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Comparison of spatial and temporal variations in p-PAH, BC, and p-PAH/BC ratio in six US counties

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ABSTRACT

An ambient air monitoring campaign was performed in six counties (Sacramento, CA; Maricopa, AZ; Anoka, MN; Jefferson, KY; Harris, TX; and Pinellas, FL) between January 2008 and September 2009. The purpose of this paper is to compare the spatial and temporal variability of black carbon (BC) and particle-bound polycyclic aromatic hydrocarbons (p-PAHs), across these counties using continuous monitoring instruments – an Aethalometer and a Photoelectric Aerosol Sensor reporting in units of μg m^{-3} and fA, respectively. We explored temporal trends in these measurements to assess the potential impact of local combustion sources on air quality. Median BC concentrations ranged from 0.13 to 0.53 μg m^{-3}; and median p-PAH values ranged from 0.31 to 4.18 fA. Hourly BC and p-PAH were elevated during morning rush hour and rapidly decreased later in the morning. Nighttime increases in BC and p-PAH were also observed in most counties. Diurnal patterns of BC and p-PAH were different on weekdays compared to weekends. Profiles of hourly ratios of p-PAH/BC in combination with meteorological data can provide insight into potential sources across the sites. Hourly ratios of p-PAH/BC which peaked during early morning and late afternoon hours suggest a dominating contribution of motor vehicle sources in four of the six counties. In two counties, hourly ratios remained elevated for several hours after rush hour and did not show a distinctive peak suggesting additional sources of BC and p-PAH. Such profiles were seen in both Jefferson KY and Harris TX, and may be attributed to coal combustion, petro-chemical industry and shipping activities, respectively. These results suggest that measurements of BC and p-PAH, combined with meteorological information and emission data are potentially useful to identify combustion sources impacting air quality. More research combining BC and p-PAH measurements with detailed source apportionment data is needed to more fully evaluate the utility of these real-time measures.

1. Introduction

Recent epidemiological studies have suggested that a light absorbing carbon, alternatively known as black carbon (BC) or elemental carbon (EC), is associated with increased cardiovascular and respiratory effects (McCreanor et al., 2007; Bell et al., 2009; Peng et al., 2009). Although ambient BC originates from various combustion sources such as motor vehicles, power plants fueled by coal or oil, biomass, and natural gas (LaRosa et al., 2002; Wallace, 2005; Reisinger et al., 2008; Chow et al., 2010), individual combustion sources may vary by geographic location. Similar to BC, particle-bound polycyclic aromatic hydrocarbons (p-PAHs) are products of incomplete combustion. p-PAHs have been associated with induction of oxidative stress (Wei et al., 2009; Bae et al., 2010) possibly resulting in acute respiratory responses including asthma (Delfino, 2002; Delfino et al., 2009). Since BC and p-PAH are both products of combustion, understanding the short-term temporal relationship between these two components of particulate matter (PM) may help to identify the contribution of combustion sources to local air quality.

Numerous studies have been conducted to examine source contribution to ambient PM air pollution. Several of these studies have relied on the chemical characterization of PM to identify components including BC (or EC) and individual PAH compounds. Sample collection for these studies requires the collection of an integrated sample using filter media or impaction substrates. The time period for sample collection can range from several hours to several days. PAH profiles have been used to distinguish between different fuel sources and there appears to be a generally consistent pattern of PAH compounds associated with various

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fuels (Li and Kamens, 1993; Rogge et al., 1993; Morawska et al., 2001). For example, benzo(b)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, and coronene have been used to distinguish diesel exhaust, gasoline emissions, and wood smoke (Li and Kamens, 1993). While this filter-based laboratory analysis approach has been shown to be useful for characterizing combustion sources, it requires extensive resources, time, highly specialized analytical equipment, and labor to obtain the source profile.

A different approach to source characterization is source apportionment studies, which include receptor modeling, such as a chemical mass balance model and factor analysis. This approach is useful for determining contributions of various combustion sources to a location of interest (Bullock et al., 2008; Kim and Hopke, 2008; Lee et al., 2008). For example, Kim and Hopke (2008) used 24-hr integrated $PM_{2.5}$ speciation data collected in Seattle, WA to assess combustion sources over 5 years. The study identified seven to ten major ambient $PM_{2.5}$ sources using positive matrix factorization and demonstrated spatial and seasonal variability of $PM_{2.5}$ sources across the Seattle urban area.

While these approaches are valuable for characterizing sources influencing ambient air pollution over extended time periods, they provide limited insight about temporal heterogeneity of local area sources over short time periods (e.g., hourly and daily). As a result, recent studies have focused on the collection of highly time resolved BC and p-PAH concentration data in order to better investigate the temporal variability of sources over short time periods. Both BC and p-PAH have been measured alone or concurrently using direct reading instruments to evaluate specific source contribution such as motor vehicles (Westerdahl et al., 2005; Zhu et al., 2008), airport emissions (Westerdahl et al., 2008), smoking (Klepeis et al., 2007), candle burning (Lung et al., 2003), cooking, wood smoke and fireplace usage (Wallace, 2005). Although these studies were able to capture the highly variable and rapidly changing concentrations generated by specifically targeted sources over a short-term period (e.g., minutes and hours), they provided limited information on the overall impact of the mixture of sources to local ambient air quality.

As BC is chemically inert and not rapidly depleted by dry deposition, airborne BC is found not only close to combustion sources but also in areas remote from these sources (Bond and Sun, 2005). In addition, although PAHs can be transformed to secondary organic aerosols under sunlight in the atmosphere, p-PAH attached to BC may persist and be transported to distant areas. As part of a larger investigation we conducted a study across the US using continuously measured BC and p-PAH in order to evaluate spatial and temporal trends in PM composition. The purpose of this paper is to: (1) compare the spatial differences and short-term variability in BC and p-PAH concentrations in six US counties; and (2) to explore the use of p-PAH to BC ratio profiles to suggest differences in local combustion sources that will allow for an assessment of differences in ambient air quality between locations.

