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Experimental Design, Methods, and Results of Ambient Particulate Matter Characterization in the Paso del Norte Region

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ABSTRACT

The increase of PM_{10} concentration in recent years and the temporal and spatial characteristics of PM pollution in the Paso del Norte airbasin are not well understood. In light of this and the new and sometimes controversial findings on the health effects of $PM_{2.5}$, the uniqueness of the PM pollution in the region, and the new National Ambient Air Quality Standard for $PM_{2.5}$, it is important to characterize both fine and coarse fractions of the atmospheric aerosols to identify the sources of PM for the Paso del Norte region. To improve understanding, an air quality study to characterize the ambient PM pollution in the region was developed by the University of Texas at El Paso in collaboration with four Southwest Consortium for Environmental Research and Policy (SCERP) universities

(University of Utah, New Mexico State University, Arizona State University, and Universidad Autónoma de Ciudad Juárez) and several U.S. and Mexican agencies.

Diseño Experimental, Métodos, y Resultados de la Caracterización de Materia Particulada Ambiental en el la Región Paso del Norte

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RESUMEN

El incremento de concentración de PM_{10} en años recientes y las características temporales y espaciales de contaminación del medio ambiente por PM en la cuenca atmosférica del Paso del Norte no son bien conocidos. En virtud de ello, y los nuevos y algunas veces controversiales descubrimientos sobre los efectos de $PM_{2.5}$ en la salud, la particularidad de la contaminación por PM en la región, y el nuevo Estándar Nacional de $PM_{2.5}$ para Calidad de Aire Ambiental, es importante el caracterizar ambos fragmentos de los aerosoles atmosféricos finos y gruesos para identificar las fuentes de PM para la región Paso del Norte. Para mejorar el conocimiento, fue desarrollado un estudio de calidad de aire para caracterizar la contaminación de PM del medio ambiente en la región por la Universidad de Texas en El Paso en cooperación con cuatro universidades del Consorcio de Investigación y Política Ambiental del Suroeste

(CIPAS), (las Universidades del Estado de Utah, Nuevo México, Estado de Arizona, y Universidad Autónoma de Ciudad Juárez) y varias agencias mexicanas y de los E.U.

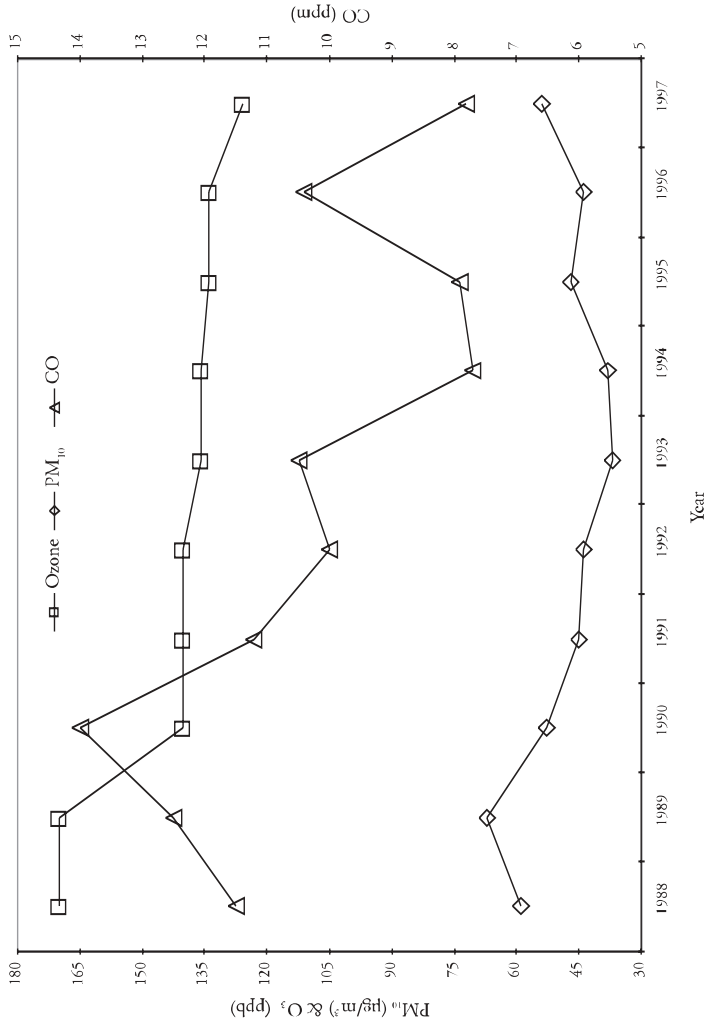
PREVIOUS STUDIES

Air quality in El Paso, Tex., has improved gradually since 1990, as shown in Figure 1. Although El Paso is still classified as non-attainment for ozone (O_3), carbon monoxide (CO), and particulate matter measuring 10 micrometers (μm) or less (PM_{10}), reductions in all three criteria pollutants have been reported by the Texas Commission on Environmental Quality (TCEQ; formerly Texas Natural Resource Conservation Commission [TNRCC]) (TNRCC 1999a, 1999b, 1999c). Ozone and carbon monoxide concentrations have decreased to levels close to or below their respective National Ambient Air Quality Standard (NAAQS). The annual average ambient PM_{10} level decreased from the peak of 67 micrograms per cubic meter ($\mu g/m^3$) in 1989 to 37 $\mu g/m^3$ in 1993, but increased to 55 $\mu g/m^3$ from 1993 to 1997.

A brief modeling feasibility study in December 1990 collected 12-hour (day and night) dichotomous samples at five sites in El Paso for gravimetric, elemental, and carbon analyses (Dattner 1994). During that study, PM_{10} exceeded the 150 $\mu g/m^3$ 24-hour standard 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 (chromium [Cr], copper [Cu], arsenic [As], lead [Pb], and cadmium [Cd]) were higher in particulate matter with an aerodynamic diameter of 2.5 μm or less ($PM_{2.5}$) than in $PM_{2.5-10}$. Surprisingly, the amount of chlorine present in El Paso air during 1990 was also higher than what was 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 (Price, et al. 1998) in central El Paso showed that

Figure 1. Annual Average PM₁₀ and Maximum One-Hour Ozone and Carbon Monoxide Concentrations for El Paso



Source: TNRCC 1999a

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geologic material ($[AlO+AlO_2]_{\text{average}} + SiO_2 + [FeO+FeO_2]_{\text{average}}$) accounted for 22% of the mass in $PM_{2.5}$, while other elements (Sum of XRF species – Al + Si + Ca + Fe + S + Cl) accounted for 2% of the total mass in $PM_{2.5}$. In addition, unexplained chlorine 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 and the results (Fitz-Simons, et al. 2000) showed that El Paso had the lowest $PM_{2.5}$ mass among major U.S. metropolitan areas. The annual mean of 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.

PROJECT DESIGN

The study was implemented in two phases: first exploratory, then full-scale. The exploratory study was designed to determine optimum spatial deployment of the PM sampling equipment and to identify major sources of PM emissions. Based on the results of the exploratory study, a full-scale study was performed to characterize the PM concentrations in the airbasin. Experimental design and results of the exploratory study have been presented and discussed elsewhere (Sheya, et al. 2000; Jeon, et al. 2001). Thus, the focus here is on the description of the full-scale study.

