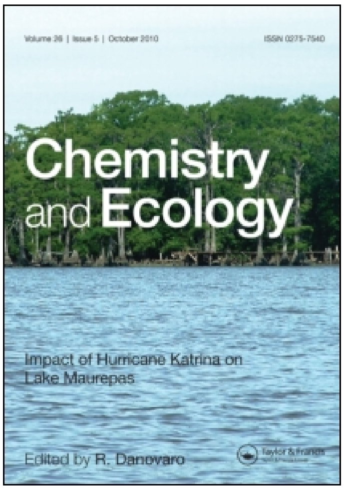

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Determination of trace elements in total suspended particles at the Southwest of Mexico City from 2003 to 2004

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The purpose of the present study is to describe the relationships of eight elements analysed in total suspended particles collected in Mexico City, during 2003 and 2004. Al, Cd, Cr, Fe, Mn, Ni, Pb and V were analysed in to the atmospheric samples and the results were treated by Principal Components Analysis and Cluster Analysis trying to identify the possible sources of aerosols in the sampling site. Factor analysis calculations allowed the elements classification, related to their source on oil combustion, crustal and urban dust, smelting industries and motor vehicle emissions. A further statistical analysis of chemical results from the atmospheric samples was also performed, in order to see what environmental concentrations of those elements have been affected by industrial and mining activities. The eight elements analysed were arranged into two groups that presents high and positive Pearson r values suggesting common emission sources.

Keywords: heavy metals measurement; total suspended particles; emission sources

1. Introduction

Atmospheric pollution by particles is a serious problem around the world, especially in countries where the industrial growth is not often followed by environmental regulations, producing high concentrations of pollutants in urban areas. In several megacities, such as Mexico City, the rapid industrialisation and urban growth produce atmospheric particles derived from many different activities that contribute to multiply respiratory diseases and chronic illnesses among the inhabitants. Also, the increasing number of motor vehicles circulating in the city increases the complexity of particulate pollution emitted from industrial sectors. For instance, total suspended particles have been found to cause health problems, because they can trigger or exacerbate diseases, such as asthma, emphysema, bronchitis, and lung cancer. Possible causes include particles composition (they may contain soluble transition metals such as copper, iron, vanadium, nickel or zinc) acidity and size [1].

In the last decades, due to its effects in the atmosphere, the study of heavy metals in particles and pluvial precipitation has increased. Metals like Pb, Cd, As, and Hg accumulate in the

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biosphere and can be toxic for living organisms, even at low concentrations. Also, the presence of particulate matter in urban areas is a significant atmospheric pollution problem. It is responsible for a decreasing in visibility and when its dimension is below $10\,\mu\text{m}$ other effects appear related with public health. For instance, particles below this aerodynamic diameter can penetrate into human respiratory tract [2,3]. Metals in inorganic fraction of atmospheric particles are linked to a higher toxic damage, than other chemical species that sometimes has a faster excretion [4].

The concentrations and size distributions of trace metals in the atmosphere are ruled by the sources, as well as by rates of wet and dry deposition, cloud processing, and chemical transformations [5]. The amount of trace metals and the size distribution of atmospheric particles influence the particles toxicity, and also control the extent the metals may be dispersed via atmospheric transport [5–8].

Natural sources of aerosols include terrestrial dust, marine aerosol, volcanic emissions and forest fires. In contrast, anthropogenic emissions of aerosols are related to industrial processes, incomplete combustions of hydrocarbons, automobile mufflers, and corrosion of metallic parts [9,10]. Energy generating plants and industrial combustion processes generate gases and particles with high amounts of metals. Their emissions contribute to the presence of heavy metals in the atmosphere.

Mexico City is considered as one of the most polluted cities of the world as a result of its rapid increase in the past 3 decades. Every day, more than 3 million vehicles and around 30,000 industries produce nitrates, TSP and fine particles $<\text{PM}_{10}$. Also, Mexico City has two power plants that consume natural gas.

