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Analysis of Temporal and Spatial Dichotomous PM Air Samples in the El Paso-Cd. Juarez Air Quality Basin

Wen-Whai Li
Department of Civil Engineering and Environmental Science and Engineering Program, University of Texas at El Paso

Ruben Orquiz
Department of Civil Engineering, University of Texas at El Paso

Jose H. Garcia and Tania T. Espino
Environmental Science and Engineering Program, University of Texas at El Paso

Nicholas E. Pingitore
Department of Geological Sciences and Environmental Science and Engineering Program, University of Texas at El Paso

Jorge Gardea-Torresdey
Department of Chemistry and Environmental Science and Engineering Program, University of Texas at El Paso

Judith Chow and John G. Watson
Desert Research Institute, Reno, Nevada

ABSTRACT

This paper presents and discusses the results obtained from the gravimetric and chemical analyses of the 24-hr average dichotomous samples collected from five sites in the El Paso-Cd. Juarez air quality basin between August 1999 and March 2000. Gravimetric analysis was performed to determine the temporal and spatial variations of $PM_{2.5}$ (particulate matter less than 2.5 μm in diameter) and $PM_{2.5-10}$ (particulate matter less than 10 μm but greater than 2.5 μm in diameter) mass concentrations. The results indicate that ~25% of the PM_{10} (i.e., $PM_{2.5}$ + $PM_{2.5-10}$) concentration is composed of $PM_{2.5}$. Concurrent measurements of hourly PM concentrations and wind speed showed strong diurnal patterns of the regional PM pollution. Results of X-ray fluorescence (XRF) elemental analyses were compared to similar but limited studies performed by the Texas Natural Resource Conservation Commission (TNRCC) in 1990 and 1997. Major elements from geologic sources—Al, Si, Ca, Na, K, Fe, and Ti—accounted for 35% of the total mass concentrations in the $PM_{2.5-10}$ fraction, indicating that geologic sources in the area are the dominant PM sources. Levels of toxic trace elements, mainly considered as products of anthropogenic activities, have decreased significantly from those observed in 1990 and 1997.

IMPLICATIONS

$PM_{2.5}$ and $PM_{2.5-10}$ mass and elemental concentrations were compared to those of previous studies in the El Paso-Cd. Juarez binational region. The PM concentrations were higher in Cd. Juarez than in El Paso. Both 24-hr averaged $PM_{2.5}$ and PM_{10} concentrations peaked at low- and high-wind conditions, but the ratio of $PM_{2.5}$ to PM_{10} remained low. The hourly $PM_{2.5}$ and PM_{10} concentrations and their ratio showed strong diurnal patterns that peaked in the morning and in the evening. Toxic trace elements in $PM_{2.5}$ are significantly lower today than a decade ago, while geologic elements continue to dominate the PM_{10} mass concentration.

INTRODUCTION

The Paso del Norte (PdN) air quality basin contains three cities: El Paso, TX; Sunland Park, NM; and Ciudad Juarez, Chihuahua, Mexico. Ambient PM_{10} concentrations in the

region frequently exceed the national ambient air quality standards (NAAQS) of both countries. PM in the region derives from geologic sources, industrial sources, vehicle exhaust, residential cooking and heating, and other unidentified sources. The arid weather, occasional high winds, frequent stagnations, shallow nighttime and morning mixing depths, and complex topography preclude simple explanations for excessive PM_{10} levels.

Air quality in El Paso has improved gradually since 1990, as shown in Figure 1. Although El Paso is still classified as a nonattainment area for ozone, CO, and PM_{10}, reductions in all three criteria pollutants have been reported by the Texas Natural Resource Conservation Commission (TNRCC).[1-3] Ozone and CO concentrations have decreased to levels close to or below their respective NAAQS. The annual average ambient PM_{10} level decreased from the peak of 67 μg/m^3 in 1989 to 37 μg/m^3 in 1993, but increased to 55 μg/m^3 from 1993 to 1997.[2]

A brief modeling feasibility study in December 1990 collected 12-hr (day and night) dichotomous samples at five sites in El Paso for gravimetric, elemental, and carbon analyses.[4] During that study, PM_{10} exceeded the 150-μg/m^3 24-hr standard a total of 15 times over the five sites during the 18 sample days. Substantial spatial variation of PM_{10} during air pollution episodes was observed, and nighttime concentrations were reported to be greater than daytime concentrations. Geologic material accounted for most of the mass in $PM_{2.5-10}$. Concentrations of trace elements (Cr, Cu, As, Pb, and Cd) were higher in $PM_{2.5}$ than in $PM_{2.5-10}$. Surprisingly, the amount of Cl present in El Paso air during 1990 was also higher than Cl levels found in Texas coastal cities.

Additional PM monitoring in El Paso has been performed by the state of Texas and the U.S. Environmental Protection Agency (EPA) since 1997 for the review of the proposed $PM_{2.5}$ NAAQS. A 1997 TNRCC study[5] in central El Paso showed that geologic material ($[AlO+AlO_2]_{average}$ + SiO_2 + $[FeO+FeO_2]_{average}$) accounted for 22% of the mass in $PM_{2.5}$, while other elements [sum of X-ray fluorescence (XRF) species: Al + Si + Ca + Fe + S + Cl] accounted for 2% of the total mass in $PM_{2.5}$. In addition, unexplained Cl concentrations continued to be higher in El Paso than in any city in Texas during the study period. EPA began its first nationwide network of PM monitoring in 1999. The results showed that El Paso had the lowest $PM_{2.5}$ mass among major U.S. metropolitan areas.[6] The annual mean of the daily $PM_{2.5}/PM_{10}$ ratio for El Paso varied from 0.15 to 0.32, with a seven-site average of 0.27. This ratio is considered a qualitative reference because the $PM_{2.5}$ and PM_{10} monitors do not use identical monitoring protocols.[6] The recurring increase of PM_{10} concentration in recent years and the temporal and spatial characteristics of PM pollution in the air basin are not understood. To improve understanding, the University of Texas at El Paso (UTEP) PM air monitoring program was conducted in 1999–2000, during which $PM_{2.5}$ and $PM_{2.5-10}$ samples were collected at several locations in the air basin. The objectives were to determine (1) the temporal and spatial variations of $PM_{2.5}$ and $PM_{2.5-10}$; (2) relationships between $PM_{2.5}$ and $PM_{2.5-10}$; and (3) the elemental constituents of $PM_{2.5}$ and $PM_{2.5-10}$.

