Intra-urban spatial variability of PM$_{2.5}$-bound carbonaceous components

Mingjie Xie[a], **Teresa L. Coons**[a], **Steven J. Dutton**[b], **Jana B. Milford**[a], **Shelly L. Miller**[a], **Jennifer L. Peel**[c], **Sverre Vedal**[d], and **Michael P. Hannigan**[a,*]

Michael P. Hannigan: hannigan@colorado.edu

[a]Department of Mechanical Engineering, College of Engineering and Applied Science, University of Colorado, Boulder, CO 80309, USA

[b]National Center for Environmental Assessment, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA

[c]Department of Environmental and Radiological Health Sciences, Colorado State University, Fort Collins, CO 80523, USA

[d]Department of Environmental and Occupational Health Sciences, School of Public Health and Community Medicine, University of Washington, Seattle, WA 98195, USA

Abstract

The Denver Aerosol Sources and Health (DASH) study was designed to evaluate associations between PM$_{2.5}$ species and sources and adverse human health effects. The DASH study generated a five-year (2003–2007) time series of daily speciated PM$_{2.5}$ concentration measurements from a single, special-purpose monitoring site in Denver, CO. To evaluate the ability of this site to adequately represent the short term temporal variability of PM$_{2.5}$ concentrations in the five county Denver metropolitan area, a one year supplemental set of PM$_{2.5}$ samples was collected every sixth day at the original DASH monitoring site and concurrently at three additional sites. Two of the four sites, including the original DASH site, were located in residential areas at least 1.9 km from interstate highways. The other two sites were located within 0.3 km of interstate highways. Concentrations of elemental carbon (EC), organic carbon (OC), and 58 organic molecular markers were measured at each site. To assess spatial variability, site pairs were compared using the Pearson correlation coefficient (r) and coefficient of divergence (COD), a statistic that provides information on the degree of uniformity between monitoring sites. Biweekly co-located samples collected from July 2004 to September 2005 were also analyzed and used to estimate the uncertainty associated with sampling and analytical measurement for each species. In general, the two near-highway sites exhibited higher concentrations of EC, OC, polycyclic aromatic hydrocarbons (PAHs), and steranes than did the more residential sites. Lower spatial heterogeneity based on r and COD was inferred for all carbonaceous species after considering their divergence

*Corresponding author. Department of Mechanical Engineering, Engineering Center, 427 UCB, Boulder, CO 80309-0427, USA. Tel.: +1 303 735 5045; fax: +1 303 492 3498.

and lack of perfect correlations in co-located samples. Ratio–ratio plots combined with available gasoline- and diesel-powered motor vehicle emissions profiles for the region suggested a greater impact to high molecular weight (HMW) PAHs from diesel-powered vehicles at the near-highway sites and a more uniformly distributed impact to ambient hopanes from gasoline-powered motor vehicles at all four sites.

Keywords

Particulate matter; PM$_{2.5}$; Organic molecular marker; Spatial variability; Co-located samples; Motor vehicle influence

1. Introduction

Numerous studies have found that both short- and long-term exposures to ambient particles less than 2.5 μm in diameter (PM$_{2.5}$) are associated with increased risk of mortality, as well as respiratory illness, lung cancer, asthma and heart disease (e.g., Dockery et al.,1993; Pope et al., 2002; U.S. EPA, 2009; Zanobetti and Schwartz, 2009). PM$_{2.5}$ is a complex mixture of chemicals often emitted directly from combustion sources or formed from atmospheric transformation of gas-phase precursors. To examine the associations between increased health risks and distinct sources that contribute to PM$_{2.5}$, several epidemiologic studies have applied receptor models to identify and quantify source impacts (e.g., Laden et al., 2000; Ito et al., 2005). Such studies have suggested links between health effects and sources in particular regions, but the collective evidence on this association from different studies remains inconclusive (Stanek et al., 2011). This variability in the evidence could be due to differences in PM$_{2.5}$ sources and composition across studies, or to exposure estimation error resulting from spatial variability in PM$_{2.5}$ sources and composition within individual study areas (Ito et al., 2004; Kim et al., 2005; Marmur et al., 2006). Heterogeneity in PM$_{2.5}$ components and sources or substantial differences in the magnitude of concentrations across an urban area can lead to biased health effects estimates (Zeger et al., 2001).

The Denver Aerosol Sources and Health (DASH) study was designed to evaluate chemical components and sources of PM$_{2.5}$ in relation to acute risk of mortality and morbidity (Vedal et al., 2009). The DASH study obtained a five-year (2002e2006) time series of daily speciated PM$_{2.5}$ measurements from a single special-purpose monitoring site in Denver, CO. Speciation measurements included inorganic ions, elemental carbon (EC), total organic carbon (OC), and organic molecular markers. The resulting time series provide significant insight into the temporal variability of PM$_{2.5}$ components and source contributions in Denver (Dutton et al., 2009a,b; Dutton et al., 2010a,b). Moreover, preliminary results for the DASH project indicated that in Denver, roadway-associated sources, especially diesel emissions characterized by EC, might be more strongly linked with respiratory hospital admissions and mortality than PM$_{2.5}$ mass and other PM components (Peel et al., 2009).

To understand the limitations of the single site used in the DASH study, we collected one year of supplemental PM$_{2.5}$ samples at three additional sites to investigate the spatial variability of PM$_{2.5}$ components and source contributions in Denver. To frame the spatial variability, uncertainty associated with sampling and analytical measurement needs to be

addressed. For example, assume measurements taken at two sites in an urban area are correlated with an *r* value of 0.6. This degree of correlation across sites might be viewed as relatively high, if side-by-side measurements from a single site are only correlated with an *r* value of 0.7 due to uncertainty in each measurement. To assess the side-by-side uncertainty in this study, $PM_{2.5}$ concentrations were measured biweekly from mid-July 2004 to late September 2005, using two co-located samplers. Finally, spatial distributions of diesel- and gasoline-powered motor vehicle source influences are discussed based on the comparison of the ambient data to published source profiles.

