



## Aerosol and Air Toxics Exposure in El Paso, Texas: A Pilot Study

L.-W. Antony Chen<sup>1</sup>, Richard J. Tropp<sup>1</sup>, Wen-Whai Li<sup>2</sup>, Dongzi Zhu<sup>1</sup>, Judith C. Chow<sup>1,3</sup>, John G. Watson<sup>1,3</sup>, Barbara Zielinska<sup>1</sup>

<sup>1</sup> Division of Atmospheric Sciences, Desert Research Institute, 2215 Raggio Parkway, Reno, NV 89512, U.S.A.

<sup>2</sup> Department of Civil Engineering, University of Texas at El Paso, El Paso, TX 79968, U.S.A.

<sup>3</sup> State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, 10 Fenghui South Road, Xi'an High-Tech Zone, Xi'an 710075, China

### ABSTRACT

The Paso del Norte (PdN) region is one of the largest metropolitan areas along the U.S.-Mexico border. Different emission regulations between the two countries, particularly with respect to on-road vehicle and domestic burning, have impacted the regional concentration and human exposure of air toxics (e.g., metals, polycyclic aromatic hydrocarbons [PAHs], and carbonyls). Comprehensive air quality measurements were conducted using a mobile monitoring system at two urban-scale sites within El Paso, Texas in December 2008 as a pilot study to understand aerosol and air toxics exposure and sources in the PdN region. The measurements show clear diurnal variations due to traffic emissions and a major pollution episode likely caused by both motor vehicles and domestic burning. Wind analysis further confirms the importance of cross-border transport on elevated pollutant concentrations at the monitoring sites. The traffic-dominated periods are characterized by high fractions of black carbon, particle-bound PAHs (p-PAHs), and carbonyls in comparison with dust-related periods. During the particular pollution episode, high levels of elemental chlorine and vinyl chloride were observed that might relate to unregulated domestic burning of polyvinyl chloride (PVC) products. Although most pollution indicators show a substantial improvement in air quality over the last decade, short-term exposure to some p-PAHs, e.g., benzo[a]pyrene, is still close to the health effects screening level. Bi-national efforts are required to further reduce air toxics emissions.

**Keyword:** Cross-border air quality; PAHs; PM<sub>2.5</sub>; Carbonyls; Mobile monitoring system; Pollution wind rose.

### INTRODUCTION

The Paso del Norte (PdN) region is in a basin formed by mountains that surround El Paso, Texas and Sunland Park, New Mexico in the United States, and Ciudad Juárez, Chihuahua in Mexico. It is one of the largest metropolitan areas along the U.S.-Mexico border with over 2 million residents, two-thirds of whom reside on the Mexican side. Each year, over 18 million vehicles cross the three international ports of entry between El Paso and Ciudad Juárez. Different emission regulations between the two countries, particularly with respect to on-road vehicle exhaust and domestic refuse burning, have impacted human exposure to aerosol and air toxics in the region. El Paso is currently classified by the United States Environmental Protection Agency (U.S. EPA) as a PM<sub>10</sub> (particles with aerodynamic diameters < 10 µm) non-attainment area. Li *et al.* (2005)

showed that about 25% of ambient PM<sub>10</sub> is fine particles (e.g., PM<sub>2.5</sub>) dominated by organic and elemental carbon (OC and EC, respectively). McCarthy *et al.* (2004) found that El Paso experienced elevated formaldehyde and acetaldehyde concentrations during 1997 relative to other cities in the United States. These two carbonyls are important hazardous air pollutants (HAPs) included in the National-Scale Air Toxics Assessment since 1996 (NATA, <http://www.epa.gov/nata/>).

El Paso air quality is monitored by the Texas Commission on Environmental Quality (TCEQ) for criteria pollutants (i.e., carbon monoxide [CO], nitrogen oxide [NO], nitrogen dioxides [NO<sub>2</sub>], ozone [O<sub>3</sub>], sulfur dioxide [SO<sub>2</sub>], and particulate matter [PM] as PM<sub>10</sub> and PM<sub>2.5</sub>) at the two State and Local Air Monitoring Stations (SLAMS) sites located on the University of Texas, El Paso (UTEP) campus and at Chamizal National Memorial (CNM) near the Bowie High School (Fig. 1). Twenty-four hour integrated filter-based PM<sub>10</sub> and PM<sub>2.5</sub> samples are acquired from these two sites on an every-third-day schedule along with continuous hourly PM<sub>10</sub> and PM<sub>2.5</sub> by tapered element oscillating microbalance (TEOM 1400a, Thermo Scientific Inc., Waltham, MA). The CNM site is part of the U.S.

\* Corresponding author. Tel.: (775) 674-7028;  
Fax: (775) 674-7009  
E-mail address: Antony.Chen@dri.edu



**Fig. 1.** Location of ambient monitoring sites in El Paso, Texas for: (a) the University of Texas at El Paso (UTEP) site: 106.501152°W, 31.768333°N, Elev. 1166.6 m; and (b) the Chamizal National Memorial (CNM)/Bowie High School site: 106.457892°W, 31.764529°N, Elev. 1121.7 m. Downtown El Paso is located between the two sites. The yellow line indicates the U.S.-Mexico border.

EPA Photochemical Assessment Monitoring Stations (PAMS) network that is equipped with an automatic gas chromatography (auto-GC) system for measuring hourly volatile organic compounds (VOCs;  $C_3$ – $C_8$ ) following an EPA TO-14-equivalent method (U.S.EPA, 1999). This method does not quantify formaldehyde or acetaldehyde. PM air toxics, such as elemental arsenic (As), cadmium (Cd), lead (Pb), polycyclic aromatic hydrocarbons (PAHs), and diesel particulate matter (DPM), are not measured at sufficient time resolution for investigating short-term exposures and potential sources.

To better understand these issues and to address multipollutant/multieffect relationships (Chow and Watson, 2011), a mobile monitoring system was deployed at the UTEP and CNM sites during a winter intensive observing period (IOP) in 2008 as part of the El Paso Air Toxics Study (Chen *et al.*, 2010a). Time-resolved (minutes to hourly) aerosol and air toxics measurements were made with an emphasis on carbonyls and particle-bound air toxics to complement the SLAMS measurements. Origins of pollutants were assessed by relating the air toxics level to auxiliary meteorological data such as wind speed (WS) and wind direction (WD) acquired on site and to known patterns of source emissions.

## EXPERIMENTAL APPROACHES

### Monitoring Locations and Periods

The PdN airshed experiences a variety of mobile sources throughout the year. In winter, excessive PM and air toxics levels could also be caused by unregulated waste burning and wildfires originating in the Mexican territory, and

enhanced by lower mixing heights and inversions. The IOP was selected to coincide with elevated criteria air pollutant concentrations often found in winter (Li *et al.*, 2001; Noble *et al.*, 2003). At the UTEP site, the mobile monitoring system was located in the parking area in front of the UTEP SLAMS site and next to a site operated by Asarco LLC. For the CNM site, the system was located at Bowie High School about a block from the SLAMS/PAMS site. With its proximity (< 100 m) to the busy Border Highway, CNM was expected to be more influenced by on-road traffic emissions than UTEP, though both sites represented neighborhood- (0.5–4 km) to urban- (4–100 km) scale exposure of local communities.

The mobile monitoring system was operated at the UTEP site between 12/11–14/2008, and then moved to the CNM site for sampling during 12/15–18/2008. Continuous instruments were fully functional. Filter-based and 2,4-Dinitrophenylhydrazine (DNPH) cartridge samples were generally collected five times a day, i.e., local standard time (LST) *a*) 1600–2400 (evening traffic and nighttime activities), *b*) 0000–0500 (nocturnal inversion layer), *c*) 0500–1000 (morning traffic), *d*) 1000–1300 (early afternoon photochemical smog), and *e*) 1300–1600 (late afternoon photochemical smog). There were a few occasions where sampling periods *d* and *e* were merged into a single sampling period (i.e., 1000–1600 LST) for a longer exposure time and better detection limits. Eight canister samples, each of which coincided with one of the time-integrated sampling periods, were acquired for evaluating the auto-GC measurements. Unfortunately auto-GC data at the CNM site were not available for the IOP due to an instrument malfunction.