THE AIR MONITORING PROGRAM

Site Description

The PM monitoring program began August 1, 1999, and ended July 31, 2000. During this period, 24-hr dichotomous samples were collected on alternate days at two El Paso sites: Chamizal National Park (Chamizal) and Sun Metro Bus Terminal (Sun Metro), as shown in Figure 2. Only air samples collected before March 7, 2000, are discussed in this paper. Three additional sites in Cd. Juarez (Club 20-30, Advanced Transformer, and Mission) were added to the sampling program during the winter months

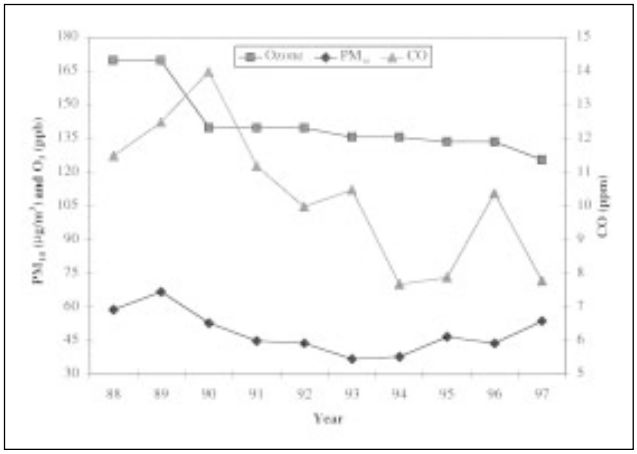

Figure 1. Annual average PM_{10} and maximum 1-hr ozone and CO concentrations for El Paso.

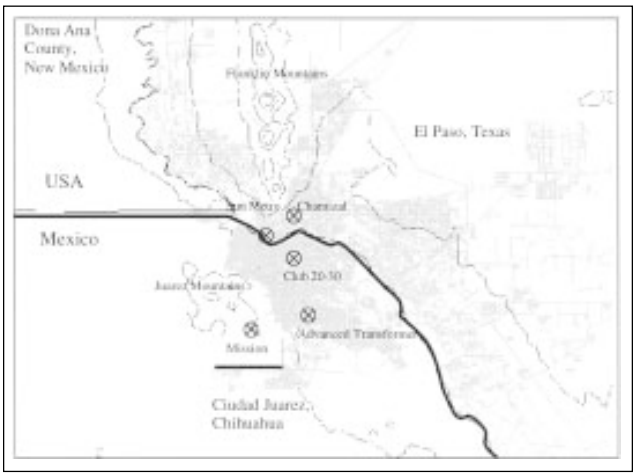

Figure 2. Locations of air monitoring sites.

(January 3–March 7, 2000). Figure 2 shows the locations of the five monitoring sites and the major geologic features in the Paso del Norte air basin.

In the United States, the Chamizal site is located in south El Paso, west of the Cordova International Bridge, in a mixed residential, semi-industrial area. It is part of EPA's State and Local Air Monitoring Stations (SLAMS) and Photochemical Air Monitoring Stations (PAMS) networks where daily, 24-hr Federal Reference Method (FRM) $PM_{2.5}$ samples are collected, and hourly PM and meteorological data are continuously recorded. The Sun Metro site, an urban commercial/industrial site ~4 km from Chamizal, is located in southwest El Paso just north of the Rio Grande and south of highway I-10. The site is collocated with a TNRCC Continuous Air Monitoring Site (CAMS) where hourly PM and meteorological data are continuously recorded.

In Mexico, the Club 20-30 site is located in a residential area east of downtown Cd. Juarez. The Advanced Transformer site is located near maquiladoras that make electronic components and automotive parts; brick kilns operate to the south. These two sites are comanaged by the Environmental Department of Cd. Juarez and the El Paso City and County Health and Environmental District. The Mission site is located in the Juarez Mountains foothills southwest of the air basin. The site is surrounded by unpaved roads and represents a typical residential community in the outskirts of Cd. Juarez. A cement factory is located ~2 mi to the south of the site.

These locations represent different activities in the air basin and supplement the study measurements with FRM $PM_{2.5}$, hourly PM, and meteorological data. Continuous hourly monitoring of PM_{10} by a beta attenuation monitor (BAM) was replaced with a tapered element oscillating microbalance (TEOM) for $PM_{2.5}$ on January 1, 2001, due to a change in PM monitoring strategy in Texas. Both the BAM and the TEOM were in operation at Sun Metro during the UTEP study period.

Sample Collection, Handling, and Processing

Two dichotomous air samplers[7,8] were placed at each of the two U.S. sites, where one sampler was operated every other day to collect 24-hr air samples and the other was operated selectively for collocated samples. Only one dichotomous sampler was operated at each of the three Mexico sites. Twenty-four-hour samples were collected from 0001 to 2359 MST on 37-mm-diameter ringed Teflon filters (Gelman Science Inc., ID No. R2PJ037) at an actual [not adjusted to standard temperature and pressure (STP)] flow rate of 1 m^3/hr. The filter had a high particle collection efficiency of 99%, measured using the DOP test with a 0.3-μm particle at the sampler's operating face velocity.[9] Quality control was managed by following EPA guidelines and procedures for PM monitoring[10] and gravimetric weighing.[11] A mini-Buck bubble calibrator (Model M-30), a primary standard calibration device traceable to NIST, was used to calibrate the rotameters on the dichotomous samplers.[12] Collocated samples were collected at the El Paso sites for every 10 samples. All samplers (except at the Mission site) were positioned at least 8 feet from the TNRCC's 8-foot-tall instrument shacks, with the inlet head standing 5 feet above the ground. The sampler at the Mission site was positioned on the roof of a one-story cinderblock storage structure, and the inlet head was 5 feet above the roof.

