

COMPARATIVE STUDY OF ELEMENTAL CONTENTS IN ATMOSPHERIC AEROSOLS FROM THREE SITES IN MEXICO CITY USING PIXE

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ABSTRACT

A study of the elemental concentrations found in samples of atmospheric aerosols from three sites in the Mexico City Metropolitan Area is presented. The samples were collected during the Winter and Spring of 1994 using Stacking Filter Units (SFU), devised to separate particles with sizes between 2.5 μm and 15 μm (coarse fraction) and smaller than 2.5 μm (fine fraction). Elemental analyses were performed using Particle Induced X-ray Emission (PIXE), which allowed simultaneous detection of 14 elements heavier than Al. By means of analysis of variance, comparisons among the elemental contents in the three sites are given for both fractions, showing that, although variations are observed for some elements, in the fine fraction no definite pattern is found with respect to the site. On the other hand, in the coarse fraction the soil-derived elements Si, K, Ca, Ti, and Fe are the most important contributors to total mass.

RESUMEN

Se presenta un estudio de las concentraciones elementales encontradas en muestras de aerosoles atmosféricos de tres sitios en la Zona Metropolitana de la Ciudad de México. Las muestras se colectaron durante el invierno y la primavera de 1994 utilizando Unidades de Filtros Apilados (SFU), diseñadas para separar partículas con tamaños entre 2.5 μm y 15 μm (fracción gruesa) y menores que 2.5 μm (fracción fina). Se efectuaron análisis elementales con la Emisión de Rayos X Inducida por Partículas Cargadas (PIXE), que permitió la detección simultánea de 14 elementos más pesados que Al. Por medio de análisis de varianza se hacen las comparaciones entre los contenidos elementales de ambas fracciones para los tres sitios, mostrando que, aunque se observan variaciones para algunos elementos, en la fracción fina no hay un patrón definido en cuanto al sitio. Por otro lado, en la fracción gruesa se encuentra que los elementos originados por el suelo Si, K, Ca, Ti y Fe son los contribuyentes más importantes a la masa total.

INTRODUCTION

The atmospheric pollution problem in the Mexico City Metropolitan Area (MCMA) presents different aspects that need to be tackled from equally distinct sides (Riveros 1994). Among the major urban pollutants are atmospheric aerosols, which are mostly responsible for the decrease in visibility, although they also affect the human respiratory tract, contribute to acid rain, and cause damage to buildings (López-

Suárez 1996, Paredes-Gutiérrez 1996). Traditionally, Total Suspended Particles (TSP) have been measured in many urban areas, although the information from these studies is strongly limited, as many of those particles can not enter the human respiratory tract, and the scattering of light is mostly due to the fine fraction of the TSP. The Metropolitan Commission for Prevention and Control of Pollution, through the Automatic Network of Atmospheric Monitoring (RAMA), provides measurements of mass concentrations of particulate

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matter with sizes below 10 μm (PM10). However, simple mass concentration data does not give information about the possible toxicity or other effects of those particles, as no knowledge of their composition exists. Therefore, further studies are required to find out what the aerosol composition is. In this line, it is of interest to investigate the differences between particles having different dimensions, because different sources emit aerosols with various sizes. So, anthropogenic elements typically have Mean Aerodynamic Diameters (MAD) below 2.5 μm , while natural sources produce larger particles. There is a need, thus, to determine whether any zones of the MCMA are more affected by sources of smaller particles, that is, anthropogenic, than others.

In order to determine elemental concentrations of a variety of samples the use of Particle Induced X-ray Emission (PIXE) is recommended (IAEA 1995a, Johansson and Campbell 1988) as it presents advantages over other techniques that can be used for aerosol analyses. It is a method based on charged particle accelerators, that allows fast simultaneous analysis of all elements with atomic number larger than 12, with a good sensitivity and, in general, the sample is not destroyed. PIXE does not offer information on chemical states or contents of light elements, although it can be complemented with other techniques to achieve a more comprehensive view of the aerosol characteristics. Examples of them are ion chromatography (which gives information on compounds as nitrates and sulfates), proton elastic scattering analysis (for measurement of hydrogen), and proton induced gamma-ray emission (for detection of light elements, like carbon, nitrogen, oxygen or fluorine).

