

USE OF ICP/MS TO DETERMINE ELEMENTAL COMPOSITION OF AIR PARTICULATES IN EL PASO/JUAREZ AIRSHED

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ABSTRACT

Air quality is a fundamental environmental challenge in urban areas along the U.S.-Mexico border. In the El Paso, Texas-Juarez, Mexico airshed, current understanding of the composition, toxicity, and origin of particulates is limited.

In this project we are using Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) to determine the elemental composition of particulates in ambient air filters collected in El Paso and Juarez over a 30-year period. ICP/MS permits simultaneous determination of the concentrations of up to 65 elements in a liquid or dissolved solid, typically at ppb levels in the solution. ICP/MS is considered the current "ultimate weapon" in the search for low detection limits. This technique also provides useful isotopic information for appropriate toxic elements such as lead.

So far we have found elevated levels of copper, lead, arsenic, and chromium in the El Paso-Juarez 1996 particulate matter. The metal distribution varies depending on sampling season. We believe that there may be three point or limited area sources responsible for the presence of these metals, two in Juarez and one in El Paso.

Key words: particulate matter, air quality, El Paso-Juarez, ICP-MS

INTRODUCTION

El Paso and Ciudad Juarez are contiguous cities which straddle the U. S.-Mexico border, separated by the Rio Grande, which cuts through the Franklin Mountains and the Sierra de Juarez. These cities are at high elevations, 1200-2100 m. Air movement is confined by the mountains and atmospheric inversions are common, especially in the cold seasons. Air quality in this urban area is an environmental challenge and particulate matter is a specific problem in the El Paso-Juarez airshed.

Toxic elements present in the air might be a threat to public health. They can cause acute and chronic health effects (Amdur, 1995), as has occurred in the three classic episodes that were observed at Meuse Valley, Belgium; Donora, Pennsylvania; and London. Trace metals in the lungs could catalyze the formation of oxidants which in turn produce tissue damage. Metals on the surface of irritant particles can be more efficiently transferred to the lungs (Hughes et al., 1998). Recently Chianelli et al. (1997) studied the components of atmospheric nanoparticles in Mexico City and Hughes et al. (1998) characterized ultrafine particles in the Los Angeles atmosphere. Such toxic metals as lead and mercury have been studied in aerosols, house dust, gasoline, and blood, to determine their concentrations and to link them to their origin, and thus protect public health in different urban areas (Adgate et al., 1998; Chow and Johnstone, 1965; Fitzgerald et al., 1998; Grousset et al., 1998; Hanisch, 1998; Hirao and Patterson, 1974; Hurst et al., 1996; Lindberg and Stratton, 1998; Palazuelos, 1996; Romieu et al., 1995; and Tera et al., 1985). In the 1970s

Rhodes et al. (1972) utilized X-ray fluorescence to analyze air particulates in 38 stations throughout Texas in a statewide project. Dzuby and Stevens (1975) also used X-ray fluorescence for ambient air analysis. However, little is known about the elemental composition of particulates in the El Paso-Juarez urban area and in general in other U. S.-Mexico border cities.

In this project we are examining and analyzing contemporary, recent, and older ambient air filter samples (mainly PM-10 filters). Our objective is to generate data on elemental composition of particulate matter in the El Paso-Juarez airshed for mapping and understanding the evolution of air pollution in this binational area.

In this study we report elemental composition of particulates trapped on filters collected at 10 sites (during 1996), five in El Paso and five in Ciudad Juarez. We utilized X-ray micro-fluorescence as a screening tool to analyze the filters. Particulates were digested in sealed teflon bombs by microwave assisted extraction (MAE), which appears superior to the traditional hot-plate method (Lorentzen et al., 1996). The extract was analyzed by inductively coupled plasma/mass spectrometry (ICP/MS). The analytical technique was selected for its high sensitivity and selectivity in which up to 65 elements can be resolved simultaneously. However, we focus on only four toxic elements in this paper due to their local importance. In addition ICP/MS permitted the analysis of lead isotopes, which may allow linking them with their possible sources through their isotopic ratios.

