

A study of elemental contents in atmospheric aerosols in Mexico City

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RESUMEN

Se analizaron muestras de partículas suspendidas en el aire con tamaños comprendidos entre 0 y 15 μm en la Ciudad de México para evaluar su composición elemental. Las muestras se colectaron durante una semana, en agosto de 1990, usando una Unidad de Filtros Apilados (Stacking Filter Unit o SFU), mediante la cual se separan partículas con tamaños de 2.5 a 15 μm (gruesas) y menores que 2.5 μm (finas). El período de colección fue de 6:00 a 12:00 hrs. El análisis con Emisión de Rayos X Inducida por Protones (PIXE) permitió la cuantificación de elementos con número atómico mayor que 10; la Dispersión Elástica de Protones (PESA) proporcionó información acerca del contenido de hidrógeno; mientras que el carbón elemental (hollín) se midió con el Método de la Placa Integradora de Láser (LIPM). Además, se midió la masa gravimétrica de las partículas depositadas en los filtros. Los resultados ofrecen la posibilidad de identificar las fuentes de los elementos medidos, a través de Análisis de Cúmulos. La comparación entre la masa gravimétrica y la masa reconstruida a partir del análisis elemental reafirmó los valores obtenidos para este último.

ABSTRACT

Samples of airborne particulate matter with sizes between 0 and 15 μm in Mexico City were analyzed in order to evaluate its elemental composition. Samples were collected during one week in August 1990, using a Stacking Filter Unit (SFU), resulting in the separation between particles having sizes 2.5 to 15 μm (coarse), and smaller than 2.5 μm (fine). The collection period was from 6:00 to 12:00 hrs. Analyses with proton Induced X-ray Emission (PIXE) allowed the quantification of elements with atomic number greater than 10; Proton Elastic Scattering Analysis (PESA) gave information on hydrogen contents; and elemental carbon (soot) was measured by means of the Laser Integrating Plate Method (LIPM). Also, the gravimetric mass of the deposited matter was measured. The results permit then the possible identification of sources of the measured elements, with the help of Cluster Analysis. Moreover, the comparison of the gravimetric mass with the mass reconstructed from the elemental analysis supports the values obtained in the latter.

Introduction

The air quality degradation in Mexico City has been subject to a dramatic and disquieting growth in the last twenty years. Besides the large increase in the population (now reaching 20 million inhabitants), with the subsequent multiplication of motor vehicles, its geographical and climatic situation has largely contributed to the problem. Located in a 2,240 m a.s.l. basin encircled by

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high ridges south and west, and lower elevations north and east, the frequent thermal inversions concentrate the pollutants, specially during the early hours and in the dry winter season.

Due to its proportion, many different approaches have been taken to tackle the problem. Several studies have been conducted by research groups in local institutions (Bravo, 1986; Báez, 1988; Salazar, 1989; Falcón, 1989; Bravo, 1989). However, no systematic lines had been followed to trace various pollutants that have effects on public health, and building and monument damage, for example. Aldape and coworkers (1991a; 1991b) presented studies that show the variability of some of these contaminants, in elemental concentrations, during daily, seasonal and annual periods, and thus show a first attempt in this kind of systematic studies. The results are, however, limited because of the lack of information on particle size, no control of maximum particle size, and no measurement of particulate mass.

Because of this, further research on the elemental composition of aerosols in Mexico City is required, including, even on a limited basis, information on particle sizes. Thus, the present work represents an effort to determine the concentration of several elements in the forementioned aerosols, for two different particle sizes (in the range of respirable matter), during one week in the summer of 1990. This paper is the third in a series of studies, result of the cooperation between Mexican and American institutions, as a part of the UC-MEXUS Program (Aldape *et al.*, 1991a, Aldape *et al.*, 1991b), and is also aimed to show the possibilities of these methods as routinary in the monitoring of the referred pollutants. Moreover, it is hoped that these new data will assist in putting the earlier Aldape *et al.* (1991a; 1991b) results in perspective.

Experimental procedures

The sampling site was the Museo Tecnológico, located in the Chapultepec Park, about 7 km west from Downtown Mexico City. Figure 1 displays a map of the Federal District, showing major elevations and some important avenues, together with the location of the site and Downtown as a reference point. The samples were collected from August 22 to August 28, 1990, in six hours periods, starting at 6:00 in the morning. This period was selected because at these hours the concentration of pollutants is much higher than in other periods, as shown by Aldape *et al.* (1991a). The sampler unit was a Stacking Filter Unit (SFU) of the Davis design. This system allows the collection of particles with sizes 0 to 15 μm , giving also a separation between particles with sizes from 2.5 to 15 μm (deposited on a 2.5 μm Nuclepore filter, and thereon described as coarse mass), and 0 to 2.5 μm (deposited on a teflon filter, and known as fine mass). The operation of this unit and comparison with other collection devices are described elsewhere (Cahill *et al.*, 1977; Cahill *et al.*, 1990a; Cahill, 1990b; Mathai *et al.*, 1990), but in summary it is fully comparable with other PM-15 and PM-2.5 samplers. It also has the advantages of ease of operation and low cost.

The elemental analyses of the deposited particles were done using four different techniques. Gravimetric mass was determined by pre- and post- weighing the filters with a Cahn-28 electrobalance. For elemental carbon (soot), the Laser Integrating Plate Method (LIPM) was used. This technique relates laser absorption by the loaded teflon filter to soot concentration (Cahill *et al.*, 1984; Gerber and Hindman, 1982). Hydrogen contents were determined with Proton Elastic Scattering Analysis (PESA), which is based on the forward scattering of protons by an incoming proton beam with energies in the range of a few MeV (Kusko *et al.*, 1988), and it was possible only on the fine mass, because the teflon filters were originally hydrogen-free. Finally, concentration of elements heavier than neon was carried out by means of Proton Induced X-ray Emission (PIXE). The capabilities of this technique on aerosol analyses have been well discussed

and established (Johansson and Campbell, 1988; Cahill *et al.*, 1990c). The PESA and PIXE analyses of the filters were done with the 150 cm isochronous cyclotron at Crocker Nuclear Laboratory, University of California-Davis. A detailed description of the system was presented somewhere else (Cahill *et al.*, 1987). The energy of the proton beam was 4.5 MeV, and accurate calibration of the system was based on thin film standards. The filters were irradiated for 100 seconds each, with an average beam current of 30 nA, following standard protocols of Crocker Nuclear Laboratory for aerosol analyses. With the techniques mentioned above, typically 93% of the fine mass can be ascribed to chemical species. The remaining is dominantly water.