Analysis of Mass Concentrations

Filters were conditioned at 25 ± 5 ºC and 30 ± 5% RH for 24 hr, pre-weighed, and stored in petri dishes for less than 30 days prior to sampling. Loaded filters were removed from the field and transported to the laboratory at UTEP for gravimetric analysis with a CAHN model C-33 microbalance (±1 μg sensitivity)[13] after conditioning. Mass concentrations were reported as micrograms of PM per cubic meter of air (μg/m^3) at EPA's STP conditions of 298 K and 760 mmHg. The adjustment for EPA standard conditions is required for determining compliance with the federal PM_{10} standard, but not for compliance with the federal $PM_{2.5}$ standard.

XRF Elemental Analysis

$PM_{2.5}$ and $PM_{2.5-10}$ Teflon filters were analyzed by XRF analysis for 38 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Au, Hg, Tl, Pb, and U). Calibration standards, sensitivity factors for each excitation condition, quality control standards and procedures, and detailed laboratory methods and operation procedures were kept the same as those used at the Desert Research Institute (DRI).[14,15]

RESULTS AND DISCUSSION

Mass Concentrations

Collocated Samples. Superior collocated precision of ±1% for both $PM_{2.5}$ and $PM_{2.5-10}$ was observed in the current study. Regression statistics for samples collected at Chamizal and Sun Metro showed high correlations ($r^2 = 0.99$), near-unity slope (1.03), and low intercepts (<3 μg/m^3).

Comparison to TNRCC's Beta Attenuation Monitor. Figure 3 shows substantially poorer comparisons between the dichotomous sampler PM_{10} and that derived from the BAM. On average, the BAM reported lower PM_{10} than the dichotomous samplers by 20–40%. The difference became more pronounced at high concentrations. Previous studies on the compatibility between the BAM and integrated

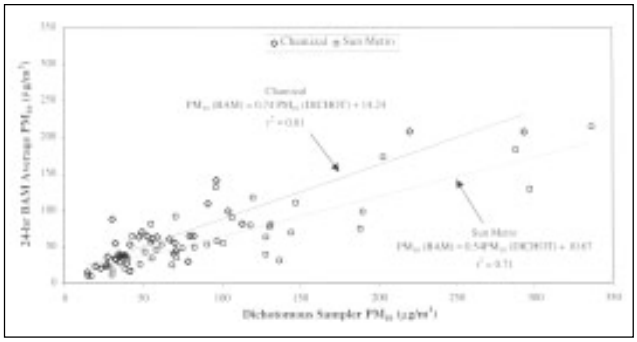

Figure 3. Comparison of PM_{10} concentrations acquired by the dichotomous monitor and BAM at Chamizal and Sun Metro for the period of December 2, 1999, to March 7, 2000. All concentrations were reported under STP conditions.

samplers showed that the BAM tends to observe lower PM concentrations (0.57~1.10 of that observed by sequential filter samplers and 0.85~1.0 of that observed by dichotomous samplers) and scattered distributions (less than 70% of all paired BAM and dichotomous data fall within ±3σ interval) than other filter-based monitors.[16] Discrepancies between the BAM and dichotomous sampler at high PM_{10} concentrations could be caused by the amount of particles with sizes greater than 10 μm[17] on the filter or the difference in humidity, calibration standards, and the beta attenuation coefficient for soot and geologic aerosols.[18-20]

Temporal Variation of PM Concentrations. Figure 4 presents the time series plot of PM_{10} and $PM_{2.5}$ concentrations for samples acquired on an every-other-day schedule at Chamizal. Regardless of the PM_{10} concentrations, $PM_{2.5}$ consisted of only a small, but steady, fraction of PM_{10}, indicating that anthropogenic emissions (in the form of $PM_{2.5}$) in this area are rather independent of the temporal variation of 24-hr average PM_{10} concentrations. The temporal variation of PM concentrations at Sun Metro is shown in Figure 5. The average $PM_{2.5}$ and PM_{10} concentrations of

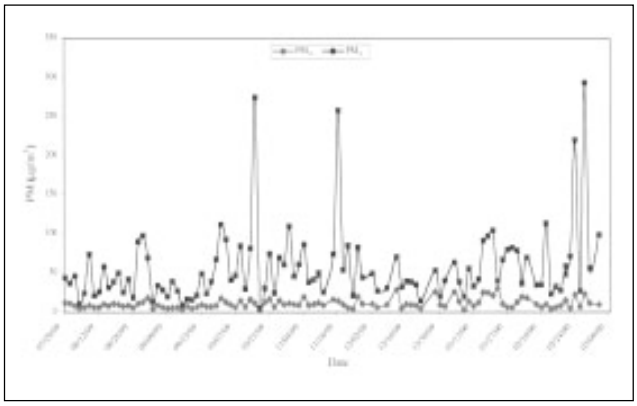

Figure 4. Temporal PM_{10} and $PM_{2.5}$ variations at Chamizal. Line break refers to missing data.

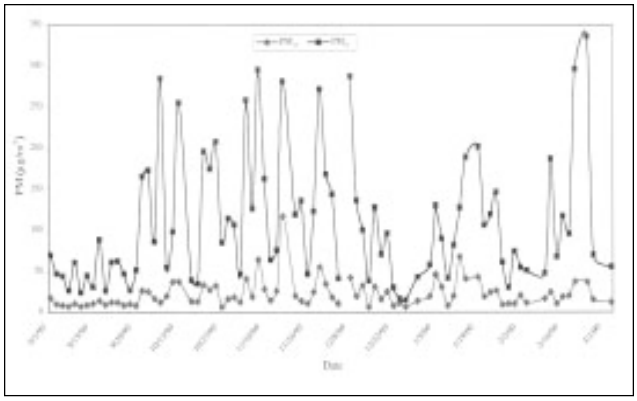

Figure 5. Temporal PM variations at Sun Metro. Line break refers to missing data.

22.5 and 109 μg/m³ at Sun Metro were considerably higher than Chamizal's 11.0 and 56.9 μg/m³, respectively. Table 1 summarizes the monthly average PM concentrations and temperatures obtained for the two El Paso sites. Both $PM_{2.5}$ and PM_{10} increased during winter months, as temperature inversions increased in frequency and duration and wood burning intensified. Because of the nearby highway and unpaved residential area in Cd. Juarez, the PM concentrations at Sun Metro were expected to be higher than those at Chamizal. Although it appears in Figure 5 that $PM_{2.5}$ followed the pattern of PM_{10} at Sun Metro, Table 2 shows that the 24-hr average PM_{10} concentrations at both U.S. sites were strongly correlated to $PM_{2.5-10}$ (with $r^2 = 0.97$ for both sites) and weakly associated with $PM_{2.5}$ (with $r^2 = 0.21$ and 0.28, respectively). As mentioned previously, the slightly higher correlation between $PM_{2.5}$ and PM_{10} at Sun Metro could be caused by the proximity to a highway.