MATERIALS AND METHODS

Pure quartz fiber (silicon dioxide) filters measuring 8 by 10 inches (20.3 x 25.4 cm) were placed on a high-volume sampler system (impaction type with size-selective inlet). The filters collected particulate matter with a pore size of 10 micrometers or less. The sampling was done by drawing ambient air through the filter material by using a pump. Air samples were taken continuously during periods of 24 hours, every sixth day. The typical mass loadings on a low to medium volume sample are less than 5 mg (Chow et al., 1995). El Paso County Health and Environmental District and the Texas Natural Resources Conservation Commission (TNRCC) were the agencies in charge of the sampling and storage. Access was provided by these agencies, which maintain a library of particulate matter filters, and also total suspended particulate (TSP) filters. Long records of particulate filter samples were collected and stored for many years (Clement, 1997). In order to select filters from several dates during 1996, we gathered pertinent weather information. Wind velocities and directions, and geographic coverage were obtained. A representative day with calm conditions (wind velocities of less than 9 miles per hour) during each of spring, summer, fall, and winter of 1996 was selected. The sites located in El Paso were Tillman, Tillman B, Ivanhoe, Northeast, and Riverside, and the sites located in Ciudad Juarez were Tecno, Tecno2, 20-30, Zenco, Advance, and Pesta. Site locations are shown in Figure 1.

X-ray micro-fluorescence (XRMF) analyses were performed on the filters. XRMF can detect elements with atomic numbers ranging from 11 (sodium) to 92 (uranium) (Chow et al., 1995). In

this method X-rays are beamed directly onto selected areas of the particulate matter. Beam X-rays eject core electrons in the sample and upon replacement characteristic X-rays are emitted, identifying the elements present (Fatoki et al., 1996).

For ICP/MS analyses, samples were prepared by microwave assisted extraction (MAE). Preference for this method over the traditional EPA method 3050B was based on its efficiency and effectiveness (Lorentzen et al., 1996). Microwave heating leads to improved precision compared to conventional heating sources. The filters were cut longitudinally into strips of 1 x 8 inches (2.54 x 20.3 cm) for digestion, weighed, and placed into the microwave vessels by folding them. Deionized class I water and 10 ml of high purity nitric acid were added to each vessel. Known concentrations of NIST-traceable standards (spikes) were added to laboratory-fortified blanks and laboratory-fortified samples which were processed with each set of samples digested. A laboratory reagent blank was also processed with each sample set. The microwave functioned at 81% power during two stages of 25 and 45 min. After the microwave vessels were cooled, the acid extracts were brought to a final volume of 50 ml. The 50-ml extracts were then stored in HDPE bottles until they were analyzed, and the remaining portion of the filter was stored.

Subsequently, the extracts were analyzed using an HP 4500 Inductively Coupled Plasma/Mass Spectrometer (ICP/MS). This method allowed us to perform multi-element determination of trace elements. In this method, the extract solution is introduced by pneumatic nebulization into a radio-frequency-generated argon plasma where energy transfer processes cause analyte desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier and the ion information is then processed by a PC-based data handling system. Interferences by polyatomic ions from gas, air, reagents, and sample matrixes were noted and corrected as appropriate (U. S. Environmental Protection Agency, 1997). When reviewing the spectroscopic data it was found that the laboratory blanks of unused filter strips contained the major elements Na, Mg, Al, Ca, and Fe. Therefore, filter-blank background subtraction was performed in the final calculations.

The ICP/MS analyses were performed using the quantitative mode. Standards prepared from NIST-traceable multi-element solutions were used to calibrate the ICP/MS. Prior to analysis of samples, a quality control sample prepared from NIST multi-element solutions was analyzed to verify the calibration.

RESULTS AND DISCUSSION

We first screened the PM-10 filters for elemental composition by using XRMF since this is a non-destructive method. The XRMF technique gave us information on the major elements such as

calcium, iron, aluminum, and magnesium, and on filter constituents, and since it has microscopic capability we were able to address such issues as cross-contamination.