### Mobile Monitoring System

The mobile monitoring system was developed at the Desert Research Institute (DRI; Reno, NV) to characterize gases and PM in a pollution plume (Nussbaum *et al.*, 2009). The system draws air through a conductive tubing (5.08-cm i.d.) into a manifold where the sample stream is distributed to the continuous ( $\leq 2$ -min time resolution) and time-integrated (one to several hours) samplers. Gas analyzers included a trace (parts per billion volume [ppbv])-level NO/NO<sub>x</sub>/ammonia (NH<sub>3</sub>) analyzer (TEI 17C, Thermo Environmental Instruments, Inc., Waltham, MA) and a CO<sub>2</sub>/H<sub>2</sub>O analyzer (LI-840, LiCor Biosciences, Lincoln, NE). Both analyzers were calibrated with standards traceable to the National Institute of Standard and Technology (NIST) before and after the field experiment. The detection ranges (10-s average) were 0.001–10 and 0.1–3000 ppbv for the TEI and LiCor analyzers, respectively. The precision of gas measurements is estimated to be  $\sim 5\%$  if they are within the instrumental detection range.

A Magee seven-wavelength aethalometer (Model AE31, Magee Scientific Company, Berkeley, CA) was used to measure light absorption ( $b_{abs}$ ) at wavelengths ( $\lambda$ ) of 370, 450, 571, 590, 660, 880, and 950 nm. Using a wavelength-dependent absorption coefficient (e.g., 16.6 m<sup>2</sup>/g at  $\lambda = 880$  nm),  $b_{abs}$  can be converted to a “black carbon” (BC) concentration, which often serves as a surrogate for DPM in urban environments (Chow *et al.*, 2009; Wang *et al.*, 2011). Particle-bound PAH (p-PAH) concentrations were quantified with a photoelectric aerosol sensor (PAS 2000; EcoChem Analytics, TX), which uses an excimer lamp producing ultraviolet (UV) radiation ( $\lambda = 225$  nm) to photo-ionize the sampled particles. The charged particle current, measured with an electrometer, is proportional to the concentration of p-PAHs (greater than 4-benzene rings). p-PAHs are common byproducts of BC or EC from combustion sources. They are often found to correlate well with BC (Arnott *et al.*, 2005; Chow *et al.*, 2009). In addition, the monitoring system included two DustTraks (TSI, Inc., Shoreview, MN) for PM<sub>10</sub> and PM<sub>2.5</sub> (Watson *et al.*, 2011) and an Electrical Low Pressure Impactor (ELPI, Dekati Instruments, Finland) for particle number-size distribution.

Time-integrated filter samples downstream of Teflon-coated Bendix 240 cyclones operated at 113 L/min were used for PM<sub>2.5</sub> chemical speciation. Teflon-membrane and quartz-fiber filters were installed in two parallel channels, each of which drew air at 25 L/min, leaving a 63 L/min bypass flow. The Teflon-membrane filter was for gravimetric mass and elemental measurements while the quartz-fiber filter was for OC and EC analysis.

Volatile carbonyls including formaldehyde and acetaldehyde were collected on DNPH cartridges in parallel with the filter sampler. The flow rate was set at  $\sim 1.2$  L/min. A canister sampler was also installed in parallel to the DNPH channel with an upstream filter to remove particles before sampling. Canisters of 6 and 12 liters were used, and the flow rate was set according to the sampling duration, typically between 0.1 and 0.3 L/min.

### Laboratory Analysis Methods

PM<sub>2.5</sub> mass was measured gravimetrically as the difference between pre- and post-sampling masses measured on a 47-mm diameter Teflon-membrane filter. Weighing was performed on an MT5 (Mettler Toledo, Placerville, CA) electromicrobalance with  $\pm 1$   $\mu$ g sensitivity. After gravimetric analyses, samples collected on the Teflon-membrane filters were also analyzed by energy dispersive X-ray fluorescence (ED-XRF, Epsilon 5, PanAnalytical, the Netherlands) for 51 elements from sodium (Na) to uranium (U) (Watson *et al.*, 1999).

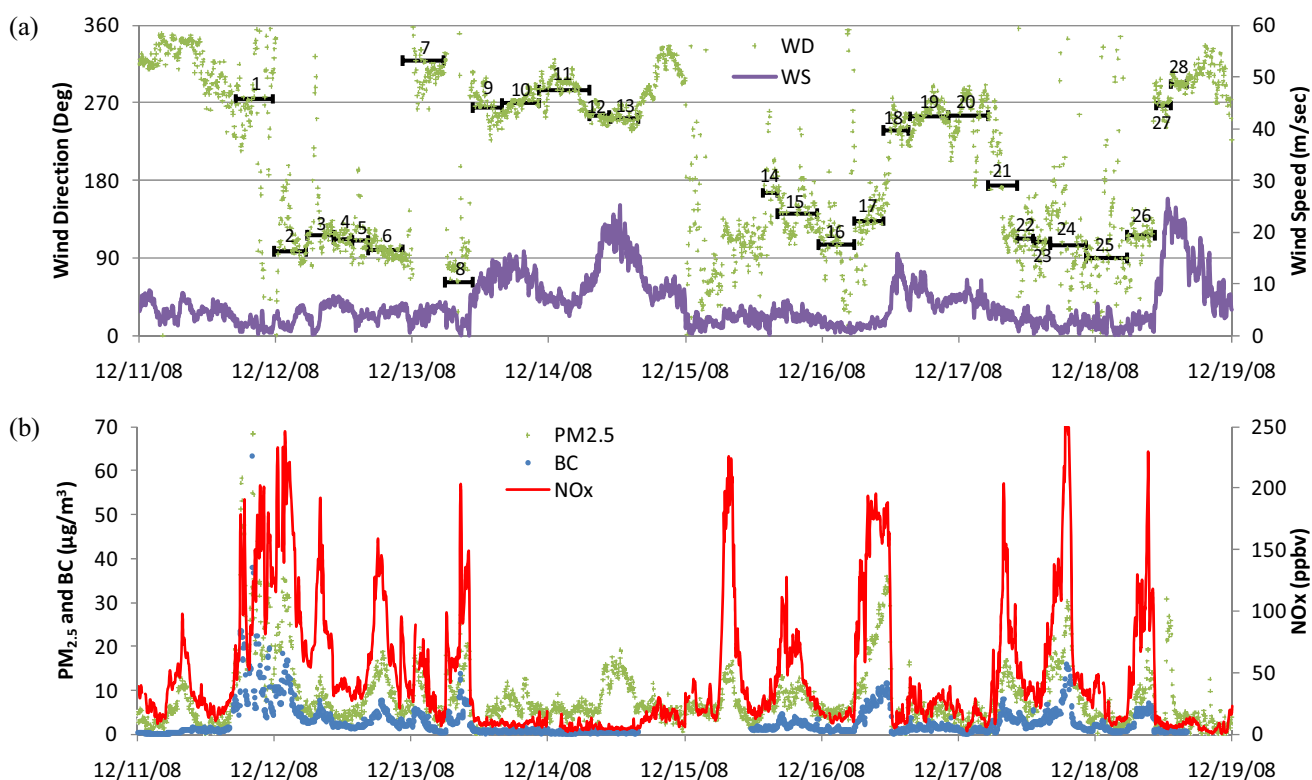
OC, EC, and their 8 thermal carbon fractions on quartz-fiber filters were quantified by the DRI Model 2001 carbon analyzer (Atmoslytic, Inc., Calabasas, CA) following the IMPROVE\_A thermal/optical reflectance (TOR) protocol (Chow *et al.*, 2007a; 2011). Quartz-fiber filter remnants were then submitted to thermal-desorption (TD)-GC/mass spectrometry (MS) analysis for speciating p-PAHs as well as alkanes, hopanes, and steranes. The analysis followed the method of Ho and Yu (2004) and Ho *et al.* (2008; 2011), in which the sample is heated to 275°C within the GC injection port. The evolved organic gases concentrate at the entry to the GC column, which then is ramped to 400°C so that the organic compounds can be separated as they pass through the column in an inert helium carrier gas for detection and identification by a mass spectrometer. The lowest quantifiable limits (LQLs) are typically 0.1–0.5 ng/cm<sup>2</sup> of filter (Chow *et al.*, 2007b).