2. Methods

2.1. $PM_{2.5}$ sampling sites

The primary sampling site for the DASH study was located on the rooftop of Palmer Elementary School (PAL), where daily samples were collected beginning on July 1, 2002. The three additional sites began sample collection on March 1, 2008 and were located to the north, northwest and southwest of PAL, as shown in Fig. 1. PAL is in a large residential area with relatively dense population, far from industrial point sources, and with the nearest major interstate highway (I-25) located 5.2 km to the southwest (Vedal et al., 2009). The supplemental site northwest of PAL was located on the rooftop of Edison Elementary School (EDI). EDI is also in a residential neighborhood far from industrial point sources, with the nearest major interstate highways located 1.9 km to the north (I-70) and 3.0 km to the southeast (I-25). In contrast, the other two sites were located in more industrial areas and closer to major interstate highways. The site to the north was located on the rooftop of Alsup Elementary School (ALS) in the north end of the major industrial area of Denver and 0.3 km from I-76. The site to the southwest was located on the roof of the Denver Municipal Animal Shelter (MAS), surrounded by small industrial facilities and only 0.2 km from the major north-south interstate highway (I-25). The MAS site was selected to leverage co-located multi-pollutant measurements taken as part of the State of Colorado's NCore monitoring program for Denver (U.S. EPA, 2011). These locations provide for comparisons between two comparatively residential sites (PAL and EDI) and two sites with greater expected roadway influences (MAS and ALS).

2.2. Sample collection and chemical characterization

Twenty-four hour $PM_{2.5}$ filter samples were collected at the four sites every sixth day from March 1, 2008 to March 14, 2009. Hourly observed meteorological data for this period were obtained from nearby monitoring stations operated by the Colorado Department of Public Health and Environment (CDPHE) (Table 1). Prior to conducting multi-site sampling, bi-weekly co-located samples were collected at PAL from July 2004 to September 2005. Details of the sampling set up, protocols, and chemical analysis were discussed previously (Dutton et al., 2009a,b). Briefly, $PM_{2.5}$ was separated by aerodynamic diameter using a cyclone incorporating a 2.5 μm size cut at a flow rate of 92 L min^{-1}. After the cyclone, the airstream was split with 20 L min^{-1} passing through a 47 mm diameter, 2 μm pore size Teflon (PTFE) filter and 72 L min^{-1} passing through a 90 mm diameter pre-baked (500 °C) quartz fiber filter. This paper focuses on the EC, OC, and organic molecular marker measurements obtained from the quartz fiber filters.

EC and OC were measured on 1.5 cm^2 punches taken from the quartz filters, using a Sunset Laboratory ECOC analyzer operated under the NIOSH 5040 thermal optical transmission (TOT) method. Organic molecular markers were extracted from the filters with reagent grade methylene chloride and analyzed using an Agilent 6890N gas chromatograph coupled with an Agilent 5975 mass spectrometer. High volume injection (50 μL) achieved by programmable temperature vaporization was applied to improve the detection limit (Dutton et al., 2009b). Fifty-eight organic molecular marker compounds were quantified for each sample, including *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (oxy-PAHs), steranes, *n*-alkanoic acids, sterols and methoxyphenols. Samples were run in sequences incorporating 14 samples, 2 field blanks, 6 solvent blanks and 5 dilutions of quantification standards. Quadratic calibration curves were generated for each molecular marker from all available runs of quantification standards in a given batch (4–7 sequences). Example calibration curves from one of the three batches are shown in Figure S1 (Supporting information); Table S1 presents the fraction of the compounds detected in samples of that batch falling in the calibration range. The calibration curves were used along with the known mass of internal standards pre-spiked before filter extraction to determine the final mass amount of each molecular marker by converting peak area ratios to mass ratios. In this work, all components were field-blank corrected by subtracting off the median blank value within a given analysis batch. More details of the quantification method are given in the supporting information after Figure S1. The 31 pairs of co-located samples were analyzed using the same protocols as the spatial samples. Table S2 presents statistics for each species quantified at the four sites, and Table S3 presents those for the co-located samples.

2.3. Uncertainty estimation

Quantification uncertainties for EC were estimated using the calculation recommended by the instrument manufacturer (Sunset Laboratory) and those for OC based on laboratory observations (Schauer et al., 2003). For the organic molecular markers, quantification uncertainty was estimated empirically from the analytical calibration curve (Dutton et al., 2009b). The root sum of squares (RSS) method (NIST, 1994) was used to propagate the uncertainty for point–wise uncertainty estimation, involving uncertainty in instrumental analysis, blank correction (standard deviation of field blanks within each batch) and sample air volume (Dutton et al., 2009b). These quantification uncertainties are reported as signal to noise (S/N, mean concentration/mean uncertainty) ratios in Tables S2 and S3.

2.4. Statistical analysis

In this study, the spatial characteristics of concentrations of carbonaceous species were evaluated using Pearson correlation coefficients (r) and coefficients of divergence (COD). Pearson correlation coefficients show the degree of correspondence of the chemical components between two sampling sites (Wongphatarakul et al., 1998). High *r* values (close to unity) indicate that concentrations of the chemical component are proportional between the two sites throughout the sampling period. COD is applied to further evaluate the similarity between concentrations at two different monitoring sites and is defined as

$$\mathrm{COD}_{fn} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{x_{if}-x_{ih}}{x_{if}+x_{ih}}\right)^2}$$

where x_{if} and x_{ih} are the concentrations of one species for the ith time period at sites f and h, respectively, and n is the number of observations. Values approaching 0 represent uniformity between pairs of samples, while values approaching 1 represent complete divergence (Wongphatarakul et al., 1998; Kim et al., 2005). From previous studies (Wongphatarakul et al., 1998; Kim et al., 2005; Wilson et al., 2005), Krudysz et al. (2008) inferred a boundary COD value of 0.2, where COD values >0.20 are defined as heterogeneous spatial distribution and values <0.20 represent spatially homogeneous air pollutants.

3. Results and discussion

3.1. General description of measurement data

3.1.1. Spatial samples—Table S2 lists statistics for concentrations of each species at each site, including mean, median, coefficient of variation (CV, standard deviation/mean concentration), S/N ratio and the percentage of observations below detection limit (BDL). The data obtained on Nov. 25, 2008 (during the Thanksgiving holiday) were not included in Table S2 due to the extremely high concentrations observed on that day for all categories of carbonaceous species (Figure S2). The elevated concentrations are probably attributable to heavy traffic combined with a stagnant atmosphere and cold weather (Figure S3). Further discussion of the Nov. 25th data is provided in the supplemental information. During the rest of the sampling campaign, total n-alkanoic acids were the most abundant and evenly distributed of the molecular marker classes, followed by n-alkanes and methoxyphenols. PAHs, oxy-PAHs and steranes exhibited lower concentrations by 1—2 orders of magnitude than the n-alkanoic acids. The odd-even patterns of n-alkanes were similar among the four sites, peaking at C_{29} and C_{31} (Table S2), consistent with the patterns observed in leaf abrasion products (Rogge et al., 1993b). Lower S/N ratios for some species (e.g., tridecanoic acid and heptadecanoic acid) suggest higher analytical uncertainty, and correspond to a larger number of observations below detection limits. The CV value is a robust metric used to assess the temporal variation of species concentrations (Dutton et al., 2009b; Krudysz et al., 2009). At all four sampling sites, the CVs of most organic molecular markers were close to or higher than unity. The highest CV values were observed for retene (1.2–1.7), n-alkanoic acids (1.0–1.7) and methoxyphenols (1.1–2.9). In contrast, CVs for bulk species were lower than unity, ranging from 0.5 to 0.7. These results are Dutton et al. (2009a,b).

