75th percentile, and the band in each box denotes the median........ 22
Figure 2-7 Diurnal trends of the effective density averaged over the whole measurement period for BP (a) and CS (b) modes.......................................................... 23
Figure 2-8 Diurnal trends of the effective densities averaged over each measurement period for different selected sizes in BP (a) and CS (b) modes................................. 26
Figure 2-9 The diurnal trends of mAMS non-refractory species and BP density averaged over the four measurement sizes, during June 2016 campaign. The mAMS species mass concentrations were summed over d_{aer}=70-268 nm corresponding to the density measurement size range. The hourly mass fractions were calculated based on the average of 50-80 data points during the campaign (corresponding to 1-min averages when all the mAMS integrated mass distributions resulted in positive mass concentrations). The density values for the four measured particle sizes were averaged by hour of the day. ... 29
Figure 3-1 Schematic diagram of the experimental setup for ambient particle size distribution and effective density measurement. .......................................................... 33
Figure 3-2 Summary of meteorological conditions, particle size distribution and particle effective density during campaigns. a) temperature and humidity trend, b) wind speed and direction, c) BP mode particle size spectra, d) CS mode particle size spectra, e) particle number concentration, and f) BP mode particle effective density variation during June 2016 measurement period g) temperature and humidity trend, h) wind speed and direction, i) BP mode particle size spectra, j) CS mode particle size spectra, k) particle number concentration, and l) BP mode particle effective density variation during September 2015 measurement period......................................................... 38
Figure 3-3 Time series of volatile and non-volatile suspended particle mass concentrations in (a) June 2016 (b) September 2015 measurement period. ....................... 41
Figure 3-4 Time course of PM dose at different regions of the human respiratory system during (a) June 2016 and (b) September 2015 measurement periods.......................... 43
Figure 3-5 Scatterplot matrix between deposited mass in the human respiratoroty system and aerosol metrics in (a) June 2016 and (b) September 2015 campaign. ............... 46
Figure 3-6 Particle number and mass distributions. a) Average number and b) mass particle size distribution for June 2016 data; c) Average number and d) mass particle size distribution for June 2016 data. Size independent and time-varying particle effective density were used for mass calculation of the BP mode. Size-dependent and time-varying particle effective density were used for mass calculation of CS mode................. 48
Figure 3-7 Correlations between accumulated deposited mass vs. aerosol properties in June 2016 campaign assuming all ambient aerosol are hygroscopic. The accumulated deposited mass was estimated by applying Löndahl et al. (2009)’s size-dependent deposition fraction of curbside hygroscopic aerosol group on our PM$_{IPSD}$. .....................
List of Tables

Table 2-1 Summary of the meteorological condition .......................................................... 17
Definitions/Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>Black Carbon</td>
</tr>
<tr>
<td>CARB</td>
<td>California Air Resources Board</td>
</tr>
<tr>
<td>CE-CERT</td>
<td>College of Engineering-Center for Environmental Research and Technology</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensation Particle Counter</td>
</tr>
<tr>
<td>CPMA</td>
<td>Centrifugal Particle Mass Analyzer</td>
</tr>
<tr>
<td>CS</td>
<td>Catalytic Stripper</td>
</tr>
<tr>
<td>$d_m$</td>
<td>Mobility equivalent diameter</td>
</tr>
<tr>
<td>$D_m$ or $D_f$</td>
<td>Mass-Mobility Exponent</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analyzer</td>
</tr>
<tr>
<td>DOS</td>
<td>Diocyl Sebacate</td>
</tr>
<tr>
<td>EAD</td>
<td>Electrical Aerosol Detector</td>
</tr>
<tr>
<td>EEPS</td>
<td>Engine Exhaust Particle Sizer</td>
</tr>
<tr>
<td>GMDs</td>
<td>Geometric Mean Diameters</td>
</tr>
<tr>
<td>GSA</td>
<td>Geometric surface area</td>
</tr>
<tr>
<td>GSD</td>
<td>Geometric standard deviation</td>
</tr>
<tr>
<td>HOA</td>
<td>Hydrocarbon-like Organic Aerosol</td>
</tr>
<tr>
<td>MAAP</td>
<td>Multi-Angle Absorption Photometer</td>
</tr>
<tr>
<td>mAMS</td>
<td>Aerosol Mass Spectrometer</td>
</tr>
<tr>
<td>NAAQS</td>
<td>National Ambient Air Quality Standards</td>
</tr>
<tr>
<td>NCST</td>
<td>National Center for Sustainable Transportation</td>
</tr>
<tr>
<td>OC</td>
<td>Organic Carbon</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PM</td>
<td>Particulate Matter</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle size distribution</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>SCAQMD</td>
<td>South Coast Air Quality Management District</td>
</tr>
<tr>
<td>SMPS</td>
<td>Scanning Mobility Particle Sizer</td>
</tr>
<tr>
<td>SPN</td>
<td>Solid Particle Number</td>
</tr>
<tr>
<td>UCR</td>
<td>University of California at Riverside</td>
</tr>
<tr>
<td>$\rho_{eff}$</td>
<td>Effective density</td>
</tr>
</tbody>
</table>
1 Background

Atmospheric aerosol plays an important role in human health, air quality, and climate change. Atmospheric aerosol is complex and dynamic in its chemical composition and physical mixing state. Effective density is an important property to understand the mixing state, transport, and depositional characteristics of particles in the ambient atmosphere and human respiratory system. Conventionally, average bulk density is used to convert lung-deposited particle number to mass by assuming spherical particle shape, which leads to some degree of uncertainties in the estimated deposited mass.

Since McMurry et al. (2002) have developed an online size-resolved effective density measurement method using Differential Mobility Analyzer (DMA)-Aerosol Particle Mass analyzer (APM) technique, this technique has been applied to fresh soot and ambient aerosol to examine morphology and mass-mobility relationships (Geller et al., 2006; Levy et al., 2014; Rissler et al., 2014).

Effective density, $\rho_{\text{eff}}$, is defined as the ratio of particle mass ($m$) to volume of a sphere with the mobility equivalent diameter ($d_m$):

$$\rho_{\text{eff}} = \frac{6m}{\pi d_m^3}$$

(Equation 1-1)

The mass-mobility exponent ($D_m$) is an indirect measure of the morphology of irregularly shaped fractal-like particles. $D_m$ can be determined from known effective densities of particles at different mobility sizes (Park et al., 2003):

$$\rho_{\text{eff}} = C d_m^{D_m-3}$$

(Equation 1-2)
The mass-mobility exponent is the same as the fractal dimension, $D_f$, when the ratio between radius of gyration ($R_g$) and mobility diameter ($d_m$) is constant (Maricq and Xu, 2004; Park et al., 2003; Sorensen, 2011).

$\rho_{eff}$ and $D_f$ (or $D_m$) can be determined by measuring particle mass at different mobility diameters using a DMA-APM system (McMurry et al., 2002) or DMA-centrifugal particle mass analyzer (CPMA) (Olfert and Collings, 2005). The CPMA technique works similarly to APM and has a better instrument inversion transfer function than the APM (Olfert et al., 2007).

