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Characterization and Nonparametric Regression of Rural and Urban Coarse Particulate Matter Mass Concentrations in Northeastern Colorado

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The Colorado Coarse Rural Urban Sources and Health study (CCRUSH) is an ongoing study of the relationship between coarse particulate mass concentrations ($PM_{10–2.5}$, particulate matter with diameter between 2.5 and 10 μm) and selected health effects. For two urban monitoring sites in Denver, CO, and two comparatively rural sites in Greeley, CO, hourly mass concentrations of $PM_{10–2.5}$ and fine particulate matter ($PM_{2.5}$, diameter less than 2.5 μm) have been measured by using dichotomous tapered element oscillating microbalances (TEOMs) with Filter Dynamics Measurement Systems (FDMS). This paper presents air quality results from just over a year of $PM_{2.5}$ and $PM_{10–2.5}$ measurements. Average $PM_{2.5}$ concentrations ranged from 7.7 to 9.2 $\mu g\ m^{-3}$ across the four sites with higher concentrations in Denver than Greeley. Average $PM_{10–2.5}$ concentrations ranged from 9.0 to 15.5 $\mu g\ m^{-3}$ with the highest values at the site in northeast Denver. Temporal variability in $PM_{10–2.5}$ was higher than that in $PM_{2.5}$ concentrations at all four sites. The two Greeley sites displayed moderate spatial correlation for $PM_{2.5}$ and high correlation for $PM_{10–2.5}$, whereas the two Denver sites showed lower spatial correlation for both PM sizes. $PM_{10–2.5}$ concentrations in Denver were highest with winds from the direction of the city's urban core. $PM_{10–2.5}$ concentrations in Greeley were moderately elevated with winds from the southwest to the northwest, coming from Denver and other large Front Range communities. Wind speed regressions for $PM_{10–2.5}$ at the Denver sites primarily exhibited resuspension effects, while $PM_{10–2.5}$ concentrations in Greeley showed relatively complex wind speed dependence.

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1. INTRODUCTION

Coarse particulate matter in the size range from 2.5 to 10 μm ($PM_{10–2.5}$) is believed to be important for human health because particles in this size range are capable of penetrating the thoracic region of the lungs when inhaled (Chan and Lippmann 1980). Size-resolved and chemically speciated data indicate that compared to particulate matter less than 2.5 μm in diameter ($PM_{2.5}$), $PM_{10–2.5}$ is more likely to contain crustal elements such as aluminum, iron, and calcium, but may also contain ions, transition metals, organic, and biological material (Milford and Davidson 1985, 1987; Boreson et al. 2004; Hueglin et al. 2005). $PM_{10–2.5}$ is commonly derived from abrasive mechanical processes, including construction and agricultural activities, resuspended road dust, vegetative debris, and sea spray (Duce et al. 1976; Patterson and Gillette 1977), with emissions from many of these processes depending strongly on the wind speed (Harrison et al. 2001). It is also produced from incomplete combustion of solid fuels such as coal and biomass (U.S. EPA 1995).

Brunekreef and Forsberg (2005) reviewed nearly 60 studies that evaluated health effects of short-term exposure to $PM_{10–2.5}$ and concluded that for some endpoints, including chronic obstructive pulmonary disease, asthma, and respiratory admissions, $PM_{10–2.5}$ could have as strong or a stronger effect than $PM_{2.5}$. Short-term increases in $PM_{10–2.5}$ have also been positively associated with mortality in several studies (Castillejos

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et al. 2000; Mar et al. 2000; Ostro et al. 2000; Villeneuve et al. 2003; Zanobetti and Schwartz 2009). In a recent review of studies of the health effects associated with short-term exposure to ambient $PM_{10–2.5}$, the U.S. Environmental Protection Agency (EPA) concluded that existing evidence is suggestive of a causal relationship between exposures and mortality, cardiovascular effects, and respiratory effects (U.S. EPA 2009). EPA also recognized several critical uncertainties in epidemiology studies of $PM_{10–2.5}$ impacts, including relatively high exposure error compared to $PM_{2.5}$, due to greater expected spatial variability in $PM_{10–2.5}$ concentrations, and limitations in the characterization of spatial distributions. Many epidemiologic studies published to date have used differences between PM_{10} and $PM_{2.5}$ concentrations measured at colocated monitors and in some cases, monitors located at different sites within the same county to estimate $PM_{10–2.5}$, which contributes further uncertainty in exposure estimation. Furthermore, epidemiologic studies of $PM_{10–2.5}$ have mostly focused on urban areas, where large populations result in greater power for detecting statistically significant effects. Because sources of $PM_{10–2.5}$ may be different in urban compared to rural regions, the associations with health effects may also be different in smaller communities or rural areas.

Because of their size, coarse particles are removed from the atmosphere more quickly than fine particles. As a consequence of both deposition velocity and the intermittent nature of many source processes, concentrations of $PM_{10–2.5}$ are expected to be more spatially and temporally variable than $PM_{2.5}$ concentrations. Wilson et al. (2005) reviewed prior studies and found that reported correlation coefficients between sites within several cities ranged from 0.14 to 0.60 for 24-h average $PM_{10–2.5}$ concentrations; these values are generally lower than those observed for $PM_{2.5}$ or PM_{10}. Chen et al. (2007) found an average correlation coefficient of 0.75 between 24-h average $PM_{10–2.5}$ concentrations measured for about 70 days at a central monitor in Chapel Hill, NC, and monitors placed at residences within about a 60 km radius. With a year of weekly monitoring at 10 sites across the Los Angeles basin, Pakbin et al. (2010) found pairwise correlations ranging from 0.04 for 24-h average $PM_{10–2.5}$ concentrations from an industrial site in Long Beach and concentrations at 2 suburban monitors located about 30 and 70 km away, to 0.80 for $PM_{10–2.5}$ concentrations at a pair of coastal sites located within a few kilometers of each other.

Most studies of seasonal variability in $PM_{10–2.5}$ concentrations have observed the highest concentrations in summer, but exceptions occur due to specific source activity patterns (Thornburg et al. 2009; Pakbin et al. 2010). Harrison et al. (2001) measured $PM_{10–2.5}$ continuously at five sites in England over a 3-year period. They observed higher $PM_{10–2.5}$ concentrations on weekdays than on weekends and found that the fraction of PM_{10} contributed by $PM_{10–2.5}$ was highest in the spring and summer. Moore et al. (2010) reported correlation coefficients of 0.1–0.4 for continuous hourly $PM_{10–2.5}$ concentrations measured at 3 sites across the Los Angeles basin. In their study, the most pronounced diurnal variation in $PM_{10–2.5}$ concentrations was observed at a site near Riverside, CA, with less diurnal variability in concentrations measured near downtown Los Angeles and at a desert location about 110 km NW of downtown. Daytime or evening maxima were observed at all three locations.

This paper presents just over a year of mass concentration data from continuous $PM_{10–2.5}$ and $PM_{2.5}$ sampling conducted in Denver and Greeley, CO, as part of the Colorado Coarse Rural Urban Sources and Health (CCRUSH) study. CCRUSH is a multiyear study of the relationship between $PM_{10–2.5}$ mass concentrations and adverse health effects, including cardiopulmonary emergency department visits and adverse birth outcomes. Denver and Greeley were selected for the study to allow comparison of the composition and relative health effects of coarse PM in urban and rural communities. For two sites in Denver and two sites in Greeley, continuous hourly mass concentrations of $PM_{10–2.5}$ and $PM_{2.5}$ were measured using dichotomous tapered element oscillating microbalances (TEOMs). Sampling began in January 2009 and will continue for three years. At the end of the sampling period, the mass concentration data will be analyzed with local data on birth outcomes and emergency department visits to assess and compare the associations between the two communities.

This paper examines spatial and temporal variations in hourly and 24-h average concentration values for $PM_{10–2.5}$ and $PM_{2.5}$. It also examines the influence of hourly wind speed and wind direction on the mass concentrations. Nonparametric regression (NPR; Henry et al. 2002, 2009; Kim and Hopke 2004; Yu et al. 2004) was used to characterize the wind speed and wind direction relationships, and help understand differences in mass concentrations across sampling locations.

2. METHODS

2.1. Sampling Locations

Continuous particulate mass concentrations were measured at two locations in Denver and two in Greeley, CO. Greeley has a population of 92,625 (U.S. Census 2009b) and an area of 77.7 km^2, and is located within Weld County. Weld County has a population of 254,759 (U.S. Census 2009a) and an area of 10,417 km^2. Agriculture and oil and gas extraction are among the county's leading economic activities. In contrast, the City and County of Denver has a population of 610,345 (U.S. Census 2009c) and an area of 401.3 km^2, with a highly mixed economy (the urban area[1] of Denver–Aurora has a population of 1.98 million and an area of 1291.9 km^2). Denver is transected by major interstate highways and experiences much greater traffic volumes than Greeley. Correspondingly, $PM_{10–2.5}$ concentrations in Denver are expected to be dominated by resuspended urban

[1]An urban area consists of core census block groups or blocks that have a population density of at least 1,000 people per square mile (386 people/km^2) and surrounding census blocks that have an overall density of at least 500 people per square mile (193 people/km^2) (U.S. Census, 2000).

