Source characterisation of airborne particles in Seville (Spain) by multivariate statistical analyses

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Abstract—Metal contamination (Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) in suspended particles was studied at twelve monitoring stations in Seville. The metal concentrations in cellulose filter samples were analyzed by FAAS (flame atomic absorption spectrophotometric) and GFAAS (graphite furnace atomic absorption spectrophotometry). We found that the sum and the percentages of metals analyzed with respect to the Total Suspended Particles (TSP) were low. The study shows that Al and Fe are the major metal elements with concentrations of around 860 ng m^{-3} which together represent 90.6% of the sum of metals. Three statistical groups of metals were found by factor analysis and cluster analysis: Fe, Al and Mn; Zn, Cd and Cr; and Pb and Cu. These techniques, applied in the lmonitoring stations, were effective at associating the groupings obtained with the different environmental locations of the city and with the origin of the metals in different areas of the same city. Areas of the city influenced by traffic and industry were distinguished, especially those influenced by metal foundry industries (Camas, Puerto Este, Pinomontano and La Liebre). A second group comprises areas influenced by traffic alone (Los Remedios. Larana, Resolana, Recaredo and Luis Montoto). The remaining sites correspond to areas influenced by emission sources (Reina Mercedes, Bellavista and Torreblanca).

Key-words: heavy metals, factorial analysis, particulate matter, air pollution.

1. Introduction

The presence of harmful substances in the atmosphere is particularly worrying because of the number of people that can be affected. Also, air pollution can have significant negative effects on a wide range of living organisms and on the rocky materials of monumental buildings. The danger depends on the nature of

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the pollutants and on its content in the atmosphere. Although there are considerable amount of data on gaseous pollutants (CO, SO_2, NO_x and O_3) this is not the case for heavy metals. Heavy metals have an important effect on biochemical mechanisms especially because they accumulate in the biomass.

In large urban areas, the considerable amount of particulate matter in the air is an important problem. The main sources of airborne particulate matter are: agriculture, industry, fuels for domestic use and motor traffic. Particles in suspension comprise the most representative variable, and determination of heavy metals in unsedimentable particles is also of great value. Because of their small size, these particles have a direct incidence on health by affecting respiration. On the other hand, they are easily transported large distances and can stay in the air for some time depending on meteorological conditions.

The aim of the present work was to determine the metal content of suspended particulate matter in Seville, which is the most densely populated city of southern Spain. It presents an extension of 142 km^2 and is situated only 10 meters above the sea level on an extensive plain crossed by the Guadalquivir River. In 1993 it had a population of 716,937 inhabitants, but on workdays the effective population increases to one million mainly with commuters from nearby towns. Seville has a Mediterranean climate with an annual average temperature of 19°C and rainfall of 580 mm. Other climatological conditions (poor winds, thermal investments) do not favour pollutant dispersion. Industry as a source of metal pollutants is rather scarce and represents about 5% of the city's economic activities. Metallic products represent only 15% of this industry.

Several studies on contamination by particulate matter in the city of Seville have been carried out in order to determine metals in sedimentable particles *(Usero et al.,* 1983a, b) and in suspended particles *(Melgarejo et al.,* 1986; *Usero et al.,* 1988; *Luis-Simon et al.,* 1995). Consequently, one of the main goals of this work was to study the evolution of the situation after the economic and urban changes experienced in the city after 1992, when the World Fair of Seville (EXPO 92) was celebrated.

2. *Experimental*

2.1 Sampling

Sampling network with twelve monitoring stations was elaborated *(Fig. 1).* It is designed to encompass practically all urban areas and some peripheral zones of Seville. In this network stations are located near to focuses of emission (industries and zones of high traffic density) as well as to others with cleaner air.

The stations can be classified into three categories according to the nearest and most significant possible pollution sources:

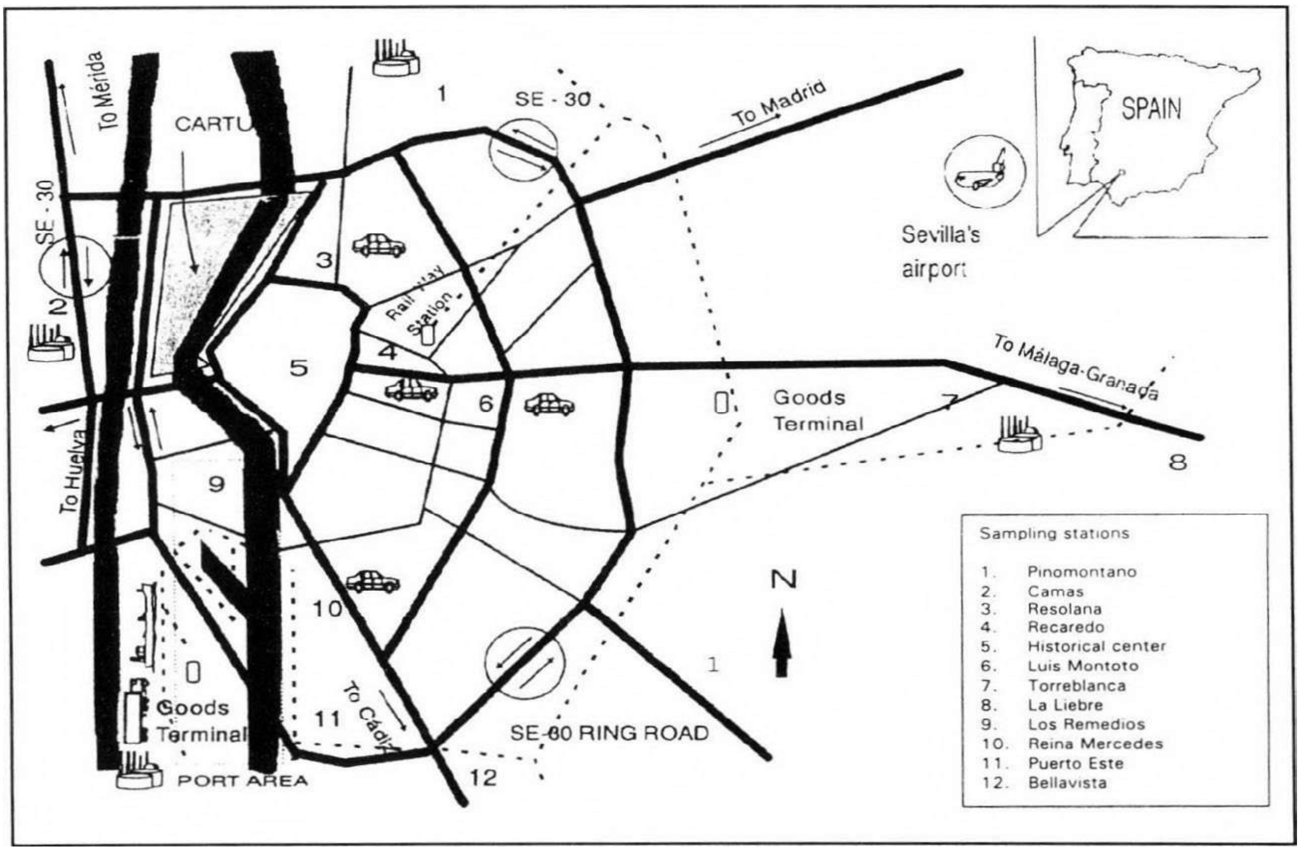


Fig. 1. Sampling network in Seville with the location of the twelve sampling.

(i) *Stations under the influence of industrial emissions.* Camas (station 1) is 6 kilometres far from the city centre, near to two foundries of iron and aluminium. Puerto Este (station 3) is near to Seville Harbour in the estuary of the Guadalquivir, in which important loading and unloading activities take place. There is a certain amount of industry nearby (fertilisers, oils, cement and construction materials, small metallurgy and shipyards). Pinomontano (station 10) is near to fertiliser and building material production plants. La Liebre (station 12) is 15 kilometres far from the city. It is next to an important cement factory, and there is a glass factory and metal foundries nearby.

(ii) *Stations under the influence of vehicle emissions.* Los Remedios (station 2), Laraha (station 5) in the historic centre, Resolana (station 6), Recaredo (station 7) and Luis Montoto (station 9). The last three sites are next to important communication routes inside the city.

(iii) *Peripheral stations with few sources of industrial emissions or traffic.* Reina Mercedes (station 4), Bellavista (station 8), near to a factory of fiber-cement and Torreblanca (station 11).

In this study, 48 samples were collected (four samples in each monitoring station on different days of the week) from Lebruary to October, 1993.

Atmospheric suspended particles were collected on 20.3 x 25.4 cm cellulose filters (Whatman-41) using a Quimisur-SMAV high volume sampler on the top roof of buildings at 4-6 m high. Approximately 1500 m3 air was collected in each 48 hour sampling period with a nominal aspiration flow of 40 m3 If1.

In order to obtain a sufficient quantity of sample and absolute concentration of metals, the relationship between the duration of the sampling and results of subsequent analytical determinations was studied. Because of the low levels of metals and the small amounts of particles collected, a sampling period of 48 hours was chosen.