The number of studies on particle effective density of ambient aerosols has gradually increased thanks to the establishment of measurement methods and advancement of instrumentation. McMurry et al. (2002) demonstrated capability of DMA-APM system and applied it first for the measurement of effective density of ambient aerosol in Atlanta, GA. They showed the measured density of 1.5 to 1.7 g/cm$^3$ agrees with the density calculated based on chemical composition for two selected sizes of 107 and 309 nm particles. Using the same technique, Geller et al. (2006) conducted measurement at various locations in Los Angeles Basin. They observed bimodal density distributions at a location where both traffic and background aerosols were present. They also showed that effective density is driven by photochemistry and meteorology at a receptor site in Riverside, California. The particle effective density of 50 nm particles rapidly dropped from 1.4 g/cm$^3$ in the mid afternoon to a value of 1.2 g/cm$^3$ by sunset. The value of 1.2 g/cm$^3$ is an assumed density for organic aerosol by Turpin and Lim (2001). Spencer et al. (2007) confirmed that effective density
varies dynamically, as much as 40%, within 16 h in Riverside, CA during photochemical seasons. They found a correlation between effective density and ambient water content. However, they assumed the correlation might be an artifact due to evaporation in the aerodynamic lens of their aerosol mass spectrometer. Levy et al. (2014) conducted continuous density measurements at US-Mexico border near Tijuana, Mexico for one-week in June, 2010. They reported mixing state and effective density of ambient particles in the size range of 46-240 nm. They showed that the 46 nm particles have the most distinctive diurnal cycle, with the lowest density in the afternoon (at 1-4 pm) likely associated with fresh black carbon emission from vehicles, and the highest in the early morning (at 1-4 am), suggesting the presence of primary organic aerosol. Levy et al. (2013) also conducted density measurement in Houston, Texas. They showed that the effective density has a minimum during morning rush hour and it increases from morning to the afternoon (i.e. 7 am to 5 pm) likely due to particle-phase sulfate and oxidized organic components. Rissler et al. (2014) conducted semi-continuous density measurement at an open street canyon in central Copenhagen, Denmark during winter season. They reported both soot and more dense particles were present in 50-400 nm size range. Additionally, they used a thermal denuder in-between DMA and APM and measured the volatile mass fraction of soot as ~10% and those of dense particles as ~80 to 100%. Yin et al. (2015) conducted a five-week long measurement in Shanghai, China during December, 2012-January, 2013. They found effective density increased with increasing particle size. They also reported a high correlation between effective density and mass fraction of secondary inorganic aerosol.
In chapter 2, density data was collected in different seasons throughout a year, along with size-dependent, non-refractory aerosol composition measured by a compact time-of-flight aerosol mass spectrometer (mini-C-ToF-AMS or mAMS, Aerodyne Research Inc.). The (CS)-DMA-CPMA system measured effective density of ambient particles in Riverside, CA in the size range of 50-152 nm, where the alveolar and tracheobronchial deposition efficiency is high (Oberdörster et al., 2005). While Rissler et al. (2014) measured the volatile mass fraction, our approach measures effective density of the non-volatile core particles. Fractal dimensions determined from the current study will reveal the degree of restructuring of the core particles. Riverside, located in Los Angeles (LA) basin, is a well-known receptor site of traffic emissions from LA. Vehicular exhaust particles are transported eastward from LA while undergoing photochemical processes, and occasionally trapped in Riverside by surrounding mountains and stagnant air at this site. Continuous measurement of effective density was conducted with the overall aim of constraining the inhalable mass budget of ambient aerosol. Diurnal evolution of effective density has significant implications on composition and mass of PM deposited onto the lung. The objective of the current study is to understand the evolution of effective density of particles in Riverside, CA at different seasons of the year. The findings of this study were subsequently used in Chapter 3 to estimate the mass based dose of aerosol that could potentially deposit in human lungs.

A specific question, of both legislative and research interest, is the choice of the appropriate metric to assess these effects (Kreyling et al., 2006). Currently, particulate mass is the metric used to regulate PM (Particulate Matter) concentrations for both ambient
air quality standards and source emissions standards (EPA, 2004). There are ample number of health effect studies and data built around this metric for several decades (Dockery et al., 1993). These studies are the scientific basis for regulations to mitigate the adverse health effects by lowering particle mass concentrations. Numerous studies have shown reduction of PM mass such as PM2.5 reduces adverse human health effects (Brook et al., 2010; Clancy et al., 2002; Delfino et al., 2005; Pope et al., 2004; Schwartz et al., 1996). These studies enabled enforcing low PM mass emitting technologies in sources, such as low PM mass emitting vehicles, benefiting society with improved air quality.

Mass metric has served very well to improve public health by cleaning air up to the current levels during the past decades. Significant health benefits have been achieved by lowering ambient PM mass concentrations. Majority of the US cities are attaining National Ambient Air Quality Standards (NAAQS) for PM2.5 while there are some areas such as central California and Los Angeles (LA) basin that have remained as non-attainment areas for a long time. Benefits on human health due to the reduction of ambient PM2.5 mass is known to have non-linear relationships (For example see Figure 1 of (Apte et al., 2015)). Underlying physics, chemistry, biology, and toxicity may have contributed to this non-linearity. There are conflicting evidences regarding further increasing health benefits of a more stringent NAAQS. Laden et al. (2006) extended the mortality analysis of the Harvard Six Cities adult cohort study, following them up for 8 years in a period of reduced air pollution concentrations, and reported that total, cardiovascular, and lung cancer mortality were each positively associated with ambient PM2.5 concentrations. They also reported reduced PM2.5 concentrations were associated with reduced mortality risk. Di et al.
(2017a; 2017b) analyzed the entire Medicare population from 2000 to 2012 residing in 39,182 zip codes and reported there is a risk of mortality by exposure to PM2.5 and ozone, even at levels below current national air quality standards. On the other hand, Enstrom (2017) re-analyzed 1982 American Cancer Society Cancer Prevention Study (CPS II) cohort data and reported no significant relationship between PM2.5 and total mortality in the CPS II cohort when the best available PM2.5 data were used. Young et al. (2017) analyzed air quality and acute deaths in California from 2000 to 2012, and found little evidence for association between air quality and acute deaths.

A specific question, of both legislative and research interest, comes to examine appropriateness of PM metrics in light of improved measurement capabilities of particle properties. Particle number, solid particle number, black carbon concentration, particle active surface area and suspended particle mass are examples of metrics of consideration discussed here.

Particle number is regarded as a non-ideal metric since there has been evidence of negative correlation between PM2.5 mass and particle number concentrations (Baldauf et al., 2016; Stanier et al., 2004). On the other hand, solid particle number (SPN) can potentially be a better metric, considering soot is a carrier for toxic compounds and SPN should have relatively good correlations with PM2.5. Toxic compounds, such as polycyclic aromatic hydrocarbons (PAHs) are adsorbed on the surface of solid particles and carried into the human respiratory system. Soot aggregates from combustion, as the most abundant solid particle type in an urban environment, act as a carrier of carcinogenic compounds. A solid particle number concentration limit of $6 \times 10^{11}$ particles/km has been included in Euro
5/6 standards for light-duty diesel vehicles (UNECE, 2008). The Euro 6 standard for heavy-duty diesel vehicles includes a solid particle number concentration limit as well, with the proposed limits of $8 \times 10^{11}$ particles/kWh for stationary cycles and $6 \times 10^{11}$ particles/kWh for transient cycles (Johnson, 2010). While the current regulatory solid particle measurement system for vehicle exhaust is a sophisticated system (Giechaskiel et al., 2008) composed of a heated and cooled dilutor, evaporation tube, and condensational particle counter (CPC), a simpler system can be designed for the measurement of ambient air. This study used integrated particle concentrations using a catalytic stripper-SMPS system. A simpler system such as a catalytic stripper-CPC system can measure solid particle number of ambient air for routine monitoring.

Previous studies suggested surface area concentrations in various environments may be suitable to present negative human health effects of aerosol exposure. Toxicological studies have found that ultrafine particles may have an increased toxicity compared to larger particles with the same composition and mass (Johnston et al., 2000; Karlsson et al., 2009) due to higher specific surface area.

Many previous studies were based on BET surface area (Brunauer et al., 1938) which requires relatively large sample amount and post-collection analysis procedures. BET surface area is not a convenient metric for routine monitoring. Geometric surface area (GSA) refers to the external surface area of particles, but does not include internal pore areas like BET. Lall and Friedlander (2006) and Lall et al. (2006) developed a theory to calculate geometric surface area of chain aggregates. Cao et al. (2017) also reported some success measuring GSA for spherical and aggregate particles. Both studies have limitations.
as they need to know types of particles before the measurement to determine GSA. Particle active surface area defines the exterior envelop surface area that is responsible for mass transfer of diffusing species. It can be measured using a diffusion charger and can be a promising and feasible metric for routine monitoring. Moshammer and Neuberger (2003) reported correlations of the measured active surface area for particle sizes ranging from 10 nm to 1 µm with lung function and pulmonary symptoms of school children in Austria. Moshammer et al. (2004) also reported the active surface area as a good indicator for ETS (environmental tobacco smoke) exposure. They found a good correlation between active surface area and nicotine concentrations in the ambient air.