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road dust, while agricultural activities (e.g., feedlots, soil preparation, and ditch burning) are expected to be relatively important sources in Greeley.

Monitors were located on the roofs of two elementary schools in Denver: Alsup and Edison, which are 11.1 km apart. Monitors were located in Greeley on the roof of Maplewood elementary school and in the heating, ventilation, and air conditioning (HVAC) system enclosure at McAuliffe elementary school. The two Greeley schools are 4.5 km apart. The city of Greeley is roughly 80 km northeast of Denver. Table 1 includes site descriptions, sampling periods, and completeness statistics for the CCRUSH data sets considered.

2.2. Particulate Matter Monitoring Methods

TEOM, model 1405-DF (ThermoFisher Scientific, Waltham, MA) ambient PM monitors were located at each site. Three monitors (Alsup, Edison, and Maplewood) were located outside on roofs and housed in enclosures (Complete Outdoor Enclosure for TEOM Series 1405, ThermoFisher Scientific, Waltham, MA) designed to maintain appropriate instrument conditions. At extreme high and low ambient temperatures, the enclosures failed to maintain appropriate instrument operating conditions, which resulted in data removal. The monitor located at McAuliffe was located just below the roof in an HVAC system crawl space and was equipped with an in-house designed foam enclosure equipped with a commercial air conditioner/heater unit set to maintain a temperature of 21.1°C.

The TEOM 1405-DF is equipped with a Filter Dynamic Measurement System (FDMS) to correct for semivolatile species evaporation from mass measurement filter surfaces. After a 16.7 L/min PM_{10} impactor inlet removes the particles larger than 10 μm from the sample stream, a round-nozzle virtual impactor is used to separate the $PM_{2.5}$ and $PM_{10–2.5}$ size fractions into dual measurement channels. Virtual impactors separate size fractions using particle inertia similar to a traditional inertial impactor. By replacing the impaction surface with a vertical collection probe with a low flow rate, virtual impactors separate larger particles that have sufficient inertia to impact the "virtual surface" of the cross-section of the collection probe inlet. Flow through the collection probe is referred to as the minor flow. The major flow, containing small particles, diverts away from the collection probe and has a collection efficiency that is less than unity due to a fraction of the smaller particles penetrating into the collection probe. This fraction is defined by the ratio of minor to inlet flow rates. Virtual impactor design and flow characteristics are described in detail elsewhere (Marple and Chien 1980; Loo and Cork 1988). The TEOM 1405-DF uses a 2.5-μm cut point virtual impactor with inlet, major ($PM_{2.5}$), and minor ($PM_{10–2.5}$) volumetric flow rates of 16.7, 15, and 1.67 L/min, respectively. Mass concentration corrections for penetration of $PM_{2.5}$ mass into the $PM_{10–2.5}$ channel are described in the data processing section below. The mass measurements are made by dual vertical oscillating tapered glass elements, one for each PM channel, with Pallflex TX-40 TEOM filters placed on the ends. Particulate mass is deposited as aerosol passes through the filter, which changes the natural oscillating frequency of the tapered glass element. The frequency change is related to filter mass change by simple vibration theory. The ambient mass concentrations are calculated by the change in mass and volumetric airflow rates.

With the FDMS system, the instrument operates by sampling in two modes that alternate every 6 min. In the "Base" measurement mode, the sample stream is held at 30°C with the aerosol passing directly to the mass measurement filter. The effect of water is reduced in the TEOM 1405-DF by the use of a Nafion™membrane diffusion dryer in each particulate channel. In the Base mode, mass can be either lost or gained from the

TABLE 1
Monitoring site descriptions, sampling periods, and completeness statistics for the CCRUSH study

	Edison	Alsup	Maplewood	McAuliffe
Coordinates	39.76 N 105.04 W	39.83 N 104.94 W	40.42 N 104.71 W	40.43 N 104.77 W
Elevation (m)	1584	1560	1433	1454
Inlet height (m)	9	6	9	10.5
Location description	Urban–Residential	Industrial–Residential	Residential	Residential
Start date/time	1/8/2009 12:00	1/16/2009 15:00	1/16/2009 18:00	1/1/2009 3:00
End date/time	1/8/2010 10:00	2/5/2010 15:00	10/16/2009 16:00	6/19/2009 10:00
Number of hourly observations	8759	9241	6551	4064
$PM_{2.5}$ No. usable hourly samples	7182	8050	5550	3963
(% completeness)	(82.0%)	(87.1%)	(84.7%)	(97.5%)
$PM_{10–2.5}$ No. usable hourly samples	7182	7910	5550	3963
(% completeness)	(82.0%)	(85.6%)	(84.7%)	(97.5%)

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filter, depending on the amount of semivolatile material present. In the "Reference" mode, after the dryer, the sample is diverted through the cooled FDMS filter, a 47 mm Pallflex TX-40 filter held at 4°C. This filter removes the particles and semivolatile material that will condense at 4°C or below. This filtered air stream is then directed through the TEOM filter and the mass change on the filter recorded. Reference mode values are commonly negative due to mass loss from the TEOM filter, but adsorption or absorption of organic gases may also occur, resulting in mass gain (Green et al. 2009). The mass change during the Reference mode due to evaporation and gas-phase sampling artifacts is assumed to be equal to the artifact contribution to the mass change that occurred during the previous Base measurement. The time series of Reference mass concentrations are thus subtracted from the Base measurements, correcting for sampling artifacts and approximating the true aerosol mass concentration. This provides a total mass concentration for each 12-min time step, with the first 6 min providing the Base and the second 6 min providing the Reference concentration. The instruments were operated at flow rates prescribed by the manufacturer: 1.67 L/min ($PM_{10–2.5}$), 3 L/min ($PM_{2.5}$), and 12 L/min (bypass). For this study, TEOMs were set up to record the raw mass concentration data (Base and Reference) for the $PM_{2.5}$ and $PM_{10–2.5}$ channels, along with ambient temperature, relative humidity, and various instrument conditions, at 6 min intervals. Raw mass concentration data are not smoothed by between-measurement averaging for unmeasured channels and do not include a correction for the penetration of $PM_{2.5}$ mass into the $PM_{10–2.5}$ channel from the virtual impactor separation. This correction was made during subsequent data processing. Flow control was set to active, and actual flow rates were used to calculate the mass concentrations.

TEOM instrument maintenance was performed monthly at each site and consists of changing TEOM and FDMS filters; cleaning the PM_{10} inlet, virtual impactor, and FDMS valve; checking for seal leaks in the mass transducer, FDMS valve, and FDMS filter holder; flow audit and calibration; and an instrument leak check. Operators ensured that the instrument was operating properly before leaving the site. Other regular maintenance was performed as needed and included exchanging Nafion diffusion dryers, pump maintenance, and replacing mass transducer, FDMS valve, and FDMS filter holder seals. Ball valves were installed between the virtual impactor and diffusion dryers to increase the ease of access to sample lines for flow audits, which were performed at a higher frequency than prescribed by the manufacturer. A single external filter on the bypass flow line was used to extend pump life.

To assure the highest quality data were used for analysis, extensive quality assurance protocols were developed. Upon arriving at a monitoring site, an instrument status log, maintenance log, comment log, and flow audit/leak check log were completed. The status log was filled out before and after maintenance to assure that the instrument conditions did not change due to operator intervention. The TEOM data were downloaded manually each month prior to instrument maintenance. The discrete section of data from the last site visit to the current visit was downloaded via the available universal serial bus (USB) port on the front of the instrument. This process closed the previous section of data before the operator interfered with instrument operation. By using the ePort software provided by Thermo Scientific, the entire TEOM database was also downloaded. The data were transferred from a field laptop or flash drive to a desktop computer immediately upon arriving back at the University of Colorado.

Discrete data sections downloaded via USB flash drive were processed by a code developed in-house. Log files for each data section were created that specified data filenames, whether maintenance occurred, whether to output hourly averages, saved data interval, number of hours to remove after maintenance occurred, and number of hours to shift the time stamp into Mountain Standard Time (MST). Rows were flagged as missing data if the status code reported the following errors: power failure, database failure, FDMS valve failure, mass transducer failures, any channel flow deviating from the set flow rate (L/min) by more than 10%, either channel reading filter loading above 90%, or heater tube temperatures (°C) deviating from set temperature by more than 2%. Instrument problems were flagged as well and included: vacuum pressures above 40.5 kPa, cooler temperatures deviating more than 0.5°C from the specified set point, or if channel relative humidity was above 98%. Data corresponding to instrument problem flags were inspected manually.