In Table S2, the average EC concentrations at ALS (0.66 µg m^{-3}) and MAS (0.48 µg m^{-3}) were higher than at PAL (0.31 µg m^{-3}) and EDI (0.32 µg m^{-3}), likely reflecting larger contributions from vehicle emissions at the sites located closer to interstate highways. Unlike EC, which is exclusively a primary species, OC is of both primary and secondary origin (Aurela et al., 2011). However, the higher OC concentrations at ALS (3.56 µg m^{-3}) and MAS (3.51 µg m^{-3}) might be mostly due to primary emissions, because average OC/EC ratios at these two sites (mean ± sd, 9.1 ± 5.0 and 6.9 ± 4.0) are lower than those at the two

more residential sites (EDI 12.2 ± 6.5, PAL 12.0 ± 6.9). The highest correlation between OC and EC concentrations was observed at ALS ($r = 0.63$) while the lowest was detected at PAL($r = 0.41$). Steranes and PAHs (not including retene) exhibited higher average concentrations at ALS (2.03 ng m^{-3} and 3.19 ng m^{-3}) and MAS (1.89 ng m^{-3} and 2.91 ng m^{-3}) than at PAL (1.43 ng m^{-3} and 1.88 ng m^{-3}) and EDI (1.52 ng m^{-3} and 2.21 ng m^{-3}), consistent with the spatial variation of EC concentrations. Sources of particulate oxy-PAHs include both direct incomplete combustion (e.g., motor vehicle exhaust, wood burning) (Fitzpatrick et al., 2007) and oxidation of parent PAHs in the environment (Walgraeve et al., 2010), so oxy-PAHs species concentrations were not always higher at the two near-highway sites. Methoxyphenols and retene, which are widely used as biomass burning tracers (Schauer et al., 2001), were found in higher concentrations at PAL (18.3 ng m^{-3} and 0.72 ng m^{-3}) and EDI (29.4 ng m^{-3} and 0.64 ng m^{-3}) than ALS (13.7 ng m^{-3} and 0.41 ng m^{-3}) and MAS (17.0 ng m^{-3} and 0.43 ng m^{-3}). In addition, larger weekend increases in total concentrations of these species were observed at PAL (145% higher than the weekday average) and EDI (92%) than at ALS (25%) and MAS (57%). These observations may be explained by the fact that EDI and PAL are closer than the other sites to residential wood combustion sources.

Table 2 compares studies that have investigated the spatial distribution of PM$_{2.5}$ components, including organic molecular markers. The total average concentrations of n-alkanes, PAHs and steranes in Denver were higher than those observed in Long Beach, CA (Krudysz et al., 2009). The average concentrations of these organic molecular markers were less varied across different sites in Denver than in Vancouver, BC (Cheng et al., 2004, 2006), Atlanta, GA (Li et al., 2009) and Hong Kong, China (Guo et al., 2003; Ho et al., 2003). Concentrations of EC and OC at the four sampling sites in Denver were lower than observed in other studies. All of the studies listed in Table 2 show smaller spatial variations for OC than EC.

3.1.2. Co-located samples—Statistics of species concentrations from 31 pairs of co-located samples obtained at the PAL site from July 2004–September 2005 are given in Table S3, including mean and median concentrations, standard deviations, S/N ratios and percentages of BDL measurements. Values of r and COD for each species between the co-located samples were also calculated to reflect the combined uncertainty associated with sampling and analytical measurement. Ideally, all species concentrations should be highly correlated ($r \sim 1$) with relatively low CODs (~ 0) between the co-located samples. In fact, co-located measurements of HMW n-alkanes (C_{32}–C_{35}), oxy-PAHs (except benzo[de]anthracene-7-one), n-alkanoic acids, cholesterols and methoxyphenols were less correlated and had higher CODs than other species (Table S3). The concentrations of the species with high side-by-side divergence (e.g., dotriacontane, tridecanoic acid, sterols and most methoxyphenols) were very low in a number of samples and prone to have relatively high quantification uncertainties, as indicated by their high percentages of measurements below the detection limit and low S/N ratios (Table S3). These low concentrations show large differences between co-located samples, leading to lower r and higher COD values than other species; the relatively small sample number ($N = 31$) of co-located samples could amplify the impacts of those low measurement values in the comparison using r and COD.

In addition, chromatogram integrations for HMW and semi-polar components have higher uncertainties than lighter and non-polar ones due to their wider peaks. Other species, including lighter n-alkanes ($C_{22} – C_{31}$), PAHs, steranes, EC and OC have relatively high correlations (r = 0.82–0.97) between co-located samples.

3.2. Analysis of spatial variability

3.2.1. Correlation coefficient (r) and coefficient of divergence (COD)—Fig. 2(a–f) shows correlation coefficients and CODs for concentrations of organic molecular markers, EC, and OC measured at the four sites from March 2008eMarch 2009. OC concentrations had higher correlation across sites ($r = 0.80–0.85$) and lower CODs (0.17–0.20) than EC, consistent with the observations of other studies (Krudysz et al., 2009; Cheung et al., 2011), which is likely caused by the smaller number of EC source types and different source strength across different sampling sites. Heavier odd n-alkanes (C_{27}, C_{29}, C_{31}, C_{33}) are primarily of biogenic origin (Simoneit and Mazurek, 1982; Rogge et al., 1993b; Cass, 1998). The heavier odd n-alkanes were highly spatially correlated ($r = 0.69–0.94$) with a clear odd to even carbon number predominance in r value, and showed an opposite pattern in CODs across all spatial site pairs. PAH (not including retene) concentrations had weaker correlations ($r = 0.27–0.66$) between all site pairs, suggesting there were different types of PAH sources contributing at the four sites. However, CODs of these compounds were lower between MAS and ALS (0.25–0.45) than for the other site pairs, which might be attributed to the similar effects of nearby roadway emissions at MAS and ALS. Steranes are primarily from lubricating oil use of both diesel and gasoline-powered vehicles (Minguillon et al., 2008), so the spatial variations of these components should be dominated by traffic emission distributions. In Fig. 2a and b, steranes had higher correlations ($r = 0.55–0.85$) and lower CODs (0.26–0.36) than in the other plots, suggesting similar impacts of roadway emissions between the two residential sites (EDI and PAL), and the two near-highway sites (MAS and ALS). The three oxygenated PAHs (xanthone, 1,8-naphthalic anhydride, anthracene-9,10-dione) and n-alkanoic acids exhibited peak concentrations in warm seasons at all four sites, and were generally more correlated across sites than PAHs and steranes. Concentrations of the biomass burning markers (methoxyphenols and retene) were generally well correlated but had higher CODs (0.31–0.56) than most of the other species. To draw conclusions about the spatial variability of one compound class relative to another, we need to understand the uncertainties associated with sampling and analytical measurement for the different compound classes.