Black Carbon (BC) mass also has the potential to be a good indicator of the aerosols’ adverse health effects. Epidemiological studies have provided evidence for the positive association of human health effects with exposure to BC. Delfino et al. (2010) found BC mass has a positive association with blood pressure but it has a weaker correlation than with aerosol organic carbon mass. Mordukhovich et al. (2009) observed positive associations between blood pressure and BC, but not with PM2.5. Janssen et al. (2011) performed a systematic review and meta-analysis of health effects of BC compared with PM mass based on data from time-series studies. They concluded that mass increase of BC led to higher mortality and more frequent hospital admissions compared to PM2.5 or PM10 mass. Toxicological studies suggest that BC may operate as a ubiquitous carrier of a wide variety of chemicals of varying toxicity to the human body (WHO, 2012). BC is a dominant component in traffic-related particles. There are a few studies suggesting the potential of
BC as a proxy to estimate health effects from the exposure to traffic related pollutants (Janssen et al., 2011; Schaap and van der Gon, 2007).

Lung-deposited particle mass is of researchers’ interest. To estimate the respiratory deposited mass, aerosol size-resolved density profile is needed. There are a few studies which applied size-resolved particle effective density to estimate the lung-deposited dose of ambient PM. Rissler et al. (2012) and Wierzbicka et al. (2014) applied differential mobility analyzer (DMA)-aerosol particle mass analyzer (APM) technique to measure size dependent density of diesel exhaust particles and used the density profile with particle size distributions to estimate the respiratory deposited particulate mass.

PM deposition in the human respiratory tract (or PM dose) is an important link between exposure to ambient particulates and observed health effects. There are limited studies reporting PM dose (or lung-deposited PM mass) of ambient particulate (Löndahl et al., 2009) and diesel exhaust (Rissler et al., 2012; Wierzbicka et al., 2014). Löndahl et al. (2006) developed a flow-through system, which was applied to human subjects, to measure the lung-deposition fraction as a function of particle size by comparing particle size distributions during inhalation and exhalation. With this technique, Löndahl et al. (2007) reported there is almost no dependence of the deposition fraction by gender and exercise level; however, higher dose was measured for male subjects and during exercise due to increased ventilation rate. They also reported the deposition fraction of hygroscopic ultrafine particles could be estimated by calculating their equilibrium size at 99.5% relative humidity (RH), i.e., the RH in the alveolar region (Anselm et al., 1990). Additionally, Löndahl et al. (2008) investigated aerosol deposition fraction and growth factor using
hygroscopic particles from biomass combustion using their flow-through system. They reported deposition fraction is affected by particle hygroscopicity and that hygroscopic ultrafine particles obtain deposition probabilities close to the minimum due to hygroscopic growth. In a follow up study, Löndahl et al. (2009) investigated deposition fraction of curbside ambient particles to understand deposition fraction of traffic related particles. They found that deposition fraction of particles from curbside was much higher than those from biomass combustion because of the lower fraction of hygroscopic particles and higher number of ultrafine particles. While Löndahl and his colleagues research provide critical information regarding deposition fraction and growth factor, involvement of human subjects prevents application of this method for routine monitoring.

The study in Chapter 3 aims to: 1) determine lung-deposited PM mass using particle size distributions determined by a scanning mobility particle sizer (SMPS), particle effective density determined by DMA-CPMA method, and lung deposition fraction curves in an SOA- (secondary organic aerosol) rich area, Riverside, CA. 2) compare correlations between the lung-deposited particle mass and ambient aerosol monitoring metrics, such as BC, SPN, suspended PM mass and active surface area to determine metrics that correlate best with lung-deposited PM mass (or PM dose). We acknowledge reactivity (and toxicity) of particles vary widely and dose by itself may not be sufficient to explain all of the adverse aerosol health effects. Despite this, physical metrics provide a common denominator for toxicity measurements and ambient monitoring. Results of this study will inform policy-makers about importance of different metrics that could be considered for developing future regulations.
2 Investigation of ambient aerosol effective density with and without using a catalytic stripper

2.1 Introduction

Particle effective density is an important property in the study of mixing state, transport, depositional characteristics of particles in the ambient atmosphere, and human respiratory system. Previous studies have reported particle effective density in various locations and specific seasons. This study collected size-dependent density data (for both unconditioned particles and non-volatile aerosol) and non-refractory aerosol composition measured by a compact time-of-flight aerosol mass spectrometer (mini-C-ToF-AMS or mAMS, Aerodyne Research Inc.) for different seasons throughout the year. The CS-DMA-CPMA system measured effective density of ambient particles in Riverside, CA in the size range of 50-152 nm, where the alveolar and tracheobronchial deposition efficiency is high (Oberdörster et al., 2005). While Rissler et al. (2014) measured the volatile mass fraction, our approach measured effective density of the non-volatile core particles. Fractal dimensions determined from this study will reveal the degree of restructuring of the core particles. The objective of the this study is to understand the evolution of particle effective density in Riverside, CA at different seasons of the year. Diurnal evolution of effective density has significant implications on composition and deposited PM mass in the lung. Furthermore, continuous measurement of effective density could serve to constrain the diurnal inhalable mass budget of ambient aerosol. A follow-up study will use the findings of this study and estimate the mass budget of aerosol that could potentially deposit in human lungs (Chapter 3).
2.2 Experimental

2.2.1 Measurement location and period

The measurements were conducted on the second floor of the Geology building at the University of California, Riverside (33.974762, -117.326313). The sampling location is 0.55 km away from the nearest highway, State Route 60, and 3.6 km away from highway 91 (Figure 2-1). The measurements were performed in four periods during summer, fall, and spring seasons: 9/16/2015-9/23/2015, 10/22/2015-10/30/2015, 3/1/2016-3/13/2016, 6/6/2016-6/15/2016, continuously (24 hours per day) in each measurement duration.

![Figure 2-1: Map of the sampling site and its distance from the closest highway.](image)

Figure 2-1: Map of the sampling site and its distance from the closest highway.
2.2.2 Instrumentation

The general experimental setup is shown in Figure 2-2. Each density measurement required 7-9 mins. Ambient particles were sampled through a 50 liter residence chamber, to provide a pseudo-steady state condition for each measurement. All instruments were located inside the building next to the sampling window. The sampling probe protruded out of the window with the exposed length of 1.5 m upstream of the chamber. A lab-made Catalytic Stripper (Abdul-Khalek and Kittelson, 1995; Martin, 2003) operating at 300 °C was employed to remove volatile particle fraction. A three-way solenoid valve (ASCO Valve, Inc, Novi, MI.) was programmed to switch the flow passage between bypass (BP mode) and Catalytic Stripper (CS mode) every 10 minutes. A DMA-CPMA-CPC (DMA model 3081, TSI, Inc.; CPMA, Cambustion, Limited; CPC model 3022, TSI, Inc.) system was placed downstream of the solenoid valve to measure particle effective density, once every 10 min. Four mobility diameters \(d_m=50, 70, 101,152\ \text{nm}\) were selected. Effective density and fractal dimension values were calculated using Equations 1 and 2, given the mass corresponding to the mode in the scan data and the \(d_m\) selected by DMA. More detailed description on applying CPMA for density measurements can be found in Olfert and Collings (2005).

