IV

Characterization of Airborne Particulate Matter in the Paso del Norte Air Quality Basin: Morphology and Chemistry

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Abstract

Five sites in the twin cities of El Paso, Tex.-Ciudad Juárez, Chih., with different topographical, industrial, and traffic conditions were selected for a detailed analysis of particulate matter (PM) from 24-hour, Sierra Anderson dichotomous samplers. Filter samples were analyzed by scanning electron microscopy for their morphology and X-ray fluorescence for elemental composition. The studies illustrate how individual particle morphology and chemical analysis can be used to identify sources and complements the source attribution studies in Chapter VI.

Five observations have been made from this study:

- Road conditions (paved or unpaved) and traffic volume influence the levels of both fine and coarse PM levels
- Industrial activities also dictate the composition of PM
- Coarse fraction of PM_{10} is strongly associated with high wind speed and mostly originates from soil

- Carbonaceous material with various forms is ubiquitous, as anticipated, although pinpointing potential sources is a difficult task
- Particles in aggregated forms of smaller components are one major component

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Caracterización de Materia Particulada Atmosférica en la Cuenca del Paso del Norte: Morfología y Química

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Resumen

Cinco sitios en las ciudades de El Paso-Ciudad Juárez con diferentes condiciones topográficas, industriales, y de tráfico fueron seleccionadas para un análisis detallado de materia particulada (PM) durante 24 horas con muestreadores dicotómicos Sierra Anderson. Las muestras de los filtros fueron analizadas por microscopía electrónica de barrido para su morfología y mediante fluorescencia de rayos X para su composición elemental. Los estudios ilustran cómo la morfología individual de las partículas y el análisis químico pueden usarse para identificar fuentes y complementa los estudios de fuentes atribuidas del capítulo VI.

Se han hecho cinco observaciones en este estudio:

- Las condiciones de la carretera (pavimentada o terracería) y el volumen de tráfico influyen en el nivel de ambos niveles finos y gruesos de PM
- Las actividades industriales también determinan la composición de PM

- El fragmento grueso de PM_{10} es fuertemente asociado con velocidades altas de viento y en su mayor parte se origina del suelo
- El material carbonado en diversas formas es ubicuo, como era esperado, aunque el indicar fuentes potenciales de manera precisa es una tarea difícil
- Las partículas en formas agregadas de componentes más pequeños son un componente mayor

Introduction

As noted already in this volume, particulate matter (PM) is a complex issue that would be better understood by knowing the sources, physical characteristics, and chemical compositions of the components. PM characterization is also believed to be a critical step for reassuring the validity of currently imposed regulations and for finding efficient abatement programs.

To understand Paso del Norte's PM issues better, five strategic sites in the twin cities of El Paso, Tex.-Ciudad Juárez, Chih., were selected for collection purposes and a series of $PM_{2.5}$ and $PM_{2.5-10}$ filters were collected. Sets of $PM_{2.5}$ and $PM_{2.5-10}$ filters were submitted for characterization of physical properties such as morphology and size via scanning electron microscopy (SEM). The SEM study was followed by analyses of elemental constituents with X-ray fluorescence (XRF) mounted on the microscope. The studies were conducted at five sites: Chamizal, Sun Metro, Club 20-30, Advanced Transformer, and Misión (the location and description of the sites are provided in Appendix Figure 1 [page 305]). Two dichotomous air samplers (Anderson Instruments) were placed at each of the two U.S. sites. One sampler was operated every other day to collect 24-hour air samples and the other was operated selectively for collocated (duplicate) samples. Only one dichotomous sampler was operated at each of the three Mexican sites. All samplers (except at the Misión site) were positioned at least eight feet away from the Texas Commission on Environmental Quality's (TCEQ) eight-foot tall instrument shacks with the inlet head standing five feet above the ground. The sampler at the Misión site was posi-

tioned on the roof of a one-story cinder block storage structure and the inlet head was five feet above the roof. The dichotomous air samplers had PM size cutoffs of $PM_{2.5}$ and PM_{10} (particulate matter that measures less than 2.5 micrometers [µm] or 10 µm or less, respectively, in diameter). However, these size cutoffs are based on a particle's aerodynamic size; a particle's morphology will affect whether a particle can pass into the dichotomous sampler. For example, some of the results in this section show particles greater than 2.5 micrometers (µm) in size being deposited on a $PM_{2.5}$ filter; this is consistent with the aerodynamic sizing cutoff of the dichotomous samplers.