3.2.2. Spatial variability framed by variability in co-located sample results—The statistics r and COD have been widely used to describe spatial variability (Kim et al., 2005; Hwang et al., 2008). However, very few studies have examined the point of reference for interpreting the degree to which they represent spatial variability versus uncertainty associated with sampling and analytical measurement (Krudysz et al., 2008). Given the divergence and lack of perfect correlation observed in co-located samples (Table S3), it is unrealistic to expect a COD near zero or value of r near 1 in comparing observations across sites, even if atmospheric concentrations are highly uniform. For reference in this study, values of r and COD for each species from co-located samples are shown in Fig. 2g; the COD values for different groups of molecular markers are averaged and overlaid on each

plot in Fig. 2. This comparison is rough, because the co-located sample comparisons are for a different time-period and include a smaller number of samples than the comparisons across sampling locations. Some species (e.g., sterols and methoxyphenols) exhibited large side-by-side divergence due to their high percentages of BDL measurements. Comparing the COD between each sampling site pair and the COD for the co-located pair, the heavy odd *n*-alkanes (C_{27}, C_{29}, C_{31}), steranes and OC have low divergence between co-located samples and slightly higher divergence across sampling locations; *n*-alkanes with a chain length ranging from C_{22} to C_{30} (not including C_{27} and C_{29}), HMW PAHs (MW = 276, 300) and EC have low divergence between co-located samples but high divergence across locations; low MW PAHs (MW 226) exhibit moderate divergence between co-located samples and higher divergence for pairs of different sites (e.g., PAL versus MAS); other species (e.g., C_{32}–C_{35}, *n*-alkanoic acids, sterols and methoxyphenols) show high divergence between co-located samples with comparable or even lower divergence across locations. Therefore, the spatial distribution of organic species in this work might be less heterogeneous than it first appears, as some of the apparent differences across locations may be due to sampling and analytical uncertainty. The impacts of quantification uncertainty on *r* and COD for side-by-side and multi-site comparisons were simulated (Table S4) and are discussed in the Supporting information. The results suggest that uncertainties in species quantification can have a substantial influence on values of *r* and COD that are used to assess spatial variability.

3.3. Spatial distribution of mobile sources influences

EC in urban environments is mainly associated with diesel vehicle emissions, while large PAHs (6–8 aromatic rings) are primarily emitted from gasoline-powered vehicles (Rogge et al., 1993a; Schauer et al., 1996; Riddle et al., 2007) and hopanes are from motor oil use (both diesel and gasoline; Kleeman et al., 2008). To better understand the relative influence of gasoline and diesel emissions spatially, two ratio–ratio plots including different motor vehicle emission markers were made for each of the four sites (Fig. 3a–h). One series of plots compares indeno[1,2,3-cd]pyrene and benzo[ghi]perylene that are normalized by EC; the other compares ba-30-norhopane and ab-hopane, again normalized by EC. Motor vehicle and wood burning profiles specifically for the Denver area (Zielinska et al., 1998; Cadle et al., 1999) were also overlaid on the plots with ambient data. If only gasoline-powered vehicle emissions or only diesel vehicle emissions are the dominant source of all three compounds, then the ambient measurements should cluster near the points of the corresponding source profiles. If both gasoline and diesel emissions are primary sources for the three compounds, then the ambient data in the plots should fall on a mixing line between the two source profiles. Finally, the ambient data can appear scattered on a ratioeeratio plot if there are three or more contributing sources (Robinson et al., 2006).

The ambient PAH data at each site fall along a relatively continuous line in all of the ratio–ratio plots (Fig. 3a–d). The ambient PAH concentrations are more likely to be explained by a combination of motor vehicle source profiles (both gasoline and diesel) than wood burning, because the line representing wood burning sources lies below that of the ambient PAH data at all sites. More ambient PAH data at PAL and EDI sites (Fig. 3a and b) correspond to gasoline and wood burning source profiles in the upper right extreme than at ALS and MAS

sites (Fig. 3c and d), indicating more diesel vehicle activity in the areas nearer to the interstate highways. The ambient PAH data also show significant influence from heavy duty diesel vehicles on a number of days, since a certain fraction of PAH to EC ratios fall below the source profiles of light duty diesel vehicle emissions and extend to the region of heavy duty diesel emissions in the lower left extreme. Unlike the PAHs, ambient hopane measurements mostly fall near the gasoline and light duty diesel source profiles at all four sites (Fig. 3e–h), supporting the conclusion that gasoline and light duty diesel emissions explain the Denver ambient hopane data (Dutton et al., 2009b).

4. Conclusions

Organic molecular markers and bulk carbon contents were analyzed in $PM_{2.5}$ samples collected every sixth day at four sampling sites for one year. Our results show that PAHs, steranes, methoxyphenols and EC concentrations were more affected by primary emissions and show distinct differences in concentrations between near-highway and residential sites. The HMW and semi-polar compound concentrations exhibit relatively less correlation and higher divergence between co-located samples, indicating high uncertainty from sampling and analytical measurements. The data and discussion in this paper also provide information on spatial variability of fine particulate organics, which was not examined in the previous DASH study. PAHs and steranes exhibited some degree of homogeneity for site pairs where each site is from a residential or a near-highway area, but showed less homogeneity for site pairs where one site was residential and one site was near-highway. OC was more strongly correlated and exhibited relatively lower CODs than EC. The spatial heterogeneity of organic molecular markers would be overestimated without considering their divergence between co-located samples. Values of r and CODs derived from co-located samples should be used as points of reference to analyze spatial variability of $PM_{2.5}$ species. In particular, the benchmark COD of 0.20 recommended by Krudysz et al. (2008) is too low to account for the influence of sampling and measurement uncertainties on CODs for many organic components in this work. The implication for DASH is that we could have high confidence in the data and representativeness from the PAL site for those compounds with low side-by-side divergence and low spatial variability, whereas compounds with either high side-by-side divergence or high spatial variability (or both) need to be treated more cautiously. From the ratio–ratio plots and overlaid source profiles, diesel vehicle emissions appear to contribute more HMW PAHs at near-highway sites than at the more residential sites. Ambient hopane concentrations at all four sites appear to be mostly explained by a combination of gasoline and light duty diesel emissions. The data sets in this study are being used to perform source apportionment. Results from that work will be presented in a future paper, which will focus on the sources of particulate organics and the spatial variability of source contributions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

References

Aurela M, Saarikoski S, Timonen H, Aalto P, Keronen P, Saarnio K, Teinilä K, Kulmala M, Hillamo R. Carbonaceous aerosol at a forested and an urban background sites in Southern Finland. Atmospheric Environment. 2011; 45:1394–1401.