A Multi-angle Absorption Photometer (MAAP Thermo Scientific model 5012) was deployed in June 2016 to measure the black carbon mass (Petzold et al., 2002). mAMS was deployed in June 2016 to characterize the non-refractory chemical nature of particles, downstream of a silica gel diffusion drier. Composition-dependent collection efficiency correction was applied to the bulk mAMS concentrations(Middlebrook et al., 2012a). In
order to compare the mAMS mass distribution data that are provided in vacuum aerodynamic diameter ($d_{va}$) with density data in the electrical mobility diameter, the following relationship was used:

$$d_{va} = d_m \frac{\rho_m}{\rho_0} S$$

(Equation 2 - 1)

Where $S$ is the Jayne shape factor, usually assumed to be 1 for spherical and <1 for non-spherical particles, $\rho_m$ is material density, and $\rho_0$ is standard density (1 g/cm$^3$) (DeCarlo et al., 2004). Here with lack of the Jayne shape factor, we roughly estimate the $d_{va}$ by using an averaged material density of $\rho_m$=1.53 g/cm$^3$, using 10-min average non-refractory and BC composition and assuming density of 1.75 g/cm$^3$ for ammonium nitrate and ammonium sulfate, 1.3 g/cm$^3$ for organic aerosol (OA), and 1.8 g/cm$^3$ for BC (Cross et al., 2007; Middlebrook et al., 2012a; Park et al., 2003). In addition with assuming $S$=1, $d_m$=50-152 nm corresponds to $d_{va}$=77-233 nm.

Figure 2-2 Schematic of the experimental setup

Early studies (McMurry et al., 2002; Olfert et al., 2007) have used poly styrene latex spheres (PSLs) to calibrate DMA-APM and DMA-CPMA systems for density measurement. In cases where the mode diameter is selected from a dried stream of nebulized PSL particles, it is known that there is up to 7% error in detecting 100 nm
standard reference material (SRM) 1963 using well-calibrated DMA systems (Mulholland et al., 1999). A well calibrated DMA size selection is known to be within ±3% (Kinney et al., 1991) in the size range of our interest, which is comparable to the accuracy of commercially available PSLs. Voltages for DMA were confirmed to be accurate within 1%, the sheath flow was within 1.5%, and sample and monodisperse flow were within 5% of the set values. Calibration tests were conducted using PSLs (Nanospheres, Thermofisher) at the four selected mobility diameters (46±2 nm, 70±3 nm, 102±3 nm, 147±3nm) which correspond to the nominal average diameters of the PSL. Errors in determined density values ranged from -6 to 5% compared to the literature values. Additional calibration tests were conducted for the four selected sizes using NaCl. As NaCl aerosol is not spherical, a shape factor was taken into account by solving the implicit equation for slip correction factor. The uncertainty in the determined density from NaCl calibration tests ranged from 4 to 7%. We chose not to use the voltage method Park et al. (2003) and Olfert et al. (2007) proposed to calibrate DMA-CPMA because newer models of CPMA are more reliable with full commercialization of the instrument, with the uncertainty being at ~ 4% for 95% confidence interval (see section 3 of Symonds et al. (2013)). Errors with the voltage calibration method can be as large as that of PSLs. Additionally, we chose to change both the rotational speed (rpm) and voltage of the CPMA to have the same mass resolution for all measurements. Quiros et al. (2015) used the same approach for their measurements of vehicular exhaust particles to determine particle effective density. They used dioctyl sebacate (DOS) particles for their calibration tests. The difference between measured and bulk DOS spheres density remained below 9.4%. We
expect similar uncertainties in our density determination. We conducted PSL calibrations before and after the measurement campaigns. The errors remained constant over the duration of the test program and no performance drift was observed.

2.3 Results and Discussions

2.3.1 Overview of meteorological conditions

The meteorological conditions of all measurement periods are summarized in Table 2-1 and Figure 2-3. The data were collected from the meteorology station at Riverside Municipal Airport, which is 9.6 km away from the sampling location. Riverside is dominated by desert-like climate. Solar radiation is strong throughout the year and as a result, the temperature and relative humidity (RH) vary dramatically during day and night time. Daily temperature reached its peak at around 3 pm and was the lowest at around 5 am before sunrise. As expected, the opposite trend was observed for RH. The different ambient RH level could have affected water content of aerosols and aerosol effective density. During the measurement periods, Riverside was mostly dominated by eastward wind, from coastal areas of Los Angeles region. During Oct. 22-30, 2015, the nighttime was dominated by wind of moderate speed from North or Northeast. During other sampling periods, the westward wind appeared mostly in the early morning. Meteorological conditions during the sampling periods were comparable to the annual trends in the region.
Table 2-1 Summary of the meteorological condition

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient temperature (°C)</td>
<td>20-42</td>
<td>16-33</td>
<td>5-27</td>
<td>15-31</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>13-85</td>
<td>9-85</td>
<td>17-93</td>
<td>32-90</td>
</tr>
<tr>
<td>(average ± standard deviation)</td>
<td>(55.4 ± 19.9)</td>
<td>(41.5 ± 21.5)</td>
<td>(62.8 ± 18.6)</td>
<td>(64.9 ± 15.4)</td>
</tr>
</tbody>
</table>

Figure 2-3 Wind rose in during the four measurement periods
2.3.2 Size-resolved effective density and fractal dimension

The size-resolved effective density values averaged over the whole measurement period for BP and CS modes are shown and compared with previous studies in Figure 2-4. Error bars indicate standard deviations of the averaged values. During the BP mode measurements, particle effective density ranged from 1.17 to 1.28 g/cm³ with slightly increasing trend as diameter increased in the 50 – 152 nm size range. This is similar to the previously reported average values, ranging from 1.29 to 1.40 g/cm³, by Geller et al. (2006) who conducted ambient measurements in Riverside in 2005. Effective density measured by Levy et al. (2014) at Tijuana ranged from 1.21 to 1.31 g/cm³ in the size range of our interest. Both Geller et al. (2006) and Levy et al. (2014) showed decreasing density trends as the diameter increased. Average mAMS non-refractory measurements of composition in June 2016 period also indicated an increase in the fraction of inorganic species and a decrease in the hydrocarbon-like fraction of organic aerosol (HOA) with size in 50-152 nm range of density observations (Figure 2-5). However, when we calculated time- and size-dependent material density of particles from chemical composition of mAMS measurements with the addition of a size-independent soot fraction, assuming particle sphericity and pure material densities of 1.75 g/cm³ for ammonium nitrate and ammonium sulfate, 1.25 g/cm³ for OA (to capture the higher contribution of fresh OA to the smaller sizes), and 1.8 g/cm³ for BC, we did not observe a significant size-dependence (Cross et al., 2007; Middlebrook et al., 2012a; Park et al., 2003). We speculate the discrepancy is in part due to the assumptions used in this calculation (e.g, size-independent soot fraction and particle sphericity), variability in the individual size distributions, as well as uncertainties.
of DMA-CPMA method. Further investigation is necessary to better understand size-dependent effective density.

Figure 2-4 Average effective densities over all the measurement periods for BP and CS modes. Data from previous studies are also included for comparison.

Size resolved effective density averaged over the whole measurement period for the thermally treated (i.e. CS mode) ambient particles ranged from 1.22 g/cm$^3$ to 1.04 g/cm$^3$, and decreasing with diameter (Figure 2-4). These are particles downstream of CS and therefore without significant semi-volatile components. It is expected that the majority of the non-volatile particles in our measurement range are soot particles. The average effective density profile resembled those of fresh soot measured in the lab by Maricq and Xu (2004) and Park et al. (2003) and they reported $D_f$ = 2.3-2.4 for fresh diesel soot and $D_f$=2.15 for flame generated fresh soot. However, the mass fractal dimension determined from this study was 2.85, indicating more compact shape, and therefore more aged soot.
compared to the fresh soot. This value is very similar to $D_f = 2.83$ which Geller et al. (2006) reported for the measurements in Riverside.

Figure 2-5 Mass fraction of dominant non-refractory species measured by mAMS during June 2016.