Equations (1)–(3) were applied to the 6-min mass concentration data to correct for $PM_{2.5}$ mass depositing in the $PM_{10–2.5}$ channel due to the virtual impactor. In the following equations, Q represents the volumetric flow rate through the indicated channel. *PM* represents the mass concentration, with the *TEOM* label indicating raw TEOM data. It was assumed that both Base and Reference channels followed the same correction, i.e., that semivolatile mass loss was proportional to the amount of total mass in each channel

$$\frac{Q_{PM10-2.5}}{Q_{Total}} = \frac{1.67\,L/m}{16.67\,L/m} = 0.1, \quad [1]$$

$$PM_{10-2.5Base} = PM_{10-2.5Base}(TEOM) - \frac{Q_{PM10-2.5}}{Q_{Total}}\left(PM_{2.5Base}(TEOM)\right), \quad [2]$$

$$PM_{10-2.5Ref} = PM_{10-2.5Ref}(TEOM) - \frac{Q_{PM10-2.5}}{Q_{Total}}\left(PM_{2.5Ref}(TEOM)\right). \quad [3]$$

The hourly average and standard error (i.e., the standard deviation divided by the square root of the number of measurements in the hour) of all downloaded variables were calculated and exported, excluding data flagged as missing. Logs used to process data were accessed to compile full data sets, filling in missing sections of data between discrete data sets with missing data flags or combining same hour measurements with a weighted average based on the number of measurements made in that

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hour in each separate data set. Three scenarios were identified that required further data processing: major events of mass loss from filter surfaces, instances of highly variable noise due to temperature aliasing from rapid or oscillating changes of enclosure temperature or other sources, or instances of elevated standard error when a nonremoval status code had been triggered. The mass loss incidents were identified if the calculated mass concentration was less than the 1st percentile of the time series and the standard error of the measurement was above the 95th percentile. The incidents of induced highly variable noise were identified if the calculated concentration was below the 1st percentile and the subsequent measurement was greater than the 99th percentile or vice versa. The third scenario was triggered when a nonzero status code was recorded and the calculated hourly mass concentration standard error was above the 95th percentile. Each occurrence of one of these three scenarios was assessed manually to determine if data should be removed for final hourly average data sets. The data were then filtered for hours with less than 75% completeness. Daily averages were calculated from cleaned hourly average data sets; days missing more than 75% of completed hours were also removed.

The data set reported in this paper has been labeled phase 1, and resulted from cutting off the currently validated results when instruments were updated to a new version of the TEOM 1405-DF firmware. This update required exchanging a physical flash card; after the update instrument settings were unintentionally reset to defaults. The start and end dates and completeness statistics for each site's phase 1 data are listed in Table 1. Sampling began on different dates at each site, and completeness varies by site based on instrument maintenance issues.

The TEOM 1405-DF is a relatively new instrument and correspondingly posed numerous challenges in our effort to produce the continuous time series of mass concentration data. Through collaboration with Thermo Scientific, solutions were found for most problems, but they nonetheless led to substantial gaps in our time series. Denver and Greeley experience significant seasonal temperature variations. The air heating and cooling systems incorporated into the Thermo Scientific TEOM 1405-DF enclosures were unable to adequately condition the space within the enclosures when ambient temperatures were very high or low. Numerous measurements from midday throughout the summer were suspect, and hence flagged for removal due to large hourly variability associated with increased TEOM mass transducer temperatures. This high measurement variability mostly originated in the Reference channel, where hourly standard errors sometimes exceeded 500 μg m^{-3}. Cold temperature extremes were less of an issue, though the operating temperatures of the FDMS systems occasionally dropped below 4°C. These changes in FDMS operating temperature were not accompanied by significant increases in the variability of mass concentration measurements so that corresponding data were not removed. A further problem with the HVAC systems occurred at Alsup and Maplewood, where insulation near the blowers peeled off and either shredded or blocked the blowers.

Malfunction of the Nafion dryer assemblies and pumps also leads to gaps in the time series. Dryer assemblies had to be replaced every 7–10 months and the pumps rebuilt every 12 months, in each case about 6 months earlier than the manufacturer's maintenance recommendations. Premature pump failure may be partly due to low ambient atmospheric pressures in Colorado, which are typically about 85.1 kPa. In addition, the bypass flow controller of the TEOM installed at McAuliffe failed when the inlet system did not adequately dispose of water vapor in the bypass line, resulting in condensation when the air was cooled in the enclosure.

Finally, a significant gap in the McAuliffe data set occurred due to seal leaks within the FDMS valve system that were not detected through the leak check process. The problem was only identified upon later inspection of the data. In response, we modified our monthly maintenance protocol to include disassembling the FDMS valve to verify that no seals failed, and to process and examine data on-site to verify the absence of leaks.

2.3. Meteorological Data

To assist with the analysis of PM mass concentration data, hourly meteorological data (temperature, RH, wind speed, and direction) were obtained from stations located at or near each of the monitoring sites. Mass concentration data from Edison were related to meteorological data from the Carriage site (39.75 N, 105.03 W), located 1.65 km to the southeast and operated by the Colorado Department of Public Health and Environment (CDPHE). Meteorological data for Alsup were collected from a CDPHE-operated meteorological station colocated with our instrument. Meteorological data for Greeley were obtained from the National Oceanic and Atmospheric Administration's (NOAA) Weld County Airport station (40.26 N, 104.38 W), located 6.7 km west and 10.9 km west of Maplewood and McAuliffe monitoring sites, respectively. Wind roses of data used for site-specific wind speed and direction regressions from Carriage, Alsup, and the Weld County Airport are shown in the online Supplemental Information. Vector-averaged wind speed was used in the data analyses.

2.4. Data Analysis and NPR

Section 3 presents standard descriptive statistics for $PM_{2.5}$ and $PM_{10-2.5}$ mass concentrations, along with the coefficient of divergence (COD), which is a measure of uniformity. The results of NPR of concentrations versus wind speed and direction are also presented. All data analyses used concentration data that were error-code-filtered. No negative data filtering or replacement was performed in any of the analyses, except when calculating the COD.

The COD (Wilson et al. 2005) for a set of measurements, X, is defined by

$$\mathrm{COD} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{X_{ij}-X_{ih}}{X_{ij}+X_{ih}}\right)^2} \qquad [4]$$

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where i is the sample, and j and h index different measurement sites. A COD value of 0 represents perfect uniformity, and a value of 1 represents total heterogeneity. The COD loses meaning when negative values are included, so in calculating this statistic, negative values in the data set were replaced with zeros.

The data set used in the NPR was different than that used in the other analyses, as it required wind data and mass concentrations for each hour, both of which had missing data. Additionally, any data point with a corresponding wind speed value below 1 ms^{-1} was excluded from the NPR analysis. Exclusion of these periods with relatively calm winds sharply reduced the number of observations used in the NPR analyses compared to the full sets of hourly mass concentration data.

NPR was used to estimate the expected concentration C_i from each wind direction or wind speed i by including all observations using weighting kernels, giving less weight to observations far from the point at which the estimate is being calculated and vice versa. The Gaussian kernel

$$K_1(x) = (2\pi)^{-\frac{1}{2}} e^{(-0.5x^2)}, \quad -\infty < x < \infty, \quad x = \frac{\theta - W_i}{\Delta\theta} \qquad [5]$$

was used for the wind direction regressions and the Epanechnikov kernel

$$K_2(x) = 0.75\left(1 - x^2\right), \quad -1 < x < 1 \qquad [6]$$

was used for wind speed regressions (Henry et al. 2002). In the kernels, θ is the wind direction or speed for which the estimate is made, W_i is the wind speed or wind direction value at time i, and $\Delta\theta$ is the smoothing parameter. The concentration $C(\theta)$ at a given wind speed or direction is then estimated by the Nadaraya–Watson estimator, defined as

$$C(\theta) = \frac{\sum_{i=1}^{n} K\left(\frac{\theta - W_i}{\Delta\theta}\right) C_i}{\sum_{i=1}^{n} K\left(\frac{\theta - W_i}{\Delta\theta}\right)}, \qquad [7]$$

where K references the appropriate kernel. In this work, the optimal value of the smoothing parameter was found for each data set and meteorological variable by cross-validation. Smoothing parameters were then averaged over all sites for each size fraction and meteorological variable, to allow for more direct comparison of the results. The resulting smoothing parameters are 23.13° for $PM_{2.5}$ with wind direction; 10.88° for $PM_{10-2.5}$ with wind direction; 0.55 ms^{-1} for $PM_{2.5}$ with wind speed; and 1.2 ms^{-1} for $PM_{10-2.5}$ with wind speed. Ninety-five percent confidence intervals of the regression estimates were calculated as described in Henry et al. (2002).

2.5. Comparison with Other PM Data Sets

As part of this study, comparisons were made to $PM_{2.5}$ and $PM_{10-2.5}$ data from other studies and locations. These comparisons are complicated by the use of different instruments and measurement methods. Federal reference methods (FRMs) and federal equivalence methods (FEMs) for PM have been discussed previously (U.S. EPA 2004, 2009). The FRM for $PM_{10-2.5}$ is calculated as the numeric difference between concurrent and colocated PM_{10} and $PM_{2.5}$ concentrations as measured by FRM low-volume filter samplers of the same make and model (U.S. EPA 2009). The TEOM 1400AB and 1405 have been designated as FEM methods for PM_{10}. The TEOM 1405-DF has been designated as an FEM method for $PM_{2.5}$, but not (to date) as an FEM for $PM_{10-2.5}$ (U.S. EPA 2010).