Cadle SH, Mulawa PA, Hunsanger EC, Nelson K, Ragazzi RA, Barrett R, Gallagher GL, Lawson DR, Knapp KT, Snow R. Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. Environmental Science and Technology. 1999; 33:2328–2339.

Cass GR. Organic molecular tracers for particulate air pollution sources. Trac-Trends in Analytical Chemistry. 1998; 17:356–366.

Cheng Y, Li SM, Leithead A, Brickell PC, Leaitch WR. Characterizations of cis-pinonic acid and n-fatty acids on fine aerosols in the Lower Fraser Valley during Pacific 2001 Air Quality Study. Atmospheric Environment. 2004; 38:5789–5800.

Cheng Y, Li SM, Leithead A, Brook JR. Spatial and diurnal distributions of n-alkanes and n-alkan-2-ones on PM2.5 aerosols in the Lower Fraser Valley, Canada. Atmospheric Environment. 2006; 40:2706–2720.

Cheung K, Daher N, Kam W, Shafer MM, Ning Z, Schauer JJ, Sioutas C. Spatial and temporal variation of chemical composition and mass closure of ambient coarse particulate matter (PM10–2.5) in the Los Angeles area. Atmospheric Environment. 2011; 45:2651–2662.

Dockery DW, Pope CA, Xu X, Spengler JD, Ware JH, Fay ME, Ferris BG, Speizer FE. An association between air pollution and mortality in six U.S. Cities. New England Journal of Medicine. 1993; 329:1753–1759. [PubMed: 8179653]

Dutton SJ, Rajagopalan B, Vedal S, Hannigan MP. Temporal patterns in daily measurements of inorganic and organic speciated PM2.5 in Denver. Atmospheric Environment. 2010a; 44:987–998. [PubMed: 23486844]

Dutton SJ, Schauer JJ, Vedal S, Hannigan MP. PM2.5 characterization for time series studies: pointwise uncertainty estimation and bulk speciation methods applied in Denver. Atmospheric Environment. 2009a; 43:1136–1146. [PubMed: 20126292]

Dutton SJ, Vedal S, Piedrahita R, Milford JB, Miller SL, Hannigan MP. Source apportionment using positive matrix factorization on daily measurements of inorganic and organic speciated PM2.5. Atmospheric Environment. 2010b; 44:2731–2741. [PubMed: 22768005]

Dutton SJ, Williams DE, Garcia JK, Vedal S, Hannigan MP. PM2.5 characterization for time series studies: organic molecular marker speciation methods and observations from daily measurements in Denver. Atmospheric Environment. 2009b; 43:2018–2030. [PubMed: 20161318]

Fitzpatrick EM, Ross AB, Bates J, Andrews G, Jones JM, Phylaktou H, Pourkashanian M, Williams A. Emission of oxygenated species from the combustion of pine wood and its relation to soot formation. Process Safety and Environmental Protection. 2007; 85:430–440.

Guo H, Lee SC, Ho KF, Wang XM, Zou SC. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. Atmospheric Environment. 2003; 37:5307–5317.

Ho KF, Lee SC, Chan CK, Yu JC, Chow JC, Yao XH. Characterization of chemical species in PM2.5 and PM10 aerosols in Hong Kong. Atmospheric Environment. 2003; 37:31–39.

Hwang I, Hopke PK, Pinto JP. Source apportionment and spatial distributions of coarse particles during the regional air pollution study. Environmental Science and Technology. 2008; 42:3524–3530. [PubMed: 18546684]

Ito K, Christensen WF, Eatough DJ, Henry RC, Kim E, Laden F, Lall R, Larson TV, Neas L, Hopke PK, Thurston GD. PM source apportionment and health effects: 2. An investigation of intermethod

variability in associations between source-apportioned fine particle mass and daily mortality in Washington, DC. Journal of Exposure Science and Environmental Epidemiology. 2005; 16:300–310. [PubMed: 16304602]

Ito K, Xue N, Thurston G. Spatial variation of PM2.5 chemical species and source-apportioned mass concentrations in New York City. Atmospheric Environment. 2004; 38:5269–5282.

Kim E, Hopke PK, Pinto JP, Wilson WE. Spatial variability of fine particle mass, components, and source contributions during the regional air pollution study in St. Louis. Environmental Science and Technology. 2005; 39:4172–4179. [PubMed: 15984797]

Kleeman MJ, Riddle SG, Robert MA, Jakober CA. Lubricating oil and fuel contributions to particulate matter emissions from light-duty gasoline and heavy-duty diesel vehicles. Environmental Science and Technology. 2008; 42:235–242. [PubMed: 18350902]

Krudysz M, Dutton S, Brinkman G, Hannigan M, Fine P, Sioutas C, Froines J. Intra-community spatial variation of size-fractionated organic compounds in Long Beach, California. Air Quality, Atmosphere and Health. 2009; 2:69–88.

Krudysz MA, Froines JR, Fine PM, Sioutas C. Intra-community spatial variation of size-fractionated PM mass, OC, EC, and trace elements in the Long Beach, CA area. Atmospheric Environment. 2008; 42:5374–5389.

Laden F, Neas LM, Dockery DW, Schwartz J. Association of fine particulate matter from different sources with daily mortality in six U.S. Cities Environmental Health Perspectives. 2000; 108

Li Z, Porter EN, Sjödin A, Needham LL, Lee S, Russell AG, Mulholland JA. Characterization of PM2.5-bound polycyclic aromatic hydrocarbons in AtlantaeSeasonal variations at urban, suburban, and rural ambient air monitoring sites. Atmospheric Environment. 2009; 43:4187–4193.

Marmur A, Park SK, Mulholland JA, Tolbert PE, Russell AG. Source apportionment of PM2.5 in the southeastern United States using receptor and emissions-based models: conceptual differences and implications for time-series health studies. Atmospheric Environment. 2006; 40:2533–2551.