Ten filters collected on January 15, 2000, at the five locations throughout the Paso del Norte airbasin were subjected to SEM and XRF. The study was performed with a Phillips Scanning Electron Microscope model XL30 equipped with an Energy Dispersive X-Ray Spectrometer (EDX) for elemental chemical analysis by XRF. Due to interference experienced using the filter supports, the filters were placed in a double roll of carbon and inside an aluminum pan for the analysis. Different representative areas were selected for each filter to perform the elemental chemical analysis. The observations were performed at 25 kilovolts (kV) of energy for electron acceleration with a 65 microampere (µA) emission current at high vacuum with varying amplifications. The chemical XRF analysis was performed at 25kV energy with 65 µA of current, obtaining the XRF spectra for different particles.

Results

Teflon filters were used for the 24-hour collection period. There is a visible and inherent difference in color—$PM_{2.5}$ is black and $PM_{2.5\text{-}10}$ is light brown to gray. One can make the assumption that each filter is loaded with different chemical constituents. Each constituent has a different density and therefore a different mass. $PM_{2.5}$ tends to contain more organic constituents while $PM_{2.5\text{-}10}$ is considered to be more geologic.

To determine the morphology of PM, a set of samples were subjected to SEM analyses. The selected specimens were collected at the five sites on January 15, 2000. Certain representative particles of

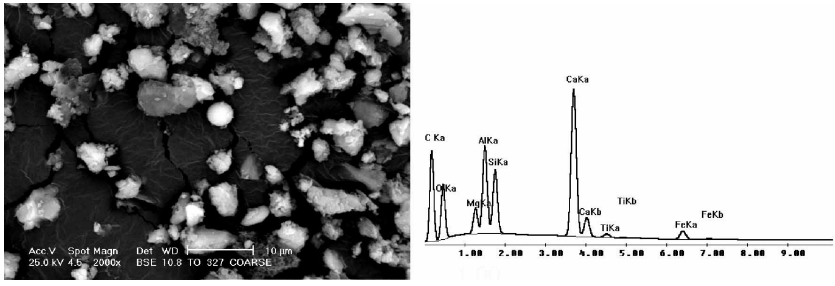
different shapes from each filter were subjected to XRF analyses for elemental determination. The Materials Science Division of the Instituto Nacional de Investigaciones Nucleare, located in Mexico City, conducted the analysis.

The SEM images showed that the shapes of the $PM_{2.5}$ particles were quite diverse, although the majority were irregularly shaped. Most of the PM ranged in size from 1 μm to 2.5 μm. Some of the particles were spherical, and some had a laminar shape, approximately 5 μm in size, with smaller particles adhered to the surfaces of the dominant particles. It is also notable that many particles were present in aggregated or cumulus forms. The cumulus particles formed long chains of up to 5 μm in longitudinal length. Representative electron micrographs are shown in Figures 1 and 2. Particle classes useful for identification include the following:

1. Soot particles. These are emitted by a wide range of combustors, including poorly operated furnaces, diesel engines, and forest fires. The soot particles typically consist of chains of primary particles with a characteristic dimension of 20 nanometers (nm) to 60 nm, such as those seen in Figure 3. The soot particles also occur as clusters (Figure 4). The XRF analysis of the cluster shows the dominance of carbon. It also shows that trace amounts of calcium (Ca) and sulfur (S) are a trait of diesel-generated soot. The inorganic content of the soot particle provides an indication of its source.
2. Spherical particles. Spherical particles such as those seen toward the middle of Figure 1 are typically associated with particles that have been formed in a high-temperature furnace, such as a coal-fired boiler. These are typically alumino-silicates, often with significant concentrations of iron that come from pyrites and other iron-containing minerals in coal. Smelting operations will also generate spherical particles, including elements specific to the ores being processed.
3. Cubical particles. Sodium chloride produced by the evaporation of saline solutions form cubical particles such as those seen in Figure 5, as confirmed by the elemental composition obtained using XRF.