2. Materials and methods

2.1. Sampling locations

Sampling locations were selected as part of an integrated research program conducted by the EPA funded Johns Hopkins Particulate Matter Research Center (JHPMRC) designed to evaluate the impact of PM composition on health. As part of the JHPMRC, PM was collected from counties identified by study epidemiologists as representing greater or lesser risk to health from exposure to ambient PM. The measurement of BC and p-PAH was an ongoing part of the JHPMRC research efforts. This paper presents a detailed evaluation of BC and p-PAH data collected in six counties.

BC and p-PAH sampling was carried out during the period of January 2008 – September 2009 in the counties listed in Table 1. Sampling duration ranged between 32 and 54 days at each site. In each county we located our sampling equipment at an existing local air quality monitoring site. Land use classification for each site was designated by US EPA. Details of $PM_{2.5}$ emissions profile data at each site are provided in Supporting information Table S1 (US EPA, 2010). Field investigators travelled to each site to set up the equipment and maintained the site daily. Once established, the site was managed by one member of the JHPMRC study team who visited the site each day to conduct a daily site check and a weekly data download.

Sacramento County, CA: Monitoring occurred January 17 – March 11, 2008. The monitoring site was located behind City Hall of the City of Folsom away from busy roads and freeways and surrounded by residential neighborhoods, The City of Folsom is approximately 30 km east of Sacramento. The 50 freeway is located 2.5 km south and I-80 is located 6 km north from the site. Within a 75 km radius of the site, local sources emitted 613 tons of $PM_{2.5}$ in 2008. *Maricopa County, AZ*: Monitoring occurred June 6 – July 18, 2008. The site was

Table 1
Site descriptions and number of days sampling conducted at each site.

		Sacramento, CA	Maricopa, AZ	Anoka, MN	Harris, TX	Pinellas, FL	Jefferson, KY
EPA land use description		Residential	Residential	Commercial	Residential	Residential	Residential
Sampling periods (Days)		Jan–Mar 2008 (54)	Jun–Jul 2008 (42)	Sep–Oct 2008 (32)	Jan–Feb 2009 (36)	Apr–May2009 (41)	Aug–Sep 2009 (40)
Coordinates		38.683285, −121.164433	33.483904, −112.1426	45.137629, −93.207783	29.669944, −95.12851	27.98625, −82.78212	38.1377, −85.578926
Distance to nearest Hwy		2.5 km to SE US-50 & 6 km to NW I-80	1.5 km to E I-17	1.5 km to E I-35W	5 km to SW I-45	1.5 km to E Rd-1	0.5 km to N I-265
Traffic counts per day (Truck Counts; %)[a]		147,500 (10.5%)	170,945 (N/A)	137,000 (5.3%)	209,934 (10.9%)	87,500 (3.6%)	151,703 (6.4%)
Estimated annual $PM_{2.5}$ emission (tons)[b]	Chemical and pharmaceutical	5	15	25	4848	80	623
	Electric and gas generating facilities	93	181	719	1482	4239	2228
	Petroleum, refinery facilities	21	23	742	3388	27	11
	Total	613	1133	2870	10,550	4691	3991

[a] Traffic counts on highways was obtained from local state agencies. See list of references in Supporting information.
[b] Estimated annual $PM_{2.5}$ emissions are obtained from the National Emission Inventory (US EPA). The estimated annual $PM_{2.5}$ emissions are obtained at each monitoring site within 75 km of radius. Detailed annual $PM_{2.5}$ emissions are summarized in Supporting information Table S1.

a vacant residential housing lot, located in a residential neighborhood. The site was 1.5 km west from a freeway. Within a 75 km radius of the site, 1133 tons of $PM_{2.5}$ were emitted from local sources.

Anoka County, MN: Monitoring occurred September 19 – October 21, 2008. The monitoring site was located at a small airport catering to private aircrafts. The site was 1.5 km west from a highway. $PM_{2.5}$ emissions are less than 3000 tons.

Jefferson County KY: Monitoring occurred August 2 – September 11, 2009. The site was located behind an elementary school. The site was 0.5 km south from a highway. Within a 75 km radius from the monitoring site there were coal powered electric and gas generating facilities with $PM_{2.5}$ emissions of 2228 tons $year^{-1}$ (approximately 56% of particle emission).

Pinellas County FL: Monitoring occurred April 17 – May 28, 2009. The site was located at a local elementary school. The school was located in a residential neighborhood not directly impacted by major highways or other industrial combustion sources. The site was 1.5 km west from a freeway. Electric and gas generating facilities were the primary $PM_{2.5}$ emitters (4239 tons $year^{-1}$).

Harris County TX: Monitoring occurred January 15 – February 20, 2009. The site was established at a Speciation and Trends Network site, located in a residential area next to a baseball field. Within a 75 km radius of the monitoring site organic chemical industry and petroleum refinery facilities emit more than 8000 tons of $PM_{2.5}$ per year.

2.2. BC and PAH measurements

Ambient BC concentration was measured using an Aethalometer (Model AE-14; Magee Scientific, Berkeley, CA), which quantifies the absorption of 880-nm light (incandescent transmission) absorbed by BC-containing particles impacted on a quartz fiber filter tape. When the percent-transmission through the deposition area decreases to a specified control level, the Aethalometer automatically advances the tape to a clean deposition area. The sampling air flow rate was 3.4 L min^{-1} through a 0.375-in. diameter stainless steel tube that was located 5 m above the ground. The Aethalometer was programmed to automatically data-log BC concentrations in μg m^{-3} at 5-min intervals over the sampling period in each location. The Aethalometer was calibrated by the manufacturer prior to deployment in the field.