Site Description

The PM monitoring program began August 1, 1999, and ended March 7, 2000. It started with collection of 24-hour dichotomous samples on alternate days at two El Paso sites—Chamizal National Park (Chamizal) and Sun Metro Bus Terminal (Sun Metro), as shown in Appendix Figure 1 (page 305). Three additional sites in Ciudad Juárez (Club 20-30, Advanced Transformer, and Misión) were added to the sampling program during the winter months (January 3, 2000–March 7, 2000). Appendix Figure 1 (page 305) shows the locations of the five monitoring sites and the major geologic features in the Paso del Norte airbasin. These locations represent different activities in the airbasin and supplement the study

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measurements with Federal Reference Method (FRM) PM_{2.5}, hourly PM, and meteorological data. Continuous hourly monitoring of PM₁₀ by Beta Attenuation Monitor (BAM) was replaced by 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 BAM and TEOM were in operation at Sun Metro during the University of Texas at El Paso (UTEP) study period.

Sample Collection, Handling, and Processing

Two dichotomous air samplers (EPA 1998; Lodge 1989) were placed at each of the two U.S. sites where one sampler was operated every other day to collect 24-hour air samples and the other was operated selectively for collocated samples. Only one dichotomous sampler was operated at each of the three Mexican sites. Samples were collected every 24 hours from 0001 to 2359 MST on 37 millimeter (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 1.0 cubic meter per hour (m³/hr). The filter has high particle collection efficiency, 99%, which is measured using the DOP test with a 0.3- μ m particle at the sampler's operating face velocity (Lodge 1989). Quality control was managed by following EPA guidelines and procedures for PM monitoring (EPA 1994) and gravimetric weighing (EPA 1998). A mini-Buck bubble calibrator (Model M-30), a primary standard calibration device traceable to the National Institutes of Standards and Technology (NIST), was used to calibrate the rotameters on the dichotomous samplers (A. P. Buck 1987). Collocated samples were collected at the El Paso sites for every 10 samples. All samplers (except at the Misión site) were positioned at least eight feet away from TCEQ's eight-foot tall instrument shacks with the inlet head standing five feet above the ground. The sampler at the Misión site was positioned on the roof of a one-story cinder block storage structure and the inlet head was five feet above the roof.

Analysis of Mass

Filters were conditioned at $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and $30\% \pm 5\%$ RH for 24 hours, 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 ($\pm 1 \mu\text{g}$ sensitivity) after conditioning (Orion 1997). Mass concentrations were reported as micrograms of PM per cubic meter of air at EPA's STP conditions of 298°K and 760 millimeters (mm) mercury (Hg). The adjustment for EPA standard conditions is required for determining compliance with the federal PM_{10} standard, but not for compliance with the federal $\text{PM}_{2.5}$ standard.

X-Ray Fluorescence Elemental Analysis

$\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ Teflon filters were analyzed by x-ray fluorescence (XRF) analysis for 38 elements¹. Calibration standards, sensitivity factors for each excitation condition, quality control standards and procedures, and detailed laboratory methods and operation procedures are kept the same as those used at the Desert Research Institute (DRI) (Watson, et al. 1999; Chow 1995).

RESULTS AND DISCUSSION

Mass Concentrations: Collocated Samples

Superior collocated precision of $\pm 1\%$ for both $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ was observed in the current study. Regression statistics for samples collected at the Chamizal and Sun Metro sites show high correlations ($R^2 = 0.99$), near-unity slope (1.03), and low intercepts ($< 3 \mu\text{g}/\text{m}^3$).

Comparison to TCEQ's BAM

Figure 2 shows substantially poorer comparisons between the dichotomous sampler PM_{10} and what was derived from BAM. On average, BAM reported lower PM_{10} than the dichotomous samplers

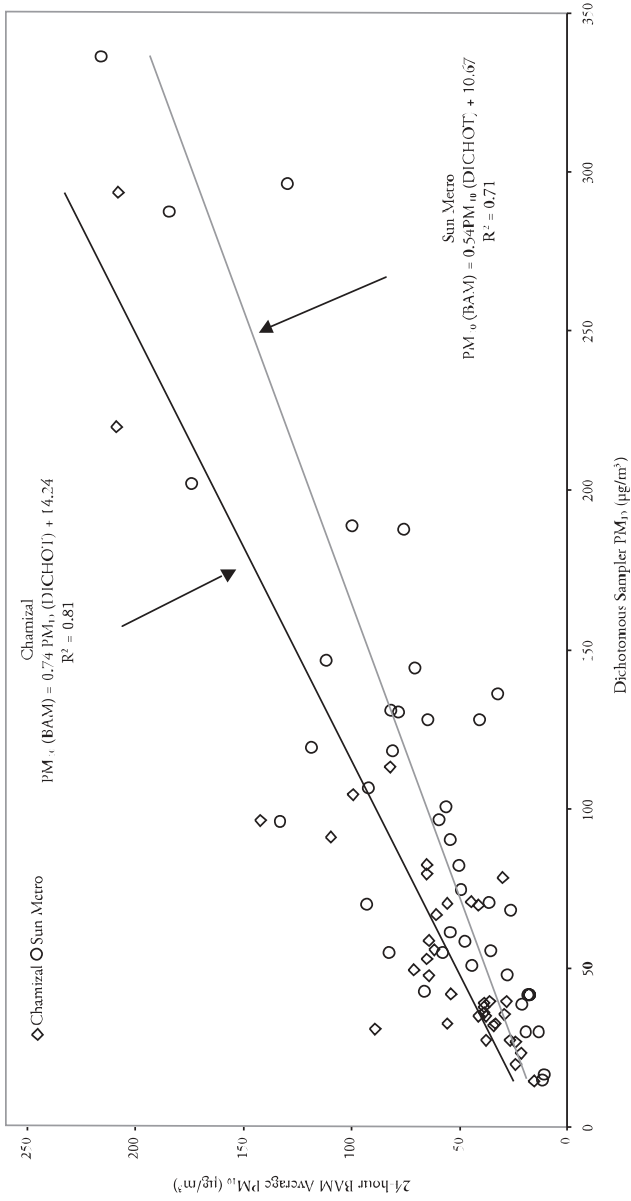
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by 20% to 40%. The difference became more pronounced at high concentrations. Previous studies on the compatibility between BAM and integrated samplers showed that BAM tends to observe lower PM concentrations (0.57 - 1.10 of that observed by sequential 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 $\pm 3\sigma$ interval) than other filter-based monitors (Watson, et al. 1998). Discrepancies between BAM and the dichotomous sampler at high PM₁₀ concentrations could be caused by the amount of particles with sizes greater than 10 μm (Hinds 1999) on the filter or the difference in humidity, calibration standards, and the beta attenuation coefficient for soot and geologic aerosols (Macias and Husar 1976; Jaklevic, et al. 1981; Wedding and Weigand 1993).