As described above, the TEOM 1405-DF has been designed to minimize sampling artifacts, both positive and negative. Positive artifacts are a result of excess mass collection typically caused by gas-phase adsorption onto the collection media. Negative artifacts are a result of reduced mass collection typically caused by semivolatile species that were in the particle phase but shift to the gas phase after collection due to collection temperatures that are higher than ambient or pressures that are slightly less than ambient. For example, when $PM_{2.5}$ concentrations were measured by a pair of TEOMs, one operated at 50°C and the other operated at 30°C, the TEOM held at a higher temperature yielded consistently lower concentrations, as at the higher temperature, the sensor collected less semivolatile and condensable mass (Grover et al. 2005; Zhu et al. 2006). The TEOM 1405-DF operates at 30°C and also utilizes an FDMS that adjusts for filter adsorption artifacts. The results from previous studies generally show that for $PM_{2.5}$, the TEOM FDMS measures higher concentrations than the FRM, especially as the ambient temperature increases (Grover et al. 2005; Schwab et al. 2006; Zhu et al. 2006), the FRM does not adjust for adsorption artifacts (Solomon and Sioutas 2008). In the end, it is important to remember that comparison across studies that have used different measurement techniques will have slight biases associated with the technique differences. Thus, the $PM_{10-2.5}$ data discussed below should be viewed as only roughly comparable across studies.

3. RESULTS AND DISCUSSION

3.1. Summary Statistics and Spatial Trends

Table 2 presents the summary statistics for the 24-h average $PM_{2.5}$ and $PM_{10-2.5}$ concentrations measured at the four study sites. Average $PM_{2.5}$ concentrations ranged from 7.7 to 9.2 $\mu g\ m^{-3}$ across the four sites. Average concentrations of $PM_{2.5}$ were somewhat higher at the two Denver sites than at the two sites in Greeley. Average $PM_{10-2.5}$ concentrations ranged from 9.0 to 15.5 $\mu g\ m^{-3}$. $PM_{10-2.5}$ concentrations were sharply higher at the Alsup site in northeast Denver than at the other three locations. Temporal variability in $PM_{10-2.5}$ concentrations was higher than that in $PM_{2.5}$ concentrations, with COV values for 24-h average $PM_{10-2.5}$ ranging from 0.6 to 0.8 and those for $PM_{2.5}$ all near 0.5. Across the four sites, 95th percentile 24-h average concentrations ranged from 14.7 to 17.9 $\mu g\ m^{-3}$ for $PM_{2.5}$ and from 18.9 to 36.0 $\mu g\ m^{-3}$ for $PM_{10-2.5}$.

The 2 Greeley sites, which are separated by a distance of 4.5 km, had the highest spatial correlation for 24-h average

TABLE 2
Summary statistics for 24-h average $PM_{2.5}$ and $PM_{10-2.5}$ concentrations

$PM_{2.5}$	Edison	Alsup	Maplewood	McAuliffe
N (days)	299	328	211	158
Mean ($\mu g\ m^{-3}$)	8.7	9.2	7.7	8.6
Median ($\mu g\ m^{-3}$)	7.6	8.2	7.0	7.8
St. Dev. ($\mu g\ m^{-3}$)	4.6	4.7	3.8	4.0
COV	0.5	0.5	0.5	0.5
5th percentile ($\mu g\ m^{-3}$)	2.8	4.0	3.3	4.3
95th percentile ($\mu g\ m^{-3}$)	17.9	17.7	14.7	15.0
COD				
Edison	0.00	0.21	0.27	0.23
Alsup		0.00	0.24	0.17
Maplewood			0.00	0.13
McAuliffe				0.00
Pearson's *R*				
Edison	1.00	0.64	0.35	0.44
Alsup		1.00	0.48	0.60
Maplewood			1.00	0.82
McAuliffe				1.00
$PM_{10-2.5}$	Edison	Alsup	Maplewood	McAuliffe
N (days)	299	323	211	158
Mean ($\mu g\ m^{-3}$)	9.0	15.5	9.6	9.8
Median ($\mu g\ m^{-3}$)	8.0	13.3	8.2	7.7
St. Dev. ($\mu g\ m^{-3}$)	5.4	11.4	7.7	7.8
COV	0.6	0.7	0.8	0.8
5th percentile ($\mu g\ m^{-3}$)	2.1	1.7	1.5	1.5
95th percentile ($\mu g\ m^{-3}$)	18.9	36.0	21.4	24.6
COD				
Edison	0.00	0.30	0.25	0.23
Alsup		0.00	0.31	0.31
Maplewood			0.00	0.15
McAuliffe				0.00
Pearson's *R*				
Edison	1.00	0.70	0.69	0.72
Alsup		1.00	0.66	0.68
Maplewood			1.00	0.97
McAuliffe				1.00

concentrations of both $PM_{2.5}$ and $PM_{10-2.5}$, with Pearson's *R* values of 0.82 for $PM_{2.5}$ and 0.97 for $PM_{10-2.5}$. Concentrations measured at the two Denver sites, separated by a distance of 11.1 km, showed lower correlation. For the Denver sites, the Pearson's *R* values were 0.64 for $PM_{2.5}$ and 0.70 for $PM_{10-2.5}$. The COD was calculated among all site pairs. The pair of Greeley sites displayed the most homogeneous 24-h average $PM_{2.5}$ and $PM_{10-2.5}$ concentrations (COD = 0.13 for $PM_{2.5}$ and 0.15 for $PM_{10-2.5}$), while the pair of Edison and Alsup was somewhat more heterogeneous (COD = 0.21 for $PM_{2.5}$ and 0.30 for $PM_{10-2.5}$). The heterogeneity of $PM_{10-2.5}$ concentrations in Denver is influenced by the relatively high concentrations at Alsup. A point source close to Alsup appears to contribute to the elevated concentrations seen there, as discussed below in Section 3.3.

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The finding of lower correlation and higher COD values for $PM_{2.5}$ and $PM_{10-2.5}$ in Denver than in Greeley is consistent with expectations, as the Denver monitors are separated by a greater distance and are located in more sharply contrasting neighborhoods. The finding of higher correlation for $PM_{10-2.5}$ than for $PM_{2.5}$ in both communities is unexpected, as prior studies have generally observed the opposite. The relatively low correlations for $PM_{2.5}$ found in our study may be partly due to noise in the $PM_{2.5}$ channel. In comparison, the $PM_{10-2.5}$ channel is quite stable.

3.2. Temporal Patterns

Table 3 compares the median concentrations of $PM_{2.5}$ and $PM_{10-2.5}$ between weekends and weekdays at each site, as well as between day (6 a.m.–6 p.m.) and night (6 p.m.–6 a.m.). Significance of differences was assessed using the Kruskal–Wallis test. For $PM_{2.5}$, weekend concentrations were higher than weekday concentrations at all four sites, though the difference is not statistically significant at Edison and Alsup. This result was surprising, as traffic and industrial activity leading to emissions of $PM_{2.5}$ and its precursors are expected to be higher on weekdays than weekends. In contrast to the current study, the Denver Aerosol Sources and Health study (DASH; Vedal et al. 2009), which performed daily $PM_{2.5}$ filter sampling for 4.5 years at Palmer Elementary School in Denver, found a significantly higher weekday median (7.1 μg m^{-3}) than weekend median (6.5 μg m^{-3}) (unpublished statistics). We do not yet have an explanation for the discrepancy.

In contrast to $PM_{2.5}$, concentrations of $PM_{10-2.5}$ followed the expected pattern, with weekday concentrations found to be uniformly significantly higher than weekend concentrations. Likewise, Harrison et al. (2001) reported higher $PM_{10-2.5}$ concentrations on weekdays than weekends for two sites in London and across all seasons. As can be shown in Table 3, daytime concentrations of $PM_{2.5}$ were higher than nighttime concentrations at Edison and McAuliffe, whereas the opposite was true for Alsup. Maplewood shows no statistically significant difference between day and night concentrations, though the nighttime median is slightly larger. Daytime concentrations of $PM_{10-2.5}$ were significantly higher than nighttime concentrations at all four sampling sites. The diurnal patterns underlying these results are discussed below.

Figure 1 shows the median hourly concentrations of $PM_{2.5}$ and $PM_{10-2.5}$ for each monitoring location. Across all four locations, median hourly average concentrations of $PM_{2.5}$ were less variable as a function of time of day than median $PM_{10-2.5}$ concentrations. $PM_{2.5}$ concentrations at all sites generally increased in the morning from about 6 to 10 a.m., decreased during the afternoon, and then increased again in the evening. Relatively high $PM_{2.5}$ concentrations in the morning hours are likely due to temperature inversions in addition to source activity. The Alsup site showed the strongest peak in $PM_{2.5}$ concentrations. This peak occurred at 7 a.m., slightly earlier than the morning peaks at the other sites.