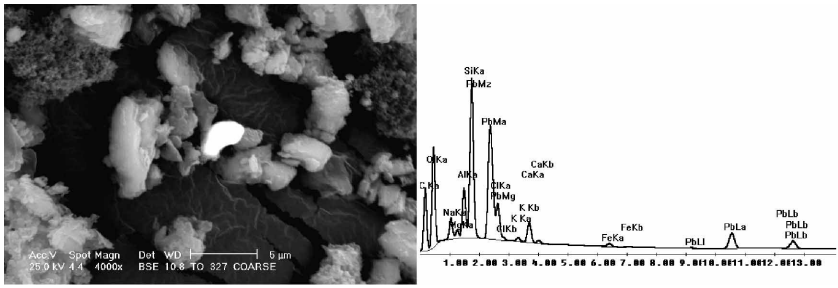
4. Irregularly shaped minerals. Crustal material suspended by the wind and particles generated during the processing of limestone and other minerals have irregular shapes indicative of the minerals being processed.
5. Cumulus Inorganic Particles. Agglomerates of smaller mineral particles of primary size of one micron to several microns were often observed. Cumulus particles were comprised of carbon, oxygen, silicon, calcium, aluminum, sodium, sulfur, chlorine, potassium, and iron (Figure 6). The origin of these is uncertain.

Figure 1. SEM Image with XRF of Spherical Particles from the Chamizal Site



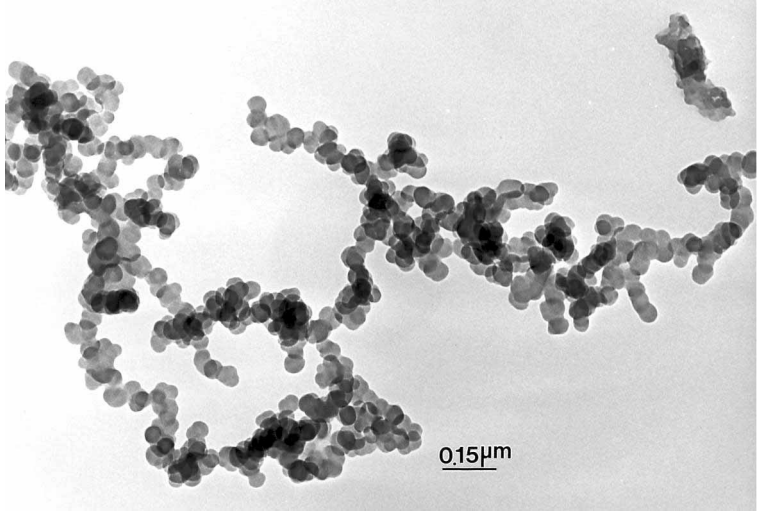
Source: Authors

Figure 2. SEM Image with XRF of Irregular Shiny Particles from the Chamizal Site



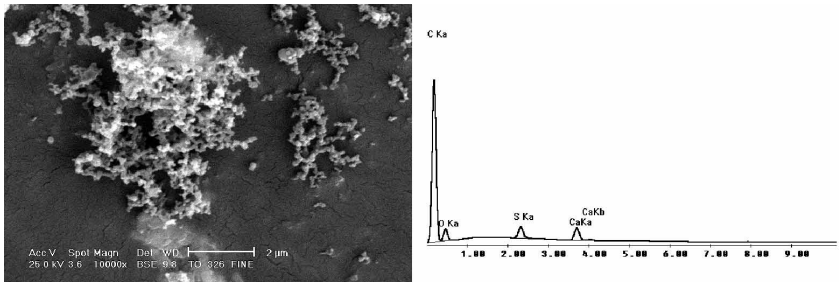
Source: Authors

Figure 3. Transmission Electron Microscopy (TEM) Image of Particles from a Diesel Engine