Given the large variability in the averaged density values over the whole measurement period, we examine the trends of density with aerosol size in each sampling period separately (Figure 2-6). Relatively large standard deviation for each period suggests effective density of ambient particles vary significantly daily and hourly. For ambient particles measured in BP mode, the measurement during October showed the highest and March the lowest effective density, while densities in September and June were comparable in terms of both average and median values. This may be the result of an interplay between transport and photochemistry. October period had lower temperatures than September. If photochemistry was the only driver, we expect to observe the highest densities during September. Densities for each measurement period are also plotted in box-whisker plots. Mean and median effective density of ambient particles in BP mode slightly increased as the particle size increased. Previous studies (Geller et al., 2006; Spencer et al., 2007)
conducted in Riverside showed either nearly constant or decreasing densities as particle
diameter increased while measurements in Shanghai China by Yin et al. (2015) showed an
increase in effective density as particle size increased. The increasing trends of density with
aerosol size will be further discussed in Section 3.3 along with aerosol chemical
composition results. Measurement conducted in March showed the least variability of the
data while the one conducted in October showed the largest variability, consistent with
wind direction variability in October (Figure 2-3) and the potential for sampling different
types/age aerosols. Effective densities of the non-volatiles particles (in CS mode) showed
a different trend. Average density showed the smallest values for March and the largest
values for June (Figure 2-6). Additionally, mean and median effective density values were
very similar for 50-101 nm particles while they decreased for the 152 nm particles during
all measurement periods, except for the June period. The lowest variability in the CS-mode
density of all particle sizes was also observed during June. We speculate that non-volatile
particles may have been more compacted during the June period. Measurement during
October period showed the largest variation of densities in CS mode, similar to what was
observed in BP mode.
2.3.3 Diurnal trends of effective density

Diurnal trends of average effective density of the whole measurement period are shown in Figure 2-7. Overall, density of particles in BP mode showed less variation during the day compared to those of CS mode. The 50 nm size particles showed the least variation in density for CS mode. This is likely due to a more compact morphology for small particles compared to larger size. For particles in CS mode, the largest size (i.e. 152 nm) showed the largest variation in density. Particle effective density in BP mode varied from 0.88 g/cm$^3$ to 1.40 g/cm$^3$ while those in CS mode varied from 0.49 g/cm$^3$ to 1.26 g/cm$^3$.
Figure 2-7 Diurnal trends of the effective density averaged over the whole measurement period for BP (a) and CS (b) modes.
For further investigation, diurnal profiles of particle effective density for each test measurement period were plotted in Figure 2-8 as a function of selected mobility diameters. Strong diurnal trends were observed over all four sampling periods. The lowest values of effective density were observed during the morning rush hour while the values became larger after sunrise, when photochemistry becomes active, which is consistent with Levy et al. (2013)’s study in Houston. As mentioned above, we attribute the large variation in 2015 October period in part to the dynamic meteorological conditions, i.e. varying upstream wind speed and directions. The diurnal trends appeared more pronounced for particles in CS mode and larger sizes (101, 152 nm) compared to particles in BP mode and smaller particles (50 nm, 70 nm). We speculate that nonvolatile particles, which are most likely soot, may have undergone some degree of restructuring in CS mode measurements in the current study and that the degree of restructuring is likely related to the amount and type of volatile materials coated on the particles. Restructuring of soot aggregates is due to increased surface tension during evaporation of coated material; therefore, the extent of soot restructuring is material dependent (Bhandari et al., 2017). Evaporation of coated material can take place in the atmosphere when particles undergo dilution or temperature changes as well as during measurements in cases when a thermal denuder or catalytic stripper is used. Cross et al. (2010) reported the effect of coating and denuding on the soot optical properties using sulfuric acid and DOS as the coating material. Their study showed that there was a stronger restructuring of the soot core using sulfuric acid compared to DOS. Xue et al. (2009) also found restructuring of soot aggregates when they were first
coated with glutaric acid and then denuded while there was no evidence for restructuring if coating was with succinic acid. Ghazi and Olfert (2013) also reported a dependence for soot restructuring on the mass of different coating material types until the amount of coating material exceeded a critical mass, leading to a complete collapse of the aggregate (i.e. $D_f=3$).
Figure 2-8 Diurnal trends of the effective densities averaged over each measurement period for different selected sizes in BP (a) and CS (b) modes.
To further understand the influence of chemical composition on the particle effective density, mAMS data during 2016 June measurement period were analyzed for both BP and CS modes. Average, size-dependent mass fractions of the non-refractory species of BP mode are shown in Figure 2-5. Ammonium sulfate (AS) and ammonium nitrate (AN) mass concentrations were calculated using the measured sulfate and nitrate mass concentrations while assuming full neutralization of these anions by ammonium. This assumption was supported by the bulk mass concentrations of ammonium, nitrate, and sulfate as measured by mAMS. Traces of oxygenated organic aerosol (OOA) and hydrocarbon-like OA (HOA) were estimated using simple parameterizations based on the mass distributions of ion fragments at $m/z$ 44 and 57 amu (Ng et al., 2010). With this simple parameterization, the sum of OOA and HOA explained ~80% of total organics in the size range of density measurements. As apparent in Figure 2-5, organics (more specifically, OOA) dominated the mass in the size range of the density measurement for BP mode while AN dominated the mass at larger sizes. Diurnal mass fractions of non-refractory species in sizes corresponding to the density measurements are shown in Figure 2-9. AN mass fraction peaked ~2-10 am, consistent with favorable partitioning of ammonium nitrate, which is semivolatile, to the aerosol phase at lower temperatures and higher RH conditions during the early hours of the day (e.g., Drewnick et al., 2004; Jimenez et al., 2003). On the other hand, OA mass fraction showed a rapid increase ~9-11 am, with a gradual increase until 6pm, and a decrease afterwards. OA and AN mass fractions correlated positively and negatively with BP mode particle density averaged over the four size selections very well.
with $r^2$ 0.78 and 0.62 respectively. However, particle effective density increased during the day when the fraction of lower density material (i.e. OA) increased and the fraction of the relatively denser AN decreased. An explanation for this counter-intuitive observation is that possibly the particles are internally mixed (as opposed to externally mixed) and OA filled the void areas of soot aggregates in the size range of our interest better than AN. With the decrease in AN content, aerosol hygroscopicity and thus water content must have decreased too and so one could expect a higher aerosol density since OA is typically more dense than water. We found unimodal distributions in most of the size selected mass distribution measurements and a very weak bimodality was found only for a few measurements, indicating only one mixing state, likely internally mixed state, was prevalent in our size range of interest. We also compared PM mass, determined by the product of effective density and volumes from mobility diameter, with total –non-refractory aerosol mass determined by mAMS. Interestingly the PM mass determined by using particle size distributions and density profiles showed an excellent correlation with the measured OA ($R^2=0.87$) while the correlation became much weaker with total mass by mAMS ($R^2=0.14$) in the size range from 50 to 152 nm in mobility diameter, supporting our hypothesis of OA filling the void of aggregates that provided the most surface area for adsorption of OA in the first place. Lack of a high correlation between PM mass determined by particle size distributions and inorganic mass is expected considering a large fraction of the inorganic species were present at sizes much larger than the size range of our particle size distribution measurement. Detailed comparisons among different metrics will be discussed in more detail in the follow up paper where the focus is to find a metric which
best correlates with lung deposited PM mass. The mAMS measurement during CS mode resulted in negligible detection of non-refractory material, with average concentrations less than 6% of that in BP mode. We speculate the extent of restructuring of soot in the CS mode may have been related to the volatile mass fraction in the BP mode. Particles may have been restructured to some extent when volatile species coated on the soot surface evaporated in the CS. It should be noted that mobility size selection for density measurements was performed downstream of the CS indicating that the original particle sizes are larger than the selected sizes. This approach makes it difficult to understand the extent of atmospheric aging or restructuring of the soot before thermal denuding with the CS. Further studies with alternative sampling methods are necessary to untangle these effects.