A total of 38 filters were used for this project, all sampled during 1996. ICP/MS analysis was performed to evaluate 65 elements. The concentrations of chromium, copper, arsenic, and lead for the fall of 1996 are shown in Table 1 and Figure 2. The Tillman and TillmanB sites are duplicate samples from identical samplers at the same site, as are JTecno and JTecno2 in Ciudad Juarez. These duplicate sampling sites yielded consistent analytical results. The copper concentration found in the Tillman site (located in downtown El Paso) was between 415 and 457 nanograms per cubic meter (ng/m^3). Copper concentrations were lower at the other El Paso sites. The Tillman sites also contained higher levels of chromium, arsenic, and lead. In Ciudad Juarez, copper concentrations in particulate matter ranged from 66 to 291 ng/m^3 at the different locations. The concentrations of the four elements were lower than at the downtown El Paso Tillman site. One can observe two points in Ciudad Juarez that are high in copper, with concentrations ranging from 209 to 291 ng/m^3 . The Ciudad Juarez downtown site, Pesta, had the highest Juarez concentrations of chromium and arsenic during the fall of 1996.

Table 2 and Figure 3 display the results obtained for the summer of 1996. Concentrations for the four elements are lower when compared to the fall results. These results were very similar for the sites in both cities.

For the spring of 1996, lower concentrations of the toxic elements were obtained than in the fall (Table 3, Figure 4). However, the toxic metal levels from the spring are a little higher than those for the summer of 1996.

Table 4 and Figure 5 show higher copper, arsenic, chromium and lead concentrations in the downtown El Paso site (Tillman) for the winter of 1996. Copper concentrations (315 to 357 ng/m^3) for the winter were somewhat lower than the 415 and 457 ng/m^3 copper concentrations for the fall. There were no significant differences in the Ciudad Juarez data.

The elevated metal concentrations during the winter and fall (as compared to the summer and spring) could be due to thermal inversions during these cooler periods.

The aerial distribution of these elements suggests one anomalous source of these elements in El Paso and two in Juarez, in addition to typical urban sources. Possible candidates include a large smelter (chiefly Cu ores) and "twin plants" which perform manufacturing and assembly operations in Juarez. The latter activities include electronic soldering and magnet fabrication.

We also determined the lead isotopes in the filter extracts for the fall of 1996. Isotopic lead ratios that were examined are 204/206, 207/206 and 208/206. The lead isotopic ratios for El Paso and Ciudad Juarez are shown in Table 5; the lead isotopic ratios show a limited range of values. However, when we graph the 208/206 versus the 207/206 ratio for the various sites, we can see possible differences (see Figure 6).

We plan in the near future to compare lead isotopic ratios to data available on soils, plants and house dust. In addition, we are gathering information on isotopic ratios in mobile sources from Juarez, Mexico, through the analysis of tetraethyl lead in the old Mexican Nova gasoline.

CONCLUSIONS

We have found elevated levels of copper, lead, arsenic, and chromium in El Paso-Ciudad Juarez particulate matter during the fall and winter of 1996. Lower concentrations were found during the summer and spring. Therefore, the metal distribution seems to vary depending on sampling season. We believe that there may be three point or limited area sources responsible for the presence of these metals, two in Juarez and one in El Paso. These potentially include a large ore smelter and "twin plant" fabrication and electronics assembly activities.

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Table 1. Results for the fall of 1996.

Site	52 Cr ng/m ³	63 Cu ng/m ³	75 As ng/m ³	208 Pb ng/m ³
El Paso				
Tillman	12.5	415	38.6	75.4
TillmanB	10.0	157	39.4	122
Ivanhoe	2.8	141	9.2	4.7
Northeast	2.0	48.6	12.7	4.9
Riverside	5.5	108	6.5	16.3
Ciudad Juarez				
JTecno	5.1	125	6.7	32.6
JTecno2	2.4	66.1	3.1	15.7
JPesta	12.5	174	52.7	89.9
JAdvance	8.2	209	39.7	133
J20-30	7.6	291	25.0	121

Table 2. Results for the summer of 1996.