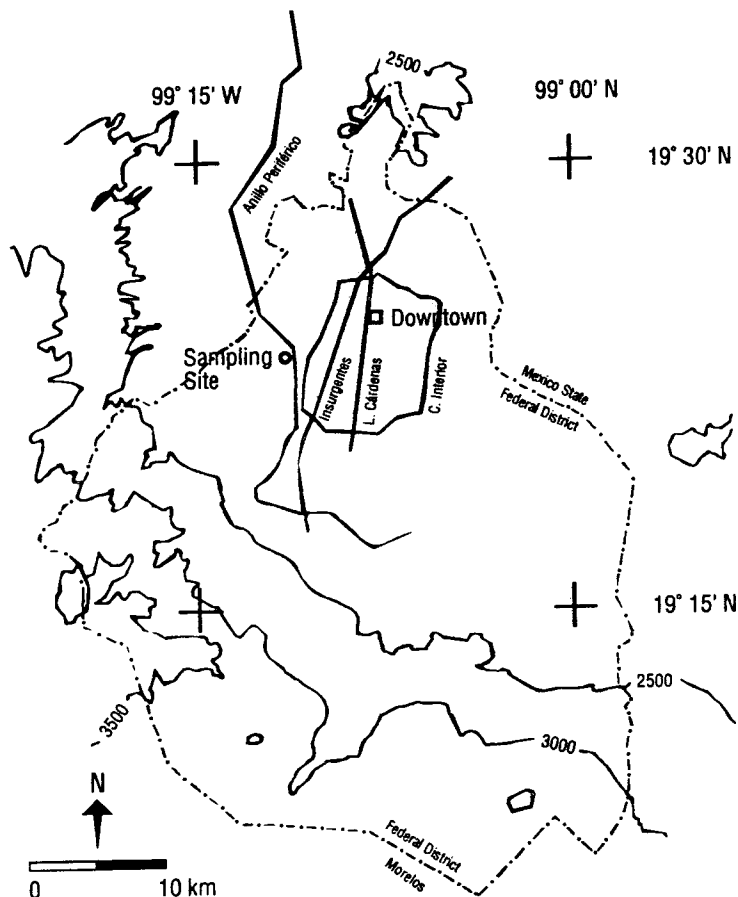


Fig. 1. Map of the Federal District, showing the sampling location, Downtown Mexico City, the most important avenues, and major elevations (in m).

Results and Discussion

Concentrations

The resulting PESA and PIXE spectra were analyzed on-line with the computer code RACE (Harrison and Eldred, 1974), which provides the concentrations of the measured elements in ng/m^3 . Uncertainties in the concentrations range from 2% for heavy and abundant elements (like Fe, Zn, or Pb) to 20% for very light or scarce elements, such as Na or Ni. PIXE allowed the detection of 18 elements in the fine mass, and 21 in the coarse mass. Tables I and II show the maximum, minimum, arithmetic mean concentrations, and standard errors for a 0.05 confidence level, measured in the fine and coarse mass respectively, together with the number of cases in

which the elements were found. As can be seen from the tables, in the fine mass 17 elements appeared systematically, besides H and C from PESA and LIPM, respectively. On the other hand, in the coarse mass only 18 elements have more than 50% of appearances. The elements reported by Salazar *et al.* (1989) were also found in this study.

Table I. Elemental Concentrations (ng/m³) in Fine Mass.¹

Element	Appearances	Minimum	Maximum	Mean
H	7	2311	3370	2808±167
C	7	2775	4193	3395±198
Na	7	183	514	316±157
Al	5	22	356	157±50
Si	7	241	1026	543±97
S	7	3209	5243	4282±258
K	7	210	579	347±59
Ca	7	166	457	331±51
Ti	7	6.6	36	16±4
V	7	50	124	85±10
Cr	7	5.7	19	11±2
Mn	7	5.5	32	12±3
Fe	7	136	356	240±31
Ni	7	5.5	13	9.6±1
Cu	7	14.7	181	74±26
Zn	7	125	1091	491±114
Se	6	2.87	8.6	5.5±0.7
Br	7	8.2	17	12±1
Ag	2	16	21	18.5
Pb	7	400	938	563±72

¹Uncertainties in the mean correspond to a 0.05 confidence level.

Table II. Elemental Concentrations (ng/m³) in Coarse Mass.¹

Element	Appearances	Minimum	Maximum	Mean
Na	1		501	
Mg	1		199	
Al	7	277	3558	1470±436
Si	7	1654	4093	2907±342
P	4	142	500	281±55
S	7	1130	1701	1424±71
K	6	73	661	356±70
Ca	7	1291	3667	2362±339
Ti	7	80	227	142±20
V	4	34	118	64±14
Cr	5	32	81	56±7
Mn	7	38	158	81±14
Fe	7	552	1183	797±97
Ni	4	16	41	24±3
Cu	6	7.9	80	31±10
Zn	7	40	218	157±24
Br	7	100	135	112±5
Rb	4	7.2	31	16±3
Sr	4	7.5	28	14±3
Zr	1		5	
Pb	7	112	232	177±14

¹Uncertainties in the mean correspond to a 0.05 confidence level.