Beforehand, a preliminary assay was done to select the most suitable filter. Although some authors prefer to use glass-fiber filters (*Obiols et al.,* 1986; *Clevenger et al.,* 1991), in our experience cellulose ones were preferable for the analyzed parameters {*Usero et al.* 1988; *Luis-Simon et al.,* 1995), because of the chemical stability, low concentration of blanks and low cost. These filters can easily break down, and values corresponding to blanks are lower than glass-fiber values. These showed high levels of impurities of iron, aluminium and especially zinc (*Berg et al.,* 1993), and reactivity with metals (*Zatka et al.,* (1992). In addition, several experiments were done to improve the method for chemical attack of samples in teflon vessels. The proportions and types of acids used in the digestion mixture, temperature, time and other variables were noted in order to optimise the blanks and efficacy of attacks. Other mixtures and heating procedures {*Obiols et al.,* 1986; *Frenzel,* 1991), have been studied, but we obtained the best results in the method recorded below.

2.2 *Apparatus and reagents*

Samples were analyzed by flame atomic absorption spectrophotometry (FAAS Perkin-Elmer 3100) for the majority metals Fe, Al, Zn, Cu and Pb, and by graphite furnace atomic absorption spectrophotometry (GFAAS Perkin-Elmer 2380 with HGA Programmer Perkin-Elmer 300) for the trace metals Cd, Co, Ni, Mn and Cr.

All the reagents employed were of analytical grade, and Milli-Q water was used.

2.3 Methodology for the chemical analysis

A quarter of cellulose filter was finely divided into 1 cm2 pieces prior to chemical treatment, consisting of acid digestion by heating in a closed teflon vessel under pressure.

First, the sample was treated in an open vessel with 20 mf of concentrated nitric acid and then it was evaporated to half of the volume in a sandbath at 180°C. Afterwards, 20 mf of water plus 2 mf of perchloric acid were added. The closed vessel was introduced into a stove at 120°C for six hours. The treated sample solution was decanted from the washed silica-carbonaceous residue, placed in a 50-mℓ standard flask and diluted to the mark with Milli-Q water. Treated samples were then analyzed by FAAS or GFAAS.

Blanks were determined for all metals. The previously described procedure was repeated with four unused filters and the average value of the blanks was subtracted from samples.

2.4 *Multivariate analyses*

To draw conclusions from the data, multivariate analyses were applied to the average of the four concentrations obtained for each metal in each monitoring station. Statistical models of parameter correlation, factor analysis and cluster analysis of variables and cases were applied using the CSS: STATISTICA (StatSoft) software package. The data matrix represents the total contents for the 10 metals and the 12 monitoring stations. Another matrix with an additional column corresponding to values of total suspended particles (TSP) was also studied.

3. *Results and discussion*

To interpret the data, in addition to plots and basic statistics of the results, other models of multivariate statistics, called pattern recognition, were also applied. These models can handle a large amount of numerical data reducing the variables to a few factors, which allow us to evaluate their combined effect and to classify metals by emission sources.

3.1 *Heavy metal composition*

Concentration values for total particles in suspension (TSP) and metal concentrations appear in *Table 1* (expressed in nanogram of the element per cubic meter of sampled air).

Values for TSP, the sum of metals (S) and their relative percentages in the TSP (S/TSP%) for each sample are recorded in *Fig. 2.* Regarding these data globally, the following considerations can be made:

The sites with the highest levels of TSP are 5 and 1, and these, therefore, have low S/TSP% values. Stations 8 and 2 behave similarly, due to the even lower absolute amounts of metals.

The sites with the lowest levels of TSP (stations 9, 10 and 4) coincided with the areas of the city with the highest relative metal percentages.

These observations can be explained as follows: Evolution of S/TSP% in the graph follows the same profile as the total sum of metals (Fig. 2), because the largest variation among the different stations is given for this variable. If the TSP value is low and the sum of metals is medium or high, the metallic richness is high (sites 9, 10, 4), but if the TSP value is high and the sum of

Table 1. Average metals concentrations (ng m 3) and total suspended particles (TSP) in Seville from February to October, 1993