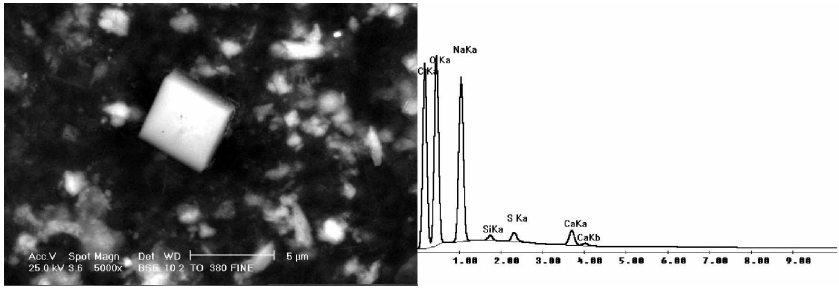
Source: Authors

Figure 4. SEM Image with XRF of Shiny Particles from the Chamizal Site



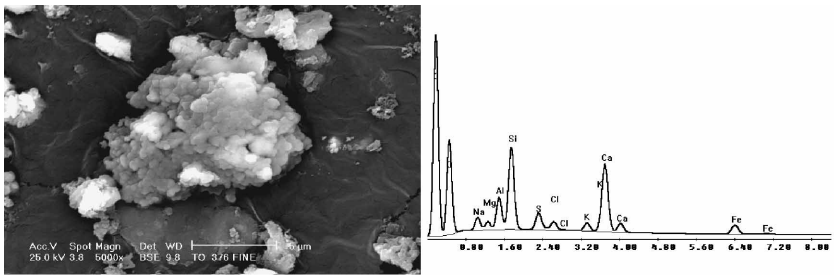
Source: Authors

Figure 5. SEM Image with XRF of Cubical Shaped Particles from the Misión Site



Source: Authors

Figure 6. SEM Image with XRF of Conglomerated Particles from the Club 20-30 Site



Source: Authors

The above classes of compounds were found at the five sites in amounts reflecting the local emissions sources. A summary of the observations at the different sites is presented below.

Samples Collected at Chamizal

The PM_{10} concentration at the Chamizal National Park site was 41.9 micrograms per cubic meter (µg/m³). The $PM_{2.5}$ concentration was 12.2 µg/m³, and the $PM_{2.5-10}$ concentration was 29.7 µg/m³. The average wind speed recorded for the day was 1.6 meters per second (m/s). The average wind gust for the day was 4.2 m/s and the maximum wind gust was 7.3 m/s.

The XRF elemental analysis determined that some spherical particles had a high iron content and others had high copper, titanium, or aluminum content. XRF analysis performed on laminar adhered particles indicates a high lead content. The lead and copper are indicative of metallurgical processing. Substantial amounts of carbon and calcium were found in the particles forming long chains, as would be expected in diesel soot. Sulfur was detected in the majority of analyzed particles.

From the SEM images of the $PM_{2.5-10}$ filter it was observed that particles were of various shapes, some spherical and some irregular. The size ranged from 0.5 µm to 11.0 µm. XRF performed on the particles of spherical shape found high contents of calcium, silicon,

and aluminum with low iron content, which is indicative of a high-temperature origin. Irregularly shaped particles, on the other hand, had high heavy metal content of elements such as lead and iron.

Samples Collected at Sun Metro

At the Sun Metro Bus Station Site, the PM_{10} concentration was 189 $\mu g/m^3$, the $PM_{2.5}$ concentration was 41.5 $\mu g/m^3$, and the $PM_{2.5-10}$ concentration was 148 $\mu g/m^3$. The average wind speed recorded for the day was 2.02 m/s. The average wind gusts for the day were 3.7 m/s with maximum hourly gusts of up to 4.9 m/s.

$PM_{2.5}$ particles observed from the SEM images ranged from 0.6 µm to 16 µm with various irregular shapes, including spherical. The larger particles appeared to be made up of clusters of smaller particles. In a recent study (Bang and Murr 2003), more than 70% of the particles collected from ambient air in the El Paso-Ciudad Juárez region were clusters of smaller particles. Chemical analysis determined high iron, silicon, and calcium contents, with small quantities of magnesium and sulfur in some of the particles. Irregularly shaped particles contained high levels of iron and low levels of sulfur.