In the present work, a comparison of elemental contents in samples of atmospheric aerosols collected during the first half of 1994 from three sites in the MCMA is given. Elemental concentrations were measured with PIXE, and examples of further information that may be achieved after analyzing those concentrations are shown. Results for both coarse and fine aerosols are presented. Although several studies about elemental composition of atmospheric aerosols in the MCMA have already been published (Falcón 1988, Rosas 1995, Aldape *et al.* 1996, Miranda *et al.* 1996), they either are more limited on the number of elements analyzed, on the number of sites where sampling occurred, or on the sampling periods.

MATERIALS AND METHODS

Aerosols samples were collected from January 1994 to April 1994, in three different sites. Their characteristics are shown in **table I**. The sites were chosen because they were expected to be highly polluted. The Naucalpan site (W) is close to an important industrial zone; the Ecatepec site (NE) is close to a major dust storm zone; while the Ciudad Universitaria site (SW) should be strongly polluted due to particle transport by the wind. The sampling equipment was the Stacking Filter Unit (SFU) of the Davis design (Cahill *et al.* 1990), which

TABLE I. SAMPLING SITES PARAMETERS

Characteristic	SW	W	NE
Latitude	19°18'N	19°24'N	19°33'N
Longitude	99°10'W	99°16'W	99°2'W
Altitude	2300 masl	2500 masl	2300 masl
Distance from industry	2 km	5 km	2 km
Traffic density	Medium	Low	High
Type	School	Residential	Residential

separates particles with MAD between 2.5 μm and 15 μm in the coarse fraction, and particles with MAD below 2.5 μm in the fine fraction. The coarse fraction is deposited onto 8 μm pore size polycarbonate membrane filters (Nuclepore, Costar Corp.), and the fine fraction is collected on 3 μm pore size Teflon filters (Teflo, Gelman Sciences Inc.). Sampling was done once a week, from 8:00 h to 14:00 h, simultaneously at the three sites. The total mass of the deposited particles was measured by pre- and post-weighing the filters with an Ohaus 200GD electrobalance (sensitivity 10 μg , resolution 10 μg). Quality control procedures for sample preparation and handling are described elsewhere (Miranda *et al.* 1996). Air flow in the SFU's was calibrated through an MKS 358C mass flow meter (MKS Instruments, Andover, MA, USA).

PIXE analyses were carried out with the 5.5 MV Van de Graaff accelerator at the Instituto de Física, UNAM, using a 2.2 MeV proton beam. The experimental setup is displayed in **figure 1**. The resolution of the detection system is 180 eV at 5.9 keV. Typical beam currents were 5 nA, and total integrated charges were 1 μC . The detection system was calibrated by means of MicroMatter (Deer Harbor, Washington, USA) thin film standards. A representative minimum detection limits curve for the elemental contents determination in the fine fraction is shown in **figure 2**, which presents data only for elements with atomic number between 13 (Al) and

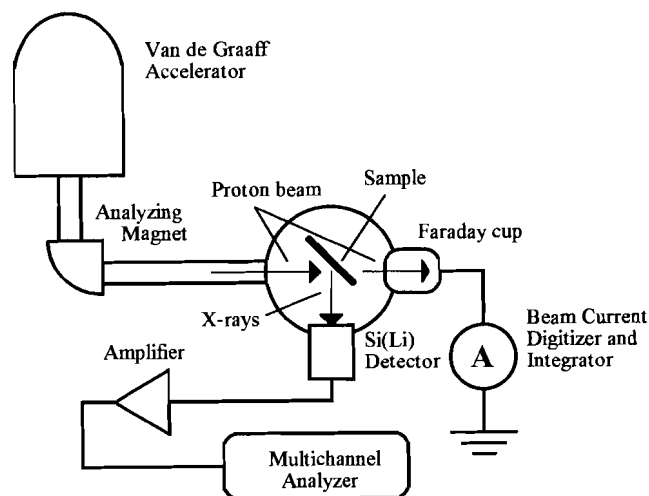


FIG. 1. Experimental setup for PIXE analyses of atmospheric aerosol samples. The amplifier is an Ortec 672 and the multichannel analyzer is an Ortec ACE add-on card attached to a personal computer