Concurrent real-time measurements of p-PAH were obtained using a Photoelectric Aerosol Sensor (PAS2000, EcoChem Inc., League City, TX), which photoionizes particle-bound PAHs (three or more ringed PAHs) by exposing the aerosol to ultraviolet light of 220 nm. The flow rate was set to 2.0 L min^{-1} through 0.25-in. stainless tubing located 5 m above the ground. The inlet of the PAS2000 was approximately 3 m from the inlet of the Aethalometer. The time resolution for this study was 5 min and synchronized with the Aethalometer at each location. The instrument reports detection of p-PAH in units of fA. A limit of detection was calculated to be 0.61 fA when a HEPA filter was placed onto the inlet of the instrument. The PAS2000 was maintained by the manufacturer prior to deployment in the field. Lamp intensity, flow rate, data readings, and operations were checked daily to ensure the equipment was operating within manufacturers specifications.

2.3. Weather data

Weather data corresponding to sampling periods for each location were available from the National Climate Data Center (NOAA, 2010). Wind speed (m s^{-1}) and wind direction were obtained from the nearest weather monitoring station to each site (<25 km).

2.4. Data management and data analysis

Weekly raw data files for each instrument were manually reviewed for completeness. Any identified problems were highlighted and logged. The weekly files for each instrument were then collapsed into a composite data set for the entire monitoring period at each site. An additional level of quality assurance was provided by culling and validating the raw data based on daily operating status as recorded in the monitoring site log book and daily checklists. Raw data were uploaded into SAS 9.2 (SAS Inc., Cary, NC) for further cleaning. Repetitive observations, such as two or more identical observations for each time point, were flagged and removed after verification. Additionally, negative observations, possible outliers (>99th percentiles), and missing observations were flagged. For BC data cleaning and quality control, we followed the procedure described previously (deCastro et al., 2008). Briefly, data were adjusted for random voltage fluctuations, and tape advances. Random voltage fluctuations, defined as consecutive pairs of extreme observations were replaced with the mean of the consecutive observations to correct the voltage fluctuations. When the deposition area became overloaded, tape advances resulted in no data collection for two consecutive 5-min intervals. Observations missing during these tape advances were imputed with the average of the six preceding and five subsequent observations. After correcting voltage fluctuations and tape advances, observations below the LOD (0.05 μg m^{-3}) were replaced with LOD/2 (0.025 μg m^{-3}). Then the data were smoothed with an average of each observation with its preceding observation using a computerized spreadsheet template provided by Magee Scientific (Hansen, 1999).

For p-PAH data cleaning, observations below the limit of detection (LOD = 0.61 fA) were replaced by one half the LOD (0.31 fA). Due to the large fraction of values less than the LOD, a sensitivity analysis was conducted to assess the impact of replacing the observations below the LOD with either zero or LOD/$\sqrt{2}$. Replacement of all values below the LOD with either zero or LOD/$\sqrt{2}$ resulted in small changes (generally less than 25%) in the distribution descriptors (results not shown).

3. Results and discussion

3.1. Meteorological results

Fig. 1 shows wind direction and speed for each location during sampling periods. In Sacramento winds came from the southeast and northwest with prevailing winds between 6 and 12 m s^{-1} (Fig. 1a). In Maricopa weak winds came from the east (<3 m s^{-1}) and west (<9 m s^{-1}) (Fig. 1b). The Maricopa site was upwind and downwind of a freeway. Fig. 1c shows wind direction was dominant from the southeast with wind speed ranging between 3 and 9 m s^{-1} in Anoka; and Fig. 1d shows both weak (<3 m s^{-1}) and strong winds (>9 m s^{-1}) from the north in Jefferson. In Pinellas winds came from the east with moderate speeds (3–9 m s^{-1}) (Fig. 1e). Finally, winds came from the southeast with moderate speeds (3–9 m s^{-1}) in Harris (Fig. 1f). Wind roses for each site stratified by morning (05:00–12:00) and evening/nighttime (16:00–24:00) are presented in supporting information (See Supporting information for Figs. S1–S4).

3.2. BC and p-PAH concentration differences by location

Table 2 presents a summary of BC sampling results by location. In total, we collected 66,793 valid observations. The valid number of observations ranged from 8393 to 15,495 across the six locations. More than 97% of BC data collected were above LOD (0.05 μg m^{-3})