$PM_{10-2.5}$ concentrations at Alsup peaked at about 8 a.m. and then declined until about 2 a.m. For both $PM_{2.5}$ and $PM_{10-2.5}$, the relatively pronounced morning peaks at Alsup appear to reflect the influence of relatively heavy industrial activity and traffic at this particular location. At Edison, $PM_{10-2.5}$ concentrations peak at 11 a.m. and then decline relatively steadily until 4 a.m. The $PM_{10-2.5}$ concentrations at the two Greeley sites were higher during the daytime hours than at night, but do not exhibit the afternoon decrease seen for $PM_{10-2.5}$ in Denver and for $PM_{2.5}$ at all locations. This suggests that the strength of $PM_{10-2.5}$ sources affecting the Greeley monitors increases in the afternoon, roughly compensating for the enhanced dilution

TABLE 3
Comparison of median 1-h average concentrations by weekday/weekend and day/night

$PM_{2.5}$	Edison	Alsup	Maplewood	McAuliffe
Weekday (μg m^{-3})	6.28	7.67	6.48	6.75
Weekend (μg m^{-3})	6.73	7.71	7.29	7.13
p value	.051	.284	.001*	.014*
Day (μg m^{-3})	6.63	7.48	6.79	7.47
Night (μg m^{-3})	5.88	7.83	6.99	6.59
p value	.001*	.011*	.701	.000*
$PM_{10-2.5}$	Edison	Alsup	Maplewood	McAuliffe
Weekday (μg m^{-3})	8.26	11.77	6.24	6.31
Weekend (μg m^{-3})	5.68	7.30	4.95	4.19
p value	.000*	.000*	.000*	.000*
Day (μg m^{-3})	8.32	12.03	6.87	6.86
Night (μg m^{-3})	5.24	8.66	5.19	4.79
p value	.000*	.000*	.000*	.000*

*Statistically significant at the .05 level.

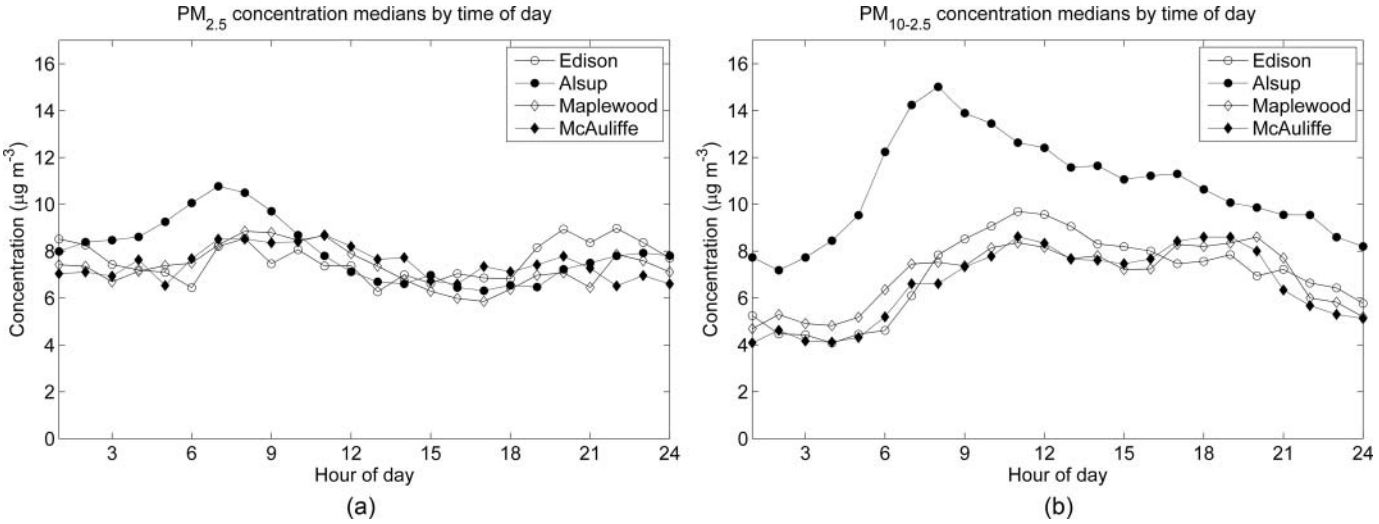

FIG. 1. Median mass concentrations (μg m^{-3}) by time of day at the 4 monitoring sites for (a) $PM_{2.5}$ and (b) $PM_{10–2.5}$.

that occurs as the mixing layer grows. The finding that $PM_{10–2.5}$ exhibits relatively strong diurnal variability compared to $PM_{2.5}$ is consistent with the shorter residence time of $PM_{10–2.5}$ in the atmosphere. Harrison et al. (2001) and Moore et al. (2010) similarly found elevated $PM_{10–2.5}$ concentrations during daytime hours, at monitoring sites in London and the Los Angeles area, respectively.

Figure 2 shows the median concentrations of $PM_{2.5}$ and $PM_{10–2.5}$ plotted by month. In each size regime, the four sites showed similar monthly patterns. $PM_{2.5}$ concentrations showed relatively little monthly variation compared to concentrations of $PM_{10–2.5}$. The highest median concentrations of $PM_{10–2.5}$ were measured during July, August, and September as well as select winter months. This is consistent with the expectation that $PM_{10–2.5}$ is partly derived from resuspension processes that are enhanced under dry and windy conditions. Additional seasonal analysis will be performed when the 3-year time series of concentrations is complete.

3.3. NPR Results

NPR results showing relationships of hourly $PM_{2.5}$ and $PM_{10–2.5}$ concentrations with wind speed and wind direction are presented for each site in Figures 3–6. In each figure, the top panels show scatter plots of concentration versus wind direction and wind speed, and the bottom panels show the NPR results. The dark center line represents the values predicted by the regression ($C(\theta)$; where θ is the wind direction or speed), and the lighter lines are the 95% confidence intervals based on the assumption that predicted values are means of normal distributions at each θ value. Wind direction data are arranged clockwise from north at 0°. Note that the hourly average concentrations shown in these figures reach sharply higher values

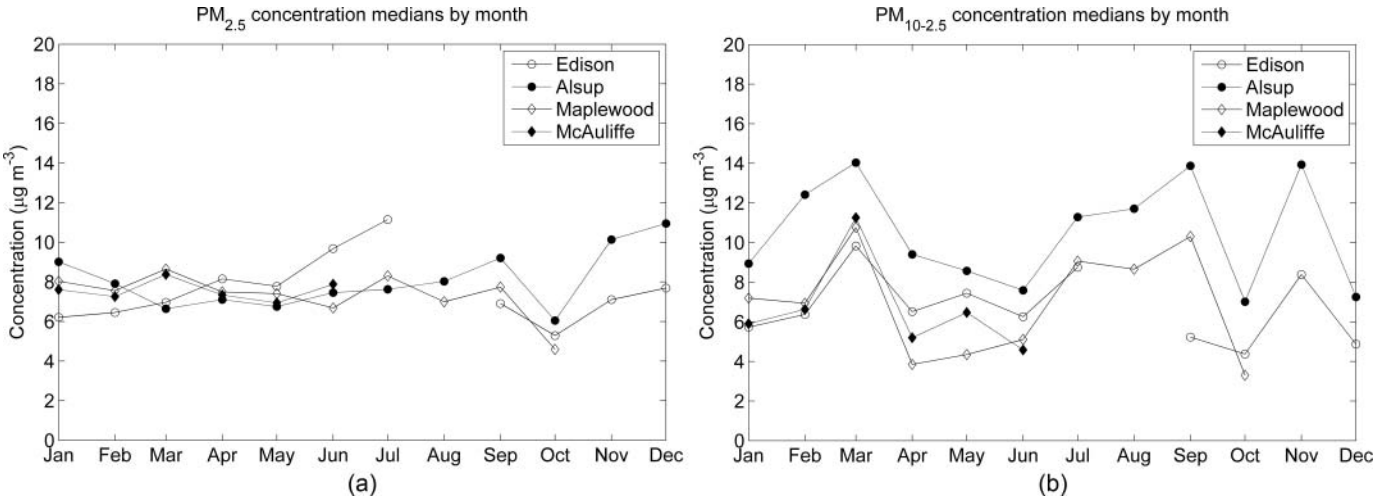

FIG. 2. Monthly median mass concentrations (μg m^{-3}) at the 4 monitoring sites for (a) $PM_{2.5}$ and (b) $PM_{10–2.5}$.

