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X-Ray Fluorescence Analysis of Fine Atmospheric Aerosols from a Site in Mexico City

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Abstract A study was performed in the Winter of the year 2015 in a Southwestern site in the MAMC (Ciudad Universitaria), collecting $PM_{2.5}$ samples with a MiniVol. As a part of wider study focused to fully characterize aerosols at this site, an X-ray Fluorescence (XRF) spectrometer (based on an Rh X-ray tube) built to analyze environmental samples, was used to characterize the sample set. A total of 16 elements (Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, and Pb) were detected in most samples and mean concentrations were calculated. Cluster analysis was also applied to the elemental concentrations to find possible correlations among the elements.

Keywords: XRF, atmospheric aerosols

1. INTRODUCTION

Airborne particles with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) are associated with human morbidity and mortality [6]. $PM_{2.5}$are incorporated into the atmosphere by natural and anthropogenic sources and form a complex mixture of different chemical and physical characteristics.

Mexican environmental legislation establishes 45 μg $m^{-3}$of $PM_{2.5}$as the maximum concentration in the atmosphere during 24-h average(SSA, 2014). In Mexico City, although the Atmospheric Monitoring System (also known as *RAMA*) measures the mass concentration of $PM_{2.5}$, it is necessary to obtain more information regarding the composition and the origin of these particles. In order to obtain the sources of emission, several methods have been developed using information on elemental contents obtained through techniques like X-Ray Fluorescence (XRF). This technique is preferred in many cases because

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it obtains many elemental concentrations with low detection limits and non-destructively. XRF may not be applicable to all aerosol samples, and in its most commonly applied form accurately quantify elements with atomic numbers larger than 13 (Al) [7].

In the present work, the elemental composition of 63 samples of $PM_{2.5}$ collected during Winter 2015 in a Southwest site in the Metropolitan Area of Mexico City (MAMC), Ciudad Universitaria, were analyzed by XRF and a first approach to the identification of the emission sources was carried out.

2. EXPERIMENTAL

Aerosol samples were collected from January 16, 2015 to March 26, 2015 at the Universidad Nacional Autónoma de México main campus (southwestern area of the MAMC) during the Winter season. Site characteristics are: latitude 19° 19' N, longitude 99° 10' W, altitude 2280 m a.s.l. Two low volume samplers, MiniVol TAS (Airmetrics, OR, USA),operating at 5 L min-1 ± 10 %, were employed to collect the samples. The particles are deposited onto polycarbonate membrane filters (SPI, USA, 47 mm, 0.4 μm) and quartz filters (Pallflex, USA, 47 mm). Sampling was performed from 11:30 h to 11:00 h of the next day (23.5 h), and a total 63 samples were acquired. Gravimetric mass of the deposited particles was measured by pre and post weighting the filters with a Sartorius BA2105 electrobalance (resolution 10 μg).

XRF analyses were performed with an X-ray Fluorescence (XRF) spectrometer developed for environmental applications at the Instituto de Física, UNAM (IFUNAM) [2]. An Oxford Instruments X-Ray tube with Rh anode, as well as an Amptek Si-PIN X-Ray detector (resolution 160 eV at 5.9 keV), were employed. The tube operated at 50 kV and current of 500 μA, irradiating during 900 s per spectrum. The detection systemefficiencies were measured using thin film standards (MicroMatter Co., Canada) in every case. The resulting spectra were integrated with AXIL program. Uncertainties in elemental concentrations were evaluated following the method described by [3].

3. RESULTS AND DISCUSSION

Table 1 shows the 24 h average elemental and gravimetric mass concentration found in the samples; values of $PM_{2.5}$ concentration reported by AMS are included. For all days the $PM_{2.5}$ concentration measured with polycarbonate filters and data reported by AMS were below 45 μg m^{-3}, the maximum value permitted in 24 h average. The mass concentration in quartz filters tends

Table 1: 24 h average elemental concentrations in $PM_{2.5}$ ($\mu g\ m^{-3}$)

Element	Mean	Uncertainty[a]	Minimum	Maximum	N[b]
$PM_{2.5}$ (quartz)	19	N.C.	1	56	60
$PM_{2.5}$ (polyc)	18	N.C.	4	43	63
$PM_{2.5}$ (AMS)	17	N.C.	5	42	63
Al	1.511	(0.277)	0.067	7.094	63
Si	0.688	(0.059)	0.322	4.483	63
P	0.268	(0.022)	0.094	0.517	63
S	1.520	(0.060)	0.513	3.775	63
Cl	3.085	(0.106)	0.069	6.515	63
K	0.160	(0.015)	0.005	0.441	48
Ca	0.133	(0.016)	0.055	0.272	63
Ti	0.095	(0.011)	0.019	0.320	62
V	0.028	(0.004)	0.001	0.083	56
Cr	0.220	(0.016)	0.128	0.303	63
Mn	0.106	(0.010)	0.052	0.166	63
Fe	0.283	(0.017)	0.157	0.412	63
Ni	0.021	(0.003)	0.002	0.051	45
Cu	0.034	(0.005)	0.002	0.075	61
Zn	0.070	(0.007)	0.012	0.202	63
Pb	0.145	(0.020)	0.019	0.274	63

a. Numbers in parenthesis represent the combined uncertainty

b. Numbers of valid observations

c. N.C.: not calculated

to be more variable, maybe because quartz may absorb humidity from the ambient. Either way, there is no statistical difference between the medians of the 3 methods at 95 % confidence. 16 elements were found in the samples. The number of valid observations was relatively small for K and Ni. The quantification of Cl was not accurate because of the L lines of the Rh emitted by the X-Ray tube. Rh L lines interfere with Cl K lines.