Temporal Variation of PM Concentrations

Figure 3 presents the time series plot of PM₁₀ and PM_{2.5} concentration for samples acquired on an every-other-day schedule at Chamizal. Regardless of the PM₁₀ concentrations, PM_{2.5} consists of only a small but steady fraction of PM₁₀, indicating that anthropogenic emissions (in the form of PM_{2.5}) in this area, are rather independent of the temporal variation of 24-hour average PM₁₀ concentrations. The temporal variation of PM concentrations at Sun Metro is shown in Figure 4. The average PM_{2.5} and PM₁₀ concentrations of 22.5 $\mu\text{g}/\text{m}^3$ and 109 $\mu\text{g}/\text{m}^3$ at Sun Metro are considerably higher than Chamizal's 11.0 $\mu\text{g}/\text{m}^3$ of PM_{2.5} and 56.9 $\mu\text{g}/\text{m}^3$ of PM₁₀. Table 1 summarizes the monthly average PM concentrations and temperatures obtained for the two El Paso sites. Both PM_{2.5} and PM₁₀ increase during winter months as temperature inversions increase in frequency and duration and wood burning intensifies. Because of the nearby highway and unpaved residential area in Ciudad Juárez, the PM concentrations at Sun Metro were expected to be higher than at Chamizal. Although it appears in Figure 4 that PM_{2.5} follows the pattern of PM₁₀ at Sun Metro, Table 2 shows that the 24-hour average PM₁₀ 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, respec-

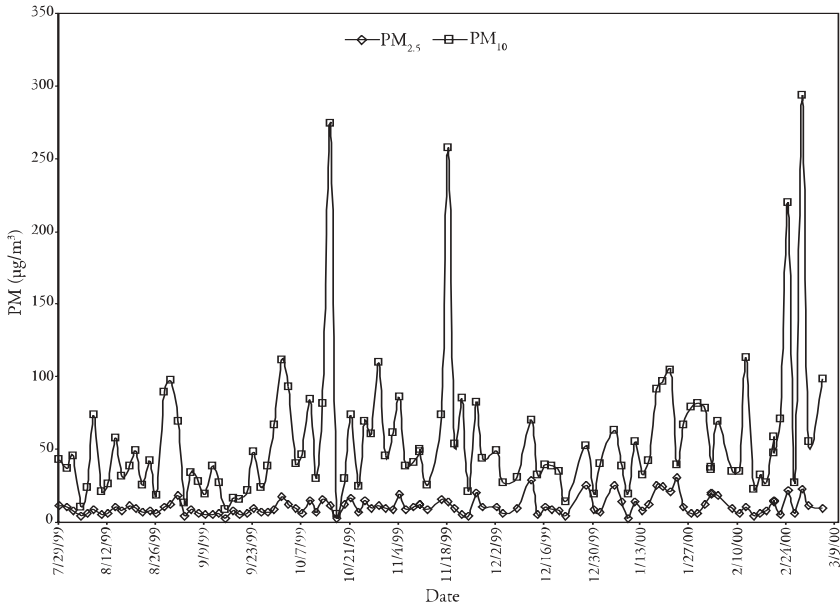
Figure 2. Comparison of PM₁₀ Concentrations Acquired by the Dichotomous and Beta Attenuation Monitors at Chamizal and Sun Metro for the Period of December 2, 1999, through March 7, 2000



Note: All concentrations were reported under STP conditions.
 Source: Authors

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Figure 3. Temporal PM₁₀ and PM_{2.5} Variation at Chamizal



Note: Line break refers to missing data.

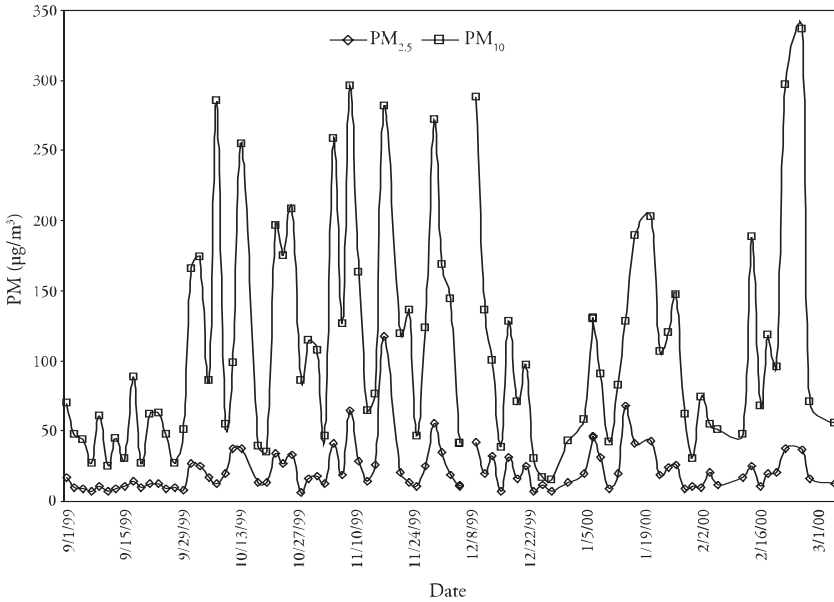
Source: Authors

tively). As mentioned previously, the slightly higher correlation between PM_{2.5} and PM₁₀ at Sun Metro could be caused by its proximity to a highway.

The average wintertime PM_{2.5}:PM₁₀ ratio at Chamizal, 0.22, agrees well with the EPA's annual mean of 0.23 at the same site. The ratios for both sites fall within the range (0.15 to 0.32) reported by EPA (Fitz-Simons, et al. 2000). These ratios are significantly lower than 0.5, a value reported for a typical arid city at Spokane, Wash., (Haller, et al. 1999) where the ratio varies from 0.20 to 0.37 during dust storms and 0.33 to 0.75 during non-dust storm days (Claibon, et al. 2000).

Based on the observed PM_{2.5}:PM₁₀ ratios and PM₁₀ concentrations, many of the high PM₁₀ days would have been attributed to fugitive dust generated by high winds. However, concurrent wind measurements at the sites do not support such an argument. For

Figure 4. Temporal PM Variations at Sun Metro



Note: Line break refers to missing data.

