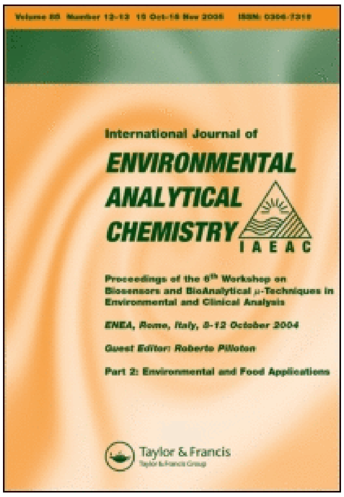

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A Determination of the Sources in the Seville Urban Aerosol

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A Determination of the Sources in the Seville Urban Aerosol

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Measurements made of the composition of total suspended particulate (TSP) matter collected at 5 sites in Seville, were examined by use of factor analysis and chemical element balance. The results show that soil-derived aerosol makes up the largest fraction of the TSP (37%), followed by limestone (17%). Small contributions (less than 5% each) from refuse incineration, motor vehicles, marine aerosol and fuel oil combustion were also identified. Most of the analyzed elements are reasonably well fitted, with predicted/observed ratio near to 1.

KEY WORDS: Particulate matter, TSP, aerosols, factor analysis, chemical element balance.

INTRODUCTION

The determination of the composition and sources of urban air particulate matter is becoming increasingly important in order to provide data which can be used to predict the effects of regulatory and other changes in emission source characteristics, and also to monitor the efficiency of such changes.

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The majority of recent source-resolution works utilize the receptor models for identifying and quantifying the source of ambient aerosol measured at a receptor site.

The initial receptor model was the chemical element balance (CEB) approach originally introduced by Miller *et al.*[1] In this model, it is assumed that the number and the elemental composition of the particle sources are known. The observed elemental distribution is then assumed to be a linear function of the probable sources. This approach has produced some very good fits to the data in recent studies done in Washington, DC[2] and Chicago.[3]

Chemical element balance methods, however, have a major drawback in that they require an *a priori* knowledge of both the number and composition of the suspected source emissions.

Another form of statistical analysis, factor analysis (FA), has also been used to identify sources of airborne particulate matter. The major advantage of this method is that it requires no prior assumptions about the nature of the sources. Factor analysis has been used to identify sources of airborne particulate matter in Tucson,[4] St. Louis[5] and Greenland.[6] In these applications of the FA, the actual mass contributions of each of the identified sources to each sample could not be determined.

Recently Alpert, Hopke and Roscoe[7–13] have developed a new form of factor analysis, called target transformation factor analysis (TTFA) which allows a similar analysis to that of the CEB and supplies quantitative information on the emission sources. However the advantages of the TTFA on other receptor models have not yet been clearly established since, as the CEB, it requires the knowledge of the elemental composition of the possible sources.

Several reviews of receptor model methodologies have been published.[14–20]

In this paper, we have used factor analysis to give first indications of the major sources of airborne particulate in Seville, with regard to these sources the CEB has been applied to determine the actual mass contribution of each of the identified sources in the studied area.

Seville is the largest city of Southern Spain, has a metropolitan population of 750,000. Seville is located at 37° 4′ N and 6° 0′ W in a valley at an altitude of 8 m above sea level and has an annual average precipitation of 571.8 mm. In the Seville valley there are no important industrial activities.

SAMPLING AND ANALYSIS

Ambient 24 h average particulate samples were collected every fifteen days from November 1984 through November 1985 at 5 air monitoring sites in the urban area of Seville, as shown in Figure 1. The locations were chosen as being fairly representative of different parts of Seville. For this reason, the selection of the number and locations of the sampling sites, took into account WHO[21] and EPA[22] recommendations.

The aerosol samples were collected on 12 × 10″ Whatman 41 filters, using a standard high volume air sampler at a flow rate of $33\,m^3\,h^{-1}$.