Station	Al	Fe	Zn	Pb	Cu	Mn	Ni	Co	Cr	Cd	TSPx1O“3
№ 1	895.3	1131.2	74.1	16.4	9.3	11.6	4.7	1.8	0.9	0.9	176.8
№ 2	467.1	421.0	53.5	43.6	19.0	8.3	3.1	1.2	0.8	0.4	155.1
№ 3	1179.4	1491.6	158.4	48.5	24.4	23.0	24.5	9.3	3.9	1.3	140.6
№ 4	445.9	621.3	79.1	91.5	38.8	8.5	4.9	2.0	1.2	0.8	75.3
№ 5	859.5	818.8	70.3	74.5	39.6	10.2	6.7	2.6	2.1	0.6	186.1
№ 6	1299.2	1217.2	75.7	76.3	53.7	18.2	5.6	4.0	2.7	0.4	139.2
№ 7	694.2	938.1	111.5	198.1	80.9	12.2	3.3	5.9	1.1	1.1	123.9
№ 8	276.1	213.5	143.9	26.1	27.0	3.3	3.9	2.7	2.5	1.4	146.8
№ 9	1192.4	1058.2	52.0	66.5	51.1	15.8	4.4	3.5	1.2	0.3	94.3
№ 10	1036.8	636.1	64.3	35.9	39.1	9.6	4.6	1.8	0.9	0.5	80.7
№ 11	1268.0	876.8	134.4	34.3	21.4	18.8	17.8	3.7	1.5	0.5	138.8
№ 12	708.0	893.8	73.7	18.0	45.6	17.5	4.7	5.2	0.3	0.5	143.1
Mean	860.2	859.8	90.9	60.8	37.5	13.1	7.4	3.6	1.6	0.7	133.4
Range	276-1299	214-1492	52-158	16-198	9-81	3-23	3-25	1.2-9.3	0.3-3.9	0.3-1.4	75-186