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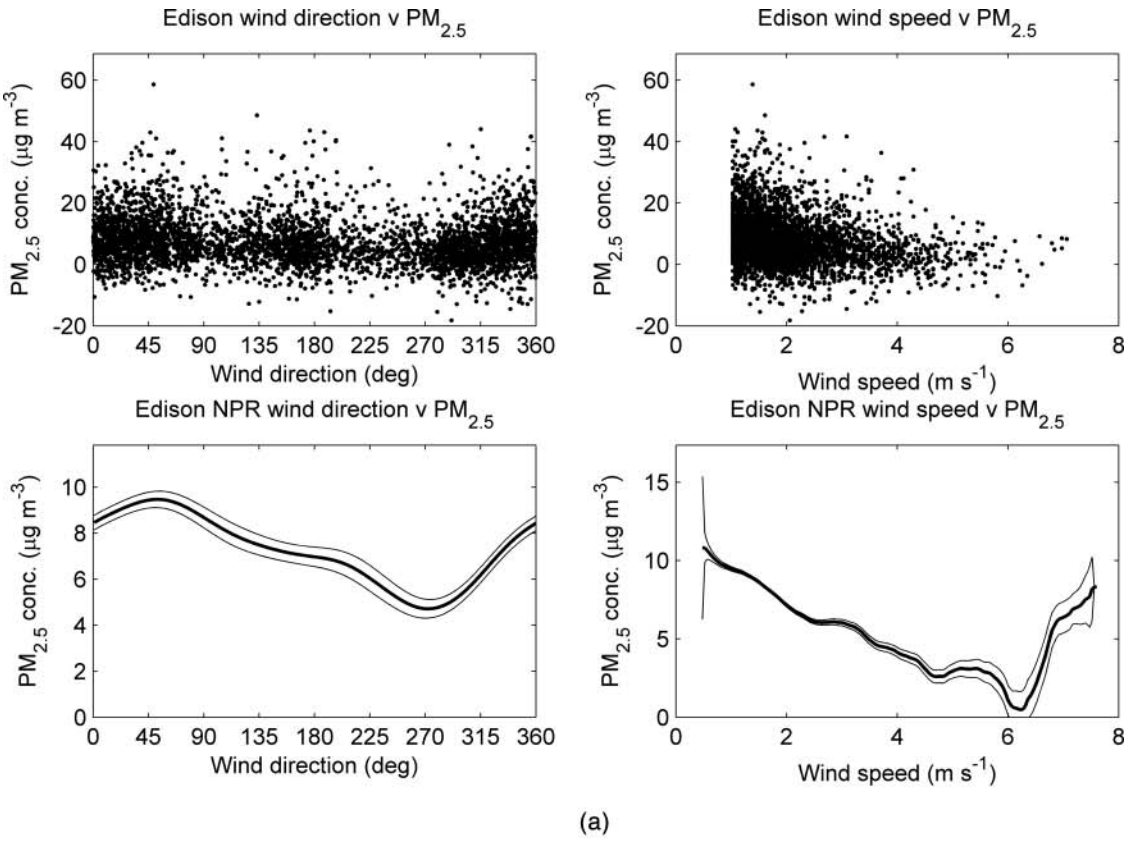

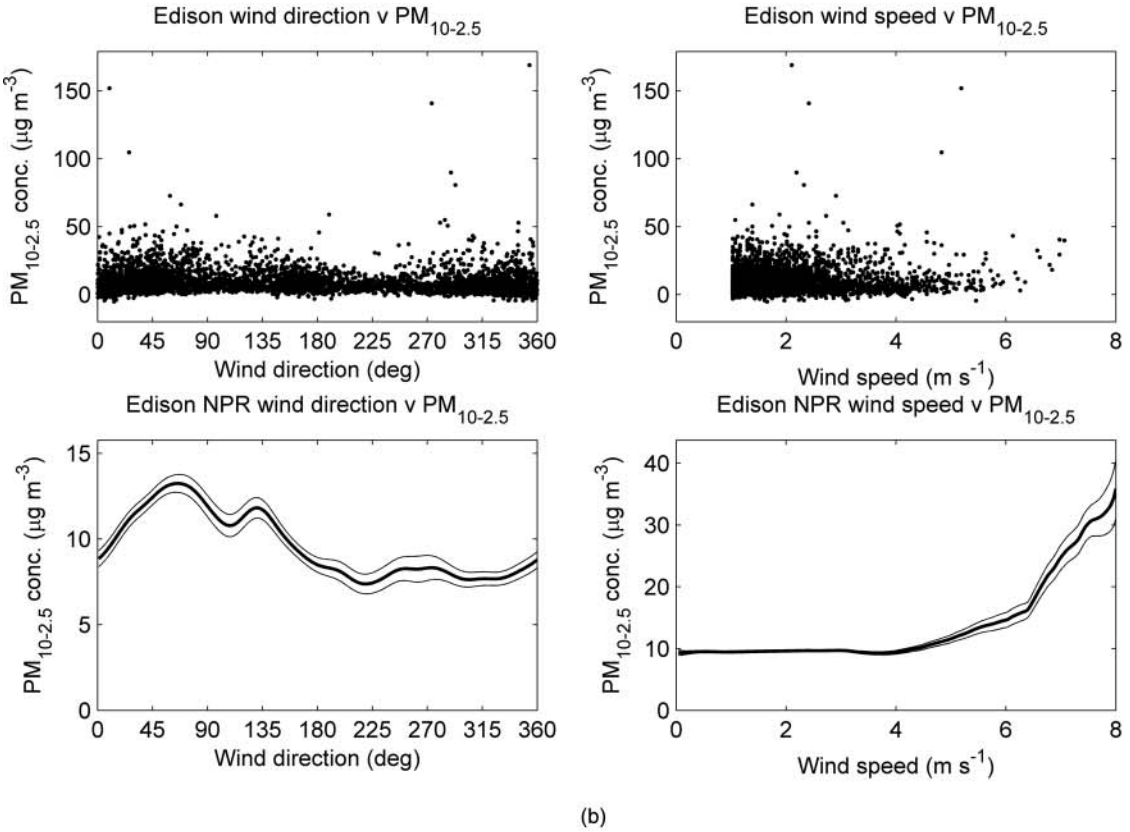

FIG. 3. NPR results for (a) $PM_{2.5}$ ($n = 4028$) and (b) $PM_{10-2.5}$ ($n = 4028$) mass concentrations ($\mu g\ m^{-3}$) at Edison, showing relationships with wind direction (degrees clockwise from north) and wind speed (ms^{-1}).

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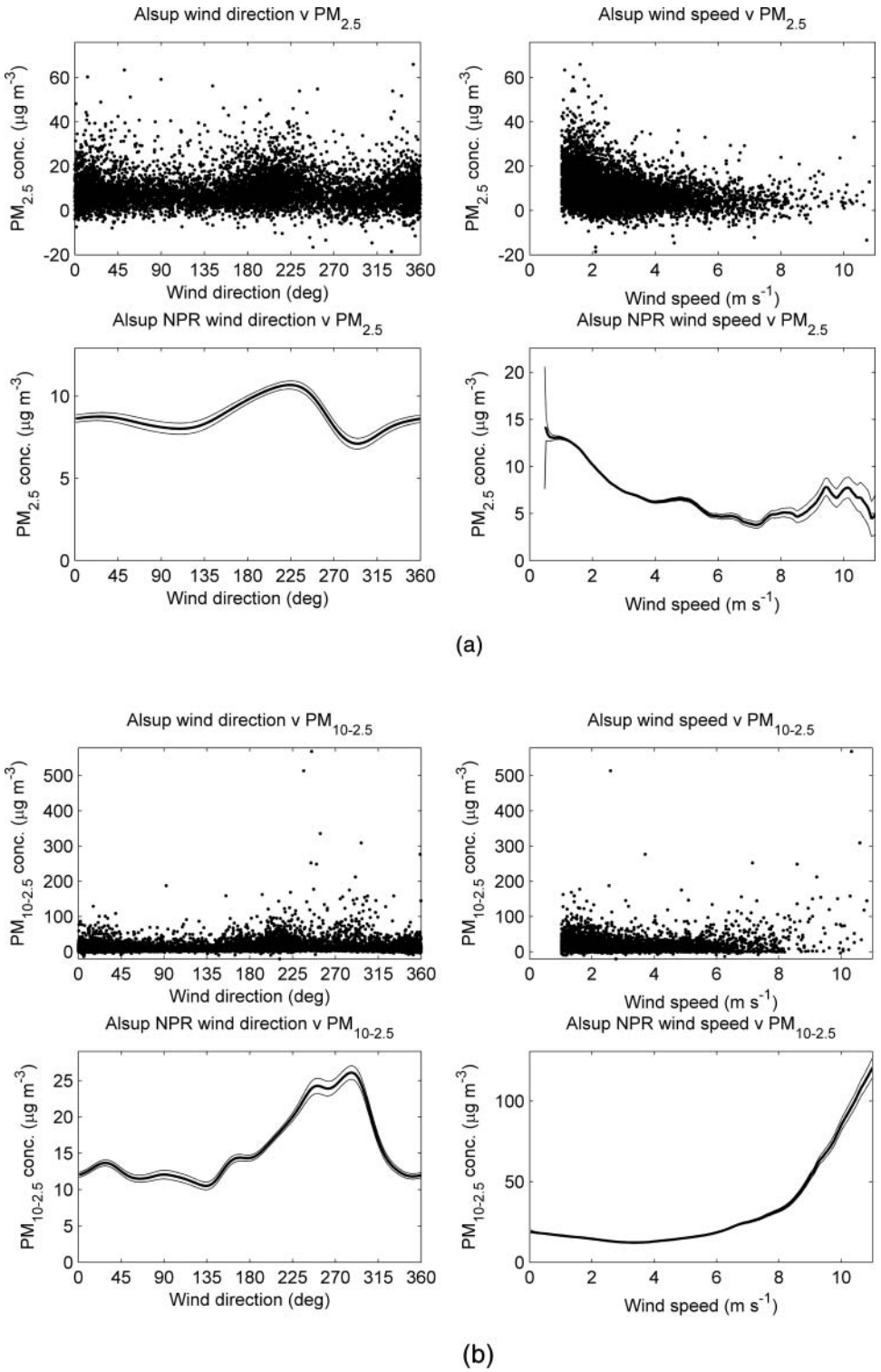

FIG. 4. NPR results for (a) $PM_{2.5}$ ($n = 7626$) and (b) $PM_{10–2.5}$ ($n = 7496$) mass concentrations ($\mu g\ m^{-3}$) at Alsup, showing relationships with wind direction (degrees clockwise from north) and wind speed (ms^{-1}).