The 120 samples were digested in a HNO_3-$HClO_4$ mixture and analyzed for Al, Cr, Fe, Mn, Ni, Pb, V, Zn, Ca, Mg, Co, Cd and Ti by atomic absorption spectroscopy and Na and K by atomic emission. The calibrations were periodically repeated to check accuracy. The concentrations of the different elements were obtained with reference to blank filters. TSP concentrations were determined by weighing the filters before and after sampling, after equilibration at 20 °C and 50% r.h. for 24 h.[23–25]

RESULTS AND DISCUSSION

Table 1 lists study-period average, standard deviations and ranges of TSP and trace metal concentrations in the urban aerosol of Seville.

Factor analysis

The concentrations of 15 elements in the 120 samples were subjected to principal component analysis (a particular type of factor analysis) followed by varimax rotation, using the Biomedical Computer Program BMDP4M described in Dixon *et al.*[26]

In factor analysis the variables are standardized to zero mean and unit standard deviation

$$Z_{ij}=\frac{X_{ij}-X_i}{\sigma i}$$

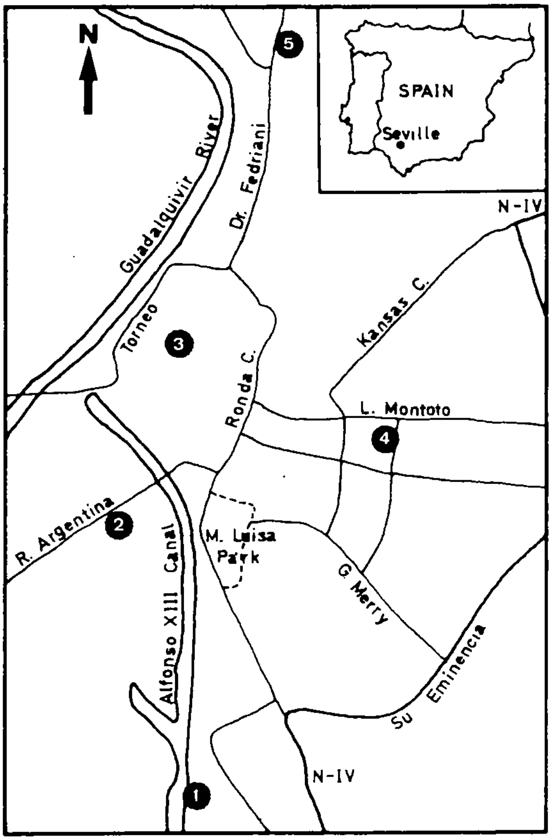

Figure 1 Location of sampling stations.

where Z_{ij} is the standardized value of the ith element for the jth sample, $\bar{X}_i$ the mean value for the ith element, and σ_i is the standard deviation of the distribution of value of the element. Factor analysis is therefore independent of level and scale.

As the data seem to be log-normally distributed we use

$$X_{ij} = \log C_{ij}$$

where C is the concentration.

The results of the principal component analysis are given in Table

Table 1 Summary of particulate concentrations at Seville November 1984–November 1985 (120 samples)

Element	*Arithmetic mean*	*Range*	*Standard deviation*
Ca	14 160	1 770–48 860	8 920
Al	3 070	470– 8 440	1 640
Na	1 370	460– 4 390	639
Zn	340	20– 2 070	350
Pb	680	50– 3 090	640
V	37.9	9.4–292.1	35.7
K	2 860	630– 8 660	2 380
Fe	3 570	950– 9 940	1 680
Mg	1 320	200– 3 100	600
Co	4.6	1.5– 40.4	3.6
Cd	3.3	1.0– 13.8	2.4
Mn	19.6	4.7–127.5	12.9
Cr	16.0	5.6– 49.8	7.6
Ni	26.0	1.1–109.7	21.3
Ti	100	21– 366	57
TSP	210 000	32 000–524 000	95 000

Units are $ng\,m^{-3}$.

2. Only components with eigenvalues greater than 1, after rotation, were included.[27,28] The five principal components account for 75% of the total variance. Most of the communalities are greater than 0.7, suggesting that the extraction of the five factors is reasonable for this study.

To facilitate the physical interpretation of the five principal components presented in Table 2, plots of the trace elements relative to the pairs of principal components PC1–PC2, PC2–PC4 and PC3–PC5 are given respectively in Figures 2, 3 and 4.

The first component appears to represent soil aerosol impact at Seville, since it is highly correlated with the crustal elements Al, Ti, Fe, Ca, etc. (see Figure 2). The interpretation of the second component is still clearer, since it is correlated with both V and Ni, two elements highly enriched in emissions from fuel oil combustion.