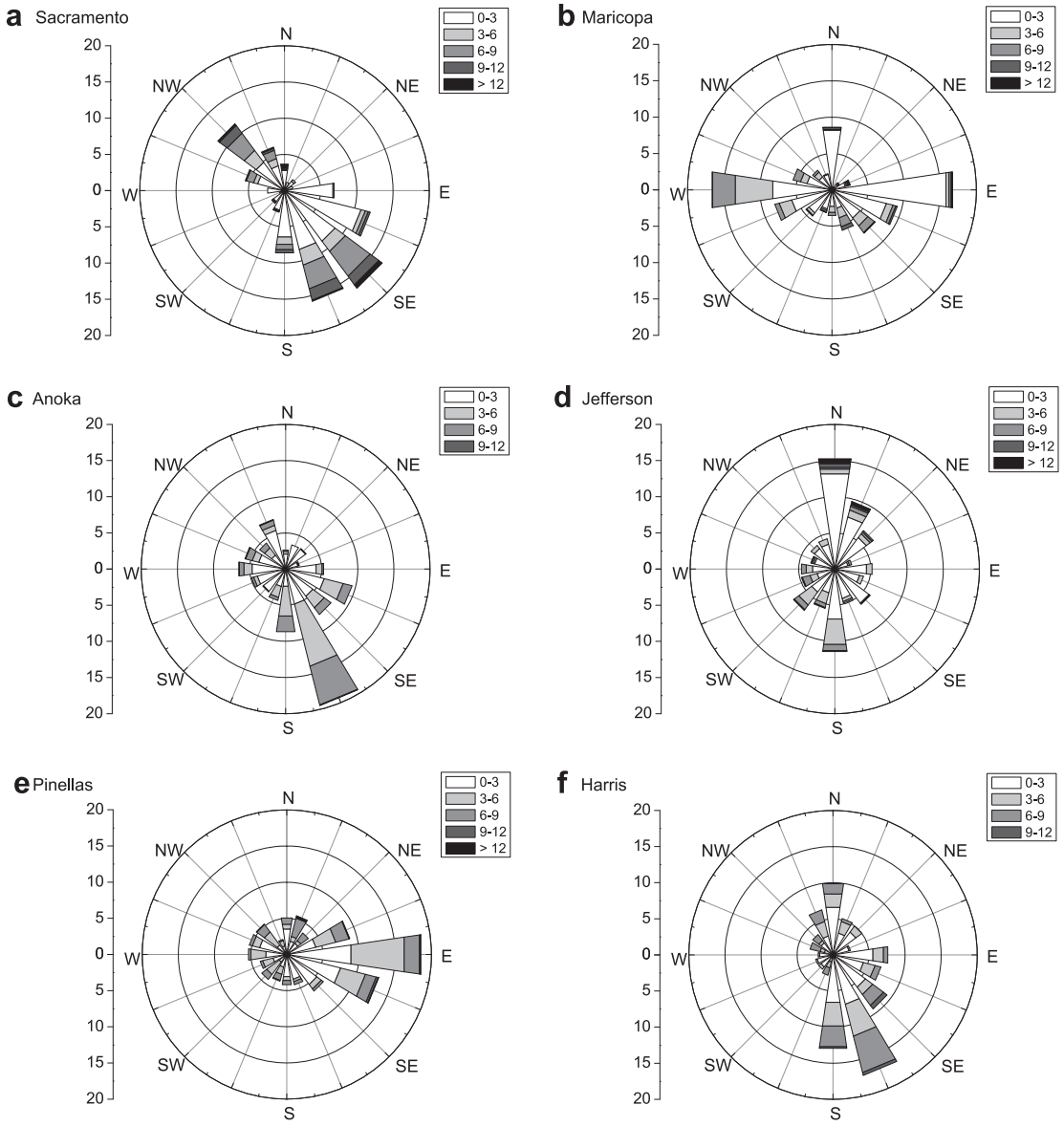

Fig. 1. Wind direction and speed at each monitoring site during sampling periods. Numbers on ordinate axis refer to percentage of wind speed categorized by 0–3 m s^{-1}; 3–6 m s^{-1}; 6–9 m s^{-1}; 9–12 m s^{-1}; and >12 m s^{-1}. Calm wind (wind speed = 0 m s^{-1}) was not included in the figure.

Table 2
Summary of descriptive statistics for hourly black carbon and particle-bound PAH at each site.

County		No.	>LOD[a] (%)	Median	Mean	Min	25th percentile	75th percentile	Max
BC (μg m^{-3})	Sacramento, CA	15,495	99.5	0.38	0.51	<0.025	0.19	0.70	4.20
	Maricopa, AZ	10,060	97.7	0.53	0.82	<0.025	0.33	1.01	6.77
	Anoka, MN	9611	98.9	0.26	0.33	<0.025	0.13	0.41	2.69
	Harris, TX	8393	97.3	0.28	0.35	<0.025	0.17	0.44	1.90
	Pinellas, FL	12,059	98.6	0.13	0.16	<0.025	0.09	0.19	2.82
	Jefferson, KY	11,175	99.2	0.28	0.33	<0.025	0.18	0.41	1.63
p-PAH (fA)	Sacramento, CA	15,791	43.9	0.31	1.72	<0.31	0.31	1.64	26.8
	Maricopa, AZ	11,617	59.1	0.84	3.23	<0.31	0.31	3.33	42.2
	Anoka, MN	9704	32.7	0.31	1.53	<0.31	0.31	1.12	28.6
	Harris, TX	10,251	90.1	2.18	3.07	<0.31	1.29	3.65	37.1
	Pinellas, FL	12,104	23.0	0.31	0.77	<0.31	0.31	0.31	11.0
	Jefferson, KY	11,227	99.4	4.18	4.88	<0.31	3.19	5.40	25.3

[a] Calculated Limit of Detections (LOD) were 0.05 μg m^{-3} and 0.61 fA for BC and p-PAH, respectively.

for all locations. There was more than a four-fold difference in the median BC concentrations among the six counties. Median concentrations were highest in Maricopa (0.53 μg m^{-3}) followed by Sacramento; Harris; Jefferson; Anoka; and Pinellas (0.13 μg m^{-3}).