Source: Authors

example, two of the highest 24-hour PM₁₀ 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 µg/m³ and 14.7 µg/m³, which resulted in PM_{2.5}:PM₁₀ ratios of 0.04 and 0.06. The average wind speeds for these two days, however, were not considered high—4.3 meters per second (m/s) (with occasional gusts up to 8.9 m/s) and 2.8 m/s, respectively. Wind gusts reaching 8.9 m/s may have made a significant impact on the elevated PM₁₀ concentration on October 15. Additionally, on January 19 at Sun Metro, the average wind speed for the day was 3.2 m/s (with maximum wind gusts of up to 4.6 m/s) and the PM₁₀ and PM_{2.5} concentrations were 203 µg/m³ and 43.1 µg/m³, respectively. On February 12, the PM₁₀ and PM_{2.5} concentrations were 188 µg/m³ and 24.8 µg/m³, with average wind speed of 5.1 m/s and occasional wind gusts up to 10.3 m/s. When wind gusts reach levels of 13.1 m/s, as on February 24, the PM₁₀ and PM_{2.5}

Table 1. Summary of 24-Hour-Average PM Concentrations ($\mu\text{g}/\text{m}^3$) and Temperatures ($^{\circ}\text{F}$) at the Two El Paso Sites

Month	Chemical			Sun Metro		
	PM _{2.5} \pm STD	PM ₁₀ \pm STD	Temp.	PM _{2.5} \pm STD	PM ₁₀ \pm STD	Temp.
August 1999	8.6 \pm 2.4	43.5 \pm 24.6	84.5	No sample collected		
September 1999	7.2 \pm 3.6	31.5 \pm 18.4	78.5	10.5 \pm 2.7	47.8 \pm 18.8	77.1
October 1999	11.2 \pm 4.3	73.8 \pm 61.8	68.0	22.6 \pm 9.9	138.9 \pm 76.9	66.6
November 1999	11.5 \pm 4.6	69.2 \pm 58.2	60.9	34.6 \pm 28.8	155.8 \pm 88.5	59.3
December 1999	11.6 \pm 8.0	37.3 \pm 15.8	47.3	18.2 \pm 11.0	85.2 \pm 73.3	45.9
January 2000	12.7 \pm 7.5	58.2 \pm 26.0	53.4	28.4 \pm 17.5	106.4 \pm 50.5	51.6
February 2000	12.5 \pm 6.7	75.1 \pm 78.5	57.5	21.5 \pm 9.4	133.0 \pm 106.0	55.8
Average	10.95	56.9		22.5	109.0	

Source: Authors

Table 2. Summary of 24-Hour-Average Winter Month PM Concentrations ($\mu\text{g}/\text{m}^3$) at All Sites

UTEP Study Average Values (January 3 through March 7, 2000)							
Site Name	PM _{2.5} ($\mu\text{g}/\text{m}^3$)	PM _{2.5-10} ($\mu\text{g}/\text{m}^3$)	PM ₁₀ ($\mu\text{g}/\text{m}^3$)	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 \pm S.D.	Avg \pm S.D.	Avg \pm S.D.	Avg \pm S.D.			
Chamizal ^a	12.6 \pm 6.50	57.7 \pm 54.7	70.3 \pm 57.9	0.22 \pm 0.12	0.21	0.97	
Sun Metro ^a	23.1 \pm 14.2	90.0 \pm 71.0	113.0 \pm 79.2	0.23 \pm 0.10	0.28	0.97	
Club 20-30 ^b	20.0 \pm 11.5	36.0 \pm 17.0	56.3 \pm 26.0	0.36 \pm 0.10	0.73	0.87	
Advance Transformer ^b	50.9 \pm 59.3	146.0 \pm 68.5	197.0 \pm 107.0	0.23 \pm 0.11	0.56	0.67	
Misión ^b	26.8 \pm 11.6	142.0 \pm 50.7	169.0 \pm 58.2	0.16 \pm 0.60	0.49	0.97	

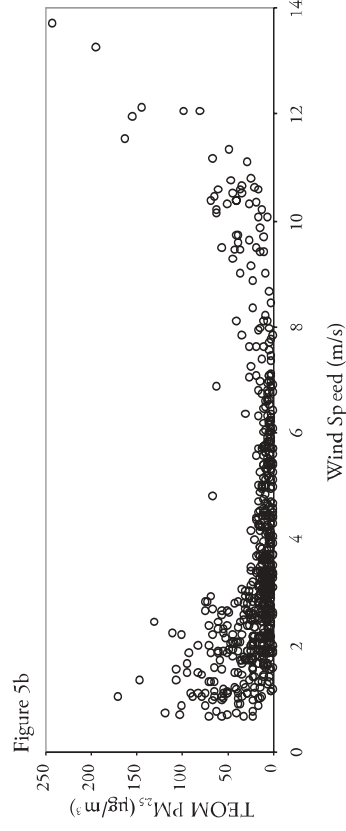
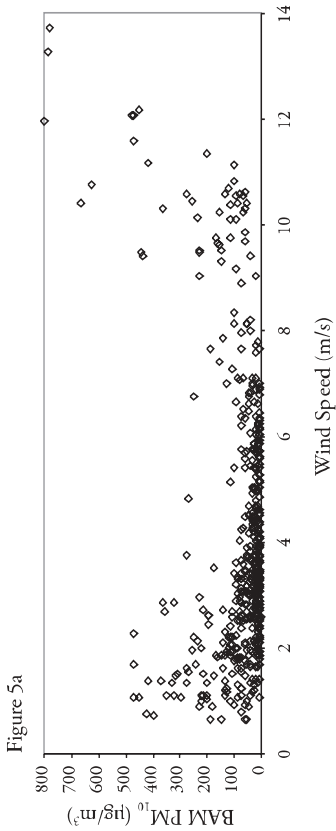
Notes: ^aEl Paso; ^bCiudad Juárez
Source: Authors

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concentrations reached $337 \mu\text{g}/\text{m}^3$ and $37.2 \mu\text{g}/\text{m}^3$, respectively. The $\text{PM}_{2.5}:\text{PM}_{10}$ ratio was 0.21 for January 19, 0.13 for February 12, and dropped to 0.11 on February 24, which is consistent with the changes in wind speed and maximum wind gusts.