The average wintertime $PM_{2.5}/PM_{10}$ ratio at Chamizal, 0.22, agrees well with EPA's annual mean of 0.23 at the same site, and the ratios for both sites fall within the range (0.15–0.32) reported by EPA.[6] These ratios are significantly lower than 0.5, a value reported for a typical arid city (Spokane, WA),[21] where the ratio varies from 0.20 to 0.37 during dust storms and 0.33 to 0.75 during non-dust storm days.[22] Based on the observed $PM_{2.5}/PM_{10}$ ratios and PM_{10} concentrations, many of the high PM_{10} days would have been attributed to fugitive dust generated by high winds. However, concurrent wind measurements at the sites do not support this argument.

For instance, two of the highest 24-hr PM_{10} concentrations measured at Chamizal were 275 μg/m³ on October 15 and 258 μg/m³ on November 18. The respective $PM_{2.5}$ concentrations for these two days at Chamizal were 11.2 and 14.7 μg/m³, which resulted in $PM_{2.5}/PM_{10}$ ratios of 0.04 and 0.06. The average wind speeds for these two days, however, were not considered high: 4.3 m/sec (with occasional gusts up to 8.9 m/sec) and 2.8 m/sec, respectively. Wind gusts reaching 8.9 m/sec may have made a

Table 1. Summary of 24-hr-average PM concentrations (μg/m^3) and temperatures (°F) at the two El Paso sites.

	Chamizal			Sun Metro		
Month	$PM_{2.5}$ ± STD	PM_{10} ± STD	Temp.	$PM_{2.5}$ ± STD	PM_{10} ± STD	Temp.
Aug 99	8.6 ± 2.4	43.5 ± 24.6	84.5	N/C N/C	N/C N/C	N/C
Sep 99	7.2 ± 3.6	31.5 ± 18.4	78.5	10.5 ± 2.7	47.8 ± 18.8	77.1
Oct 99	11.2 ± 4.3	73.8 ± 61.8	68	22.6 ± 9.9	138.9 ± 76.9	66.6
Nov 99	11.5 ± 4.6	69.2 ± 58.2	60.9	34.6 ± 28.8	155.8 ± 88.5	59.3
Dec 99	11.6 ± 8.0	37.3 ± 15.8	47.3	18.2 ± 11	85.2 ± 73.3	45.9
Jan 00	12.7 ± 7.5	58.2 ± 26	53.4	28.4 ± 17.5	106.4 ± 50.5	51.6
Feb 00	12.5 ± 6.7	75.1 ± 78.5	57.5	21.5 ± 9.4	133 ± 106	55.8
Average	10.95	56.9		22.5	109	

Note: N/C is no samples collected.

significant impact on the elevated PM_{10} concentration on October 15. In addition, on January 19 at Sun Metro, the average wind speed for the day was 3.2 m/sec (with maximum wind gusts of up to 4.6 m/sec), and the PM_{10} and $PM_{2.5}$ concentrations were 203 and 43.1 μg/m^3, respectively. On February 12, the PM_{10} and $PM_{2.5}$ concentrations were 188 and 24.8 μg/m^3, with an average wind speed of 5.1 m/sec and occasional wind gusts up to 10.3 m/sec. When wind gusts reached levels of 13.1 m/sec, as on February 24, the PM_{10} and $PM_{2.5}$ concentrations reached 337 and 37.2 μg/m^3, respectively. The $PM_{2.5}/PM_{10}$ ratio was 0.21 for January 19 and 0.13 for February 12, and decreased to 0.11 on February 24, which is consistent with the changes in wind speed and maximum wind gusts.

The low-wind–high-PM and high-wind–high-PM phenomena have been observed at several locations and throughout the year in the air basin.[23] Figure 6, based on the hourly BAM PM_{10} and TEOM $PM_{2.5}$ data,[24,25] shows that hours with low or extremely high wind speeds (exceeding the wind erosion threshold wind speed of ~7 m/sec) tend to yield higher PM concentrations than hours with light/moderate wind speeds. Furthermore, the hourly PM data show a strong diurnal pattern. Both $PM_{2.5}$ and PM_{10} peak at two distinct time intervals in Figure 7. The first PM peak was during the morning hours, when ground-based inversions occurred and morning traffic began. The second PM peak occurred in the evening, when radiation inversions started to form and wood burning and home cooking prevailed in the air basin. Similar diurnal variations in PM_{10} were observed in southern California. Pronounced morning and evening peaks in PM_{10} were observed at both urban and rural sites.[26] However, the most pronounced peak was observed at a suburban location where shifts in meteorology (winds and atmospheric pressure) were considered the major causes of the peak.[26]

Figure 7 also shows the average hourly $PM_{2.5}/PM_{10}$ ratio, which peaked at the same time intervals as $PM_{2.5}$ and PM_{10} but arrived 1 hr ahead of the $PM_{2.5}$ and 2 hr before the PM_{10}. The hourly $PM_{2.5}/PM_{10}$ ratios (0.3~0.6) observed by the continuous monitors appeared to be much higher than the 24-hr averages (0.15–0.32) obtained by our dichotomous samplers. Errors caused by measurement imprecision, systematic bias caused by different monitoring devices, characteristics of wind-direction related emissions, and dominance of $PM_{2.5-10}$ in PM_{10} during higher PM hours all could contribute to the discrepancies. Time-resolved PM monitoring and associated chemical specification during the peak hours would provide further information for understanding the causes of the low daily $PM_{2.5-10}/PM_{10}$ ratios and for controlling the PM pollution in the air basin.