The reported median BC concentrations in this study are similar to published results from studies conducted in suburban or rural areas. In the southeastern US, ambient levels of BC were reported between 0.26 and 0.38 μg m^{-3} in North Carolina (Im et al., 2001). In suburban New York, the concentrations of BC in ambient air ranged between 0.66 and 0.73 μg m^{-3} (Patel et al., 2009). Wallace (2005) reported median outdoor BC concentrations as 0.41 μg m^{-3} (IQR 0.37 μg m^{-3}) in a suburb of VA. In urban areas with heavy traffic volume, daily background BC concentrations were 1.8–7 times higher than those in this study. deCastro et al. (2008) measured background BC concentrations of 0.91 μg m^{-3} in Baltimore at a site that was directly impacted by more than 150,000 vehicles per day. In Los Angeles median BC concentrations in a residential area near freeways ranged from 0.74 to 1.50 μg m^{-3} (Westerdahl et al., 2005).

p-PAH concentrations are also summarized in Table 2. Valid observations ranged from 9704 to 15,791 across the six locations. For most of the counties a significant fraction of the p-PAH measurements were below the limit of detection. Exceptions were Harris and Jefferson where 90% and 99% of the p-PAH measurements above the LOD, respectively. There was more than a thirteen-fold difference in the median p-PAH values across the six counties, with the highest median values measured in Jefferson (4.18 fA) followed by Harris (2.18 fA) and lowest in Anoka (0.31 fA) and Pinellas (0.31 fA).

In general, ambient values of p-PAH in this study agreed well with recent studies conducted in California. These studies report the average values of p-PAH ranging from 0.38 to 2.0 fA (Ning et al., 2007; Polidori et al., 2008). However, our results were lower than p-PAH measurements obtained from other suburban and metropolitan areas. For example, measured p-PAH concentrations (ca. 50 fA) in residential areas of LA were also higher than those in this study (Westerdahl et al., 2005). All of these studies were conducted using the PAS2000 model for p-PAH measurements.

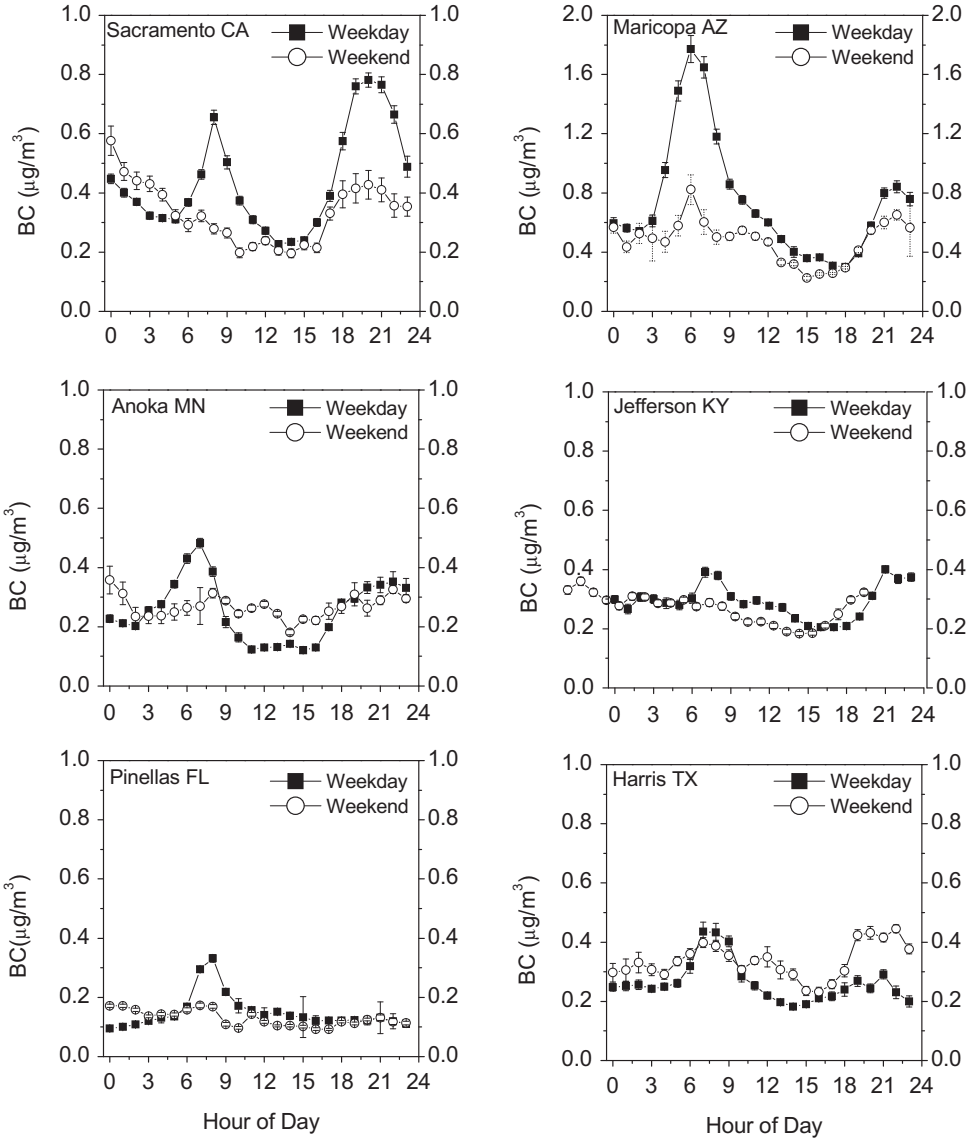

Fig. 2. Temporal variability of hourly median BC concentrations over the six counties. Closed squares represent BC concentrations on weekday and open circles represent BC concentrations on weekend, Error bars represent standard errors.

3.3. Temporal variability

The value of direct reading assessment of BC and p-PAH is the ability to assess changes over time. Fig. 2 shows the temporal variability of hourly BC concentrations over six counties for weekdays and weekends. On weekdays, diurnal patterns were observed for the six counties, with hourly median BC concentrations at each location strongly affected by morning rush hour traffic between 05:00 and 10:00.