More than 80% of the Mexico City industry is located at the North, Northeast, and the prevailing winds come from this direction [11], then the pollutants emitted in these areas are transported to the South, Southwest part of the city, where the sampling site is located.

The standard air quality for total suspended particles (TSP) in Mexico, Federal Norm NOM [12], is $210\,\mu\text{g}\,\text{m}^{-3}$ (24 h average), and for particles with aerodynamic diameter less than $10\,\mu\text{m}$ (PM_{10}) is $150\,\mu\text{g}\,\text{m}^{-3}$.

Despite the efforts of the authorities to accomplish the norms, the concentration of particles in Mexico City is usually above national and international air quality standards.

In order to provide new insights about the temporal variability of the distribution of trace elements and air quality at the Southwest of Mexico City, we analysed the total suspended particles collected during the period 2003–2004.

2. Material and methods

2.1. *Sampling site*

Mexico City has an average altitude of 2240 meters above sea level (masl), and it is located at 19°26′13″ latitude, 99°10′55″ longitude (Figure 1). The city extends over $2000\,\text{km}^2$. It is surrounded in South and West by mountain complexes, like Ajusco and Chichinautzín, over 3000 masl, and the Valley of Toluca. At the Southeast are Popocatépetl and Iztaccíhuat volcanos, at more than 5000 masl. Most of the river basin at the North is blocked by the Mountain of Guadalupe, which reaches 2600 masl [13].

The sampling site was located in the Southwest part of Mexico City, on the roof of the Centro de Ciencias de la Atmósfera building, at the Universidad Nacional Autónoma de México (UNAM) campus. The UNAM is located in the middle of a residential area. Industrial activities and traffic are less intense than in down-town or the northwestern area. Thus, the main nearby pollution sources are local soil, light traffic, and a few industries.

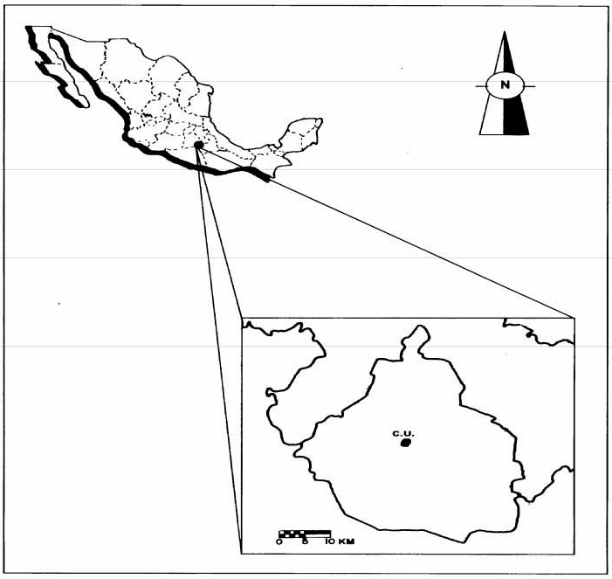

Figure 1. Sampling site location.

2.2. *Sampling method*

Particles were collected on isopore membrane filters (Millipore 0.4 μm HTTP). The sampling time was 24 h per day, with a filter volume air which ranged from 30 to 35 m^3. The present study reports the concentrations of Al, Cd, Cr, Fe, Mn, Ni, Pb and V, in 100 filters collected over a two year period (2003–2004).

2.3. *Chemical analysis*

Prior to chemical analysis, acid digestion of the filters was done with a MARS 5 analytical microwave oven, using 15 ml of 3.2N nitric acid at 110 psias, for 30 min; after digestion, the solution was poured into a 25 ml volumetric flask, then deionised water was added to the mark and kept at 4 °C until the analyses were carried out.