Figure 2-9 The diurnal trends of mAMS non-refractory species and BP density averaged over the four measurement sizes, during June 2016 campaign. The mAMS species mass concentrations were summed over \( d_{oa}=70-268 \text{ nm} \) corresponding to the density measurement size range. The hourly mass fractions were calculated based on the average of 50-80 data points during the campaign (corresponding to 1-min averages when all the mAMS integrated mass distributions resulted in positive mass concentrations). The density values for the four measured particle sizes were averaged by hour of the day.
2.4 Conclusion

Size-resolved effective density of 50-152 nm particles were measured by a (CS)-DMA-CPMA system, combined with parallel measurement of aerosol composition during 2015-2016 at Riverside, a well-known receptor site for pollution from LA area. The BP mode particle effective density ranged from 1.17 g/cm$^3$ to 1.28 g/cm$^3$, with a slightly increasing trend as particle size increased. On the other hand, effective density of particles in CS mode showed a decreasing density trend from 1.22 g/cm$^3$ to 1.04 g/cm$^3$, with a fractal dimension of 2.85. The effective density of BP and CS mode particles showed pronounced diurnal trends, with the lowest values observed during the morning traffic time and the peak in the early afternoon. The particle density of BP mode correlated well with OA mass. While diurnal density variation in BP mode seemed to be related with OA filling the void space of soot aggregate, diurnal density variation for CS mode particles appeared to be related to particle restructuring in the presence of semivolatile components. Although diurnal variations in the measured density were supported by time-dependent mAMS composition measurements, size-dependent density changes could not be clearly explained by the estimated material densities. Future studies should consider measuring mobility sizes before and after CS to quantify the amount and fraction of semivolatile components. The size-resolved density data will be used in a follow-up paper to estimate particle mass deposited in human lungs at the receptor site, Riverside CA for different seasons.
3 In search of a particle dose metric using estimated lung-deposited PM mass from particle size distributions and effective densities

3.1 Introduction

Particulate mass is used to regulate PM (Particulate Matter) concentrations in ambient air quality and source emissions standards (EPA, 2004). Mass metric has served very well to improve public health by reducing the level of particulates in the air for the past few decades. However, more recent studies suggested the benefits on human health due to the reduction of ambient PM2.5 mass is known to have non-linear relationships (Apte et al., 2015). The underlying physics, chemistry, biology, and toxicity may have contributed to this non-linearity. With an improvement in measurement capabilities of particle properties, one of the interesting questions for both legislative and research interest is to evaluate for alternative PM metrics. Particle number, solid particle number, BC mass, particle active surface area, and suspended particle mass are examples of metrics of consideration for this study.

This study takes lung-deposited PM mass as a representative indicator for adverse health effect. The first objective of this study is to determine lung-deposited PM mass using particle-size distributions determined by a scanning mobility particle sizer (SMPS), particle effective density determined by DMA-CPMA method, and lung deposition fraction curves in a secondary organic aerosol rich area, Riverside, CA. The second objective is to compare correlations between the lung-deposited particle mass and ambient aerosol monitoring metrics, such as BC, SPN, suspended PM mass, and active surface area
to determine metrics that correlate best with lung-deposited PM mass (or PM dose). We acknowledge reactivity (and toxicity) of particles vary widely and dose by itself may not be enough to explain all of the adverse health effects relating to aerosols. Despite this, physical metrics provide a common denominator for toxicity measurements and ambient monitoring. Results of this study will inform policy-makers about importance of different metrics that could be considered for developing future regulations.

3.2 Experimental

The measurements were conducted at the second floor of the Geology building at the University of California, Riverside (33.974762, -117.326313), 0.55 km away from the nearest highway (State Route 60) and 3.6 km away from highway 91. The measurements were conducted continuously during two periods: 09/16/2015-09/23/2015 and 06/06/2016-06/15/2016.

The experimental setup is shown in Figure 3-1. Ambient particles were sampled through a residence chamber with residence time of 4.4 minutes to provide pseudo-steady state condition for each measurement. All the instruments were placed indoors at a constant temperature of 25 °C.

* DMA is operated with sheath flow rate 7.5 LPM and sampling flow rate of 1.5 LPM.
Figure 3-1 Schematic diagram of the experimental setup for ambient particle size distribution and effective density measurement.

An aethalometer (Magee Scientific model AE33) measured the BC mass concentration in September 2015 campaign, and MAAP (Thermo Scientific model 5012) measured the BC in June 2016 campaign. An Electrical Aerosol Detector (EAD TSI model 3070A) measured active surface area based on diffusion charging. A lab-made Catalytic Stripper (CS, (Abdul-Khalek and Kittelson, 1995; Stenitzer, 2003)) operating at 300 °C was used to remove semivolatile components of ambient aerosols. The wall loss in the CS mode was corrected by an experimentally-determined, size-dependent penetration efficiency curve. A three-way solenoid valve (ASCO Valve, Inc) was programmed to switch the flow passage between ambient (BP mode) and the CS (CS mode) every 10 minutes. A DMA-centrifugal particle mass analyzer (CPMA)-CPC (DMA model 3081, TSI, Inc.; CPMA, Cambustion, Limited; CPC model 3022, TSI, Inc.) system was placed downstream of the solenoid valve to measure particle effective density, once every 10 min. Four mobility diameters (d_m= 50, 70, 101, 152 nm) covering the range where the alveolar and tracheobronchial deposited mass fraction is relatively high (Oberdörster et al. (2005)) were selected. Detailed description of the density measurement setup of this study was reported in a previous manuscript (Lin et al., 2018). A Scanning Mobility Particle Sizer (SMPS) consisting of a Differential Mobility Analyzer (TSI model 3081) and Condensation Particle Counter (CPC TSI model 3022) was used to measure particle size distributions (PSDs) in the range of 10 -346 nm.
A compact time-of-flight aerosol mass spectrometer (mini-AMS or mAMS) measured non-refractory dry aerosol composition in June 2016 campaign. Composition-dependent collection efficiency correction was applied to the bulk mAMS concentrations (Middlebrook et al., 2012b).

3.3 Results and Discussions

3.3.1 Particle size spectra with and without using CS

Temperature and RH in Figure 3-2a show strong diurnal trends from 6/6 to 6/10 and 6/12 to 6/13. On the other hand, much weaker diurnal temperature and RH trends were observed on 6/11. Westerly wind was dominant with the average wind speed of 4 m/s during the period as shown in Figure 3-2b. Figures 3-2c and 2d show particle spectra for BP mode and CS mode. Note that wall loss in the CS was corrected for CS mode particle spectra using experimentally determined penetration curve for the CS. Maximum particle concentrations were observed during 6-7pm as temperature-driven mixing (or dilution) rapidly slows down. Figure 3-2e shows PN for CS and BP modes. Strong diurnal trends were observed except on 6/11. CS mode particle concentration was the lowest (~4000 particles/cm$^3$) at 6-7am and the highest (~15,000 particles/cm$^3$) at 6-7 pm. The BP mode particle concentration was the highest (~30000 particles/cm$^3$) at ~7pm. Figure 3-2c shows that particle mode diameter increased from ~20 nm at ~9am to ~90 nm at ~12pm, and decreased from noon to night time to 10-30 nm. Time dependent and size independent BP mode particle effective density, shown in Figure 3-2f, was obtained by averaging the nearest size-dependent particle effective density at each time. We published in depth analysis of the effective density analysis separately in our previous work (Lin et al., 2018)
. We found the CS mode particle effective density is clearly size-dependent and can be characterized by mass-mobility exponent. We also found BP mode effective density has a slight size-dependency, but the variance was within the measurement uncertainty. As such, we decided to determine size- independent (or size-averaged) particle effective density at each time to calculate suspended PM mass (PM$_{IPSD}$) for the BP mode. Size- independent BP mode particle effective density showed strong diurnal trend from 6/6 to 6/10 while the diurnal trend got weaker from 6/12 to 6/13.
Figure 3-2 Summary of meteorological conditions, particle size distribution and particle effective density during campaigns. a) temperature and humidity trend, b) wind speed and direction, c) BP mode particle size spectra, d) CS mode particle size spectra, e) particle number concentration, and f) BP mode particle effective density variation during June 2016 measurement period g) temperature and humidity trend, h) wind speed and direction, i) BP mode particle size spectra, j) CS mode particle size spectra, k) particle number concentration, and l) BP mode particle effective density variation during September 2015 measurement period.
Temperature and RH in Figure 3-2g show strong diurnal trends from 9/17 to 9/21. On the other hand, slightly weaker diurnal temperature and RH trends were observed on 9/16 and 9/22. Westerly wind was dominant from 9/17 to 9/19 with the average wind speed of 3.2 m/s during the period as shown in Figure 2h. Figures 2i and 2j show particle spectra for BP mode and CS mode. Particle size distributions showed broader atmospheric accumulation mode particles compared to those in the June measurement period (Figures 2c and 2d). The time for maximum particle concentrations varied daily during September measurement period as shown in Figures 3-2k and 3-2l. Time-dependent and size-independent BP mode particle effective density are shown in Figure 3-2m.