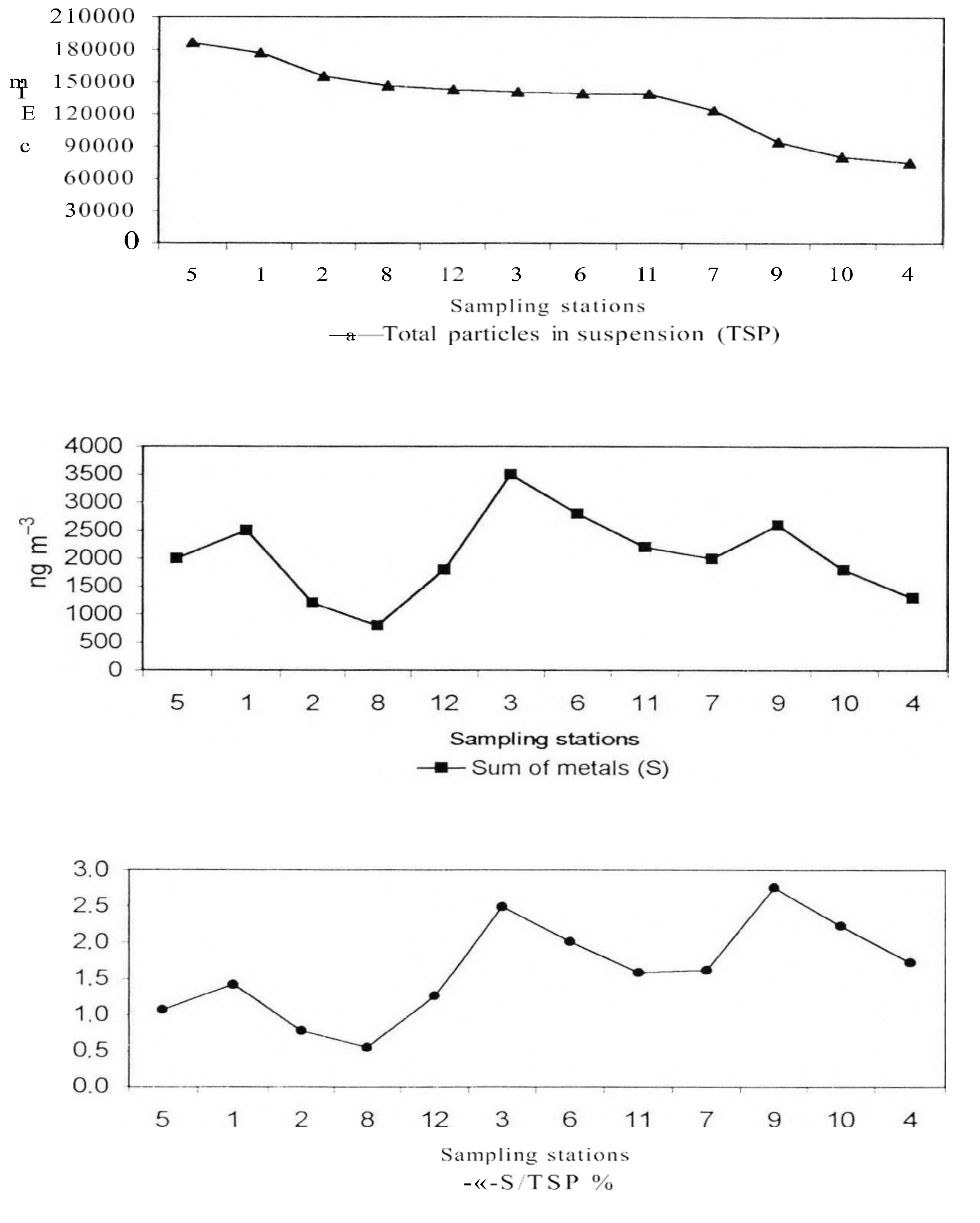


Fig. 2. Average of total particles in suspension (TSP), sum of metals (S) and their relative percentages in the TSP (S/TSP%) parameters at the twelve sampling stations of Seville.

metals is low, the metallic richness is low (sites 2, 8). Therefore, the values of S/TSP% reflect the metallic richness of particles, although the parameter that measures the degree of metal pollution is the total sum of all the metals (S). However, the parameter S/TSP% is useful to assess the level of metal contamination in conditions in which, mainly due to the rains, TSP and S levels diminish considerably. Therefore, in spite of varying meteorological conditions, metal concentrations on different days or in different seasons would give some indication of the degree of metal contamination of the particles.

Values of metal pollution (S) (Fig. 2) reflect that the highest levels are found in Puerto Este (3), Resolana (6), Luis Montoto (9) and Torreblanca (11). The least contaminated sites are Bellavista (8), Los Remedios (2) and Reina Mercedes (4).

Regarding individual heavy metal contents (Table 1) we observed the highest average concentrations for Al and Fe with 860 ng nT3 for both elements. The metals Zn, Pb and Cu presented concentrations an order of magnitude below the above value (91-38 ng n r3), and finally, Mn, Ni, Co, Cr and Cd showed even lower amounts (13-0.7 ng m'3).

Table 2 presents the results of two experiments: the average individual metal content (C), the metallic fractions (C/TSP%) and the relative metallic composition (C/S%) obtained in 1985 *(Usero et al.,* 1988) and 1993. The comparison reveals a reduction in metal concentrations (C) from 1985 to the present day. They are four times lower for Al, Fe, Zn, Ni and Cd and even ten times lower for Pb and Cr. On the other hand, these parameters remained more or less constant for Mn and Co. Similar values of relative composition (C/S%) show that the same contamination sources remained in Seville. However, lead and chrome are notable exceptions, since their concentrations suffered a greater decrease. The metallic fraction on particulate matter (C/TSP%) was also diminished since TSP levels were only reduced from 210,000 to 133,400 ng n f3.

3.2 Correlation of metals

Table 3 includes the correlation matrix of the studied parameters. Tabulated values show that Mn significantly correlates with Fe, Al and Co ($r > 0.73$) and to a lesser extent with Ni ($r = 0.69$). These elements are presumably of soil or agricultural origin. A good correlation between elements mainly from vehicular emissions such as Pb and Cu ($r = 0.81$) is also observed. Zn correlates with Cd and Cr moderately well ($r > 0.64$) and to a lesser extent with Co and Ni (r coefficients of 0.62 and 0.69). All these elements are from waste stored in uncontrolled dumps, where burning and incineration often take place. Also, in the case of Ni and Co the significant correlation with earth metals marks a mixed origin. In the following factor and cluster analysis, TSP was ignored because of its low correlation with the remaining parameters.

Table 2. Comparative study of 1985 and 1993 in Seville

	1985*			1993"		
TSP	210.000 ng m 3			133.400 ng n r3		
Metal	C	C/TSP%	C/S%	c	C/TSP%	C/S%
Al	3070.0	1.462	39.72	860.2	0.645	45.32
Fe	3570.0	1.700	46.18	859.8	0.644	45.30
Zn	340.0	0.162	4.40	90.9	0.068	4.79
Pb	680.0	0.324	8.80	60.8	0.046	3.20
Cu***				(37.5)	(0.028)	
Mn	19.6	0.009	0.25	13.1	0.010	0.69
Ni	26.0	0.012	0.34	7.4	0.006	0.39
Co	4.6	0.002	0.06	3.6	0.003	0.19
Cr	16.0	0.008	0.21	1.6	0.001	0.08
Cd	3.3	0.002	0.04	0.7	0.001	0.04
Sum	7729.5	3.681	100.00	1898.1	1.424	100.00

C: total contents in ng m"3
C/TSP%: metallic fraction
S: sum of total contents in ng m-3
C/S %: relative composition
* see *Usero et al.,* 1988
** present work
*** the metal not was analyzed in 1985