Site	52 Cr ng/m ³	63 Cu ng/m ³	75 As ng/m ³	208 Pb ng/m ³
El Paso				
Tillman	2.1	57.7	3.1	5.9
TillmanB	1.9	91.1	3.4	6.5
Ivanhoe	1.4	30.9	6.6	3.8
Northeast	1.6	47.5	5.8	2.8
Riverside	2.3	42.3	6.7	4.8
Ciudad Juarez				
JPesta	3.6	95.9	7.0	12.9
JAdvance	3.0	116	3.1	6.7
JZenco	5.6	87.6	5.5	30.2

Table 3. Results for the spring of 1996.

Site	52 Cr ng/m ³	63 Cu ng/m ³	75 As ng/m ³	208 Pb ng/m ³
El Paso				
Tillman	3.6	36.1	1.8	6.3
TillmanB	3.3	31.0	1.5	5.9
Ivanhoe	3.4	17.0	2.5	3.4
Northeast	4.3	31.1	2.1	3.5
Riverside	4.8	19.8	7.8	6.7
Ciudad Juarez				
JTecno	3.0	69.3	2.1	26.9
JTecno2	2.3	67.0	1.7	22.8
JPesta	3.0	64.7	3.6	12.9
JAdvance	4.7	40.9	3.9	21.6

Table 4. Results for the winter of 1996.

Site	52 Cr ng/m ³	63 Cu ng/m ³	75 As ng/m ³	208 Pb ng/m ³
El Paso				
Tillman	10.8	315	66.1	98.2
TillmanB	12.9	357	68.9	103
Ivanhoe	2.2	121	38.5	23.0
Northeast	1.7	114	20.3	17.1
Riverside	4.2	141	23.0	38.0
Ciudad Juarez				
JTecno	7.5	156	22.9	59.2
JTecno2	5.0	180	21.0	60.3
JPesta	6.3	163	24.6	62.4
JAdvance	6.2	96.2	11.4	70.9
JZenco	6.1	128	16.4	71.4

Table 5. Fall 1996, lead isotopic ratios.

	204/206	207/206	208/206
El Paso			
Tillman	0.053	0.834	2.072
TillmanB	0.052	0.835	2.073
Ivanhoe	0.054	0.830	2.050
Northeast	0.053	0.827	2.049
Riverside	0.053	0.834	2.068
Ciudad Juarez			
JTechno	0.052	0.827	2.066
JTechno2	0.053	0.828	2.068
JPesta	0.052	0.832	2.079
JAdvance	0.052	0.829	2.077
J20-30	0.052	0.832	2.084

Figure 1. Location of the five sampling sites in El Paso and the five sites in Ciudad Juarez.