Minguillon MC, Arhami M, Schauer JJ, Sioutas C. Seasonal and spatial variations of sources of fine and quasi-ultrafine particulate matter in neighborhoods near the Los Angeles-Long Beach harbor. Atmospheric Environment. 2008; 42:7317–7328.

NIST. Technical Note 1297, 1994 Edition: Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. National Institute of Standards and Technology. 1994. Available from: http://physics.nist.gov/Pubs

Peel J, Kim S, Hannigan M, Dutton S, Clark M, Vedal S. Fine particulate matter chemical speciation and hospital admissions in Denver: the Denver aerosol sources and health study (DASH). American Association for Aerosol Research. 2009; 295

Pope CA, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurston GD. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. JAMA: The Journal of the American Medical Association. 2002; 287:1132–1141.

Riddle SG, Jakober CA, Robert MA, Cahill TM, Charles MJ, Kleeman MJ. Large PAHs detected in fine particulate matter emitted from light-duty gasoline vehicles. Atmospheric Environment. 2007; 41:8658–8668.

Robinson AL, Subramanian R, Donahue NM, Bernardo-Bricker A, Rogge WF. Source apportionment of molecular markers and organic aerosols-1. Polycyclic aromatic hydrocarbons and methodology for data visualization. Environmental Science and Technology. 2006; 40:7803–7810. [PubMed: 17256531]

Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosol . 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environmental Science and Technology. 1993a; 27:636–651.

Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. Sources of fine organic aerosol . 4. Particulate abrasion products from leaf surfaces of urban plants. Environmental Science and Technology. 1993b; 27:2700–2711.

Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. Measurement of emissions from air pollution sources. 3. C-1-C-29 organic compounds from fireplace combustion of wood. Environmental Science and Technology. 2001; 35:1716–1728. [PubMed: 11355184]

Schauer JJ, Mader BT, Deminter JT, Heidemann G, Bae MS, Seinfeld JH, Flagan RC, Cary RA, Smith D, Huebert BJ, Bertram T, Howell S, Kline JT, Quinn P, Bates T, Turpin B, Lim HJ, Yu JZ, Yang H, Keywood MD. ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. Environmental Science and Technology. 2003; 37:993–1001. [PubMed: 12666931]

Schauer JJ, Rogge WF, Hildemann LM, Mazurek MA, Cass GR. Source apportionment of airborne particulate matter using organic compounds as tracers. Atmospheric Environment. 1996; 30:3837–3855.

Simoneit BRT, Mazurek MA. Organic-matter of the troposphere. 2. Natural background of biogenic lipid matter in aerosols over the rural western United States. Atmospheric Environment. 1982; 16:2139–2159.

Stanek LW, Sacks JD, Dutton SJ, Dubois JJB. Attributing health effects to apportioned components and sources of particulate matter: an evaluation of collective results. Atmospheric Environment. 2011; 45:5655–5663.

U.S. EPA. Integrated Science Assessment for Particulate Matter (Final Report). U.S. Environmental Protection Agency; Washington, DC: 2009. EPA/600/R-08/139F

U.S. EPA. NCore Multipollutant Monitoring Network. 2011. Retrieved September 12,2011 from: http://www.epa.gov/ttnamti1/ncore/

Vedal S, Hannigan MP, Dutton SJ, Miller SL, Milford JB, Rabinovitch N, Kim SY, Sheppard L. The Denver aerosol sources and health (DASH) study: overview and early findings. Atmospheric Environment. 2009; 43:1666–1673. [PubMed: 22723735]

Walgraeve C, Demeestere K, Dewulf J, Zimmermann R, Van Langenhove H. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: molecular characterization and occurrence. Atmospheric Environment. 2010; 44:1831–1846.

Wilson JG, Kingham S, Pearce J, Sturman AP. A review of intraurban variations in particulate air pollution: implications for epidemiological research. Atmospheric Environment. 2005; 39:6444–6462.

Wongphatarakul V, Friedlander SK, Pinto JP. A comparative study of PM2.5 ambient aerosol chemical databases. Environmental Science and Technology. 1998; 32:3926–3934.

Zanobetti A, Schwartz J. The effect of fine and coarse particulate air pollution on mortality: a national analysis. Environmental Health Perspectives. 2009; 117

Zeger SL, Thomas D, Dominici F, Samet JM, Schwarz J, Dockery D, Cohen A. Exposure measurement error in time-series studies of air pollution: concepts and consequences (vol. 108, pg 419, 2000). Environmental Health Perspectives. 2001; 109:A517. [PubMed: 11762306]

Zielinska, B.; McDonald, J.; Hayes, T.; Chow, JC.; Fujita, EM.; Watson, JG. Prepared for Colorado State University, Fort Collins, CO In: Volume B: Source Measurements. Desert Research Institute; Reno, NV: 1998. Northern Front Range Air Quality Study Final Report.

Highlights

- Concentrations of $PM_{2.5}$ associated carbonaceous species were measured from 4 urban sites in Denver.

- Spatial variability was assessed using the Pearson correlation coefficient (r) and coefficient of divergence (COD).

- Near-highway sites exhibited higher concentrations of EC, OC, PAHs, and steranes than residential sites.

- Large uncertainties associated with sampling and species quantification will bias the estimation of r and CODs.