BC concentrations during weekdays and weekends were highest in Maricopa. (Note the scale on the *y*-axis used for Maricopa presented in Fig. 2 is twice that of the other counties.) The hourly median morning rush hour BC peak in Maricopa was 1.77 $\mu g\ m^{-3}$ compared to rush hour peaks ranging from 0.33 to 0.66 $\mu g\ m^{-3}$ in the other counties. In general, the hourly BC median concentration in Maricopa was 2–3 times higher than the hourly BC median concentration in the other counties. While traffic volume in Maricopa is not significantly different from the other counties as indicated by daily counts on the nearest roadway, the geographical configuration of the county may explain the elevated concentrations (Table 1). Maricopa County is a bowl created by mountains that surround it in all directions. In addition, an analysis of morning (2.9 m s^{-1}) vs. evening/nighttime (4.5 m s^{-1}) wind speeds during the monitoring periods, show the morning wind activity to be lowest in Maricopa county potentially explaining the elevation in BC relative to the other sites.

Also of note, is the nighttime BC peak in Sacramento, which was higher than the peak seen during the morning rush hour. An analysis of morning vs. evening/nighttime wind speed and direction for Sacramento show strong winds coming from the southeast during the evening/nighttime (Fig. S2). As mentioned above, the site was directly north of a freeway which carried a significant fraction (10.5%) of truck traffic (Table 1).

Fig. 2 displays the temporal patterns of BC by hour during weekends for the six counties. As expected, a morning rush hour peak was not apparent during the weekend time periods in all counties except Maricopa, where a small rush hour peak is suggested. Notably, nighttime peaks of BC during weekend were also observed in Sacramento, Jefferson, and Harris.

Fig. 3 shows the temporal patterns of p-PAH during the weekday and weekend for the six counties. Overall temporal patterns of p-PAH during the weekday were similar to those of BC. Typically, hourly median values of p-PAH were increased between 05:00 and 07:00 and then decreased throughout the remainder of the morning and the afternoon. Like BC, the strongest diurnal patterns were noted in Maricopa. The peak hourly median p-PAH in Maricopa, 12.4 fA, was observed at 06:00 while the highest hourly median p-PAH in the remaining five counties ranged between 7.08 fA (Jefferson) and 2.54 fA (Pinellas) during morning rush hour periods. A strong nighttime p-PAH peak was observed in Sacramento similar to that seen for BC. During the weekend, evening peaks were also observed in Sacramento, Maricopa and Harris. The highest hourly median of p-PAH were 1.21, 2.41 and 2.24 fA for Sacramento, Maricopa and Harris, respectively.

The results of this study indicate that ambient levels of BC and p-PAH were drastically higher on weekdays than on weekends and in the morning rush hour than in the afternoon. These results are consistent with previous studies indicating that a higher volume of traffic on weekdays and in the morning is a major contributor to increase carbon in ambient air (Dubowsky et al., 1999; Wallace, 2005; deCastro et al., 2008; Lee et al., 2008). Although traffic counts were not directly measured in this study, traffic volume increase has been associated with increases in BC in urban areas. deCastro et al. (2008) observed that increased traffic volume during rush hour resulted in at least one order of magnitude increase in hourly median BC during morning rush hour peak compared to the overall median. Patel et al. (2009) also demonstrated that an increase in hourly vehicle count during rush hour was associated with 0.07–0.62 $\mu g\ m^{-3}$ increase in hourly average BC at New York City school districts located near a major highway.

3.4. p-PAH and BC ratio

In order to further explore the temporal relationship of these two measures we calculated the ratio of p-PAH to BC. Other investigators have used trends in p-PAH/BC ratios to evaluate potential sources (Thornhill et al., 2008; Arnott et al., 2005). The ratio of p-PAH values to BC concentration varies by location. Table 3 shows that the ratio for Jefferson (median = 14.7) was significantly higher than those in the rest of the sites ($p < 0.001$). The ratio for Harris (median = 8.28) was the second highest and significantly different from the other sites as well ($p < 0.001$). The ratios among the rest of the sites were not significantly different from each other (2.23–3.05).

Fig. 4 shows the temporal variability of this ratio for each county. The temporal pattern of these ratios suggests that sources contributing to the aerosol mixture differ between counties. Diurnal patterns were observed during weekdays for all six counties (Fig. 4a) with the ratio increased during the morning rush hour period (05:00–09:00) and rapidly decreasing after 09:00. The relative elevation in the ratio for Jefferson and Harris indicates an enrichment of p-PAH, suggesting sources in addition to traffic. The diurnal pattern of the ratio also differs from those seen from the p-PAH and BC data (Results 3.2 and 3.3). Unlike the profiles seen for the individual measurements an increase in the ratios was observed in the morning and not during evening/nighttime, with the exception of Jefferson. These results suggest that traffic in the morning is a greater source of p-PAH than in other times of the day. Wallace (2005) reported that the ratio of p-PAH/BC increased by a factor of 2.4 during the morning rush hour period in a residential area of VA as compared to the rest of the day. In this study the change in the ratio from the morning rush hour as compared to the evening ranged from a factor of 2.1 to 4.4. These findings suggest that changes in ratios of p-PAH to BC may be a more useful indicator of the traffic contribution to local air quality than the single measures of BC or p-PAH.

Fig. 4b shows temporal patterns of p-PAH/BC during the weekend. With the exception of Maricopa where a traffic profile was still evident, the ratios show no distinctive pattern. However, similar to the weekday, ratios for Harris and Jefferson were significantly elevated relative to the remaining counties. In Harris, the maximum ratio (median = 10.3) was observed at 10:00 while in Jefferson the ratios increased continuously until 19:00 when it peaked at 16.8 (median).