SEM images of the $PM_{2.5-10}$ filters revealed that the size varied from 1 µm to 7.7 µm; the majority were of irregular shape and some had spherically shaped particles. It was observed that small particles were adhered to larger particles, and in fact, some large particles are made up of an accumulation of smaller particles. XRF analysis demonstrates that in general, particles are comprised mainly of carbon, oxygen, silicon, and low quantities of aluminum and calcium. Spherical particles contain high concentrations of iron, oxygen, and carbon. Cumulus particles had carbon and calcium with small quantities of sulfur and potassium, again indicative of diesel soot.

Samples Collected at Club 20-30 in Ciudad Juárez

At the Club 20-30 site, the PM_{10} concentration was 76.9 µg/m³ for the day, the $PM_{2.5}$ concentration was 31.1 µg/m³, and the $PM_{2.5-10}$ concentration was 45.5 µg/m³. The average wind speed recorded for the day was 0.84 m/s.

From the SEM images of the $PM_{2.5}$ filter it was observed that particles were of various shapes with sizes ranging from 0.8 µm to 20 µm. Most of the particles are of irregular shape, some were large spherical particles. Accumulation of particles of approximately 0.6 µm combined to form cumulus larger than 10 µm. Elemental analysis determined that the larger particles (those greater than 15 µm) exhibit carbon, oxygen, silicon, sodium, and calcium in substantial quantities. Cumulus inorganic particles were also observed (Figure 6).

The SEM images showed that the $PM_{2.5-10}$ particles were of diverse sizes and shapes. Spherical particles ranged from 2 µm to 3.9 µm, and rectangular particles ranged from 2.8 µm to 9 µm long. Others with semi-spherical shapes ranged up to 13.5 µm. Elemental analysis indicates that a large portion of the spherical particles contain elevated concentrations of carbon, oxygen, and silicon and lesser quantities of magnesium, sodium, aluminum, sulfur, calcium, and silicon. Rectangular particles, including cube-shaped particles, had high concentrations of sodium and chlorine, including carbon, oxygen, and a substantial concentration of iron.

Samples Collected at Advanced Transformer in Ciudad Juárez

The PM_{10} concentration at the Advanced Transformer site was 238 µg/m³. The $PM_{2.5}$ concentration was 85.8 µg/m³, and the $PM_{2.5-10}$ concentration was 152 µg/m³. The average wind speed recorded for the day was 0.9 m/s.

The SEM images of the $PM_{2.5}$ filter showed that the morphology of the particles was irregular. Also, there were particles that formed layers. The $PM_{2.5}$ particles ranged from 0.78 µm to 4 µm, with the larger particles formed by aggregation or agglomerations of smaller

particles. Elemental analyses on some irregularly shaped particles represented high concentrations of carbon and calcium. There were elevated portions of titanium accompanied by lower portions of iron in a spherical particle.

The SEM images of the $PM_{2.5-10}$ filter showed that the particles were of irregular shape and some particles had a cubical shape. The sizes ranged from 0.6 µm to 8 µm while the cubical particles, indicative of sodium chloride (NaCl), ranged from 0.6 µm to 1.9 µm. Small particles arranged together and simulating chains were comprised of high concentrations of calcium with lesser quantities of aluminum and silicon. Some irregularly shaped particles contained substantial portions of metals. Again, cube-shaped particles had substantial quantities of sodium, chlorine, and calcium.

Samples Collected at Misión in Ciudad Juárez

The PM_{10} concentration at the Misión Site was 214 µg/m^3. The $PM_{2.5}$ concentration was 44.3 µg/m^3, and the $PM_{2.5-10}$ concentration was 170 µg/m^3. Meteorological data were not available at this site.