Carbonyls collected by drawing air through a cartridge impregnated with acidified DNPH were measured in the laboratory using high performance liquid chromatography (HPLC) (i.e., EPA Method TO-11). Typically, carbonyl compounds of carbon number 1 to 6 (C<sub>1</sub>–C<sub>6</sub>), including benzaldehyde, are measured effectively by this technique, with a detection limit of  $\sim 0.05$  ppbv (Zielinska *et al.*, 1998). Canister air samples of known volume were passed through a cryogenically cooled trap, cooled with liquid argon, cryogenically trapping out C<sub>3</sub> and heavier VOCs without trapping methane (i.e., non-methane hydrocarbons). The trapped VOCs were then heated to 120°C and injected into a GC capillary column (i.e., EPA Method TO-14a). The method's minimum detection limit for C<sub>3</sub>–C<sub>8</sub> is 0.01–0.05 ppbv (Zielinska *et al.*, 2001).

## RESULTS AND DISCUSSION

### Time Series and Wind Roses Analysis

Fig. 2(a) shows the time series of WD and WS over the ambient monitoring period and average WD corresponding to 28 time-integrated samples (See Supplemental Table S-1). Winds shifted back and forth between the northwesterly (270°–360°) and southeasterly (90°–180°) directions. Since Ciudad Juarez is located south of El Paso, the southeasterly winds probably carried more cross-border transport. Densely populated areas are also located to the east of El Paso on the U.S. side. Immediately to the northwest of El Paso are several small villages, part of El Paso County, and the city of Sunland Park, New Mexico (population  $\sim 14,000$ ). WS usually did not exceed 10 m/s. Higher WS ( $> 10$  m/s) were associated with westerly winds.



**Fig. 2.** Time series of 5-min measurements for: (a) wind direction (green) and wind speed (purple); and (b) PM<sub>2.5</sub> (green), BC (blue), and NO<sub>x</sub> (red) concentrations during the El Paso intensive observing period (IOP) from 12/11–19/08. Data were acquired at the UTEP and CNM sites before and after 12/15/2008, respectively. Black bars in (a) indicate average wind directions corresponding to 28 time-integrated sample numbers.

As shown in Fig. 2(b), five-minute NO<sub>x</sub> and PM<sub>2.5</sub> measured by TCEQ tracked well with BC ( $\lambda = 880$  nm) measured by the mobile monitoring system. The diurnal pattern includes morning-rush-hour highs around 0800 LST on weekdays (12/11–12/2008 and 12/15–18/2008). Evening rush hours are only evident on 12/12, 12/15, and 12/17/2008, partly due to relatively strong easterly-to-northeasterly winds during the evenings of 12/16 and 12/18/2008. An overnight episode (Episode I) occurred from the afternoon of 12/11/2008 through the morning of 12/12/2008 when 5-min PM<sub>2.5</sub> mass and BC concentrations reached 68.4 and 63.4  $\mu\text{g}/\text{m}^3$ , respectively. This episode illustrates the effect of calm winds coupled with surface cooling leading to the accumulation of local pollutants. By 6 am, 12/12/2008, the surface temperature dropped to  $\sim 2^\circ\text{C}$ , the lowest point through the end of IOP. While NO<sub>x</sub> and BC concentrations approached nearly zero (i.e., detection limits) from noon 12/13/2008 through 1400 12/14/2008, PM<sub>2.5</sub> mass increased to  $\sim 20$   $\mu\text{g}/\text{m}^3$ . Elevated PM<sub>2.5</sub> mass were attributed to fugitive dust caused by high wind conditions (up to 25 m/s) during the period. Concurrent high PM<sub>10</sub> levels (not shown) support this proposition.

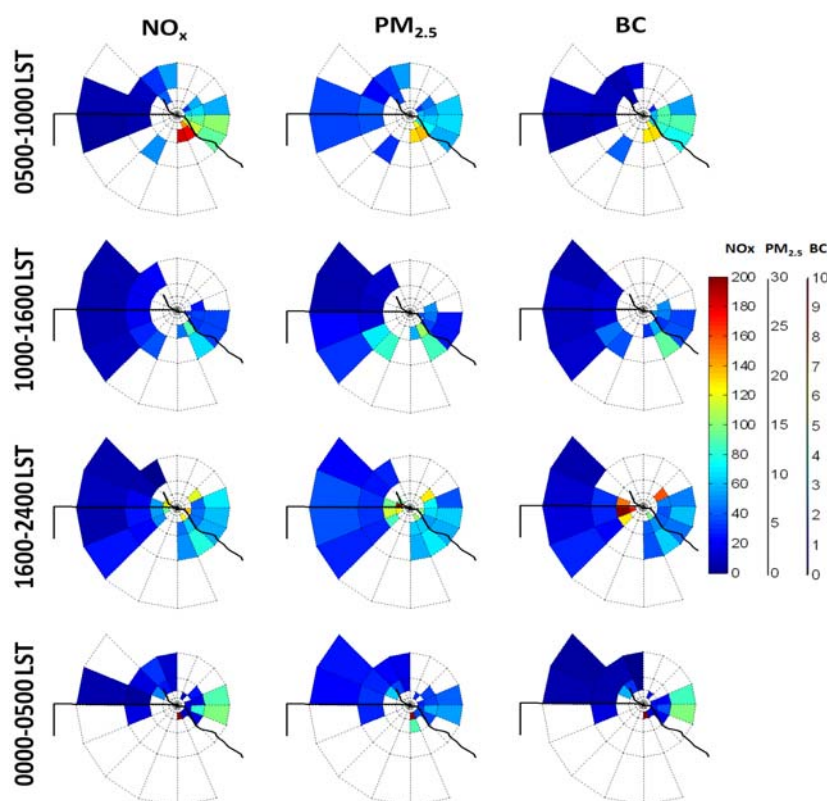
Wind roses categorizing pollutant concentrations by WD and WS (Fig. 3) confirm that, during the morning rush hours (0500–1000 LST), elevated NO<sub>x</sub>, PM<sub>2.5</sub>, and BC concentrations resulted from southeasterly transport, particularly those across the U.S.-Mexico border. On the other hand, northwesterly winds brought in the cleanest air.

The effect of wind speed is not obvious, though WS was rarely below 1 m/s or over 7 m/s for 0500–1000 LST. Lower traffic emissions and possibly a deeper mixing layer led to lower pollutant concentrations during 1000–1600 LST. Pollution built up again into the evening hours (1600–2400 LST); however, the highest PM<sub>2.5</sub> and BC concentrations were associated with westerly transport. This primarily reflects the Episode I (12/11–12/2008) conditions, which also produced the highest pollutant levels under calm southeasterly winds after midnight (i.e., 0000–0500 LST, see Fig. 3). Episode I is unlikely to be dominated by evening traffic emissions. Except Episode I, elevated NO<sub>x</sub> and BC concentrations during 0000–0500 LST were often observed for winds from the east with WS  $> 4$  m/s. Late-night/early-morning traffic volumes were low while domestic heating demand peaked. El Paso local sources might be as important during this period.

#### Air Quality Conditions during IOP

Table 1 summarizes gas and PM pollutant concentrations during the IOP. Except for PM<sub>10</sub>, IOP measurements at the CNM site are representative of the monthly means. Although CO measurements at CNM are missing for the IOP, it is possibly also within  $\pm 10\%$  of the monthly mean (421 ppbv). The UTEP site exhibited substantially (50–100%) higher NO, NO<sub>x</sub>, PM<sub>2.5</sub>, and PM<sub>10</sub> concentrations during the IOP than the monthly means partly due to the influence of Episode I. All criteria pollutant concentrations





**Fig. 3.** Wind rose analysis based on 5-min measurements of wind direction and wind speed (WD/WS) and  $\text{NO}_x$ ,  $\text{PM}_{2.5}$ , and BC concentrations in Fig. 2. Sectors are formed by 16 WD ( $22.5^\circ$  each starting at true north) and 8 WS (i.e.,  $> 14$ ,  $7-14$ ,  $4-7$ ,  $2-4$ ,  $1-2$ ,  $0.5-1$ ,  $0.3-0.5$ , and  $< 0.3$  m/sec) sectors. Colors indicate average concentration ( $\text{NO}_x$  in ppbv;  $\text{PM}_{2.5}$  and BC in  $\mu\text{g}/\text{m}^3$ ) within each sector. Sectors with less than six data points were not included. Separating UTEP and CNM observations does not show appreciable differences.