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A comparison is developed in Table III of the mean values measured for the elements found in fine as well as coarse fraction, which added to each other give the total mass, with the mean values in August 1988, August 1989, and Summer 1988, given by Aldape and collaborators (1991a; 1991b), together with the results reported by Falcón *et al.* (1989) for PM10 24 hours average mass concentrations of Fe, Cu, and Pb in April 1988 in a Mexico City's Northwestern site. It is worth noticing that, for most elements, the mean values in Aldape's 1988 and 1989 studies are closer to the coarse mass concentrations. This fact can be due to either two reasons: 1) the particle size collected by Aldape *et al.* (1991a, 1991b) is similar to the coarse mass, which is plausible since their sampler collected all particle size on its open, upward-facing filter; or 2) the elemental concentrations in 1990 are much larger than those of 1988 and 1989. Further studies may provide an answer to this issue. As opposed to this, the Pb concentrations presented in this work and the one given by Falcón *et al.* (1989) are very similar, although the latter results correspond to PM10 particulates and 24-hours average. This fact may suggest that most of the lead is present only in particles having these sizes, which are included in the samples collected during the present work. Moreover, as Aldape *et al.* (1991a) demonstrated, in many cases the Pb concentrations are much higher in the sampling period used here, and probably the 24-hours average is strongly dominated by the 6:00 to 12:00 hours period. The seasonal variations found by Aldape *et al.* (1991b), on the other hand, show that August and April correspond roughly to the same Pb concentration regime, supporting in part the agreement between the present results and those of Falcón *et al.* (1989). The higher values of Fe and Cu reported by Falcón *et al.* (1989) might be explained by the circumstance that August is in the middle of the rainy season, while April is at the end of the dry season, when soil-derived pollutants have higher concentrations (Aldape *et al.*, 1991b).

Table III. Comparison of Elemental Concentrations in Different Studies.¹

Element	August 1990	August 1990	August 1990	August 1988	August 1989	Summer 1988	4/1/1988 ²
	Fine Mass	Coarse Mass	Total	Aldape 1991b	Aldape 1991b	Aldape 1991a	Falcón 1989
H	2808	NM	2808	NM	NM	NM	NM
C	7719	NM	7719	3384	3648	2246	NM
Na	316	NO	316	NO	NO	181	NM
Al	157	1470	1628	1807	1188	794	NM
Si	543	2907	3450	1355	1225	1228	NM
P	NO	281	281	NO	NO	NO	NM
S	4282	1424	5706	1485	1912	1051	NM
K	347	356	704	188	235	174	NM
Ca	332	2362	2694	949	1498	719	NM
Ti	16	142	158	34	21	33	NM
V	85	64	149	69	59	52	NM
Cr	11	56	67	NO	NO	6	NM
Mn	12	81	94	14	20	22	NM
Fe	240	797	1037	447	557	412	2340
Ni	10	24	33	NO	NO	4	NM
Cu	74	31	105	17	22	24	660
Zn	491	157	648	152	304	192	NM
Se	6	NO	6	NO	NO	3	NM
Br	12	112	124	206	235	123	NM
Rb	NO	16	16	13	21	7	NM
Sr	NO	14	14	3	6	NO	NM
Pb	563	177	740	339	263	203	770

¹ Concentrations in ng/m³; NM = Not measured; NO = Not observed.

² Results for PM10.

Afterward, mean enrichment factors (EF) were calculated for both fine and coarse mass, taking Si as reference, which is an element with a predominant soil provenance. The results can be seen in Figure 2, where soil-related elements have EF below 5, such as Al, K (coarse), Ca, Ti, Fe, Rb, and Sr. Elements with anthropogenic origin are also identified because of their large EF, especially C, S, V, Cu, Zn, Se, and Pb. This procedure, however, provides no information on the sources of anthropogenic or other natural elements.

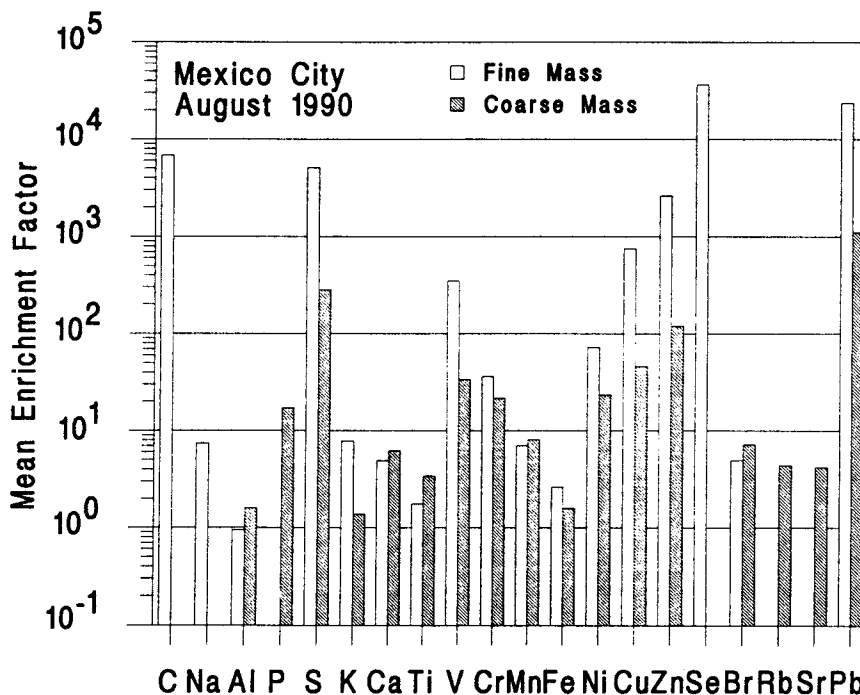


Fig. 2. Mean enrichment factors of measured elements, relative to earth crust Si, for the fine and coarse mass fractions.

Reconstructed mass

The next step is an attempt to reconstruct the total mass deposited on the teflon filters from the elemental concentrations measured with PIXE, PESA, and LIPM. To achieve this, the following expression is used:

$$RCM = Soil + 1.2 NSK + Sulfate + Organic + Other, \tag{1}$$

where RCM is the reconstructed mass, Soil represents the concentration of soil-derived particulates, Sulfate is the ammonium sulfate concentration, Organic is the concentration of organic matter in the aerosol, and Other is the sum of the remaining elements measured. Soil is calculated from the elements identified as soil-originated, i.e., Al, Si, Ca, Ti and Fe, from the formula:

$$Soil = 2.20Al + 2.49Si + 1.63Ca + 1.94Ti + 2.38Fe, \tag{2}$$

with Al, Si, Ca, ti and Fe representing the concentrations of the respective elements. This equation is obtained through the oxide forms and crustal ratio of these elements. Also, NSK

in eq. (1) is the concentration of potassium with a source other than soil, and which is often related to smoke, and whose value can be obtained by means of the equation

$$NSK = K - 0.52Fe, \quad (3)$$

in which again K and Fe stand for elemental concentrations of those elements. The factor 0.52 in this formula comes from the K/Fe crustal ratio. On the other hand, Sulfate is evaluated through

$$\text{Sulfate} = 4.125S. \quad (4)$$

Here, S represents sulfur concentration, and the expression comes from a consideration of the ratio of ammonium sulfate to sulfur mass in this compound. Finally, Organics can be known from the difference of total hydrogen concentration to that in the same ammonium sulfate:

$$\text{Organics} = 11(H - 0.25S). \quad (5)$$

Using eqs. (1)-(5), the reconstruction of mass is straightforward. The comparison of RCM and gravimetric mass as measured with the electrobalance is presented in Figure 3. It is apparent that the agreement between both procedures is good, supporting then the values obtained by the other three analytical techniques.