- CODs derived from co-located samples are useful points of reference to analyze spatial variability of $PM_{2.5}$ species.
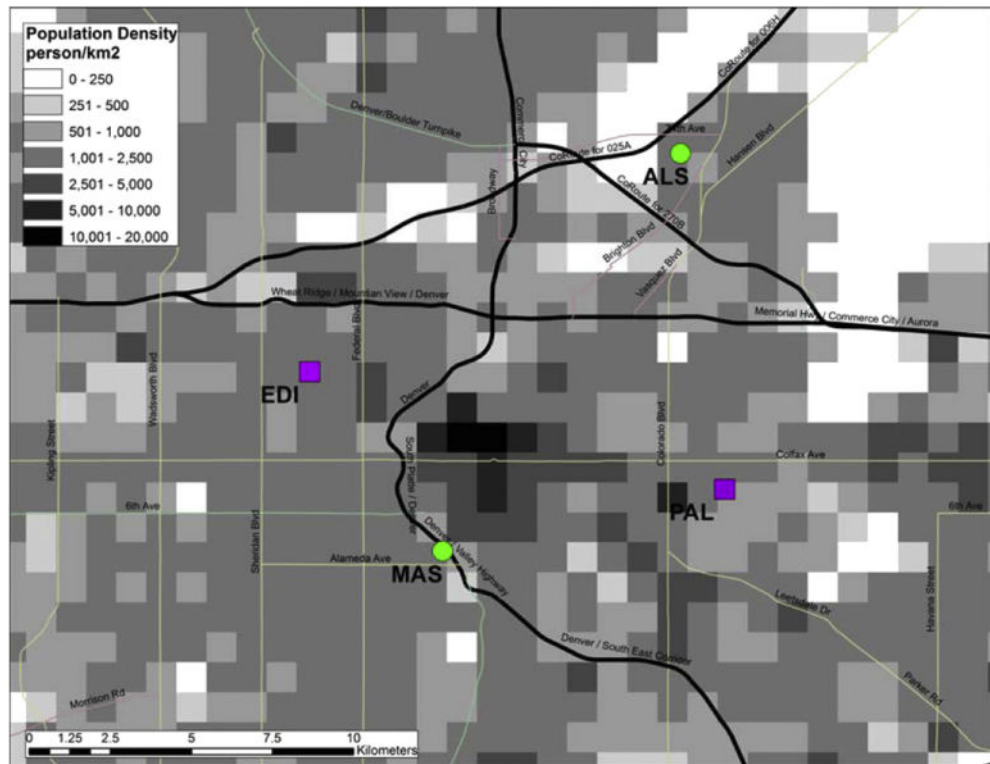
Fig. 1.
Locations of the four sampling sites in Denver urban area: (1) Palmer Elementary School (PAL); (2) Edison Elementary School (EDI); (3) Alsup Elementary School (ALS); (4) Municipal Animal Shelter (MAS).
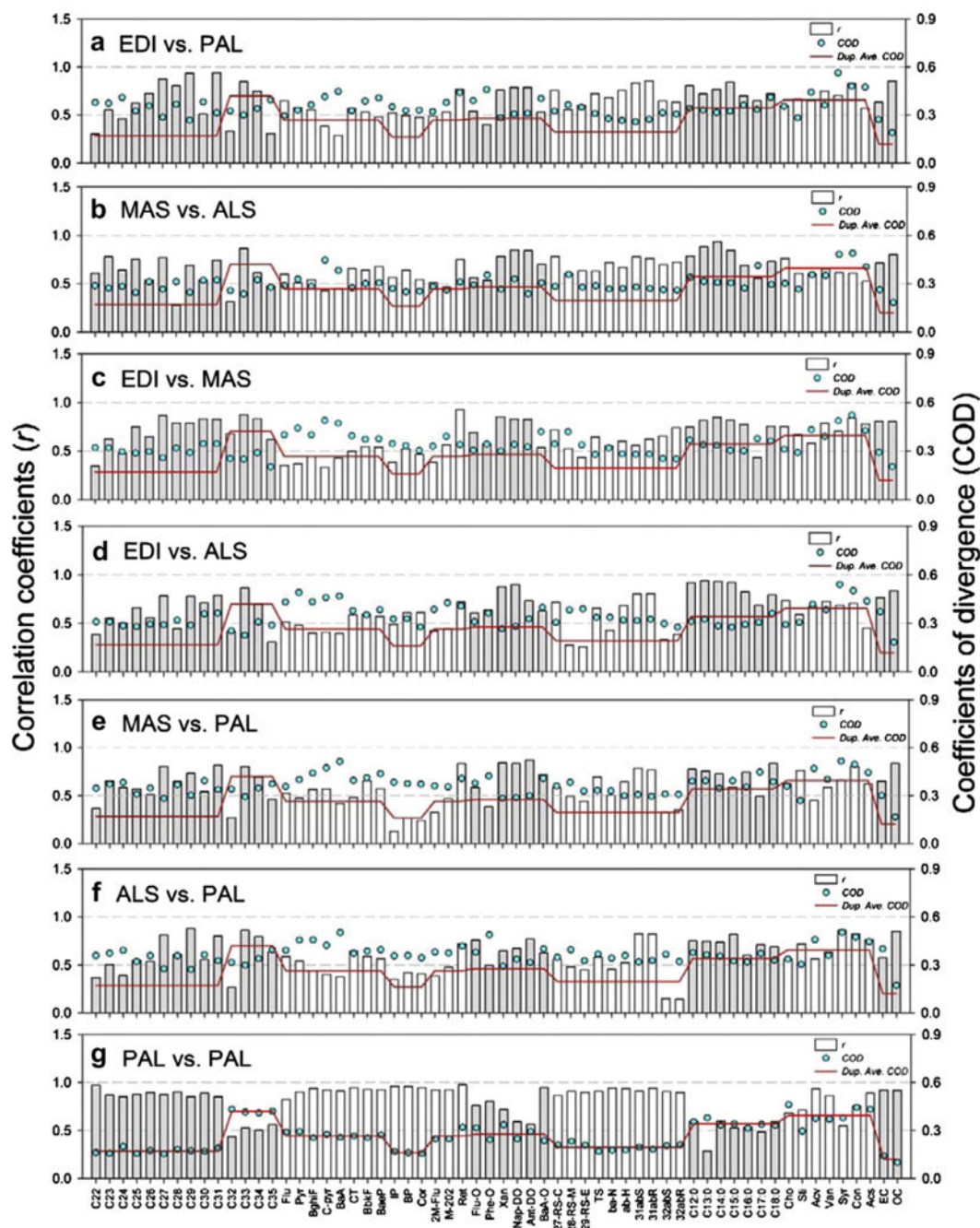
Fig. 2.
Pearson correlation coefficients (bars) and coefficients of divergence (light blue circles) for organic molecular markers and bulk carbon contents obtained at the 4 sampling sites (a–f) as well as the co-located samples at PAL site (g). CODs of collocated samples were averaged in groups and overlaid on each plot. Bars are shaded to show compound class separations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
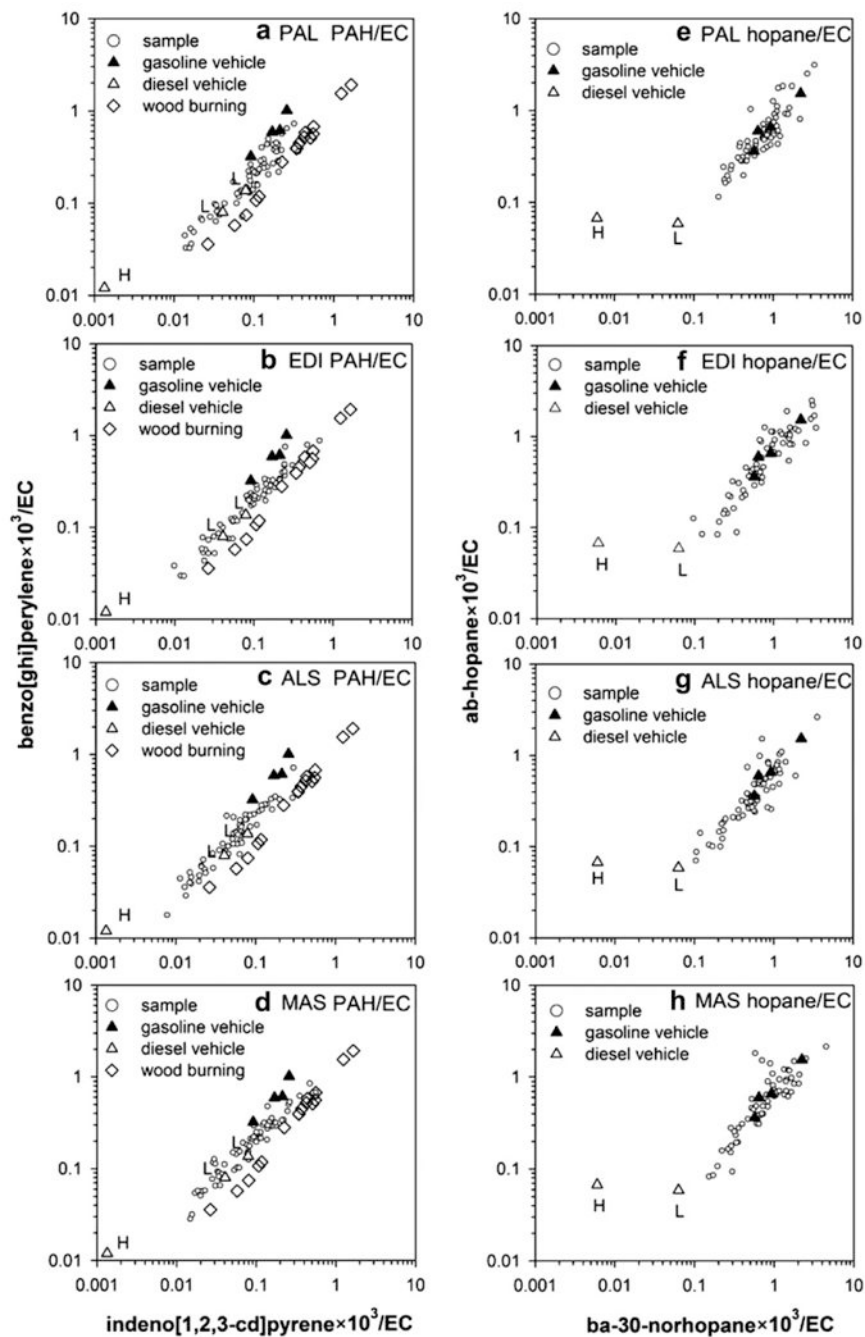
Fig. 3.
Ratio–ratio plots for two polycyclic aromatic hydrocarbons (PAHs) normalized by EC (a–d) and two hopanes normalized by EC (e–f) at each of the four sites. Gasoline, diesel (L light duty, H heavy duty) and wood burning (different woods and burning conditions in fireplace and woodstove) source profiles overlaid were obtained from Cadle et al. (1999) (only for light duty diesel associated PAHs in Denver) and NFRAQS study (Zielinska et al., 1998).