Spatial Variation of PM Concentrations. Figure 8 contains the temporal variation of 24-hr PM_{10} and $PM_{2.5}$ at the three Cd. Juarez sites. The $PM_{2.5}$ concentrations visibly followed the PM_{10} trend. At the Cd. Juarez downtown site (Club 20-30), the PM_{10} concentration was consistently lower than that observed at the other Cd. Juarez sites. However, the average $PM_{2.5}/PM_{10}$ ratio, 0.36 with a Φ value of 0.11, appeared to be the highest among all U.S. and Mexico sites, obviously affected by the increased anthropogenic (most likely the mobile) emissions in downtown Cd. Juarez.

At the Mission site, it was expected that the PM_{10} concentration would be high and mostly made up of $PM_{2.5-10}$. Indeed, Table 2 shows that the average $PM_{2.5-10}$ concentration at this site was 142 μg/m^3, a value much higher than that monitored in El Paso or downtown Cd. Juarez. The high PM concentrations could be attributed to a cement factory located in the vicinity and the large number of wood stoves, unpaved roads, and kerosene heaters in the area. Also as expected, the $PM_{2.5}/PM_{10}$ ratio, 0.16 (with a

Table 2. Summary of 24-hr-average winter month PM concentrations (μg/m^3) at all sites.

	UTEP Study Average Values (Jan 7 through March 7, 2000)					
Site Name	$PM_{2.5}$ μg/m^3	$PM_{2.5-10}$ μg/m^3	PM_{10} μg/m^3	$PM_{2.5}/PM_{10}$ Ratio (unitless)	r^2 for $PM_{2.5}$ to PM_{10}	r^2 for $PM_{2.5-10}$ to PM_{10}
	Avg ± S.D.	Avg ± S.D.	Avg ± S.D.	Avg ± S.D.		
Chamizal[a]	12.6 ± 6.5	57.7 ± 54.7	70.3 ± 57.9	0.22 ± 0.118	0.21	0.97
Sun Metro[a]	23.1 ± 14.2	90.0 ± 71	113 ± 79.2	0.23 ± 0.099	0.28	0.97
Mission[b]	26.8 ± 11.6	142 ± 50.7	169 ± 58.2	0.16 ± 0.055	0.49	0.97
Club 20-30[b]	20.0 ± 11.5	36.0 ± 17.0	56.3 ± 26	0.36 ± 0.105	0.73	0.87
Adv. Transformer[b]	50.9 ± 59.3	146 ± 68.5	197 ± 107	0.23 ± 0.112	0.56	0.67

[a]El Paso, TX; [b]Cd. Juarez, Chihuahua, Mexico.

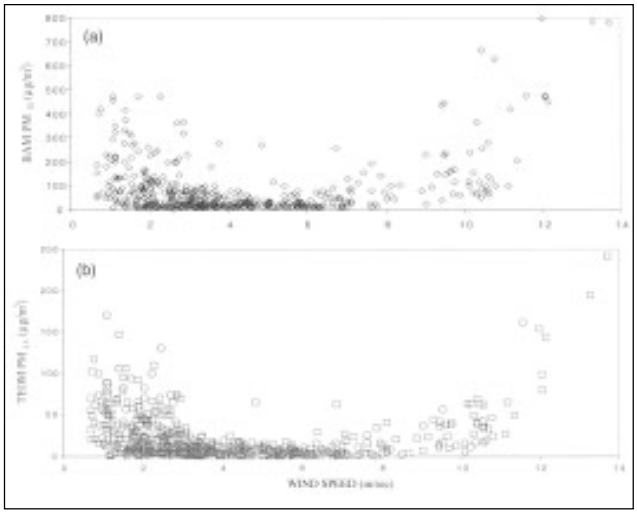

Figure 6. Relationship of hourly PM_{10} and $PM_{2.5}$ with wind speed at Sun Metro for the period of December 1, 1999, through February 28, 2000.

Φ value of 0.06), was significantly lower than at the other sites and is a good indication of the dominance of PM pollution by geologic sources. Table 2 shows that $PM_{2.5\text{-}10}$ dominated the PM_{10} at Mission and the two El Paso sites (with $r^2 = 0.97$ at all three sites).

At Advanced Transformer, the average $PM_{2.5}$ concentration of 50.9 μg/m³ and the PM_{10} concentration of 197 μg/m³ were the highest of all sites (see Table 2), reflecting the unique mixed emission sources (brick kilns, automobiles, unpaved roads, and industrial sources) in the immediate vicinity. For the Cd. Juarez sites, $PM_{2.5}$ correlated moderately to PM_{10} (with r^2 varying from 0.49 to 0.73), as seen in Table 2, indicating that anthropogenic emissions are more pronounced in Cd. Juarez than in El Paso.

PM pollution in the area appears to be dominated by $PM_{2.5\text{-}10}$ and increases from El Paso toward the outskirts of Cd. Juarez. $PM_{2.5\text{-}10}$ is likely to be fugitive dust generated by wind erosion (when wind speeds exceeded 7 m/sec) from bare soil or by vehicular movement/mechanical

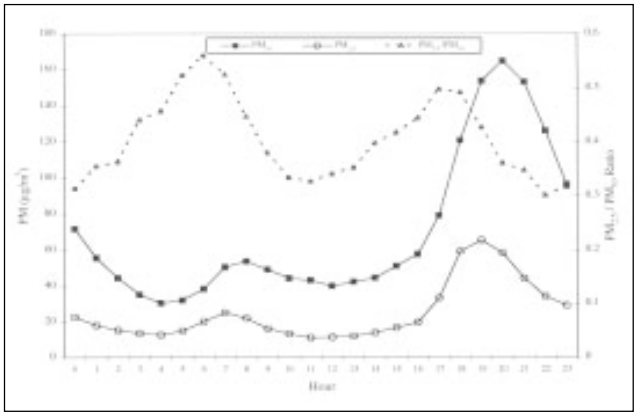

Figure 7. PM_{10}, $PM_{2.5}$, and $PM_{2.5}/PM_{10}$ diurnal variations at Sun Metro for the period of December 1, 1999, through February 28, 2000.

