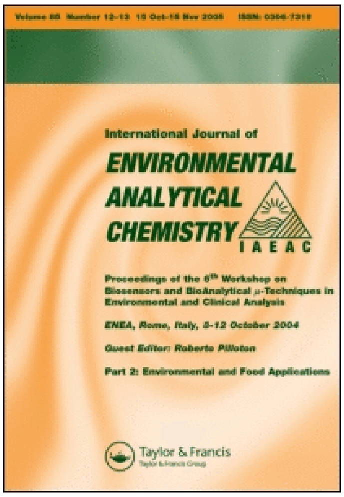

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A Quantitative Determination of Atmospheric Deposition Sources in the "Campo de Gibraltar" Region, Using Factor Analysis and Chemical Element Balance

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A Quantitative Determination of Atmospheric Deposition Sources in the "Campo de Gibraltar" Region, Using Factor Analysis and Chemical Element Balance

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Factor analysis and chemical element balance were employed to identify and quantify the major atmospheric deposition sources at 12 sampling stations in the "Campo de Gibraltar" Region. The data were best represented with 5 sources: soil, marine aerosol, residual fuel oil, refuse and limestone. Predicted concentrations account for about 80% of measured total deposition.

KEY WORDS: Dustfall, chemical element balance, factor analysis, principal components analysis, receptor models, source characterization.

INTRODUCTION

In the development of programs for the control and reduction of the levels of particles in the atmospheric environment, the knowledge of the relative contributions of particulate emission sources is becoming increasingly important.

Source oriented dispersion models, based on emission inventories and meteorological parameters, have been the primary tools used to

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estimate the impact of particle sources at a receptor site. However, there are many investigator[1–3] who consider that the results obtained by applying these models are only approximate. This is due to the complexity and random nature of the dispersion in the atmosphere, together with the inaccuracy in the inventory of the emission sources.

Because of the great uncertainties of source oriented dispersion models, receptor models have been developed during the last years. They are used to determine the source contributions to ambient particulate matter loadings at a sampling site based on common properties between source and receptor. The number and variations of these receptor models have grown very fast over the past few years, Watson *et al.*,[4–6] Core,[7] Gordon,[1] Cooper *et al.*[8] and Henry *et al.*[9] offer excellent reviews of the receptor models and discuss their boundary conditions, strengths and weaknesses.

Among the several types of receptor models, the most widely used are: chemical element balance and factor analysis.

The chemical element balance (CEB) is based on the principles established by Miller *et al.*[10] and Friedlander.[11]

According to the CEB model, the composition of particles at the receptor is a linear combination of concentration patterns of particles from the contributing sources; i.e., the concentration of element i in the particulate sample is given by

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

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 whose predicted-to-observed concentration ratios can serve as a measure of the quality of the fit.

Factor analysis (FA) has proven to be of value in identifying sources in atmospheric particle studies.[12–15]

In the FA model it is assumed that the variations of the n variables x_z can be described as a sum of two independent terms

$$x_{zi} = \sum_{p=1}^{m} a_{zp} F_{pi} + \varepsilon_{zi},$$

or in matrix notation,

$$X = AF + G.$$

The first term is the common factor term containing m independent (orthogonal) factors F_p, which are stochastic variables (with zero mean and unit variance) taking the values F_{pi} in sample i.

The second term G contains the residuals ε which are not explained. The residuals include both analytical and sampling errors as well as errors due to the possible inadequacy of the model. They are considered as random errors.

The so-called factor loadings a_{zp} are in fact correlation coefficients between variable z and factor p. Without loss of generality, the system of m orthogonal factor-vectors can be rotated so as to either maximize or minimize the factor loadings.

The communality h^2 is defined as the sum

$$h_z^2 = \sum_{p=1}^{m} a_{zp}^2 \leqq 1,$$

and it is the fraction of the (unit) variance of variable z that is explained by the model. The communality if therefore a measure of the quality of the model.