**Table 1.** Average air quality indicators at El Paso, Texas during this and other winter air quality studies at the University of Texas, El Paso (UTEP), Chamizal National Memorial (CNM), and downtown sites. Units are ppbv for gaseous species and  $\mu\text{g}/\text{m}^3$  for particulate species.

|                        | December 2008 IOP   |                     | December 2008 Monthly Average |      | Winter 1999 <sup>a</sup> |                    | Winter 1996–1997 <sup>b</sup> |
|------------------------|---------------------|---------------------|-------------------------------|------|--------------------------|--------------------|-------------------------------|
| Site                   | UTEP                | CNM                 | UTEP                          | CNM  | Downtown                 | CNM                | Downtown                      |
| CO                     | 420                 | -                   | 293                           | 421  | 1100                     | 1100               |                               |
| NO                     | 34                  | 31                  | 17                            | 29   | 68                       | 50                 |                               |
| $\text{NO}_2$          | 20                  | 21                  | 18                            | 19   | 34                       | 28                 |                               |
| $\text{NO}_x$          | 53                  | 52                  | 35                            | 48   | 102                      | 78                 |                               |
| $\text{NO}_x$          | -                   | 75 <sup>*</sup>     |                               |      |                          |                    |                               |
| Carbonyls <sup>c</sup> | 1.88 <sup>*</sup>   | 2.05 <sup>*</sup>   |                               |      |                          |                    | 8.54                          |
| $\text{PM}_{10}$       | 44.7                | 42.1                | 27.2                          | 31.7 | 91                       | 49–61 <sup>f</sup> |                               |
| $\text{PM}_{2.5}$      | 10.5                | 8.3                 | 7.1                           | 7.4  | 20                       | 12–17 <sup>f</sup> |                               |
| $\text{PM}_{2.5}$      | 12.9 <sup>*</sup>   | 9.2 <sup>*</sup>    |                               |      |                          |                    |                               |
| BC <sup>d</sup>        | 3.4 <sup>*</sup>    | 2.4 <sup>*</sup>    |                               |      |                          |                    |                               |
| p-PAHs <sup>e</sup>    | 0.0432 <sup>*</sup> | 0.0165 <sup>*</sup> |                               |      |                          |                    |                               |

<sup>\*</sup> Measured by the mobile monitoring station in this study.

<sup>a</sup> Nobel *et al.* (2003) and Li *et al.* (2001).

<sup>b</sup> Urban air toxics monitoring program (Mohamed *et al.*, 2002).

<sup>c</sup> Sum of 14 carbonyls including formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, 2-butanone, methacrolein, n-butyraldehyde, benzaldehyde, valeraldehyde, glyoxal, m-tolualdehyde, and hexaldehyde measured from time-integrated 2,4-Dinitrophenylhydrazine (DNPH) cartridges.

<sup>d</sup> Measured by the aethelometer 880 nm channel.

<sup>e</sup> Sum of 36 particle-bound PAHs from acenaphthylene to anthanthrene (see Fig. 6(a)) measured on quartz-fiber filters.

<sup>f</sup> Concentration ranges result from different monitoring methods.

-Missing or insufficient data points.

are below the U.S. EPA National Ambient Air Quality Standards (NAAQS; <http://www.epa.gov/air/criteria.html>).  $\text{NO}_x$  measured by the mobile monitoring system correlated well with TCEQ values ( $r^2 = 0.98$ ), but were 35% higher on average. Besides a potential calibration issue, the reported  $\text{NO}_x$  may contain different degrees of  $\text{NO}_y$  (reactive, odd nitrogen) components such as nitric acid ( $\text{HNO}_3$ ), nitrate ( $\text{NO}_3^-$ ), and peroxyacetyl nitrates (PANs) owing to different sampling configurations (e.g., Fehsenfeld *et al.*, 1987; Chen *et al.*, 2002).  $\text{PM}_{2.5}$  mass (based on time-integrated filters from the mobile monitoring system) agreed with the hourly TEOM  $\text{PM}_{2.5}$  within 20%. BC accounts for ~26% of  $\text{PM}_{2.5}$ , and p-PAHs are ~0.7–1.3% of BC (Table 1).

A study conducted by Noble *et al.* (2003) between 11/28/1999–12/18/1999 found generally higher pollution levels than this study, particularly with respect to CO and  $\text{PM}_{2.5}$  concentrations. CO is a marker for various combustion emissions and usually correlated well with carbonaceous aerosol (mostly in the  $\text{PM}_{2.5}$  fraction). The decreases in CO and  $\text{PM}_{2.5}$  concentrations from 1999 to 2008 are consistent with the phase-in of cleaner engines and better residential biomass burning technologies, at least on the U.S. side (Tao *et al.*, 2010; Murphy *et al.*, 2011). Carbonyls were not quantified by Noble *et al.* (2003), but more than a 75% reduction can be inferred from measurements that were part of the urban air toxics monitoring program (Mohamed *et al.*, 2002) for winter 1996–1997 (Table 1). Motor vehicles are an important source of carbonyls in urban areas (Kao, 1994; Zielinska *et al.*, 2001), though lifetimes of carbonyls are short due to rapid photolysis and reactions with hydroxyl radicals (Wang *et al.*, 2010).

### Episodic Aerosol Characteristics

The highest 10 time-integrated  $\text{PM}_{2.5}$  concentrations (out of 28 samples in Fig. 2(a)) ranged from 35.0 to 11.4  $\mu\text{g}/\text{m}^3$ . These are clustered into four types of episodes according to  $\text{PM}_{2.5}$  chemical composition (Fig. 4). Details of the Matlab® dendrogram-based clustering are presented in the supplementary information. Group A that contains samples #1, #2, and #24 is named “Episode I-like” since sample #1 and #2 defined Episode I. Sample #1 and #24 might also capture mobile emissions during evening rush hours. Group B (samples #13 and #28) is consistent with high WS periods at UTEP and CNM, respectively, and likely “Dusty”. Group C contains samples #3 and #8 corresponding to morning rush hours (0500–1000 LST) and easterly-to-southeasterly transport at UTEP. Group D is the counterpart of Group C at the CNM site containing samples #17, #18, and #26, although sample #18 (1000–1600 LST) does not correspond to the morning rush hour and was collected during a period with higher WS. The respective sampling dates for each sample ID # and Group are summarized in Table S-1 of the Supplemental Information.

The crustal fraction in  $\text{PM}_{2.5}$ , as determined from aluminum (Al), silicon (Si), calcium (Ca), iron (Fe), and titanium (Ti) concentrations (Malm *et al.*, 1994; Chen *et al.*, 2010b), distinguishes the Dusty samples in Group B where crustal material accounts for > 40% of  $\text{PM}_{2.5}$  mass. CNM-Mobile samples (Group D) show higher crustal

fractions than UTEP-Mobile samples (Group C), likely due to higher speed traffic on the Border Highway. Among the 10 samples, the lowest crustal contributions were found during Episode I (samples #1 and #2) and morning rush hours at the UTEP site.