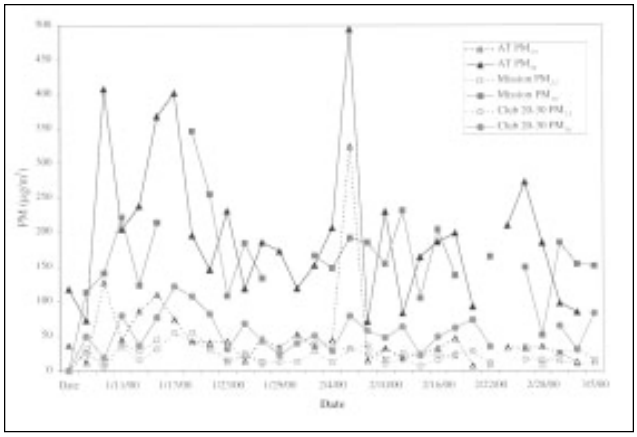

Figure 8. Temporal variation of PM_{10} and $PM_{2.5}$ at the Cd. Juarez sites. Line break refers to missing data.

disturbance on a paved or unpaved surface. Contributions to PM pollution by mobile emissions (primarily as $PM_{2.5}$) may be quite localized (both temporally and spatially) and do not significantly affect the overall 24-hr averaged PM_{10} concentrations in the air basin. Perhaps $PM_{2.5}$ in the area is dominated by resuspension of urban dust due to vehicular movement and the frequently occurring temperature inversions that are likely to trap PM in the air basin.

Elemental Analysis

A total of 149 filters collected at the five sites were analyzed using XRF for rapid evaluation of the elemental composition of PM. XRF analysis was performed for samples collected at Chamizal and Sun Metro for September 1999 and from December 2, 1999, to March 5, 2000. At the Cd. Juarez sites, filters were analyzed for samples collected from January 3 to March 7, 2000.

Element Concentrations. Figure 9 shows the average ambient toxic trace element concentrations (Cu, Cr, As, Cd, and Pb) at all sites. These elements were selected for their association with operations of local industrial sources. Concentrations for the five indicator elements were higher

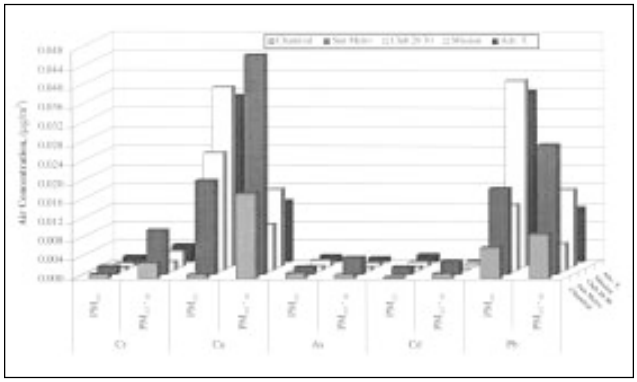

Figure 9. Average toxic trace element concentrations at all sites.

in $PM_{2.5-10}$ than in $PM_{2.5}$ for the El Paso sites, but lower (except Cr) in $PM_{2.5}$ than in $PM_{2.5-10}$ for the Cd. Juarez sites. This observation is opposite to what was discovered in 1990. It implies that the toxic trace elements in El Paso are more likely caused by wind erosion of natural surfaces or mechanical disturbance of road dust, but less likely to be caused by anthropogenic emissions of smelters or foundries. Localized emission sources in Cd. Juarez could be the reason for higher trace element concentrations in $PM_{2.5}$. Nevertheless, toxic trace elements in the Paso del Norte air are relatively low compared with the concentration ranges of these elements associated with PM in the atmosphere reported for rural or urban areas in the United States, Canada, or Europe.[27]

Geologic elements (Al, Si, Ca, Fe, Ti, and K) appeared to dominate the coarse fraction of PM_{10} (Figure 10). These elements were expected to be of higher concentrations as low $PM_{2.5}/PM_{10}$ ratios and high correlations between $PM_{2.5-10}$ and PM_{10} were observed at all sites. Based on the results of the XRF analysis, geologic elements accounted for 35% of $PM_{2.5-10}$ and 12% of $PM_{2.5}$ concentrations. PM concentrations at all Cd. Juarez sites, particularly the rural Mission site, were heavily weighted by the geologic elements, signifying the impacts of unpaved roads and surrounding desert on local air quality. The central Cd. Juarez site, which is far from the unpaved roads and bare soil of the desert, showed low concentrations for all geologic elements.

Figure 10 also shows that sulfur concentrations are low but similar in the fine and coarse fractions of PM. Potential sulfur emission sources in the region are fuel combustion and re-entrainment of fallout from past smelting of sulfide-containing ores. Occasional high Cl concentrations (not seen in the average concentration) were detected in $PM_{2.5}$, indicating the existence of possible anthropogenic sources of Cl-containing substances. Cl levels at Sun Metro and Advance Transformer appeared to be higher than at other areas in the air basin. Nevertheless, the level has decreased significantly from what was observed in 1990, but remained at approximately the same level as reported in TNRCC's 1997 statewide $PM_{2.5}$ study.

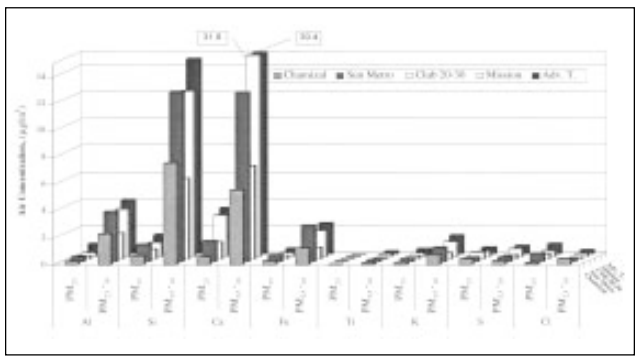

Figure 10. Average element concentrations of geologic origin and Cl and S at all sites.

PM Pollution Trend. Tables 3 and 4 compare the elemental composition of $PM_{2.5}$ and $PM_{2.5-10}$ observed in this study to that observed by TNRCC in 1990 and 1997. The 1990 TNRCC study was conducted using the same dichotomous samplers and sampling media as used in the current study. The 1997 TNRCC study used FRM $PM_{2.5}$ samplers. All samples were analyzed by DRI using the XRF method. Laboratory procedures, calibration standards, instrument precisions, and detection limits (documented by DRI[14] or available in the literature[27]) for the three studies were either identical or similar. Although the comparison may still include uncertainties, it provides the best available information of historical PM data for the air basin.