As a further step in the analysis, Fig.1 shows the correlation matrix for the elements present in $PM_{2.5}$. The numbers represent Pearson correlation coefficients for values significant at a confidence level of 95 %. Al and Si

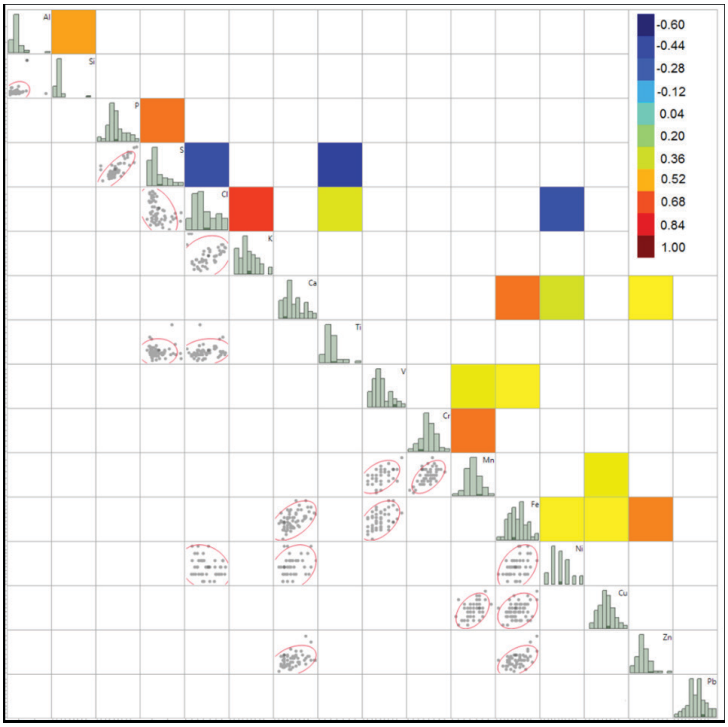

Figure 1: Scatterplot and correlation matrix of elements present in $PM_{2.5}$. Significant values ($p < 0.05$) of Pearson correlation coefficients are presented.

present strong correlation maybe because of a soil-related origin [4]. S and P are considered markers for biomass burning emission [1], which suggest an explanation for the strong positive correlation obtained in the analysis. The matrix shows positive correlation with elements markers for industrial sources like Cr and Mn [4].

With the objective of classifying the elements in a small number of groups based on the similarities among them, a cluster analysis (Ward's amalgamation method and 1-Pearson linkage distance) was made and the resultant dendrogramis shown in Fig. 2. The first group at a distance of ~2.0 is conformed by elements present in biomass burning: K, Cl and Ti [2]. At a distance of ~1.5 the cluster shows three groups: one includes elements like Al and Si (soil-related origin) and S and P (markers of biomass burning), while the other is formed by elements produced by industrial processes: Cu, Cr, Mn and V associated with fossil fuel combustion. The last distance shows othersoil-

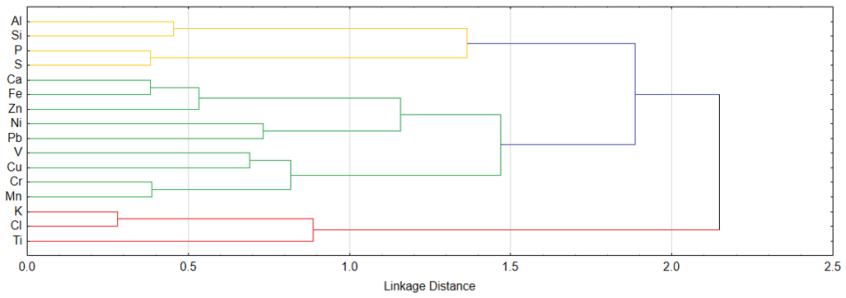

Figure 2: Dendrogram obtained from Cluster analysis for the elements present in $PM_{2.5}$

related elements,like Ca, Fe and Zn. Finally, another group conformed by Ni and Pb, elements present in fossil fuel combustion.

4. CONCLUSIONS

During the whole campaign the concentration of $PM_{2.5}$ was below the limit established by official regulation (SSA, 2014). The most abundance elements in $PM_{2.5}$ were Al, Si, and S, the values for Cl are over estimated by this method analysis. The correlation matrix and cluster analysis suggest biogenic and anthropological emission sources like biomass burning, soil-related emissions, fossil fuel combustion and industrial emissions. Although this statistical tools may help to find the source of atmospheric aerosol, in future techniques like Positive Matrix Factorization (PMF) or Principal Component Analysis (PCA) will be used to determine source contributions.

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