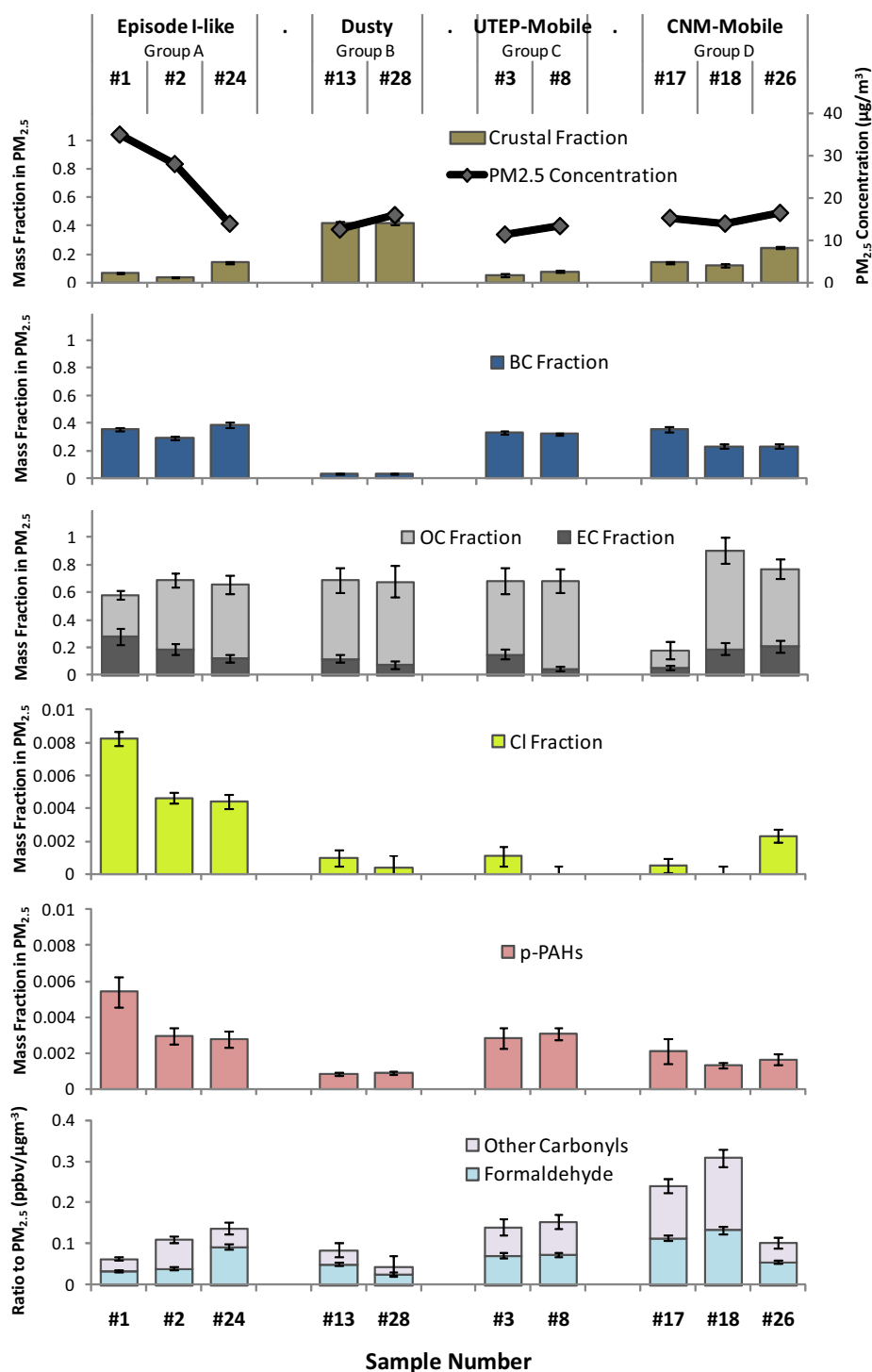
The Group B “Dusty” samples are also characterized by relatively low BC, p-PAH, and  $\text{NO}_x$  (not shown) concentrations as compared to  $\text{PM}_{2.5}$ . For OC and EC, the inter-group differences are not as pronounced. It should be noted that OC sampling artifacts owing to adsorption of VOCs on quartz-fiber filters (Watson *et al.*, 2009; Chow *et al.*, 2010) were not corrected in these samples, and this may explain why the sum of mass fractions for samples #13 and #28 exceeds 100%. The very low OC in sample #17 leads to an unusual OC/ $\text{PM}_{2.5}$  ratio (0.12). Some measurement errors on this sample are suspected though not confirmed.

There are no appreciable distinctions between the Episode I-like (Group A) and Mobile-UTEP (Group C) samples with respect to crustal material, BC, OC/EC, and p-PAHs fractions in  $\text{PM}_{2.5}$ . However, the elemental chlorine (Cl) content does differ. The high Cl fraction during Episode I (up to 0.8%  $\text{PM}_{2.5}$ ) implies PM sources in addition to mobile emissions. Residential or other types of wood combustion are not likely the cause due to a lack of concurrent enrichment in potassium (K). Tropp *et al.* (1998; 2004) also noted that Cl concentrations were elevated in El Paso without a corresponding source of sodium (Na, a sea salt marker). They hypothesized the potential of domestic refuse burning contributions, as such combustion usually contains polyvinyl chloride (PVC) products which release particulate Cl and chlorinated VOCs such as vinyl chloride when combusted (Shue *et al.*, 2009). A canister sample taken with sample #1 shows vinyl chloride of 0.27 ppbv, much higher than any other samples (< 0.01 ppbv).

Formaldehyde and the sum of 14 carbonyls (see footnote c of Table 1 for a list of carbonyls) to  $\text{PM}_{2.5}$  ratios were relatively low during Episode I compared with mobile-dominated periods and sample #24 (Fig. 4). Mobile emissions may still be the most important primary source of carbonyls in El Paso while burning contributions are limited. The highest formaldehyde concentration (~2 ppbv) occurred on samples #17 and #18 at the CNM site when the total carbonyl concentration reached 4–5 ppbv. Most elemental air toxics, including chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), As, selenium (Se), Cd, antimony (Sb), mercury (Hg), and Pb, were either below the detection limits or show no apparent enrichment across different groups of samples.

### Organic Aerosol Speciation

The sum of the 36 p-PAHs (by TD-GC/MS, see Fig. 6(a) for a list of p-PAHs) averages 43.2 and 16.5  $\text{ng}/\text{m}^3$  at the UTEP and CNM sites, respectively, on the same order of magnitude as the PAS-detected (with factory calibration) PAHs of 21.0 and 16.0  $\text{ng}/\text{m}^3$ , respectively. The two datasets tracked each other well (see Fig. 5,  $r^2 = 0.85$ ). The PAS analyzer is known to respond to BC in addition to PAHs (Arnott *et al.*, 2005); strong correlations ( $r^2 = 0.96$ ) were found between BC and PAS p-PAHs during the IOP.

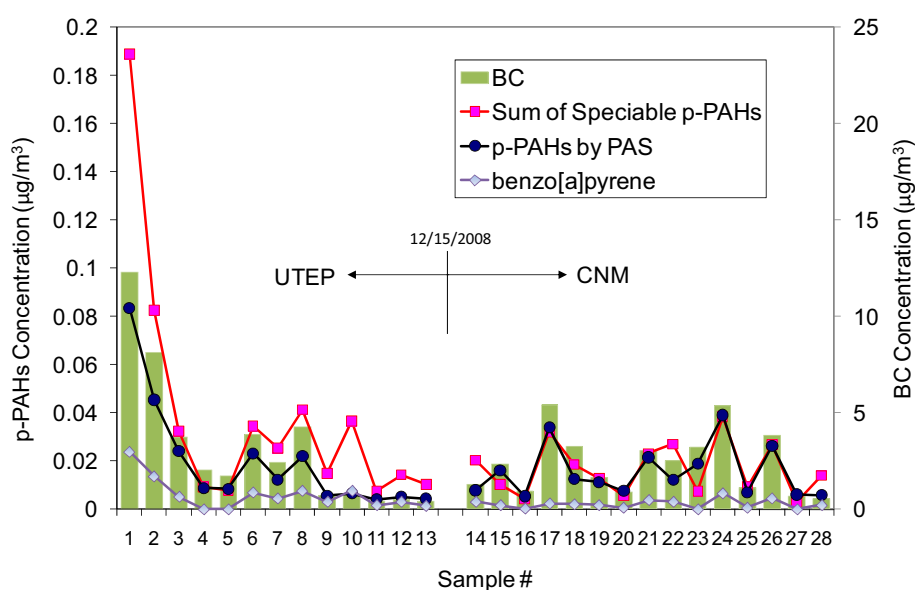


**Fig. 4.** PM<sub>2.5</sub> concentration and chemical characteristics for 10 episodic samples by group. See Fig. 2(a) for the definition of sample numbers on x-axis.

The most abundant p-PAHs include cyclopenta[cd]pyrene, anthanthrene, benzo[a]pyrene, benzo[j+k]fluoranthene, perylene, and benzo[ghi]perylene, all of which, except for anthanthrene, are correlated well with one another ( $r^2 = 0.82\text{--}0.96$ ). Benzo[k]fluoranthene, benzo[a]pyrene, and benzo[ghi]perylene are among the 16 U.S. EPA priority PAHs. A short-term concentration of benzo[a]pyrene of 24 ng/m<sup>3</sup>, which is at 80% of TCEQ (2010)'s 1-hr effects

screening level of 30 ng/m<sup>3</sup> and similar to the levels in China's urban centers (e.g., Shi *et al.*, 2009; Shen *et al.*, 2010), was observed on 12/11/2008 (Fig. 5). p-PAHs are potentially underestimated risk contributors in El Paso.