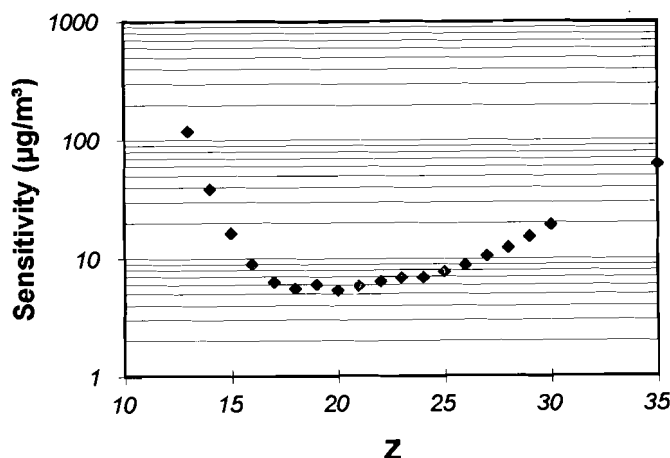


FIG 2. Sensitivity curve (μg of an element per m^3 of air) for a typical PIXE analysis of an aerosol sample, using a 2.2 MeV proton beam and a $5 \mu\text{C}$ integrated charge

35 (Br). These elements are analyzed with their K X-ray line. Other heavy elements, like Pb, are measured using their L lines, thus corresponding to a different sensitivity curve. However, the sensitivity for Pb is $\sim 45 \mu\text{g}/\text{m}^3$. Quality assurance experiments for PIXE analyses were done previously with X-ray Fluorescence (Miranda et al. 1994). X-ray spectra were analyzed by means of the Quantitative X-ray Analysis System (QXAS) computer code (IAEA 1995b).

RESULTS AND DISCUSSION

About 1100 elemental concentrations were measured. Average elemental contents in the fine fraction are displayed in table II, while those for the coarse fraction are given in table III. Also, mass concentrations and the number of samples are included for both components.

From the figures in table II it is possible to note that concentrations of the elements in the fine fraction are almost constant in the three sites. In spite of showing different concentrations of some elements (S, Fe, Pb) within the uncertainty, analysis of variance at a 95% confidence level (Kreyszig 1985) of this sample set does not show differences in the means of the detected elements nor on the mass, thus supporting the statement about the uniformity of aerosol composition, or otherwise pointing to a need for more samples. The results from this analysis of variance are given in table IV, both for the fine and the coarse fractions.

Regarding the coarse fraction, it is observed that the main contribution comes from soil-derived elements (Si, K, Ca, Ti, and Fe). This has already been observed in previous size-segregated studies in the MCMA (Miranda et al. 1992, 1994, 1996). Again, analysis of variance shows no difference on the elemental concentrations, although it does indicate a lower gravimetric mass concentration in the SW site (see table IV). The explanation is probably the presence of organic com-

TABLE II. ELEMENTAL CONCENTRATIONS OF FINE FRACTION OF AEROSOL SAMPLES FROM THREE DIFFERENT SITES IN 1994 ($\mu\text{g m}^{-3}$)

Element	SW	W	NE
Number of samples	14	12	14
Mass	72 ± 12	59 ± 11	50 ± 11
Al	3.0 ± 0.42	ND*	0.91 ± 19
Si	1.8 ± 0.15	2.0 ± 0.17	1.9 ± 0.17
P	0.22 ± 0.02	0.16 ± 0.02	0.18 ± 0.02
S	3.5 ± 0.30	2.6 ± 0.28	2.7 ± 0.34
Cl	0.14 ± 0.01	0.11 ± 0.01	0.13 ± 0.01
K	0.45 ± 0.04	0.41 ± 0.04	0.39 ± 0.04
Ca	0.33 ± 0.03	0.46 ± 0.03	0.41 ± 0.03
Ti	0.031 ± 0.003	0.030 ± 0.003	0.026 ± 0.003
V	0.37 ± 0.005	0.038 ± 0.005	0.032 ± 0.005
Cr	0.013 ± 0.002	0.011 ± 0.002	0.008 ± 0.002
Mn	0.008 ± 0.002	0.014 ± 0.003	0.008 ± 0.002
Fe	0.35 ± 0.02	0.37 ± 0.03	0.24 ± 0.02
Cu	0.017 ± 0.004	0.021 ± 0.005	0.012 ± 0.004
Zn	0.090 ± 0.01	0.13 ± 0.02	0.10 ± 0.01
Pb	0.12 ± 0.01	0.25 ± 0.05	0.10 ± 0.01

*ND = element was not detected

pounds, which cannot be measured with PIXE. Also, S contents in the coarse fraction is lower than in the fine one, as anticipated from other studies. Rather surprising, though, is the concentration of this element in the Western site, which was always below the sensitivity of the detection system. No trace of Pb, typically anthropogenic, was measured in the coarse fraction.