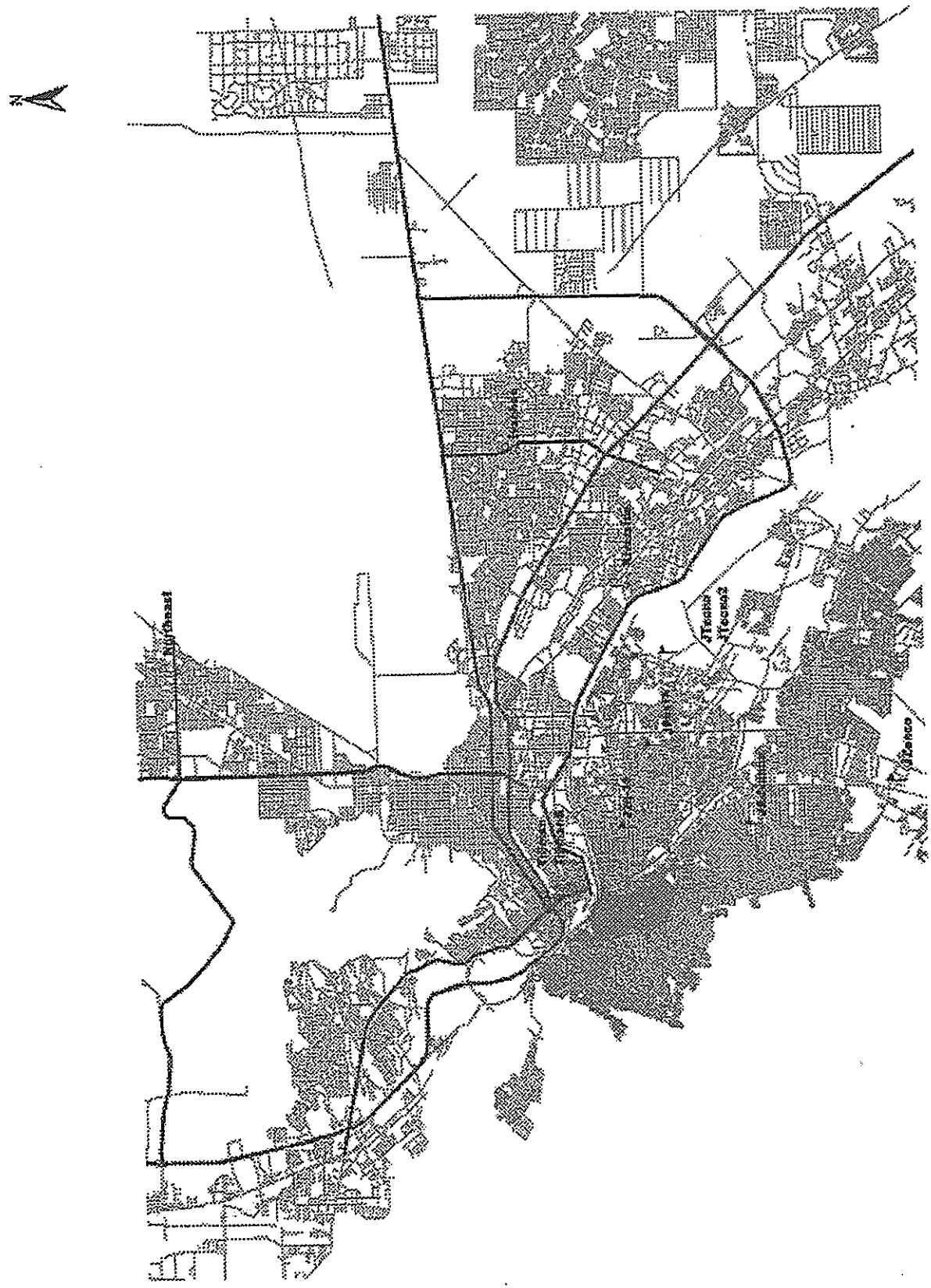


Figure 2. Concentrations in nanograms per cubic meter for copper, chromium, arsenic and lead in the PM-10 filters for the fall of 1996. The ten sites are represented on the x axis. The five sites located in El Paso are shown on the left while the five sites located in Ciudad Juarez are shown on the right.