Table 1

Meteorological statistics based on hourly observation from nearby monitoring stations during March 1, 2008–March 14, 2009. (PAL – CAMP; EDI – Carriage; ALS – Welby; MAS Denver Animal Shelter).

Parameter	Statistic	PAL	EDI	ALS	MAS
Temperature (° C)	Mean	12	11	11	11
	SD[a]	9	9	9	10
	Mean daily max[b]	19	19	18	17
	Mean daily min[c]	6	2	4	5
Scalar wind speed (km h^{-1})	Mean	7	5	8	8
	SD	2	2	4	2
	Mean daily max	13	11	17	16
	Mean daily min	3	2	2	3
Relative humidity (%)[d]	Mean	42	42		
	SD	17	16		
	Mean daily max	63	65		
	Mean daily min	25	23		

[a] Standard deviation of daily means.

[b] Mean of the daily maximum observation.

[c] Mean of the daily minimum observation.

[d] Only available for two sites, data for PAL is from DESCI (2.7 miles) and that for EDI is from Auraria (2.8 miles).

Table 2

Studies on spatial variations of PM$_{2.5}$ components.

Location	Site	Sample No.	Organic markers (ng m^{-3})					Bulk species (µg m^{-3})		
			n-alkanes	PAHs	Steranes	*n*-alkanoic acids	OC	EC	PM$_{2.5}$ mass
Denver[a]	PAL (Residential)	62	30.5	2.60	1.43	223	3.03	0.31	6.51
	EDI (Residential)	59	24.9	2.85	1.52	234	3.39	0.32	6.81
	ALS (Traffic)	63	29.4	3.60	2.03	249	3.56	0.66	9.32
	MAS (Traffic)	63	24.3	3.34	1.89	233	3.51	0.48	7.79
Long Beach[b,c]	NLB (Traffic)	10	16.6	1.07	0.43		4.03	1.32	12.9
	SLB (Traffic)	7	17.6	1.23	0.77		3.45	0.74	11.2
	Sutter (Traffic)	10	21.6	1.65	0.58		5.07	1.70	14.6
	Riley (Residential)	10	23.5	1.48	0.62		5.09	0.92	13.6
Lower Fraser Valley[d,e]	GEP (Forest)	9	10.6			60.0			2.37
	CT (Tunnel)	8	83.9			156			1.12
	SP (Urban park)	23	14.8			50.0			1.71
	SER (Urban/forest)	25	10.3			65.0			1.96
	LEL (Rural)	23	8.20			39.0			1.92
Atlanta[f]	Highway	7	40.1	11.0	7.97	67.7	8.16	4.06	22.7
	GeoTech. campus	7	25.1	3.19	3.15	32.0	5.53	0.96	16.4
Hong Kong, China[g,h]	PU (Traffic)	14	41.8				9.45	5.80	50.9
	KT (Industrial)	12	27.9				10.2	5.05	57.3

[a]This study.

[b]Krudysz et al. (2008).

[c]Krudysz et al. (2009).

[d]Cheng et al. (2004).

[e]Cheng et al. (2006).

[f]Li et al. (2009).

[g]Ho et al. (2003).

[h]Guo et al. (2003).

NIH-PA Author Manuscript

NIH-PA Author Manuscript

NIH-PA Author Manuscript