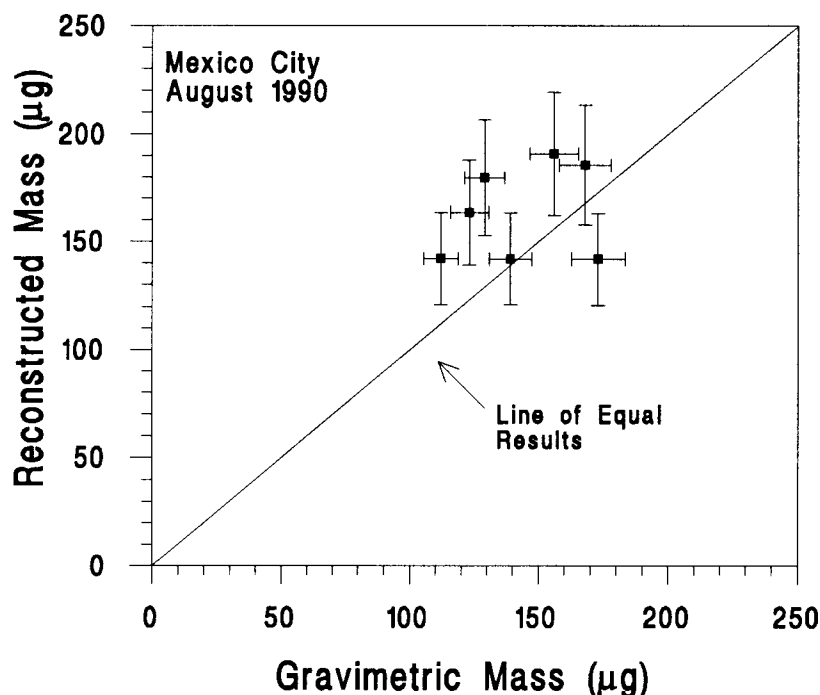


Fig. 3. Comparison between reconstructed and gravimetric masses, for the fine fraction. The line represents the values for which the reconstructed and the gravimetric masses are equal to each other.

Furthermore, in order to give an appropriate weight to the concentrations measured in Mexico City, a comparison with elemental contents resulting from analogous studies in other urban areas is suitable. Table IV displays the figures obtained by Cahill *et al.* (1990d) in Los Angeles in August 1986 for the fine mass, together with those of Mexico City. The comparison is valid, as the same kind of sampling units were used, and the sampling periods were during the summer.

Table IV. Comparison of aerosol contents (fine mass) in Mexico City (1990) and Los Angeles (1986). Values in $\mu\text{g}/\text{m}^3$.

	Mexico City 1990	Los Angeles 1986
C (soot)	3.4±0.5	5.7
H (organic)	1.7±0.4	1.6
H (total)	2.8±0.4	3.4
Sulfur	4.3±0.7	2.5
Soils*	1.6±0.7	3.2
Ni	0.010±0.003	0.014
Cu	0.074±0.070	0.021
Zn	0.49±0.30	0.244
Br	0.012±0.003	0.039
Pb	0.56±0.19	0.252

*Calculated as the sum of Al, Si, K, Ca, Ti, Mn and Fe.

Moreover, the Los Angeles results are for a 4-hours average, close to the 6-hours periods of the present work. It is not difficult to see that while soil, and organic hydrogen are lower in Mexico City, sulfur and other anthropogenic trace elements are much higher in the latter. It is also important to point out that when the Los Angeles study was done, regulations had already been imposed, thus leading to a cleaner environment. This must be contrasted to the situation in Mexico City, where similar rules have been followed only in the past two years.

Cluster analysis

An attempt to identify the possible sources of the pollutants, is the use of Cluster Analysis (CA) (Karson, 1982). In order to carry out the analyses, the computer code CSS/3 was used (StatSoft, 1991). First, the correlation matrices for the fine and coarse fractions are calculated, and are displayed in Tables V and VI, respectively. High correlation coefficients are found among several elements, a fact that suggests grouping and, therefore, common sources. Then,

Table V. Correlation Matrix for Fine Mass.¹

	H	C	Na	Al	Si	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Se	Br	Pb
H	1.000																		
C	0.736	1.000																	
Na	0.484	0.802	1.000																
Al	-0.107	-0.143	0.072	1.000															
Si	-0.571	-0.473	-0.321	0.619	1.000														
S	0.683	0.136	-0.237	0.160	-0.164	1.000													
K	-0.339	-0.150	-0.523	-0.638	0.030	-0.153	1.000												
Ca	-0.278	-0.052	-0.157	0.447	0.705	-0.053	0.128	1.000											
Ti	-0.261	-0.068	0.009	0.855	0.802	0.012	-0.220	0.618	1.000										
V	0.730	0.656	0.500	0.507	0.040	0.590	-0.488	0.202	0.465	1.000									
Cr	0.569	0.363	0.167	-0.688	-0.837	0.233	0.050	-0.387	-0.886	-0.093	1.000								
Mn	-0.457	0.049	-0.092	-0.293	0.089	-0.546	0.573	0.543	-0.040	-0.414	0.068	1.000							
Fe	-0.416	-0.053	0.008	0.505	0.853	-0.300	0.088	0.895	0.767	0.185	-0.655	0.435	1.000						
Ni	0.658	0.519	0.437	0.619	0.153	0.581	-0.603	0.340	0.491	0.958	-0.090	-0.390	0.274	1.000					
Cu	0.397	0.606	0.692	0.393	-0.281	0.048	-0.543	-0.279	0.306	0.593	-0.162	-0.308	-0.142	0.458	1.000				
Zn	0.238	0.595	0.938	-0.030	-0.256	-0.495	-0.458	-0.252	-0.076	0.218	0.104	-0.059	0.001	0.168	0.547	1.000			
Se	0.462	0.460	-0.009	-0.308	-0.603	0.404	0.225	0.051	-0.346	0.179	0.618	0.364	-0.314	0.126	0.118	-0.251	1.000		
Br	0.397	0.699	0.884	-0.040	-0.158	-0.299	-0.383	0.113	-0.066	0.377	0.268	0.114	0.217	0.399	0.296	0.858	-0.050	1.000	
Pb	0.602	0.903	0.898	-0.324	-0.531	-0.159	-0.182	-0.216	-0.287	0.393	0.458	0.063	-0.131	0.283	0.479	0.823	0.228	0.860	1.000