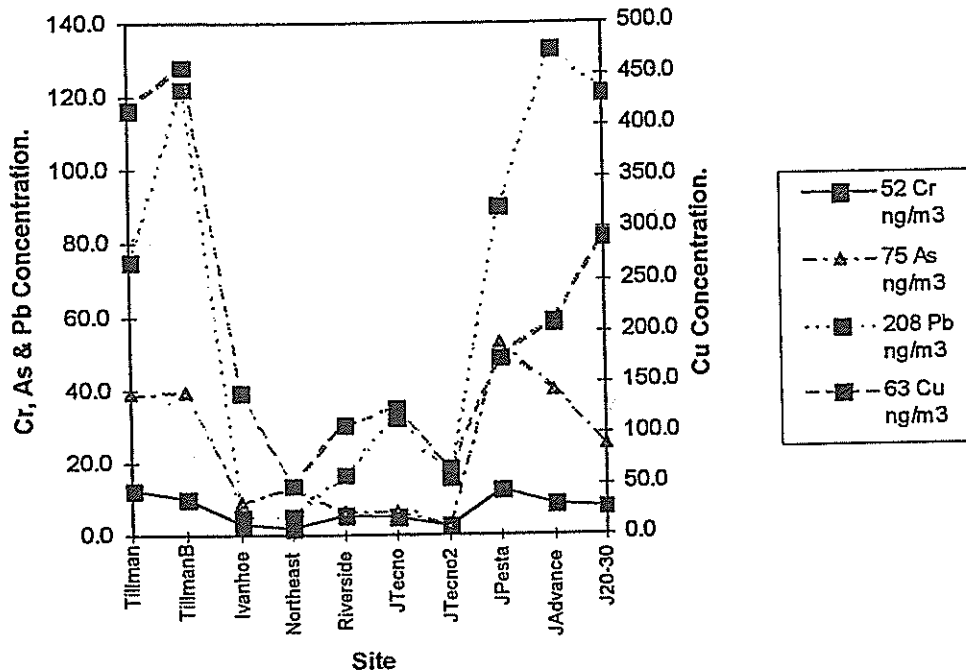


Figure 3. Concentrations in nanograms per cubic meter for copper, chromium, arsenic and lead in the PM-10 filters for the summer of 1996. The eight sites are represented on the x axis. The five sites located in El Paso are shown on the left while the three sites located in Ciudad Juarez are shown on the right.

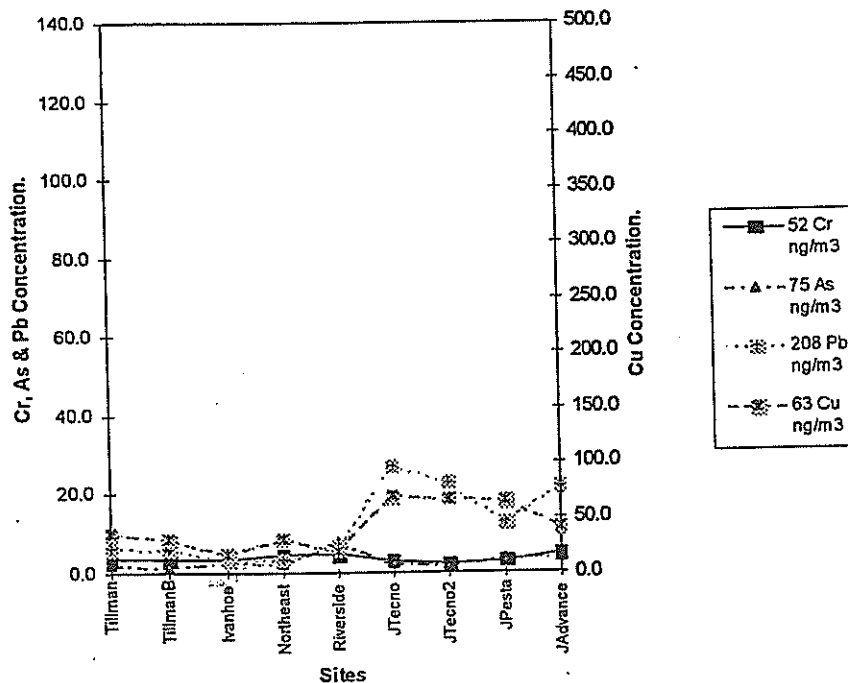


Figure 4. Concentrations in nanograms per cubic meter for copper, chromium, arsenic and lead in the PM-10 filters for the spring of 1996. The nine sites are represented on the x axis. The five sites located in El Paso are shown on the left while the four sites located in Ciudad Juarez are shown on the right.