The samples were analysed by graphite furnace atomic absorption spectrometry (GFAAS) with a 932AA double beam GBC device, coupled with a 3000 graphite furnace accessory system, which consists of a GF3000 graphite power supply and a PAL3000 furnace auto sampler, both computer controlled. A deuterium lamp for background correction, pyrolytically coated graphite tubes, boosted discharge hollow cathode lamps (Photron Super Lamp) for Cd, Fe, Ni and Pb analysis at 228.5, 248.3, 232.0 and 217.0 nm respectively, as well as a hollow cathode lamp (Photron) for Al, Cr, Mn, and V, at 309.3, 357.9, 279.5 and 318.5 nm respectively. Calibration standards were prepared with the same acid concentration as the samples. Cross check methods for standard additions were used. The detection limits, in $\mu g\, l^{-1}$ were 6.2, 0.07, 0.38, 2.04, 0.46, 0.78, 1.14 and 3.12 for Al, Cd, Cr, Fe, Mn, Ni, Pb and V, respectively. Certified standards High-Purity Standards traceable to National Institute of Standards and Technology (NIST) were used for determination of metals. Blanks were collected during sampling and were analysed in the same way as the samples, it was important to calculate the ratios of trace metals average concentrations on blanks and the average concentrations of metals on samples.

2.4. *Quality control*

Validation of the analytical method was done analysing field and laboratory blanks. The evaluation of cleaning procedure was the same that was applied to the bottles, a measured volume of deionised water of around 60 ml of the filtered sample. The method of recoveries was applied by means of the 'laboratory spike'; a volume known of the analytic is added to the sample [14,15].

2.5. *Statistics*

A statistical analysis was carried out with the integrated results of each one of the analysed metals. In this study, a Statistica/W [16] was used for data treatment and analysis, it involved three steps: (a) Experimental data sets arrangement and correlation efficient matrix building, (b) Data exploration and description by principal component analysis, and (c) Principal component factor loadings [17,18].

3. Results and discussion

Concentrations descriptive statistics (mean, minimum, maximum, percentiles 25th and 75th, geometric mean, harmonic mean and standard deviation) are reported in Table 1. For values under the metal's detection limit, half of the detection limits value was used for computational purposes. Table 1 indicates that Al and Fe have the highest concentrations, followed by Pb, Cr, Ni, Mn, V, and Cd. The geometric and the harmonic mean can be used to calculate the baseline

Table 1. Descriptive statistics: Mean, minimum (Min), maximum (Max), percentiles 25th and 75th, geometric mean, harmonic mean and standard deviation (Std. Dev), [ngm^{-3}], concentrations of metals in total suspended particulate (TSP), collected during 2003–2004.

Element	Mean	Min	Max	25th percentile	75th percentile	Geometric mean	Harmonic mean	Std. Dev
Al	1536.4	97.65	8939.1	570.04	2027.9	1047.8	691.56	1543.6
Cd	2.64	0.09	8.05	1.06	3.99	1.85	0.99	1.75
Cr	23.79	14.08	44.02	18.24	27.20	22.93	22.11	6.62
Fe	1098.6	27.88	4963.8	263.19	1593.8	623.6	315.00	1102.2
Mn	19.23	2.66	45.18	12.11	25.46	14.32	14.32	9.41
Ni	23.03	8.78	52.93	18.03	26.49	20.77	20.77	7.57
Pb	50.78	8.36	128.07	29.48	68.01	35.94	35.94	28.16
V	16.22	2.15	44.52	8.40	23.41	9.93	9.93	10.02

$N = 100$ (number of samples).

Table 2. Comparison of trace metal concentrations in total suspended particulate (TSP) ngm^{-3} for different sites.

Trace metal	This study	[a]Fernández A.J.	[b]Fernández A.J.	[c]Wu Yuh-Shen	[d]Fang G.C.
Al	1536.6				1710.0
Cd	2.62	0.210	0.32		
Cr	23.79			24.4	
Fe	1098.6	260.8	654.0	116.3	
Mn	19.23	7.43	16.5	148.8	110.0
Ni	23.03	1.44	1.97		
Pb	50.78	43.7	63.7	46.1	180.0
V	16.22	4.8	5.9		

[a]Fernández A.J. et al., 2001 [20]; [b]Fernández A.J. et al., 2002 [21]; [c]Wu Yuh-Shen et al., 2006 [22], [d]Fang et al., 2004 [23].