Both the weekday and weekend hourly p-PAH/BC profiles in both Jefferson and Harris show patterns different from those of the other counties suggesting sources other than traffic. In Jefferson, air quality may have been impacted by emissions from coal fired power plants located directly north of the site. Supporting information (Fig. S3) shows morning and evening/nighttime wind speed and direction for Jefferson during the monitoring period. In general, the strongest winds came from the northern direction. The Kentucky Office of Energy Policy (KOEP) reports 56 operating coal power plants producing 92% of Kentucky's electricity (KOEP, 2008). According to US EPA National Emission Inventory Data (NEI), the 8 coal fired power plants directly north of the site generate approximately 97% of the 2228 tons of $PM_{2.5}$ resulting from the 24 power plants located within a 75 km radius of the site (Supporting information Table S1).

In Harris, it is likely that chemical manufacturing facilities, petrochemical facilities, and shipping activities using residual fuel were substantial sources of p-PAH in the air. Those facilities are

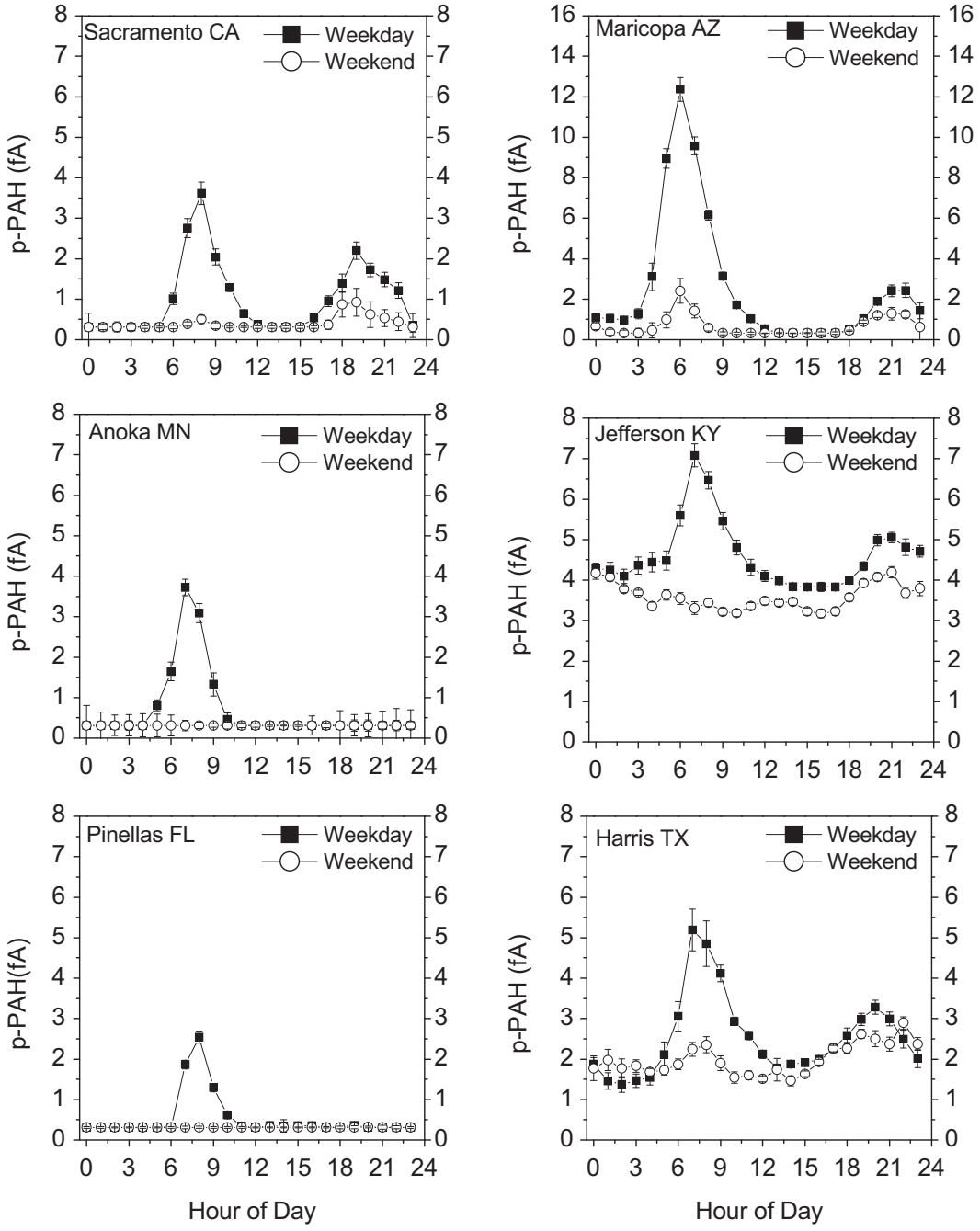

Fig. 3. Temporal variability of hourly median p-PAH concentrations over the six counties. Closed squares represent p-PAH concentrations on weekday and open circles represent p-PAH concentrations on weekend, Error bars represent standard errors.

Table 3
Summary of hourly ratio of p-PAH/BC (fA of p-PAH/μg m^{-3} of BC) in six US counties.