The sum of speciated n-alkanes (C<sub>15</sub>–C<sub>40</sub>) averaged 68.6 and 57.2 ng/m<sup>3</sup> at the UTEP and CNM sites, respectively. N-alkanes mass peaks between C<sub>25</sub>–C<sub>27</sub>. Speciated hopanes and steranes were at much lower concentrations, i.e., below



**Fig. 5.** Particle-bound polycyclic aromatic hydrocarbons (p-PAHs) measured by photoelectric aerosol sensor (PAS) and thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) methods, compared with BC measured by an aethalometer ( $\lambda = 880$  nm) for the El Paso intensive observing period (IOP). Data were acquired at the UTEP and CNM sites before and after 12/15/2008, respectively. See Fig. 2(a) for the definition of sample numbers.

4 ng/m<sup>3</sup>. C29  $\alpha\beta$ -norhopane and  $\alpha\alpha\alpha$  20S-cholestane are the most abundant hopane and sterane, respectively (Chen *et al.*, 2010a). No significant correlations were found among p-PAHs, n-alkanes, and hopanes/steranes, consistent with their origination from various sources.

A mobile source p-PAHs profile was created by compositing five samples in the UTEP-Mobile and CNM-Mobile groups (Fig. 6(a)). Several species, such as benzo[a]pyrene, benzo[ghi]perylene, 9-fluorenone, 1-methyl phenanthrene, and cyclopenta[cd]pyrene show a good intra-group consistency. The p-PAHs profiles during Episode I (i.e., samples #1 and #2) do not differ from the mobile p-PAHs significantly except for slightly lower 9-fluorenone and higher cyclopenta[cd]pyrene fractions. Although most of the PAHs may not be used as exclusive source markers, the inter-group consistency suggests motor vehicles to be the dominant source of p-PAHs in El Paso. The distribution of n-alkanes, however, shows differences between the Episode I and the mobile groups (Fig. 6(b)). Lower-carbon-number n-alkanes (e.g., < C<sub>25</sub>) are more associated with petrogenic than biomass/waste combustion sources (Zheng *et al.*, 2000; He *et al.*, 2010). Higher concentrations of these alkanes in mobile group samples may result from unburned fuel and/or lubricate oil. The motor vehicle fractional contributions were expected to be lower during Episode I due to contributions from other combustion sources.

## CONCLUSIONS

The DRI mobile monitoring system proved useful and cost-effective for evaluating short-term air toxics exposure at multiple locations. It covers a wide range of parameters, including both gaseous (e.g., NO<sub>x</sub>, VOCs) and particulate (PM<sub>10</sub>/PM<sub>2.5</sub> mass and chemical composition) pollutants,

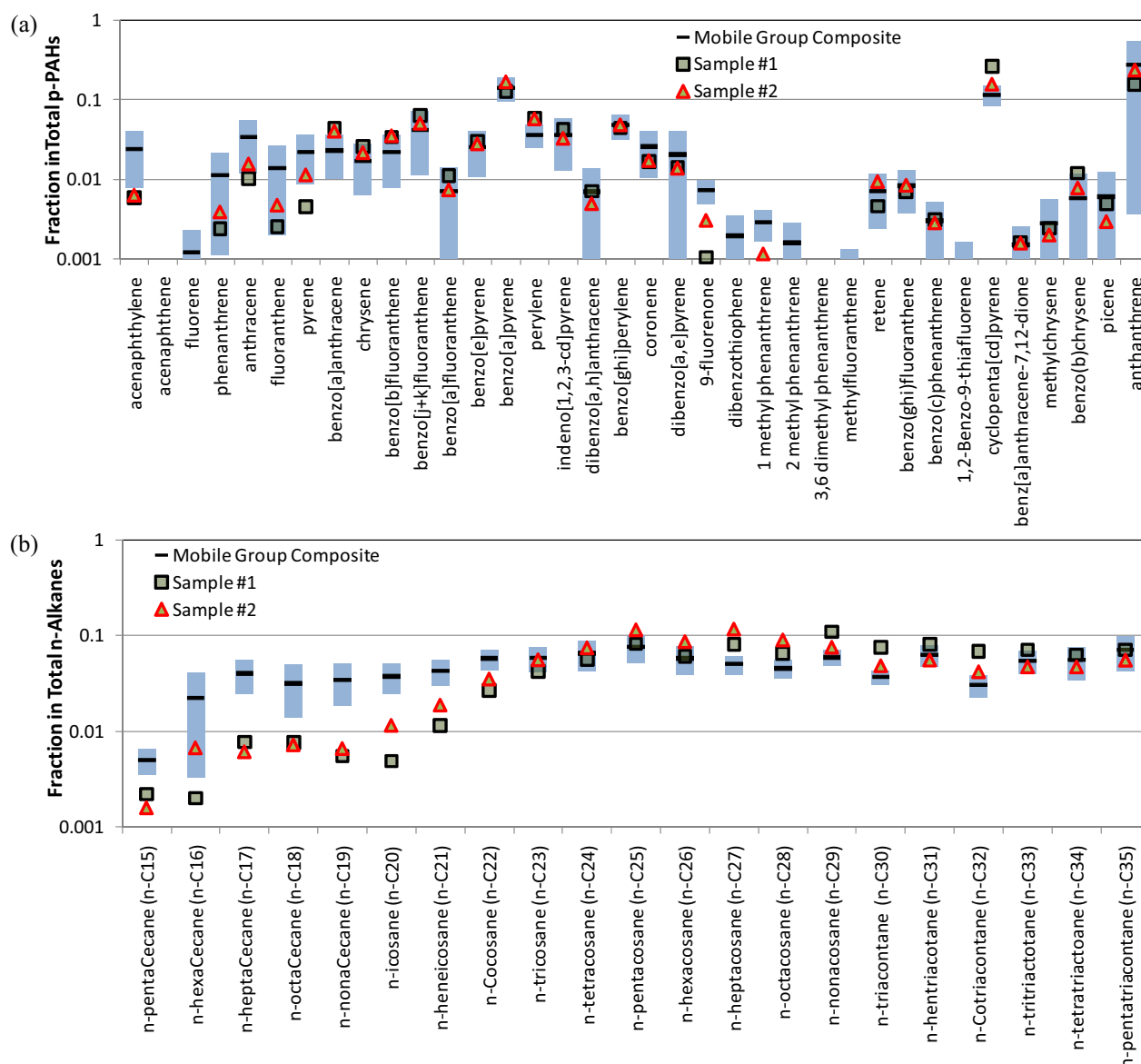
measured either continuously (2-min time resolution or less) or in a time-integrated (one to several hours) manner complementing measurements from the fixed monitoring sites. This system allows ambient and source measurements to be made by identical approaches, thereby reducing uncertainties in receptor modeling which uses both ambient and source information.

Although this study focused on a short IOP at two community exposure sites in El Paso, it reveals clear diurnal variations due to traffic pattern and a major overnight episode (Episode I) with peak PM<sub>2.5</sub> concentration reaching 68.4 µg/m<sup>3</sup>. Wind analysis demonstrates that high pollution (NO<sub>x</sub>, PM<sub>2.5</sub>, and BC) levels during morning rush hours were often associated with calm winds (< 4 m/s) and southeasterly transport across the U.S.-Mexico border. Episode I started with a slow westerly transport swirling, generally via south, to the east. Elevated PM<sub>2.5</sub> and PM<sub>10</sub> were also observed occasionally with low NO<sub>x</sub> and BC concentrations but high WS that agitated road dust.

High PM<sub>2.5</sub> episodes appear to be influenced by either motor vehicle emissions or wind-blown dust. The mobile-related episodes are characterized by high fractions of BC, p-PAHs, and carbonyls while dust-related episodes feature high fractions (up to 40%) of crustal material. Episode I shows high levels of elemental Cl and vinyl chloride that suggest sources besides motor vehicle emissions. Unregulated garbage burning containing PVC products is a possible cause. The p-PAHs profiles from Episode I do not differ significantly from other mobile-dominated periods. However, the distribution of n-alkanes appears to shift towards higher carbon numbers.

Overall, PM<sub>2.5</sub>, CO, and carbonyls levels measured in this study are substantially lower than those from a decade ago. Air quality improvements correspond with technological





**Fig. 6.** Distribution of: (a) particle-bound polycyclic aromatic hydrocarbons (p-PAHs); and (b) n-Alkanes in mobile source-dominated and Episode I samples. Mobile group composites are the average of samples #3, #8, #17, #18, and #26 (defined in Fig. 2(a) and Fig. 4). Vertical blue bars indicate the standard deviation of the five samples. Episode I is represented by samples #1 and #2.

advances and effective regulatory controls, though this trend needs to be confirmed through longer-term monitoring. Short-term exposure to some p-PAHs, e.g., benzo[a]pyrene, is still close to the health effects screening level. To assure public health, it will require bi-national effort to further reduce vehicle and domestic burning emissions.