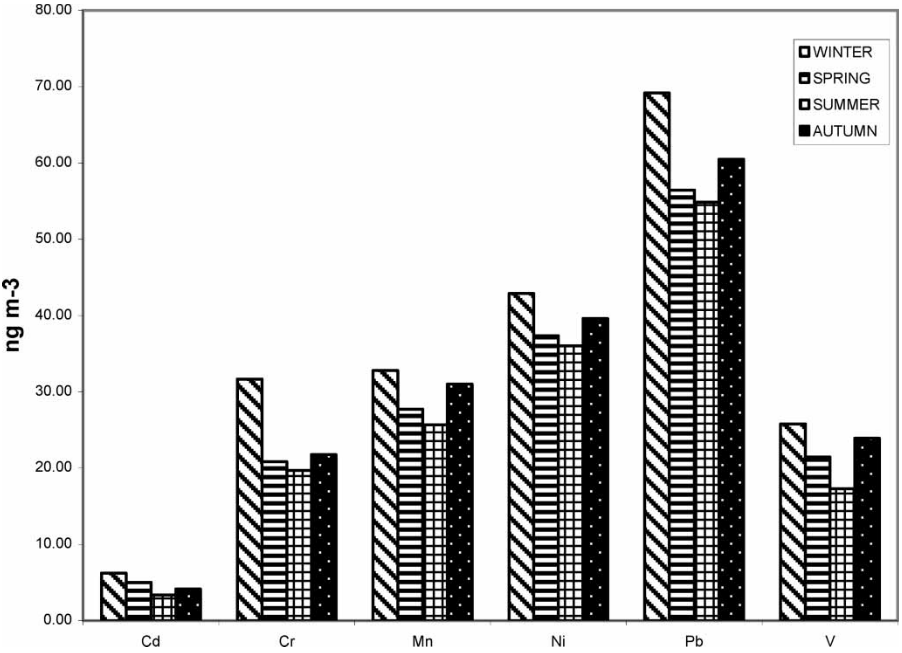

Figure 2. Bar graph corresponding to seasonal average concentrations of trace metals corresponding to 2003 and 2004.

concentrations [19]. The average values obtained in this study are compared with others available from the literature [20–23] in Table 2.

Since the sampling was 24 h day, it is not possible to obtain daily variations, but allows calculating monthly or seasonal variations (Figure 2). According to the sampling time, results were grouped in seasons: spring, summer, autumn and winter, and then were compared with each other. During these seasons, temperature inversions and calm winds, occurring almost daily, promote the increase of air pollutants in Mexico City's atmosphere. Figure 2 indicates that the highest values occurred from February to May, and the lowest values in December and January. Also, a maximum photochemical activity is expected in the spring months.

3.1. *Correlation between variables*

Correlation coefficients were calculated for each metal. If the coefficient between two metals is high, it means the source of emission for both is the same. Table 3 shows the correlation coefficients

Table 3. Spearman rank correlation among the average concentration of trace metals, during 2003-2004. Bold numbers are significant at $p < 0.05$, $N = 100$.

Variable	Al	Cd	Cr	Fe	Mn	Ni	Pb	V
Al	1.00	**0.51**	0.06	**0.64**	0.46	0.10	0.05	0.35
Cd		1.00	0.08	0.48	**0.59**	0.03	0.38	0.20
Cr			1.00	−0.02	0.15	0.09	0.44	−0.08
Fe				1.00	**0.54**	0.12	0.10	0.25
Mn					1.00	0.08	0.48	0.34
Ni						1.00	0.04	0.16
Pb							1.00	0.08
V								1.00

among the different metals on filters. The Spearman Rank Order correlation was applied to the total trace metals. The matrix correlations are shown in this table. Good correlation was found between Al and Fe. These metals are associated with coal-fired boilers, crustal components (fugitive dusts), steel making and smelter activities. A good correlation between Cd and Mn is associated with electroplating and smelter activities on industrial zones; though Mn has also a contribution from crustal material, as some authors have pointed out [24,25]. On Table 3 significant correlations are in bold.