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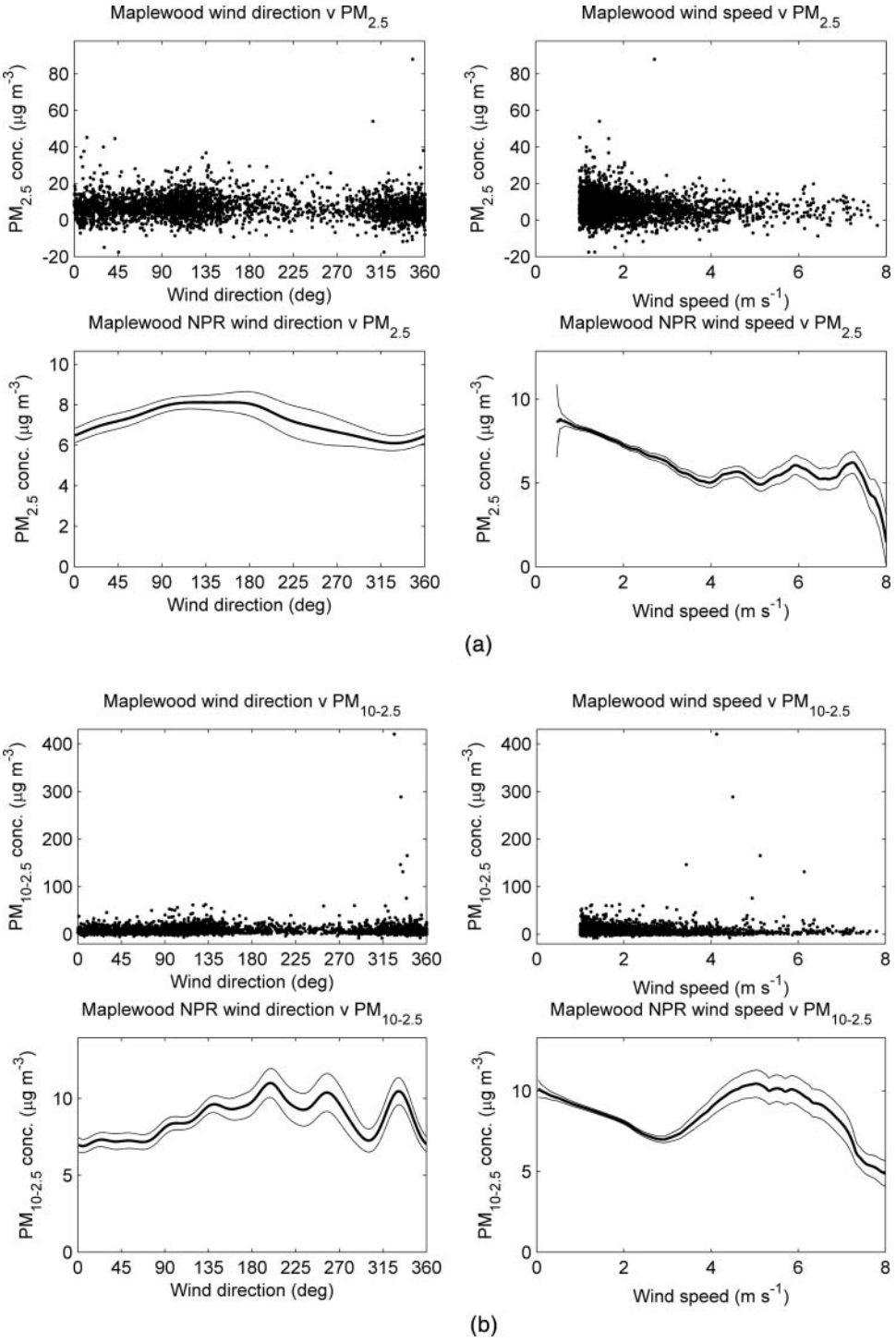

FIG. 5. NPR results for (a) $PM_{2.5}$ ($n = 2930$) and (b) $PM_{10-2.5}$ ($n = 2930$) mass concentrations (μg m^{-3}) at Maplewood, showing relationships with wind direction (degrees clockwise from north) and wind speed (ms^{-1}).

than the 24-h average concentrations summarized in Table 2. As reflected in the wider confidence limits for high wind speeds in some cases, limited data density influenced the curve shapes in these regions.

The NPR results for the Edison site (Figure 3) show higher concentration estimates for both size fractions when the wind is from the northeast. Estimated $PM_{2.5}$ concentrations at Alsup peak with winds from the southwest (Figure 4a). Estimated

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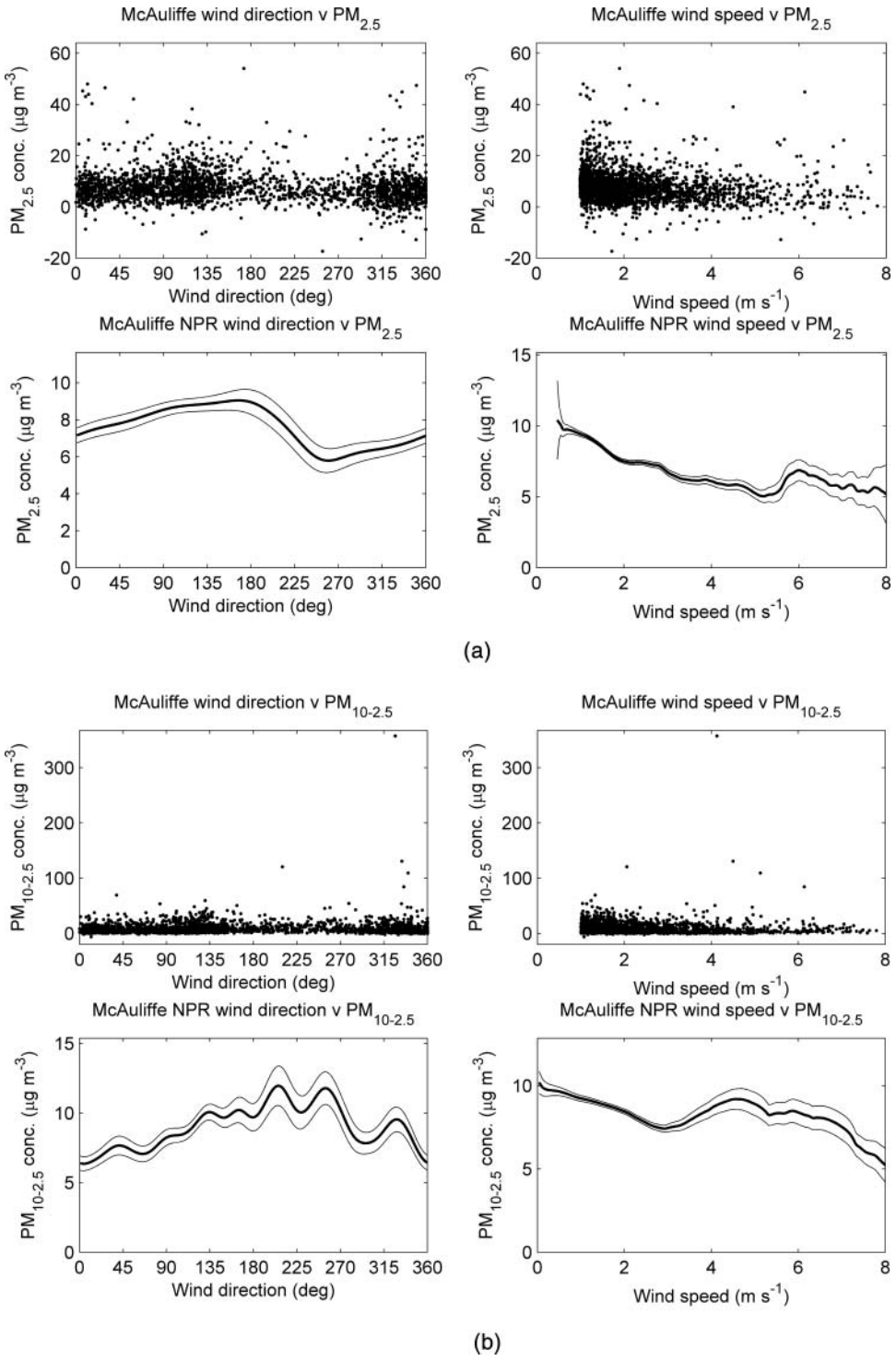

FIG. 6. NPR results for (a) $PM_{2.5}$ ($n = 2262$) and (b) $PM_{10–2.5}$ ($n = 2262$) mass concentrations ($\mu g\ m^{-3}$) at McAuliffe, showing relationships with wind direction (degrees clockwise from north) and wind speed (ms^{-1}).