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## SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

## REFERENCES

Arnott, W.P., Zielinska, B., Rogers, C.F., Sagebiel, J.C., Park, K., Chow, J.C., Moosmüller, H., Watson, J.G., Kelly, K.,

- Wagner, D., Sarofim, A., Lighty, J.S. and Palmer, G. (2005). Evaluation of 1047 nm Photoacoustic Instruments and Photoelectric Aerosol Sensors in Source-Sampling of Black Carbon Aerosol and Particle Bound PAH's from Gasoline and Diesel Powered Vehicles. *Environ. Sci. Technol.* 39: 5398–5406.
- Chen, L.W.A., Doddridge, B.G., Dickerson, R.R., Chow, J.C. and Henry, R.C. (2002). Origins of Fine Aerosol Mass in the Baltimore-Washington Corridor: Implications from Observation, Factor Analysis, and Ensemble Air Parcel Back Trajectories. *Atmos. Environ.* 36: 4541–4554.
- Chen, L.W.A., Tropp, R.J., Zhu, D., Chow, J.C., Zielinska, B. and Watson, J.G. (2010a). Characterizing and Assessing the Associations of Hazardous Air Pollutant Emissions with Environmental Indicators for the El Paso-Cd, Juarez Border Region, Prepared by Desert Research Institute, Reno, NV for Dallas, TX, U.S. EPA Region 6.
- Chen, L.W.A., Watson, J.G., Chow, J.C., DuBois, D.W. and Herschberger, L. (2010b). Chemical Mass Balance Source Apportionment for Combined PM<sub>2.5</sub> Measurements from U.S. Non-Urban and Urban Long-Term Networks. *Atmos. Environ.* 44: 4908–4918.
- Chow, J.C. and Watson, J.G. (2011). Air Quality Management of Multiple Pollutants and Multiple Effects. *Air Qual. Clim. Change* 45: 26–32.
- Chow, J.C., Watson, J.G., Chen, L.W.A., Chang, M.C.O., Robinson, N.F., Trimble, D.L. and Kohl, S.D. (2007a). The IMPROVE\_A Temperature Protocol for Thermal/Optical Carbon Analysis: Maintaining Consistency With a Long-Term Database. *J. Air Waste Manage. Assoc.* 57: 1014–1023.
- Chow, J.C., Yu, J.Z., Watson, J.G., Ho, S.S.H., Bohannan, T.L., Hays, M.D. and Fung, K.K. (2007b). The Application of Thermal Methods for Determining Chemical Composition of Carbonaceous Aerosols: A Review. *J. Environ. Sci. Health., Part A* 42: 1521–1541.
- Chow, J.C., Watson, J.G., Doraiswamy, P., Chen, L.W.A., Sodeman, D.A., Lowenthal, D.H., Park, K., Arnott, W.P. and Motallebi, N. (2009). Aerosol Light Absorption, Black Carbon, and Elemental Carbon at the Fresno Supersite, California. *Atmos. Res.* 93: 874–887.
- Chow, J.C., Watson, J.G., Chen, L.W.A., Rice, J. and Frank, N.H. (2010). Quantification of PM<sub>2.5</sub> Organic Carbon Sampling Artifacts in US Networks. *Atmos. Chem. Phys.* 10: 5223–5239.
- Chow, J.C., Watson, J.G., Robles, J., Wang, X.L., Chen, L.W.A., Trimble, D.L., Kohl, S.D., Tropp, R.J. and Fung, K.K. (2011). Quality Assurance and Quality Control for Thermal/Optical Analysis of Aerosol Samples for Organic and Elemental Carbon. *Anal. Bioanal. Chem.* 401: 3141–3152.
- Fehsenfeld, F.C., Dickerson, R.R., Hübler, G., Luke, W.T., Nunnermacker, L., Williams, E.J., Roberts, J.M., Calvert, J.G., Curran, C.M., Delany, A.C., Eubank, C.S., Fahey, D.W., Fried, A., Gandrud, B.W., Langford, A.O., Murphy, P.C., Norton, R.B., Pickering, K.E. and Ridley, B.A. (1987). A Ground-Based Intercomparison of NO, NO<sub>x</sub>, NO<sub>y</sub> Measurement Techniques. *J. Geophys. Res.* 92: 14710–14722.
- He, J., Zielinska, B. and Balasubramanian, R. (2010). Composition of Semi-Volatile Organic Compounds in the Urban Atmosphere of Singapore: Influence of Biomass Burning. *Atmos. Chem. Phys.* 10: 11401–11413.
- Ho, S.S.H. and Yu, J.Z. (2004). In-Injection Port Thermal Desorption and Subsequent Gas Chromatography-Mass Spectrometric Analysis of Polycyclic Aromatic Hydrocarbons and *n*-Alkanes in Atmospheric Aerosol Samples. *J. Chromatogr. A* 1059: 121–129.
- Ho, S.S.H., Yu, J.Z., Chow, J.C., Zielinska, B., Watson, J.G., Sit, E.H.L. and Schauer, J.J. (2008). Evaluation of an in- Injection Port Thermal Desorption-Gas Chromatography/Mass Spectrometry Method for Analysis of Non-Polar Organic Compounds in Ambient Aerosol Samples. *J. Chromatogr. A* 1200: 217–227.
- Ho, S.S.H., Chow, J.C., Watson, J.G., Ng, L.P.T., Kwok, Y., Ho, K.F. and Cao, J.J. (2011). Precautions for in- Injection Port Thermal Desorption-Gas Chromatography/Mass Spectrometry (TD-GC/MS) Applied to Aerosol Filter Samples. *Atmos. Environ.* 45: 1491–1496.
- Kao, A. (1994). Formation and Removal Reactions of Hazardous Air Pollutants (HAP). *J. Air Waste Manage. Assoc.* 44: 683–696.
- Li, W.W., Orquiz, R., Garcia, J.H., Espino, T.T., Pingitore, N.E., Gardea-Torresdey, J., Chow, J.C. and Watson, J.G. (2001). Analysis of Temporal and Spatial Dichotomous PM Air Samples in the El Paso-Cd. Juarez Air Quality Basin. *J. Air Waste Manage. Assoc.* 51: 1551–1560.
- Li, W.W., Cardenas, N., Walton, J., Trujillo, D., Morales, H. and Arimoto, R. (2005). PM Source Identification at Sunland Park, New Mexico, Using a Simple Heuristic Meteorological and Chemical Analysis. *J. Air Waste Manage. Assoc.* 55: 352–364.
- Malm, W.C., Gebhart, K.A., Molenar, J.V., Cahill, T.A., Eldred, R.A. and Huffman, D. (1994). Examining the Relationship Between Atmospheric Aerosols and Light Extinction at Mount Rainier and North Cascades National Parks. *Atmos. Environ.* 28: 347–360.
- McCarthy, M.C., Hafner, H.R., Raffuse, S.M. and Stiefer, P.S. (2004). Spatial Variability in Air Toxics - Supplementary Technical Memorandum, Report Number STI-903553-2591-STM Prepared by Sonoma Technology, Inc., Petaluma, CA for Des Plaines, IL, Lake Michigan Air Directors Consortium.
- Mohamed, M.F., Kang, D. and Aneja, V.P. (2002). Volatile Organic Compounds in Some Urban Locations in United States. *Chemosphere* 47: 863–882.
- Murphy, D.M., Chow, J.C., Leibensperger, E.M., Malm, W.C., Pitchford, M.L., Schichtel, B.A., Watson, J.G. and White, W.H. (2011). Decreases in Elemental Carbon and Fine Particle Mass in the United States. *Atmos. Chem. Phys.* 11: 4679–4686.
- Noble, C.A., Mukerjee, S., Gonzales, M., Rodes, C.E., Lawless, P.A., Natarajan, S., Myers, E.A., Norris, G.A., Smith, L., Özkaynak, H. and Neas, L.M. (2003). Continuous Measurement of Fine and Ultrafine Particulate Matter, Criteria Pollutants and Meteorological Conditions in Urban El Paso, Texas. *Atmos. Environ.* 37: 827–840.
- Nussbaum, N.J., Zhu, D., Kuhns, H.D., Mazzoleni, C.,