In general, aluminum and iron show the highest correlations at $p \leq 0.05$ for both years. Low correlations between Cr, Ni, Pb and V suggests that these trace metals have different anthropogenic or natural sources.

Figures 3a and 3b show the scatter plots and linear regression equations of Al-Fe and Cd-Mn, the correlations at 95% confidence are $r = 0.647$ and $r = 0.567$ respectively. Perhaps, particles with these metals were transported towards the collecting site, although correlations with wind directions and velocities could not be examined. Concentrations of Cd, Cr, Ni and V are linked normally with industrial sources, and are much lower in the UNAM campus, because it is in the middle of a residential zone.

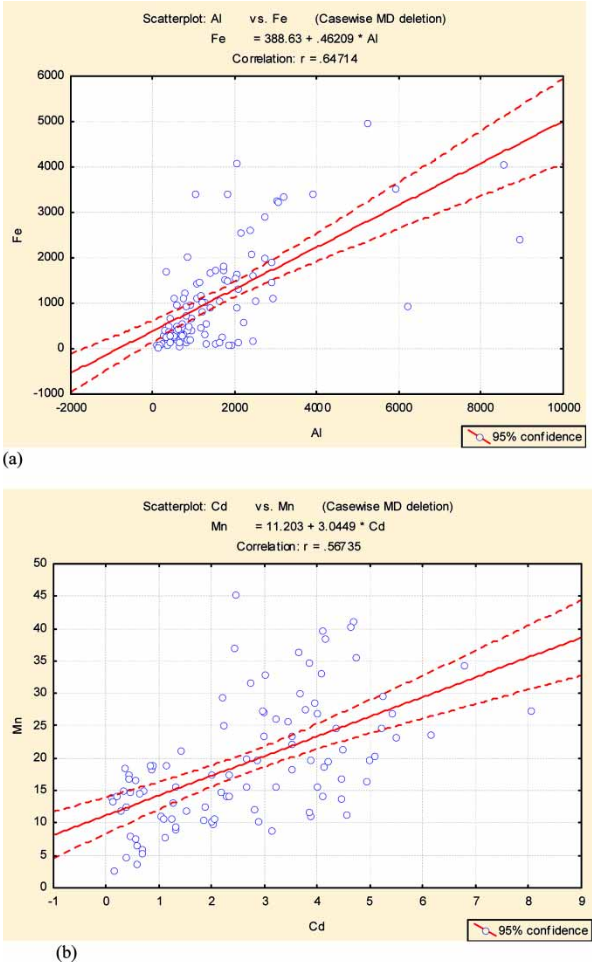

Figure 3. Scatter plot and linear regression of Fe vs Al (a) and Mn vs Cd (b).

3.2. *Enrichment factors*

To evaluate the contribution of non-crustal sources, the enrichment factor EF_c of an element was calculated using the following relation:

$$\mathrm{EFc} = \frac{(\mathrm{Cx/CAl\ sample})}{(\mathrm{Cx/CAl,\ crust})}$$

where $(C_x/C_{\mathrm{Al\ sample}})$ is the concentration ratio of an element X to Al in a sample, and $(C_x/C_{\mathrm{Al,\ crust}})$ is the same ratio in crustal material [26].

An EF_c close to 1.0 is for elements from the Earth crust. EF_c values above the unity have sources other than the crust. However, EF_c values below than 10 do not necessarily indicate a non crustal source for an element [27].

We calculate EF_c for Cd, Cr, Fe, Mn, Ni, Pb and V mean concentrations using Al as reference. The values obtained were: Fe (1.16), Mn (1.08) and Ni (16.2), denoting a crustal source. Conversely, Cr (12.5), Pb (206), partially V (6.32) and Cd (698) also have very high values, signifying that these elements are coming from anthropogenic emissions.