¹Coefficients with a significance level of 0.10 are shown in bold.

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Table VI. Correlation Matrix for Coarse Mass.¹

	Al	Si	P	S	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Rb	Sr	Pb
Al	1.000																	
Si	0.799	1.000																
P	-0.011	0.396	1.000															
S	0.441	0.528	0.606	1.000														
K	0.196	0.036	-0.327	-0.090	1.000													
Ca	0.538	0.861	0.710	0.810	-0.010	1.000												
Ti	-0.183	0.134	0.570	0.574	0.350	0.556	1.000											
V	-0.690	-0.318	0.169	-0.221	0.226	-0.068	0.610	1.000										
Cr	0.316	0.657	0.856	0.598	0.086	0.840	0.577	0.035	1.000									
Mn	0.530	0.525	0.502	0.702	-0.619	0.565	-0.105	-0.645	0.371	1.000								
Fe	0.794	0.769	0.223	0.801	-0.086	0.749	0.147	-0.493	0.342	0.732	1.000							
Ni	-0.290	-0.510	0.060	0.421	-0.122	-0.151	0.327	0.058	-0.234	0.180	0.076	1.000						
Cu	-0.454	-0.153	-0.014	-0.314	0.004	-0.103	0.260	0.825	-0.199	-0.464	-0.289	-0.072	1.000					
Zn	0.066	0.300	0.000	0.278	0.129	0.378	0.461	0.494	-0.030	-0.083	0.411	0.071	0.697	1.000				
Br	0.486	0.409	0.258	-0.097	-0.148	0.145	-0.423	-0.421	0.344	0.359	0.068	-0.459	-0.197	-0.414	1.000			
Rb	0.147	0.399	0.339	0.526	-0.199	0.547	0.258	-0.244	0.422	0.399	0.436	-0.081	-0.471	-0.021	-0.356	1.000		
Sr	-0.127	0.133	0.024	-0.080	-0.301	0.098	0.056	0.473	-0.203	-0.020	0.119	-0.073	0.863	0.783	-0.056	-0.330	1.000	
Pb	0.122	0.450	0.112	-0.350	-0.099	0.192	-0.165	0.281	0.164	-0.118	-0.048	-0.764	0.596	0.341	0.474	-0.270	0.682	1.000

¹Coefficients with a significance level of 0.10 are shown in bold.

using Pearson's rule for distance measures (Karson, 1982), and Ward's method of amalgamation (Ward, 1963), the hierarchical trees for CA are constructed, and are represented by Figures 4 and 5 for fine and coarse mass, in that order. In both cases, several groups are defined. As was concluded from the enrichment factors, some elements show an unequivocal soil origin, while the anthropogenic elements now indicate the presence of different sources.

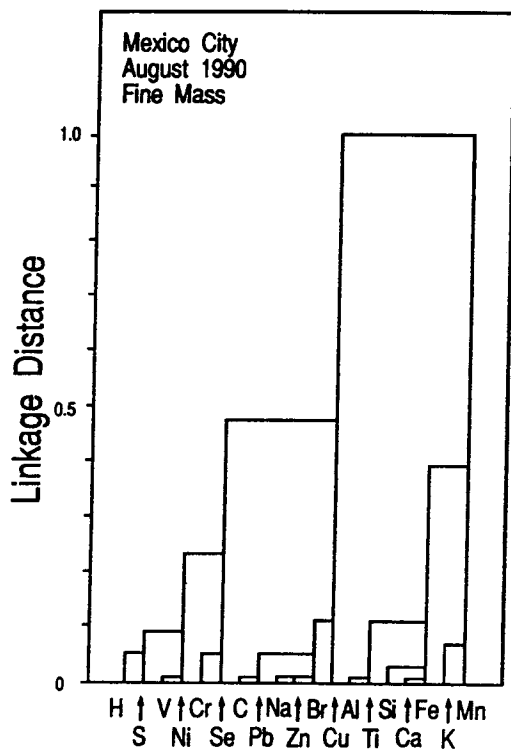


Fig. 4. Hierarchical tree for fine mass, with the vertical coordinate normalized to one for the maximum linkage distance.

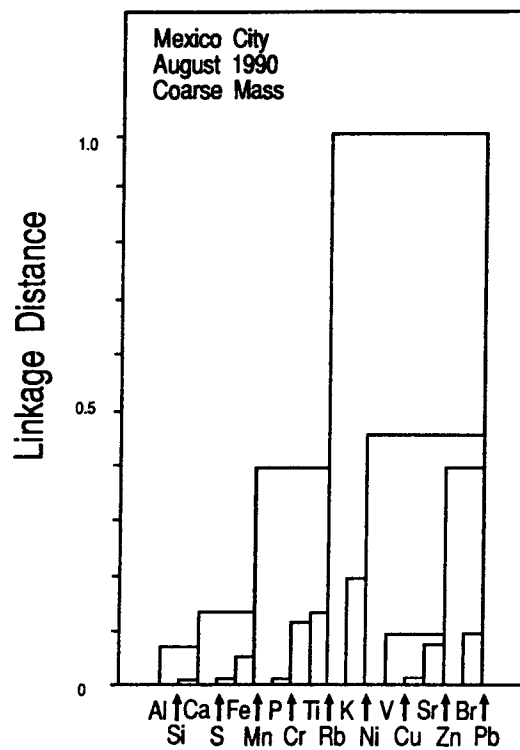


Fig. 5. Same as Figure 4, but for coarse mass.