In general, As, Cr, and Pb levels in either $PM_{2.5}$ or $PM_{2.5-10}$ were lower in 1997 and 2000 than they were a decade ago at the two El Paso sites. As and Cr levels were consistently low in the air basin throughout the study period, which may reflect the closure of a local Cu smelting operation. Levels of Pb and Cu, although reduced, were still high in the air basin. The mean concentration of almost every elemental composition was seen to decrease from 1990 to 2000 at both El Paso sites (see Table 3). $PM_{2.5}$ Pb concentrations are significantly lower today than in the previous studies, possibly because of the elimination of Pb from gasoline (eliminated recently in Cd. Juarez) and the shutdown of a major smelting operation in the city. As and other smelter emissions have experienced the same decrease in concentration as Pb. $PM_{2.5}$ Cl and S concentrations have also experienced decreases in concentration.

The student's *t* test was performed to evaluate the trend of element concentrations in the air. For $PM_{2.5}$, although the mean concentrations of geologic elements seemed to decrease over the past decade, the trend cannot be established because of significant data scattering ($1.5 > \Phi/\text{Mean} > 0.5$). For instance, Al concentrations in El Paso decreased from an average of 0.47 μg/m³ in 1990 to 0.27 μg/m³ in 2000, and Ca levels decreased from 1.27 μg/m³ in 1990 to 1.04 μg/m³ in 2000, yet the trend cannot be established based on the data. Based on the paired student's *t* tests of three data sets for the six geologic elements, it appears that the geologic elements associated with $PM_{2.5}$ in the PdN air remain at the same levels as in the past decade. However, Cl showed a decreasing trend between 1990 and 2000.

Levels of toxic trace elements in $PM_{2.5}$ decreased significantly from 1990 to 2000. The trends are statistically significant based on the paired statistical analyses for the five indicator trace elements. The decreases are quite dramatic. For instance, the As concentration in $PM_{2.5}$ decreased by 57-fold (from 0.073 to 0.0013 μg/m³) and Pb decreased by 18-fold (from 0.24 to 0.014 μg/m³) in El Paso.

The decrease in the $PM_{2.5}$ mass concentration is also obvious. $PM_{2.5}$ decreased from 32.8 and 55.6 μg/m³ in 1990

Table 3. Comparison of the UTEP winter study $PM_{2.5}$ elemental composition to those of the 1990 and 1997 TNRCC studies. Samples from the 1990 TNRCC study and the UTEP study were collected with dichotomous samplers, while the 1997 TNRCC samples were collected with the $FRM_{2.5}$ sampler. All samples were analyzed by the XRF method.

Element	Chamizal		Sun Metro Site		AdvT	Club 20-30	Mission	Central El Paso
	UTEP Study ng/m³	1990 TNRCC Study ng/m³	UTEP Study ng/m³	1990 TNRCC Study ng/m³	UTEP Study ng/m³	UTEP Study ng/m³	UTEP Study ng/m³	1997 TNRCC Study[a] ng/m³
Na	64	-	54	-	83	54	66	18
Mg	41	-	69	-	75	43	73	53
Al	190	440	357	497	761	218	285	243
Si	593	440	1264	1071	1436	726	1010	928
P	2	-	2	-	1	2	2	0.1
S	409	1169	341	1349	492	514	374	594
Cl	89	565	625	1741	742	349	405	362
K	128	186	217	365	381	183	242	191
Ca	542	559	1540	1989	3411	1257	3063	1407
Ti	8	10	19	20	28	11	18	20
V	1	7	1	9	1	1	1	3
Cr	0.4	4	2	5	1	0	1	1
Mn	4	13	9	17	15	6	11	9
Fe	231	179	508	411	397	243	291	324
Co	0.1	-	0.1	-	0.3	0.0	0.1	1
Ni	0.2	-	0.1	-	1	0.3	0.4	1
Cu	15	49	22	119	35	25	38	61
Zn	24	90	38	242	159	98	73	64
Ga	0	-	0.0	-	0.0	0.0	0.0	0
As	1	51	1	94	1	1	1	19
Se	0.0	6	0.0	21	0.0	0.0	0.1	8
Br	7	33	1	38	52	14	16	9
Rb	0.3	-	1	-	1	0.5	1	1
Sr	3	3	6	8	10	5	7	5
Y	0.2	-	0.4	-	0.3	0.3	0.2	0.0
Zr	1	-	1	-	1	1	1	1
Mo	0.1	-	0.3	-	0.2	0.1	0.2	1
Pd	0.3	-	0.5	-	1	1	1	1
Ag	0.1	-	0.3	-	0.2	1	0.0	1
Cd	0.3	5	1	8	2	1	1	2
In	0.1	-	1	-	1	1	0.0	1
Sn	1	3	3	7	3	3	3	3
Sb	2	8	14	18	23	11	15	8
Ba	17	7	22	12	21	22	18	9
La	10	-	12	-	9	15	12	8
Au	0.0	-	0.0	-	0.0	0.0	0.0	0.0
Hg	0.0	-	0.0	-	0.0	0.0	0.0	0.0
Tl	0.0	-	0.1	-	0.1	0.0	0.1	0.0
Pb	7	188	20	301	36	14	39	37
U	0.0	-	0.0	-	0.1	0.1	0.1	0.0

[a]Only 17 samples were analyzed.

Table 4. Comparison of elemental $PM_{2.5-10}$ between those of the 1990 TNRCC study and the UTEP winter study. Samples from the 1990 TNRCC study and the UTEP study were collected with dichotomous samplers. All samples were analyzed by the XRF method.