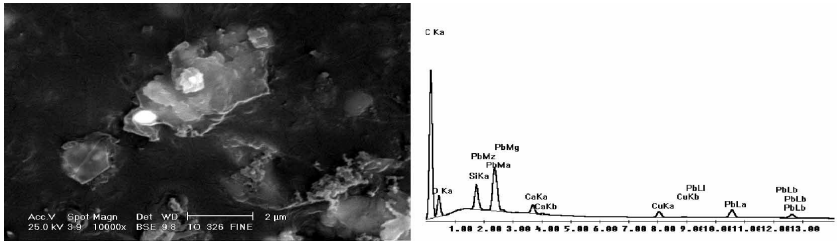
The SEM images of the $PM_{2.5}$ filter showed particles of various shapes, including irregular and spherical shapes. The sizes ranged from 0.6 µm to 1.2 µm. Other cubical shaped particles had a size range from 2 µm to 4.5 µm. Elemental analysis determined that, in general, particulates have high carbon, oxygen, silicon, and calcium contents. On the other hand, spherically shaped particles contained substantial quantities of iron. Cubical particles represent high sodium, oxygen, and carbon content and small sulfur content.

The SEM images of the $PM_{2.5-10}$ filter showed that the particles were of irregular shape, with sizes varying from 0.7 µm up to 11 µm. There were also distinct spherical particles with diameters from 1.6 µm to 5.6 µm. Cubical particles were also found on the coarse filter. Elemental analysis determined that those irregularly shaped particles, including those that were spherical, contained substantial quantities of calcium, silicon, oxygen, carbon, and sulfur. In addition, spherical particles represented high concentrations of lead, zinc, or iron, while the cubical particles presented sodium, aluminum, and calcium.

Discussion and Conclusions

Some samples collected at the Chamizal area showed layered structures with metallic particles of different sizes attached to their surfaces. Particles with layered structures of carbonaceous material are often present in ambient air (Bang and Murr 2002). Bang and Murr speculated that brake pads and linings or other graphitic materials used in various industries were a likely source of the particles with layered structures. Particles with a laminar-adhesion form contained several elements, predominantly lead, that attached on the surface of a parent particle (Figure 7). It is believed that lead elements are attached to the surface of the carbon particles in the air after they are generated from separate sources. Particles in aggregated forms with high carbon and silicon indicate an influence of various combustion activities, including automobiles. Unlike the previous case (Figure 7), the shiny particles with high carbon and sulfur are more likely to be generated from the same source without a significant time lapse.

Figure 7. SEM Image with XRF of Shiny Particles from the Chamizal Site



Source: Authors

Spherical coarse particles from the Chamizal area (Figure 1) resemble particles from natural sources, such as soil or disturbed roadsides, but are more homogeneous and regular. In Figure 2, the XRF of the coarse particles presents the mixture of elements from both natural and anthropogenic sources. The shiny particles are

probably lead with other elements mingled together. At the upper left corner of the picture, particles similar to the cumulus soot shown in Figure 4 are present.

A striking characteristic among the samples collected from the Sun Metro site when compared with those from Chamizal, regardless of their sizes and elemental compositions, is that a majority of the particles are aggregates or clusters of smaller-size components. As stated before, a similar observation was made in a more recent study (Bang and Murr 2003). In fact, the majority of the collected ultrafine PM observed under transmission electron microscopy was aggregates of much smaller particles.

Both fine and coarse particles collected from Club 20-30 show a higher percentage of elemental carbon than at other sites. The elemental composition of the particles in both categories from this site is unremarkable except that the majority seems to be suspended soil. Because the Club 20-30 site had the lowest wind speed among the five collection sites during the collection period, the elements shown in XRF studies are believed to best represent the particles generated locally. Similar forms of the conglomerated particles in Figure 6 also have been observed from the tailpipe of an old gasoline engine during a preliminary study (Bang 2003). One speculation was that, as shown in XRF data in Figure 6, carbonaceous particles intermingle with soil elements made available in the chamber during the internal combustion process.