In the case of fine mass, hydrogen and sulphur are highly correlated, as would be expected if they were present in the form of ammonium sulfate or sulfuric acid. However, if a plot of hydrogen concentration versus sulfur concentration is made (Fig. 6), the slope of the adjusted line is higher than expected for ammonium sulfate, although no other feasible compound is suggested here, as more information on nitrogen and oxygen is necessary. Also, the automotive group is well recognized, composed by C, Pb, Na, Br, Cu, and Zn. The extremely high correlation between C and Pb was also found by Aldape and coworkers (1991a; 1991b), demonstrating the existence of a common source. Moreover, a third group, likely industrial fuels, comprises V, Ni, Cr, and Se. Finally, K and Mn might be related to smoke, although they are also present as soil derived elements, and are closely linked to the soil cluster, formed by Al, Ti, Si, Ca, and Fe.

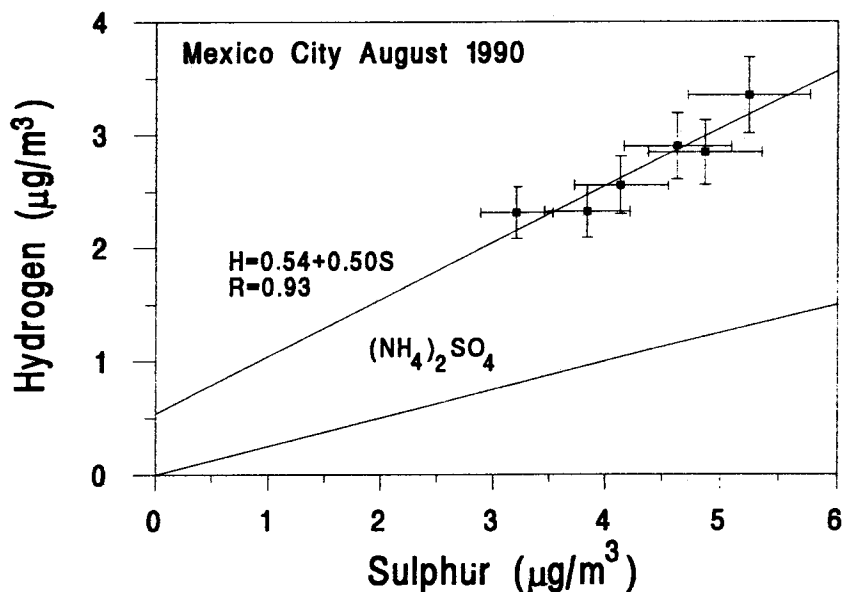


Fig. 6. Hydrogen concentration as a function of sulfur concentration for fine mass. The fitted line gives a slope equal to 0.50, as contrasted to the ammonium sulfate line, shown below, which has a slope equal to 0.25.

On the other hand, the coarse mass presents a slightly different behavior. The most important contributor is soil, not a surprising result. The automotive elements are now Br and Pb, which are known as tracers of traffic derived pollutants (Rojas *et al.*, 1990). V, Cu, Sr, and Zn characterize the industrial fuel source, while P, Cr, Ti, and Rb are in a third group, possibly soil-related, though not unambiguously placed. Additionally, K and Ni seem to have a joint source, but is not clearly understood either.

Effect of meteorological variables

As explained before, one of the principal contributors to Mexico City's pollution is the weather. Because of this, the influence of some meteorological parameters (wind velocity, temperature, relative humidity, and precipitation) was studied. During the present study, it was found that the winds had a North direction during almost all the sampling periods, with a few changes to a NNW direction. Thus, only wind velocity is considered. Figure 7 displays the relationship between the maximum wind velocity measured during the sampling period with Pb fine mass concentrations. It is important to note that the Pb concentration varies inversely with wind velocity. This is not a surprising result, as fuel pollutants are expected to be dispersed by the

wind. Moreover, Figure 8 presents the behavior of NSK from eq. (3) as a function of wind velocity. A growth in the non-soil K is seen with increasing velocity, suggesting the provenance of smoke from a source North of the sampling location.

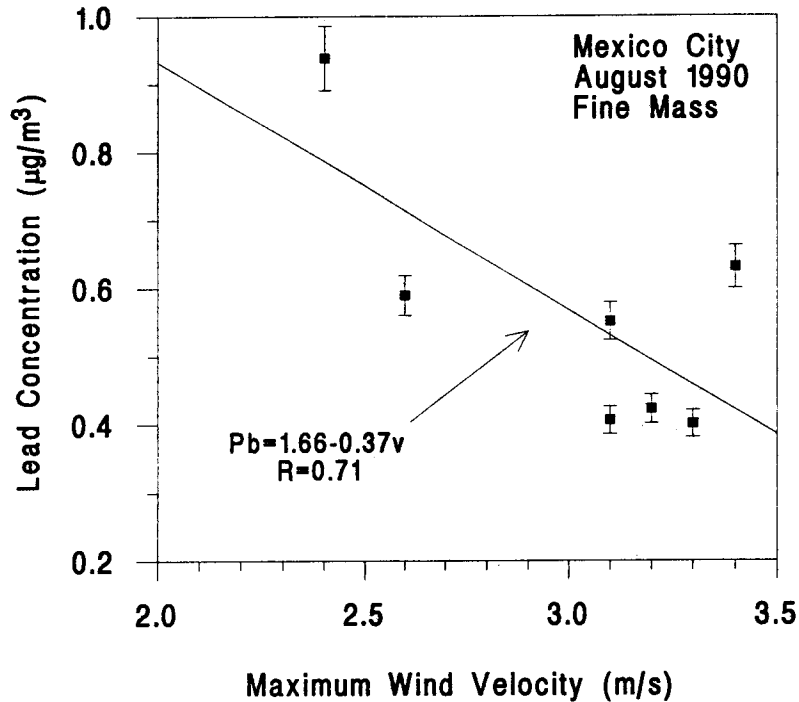


Fig. 7. Pb fine mass concentrations as a function of the maximum wind velocity. The direction of the wind was predominantly North.