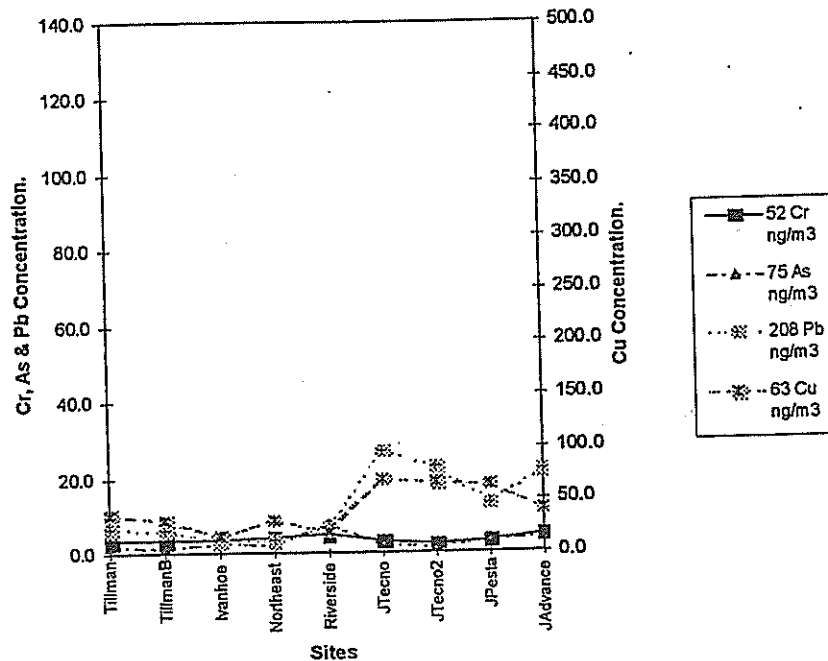


Figure 5. Concentrations in nanograms per cubic meter for copper, chromium, arsenic and lead in the PM-10 filters for the winter of 1996. The ten sites are represented on the x axis. The five sites located in El Paso are shown on the left while the five sites located in Ciudad Juarez are shown on the right.