	County	Median	Mean	Minimum	25th percentile	75th percentile	Maximum
PAH/BC Ratio	Sacramento, CA	2.23	3.02	<0.01	1.16	4.19	17.8
	Maricopa, AZ	2.48	3.58	<0.01	1.26	4.70	19.5
	Anoka, MN	2.58	3.78	0.01	1.36	55.0	18.1
	Harris, TX	8.28	8.65	0.01	4.90	11.7	27.5
	Pinellas, FL	3.05	4.16	0.09	1.96	5.06	20.2
	Jefferson, KY	14.7	18.2	0.51	10.7	21.5	61.9

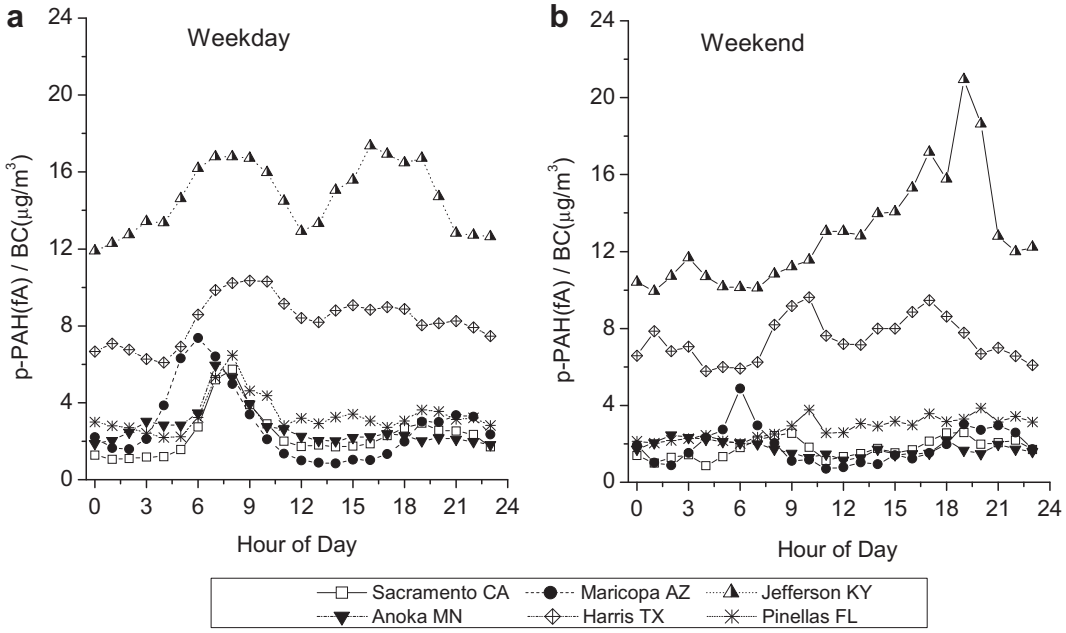

Fig. 4. Temporal patterns of hourly median ratios of p-PAH/BC over six counties. Error bars represent standard errors. (a) represents hourly median ratios of p-PAH/BC on weekday. (b) represents hourly median ratios of p-PAH/BC on weekend.

located north and southeast of the monitoring site. The morning and evening/nighttime wind roses generated for Harris (Fig. S4) suggest air quality at the site may have been continuously affected by chemical manufacturing facilities from the north and petrochemical facilities and maritime shipping operations in the port of Houston from the south. In Harris, US EPA NEI data shows 92% of particle emissions come from these stationary sources within a 75 km radius of the study site (Table S1). This observation is supported by two studies using factor analysis which estimated the source contribution of these industrialized facilities/activities at 49–77% in ambient particles for locations near Harris (Buzcu and Fraser, 2006; Xie and Berkowitz, 2006).

There are a number of limitations in this study. Because the ionization energy (5.6 eV) used by the PAS2000 to ionize surface-bound PAH can also ionize pure carbon, the signal of the PAS2000 may suffer from an interference from the pure carbon core under certain atmospheric conditions (Bukowiecki et al., 2002; Burtscher, 2005). In an urban ambient environment, however, it is unlikely that the PAS2000 is presented with pure carbon. As particles generated by combustion age, their surface characteristics become complex due to adsorption of gases and vapors, surface reactions and aggregation. While it is possible the signal was biased high due to interference by the ionization of the carbon core, it is also likely that the signal was biased low due to PAHs which were not presented on the surface as a result of being obscured by other compounds (Marr et al., 2006).

A site by site evaluation of the response of the PAS2000 to the local PAH mixture, as suggested by the manufacturer, was not conducted. While an approximate calibration of 0.3–1 ng m^{-3} of p-PAH/fA has been reported (Wallace, 2005; Childers et al., 2000), this study chose to use the direct response of the instrument (in fA) as a semi quantitative measure of the presence of p-PAH. Using the direct response provides the best measures for comparing trends over time.

Because previous studies have shown that ambient BC and p-PAH are strongly affected by meteorological factors (deCastro et al., 2008; Patel et al., 2009; Querol et al., 2008) additional information on mixing height, relative humidity, visibility, and atmospheric pressure may have improved our ability to interpret our results. Additionally, we were unable to examine seasonal variation in the temporal trends as we were only able to visit each site once.

More research combining BC and p-PAH with detailed source apportionment data are needed to more fully evaluate the utility of these real-time measures for the identification of specific source impacts.

4. Conclusions

The acquisition of time resolved observations of p-PAH and BC enabled us to examine temporal and spatial differences of carbon compounds in ambient air. Spatial differences of BC and p-PAH were observed between the six counties examined. Temporal patterns of BC and p-PAH indicate peaks in the morning associated with rush hour traffic across all counties. The temporal changes in ratios of p-PAH to BC were also useful in assessing the relative impact of morning rush hour traffic as compared to later in the day with regard to the contribution of p-PAH to the air mixture. Furthermore, the elevated ratios of p-PAH to BC in Jefferson and Harris were useful in examining local combustion sources beyond motor vehicles such as coal power plants and petrochemical facilities, respectively.

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Appendix. Supplementary information

Supporting information related to this article can be found online at doi:10.1016/j.atmosenv.2010.10.042.

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