- Chang, M.C.O., Moosmüller, H. and Watson, J.G. (2009). The In-Plume Emissions Test-Stand: A Novel Instrument Platform for the Real-Time Characterization of Combustion Emissions. *J. Air Waste Manage. Assoc.* 59: 1437–1445.
- Shen, Z.X., Han, Y.M., Cao, J.J., Tian, J., Zhu, C.S., Liu, S.X., Liu, P.P. and Wang, Y.Q. (2010). Characteristics of Traffic-Related Emissions: A Case Study in Roadside Ambient Air Over Xi'an, China. *Aerosol Air Qual. Res.* 10: 292–300.
- Shi, G.L., Feng, Y.C., Wu, J.H., Li, X., Wang, Y.Q., Xue, Y.H. and Zhu, T. (2009). Source Identification of Polycyclic Aromatic Hydrocarbons in Urban Particulate Matter of Tangshan, China. *Aerosol Air Qual. Res.* 9: 309–315.
- Shue, M.F., Liou, J.J., Tasi, J.L., Tang, H.C., Huang, W.J. and Liao, M.H. (2009). Cytotoxicity Studies on Combustion Gas of Polyvinyl Chloride (PVC) Resin. *Aerosol Air Qual. Res.* 9: 305–308.
- Tao, Z., Hewings, G. and Donaghy, K. (2010). An Economic Analysis of Midwestern US Criteria Pollutant Emissions Trends from 1970 to 2000. *Ecol. Econ.* 69: 1666–1674.
- TCEQ (2010). Effects Screening Levels, InterOffice Memorandum. Prepared by Toxicology Division, Texas Commission on Environmental Quality, Austin, TX (<http://www.dentonrc.com/s/dws/img/drc/03-11/0330screening.pdf>).
- Tropp, R.J., Kohl, S.D., Chow, J.C. and Frazier, C.A. (1998). Final Report for the Texas PM<sub>2.5</sub> Sampling and Analysis Study, Report Number 6570-685-7770.1F Prepared by Desert Research Institute, Reno, NV for Houston, TX, City of Houston, Bureau of Air Quality Control.
- Tropp, R.J., Engelbrecht, J., Kohl, S.D., Dickerson, A., Lowenthal, D.H., Chow, J.C., Watson, J.G., DuBois, D.W., Countess, R.J., Countess, S.J. and Michel, E.L. (2004). In *Proceedings, Symposium on Air Quality Measurement Methods and Technology*, Air & Waste Management Association, Pittsburgh, PA.
- U.S.EPA (1999). Toxic Organic Compounds in Ambient Air Compendium Method TO-14A: Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography, Report Number EPA/625/R-96/010b Prepared by U.S. Environmental Protection Agency, Research Triangle Park, NC.
- Wang, H.K., Huang, C.H., Chen, K.S. and Peng, Y.P. (2010). Seasonal Variation and Source Apportionment of Atmospheric Carbonyl Compounds in Urban Kaohsiung, Taiwan. *Aerosol Air Qual. Res.* 10: 559–570.
- Wang, Y., Hopke, P.K. and Utell, M.J. (2011). Urban-scale Spatial-temporal Variability of Black Carbon and Winter Residential Wood Combustion Particles. *Aerosol Air Qual. Res.* 11: 473–481.
- Watson, J.G., Chow, J.C. and Frazier, C.A. (1999). In S. and Creatchman, M. (Eds.), *Gordon and Breach Science*, Amsterdam, p. 67.
- Watson, J.G., Chow, J.C., Chen, L.W.A. and Frank, N.H. (2009). Methods to Assess Carbonaceous Aerosol Sampling Artifacts for IMPROVE and Other Long-Term Networks. *J. Air Waste Manage. Assoc.* 59: 898–911.
- Watson, J.G., Chow, J.C., Chen, L., Wang, X.L., Merrifield, T.M., Fine, P.M. and Barker, K. (2011). Measurement System Evaluation for Upwind/Downwind Sampling of Fugitive Dust Emissions. *Aerosol Air Qual. Res.* 11: 331–350.
- Zheng, M., Fang, M., Wang, F. and To, K.L. (2000). Characterization of the Solvent Extractable Organic Compounds in PM<sub>2.5</sub> Aerosols in Hong Kong. *Atmos. Environ.* 34: 2691–2702.
- Zielinska, B., Fujita, E.M., Sagebiel, J.C., Harshfield, G., Uberna, E., Hayes, T. and Keene, F. (1998). Arizona Hazardous Air Pollutants Monitoring Program. *J. Air Waste Manage. Assoc.* 48: 1038–1050.
- Zielinska, B., Sagebiel, J.C., Harshfield, G. and Pasek, R. (2001). Volatile Organic Compound Measurements in the California/Mexico Border Region during SCOS97. *Sci. Total Environ.* 276: 19–31.

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## Supplementary Information

### Definition of Sample ID/Numbers

A total of 28 time-integrated samples were acquired in this study (Fig. 2(a)). The table below shows the definition of sample numbers.

| Sampling Site | University of Texas El Paso (UTEP) |          |          |          | Chamizal National Memorial (CNM) |          |          |          |
|---------------|------------------------------------|----------|----------|----------|----------------------------------|----------|----------|----------|
| Time\Date     | 12/11/08                           | 12/12/08 | 12/13/08 | 12/14/08 | 12/15/08                         | 12/16/08 | 12/17/08 | 12/18/08 |
| 0000-0500 LST |                                    | #2       | #7       | #11      |                                  | #16      | #20      | #25      |
| 0500-1000 LST |                                    | #3       | #8       | #12      |                                  | #17      | #21      | #26      |
| 1000-1300 LST |                                    | #4       | #9       | #13      |                                  | #18      | #22      | #27      |
| 1300-1600 LST |                                    | #5       |          |          | #14                              |          | #23      | #28      |
| 1600-2400 LST | #1                                 | #6       | #10      |          | #15                              | #19      | #24      |          |

\*Color Code: Orange (Group A; Episode I-like); yellow (Group B; Dusty); blue (Group C; UTEP-Mobile); and green (Group D; CNM-Mobile).

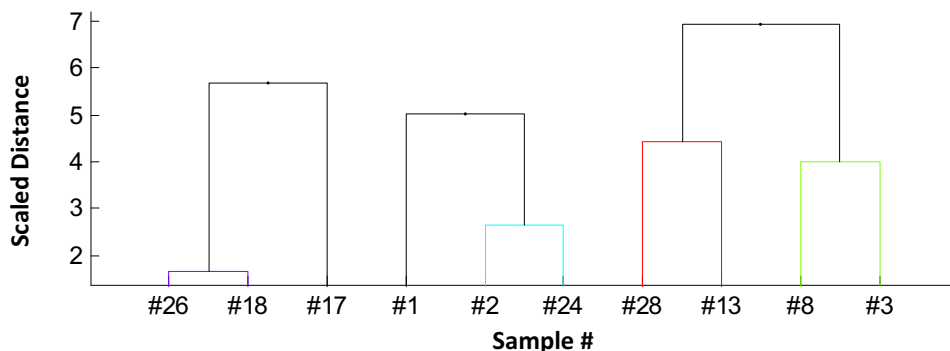
### Sample Clustering

Ten high PM<sub>2.5</sub> time-integrated samples (#1, #2, #3, #8, #13, #17, #18, #24, #26, and #28) were clustered by PM<sub>2.5</sub> chemical composition, i.e., ratios of OC, EC, TC, Al, Cl, K, Ca, Mn, Fe, Cu, Zn, Pb, BC, NO<sub>x</sub>, p-PAHs, and formaldehyde to PM<sub>2.5</sub> mass. The inter-sample distances are calculated by Mahalanobis distance:

$$d_{1,2}^2 = (x_1 - x_2)V^{-1}(x_1 - x_2)' \quad (1)$$

where  $V$  is the sample covariance matrix (as the standardization basis).

A hierarchical cluster tree was created using the Matlab® linkage function with ‘average’ distances. The cluster tree was then plotted using the Matlab® dendrogram function.



### Species Unit

PM<sub>2.5</sub> and p-PAHs concentrations measured by the mobile monitoring station were reported in different units between this paper and the original report (Chen *et al.*, 2010). In this paper, the concentrations are in volumetric µg/m<sup>3</sup> while in the report they were converted to standard volume using ambient pressure and temperature measurements. Therefore the numbers differ by a factor of ~0.8.

## REFERENCE

Chen, L.-W.A., Tropp, R.J., Zhu, D., Chow, J.C., Zielinska, B. and Watson, J.G. (2010).



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