3.3 Factor analysis of the metals

The previous correlations were confirmed by factor analysis of the variables revealing three factors which together explained 87% of the variance. The factors that contributed to less than 5% of the variance were rejected. Percentages and loadings explained in each case are included in *Table 4.* The variables obtained in each factor are the following:

Factor 1. This is formed by Al, Fe, Mn, Co and Ni (it is noteworthy that these last two elements can also be found in Factor 2). This factor explains 43% of the variance and it prevails in stations Puerto Este (11), Resolana (3), Torreblanca (7) and Luis Montoto (6) (see *Fig. 3).* These elements contribute to almost 90% of metal content in the atmosphere of Seville. Factor 1 shows the presence of elements *(Usero,* 1988) of earth crustal origin.

Factor 2. This consists of elements such as Zn, Cd and Cr. This factor explains 24% of the variance and this grouping is significant at stations of

Puerto Este (11) and Bellavista (12) (Fig. 3). This factor is associated mainly with waste combustion (*Usero,* 1988) and represents 5% of all the metals.

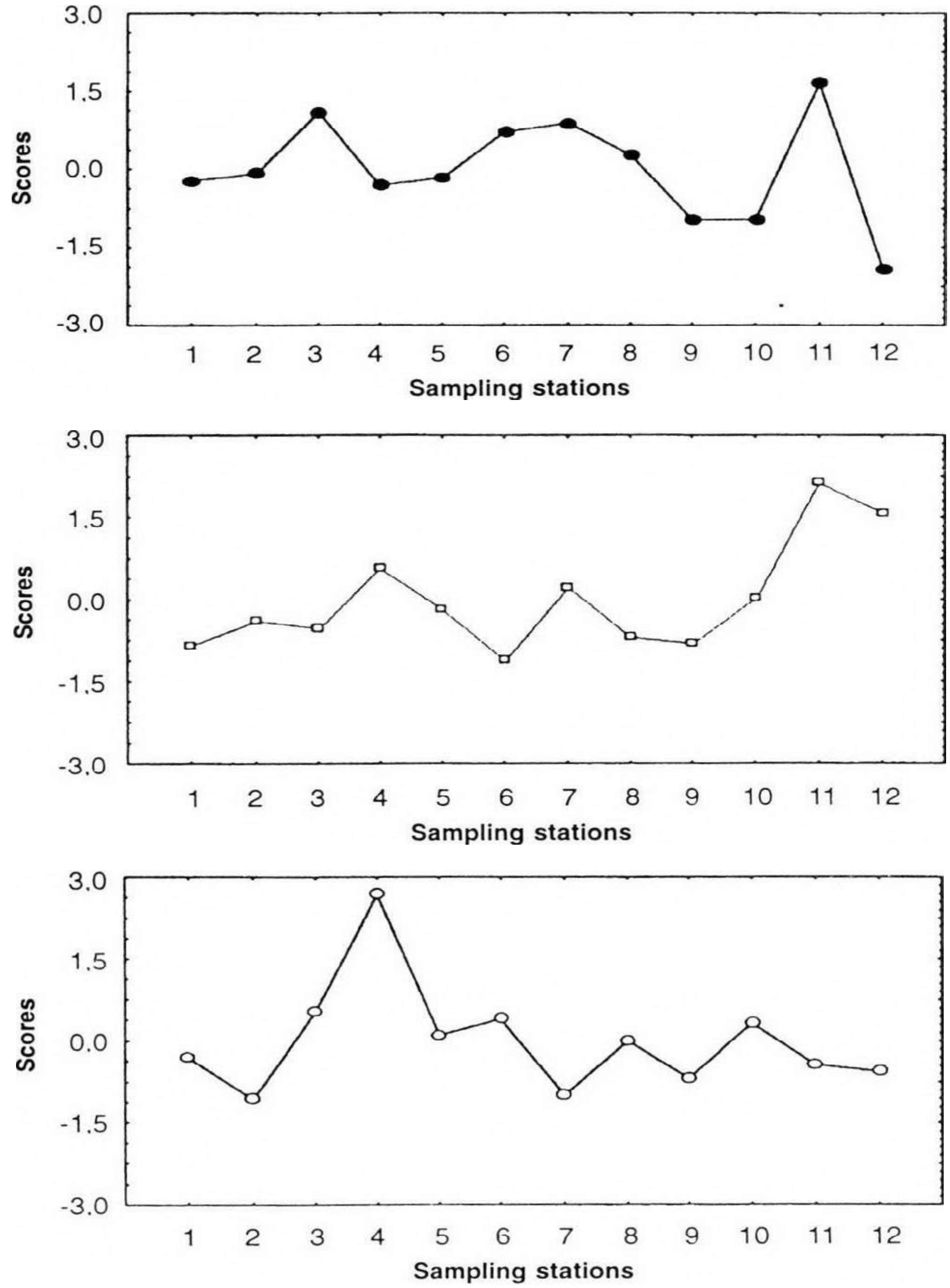
Table 3. Correlation coefficients (r) for the ten analyzed metals and TSP