TABLE III. ELEMENTAL CONCENTRATIONS OF COARSE FRACTION OF AEROSOL SAMPLES FROM THREE DIFFERENT SITES IN 1994 ($\mu\text{g m}^{-3}$)

Element	SW	W	NE
Number of samples	14	12	14
Mass	79 ± 10	150 ± 11	132 ± 17
Si	11 ± 0.80	17 ± 1.2	15 ± 1.1
S	1.1 ± 0.11	NR*	1.1 ± 0.10
Cl	0.88 ± 0.06	0.089 ± 0.066	1.2 ± 0.08
K	0.91 ± 0.08	1.4 ± 0.14	1.4 ± 0.13
Ca	5.2 ± 0.29	6.5 ± 0.39	6.8 ± 0.37
Ti	0.30 ± 0.03	0.31 ± 0.02	0.33 ± 0.02
V	0.042 ± 0.006	0.037 ± 0.006	0.033 ± 0.005
Cr	0.073 ± 0.01	0.068 ± 0.01	0.062 ± 0.01
Mn	0.066 ± 0.01	0.074 ± 0.01	0.075 ± 0.01
Fe	3.1 ± 0.18	3.6 ± 0.22	3.4 ± 0.19
Cu	ND**	0.010 ± 0.004	ND**
Zn	0.092 ± 0.02	0.12 ± 0.02	0.10 ± 0.02

*NR = element was not reliably measured

**ND = element was not detected

Remarkable differences are observed also between fine and coarse components. First, Al, P, and Cu are more abundant in the fine fraction, while Cl, Cr, and Mn have higher concentrations in the coarse one. This is somewhat startling, as Cr is normally among the anthropogenic elements, which are most of the times present as fine aerosols. However, Cl and Mn may be associated to soil derived elements. On the other hand, concentrations of other elements, like V and Zn are apparently uniform in both fractions. Again, higher values

TABLE IV. RATIO v_o OF MEAN SQUARES FOR ANALYSIS OF VARIANCE*

Element	Fine fraction	Coarse fraction
Mass	0.41	10.96
Si	0.10	1.66
P	0.30	ND**
S	0.85	0.10
Cl	0.15	2.81
K	0.26	2.89
Ca	1.48	1.07
Ti	0.14	0.13
V	0.05	0.19
Cr	0.54	0.60
Mn	1.58	0.32
Fe	2.75	0.32
Cu	1.45	0.86
Zn	0.90	0.72
Pb	1.14	ND

* The value x for which the F distribution function with (2, 39) degrees of freedom has the value 0.95 is $x = 3.24$ (Kreyszig 1985). If $v_o \leq x$, then the mean concentrations are not different from each other.

** ND = element not detected

were expected for these elements in the fine fraction.

Enrichment factors (EF) relative to Fe and to earth crust composition are also computed to estimate the possible origin of the elements. Fe is chosen as reference element because it is expected to have lower errors and uncertainties in the concentration measurement, due to its higher X-ray energy (thus reducing the uncertainty in the efficiency) and because there are rather large amounts of this element in the samples. These factors are obtained through the equation:

$$EF = \frac{\left(\frac{C_z}{C_{Fe}}\right)_s}{\left(\frac{C_z}{C_{Fe}}\right)_{EC}}, \quad (1)$$

where C_Z is the concentration of element Z, and the subscripts S and EC refer to the sample and to the average earth crust composition, respectively. Figure 3 shows the EF for elements Si, K, Ca, and Ti. Values of elemental contents in earth crust were taken from the tables by Demayo (1984). The EF for these particular elements is very close to one, as it should be expected from soil-derived elements. However, different behaviors are observed for K in the fine and coarse fractions. EF for K is higher in the fine fraction, and this can be explained by a contribution from smoke, as K is a typical tracer of this aerosol source. Moreover, the high Zn contents found in the coarse fraction are better understood when looking at its EF, because their values for all three sites are around 25, while those for the fine fraction are between 250 and 300.