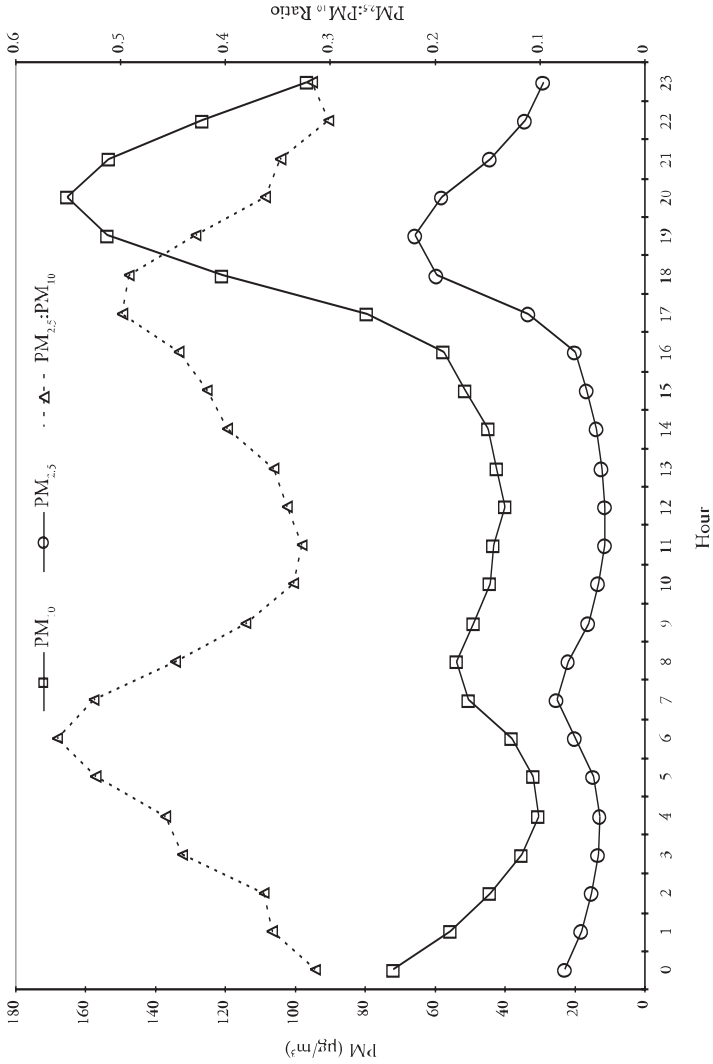
The low-wind-high-PM and high-wind-high-PM phenomena have been observed at several locations and throughout the year in the airbasin (Becerril, et al. 1999). Figure 5, based on the hourly BAM PM_{10} and TEOM $\text{PM}_{2.5}$ data (TNRCC 1999d; 1999e), shows that hours with low or extremely high wind speeds (exceeding the wind erosion threshold wind speed of approximately 7 m/s) tend to yield higher PM concentrations than hours with light-to-moderate wind speeds. Furthermore, the hourly PM data show a strong diurnal pattern. Both $\text{PM}_{2.5}$ and PM_{10} peak at two distinct time intervals in Figure 6. 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 airbasin. Similar diurnal variations in PM_{10} were observed in southern California. Pronounced morning and evening peaks in PM_{10} were observed at urban and rural sites (Doloslager and Motallebi 1999). 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 (Doloslager and Motallebi 1999). Figure 6 also shows the average hourly $\text{PM}_{2.5}:\text{PM}_{10}$ ratio. It peaks at the same time intervals as $\text{PM}_{2.5}$ and PM_{10} but arrives one hour ahead of the $\text{PM}_{2.5}$ and two hours before the PM_{10} . The hourly $\text{PM}_{2.5}:\text{PM}_{10}$ ratios (0.3 ~ 0.6) observed by the continuous monitors appear to be much higher than the 24-hour averages (0.15 to 0.32) obtained by the authors' dichotomous samplers. The phenomenon is expected when the mass of $\text{PM}_{2.5}$ generated from anthropogenic/mobile sources remains steady while coarse PM mass, mostly associated with wind-blown dust, remains low during some low-wind hours. In addition, errors caused by measurement imprecision, systematic bias caused by different monitoring devices, characteristics of wind-direction related emissions, and dominance of $\text{PM}_{2.5-10}$ in PM_{10} during higher PM hours all could contribute to the discrepancies. Time-resolved PM monitoring and associated chemical specification during the peak

Figure 5. Relationship of Hourly PM_{10} and $PM_{2.5}$ with Wind Speed at Sun Metro from December 1, 1999, through February 28, 2000



Source: Authors

Figure 6. PM_{10} , $PM_{2.5}$, and $PM_{2.5}:PM_{10}$ Diurnal Variation at Sun Metro from December 1, 1999, to February 28, 2000



Source: Authors

hours would provide further information for understanding the causes of the low daily $PM_{2.5-10}:PM_{10}$ ratios and controlling the PM pollution in the airbasin.

Spatial Variation of PM Concentrations

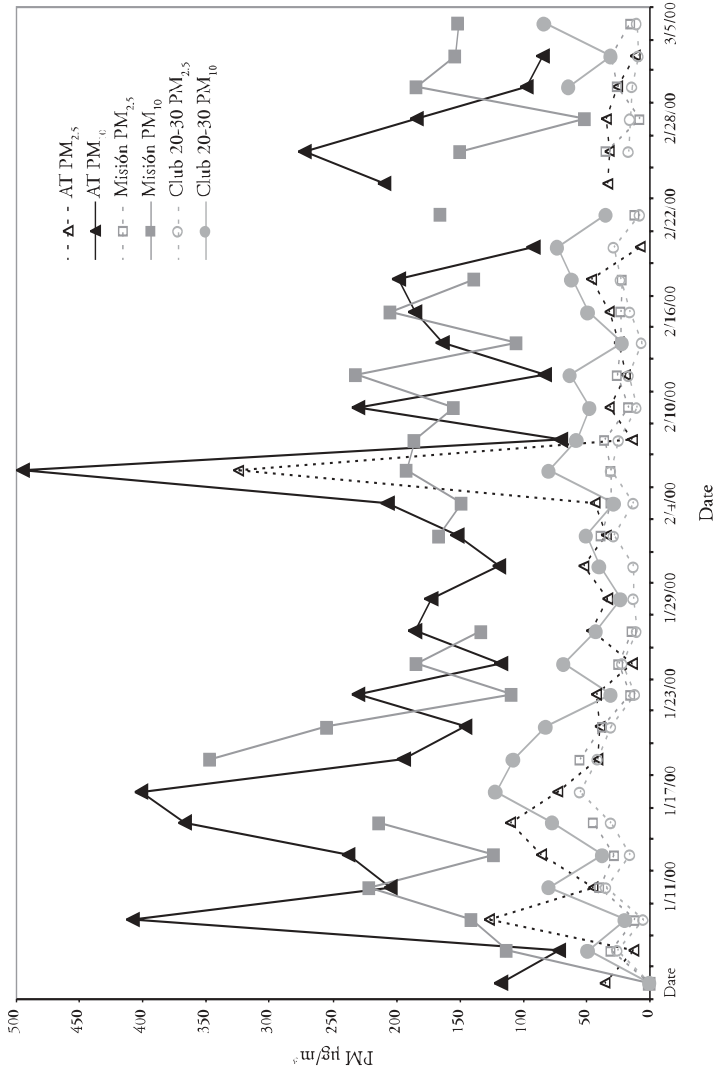
Figure 7 contains the temporal variation of 24-hour PM_{10} and $PM_{2.5}$ at the three Ciudad Juárez sites. The $PM_{2.5}$ concentrations visibly followed the PM_{10} trend. At the Ciudad Juárez downtown site (Club 20-30), the PM_{10} concentration is consistently lower than what was observed at other Ciudad Juárez sites. However, the average $PM_{2.5}:PM_{10}$ ratio, 0.36 with a Φ value of 0.11, appears to be the highest among all U.S. and Mexican sites, obviously affected by the increased anthropogenic (most likely the mobile) emissions in downtown Ciudad Juárez.

At the Misión site, it is expected that the PM_{10} concentration will 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 $142 \mu\text{g}/\text{m}^3$, a value much higher than that monitored in El Paso or downtown Ciudad Juárez. The high PM concentrations could be attributed to a cement factory located in the vicinity of the site 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 Φ value of 0.06), is significantly lower than at other sites and is a good indication of the dominance of PM pollution by geologic sources. Table 2 shows that $PM_{2.5-10}$ dominates the PM_{10} at the Misión site 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 $50.9 \mu\text{g}/\text{m}^3$ and PM_{10} concentration of $197 \mu\text{g}/\text{m}^3$ are the highest of all sites (Table 2), reflecting the unique mixed emission sources (brick kilns, automobiles, unpaved roads, and industrial sources) in the immediate vicinity of the site. For the Ciudad Juárez 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 Ciudad Juárez than in El Paso.