The third component is the motor vehicle component, since it has high loading for Pb. The fourth component is strongly related to Zn and Cd, this component may be associated with refuse incineration.

Table 2 Varimax rotation of principal component analysis

Parameter	*Component number*					*Communality*
	1	*2*	*3*	*4*	*5*	
Al	0.91	0.05	0.07	−0.06	0.19	0.88
Ti	0.91	0.01	0.08	−0.05	0.14	0.86
Fe	0.77	0.03	0.26	0.10	0.25	0.73
K	0.76	0.05	−0.21	0.23	0.41	0.85
Cr	0.74	0.07	0.41	−0.02	0.16	0.75
Mn	0.73	−0.09	0.22	0.09	0.32	0.70
Co	0.72	0.00	0.00	0.42	0.12	0.71
Mg	0.72	−0.03	0.26	0.09	0.32	0.70
Ca	0.71	−0.04	0.43	0.10	0.05	0.70
Na	0.16	0.05	−0.10	0.17	0.83	0.76
V	0.02	0.95	0.08	−0.01	0.03	0.91
Ni	0.04	0.94	0.16	0.08	0.00	0.92
Pb	0.26	0.21	0.88	0.08	−0.01	0.89
Cd	0.06	0.23	0.30	0.71	0.16	0.68
Zn	−0.14	0.00	0.22	0.84	0.27	0.85
% of total variance	35.3	12.1	9.8	9.6	8.4	

The last component is the only one with a strong dependence of Na and is attributed to the sea-salt aerosol that would be expected in the Seville area.

Chemical element balance

The results of the factor analysis suggest that the major primary sources of airborne particulate in Seville are: soil aerosol, fuel oil combustion, motor vehicle, refuse incineration, and sea-salt aerosol. Preliminary results from the previous CEB indicated the need for a high-Ca source to account for that element. Following Kowalczyk *et al.*[2] and Dzubay[29] we added a limestone component (originated from agricultural liming, construction projects, or abrasion of streets and buildings).

The method is that given by Miller *et al.*[1] and is described as follows. The concentration of any element i in the aerosol is given by:

$$C_i = \sum_j m_j X_{ij},$$

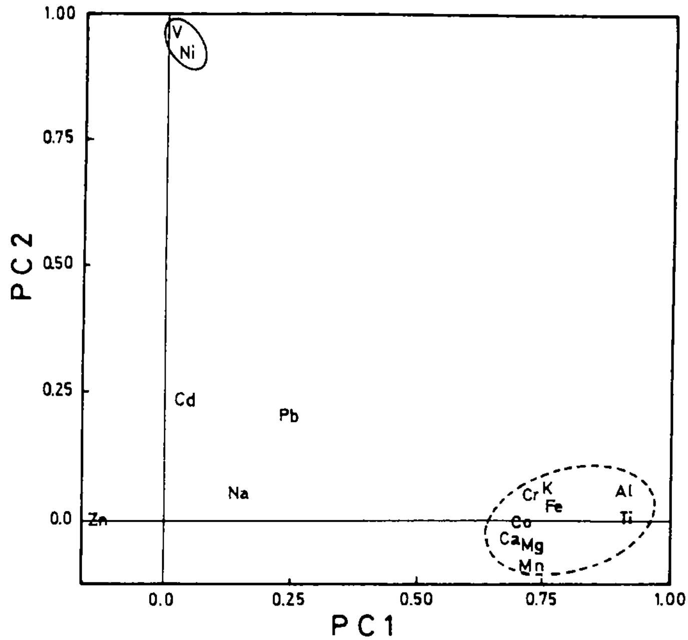

Figure 2 Principal component plot of the trace elements.