Based on the information given by the EF, i.e., that the elements Si, K, Ca, Ti and Fe all have a common soil origin, it is possible to compute a total soil contribution to the aerosol mass, following a tracer element method (Henry *et al.* 1984). Also, sulfate and non-soil K concentrations can be

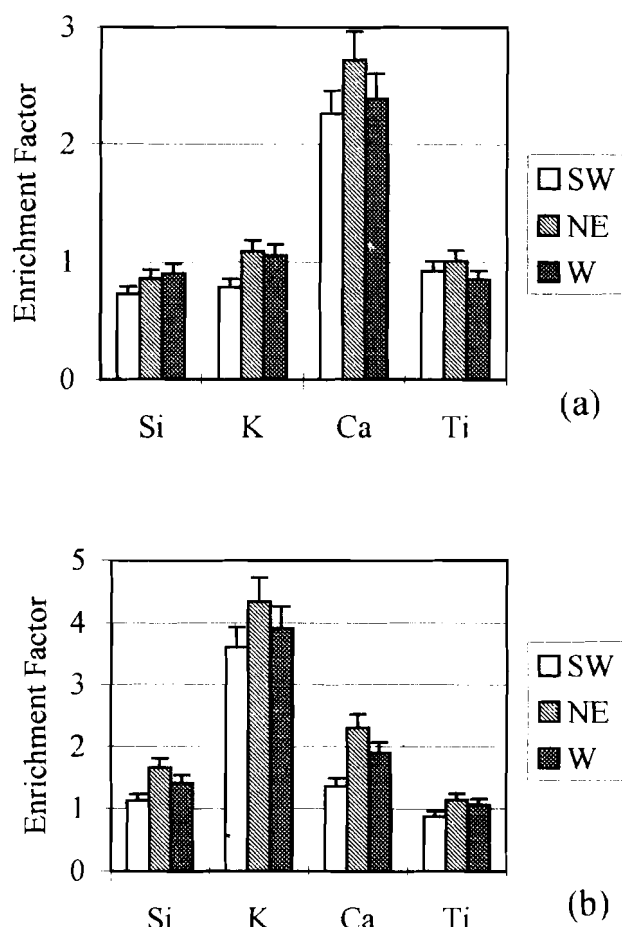


FIG. 3. Enrichment factors for Si, K, Ca and Ti compared to Fe, for (a) coarse fraction and (b) fine fraction

evaluated. This is done by using the equations (Miranda *et al.* 1994):

$$\text{Soil} = 2.20\text{Al} + 2.49\text{Si} + 1.63\text{Ca} + 1.97\text{Ti} + 2.38\text{Fe}, \quad (2)$$

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

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

where Soil denotes the soil-derived aerosols concentration (assuming that the elements are present as oxides and using average earth crust composition); NSK is the non-soil K contribution (possibly from smoke); Sulfate is the concentration of this compound, based on the assumption that S is present as ammonium sulfate, while Al, Si, S, K, Ca, Ti, and Fe represent the measured concentration of the respective element. Results of this calculation are presented in table V for the fine fraction. Again, analysis of variance shows no difference on the concentrations in the samples from the three sites. Mass deficiency with respect to gravimetric mass after adding all the contributions from PIXE analysis is explained by other compounds not analyzed by this technique, like organic matter and nitrates. The analysis of these species requires complementary techniques, such as ion chromatography.

TABLE V. SOIL, SULFATE AND NON-SOIL K CONCENTRATIONS IN AEROSOL SAMPLES FROM THREE DIFFERENT SITES IN 1994 ($\mu\text{g m}^{-3}$)

Element	SW	W	NE
Soil (fine)	13 \pm 1	7 \pm 0.5	8 \pm 0.6
Soil (coarse)	45 \pm 1	63 \pm 3	56 \pm 2
Sulfate (fine)	14 \pm 1.2	11 \pm 1.2	11 \pm 1.4
NSK (fine)	10.27 \pm 0.04	0.22 \pm 0.04	0.27 \pm 0.04

CONCLUSIONS

This work represents the first attempt to establish an aerosol monitoring network throughout the MCMA, with multielemental and sensitive analytical capabilities. The quantitative results regarding the concentrations did not allowed to determine differences in the elements present in the aerosols from the three sites, and only a gravimetric mass difference was observed in the Southwestern site. There is also a strong limitation in the number of samples considered in this study. Other works are already in progress to support or discard the uniformity hypothesis. Enrichment factors are helpful in the identification of some elements as produced by a specific source, as was the case of soil derived elements; moreover, the analytical methods are useful for the application of simple tracer element methods for source apportionment. Unfortunately, the lack of comparable information from other urban areas (Miranda 1996) prevents the authors from making any statement about the true level of aerosol pollution in the MCMA.

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