Al	1										
Cd	-0.39	1									
Co	0.36	0.41	1								
Cr	0.29	**0.51**	**0.55**	1							
Cu	0.06	-0.11	0.29	-0.11	1						
Fe	0.77	-0.04	**0.67**	0.37	0.14	1					
Mn	**0.79**	-0.20	**0.73**	0.32	0.10	**0.86**	1				
Ni	**0.52**	0.30	**0.67**	**0.64**	-0.34	**0.54**	**0.69**	1			
Pb	-0.07	0.16	0.26	0.00	**0.81**	0.12	-0.03	-0.19	1		
Zn	0.02	**0.78**	**0.62**	**0.64**	-0.14	0.13	0.23	**0.69**	0.03	1	
TSP	-0.04	0.14	0.05	0.21	-0.38	0.12	0.03	0.12	-0.24	0.14	1
	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	TSP

Factor 3. This is formed by Cu and Pb corresponding to 5% of the metal content. This factor explains 20% of the variance and its highest influence is observed at the Recaredo (4) station (Fig. 3). This reflects the effect of vehicle emissions.

Table 4. Factor loadings for the varimax rotation

Variable	Factor 1	Factor 2	Factor 3	Communality (%)
Al	0.91	0.16	-0.06	86
Cd	-0.27	-0.91	0.07	91
Co	0.63	-0.61	0.31	87
Cr	0.36	-0.73	-0.09	66
Cu	0.09	0.13	0.95	93
Fe	0.90	-0.10	0.14	85
Mn	0.97	-0.09	0.02	94
Ni	0.66	-0.60	-0.32	89
Pb	-0.03	-0.11	0.93	88
Zn	0.13	-0.93	-0.06	89
% of total variance	43.2	23.8	19.9	



Factor 3

Fig. 3. Graphical representation of the three factors in the twelve sampling stations of Seville.

3.4 Cluster analysis

Cluster analysis of variables with the standardised matrix *(Fig. 4)* was also carried out. This analysis groups together Al, Fe and Mn, the other cluster is formed by Cd, Zn, Co, Ni and Cr, and the last cluster consists of Cu and Pb.

Metals are practically classified in the same groups obtained by factor analysis, while Co and Ni show a mixed behavior between Factor 1 and Factor 2.

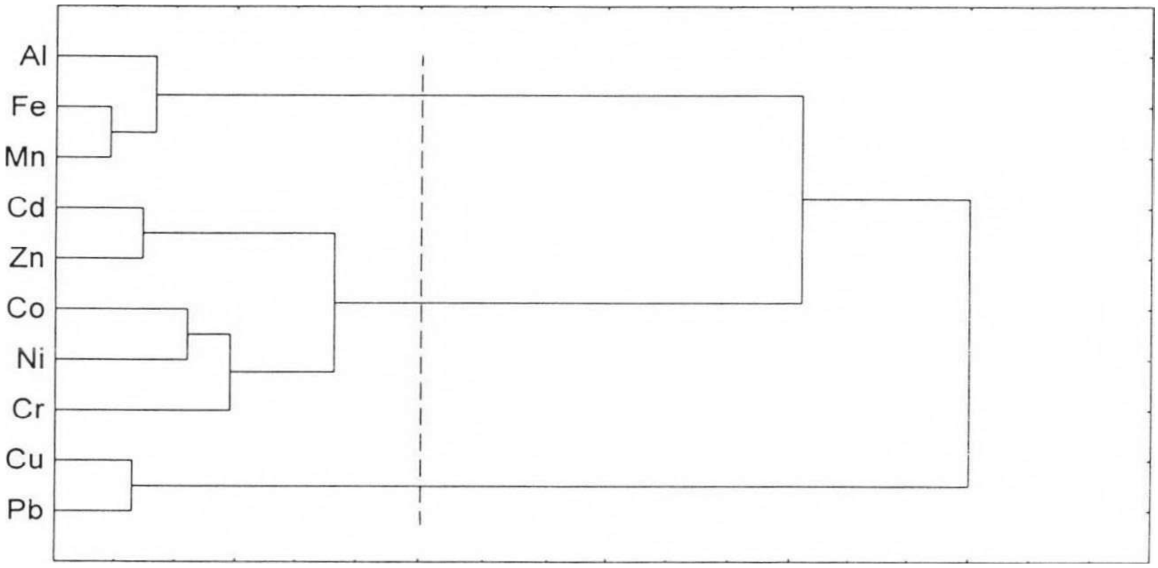


Fig. 4. Dendrogram of the cluster analysis of the ten metals.