Particle mass concentration of the BP mode, $M_{BP} \, (\mu g/m^3)$ was calculated by the following equation:

$$M_{BP} = \sum_i \rho_{avg,BP} \frac{\pi d_i^3}{6} n_i,BP$$  \hspace{1cm} (Equation 3-1)

Where the $\rho_{avg,BP}$ is the average effective density of the BP mode over the four measured particle sizes (50nm, 70nm, 100nm, 150nm) that was used to cover size range of 10-350 nm, $d_i$ is the particle diameter of the size bin from the particle size distribution, and $n_i$ is the number concentration of the size bin.

Non-volatile (or CS mode) particle mass concentration was calculated by the following equation:

$$M_{CS} = \sum_i \rho_{i,CS} \frac{\pi d_i^3}{6} n_{i,CS}$$  \hspace{1cm} (Equation 3-2)
Where $\rho_{i,CS}$ is particle effective density of the CS mode at the $i^{th}$ size bin. Particle effective density profile was obtained at each time by fitting the particle effective density measured at each selected size in the nearest time steps to mass fractal dimension equation:

$$\rho_{eff} = C d_m^{D_m-3}$$  \hspace{1cm} (Equation 3-3)

Effective density at the $i^{th}$ size bin is obtained using the constant ($C$) and mass-mobility exponent ($D_m$) determined at each time step. As the largest selected mobility diameter was 150 nm, effective density larger than 150 nm diameter was obtained by extrapolating the mass-mobility relationship (McMurry et al., 2002; Park et al., 2003).

Both volatile aerosol (obtained by subtracting CS mode from BP mode) and non-volatile ambient aerosol mass showed diurnal trends (Figure 3-3). Non-volatile ambient particle mass on 6/11 and 6/12 were much lower compared to the other dates in Figure 3-3a. Likewise, volatile PM mass showed reduced concentration. We speculate this reduction in particle mass was due to changes in meteorological conditions (such as relatively high late-afternoon temperatures on 6/11 and 6/12 suppressing boundary layer height reduction in the late afternoon, leading to less reduction in vertical mixing (or dilution)), and not due to changes in traffic pattern during the weekend. Previous studies (e.g. Bahreini et al., 2012)) have shown that mass concentration of secondary organic aerosols, the major component of submicron aerosol mass, in the Los Angeles Basin is unchanged on weekends relative to weekdays despite a significant reduction in diesel traffic emissions during the weekends. Figure 3-3b confirms that meteorological condition dictates both non-volatile and volatile PM mass at the measurement location. The volatile mass fraction
of ambient aerosol ranged from 0.51 to 0.87 (0.48 to 0.94) with the average of 0.74 (0.79) and standard deviation of 0.06 (0.05) during June period (September period).

Figure 3-3 Time series of volatile and non-volatile suspended particle mass concentrations in (a) June 2016 (b) September 2015 measurement period.

3.3.2 Calculation of the PM dose to three different areas in the human respiratory system

The area plot in Figure 3-4 shows temporal trends of deposited particle mass (or dose) in different sections of the human respiratory system. The deposited mass concentration of the BP mode, $M_{BP,\text{deposit}}$ ($\mu g/m^3$) was calculated by the following equation:

$$M_{BP,\text{deposit}} = \sum_l \rho_{avg,BP} \frac{\pi d_l^2}{6} n_l \eta_l$$

(Equation 3-4)
Where the \( \rho_{avg,BP} \) is the average effective density of the BP mode over the four measured particle sizes (50nm, 70nm, 100nm, 150nm) that was used to cover size range of 10-350 nm, \( d_i \) is the particle diameter of the size bin from the particle size distribution, \( n_i \) is the number concentration of the size bin, and \( \eta_i \) is the deposition fraction from ICRP (1994).

Nasal and alveolar regions showed 2.85 and 3.15 times higher deposited PM mass, respectively, compared to tracheobronchial regions over the size range of 10-350 nm. More specifically, the dose to alveolar region is the highest among three regions in the respiratory system, with deposited mass ranging from 0.3 - 1.0 \( \mu g/ m^3 \) for the conditions encountered during these measurement periods. The dose to nasal area was the second highest, ranging from 0.16 – 0.83 \( \mu g/ m^3 \). The dose to tracheobronchial region is the lowest (0.05 – 0.27 \( \mu g/ m^3 \)). PM dose followed the diurnal trend of PM\textsubscript{IPSD}. The deposited PM mass (or dose) in all three regions in the respiratory system consistently peaked at noon ~ 6pm and showed the lowest value near midnight. The deposited PM mass fraction, ranged from 0.32 – 0.36, and it did not vary much with time.
Figure 3-4 Time course of PM dose at different regions of the human respiratory system during (a) June 2016 and (b) September 2015 measurement periods.

3.3.3 Dose vs PM metric

Our goal is to find a physical metric, e.g. solid particle number, BC mass, or suspended PM mass, which has the best correlation with PM dose, i.e. lung-deposited PM mass. Figure 3-5a and 5b show the scatterplot matrix between deposited mass in the human
respiratory system and aerosol properties in June 2016 and September 2015 campaigns, respectively. We included mAMS-measured organic aerosol (OA) for comparison although mAMS monitoring is costly and not practical for routine monitoring.

PM$_{IPSD}$ showed the highest correlation coefficients of nearly 1 with PM dose during both June and September periods in Figure 3-5. We attribute this to the characteristics of particle size distributions at a background location. Figure 3-6 shows period-averaged particle number and mass size distributions. While number peaks are below 100 nm where the lung deposition fraction is the highest, mass peaks are at 168 nm for CS mode and 242 nm for BP mode. We may find larger contribution of ultrafine particles at locations where primary emissions are important, such as near-road locations. In that case, PM$_{IPSD}$ may have a lower correlation coefficient with PM dose.