The variance which can be ascribed to the variations of a given factor is

$$\lambda_p = \sum_z a_{zp}^2.$$

The identification of sources is made by associating the largest calculated factor loading with the marked element for each source.

The main advantage of FA in comparison to CEB, is that it requires no prior knowledge of the number and composition of the emission sources. Nevertheless, it does not allow for the contribution of specific source types to be determined quantitatively and cannot provide source information for individual samples.

In this paper, the factor analysis has been used as a qualitative technique to identify the major sources of total deposition in the "Campo de Gibraltar" (industrial zone where there are important residential areas). With regard to these sources, the CEB has been applied to determine the relative contribution of total deposition sources in the studied area.

METHODS

From September 1982 to September 1983, monthly samples of total deposition were collected by the sampling equipment designed by the British Standards Institution.[16] A map of the "Campo de Gibraltar" Region, showing the location of the 12 sampling stations, are represented in Figure 1. Each sample was analyzed for Al, Cr, Fe, Mn, Ni, Pb, V, Zn, Ca and Mg by atomic absorption, for Na and K by atomic emission, for Cl^- by conductometry titration, for: SO_4^{2-} by turbidimetric titration and NO_3^- and NH_4^+ by visible spectrophotometry after complexing with sodium salicylate and Nessler reagent, respectively.

RESULTS AND DISCUSSION

Factor analysis

In this study a particular type of factor analysis (principal components analysis) was applied to the deposition elemental data. The analysis was carried out using the Biomedical Computer Program BMDP4M described in Dixon *et al.*[17] The initial components were rotated using the orthogonal varimax method to obtain the final factor loadings presented in Table I. The four components account for 78% of the variance in the data set (23% accounted for the first one of them). These four factors account for most of the true variance of each of the measured elements.

The four components can be interpreted as different types of sources. The first component is strongly dependent on concentrations of Cl^-, Na, Mg and K and it is attributed to the sea-salt