	Chamizal		Sun Metro	Advanced Trans.	Club 20-30	Mission
Element	UTEP Study ng/m³	1990 TNRCC Study ng/m³[a]	UTEP Study ng/m³	UTEP Study ng/m³	UTEP Study ng/m³	UTEP Study ng/m³
Na	126	-	92	162	73	153
Mg	179	-	254	324	149	355
Al	2233	934	3729	3990	1919	3496
Si	7491	4242	12,652	14,525	6006	12,316
P	14	-	38	64	28	64
S	249	283	335	622	265	569
Cl	396	138	215	284	110	183
K	665	614	1071	1397	487	1080
Ca	5500	6672	12,627	30,365	6918	31,819
Ti	90	100	150	200	71	159
V	1	6	1	3	1	4
Cr	3	12	10	4	2	3
Mn	24	36	49	50	17	39
Fe	1187	1253	2714	2282	852	1932
Co	1	-	1	3	0.2	1
Ni	1	-	2	3	1	3
Cu	18	57	36	13	10	16
Zn	30	49	51	70	68	49
Ga	0	-	0.0	0.0	0.0	0.0
As	1	7	3	1	0	1
Se	0.0	1	0.0	0.1	0.0	0.0
Br	1	6	5	4	2	3
Rb	3	33	5	7	2	5
Sr	20	27	38	78	21	74
Y	1	-	2	2	1	2
Zr	5	4	8	11	3	8
Mo	1	-	2	2	0	2
Pd	1	-	0	2	0	7
Ag	1	-	2	0	0	0
Cd	1	3	3	0	0	0
In	0.4	-	0.0	3	0.3	2
Sn	2	6	2	0	1	2
Sb	2	1	1	3	2	4
Ba	46	40	64	87	32	57
La	7	-	13	3	12	3
Au	0.0	-	0.0	0.0	0.0	0.0
Hg	0.0	-	0.2	0.2	0.0	0.0
Tl	0.1	-	1	1	0	1
Pb	9	55	23	12	6	16
U	0.1	-	0.4	0.3	0.1	1

[a]TNRCC did not report element concentrations for $PM_{2.5-10}$ samples in 1990.

at Chamizal and Sun Metro to 11.0 and 22.5 μg/m³ in 2000, respectively. Consequently, the fraction of geologic elements in $PM_{2.5}$ (based on the sum of Al, Si, Ca, Fe, Ti, and K) increased from 6 to 12%, which implies that the contribution of anthropogenic emissions to $PM_{2.5}$ decreased and the overall $PM_{2.5}$ concentration in the air improved in the past decade. The ratio of trace elements to the $PM_{2.5}$ concentration also increased. The ratio of Cu to $PM_{2.5}$ increased from 0.19% in 1990 to 0.27% in 1997, but decreased to 0.12% in 2000. Table 5 shows that ratios for the dominant trace elements (except for Cr and Cu) in the region decreased less impressively from 1990 to 1997, but rather significantly (except for Cr) in 2000 after a major smelter halted its operations early that year. This is indicative of improvement in both geologic and industrial emissions in the past decade and further reduction of toxic trace elements from industrial emissions in the past year.

Table 4 compares the composition of $PM_{2.5-10}$ obtained in the present study to that measured in 1990. As expected, elements associated with geologic sources are high in $PM_{2.5-10}$. Based on the sum of the mass of the six indicator geologic elements and the mass of the $PM_{2.5-10}$ derived from Table 1, geologic elements account for ~35% of the mass of the coarse fraction of PM_{10}. Concentrations of the geologic elements associated with $PM_{2.5-10}$ were indistinguishable between 1990 and 2000, while the trace elements decreased significantly from 1990 to 2000.

Cl concentrations at all sites (except Chamizal) were high in $PM_{2.5}$ but low in $PM_{2.5-10}$. The Chamizal site is less influenced by the emission sources of Cd. Juarez because of its location and the prevailing southeast-northwest winds. The fact that Cl concentrations are high in $PM_{2.5}$ indicates the existence of local Cl sources in the southwest region of the air basin. Further investigation of the seasonal and spatial variations of Cl concentrations as well as the locations of these sources may provide answers to the unexplained high ozone concentrations in the region.

SUMMARY AND CONCLUSIONS

Our 7-month study of PM concentrations in El Paso shows that the average $PM_{2.5}$ and PM_{10} concentrations are 11 and 57 μg/m³ for Chamizal and 22 and 109 μg/m³ for Sun Metro, respectively. The PM_{10} concentration increases towards the suburban area of Cd. Juarez, while $PM_{2.5}$ peaks in areas of that city surrounded by brick kiln emissions and unpaved roads. $PM_{2.5-10}$ dominates the PM_{10} mass concentration, and geologic sources are the major contributors to $PM_{2.5-10}$. The 24-hr average $PM_{2.5}$ concentration maintains as a steady portion of PM_{10} and is less sensitive to the spatial and diurnal variations of PM pollution.

The diurnal variation of PM concentrations at Sun Metro shows that $PM_{2.5}$, PM_{10}, and the $PM_{2.5}/PM_{10}$ ratio all peak in the morning and at night. Characterization of time-resolved

Table 5. Percent fraction of trace metals in $PM_{2.5}$.

Element	1990 TNRCC Study Chami/Sun Metro	1997 TNRCC Study Central El Paso	UTEP Study El Paso Chamizal	UTEP Study El Paso Sun Metro	UTEP Study Ciudad Juarez Advanced Transformer	UTEP Study Ciudad Juarez Mission	UTEP Study Ciudad Juarez Club 20-30
Cr	0.001	0.004	0.005	0.011	0.001	0.001	0.002
Cu	0.19	0.27	0.110	0.098	0.068	0.124	0.104
As	0.164	0.086	0.009	0.009	0.003	0.004	0.002
Cd	0.015	0.008	0.003	0.006	0.003	0.003	0.003
Pb	0.552	0.163	0.046	0.078	0.070	0.122	0.055

PM concentrations will be extremely helpful in determining the sources responsible for the high morning and nighttime pollution. Trace elements in the air are lower today than historical values. Elements of geologic origin dominate the coarse fraction of PM_{10} and are persistent due to the abundance of unpaved roads and complex terrain. Further investigation using source fingerprints and chemical compositions of air samples, both organic[28] and elemental (research in progress), could provide mitigation alternatives for controlling PM pollution in the El Paso-Cd. Juarez border region.

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About the Authors

Wen-Whai Li (associate professor of civil engineering; corresponding author, e-mail: wli@utep.edu), Ruben Orquiz (M.S. candidate in the Department of Civil Engineering), Nicholas E. Pingitore (professor of geological sciences), Jorge Gardea-Torresdey (professor of chemistry), and Jose H. Garcia and Tania T. Espino (Ph.D. students in the Environmental Science and Engineering Program) are members of the air quality research group at the University of Texas at El Paso. Judith Chow and John G. Watson are research professors at the Desert Research Institute, University of Nevada at Reno.