Because of MAAP malfunctioning during the June period, we used the aethalometer data from the September measurement period to investigate the correlations between BC and PM dose. Figure 3-5b shows BC measured by Aethalometer has moderate correlation, with correlation coefficient $R^2$ ranging from 0.56 to 0.63, with PM dose.
Figure 3-5 Scatterplot matrix between deposited mass in the human respiratory system and aerosol metrics in (a) June 2016 and (b) September 2015 campaign.
(a) $dN/d\log D_p$ (#/cm$^3$) vs $D_p$ (nm)

- BP mode
- CS mode

(b) $dM/d\log D_p$ (µg/m$^3$) vs $D_p$ (nm)

- BP mode
- CS mode
Figure 3-6 Particle number and mass distributions. a) Average number and b) mass particle size distribution for June 2016 data; c) Average number and d) mass particle size distribution for June 2016 data. Size independent and time-varying particle effective density were used for mass calculation of the BP mode. Size-dependent and time-varying particle effective density were used for mass calculation of CS mode.
Table 1 summarizes correlations between dose and PM metrics shown in Figure 3-5ab. Among the metrics of our interest, the PM_{IPSD} showed the best correlation with the human respiratory system deposited mass (R^2 = 0.99-1), followed by OA (R^2 = 0.91-0.95), active surface area (R^2 = 0.80-0.90), oxygenated OA (R^2 = 0.73-0.75), PN (CS-mode) (R^2 = 0.59-0.78), BC mass (R^2 = 0.56-0.63) and, PN (BP-mode) (R^2 = 0.45-0.57). Correlations were similar for deposition in different sections of the respiratory system. As discussed earlier, PM_{IPSD} and mAMS are not ideal methods for a routine monitoring practice. However, active surface area measurements based on a diffusion charging instrument (i.e. EAD) are relatively inexpensive and easy to maintain and deploy. BC and PN (CS-mode) reported intermediate correlations in this study. We expect BC to have a higher correlation with PM dose in locations where primary emissions are more prevalent. Future health effect studies should consider including these two promising metrics (active surface area and BC) and compare effectiveness of these metrics with the current PM mass metrics determined by FEM (Federal Equivalent Method) and FRM (Federal Reference Method).
Table 3-1 Correlations ($R^2$) between deposited PM mass in the human respiratory system and PM metrics

<table>
<thead>
<tr>
<th></th>
<th>PN (BP-mode, 10-346nm, #/cm³)</th>
<th>PN (CS-mode, 10-346nm, #/cm³)</th>
<th>Active surface area (EAD, mm/cm³)</th>
<th>PM mass (IPSD, 10-346nm, μg/m³)</th>
<th>Volatile mass (IPSD, 10-346nm, μg/m³)</th>
<th>Non-volatile mass (IPSD, 10-346nm, μg/m³)</th>
<th>Org mass (AMS, 10-346nm, μg/m³)</th>
<th>OOA mass (AMS, 10-346nm, μg/m³)</th>
<th>BC mass (Aethalometer, μg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nasal</td>
<td>0.45 0.55</td>
<td>0.59 0.73</td>
<td>0.80 0.87</td>
<td>1.00 0.90</td>
<td>0.97 0.98</td>
<td>0.87 0.88</td>
<td>0.91 -</td>
<td>0.73 -</td>
<td>- 0.56</td>
</tr>
<tr>
<td>Tracheobronchial</td>
<td>0.56 0.57</td>
<td>0.68 0.78</td>
<td>0.87 0.90</td>
<td>0.99 1.00</td>
<td>0.97 0.99</td>
<td>0.88 0.86</td>
<td>0.94 -</td>
<td>0.74 -</td>
<td>- 0.64</td>
</tr>
<tr>
<td>Alveolar</td>
<td>0.57 0.57</td>
<td>0.69 0.78</td>
<td>0.87 0.90</td>
<td>0.99 1.00</td>
<td>0.98 0.99</td>
<td>0.86 0.87</td>
<td>0.95 -</td>
<td>0.75 -</td>
<td>- 0.63</td>
</tr>
<tr>
<td>Total</td>
<td>0.53 0.57</td>
<td>0.66 0.76</td>
<td>0.85 0.89</td>
<td>1.00 1.00</td>
<td>0.98 0.99</td>
<td>0.87 0.87</td>
<td>0.94 -</td>
<td>0.74 -</td>
<td>- 0.61</td>
</tr>
</tbody>
</table>

Figure 3-7 Correlations between accumulated deposited mass vs. aerosol properties in June 2016 campaign assuming all ambient aerosol are hygroscopic. The accumulated deposited mass was estimated by applying Löndahl et al. (2009)’s size-dependent deposition fraction of curbside hygroscopic aerosol group on our PM$_{IPSD}$. 

PN (BP-mode, 10-346nm, #/cm³)
PN (CS-mode, 10-346nm, #/cm³)
Active surface area (EAD, mm/cm³)
PM mass (IPSD, 10-346nm, μg/m³)
Volatile mass (IPSD, 10-346nm, μg/m³)
Non-volatile mass (IPSD, 10-346nm, μg/m³)
Org mass (AMS, 10-346nm, μg/m³)
OOA mass (AMS, 10-346nm, μg/m³)
BC mass (Aethalometer, μg/m³)
3.3.4 Effect of hygroscopic growth

The relative humidity (RH) in the lungs has been estimated to be 99.5% (Anselm et al., 1990). Particles can grow to larger size at this RH depending on their hygroscopicity. Hämeri et al. (2000) reported a growth factor (GF) of 1.72 for 50 nm ammonium sulfate assuming RH\text{dry}=40\% and RH\text{wet}=90\%. Hu et al. (2011) reported GF of \(\approx 1.36 - 1.68\) for 50 - 150 nm ammonium nitrate for RH increasing from 40\% to 86\%. Hu et al. (2011) reviewed hygroscopicity of urban ambient particles and found ambient particles exhibited growth distributions with at least one hygroscopic mode with GF = 1.15-1.68 besides the hydrophobic mode. Aerosol composition measurements previously reported in Lin et al. (2018) indicated that aerosols in the size range of 10-346 nm were dominated by OA (42.6\%) and BC (39.7\%, assuming all the measured bulk BC was in this size range), with a minor contribution from ammonium sulfate (13.2\%) and ammonium nitrate (4.5\%). Size dependent growth factor can be measured using a setup which measures particles size distribution before inhalation and after exhalation, similar to that of Löndahl et al. (2006), or can be calculated if mixing state and chemical composition are known. While we have some information about chemical composition, we do not know the aerosol mixing state or size distribution of BC. As such, we decided to use a deposition fraction (see their Figure 6) of hygroscopic particles that Löndahl et al. (2009) has determined to qualitatively assess the effect of hygroscopic growth of particles on deposition. The deposition fraction curve of hygroscopic particles shows lower values than that of dry particles from ICRP due to hygroscopic growth. Use of Löndahl et al. (2009) deposition fraction curve for hygroscopic particles will lead to less contribution of ultrafine particles to the total PM mass deposited.
in the respiratory system. Figure 3-7 shows the new correlation plots between the various metrics and total deposited PM mass in the respiratory system, assuming all particles were hygroscopic. Interestingly there was no significant difference in correlations with the metrics when hygroscopic growth was considered. That is because contribution of the ultrafine particles to the total deposited PM mass was not significant enough in this environment. This may change in different measurement locations where primary emissions dominate particle size distributions. The current analysis assumed PM toxicity is based on the mass of deposited PM. If PM toxicity is based on other metrics such as lung-deposited particle surface area or number, the correlations may change quite differently.

3.4 Conclusion

We measured ambient particle size distribution, effective density, BC, surface area and volatile fraction in September 2015 and June 2016 at Riverside, CA and investigated the correlation between these particle metrics and the respiratory deposited PM mass.

Ambient particle size distributions showed strong diurnal variations during the sampling period. Particle mode diameter was the lowest (10-30 nm) at nighttime and highest (~90nm) at noon. Particle concentration was the highest at ~7 pm (~30,000 particles/cm³ for BP mode and ~15,000 particles/cm³ for CS mode), and the lowest (~4000 particles/cm³) at 6-7 am for CS mode.

While the deposited PM mass fraction (0.32-0.36) didn’t vary much with time of the day or during the sampling periods, PM mass deposited in the human respiratory system followed trends of the suspended PM mass in the ambient air. Dose for the alveolar region
was the highest (0.3-1.0 \mu g/m^3), followed by that for the nasal region (0.16 – 0.83 \mu g/m^3), and that for tracheobronchial region (0.05 – 0.27 \mu g/m^3). All PM doses peaked at noon-6pm and reached the lowest value near midnight.

PM_{PSD} correlated best with respiratory doses, followed by OA, active surface area, and BC mass. Particle hygroscopicity did not affect correlations between metrics and lung-deposited PM mass. Considering accessibility and cost of these measurements, we propose that active surface area and BC mass measurements be considered when evaluating/monitoring the health effects caused by air pollution.
References


determinations using light scattering in conjunction with aerosol mass spectrometry. Aerosol Science and Technology 41, 343-359.