Cd and Pb EF_{crust} values show that they are non-crustal in PST. Often both metals are associated with fine particles ($<1\ \mu$m), which are generated in high temperature combustion processes and infected by smoke-stacks into the boundary layer [28,29].

3.3. *Principal Components Analysis (PCA) and Cluster Analysis (CA)*

3.3.1. *Principal Components Analysis*

In order to gain a better understanding about the sources of trace metals and the inorganic ions analyzed, Stat Soft 6.4 program was used [16] to calculate Principal Components Analysis (PCA). With the PCA it is possible to identify sources of pollutants and to validate the method applied, following the criteria described by other authors [3,30–32]. PCA is a receptor model that allows the observation of the influence of anthropogenic and natural sources through several groups of elements [30,31].

In Table 4 three factors indicate their major role on the total variance, when PCA is applied through the lineal combination of eight metals.

The first factor describes the role of metals on the total variance. Al, Cd, Fe, Mn and V are the most important, given the explained variance of 2.68 and the percent total variance of 38.26%. In the case of Al and Fe, there is high coefficient correlation between them; these metals are

Table 4. Factor analysis for all data and variables.

Variable	Factor 1	Factor 2	Factor 3
Al	**0.83**	−0.13	−0.11
Cd	**0.67**	0.42	−0.10
Cr	−0.07	**0.77**	0.11
Fe	**0.83**	−0.02	0.13
Mn	**0.72**	0.39	0.06
Ni	0.08	0.02	**0.98**
Pb	0.08	**0.89**	−0.09
V	**0.59**	−0.09	0.14
Explained variance	2.68	1.55	1.02
% Total variance	38.26	22.19	14.57

Factor loading normal varimax extraction. Principal components (bold numbers are significant at $p > 0.5$)

Table 5. Total variance explained and component matrixes (three factors selected)[a] Eigenvalues, % total variance, cumulative eigenvalues and variables with absolute loading values >0.7, in the factor analysis for 100 samples.

Value number	Eigenvalues	% Total variance	Cumulative Eigenvalues	% Cumulative
1	2.68	38.26	2.68	38.26
2	1.55	22.19	4.23	60.45
3	1.02	14.57	5.25	75.03
4	0.69	9.88	5.94	84.91
5	0.46	6.61	6.41	91.52
6	0.32	4.54	6.72	96.05
7	0.28	3.95	7.00	100.00

[a] Extraction method: Principal Component Analysis.

associated with coal-fired boilers, crustal components (fugitive dusts), steel production and high temperature furnaces. Al and Fe have also a main source apportionment and assessment of the lignite coal combustion and mobile source emissions on air quality [26,33].

The second factor suggests the Cr and Pb anthropogenic origin, with the percent total variance of 22.19%. In the third factor only Ni has loading of 0.98 indicating anthropogenic origin too; this factor gives 14.57% of the total variance.

Table 5 displays the explained total variance and component matrixes (from the three factors selected), eigenvalues, % total variance, cumulative eigenvalues, and % cumulative after maximisation of variance (varimax). According to the eigenvalues results, three principal components are considered, which account for over 75% of the total variance.

3.3.2. *Cluster Analysis*

Cluster Analysis (CA) was applied to obtain a first approach about the sources of elements analysed on the samples. Resulting dendograms (obtained through Ward's method of amalgamation and the 1-Pearson's rule for linkage measures) are observed in Figure 4. They were obtained using the computer code Statistica/W [16]. There is a clear grouping of the following elements: Cr, Pb and