$PM_{10–2.5}$ concentrations at Alsup are markedly higher with winds from the west (Figure 4b). The wind direction NPR results for both pollutants at both Denver sites point toward the more densely populated, highly traveled, and industrialized core of the city as a significant source area. There are no known major point sources near the Edison site, but the westerly peak in the NPR results for $PM_{10–2.5}$ at Alsup is likely influenced by a sand and gravel operation 1 km west of the monitor and a major

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interstate highway junction (I-76, I-270, I-25, and US-36) just west of that.

The Maplewood and McAuliffe sites have similar NPR results (Figures 5 and 6). The NPR results show that $PM_{2.5}$ concentrations are highest with southerly winds (Figures 5a and 6a). The NPR results for $PM_{10-2.5}$ for both Greeley sites show peaks corresponding to winds from the west and southwest (Figures 5b and 6b). A third peak corresponding to winds from the northwest is more pronounced in the results for Maplewood than those for McAuliffe. The predicted value centered on this peak is influenced by multiple data points with concentrations exceeding 100 μg m^{-3}. When these values are omitted from the NPR, the third peak is no longer apparent for either Maplewood or McAuliffe. We have no basis for excluding these data points; the northwesterly influence appears to be a real effect on the data sets. The densely populated portion of Colorado's Northern Front Range extends from metropolitan Denver, which is south–southwest of Greeley, to Fort Collins, which is northwest of Greeley. Emissions from these source areas may account for the peaks in Figures 5b and 6b. We are not aware of nearby point sources that are south, southwest, or northwest of the Greeley monitoring sites.

Across all four sites, the NPR results for $PM_{2.5}$ dependence on wind speed show a general dilution effect with increasing wind speed. The NPR results for Edison and Alsup show increased $PM_{2.5}$ concentrations with wind speeds above 6–7 ms^{-1}. This could be due to resuspension processes or uncertainty associated with low data density. Additional data in this wind speed range will help in interpreting this relationship.

Results for $PM_{10-2.5}$ are more complicated than those for $PM_{2.5}$. The $PM_{10-2.5}$ wind speed regressions for the two Denver sites (Figures 3b and 4b) suggest resuspension effects, with concentrations increasing with wind speeds up to 8 ms^{-1} at Edison and 10 ms^{-1} at Alsup. The $PM_{10-2.5}$ concentrations at the two Greeley sites (Figures 5b and 6b) show relatively complex wind speed dependence. They decrease for wind speeds up to about 3 ms^{-1}, increase with wind speeds between 3 and 5 ms^{-1}, and then decrease again at higher wind speeds. In comparison, Harrison et al. (2001) found a U-shaped curve for the wind speed dependence of $PM_{10-2.5}$ mass concentration measurements taken near a roadway in Birmingham Hodge Hill, England, suggesting dilution at wind speeds below about 4 ms^{-1} and resuspension at higher wind speeds. Moore et al. (2010) found positive correlation between $PM_{10-2.5}$ concentration and wind speed for three Los Angeles area sites during the dry seasons, but negligible or negative correlation in winter. Once additional data are available, seasonal analysis and consideration of additional meteorological variables related to resuspension could assist in interpreting the relationship between wind speed and $PM_{10-2.5}$ concentrations at our monitoring sites.

3.4. Comparison of 24-h Average Mass Concentrations and Spatial Correlation with other Locations

The State of Colorado (CDPHE) reports mass concentrations of $PM_{2.5}$ and PM_{10} from two urban monitoring sites in Denver: the CAMP site at 2105 Broadway (lat. 39.75, long. −104.99) and the Denver Municipal Animal Shelter (DMAS) site at 678 S. Jason Street (lat. 39.70, long. −105.00). Each site houses a TEOM 1400a equipped with an FDMS unit (Series 8500 FDMS, Thermo Scientific) for continuous $PM_{2.5}$ monitoring and a TEOM 1400AB without an FDMS unit for PM_{10} monitoring. We obtained data from 1/1/2009 to 2/28/2010 for these monitoring sites from CDPHE and estimated $PM_{10-2.5}$ concentrations by subtraction. Descriptive statistics for both size ranges were calculated for comparison with results from the four CCRUSH TEOM sites. For the given time period, the mean 24-h average $PM_{2.5}$ concentration at CAMP was 8.3 μg m^{-3}, with a 95th percentile value of 16.6 μg m^{-3} and COV of 0.5. The mean $PM_{2.5}$ concentration at DMAS was 11.1 μg m^{-3}, with a 95th percentile value of 19.6 μg m^{-3} and COV of 0.4. The mean $PM_{2.5}$ concentration at CAMP thus falls within the range observed at our 4 monitoring sites, while the concentration at DMAS is about 20%–40% higher than the mean concentrations we observed. The Pearson's R correlation coefficient for 24-h average $PM_{2.5}$ concentrations at the two CDPHE monitors, separated by 5.1 km, was 0.82. Correlation coefficients for 24-h average $PM_{2.5}$ concentrations at the CDPHE monitors paired with our Denver monitors ranged from 0.69 between Alsup and DMAS (14.7 km apart) to 0.87 between Edison and DMAS (8.8 km apart).

The mean 24-h average $PM_{10-2.5}$ concentration at CAMP was 15.7 μg m^{-3}, with a 95th percentile value of 27.5 μg m^{-3} and COV of 0.4. The mean $PM_{10-2.5}$ concentration at DMAS was 12.9 μg m^{-3}, with a 95th percentile value of 28.4 μg m^{-3} and COV of 0.7. $PM_{10-2.5}$ concentrations at the CDPHE sites are thus comparable to those we observed at Alsup, and higher than those observed at our other study sites. The Pearson's R correlation coefficient for 24-h average $PM_{10-2.5}$ concentrations at the two CDPHE monitors was 0.61. Correlation coefficients for $PM_{10-2.5}$ concentrations at the CDPHE monitors paired with our Denver monitors range from 0.60 between Alsup and CAMP (9.7 km apart) to 0.83 between Edison and DMAS (8.8 km apart).

U.S. EPA (2009) presents the distributions of 24-h average $PM_{2.5}$ and $PM_{10-2.5}$ mass concentrations measured from 2005 to 2007 from FRM monitors across the country that report to the agency's Air Quality System. For $PM_{2.5}$, the national mean 24-h average concentration was 12 μg m^{-3} and the 5th and 95th percentile values were 4 and 28 μg m^{-3}, respectively, based on nearly 350,000 observations. For Denver, U.S. EPA (2009) reports a mean 24-h average $PM_{2.5}$ concentration during 2005–2007 of 9 μg m^{-3} and 5th and 95th percentile values of 3 and 18 μg m^{-3}, respectively, based on 4192 observations. The results from the CDPHE monitors discussed above and from the TEOM sampling conducted in this study during 2009–2010 show similar mean $PM_{2.5}$ concentrations to those EPA reports for Denver, but with greater variability.

For $PM_{10-2.5}$, U.S. EPA (2009) reported concentrations estimated from colocated monitors using low-volume FRM filter samplers from 2005 to 2007. The national mean 24-h average $PM_{10-2.5}$ concentration was 13 μg m^{-3} with 5th and 95th percentile values of 1 and 33 μg m^{-3}, respectively, based on just

over 12,000 observations. For $PM_{10-2.5}$ in Denver, EPA reported a mean concentration of 20 μg m^{-3} with 5th and 95th percentile values of 4 and 42 μg m^{-3}, based on 353 observations. In comparison to the values U.S. EPA (2009) reports for Denver, the results from the CDPHE monitoring discussed above and the results from our study suggest lower mean $PM_{10-2.5}$ concentrations. Differences could be due to differences in sampling methods and monitoring locations or changes in pollutant levels over time.

As mentioned in Section 1, concentrations of $PM_{10-2.5}$ have generally been expected to be more variable than those of $PM_{2.5}$. The results from this study indicate that 24-h average $PM_{10-2.5}$ concentrations are somewhat more temporally variable than those for $PM_{2.5}$, with coefficients of variation ranging from 0.6 to 0.8 for $PM_{10-2.5}$ and near 0.5 for $PM_{2.5}$. The data from CDPHE show a comparatively low COV for $PM_{10-2.5}$ concentrations at CAMP. For both size classes, spatial correlation was relatively strong for the two monitors in Greeley, compared to the monitors located in Denver. The correlation coefficient of 0.97 for $PM_{10-2.5}$ concentrations from the 2 Greeley locations, which are located 4.5 km apart, is also relatively high compared to correlation coefficients reported for pairs of $PM_{10-2.5}$ monitors in other cities, including those with similar separation distances (Wilson et al. 2005; U.S. EPA 2009; Pabkin et al. 2010). The high correlation of $PM_{10-2.5}$ for the Greeley monitors suggests the impact of regional sources and/or meteorological influences, rather than local sources.

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