PM pollution in the area appears to be dominated by $PM_{2.5-10}$ and increases from El Paso toward the outskirts of Ciudad Juárez. $PM_{2.5-10}$ is likely to be fugitive dust generated by wind erosion

Figure 7. Temporal Variation of PM_{10} and $PM_{2.5}$ at the Ciudad Juárez Sites



Note: Line break refers to missing data.
Source: Authors

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(when wind speeds exceeded 7 m/s) from bare soil or by vehicular movement/mechanical disturbance on paved or unpaved surfaces. 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-hour averaged PM_{10} concentrations in the airbasin. 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 airbasin.

Elemental Analysis

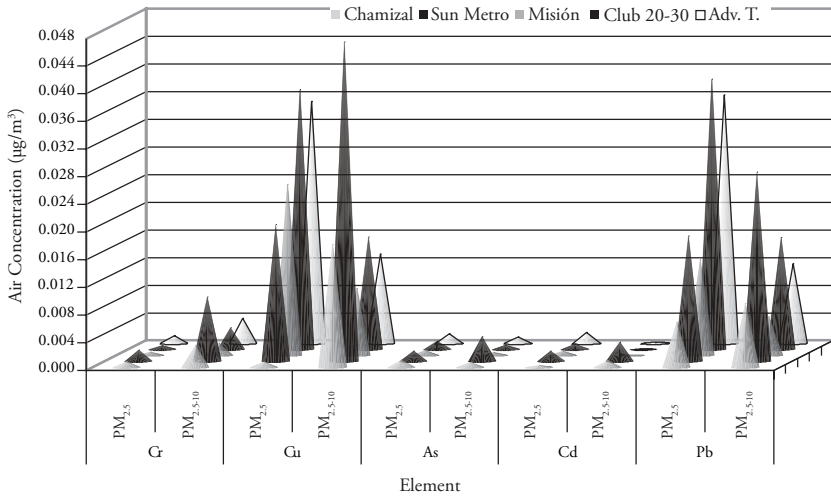
A total of 149 filters collected at the five sites were analyzed using XRF for rapid evaluation of the elemental composition of PM. XRF analysis was performed for samples collected at Chamizal and Sun Metro for the month of September 1999 and from December 2, 1999, to March 5, 2000. At the Ciudad Juárez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

Element Concentrations

Figure 8 shows the average ambient toxic trace element concentrations (copper, chromium, arsenic, cadmium, and lead) at all sites. These elements were selected for their associations with the operations of local industrial sources. Concentrations for the five indicator elements were higher in $PM_{2.5-10}$ than in $PM_{2.5}$ for the El Paso sites, but lower (except chromium) in $PM_{2.5}$ than in $PM_{2.5-10}$ for the Ciudad Juárez sites. This observation is the opposite of 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 Ciudad Juárez could be the reason for higher trace element concentrations in $PM_{2.5}$. Nevertheless, toxic trace elements in the air of Paso del Norte are relatively low compared to 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 (Schroeder, et al. 1987).

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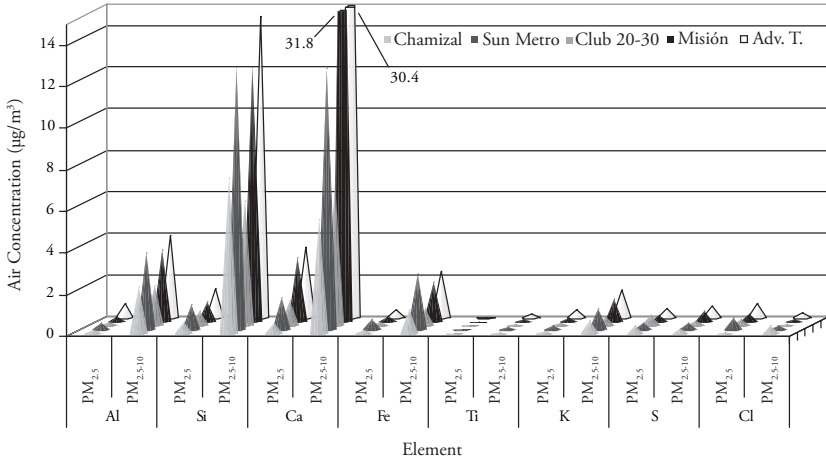
Figure 8. Average Toxic Trace Element Concentrations at All Sites



Source: Authors

Geologic elements (aluminum [Al], silicon [Si], calcium [Ca], iron [Fe], titanium [Ti], and potassium [K]) appear to dominate the coarse fraction of PM₁₀ (Figure 9). These elements are expected to be of higher concentrations because low PM_{2.5}:PM₁₀ ratios and high correlations between PM_{2.5-10} and PM₁₀ were observed at all sites. Based on the results of the XRF analysis, geologic elements account for 35% of PM_{2.5-10} and 12% of PM_{2.5} concentrations. PM concentrations at all Ciudad Juárez sites, particularly the rural Misión site, are heavily weighted by the geologic elements, signifying the impacts of unpaved roads and the surrounding desert on local air quality. The central Ciudad Juárez site, which is located far from unpaved roads and the bare soil of the desert, showed low concentrations for all geologic elements.

Figure 9. Average Element Concentrations of Geologic Origin, Chlorine (Cl), and Sulfur (S) at All Sites



Source: Authors

Figure 9 also shows that sulfur concentrations are low but similar in the fine and coarse fractions of PM. Potential emission sources in the region for sulfur are fuel combustion and re-entrainment of fallout from past smelting of sulfide-containing ores. Occasional high chlorine concentrations (not seen in the average concentration) were detected in PM_{2.5}, indicating the existence of possible anthropogenic sources of chlorine-containing substances. Chlorine levels at Sun Metro and Advance Transformer appeared to be higher than at other areas in the airbasin. 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.

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PM Trends

Tables 3 and 4 compare elemental composition of the $PM_{2.5}$ and $PM_{2.5-10}$ observed in this study to those 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. The laboratory procedures, calibration standards, instrument precisions, and detection limits for the three studies were identical or similar and are documented by DRI (Watson, et al. 1999) or available in the literature (Schroeder, et al. 1987). Although the comparison may still include uncertainties, it provides the best available information of historical PM data for the airbasin.

In general, arsenic, chromium, and lead in either $PM_{2.5}$ or $PM_{2.5-10}$ were lower in 1997 and 2000 than a decade ago at the two El Paso sites. Arsenic and chromium levels were consistently low in the airbasin throughout the study period, which may reflect the closure of a local copper smelting operation. Levels of lead and copper, although reduced, are still high in the airbasin. The mean concentration of almost every elemental composition decreased from 1990 to 2000 at both El Paso sites (Table 3). $PM_{2.5}$ lead concentrations are significantly lower today than in the previous studies. Reasons for the lower lead concentration lie in the elimination of lead from gasoline (eliminated recently in Ciudad Juárez) and the shutdown of a major smelting operation in the city. Arsenic and other smelter emissions have experienced the same decrease in concentration as lead. $PM_{2.5}$, chlorine, and sulfur concentrations have also experienced decreases in concentration.