As anticipated, the levels of both fine and coarse PM collected from Advanced Transformer, where industrial activities are more common than other sections of El Paso-Ciudad Juárez, were among the highest. The amount of carbonaceous material represented in a form of carbon in XRF is notable in these samples. The wide variation in composition and morphology (aggregates, layered structures, chains, etc.) of particles at this site are indicative of the diversity of industrial sources. The elemental composition of the layered structures shows that they are a mixture of carbonaceous material and soil components. The majority of soil components might have been added on the surfaces of carbonaceous particles produced by some industrial activities or automobiles.

The presence of some cubical particles shown in SEM pictures (sodium, calcium, and chlorine) at the Advanced Transformer site, the Club 20-30 site, and the Misión site indicate the possibility of a local source rather than long-range transfer of sodium chloride or calcium chloride, although long-range transfer from the Gulf of Mexico is a possibility. Identification of the source of chlorine or precursors of chlorine would not be an easy task, mainly due to the lack of monitoring procedures in Ciudad Juárez. However, the routine use of chlorine for disinfecting heavily concentrated healthcare buildings, including local hospitals, pharmacies, clinics, and public buildings in the Club 20-30 area, could be one major source for the high chlorine levels. Although, these are unlikely to react in the atmosphere to yield cubical sodium chloride crystals. At the time of this study, official data about chlorine use in industrial sectors were not available for Ciudad Juárez. The source identification of chlorine would be an interesting follow-up task for the future.

The presence of cement manufacturing factories in addition to unpaved roads in the heavily populated Misión site leads one to expect high levels of PM in both fine and coarse categories. The PM from this site is mostly from unpaved roads and cement factories and mixed with carbonaceous components from combustion sources located in nearby residential areas. The source of substantial quantities of iron in the PM collected at the Misión site is unclear.

Trace metal concentrations are lower today than historical values. They are mostly contained in spherically shaped particles in the $PM_{2.5}$ fraction and in irregularly shaped particles, presumably as coatings, in the $PM_{2.5-10}$ fraction. Misión had the highest lead and copper concentration in the $PM_{2.5}$ fraction, Sun Metro had the second highest levels of lead, and Sun Metro also ranked third for copper, which is expected because Sun Metro is situated nearby an old refinery. There is evidence that trace elements in $PM_{2.5}$ might be attributed to wind or mechanical erosion at some locations such as Sun Metro, but spherical shapes determined by SEM analysis suggest that trace metals in $PM_{2.5}$ are from smelting or combustion sources. On the other hand, Sun Metro had the highest lead and copper concentrations in $PM_{2.5-10}$, which were frequently associated with par-

ticles of an irregular shape. Given the site's location close to an old refinery, Sun Metro's $PM_{2.5-10}$ is likely influenced by wind or mechanical erosion.

Elements of geologic origin dominate the coarse fraction of PM_{10} and are persistent due to the abundance of unpaved roads, dry terrain, and high wind episodes, as can be seen in the high aluminum, silica, and calcium concentrations at all five sites. Misión, located in the foothills of the Sierra de Juárez Mountains; Advanced Transformer, located next to the brick kiln district with unpaved roads; and Sun Metro, located close to high geologic emission sources, had the highest silicon and calcium concentrations, as expected. In the fine fraction of PM_{10}, geologic particles were of irregular shape, which is opposite of what was observed with the trace metals, and highest at the sites close to unpaved roads, as at the Advanced Transformer and Misión sites.

The data from the five sites indicate that road conditions, industrial activities, and the volume of traffic in a region dictate the levels of both fine and coarse PM when weather-related factors are ruled out. The composition of fine and coarse PM seems to be influenced by the unique characteristics of each site.

Lead levels in both fine and coarse PM were high in the samples from the Chamizal site, which indicates that there may be a source of new lead generation, in addition to some pre-existing lead in the local environment. Automobiles crossing the international bridges, various small factories in the region, and metal recycling sites in the vicinity are all believed to be contributing sources of the high lead levels. The presence of fine lead at this site can be contrasted to the conditions at the Advanced Transformer and Misión sites, where most of the lead is in coarse form. The significance of this contrast is not well documented. However, it is thought that these differences are related to the various levels of industrial activities. Such observations can help guide future investigations of sources of lead in the atmosphere.

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