4. *Conclusions*

From our results we can conclude that, in general, atmosphere of Seville is cleaner now than several years ago. This is indicated by the average value of TSP that has reduced from 210,000 to 133,400 ng m^{-3}. On the other hand, the metal fraction in TSP has diminished considerably, i.e., suspended particles now contain smaller amounts of metals. The decrease observed for lead and chromium is especially significant. In the first case, this is due to the new underground network of railways and ring roads constructed in 1992 for the World Fair. The latter has certainly alleviated dense inner city traffic. The continual increase of the proportion of vehicles with unleaded fuel also plays an important role. The decrease in chromium is especially pronounced because of the conversion of many former uncontrolled garbage dump sites into large controlled urban waste installations far from the city center also as a consequence of urban and environmental restructurization.

The absolute metal content has also decreased. Similarly to above, this is also partially due to improvement in traffic and waste management. However, the relative concentration of the ten heavy metals studied has not changed. Metals which present with the highest concentrations are still iron and aluminium, clearly derived from soil or building activities. Zinc, lead and copper present in lower levels, manganese, nickel, cobalt, chromium and cadmium in still smaller amounts. Unexpectedly, the percentages of each metal with respect to the sum (the metal fraction) also remained constant in the last few years (Table 2). This suggests that the pollutant sources have not experienced substantial changes with time, although absolute levels have decreased. Lead and chromium are two clear exceptions to this behavior since, because of the aforementioned reasons, they are now present in much lower percentages.

Factor analysis of variables detects the principal metal sources for atmospheric particles. The main one is the land, due to agricultural works on the periphery. Thus, the metals included in this group are iron, aluminium, manganese, nickel and cobalt. Other important sources are urban wastes and traffic. Thus, Zn, Cd and Cr are components of different waste sources, while Cu and Pb are grouped as components of vehicle emissions. The soil and waste components in particles come from the city's outskirts, whereas the components of traffic origin are emitted in city centre. In this way, zones predominantly affected by the different metal sources in the city have been identified.

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References

Berg, T., Royset, O. and *Steinnes, E.,* 1993: Blank values of trace elements in aerosol filters determined by ICP-MS. *Atmos. Environ. 21A,* 2435-2439.

Clevenger, T.E., Saiwan, C. and *Koirtyohann, S.R.,* 1991: Lead speciation of particles on air filters collected in the vicinity of a lead smelter. *Environ. Sci. Technol. 25,* 1128-1133.

Frenzel, W., 1991: Microanalytical concept for multicomponent analysis of airborne particulate matter. *Fresenius J. Anal. Chem. 340,* 525-533.

Luis-Simon, F.J., Gomez-Camacho, J. and *Respaldiza, M.A.,* 1995: Study of the elemental composition of the air pollution in Seville. *Int. J. PIXE,* 5(1), 43-56.

Melgarejo, P.L., Ternero, M. and *Gracia, I.,* 1986: A study of the atmospheric lead pollution in Seville, Spain. Influence of meteorology and traffic, and relationship with other traffic-generated pollutants. *Intern. J. Environ. Anal. 24,* 283-296.

Obiols, J., Devesa, R. and *Sol, A.,* 1986: Speciation of heavy metals in suspended particulates in urban air. *Toxicol. Environ. Chem. 13,* 121-128.

Usero, J., Ternero, M. and *Gracia, I.,* 1983a: Estudio de la contaminacion atmosferica de la ciudad de Sevilla por particulas sedimentables. I. Fraccion insoluble. *Ingenieria Quimica.* 176, 149-153.

Usero, J., Ternero, M. and *Gracia, I.,* 1983b: Estudio de la contaminacion atmosferica de la ciudad de Seville por particulas sedimentables. II. Fraccion soluble. *Ingenieria Quimica. 189,* 57-62.

Usero, J., Rosa, F., Ternero, M. and *Gracia, I.,* 1988: A determination of the sources in the Seville urban aerosol. *Intern. J. Environ. Anal. Chem.* 33, 233-244.

Zatka, V.J., Warner, J.S. and *Maskery, D.,* 1992: Chemical speciation of Nickel in airborne dusts: Analytical methods and results of an interlaboratory test program. *Environ. Sci. Technol.* 26, 138-144.