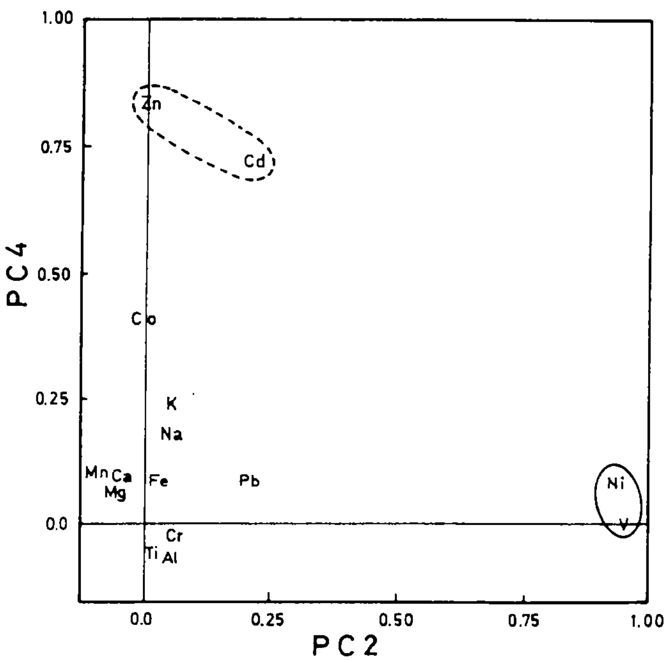

Figure 3 Principal component plot of the trace elements.

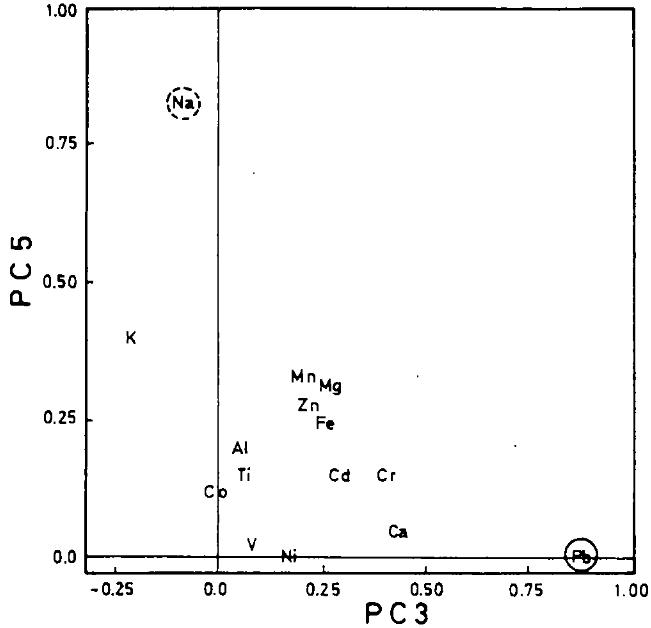

Figure 4 Principal component plot of the trace elements.

where m_j is the mass of material from source j in the sample and X_{ij} is the concentration of element i in particles from source j. If C_i and X_{ij} are known, one can solve the matrix equation for the source-strength vector m_j.

Ideally, one should use concentrations of all measured nonvolatile elements to obtain the source strengths. However in testing the CEB method, most investigators try to use a minimum of carefully chosen marker elements to determine the m_j values in order to leave a maximum of "floating" elements to test the fit. On the basics of factor analysis results, Al, V, Pb, Zn and Na were selected as marker elements for soil aerosol, fuel oil combustion, automobile exhaust, refuse incineration and sea-salt aerosol sources, respectively. The data used in the definition of the source matrix are based on the elemental composition of particles released from the indicated sources. The sources sampling apparatus used were similar to those described by Watson.[14]

Table 3 summarizes results of the CEB on the 120 samples. The

Table 3 Average results of chemical element balance of 120 samples from Seville (ng m^{-3})

Element	*Predicted Contribution*						*Total predicted*	*Predicted/ observed*
	Soil	*Limestone*	*Marine*	*Refuse*	*Motor vehicle*	*Oil*		
Al	2743.2	290.1	*	35.5	*	1.2	3070.0	1.0
Ca	1630.2	12396.2	28.4	54.6	40.2	10.4	14160.0	1.0
Na	368.4	149.5	747.4	84.9	*	19.8	1370.0	1.0
Zn	15.7	*	*	310.3	11.1	2.9	340.0	1.0
Pb	7.8	*	*	74.1	597.0	1.1	680.0	1.0
V	*	*	*	0.9	*	37.0	37.9	1.0
K	1214.8	656.3	27.0	*	*	1.1	1899.2	0.7
Fe	2664.8	422.9	*	28.2	39.0	12.7	3167.6	0.9
Mg	509.4	583.3	95.0	42.9	29.8	16.3	1276.3	1.0
Co	2.4	*	*	*	*	0.9	3.3	0.7
Cd	*	*	*	4.3	0.4	*	4.7	1.4
Mn	15.7	—	*	2.6	1.2	0.3	19.8	1.0
Cr	7.8	3.6	*	2.2	*	1.1	14.7	0.9
Ni	5.8	3.5	*	0.7	0.4	13.1	23.5	0.9
Ti	117.6	—	*	—	—	—	117.6	1.2