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Table 3. Comparison of the UTEP Winter Study PM_{2.5} Elemental Composition to Those of the 1990 and 1997 TNRCC Studies

Element	Chamizal		Sun Metro		Advance Transformer	Club 20-30	Misión	Central El Paso
	UTEP Study	1990 TNRCC Study	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	1997 TNRCC Study*
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³
Sodium	64.0	<IDL	54.0	<IDL	83.0	54.0	66.0	18.0
Magnesium	41.0	<IDL	69.0	<IDL	75.0	43.0	73.0	53.0
Aluminum	190.0	440.0	357.0	497.0	761.0	218.0	285.0	243.0
Silicon	593.0	440.0	1264.0	1071.0	1436.0	726.0	1010.0	928.0
Phosphorus	2.0	<IDL	2.0	<IDL	1.0	2.0	2.0	1.0
Sulfur	409.0	1169.0	341.0	1349.0	492.0	514.0	374.0	0.1
Chlorine	89.0	565.0	625.0	1741.0	742.0	349.0	405.0	594.0
Potassium	128.0	186.0	217.0	365.0	381.0	183.0	242.0	362.0
Calcium	542.0	559.0	1540.0	1989	3411.0	1257.0	3063.0	191.0
Titanium	8.0	10.0	19.0	20.0	28.0	11.0	18.0	1407.0
Vanadium	1.0	7.0	1.0	9.0	1.0	1.0	1.0	20.0
Chromium	0.4	4.0	1.0	5.0	1.0	0.0	1.0	3.0
Manganese	4.0	13.0	9.0	12.0	15.0	6.0	11.0	1.0
Iron	231.0	179.0	508.0	411.0	397.0	243.0	291.0	9.0
Cobalt	0.1	<IDL	0.1	<IDL	0.3	0.0	0.1	324.0
Nickel	0.2	<IDL	0.1	<IDL	1.0	0.3	0.4	1.0
Cooper	15.0	49.0	22.0	119.0	35.0	25.0	38.0	1.0
Zinc	24.0	90.0	38.0	242.0	159.0	98.0	73.0	61.0
Gallium	0.0	<IDL	0.0	<IDL	0.0	0.0	0.0	64.0
Arsenic	1.0	51.0	1.0	94.0	1.0	1.0	1.0	0.0
Selenium	0.0	6.0	0.0	21.0	0.0	0.0	0.1	19.0
Bromine	7.0	33.0	1.0	38.0	52.0	14.0	16.0	8.0
Rubidium	0.3	<IDL	1.0	<IDL	1.0	0.5	1.0	9.0
Strontium	3.0	3.0	6.0	8.0	10.0	5.0	7.0	1.0

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Table 3. continued

Element	Chamizal		Sun Metro		Advance Transformer	Club 20-30	Misión	Central El Paso
	UTEP Study	1990 TNRCC Study	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	1997 TNRCC Study*
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³
Yttrium	0.2	<IDL	0.4	<IDL	0.3	0.3	0.2	5.0
Zirconium	1.0	<IDL	1.0	<IDL	1.0	1.0	1.0	0.0
Molybdenum	0.1	<IDL	0.3	<IDL	0.2	0.1	0.2	1.0
Palladium	0.3	<IDL	0.5	<IDL	1.0	1.0	1.0	1.0
Silver	0.1	<IDL	0.3	<IDL	0.2	1.0	0.0	1.0
Cadmium	0.3	5.0	1.0	8.0	2.0	1.0	1.0	1.0
Indium	0.1	<IDL	1.0	<IDL	1.0	1.0	0.0	2.0
Tin	1.0	3.0	3.0	7.0	3.0	3.0	3.0	1.0
Antimony	2.0	8.0	14.0	18.0	23.0	11.0	15.0	3.0
Barium	17.0	7.0	22.0	12.0	21.0	22.0	18.0	8.0
Lanthanum	10.0	<IDL	12.0	<IDL	9.0	15.0	12.0	9.0
Gold	0.0	<IDL	0.0	<IDL	0.0	0.0	0.0	0.0
Mercury	0.0	<IDL	0.0	<IDL	0.0	0.0	0.0	0.0
Thallium	0.0	<IDL	0.1	<IDL	0.1	0.0	0.1	0.0
Lead	7.0	188.0	22.0	301.0	36.0	14.0	39.0	37.0
Uranium	0.0	<IDL	0.0	<IDL	0.1	0.1	0.1	0.0

Notes: 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.

*Only 17 samples were analyzed.

<IDL = Less than instrument detection limits

ng/m³ = nanograms per cubic meter

Source: Authors

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Table 4. Comparison of Elemental PM_{2.5-10} Between Those of the 1990 TNRCC Study and the UTEP Winter Study

Element	Chamizal		Sun Metro	Advance Transformer	Club 20-30	Misión
	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	UTEP Study
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³
Sodium	126.0	<IDL	92.0	162.0	73.0	153.0
Magnesium	179.0	<IDL	254.0	324.0	149.0	355.0
Aluminum	2233.0	934.0	3729.0	3990.0	1919.0	3496.0
Silicon	7491.0	4242.0	12652.0	14525.0	606.0	12316.0
Phosphorus	14.0249.0	<IDL	38.0	64.0	28.0	64.0
Sulfur	249.0	283.0	335.0	622.0	265.0	569.0
Chlorine	396.0	138.0	215.0	284.0	110.0	183.0
Potassium	665.0	614.0	1071.0	1397.0	487.0	1080.0
Calcium	5500.0	6672.0	12627.0	30365.0	6918.0	31819.0
Titanium	90.0	100.0	150.0	200.0	71.0	159.0
Vanadium	1.0	6.0	1.0	3.0	1.0	4.0
Chromium	3.0	12.0	10.0	4.0	2.0	3.0
Manganese	24.0	36.0	49.0	50.0	17.0	39.0
Iron	1187.0	1253.0	2714.0	2282.0	852.0	1932.0
Cobalt	1.0	<IDL	1.0	3.0	0.2	1.0
Nickel	1.0	<IDL	2.0	3.0	1.0	3.0
Cooper	18.0	57.0	36.0	13.0	10.0	16.0
Zinc	30.0	49.0	51.0	70.0	68.0	49.0
Gallium	0.0	<IDL	0.0	0.0	0.0	0.0
Arsenic	1.0	7.0	3.0	1.0	0.0	1.0
Selenium	0.0	1.0	0.0	0.1	0.0	0.0
Bromine	1.0	6.0	5.0	4.0	2.0	3.0
Rubidium	3.0	33.0	5.0	7.0	2.0	5.0
Strontium	20.0	27.0	38.0	78.0	21.0	74.0