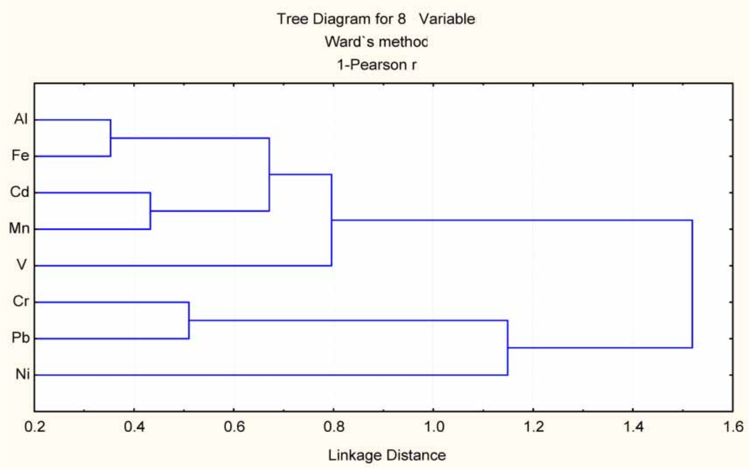

Figure 4. Ward's method of cluster analysis with Pearson correlations for the 8 variables.

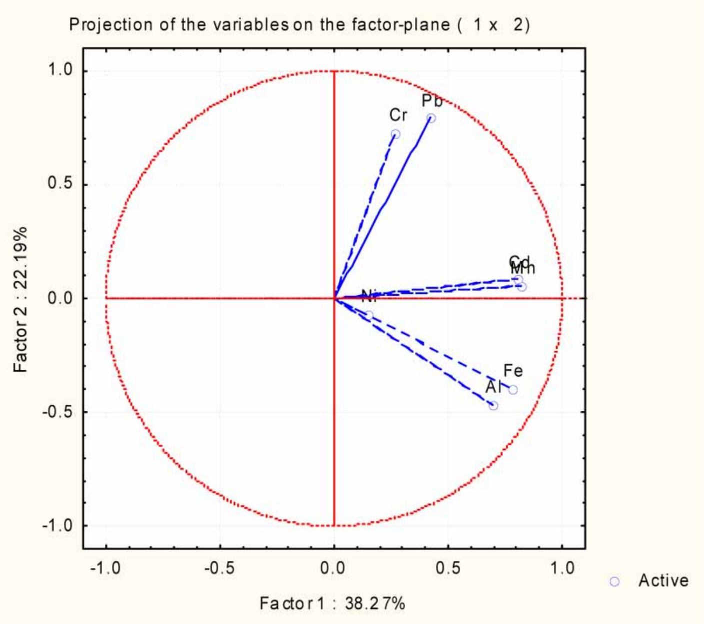

Figure 5. Eigenvalues matrix rotation (Factor 1 and 2).

Ni. In Mexico City, industrial emissions (like those from smelters), fuel combustion and traffic emissions, among others are among the most relevant sources of Cr, Pb and Ni [34].

There is a strong correlation between Al and Fe. Both metals are associated with coal-fired boilers, crustal components (fugitive dusts), steel production and smelter activities. Also, Cd is emitted by electroplating and battery production industries, Mn is related to industrial processes and V is related to combustion because is one of the main organometallic fuel constituents.

In addition, the eight elements analysed are also associated with industry or traffic [35,36]. This method is the most appropriate to evidence the correlation among variables [31]. Although CA is not substantially different from PCA, it can be used as an alternative method to confirm results [37]. The eigenvalues of the two first extracted factors are greater and the third becomes grater after the matrix rotation (Figure 5).

4. Conclusions

The application of the Principal Component Analysis (PCA) and Cluster Analysis (CA) gave a clear indication of the origin of the trace metals between anthropogenic and natural sources for the TSP. Also, PCA can assist CA for pollutant sources identification. However, identification of sources may also be related to human activities, such as industrial processes, incomplete combustion of hydrocarbons, exhaust of automobiles, worn spare parts of engines, and corrosion of metallic parts.

The elemental concentrations found at the UNAM are in many cases lower than those found in other areas of Mexico City in the past, although in some instances they are now higher than other urban areas. The results determine a different regime for the Southwest, in accordance with what was expected from the nearby emitting sources.

High concentrations of trace metals were found in Mexico City during the two years. This was expected since the Mexico City atmosphere is highly polluted and the amount of industries is big enough to contribute with heavy metals emissions. The Spearman Rank order correlations calculated for trace metals seem to indicate a common anthropogenic origin for TSP.

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