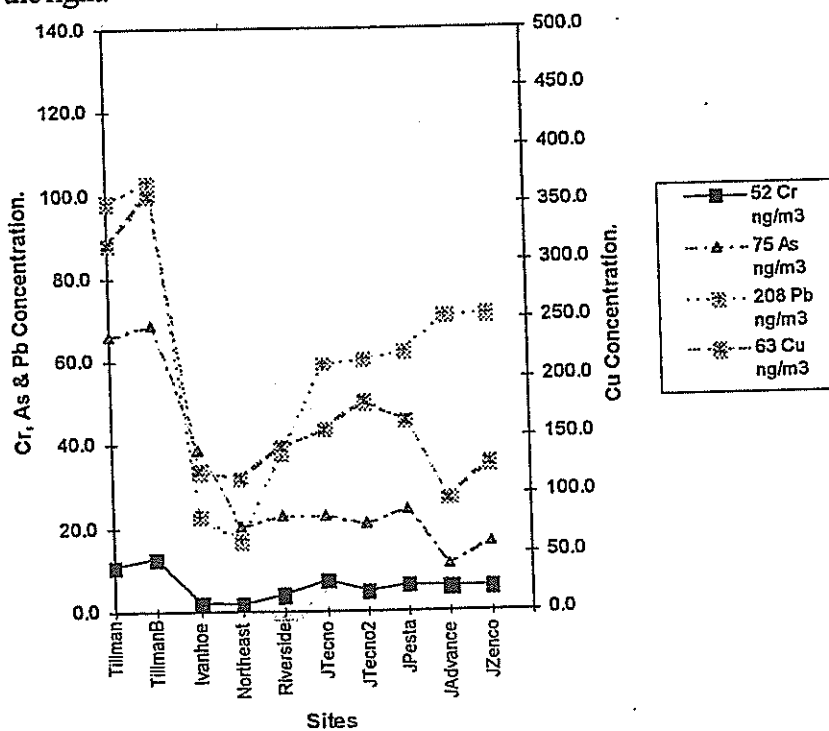
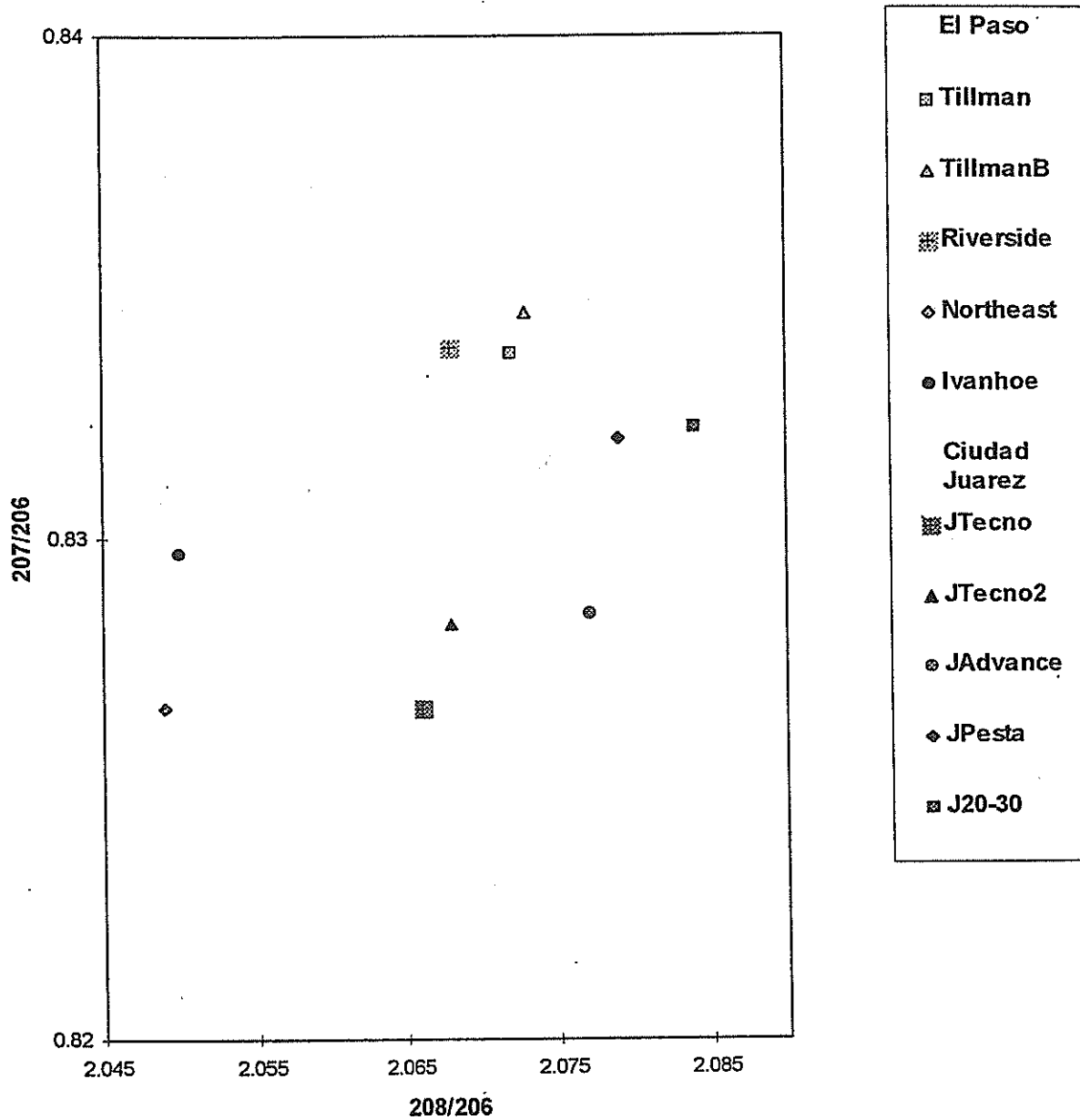
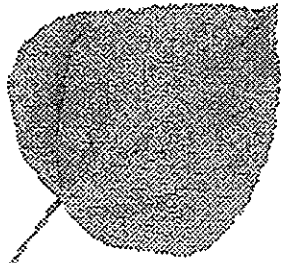


Figure 6. Lead isotopic ratios 208/206 versus 207/206 in the PM-10 filters for the fall of 1996.





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