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Table 4. continued

Element	Chamizal		Sun Metro	Advance Transformer	Club 20-30	Misión
	UTEP Study	1990 TNRCC Study	UTEP Study	UTEP Study	UTEP Study	UTEP Study
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³
Yttrium	1.0	<IDL	2.0	2.0	1.0	2.0
Zirconium	5.0	4.0	8.0	11.0	3.0	8.0
Molybdenum	1.0	<IDL	2.0	2.0	0.0	2.0
Palladium	1.0	<IDL	0.0	2.0	0.0	7.0
Silver	1.0	<IDL	2.0	0.0	0.0	0.0
Cadmium	1.0	3.0	3.0	0.0	0.0	0.0
Indium	0.4	<IDL	0.0	3.0	0.3	2.0
Tin	2.0	6.0	2.0	0.0	1.0	2.0
Antimony	2.0	1.0	1.0	3.0	2.0	4.0
Barium	46.0	40.0	64.0	87.0	32.0	57.0
Lanthanum	7.0	<IDL	13.0	3.0	12.0	3.0
Gold	0.0	<IDL	0.0	0.0	0.0	0.0
Mercury	0.0	<IDL	0.2	0.2	0.0	0.0
Thallium	0.1	<IDL	1.0	1.0	0.0	1.0
Lead	9.0	55.0	23.0	12.0	6.0	16.0
Uranium	0.1	<IDL	0.4	0.3	0.1	1.0

Notes: Samples from the 1990 TNRCC study and the UTEP study were collected with dichotomous samplers. All samples were analyzed by the XRF method.

*TNRCC did not report element concentrations for PM_{2.5-10} samples in 1990.

<IDL = Less than instrument detection limits

ng/m³ = nanograms per cubic meter

Source: Authors

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The student-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 seem to decrease over the past decade, the trend cannot be established because of significant data scattering ($1.5 > F/\text{Mean} > 0.5$). For example, aluminum concentrations in El Paso decreased from an average of $0.47 \mu\text{g}/\text{m}^3$ in 1990 to $0.27 \mu\text{g}/\text{m}^3$ in 2000 and calcium decreased from $1.27 \mu\text{g}/\text{m}^3$ in 1990 to $1.04 \mu\text{g}/\text{m}^3$ in 2000, yet the trend cannot be established based on the data. Based on the paired student-t tests of three data sets for the six geologic elements, it appears that the geologic elements associated with $PM_{2.5}$ in the Paso del Norte air remain at the same levels as in the past decade. Chlorine, however, shows 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 example, arsenic concentration in $PM_{2.5}$ decreased by 57-fold (from $0.073 \mu\text{g}/\text{m}^3$ to $0.0013 \mu\text{g}/\text{m}^3$) and lead by 18-fold (from $0.24 \mu\text{g}/\text{m}^3$ to $0.014 \mu\text{g}/\text{m}^3$) in El Paso.

The decrease in the $PM_{2.5}$ mass concentration is also obvious. $PM_{2.5}$ decreased from $32.8 \mu\text{g}/\text{m}^3$ and $55.6 \mu\text{g}/\text{m}^3$ in 1990 at Chamizal and Sun Metro to $11.0 \mu\text{g}/\text{m}^3$ and $22.5 \mu\text{g}/\text{m}^3$ in 2000, respectively. Consequently, the fraction of geologic elements in $PM_{2.5}$ (based on the sum of aluminum, silicon, calcium, iron, titanium, and potassium) 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 $PM_{2.5}$ concentration also increased. The ratio of copper 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 chromium and copper) in the region decreased less impressively from 1990 to 1997, but rather significantly (except that for chromium) until 2000 after a major smelter halted its operations in early 2000. 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.

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Table 5. Fraction of Trace Metals in PM_{2.5}

Element	1990	1997	UTEP Study				
	TNRCC Study	TNRCC Study	El Paso, Texas		Ciudad Juárez, Mexico		
	Chamizal/Sun Metro	Central El Paso	Chamizal	Sun Metro	Advanced Transformer	Misión	Club 20-30
Chromium	0.001	0.004	0.005	0.011	0.001	0.001	0.002
Cooper	0.190	0.270	0.110	0.098	0.068	0.124	0.104
Arsenic	0.164	0.086	0.009	0.009	0.003	0.004	0.002
Cadmium	0.015	0.008	0.003	0.006	0.003	0.003	0.003
Lead	0.552	0.163	0.046	0.078	0.070	0.122	0.055

Source: Authors

Table 4 compares the composition of PM_{2.5-10} obtained in the present study to those measured in 1990. Concentrations of the geologic elements associated with PM_{2.5-10} are indistinguishable between 1990 and 2000, while the trace elements decreased significantly from 1990 to 2000. 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, individual geologic elements account for about 35% of the mass for the coarse fraction of PM₁₀. Because the majority of metals in this study are related to geologic/crustal material, they are predominantly present as oxides (such as Al₂O₃, SiO₂, CaO, FeO/Fe₂O₃, and TiO₂). To account for the dominant forms of these elements, the mineral mass can be estimated by the following equation (Seinfeld 1986):

$$\text{Mineral mass} = (2.2 \times \text{Al}) + (2.49 \times \text{Si}) + (1.63 \times \text{Ca}) + (2.42 \times \text{Fe}) + (1.94 \times \text{Ti})$$

Alternatively, the mineral mass may be estimated from an indicator element (Taylor and McLennan 1995) by multiplying, for example, the aluminium concentration by 12.4 (while not including data

for silicon, calcium, etc.). Using these algorithms and the values presented in Tables 2 and 4, the mineral materials could account for up to 70% of the mass for the coarse fraction of PM_{10} .

Chlorine 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 Ciudad Juárez because of its location and the prevailing southeast-northwest winds. The fact that chlorine concentrations are high in $PM_{2.5}$ indicates the existence of local chlorine sources in the southwest region of the airbasin. Further investigation of the seasonal and spatial variations of chlorine concentrations as well as the locations of these sources may provide answers to the unexplained high ozone concentrations in the region.

SUMMARY AND CONCLUSIONS

The seven-month study of PM concentrations in El Paso shows that the average $PM_{2.5}$ and PM_{10} concentrations are $11 \mu\text{g}/\text{m}^3$ and $57 \mu\text{g}/\text{m}^3$ for Chamizal and $22 \mu\text{g}/\text{m}^3$ and $109 \mu\text{g}/\text{m}^3$ for Sun Metro, respectively. The PM_{10} concentration increases toward the suburban area of Ciudad Juárez while $PM_{2.5}$ peaks in areas 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-hour average $PM_{2.5}$ concentration is maintained 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 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, both organic and elemental (in progress), compositions of air samples could provide mitigation alternatives for controlling PM pollution in the El Paso-Ciudad Juárez border region.

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ENDNOTE

¹ aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), gallium (Ga), arsenic (As), selenium (Se), bromine (Br), rubidium (Rb), strontium (Sr), yttrium (Y), zirconium (Zr), molybdenum (Mo), palladium (Pd), silver (Ag), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), barium (Ba), lanthanum (La), gold (Au), mercury (Hg), thallium (Tl), lead (Pb), and uranium (U).

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