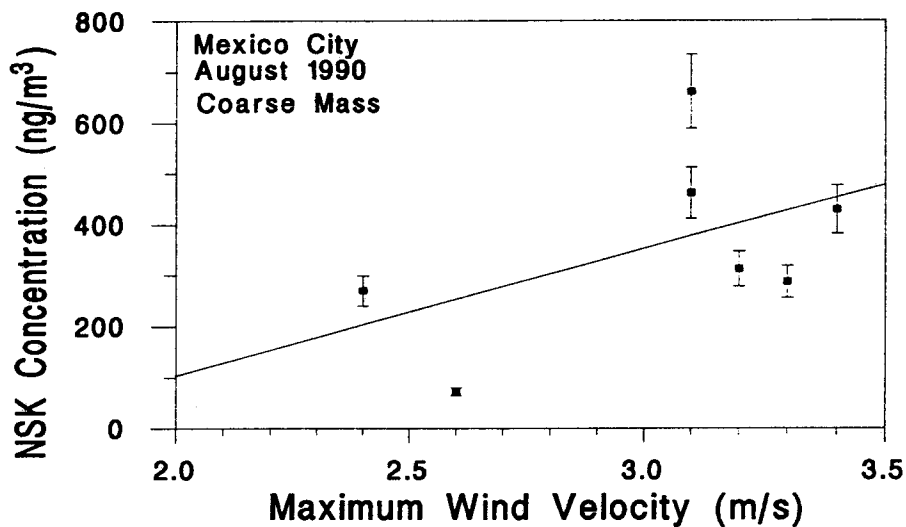


Fig. 8. Concentration of non-soil potassium (NSK) in coarse mass as a function of maximum wind velocity. The line is presented only as a guide to the eye.

Now it is interesting to look at the temperature influence on the various pollutants. Figure 9 shows a plot of H and Si concentrations as a function of the maximum temperature measured during the sampling. It is apparent that while H concentrations increase with temperature, that of Si decreases. This fact might be correlated to photo-oxidation, showing a possible increase of pollutants in the form of hydrocarbons (Ruiz-Suárez, 1989), although these elements are also highly correlated to other anthropogenic elements, as mentioned above. The cause of the decrease of Si, and soil elements in general, with temperature needs deeper studies in order to be explained. Although the quoted results are given mostly for fine mass, similar behavior of coarse mass was observed.

Furthermore, it must be mentioned that no clear correlation of the pollutants with relative humidity (in the range of 45-90% during the sampling process) was found. Moreover, no precipitation occurred along the same period, and thus no possible conclusions can be extracted.

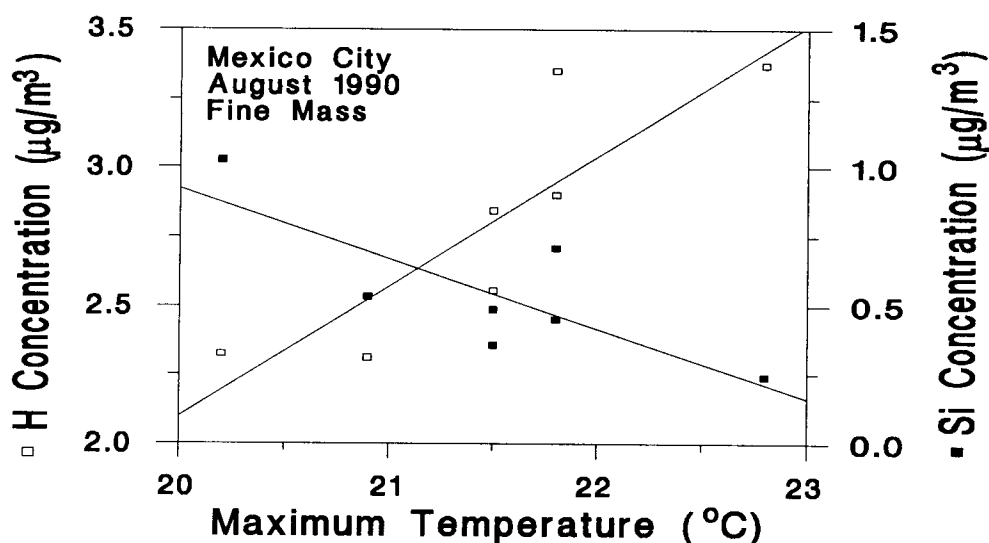


Fig. 9. H and Si concentrations (fine fraction) as a function of the maximum temperature measured during the sampling periods. The lines are drawn only as guides to the eye.

Conclusions

The results shown above permit to establish several important facts. In the first place, the elemental concentrations measured for elements such as Pb are well below the United States Environmental Protection Agency standards ($1.5 \mu\text{g}/\text{m}^3$ 24-hours average). The measured Pb concentration ($0.74 \mu\text{g}/\text{m}^3$) corresponds to the 6 hours period with the worst conditions (6:00 to 12:00 hrs), and in consequence the 24-hours average must be lower. It is necessary to see, however, that the quoted value is still high, and was measured in a relatively clean area, as is the Chapultepec Park.

Identification of possible sources with multivariate statistical techniques (Cluster Analysis) is reasonable, in spite of the very small number of samples taken for this study. Care must be taken when extracting conclusions from these analyses, due precisely to this small number. A larger set of samples will allow then a better understanding of the sources with the use of other methods, such as Principal Components or Factor Analysis. Additionally, a small sample set, like the one presented here, produces a large variability on the measured concentrations, thus reducing the confidence of the results. Nevertheless, further data are being collected, in order to

improve their reliability. As has been extensively discussed, automotive and industrial sources are found to be major sources of contaminants, although soil-derived pollutants represent also a high fraction of the total particulate matter.

The results presented here show in a small scale the potential of the analytical techniques used in the study (PIXE, PESA, and LIPM), which are mainly accelerator-based. They provide multielemental data on a single analysis run, giving information on the correlation (and from this, the sources) of the various elements. Finally, it is important to mention that systematic studies of atmospheric aerosols in Mexico City, following these procedures, are under process of being established, bearing on the work of several Mexican and foreign scientific institutions. This must give, consequently, a better knowledge and possible control of pollutants, which may result in an improvement of the air quality in Mexico City.