*Negligible.
— Unknown.

quality of the fit is indicated by the final column, which lists the predicted/observed ratio for each element in the CEB. As shown in Table 3, most of the elements have a ratio near to 1.

From the data of Table 3, Table 4 has been elaborated in which major sources of each element in the Seville urban aerosol are indicated. As might be expected, Zn and Cd are contributed primarily by refuse incineration, a majority of the V and Ni are associated with the fuel oil combustion, while automative emissions are estimated to be the largest contributor of ambient Pb. The soil is the major source of Al, Fe, Co, Ti, Cr and Mn, most of the Na are contributed by the marine aerosol and the main source of Ca is the limestone.

From the resolution and the knowledge of the weight percentage of major elements in particulate matter from the six sources, we can compute the contribution of each source to the total suspended particulate matter in Seville. We have used the following concentrations: 3.5% Al in particles from soil, 7.2% Zn in refuse-combustion particles, 4.1% V in particles from fuel oil combustion,

Table 4 Major sources of elements on particles in Seville atmosphere

Components	*Element for which component is major source*
Soil	Al, Fe, Co, Ti, Cr, Mn
Limestone	Ca
Refuse	Zn, Cd
Motor vehicle	Pb
Marine	Na
Oil	V, Ni
Soil and Limestone	Mg, K

31% Na in marine aerosol, 15% Pb in motor-vehicle particles and 34% in the limestone component.

Table 5 summarizes the average TSP contributions from the various sources in Seville as indicated by the CEB. Altogether the six sources used in the resolution account for about 126 $\mu g\, m^{-3}$ of TSP vs. measured values of about 210 $\mu g\, m^{-3}$. Thus, we account for about 60% of the measured TSP matter. Note that we do not include several species in our account, e.g., organic material and secondary aerosols, i.e., species such as $SO_4 2_-$, NO_3^-, NH_4^+ which were emitted as gases (SO_2, NO_x, NH_3) and subsequently formed particles.

The results in Table 5 indicate that the soil constitutes the most important source of the TSP matter in Seville (37% on average). The next largest contributor is the limestone which averages 17% of the TSP. All other sources each contribute 5% or less of the measured TSP matter.

SUMMARY AND CONCLUSIONS

Ambient 24 h average particulate samples were collected every fifteen days, during a year, at five sites in Seville and analyzed for 15 elements. This set of data were used in FA and CEB to identify and quantify the major particle sources in the Seville urban aerosol.

The results of the FA and CEB suggest that the major primary sources of TSP matter in Seville are: soil dust, limestone, refuse

Table 5 Average contributions of TSP matter ($\mu g\, m^{-3}$) from various sources in Seville

Component	*Predicted TSP contribution*
Soil	78.4
Limestone	36.5
Refuse	4.3
Motor vehicle	4.0
Marine	2.4
Oil	0.9
Total primary aerosols predicted	126.5
Observed TSP	210.0
Unidentified TSP	83.5

incineration, automobile exhaust, sea-salt aerosol and fuel oil combustion. As a whole, the six sources account for about 60% of the measured TSP matter. The remainder presumably being secondary aerosols and other primary sources not included in the CEB.

Soil is the dominant source of TSP matter (37%) and also of Al, Fe, Co, Ti, Cr and Mn, followed by the limestone (17%) which is the main source of Ca and the refuse incineration which is made up of Zn and Cd. Likewise, marine aerosol and auto exhaust particles are estimated to be the major sources of Na and Pb, respectively. The small contribution of fuel oil combustion to the TSP matter is consistent with the small number of such sources in Seville.

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