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REFERENCES

- Aldape, F., J. Flores-M., R. V. Díaz, J. R. Morales, T. A. Cahill, and L. Saravia, 1991a. Seasonal Study of the Composition of Atmospheric Aerosols in Mexico City. *Int. J. PIXE*, **1**, 355-371.
- Aldape, F., J. Flores-M., R. V. Díaz, J. Miranda, T. A. Cahill, and J. R. Morales, 1991b. Two Year Study of Elemental Composition of Atmospheric Aerosols in Mexico City. *Int. J. PIXE*, **1**, 373-388.
- Báez, A., M. Reyes, I. Rosas, and P. Mosiño, 1988. CO₂ Concentrations in the Highly Polluted Atmosphere of Mexico City. *Atmósfera*, **1**, 87-98.
- Bravo A., H., 1986. Particulate Carbon, a Significant Contributor to the Visibility Reduction of Mexico City. Proc. of the APCA Int.Conf. on Particulate Matter and Fugitive Dusts, Tucson, Arizona, October 1986, 113-127.
- Bravo A., H., R. Camacho, M. I. Saavedra, R. Sosa, and R. Torres, 1989. Concentrations of Nitrates and Sulfates in Total Suspended and Respirable Particles as a Result of Air Pollution Control Strategies in Mexico City. Proc. of the 82nd Ann. Meet. of the Air and Waste Management Assoc., Anaheim, June 25-30 1989, 89-15.5.
- Cahill, T. A., R. G. Flocchini, R. A. Eldred, P. J. Feeney, S. Lange, D. Shadoan, and G. M. Wolfe, 1976. Monitoring of Smog Aerosols with elemental Analysis by Accelerator Beams. National Bureau of Standards Special Publications, 422, 1119-1136.
- Cahill, T. A., L. L. Ashbaugh, J. B. Barone. R. A. Eldred, P. J. Feeney, R. G. Flocchini, C. Goodart, D. J. Shadoan, and G. M. Wolfe, 1977. Analysis of Respirable Fractions in Atmospheric Particulates via Sequential Filtrations. *J. Air. Poll.Control Assoc.* **27**, 675-678.
- Cahill, T. A., R. A. Eldred, D. Shadoan, P. J. Feeney, B. Kusko, and Y. Matsuda, 1984. Complete Elemental Analysis of Aerosols: PIXE, FAST, LIPM and Mass. *Nucl. Instr. and Meth.* **B3**, 291-295.

- Cahill, T. A., R. A. Eldred, D. Shadoan, B. P. Perley, P. J. Feeney, B. Kusko, and H. Miyake, 1987. Multiple Detector System for Rapid PIXE Analysis. *Trans. of the XII Symp. on Appl. of Ion Beams in Material Science, Tokyo*, 433-438.
- Cahill, T. A., R. A. Eldred, P. J. Feeney, P. J. Beveridge, and L. K. Wilkinson, 1990a. The Stacking Filter Unit Revisited. *Trans. of the Air and Waste Management Assoc.*, 213-222.
- Cahill, T. A. 1990b. Design Constraints on Aerosol Samplers Used in Visibility Studies in the Southwest. *Trans. of the Air and Waste Management Assoc.*, 97-108.
- Cahill, T. A., 1990c. Analysis of Air Pollutants by PIXE: the Second Decade. *Nucl. Instr. and Meth.* **B49**, 345-350.
- Cahill, T. A., M. Surovik, and I. Wittmeyer, 1990d. Visibility and Aerosols During the 1986 Carbonaceous Species Methods Comparison Study. *Aerosol Sci. and Technol.* **12**, 149-160.
- Falcón, Y. I., C. R. Ramírez, L. Nuno, and M. L. Sánchez, 1989. Mexico City Aerosol Study: PM10 Sampling and Analysis. *Proc. of the 82nd Ann. Meet. of the Air and Waste Management Assoc., Anaheim, June 25-30 1989*, 89-15.1.
- Gerber, H. E. and E. E. Hindman, 1982. *Light Absorption by Aerosol Particles* (Spectrum Press, Hampton, VA).
- Harrison, J. F. and R. A. Eldred, 1974. Automatic Data Acquisition and Reduction for Elemental Analysis of Aerosol Samples. *Adv. in X-ray Analysis* **17**, 560-583.
- Johansson, S. A. E. and J. L. Campbell, 1988. *PIXE: A Novel Technique for Elemental Analysis*. (John Wiley and Sons, Chichester).
- Karson, M. J., 1982. *Multivariate Statistical Methods*. (Iowa State University Press, Ames, Iowa).
- Kusko, B. H., T. A. Cahill, and R. A. Eldred, 1988. Non destructive Light Element Analysis by Forward Ion Scattering Techniques. *Proc. of the APCA 81st Ann. Meet., Dallas, June 19-24*. 88-53.4.
- Mathai, C. V., S. V. Hering, B. R. Appel, W. Cheng, F. Salaymeh, S. H. Cadle, P. A. Mulawa, T. A. Cahill, R. A. Eldred, M. Surovik, D. Fitz, J. E. Howes, K. T. Knapp, L. Stockburger, B. J. Turpin, J. J. Huntzicker, X. Q. Zhang, and P. H. McMurry, 1990. Intercomparison of Ambient Aerosol Samplers Used in Western Visibility and Air Quality Studies. *Environ. Sci. and Technol.* **24**, 1090-1099.
- Rojas, C. M., P. Artaxo, and R. Van Grieken, 1990. Aerosols in Santiago de Chile: a Study Using Receptor Modeling with X-ray Fluorescence and Single Particle Analysis. *Atmospheric Environment* **24B**, 227-242.
- Ruiz-Suárez, L. G., 1989. Photo-oxidation of hydrocarbons in Mexico City. Effects of Altitude. *Atmósfera*, **2**, 47-63.
- Salazar, S., J. L. Bravo, and M. A. Castellanos, 1989. Identificación de la fracción mineral del aerosol atmosférico en una zona urbana de la Ciudad de México por medio de difracción y fluorescencia de rayos X. *Atmósfera*, **2**, 103-110.
- StatSoft, 1991. *CSS:Statistica* (StatSoft Inc., Tulsa Oklahoma).
- Ward, J. H., 1963. Hierarchical Grouping to Optimize an Objective Function. *Jour. Amer. Stat. Soc.* **58**, 236.