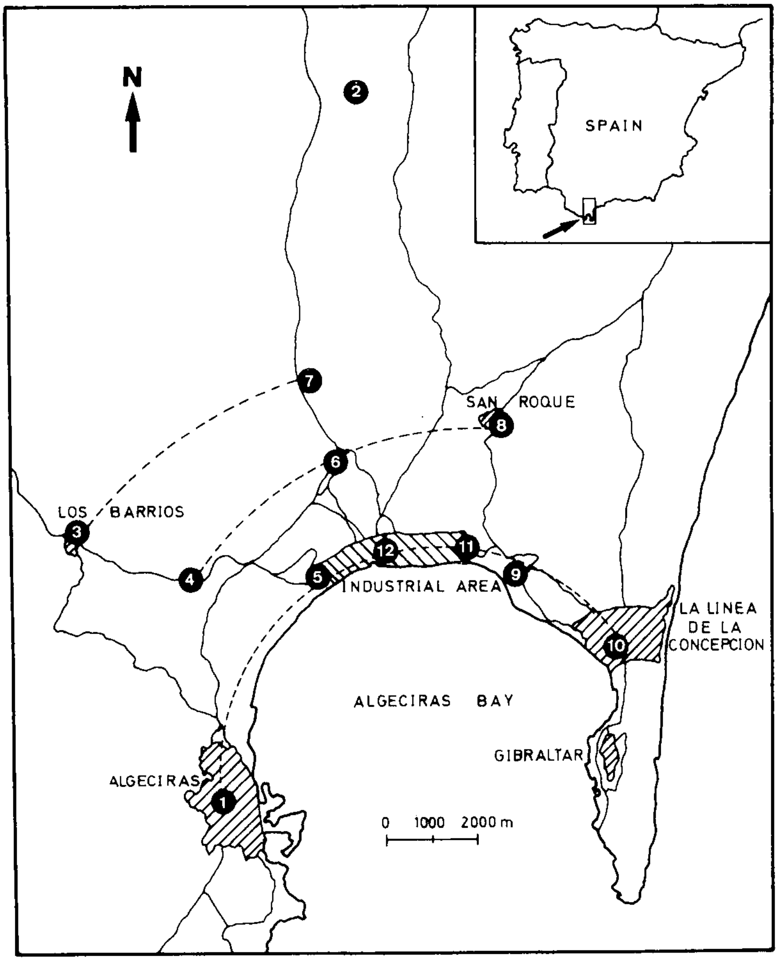

Figure 1 Location of sampling stations.

aerosol.[14,18] The second appears to represent soil aerosol impacts at the "Campo de Gibraltar", since it is highly correlated with the crustal elements Al, Mn and Fe.[15,19–20] The third can be attributed to fuel oil and refuse combustion, since it presents high factor loadings of V, Ni and Zn.[18] Finally, the fourth component has a strong dependence on NO_3^- and NH_4^+ which suggests that it is related to secondary reactions in the atmosphere.[21–22]

Table I Varimax rotation of principal component analysis.[a]

Element	Factor loadings				h^2
	1	2	3	4	
Cl^-	0.93	0	0	0	0.94
Na	0.92	0	0	0	0.95
Mg	0.86	0	0.42	0	0.94
K	0.79	0.47	0	0	0.91
Mn	0.41	0.85	0	0	0.94
Al	0.44	0.76	0	0	0.80
Pb	0	0.43	0.63	0.32	0.69
Cr	0	0.75	0	0	0.59
Ca	0	0.60	0	0.45	0.69
V	0	0	0.97	0.	0.94
Ni	0	0	0.91	0	0.92
Fe	0	0.77	0	0	0.71
Zn	0	0	0.68	0.40	0.65
NO_3^-	0	0	0	0.90	0.85
NH_4^+	0	0	0	0.86	0.77
SO_4^{2-}	0	0	0	0.60	0.57
λ	3.75	3.27	2.91	2.51	12.86 78%

[a] Loadings of <0.3 have been replaced by 0.

Chemical element balances

The results of the factorial analysis suggest that the major primary sources of total deposition in, the "Campo de Gibraltar" are: sea-salt, soil and combustion of fuel oil and refuse. Preliminary results from previous CEB indicated the need for a high-Ca source to account for that element. Following Kowalczyk *et al.*[2] and Scheff *et al.*[23] we added a limestone component (originated from agricultural liming, construction projects, or abrasion of streets and buildings).

The method used was to determine source strengths by fitting concentrations of a reduced number of carefully chosen marker elements in order to leave a lot of "floating" elements to test the fit. Marker elements used were: Na, V, Zn, Ca and Al. Sodium is a good measure of the marine component, V of oil combustion, Zn of refuse incineration, Ca of limestone and Al of soil component.[24–25]

Table II Source profile matrix (percentages)

Element	Soil	Sea-salt	Fuel-oil	Refuse	Limestone
Al	5.91	<0.01	0.41	1.08	2.41
Na	0.61	31.20	2.51	1.96	0.41
V	0.01	<0.01	5.42	<0.01	<0.01
Zn	0.01	<0.01	0.32	5.02	<0.01
Ca	2.24	1.18	1.35	1.25	35.00
Fe	3.94	<0.01	0.61	0.49	1.22
Pb	0.04	<0.01	0.05	0.23	<0.01
Cr	0.05	<0.01	0.02	0.04	—
Mn	0.06	<0.01	0.03	0.06	0.04
Ni	0.02	<0.01	1.19	0.01	<0.01
Mg	0.32	3.94	2.64	0.91	0.48
Cl^-	0.01	55.00	3.71	3.72	0.30
K	1.53	1.12	0.13	0.89	0.53

Table II lists all of the data used in the definitions of the source matrices. All data selected are based on the elemental composition of samples collected downstream of pollution control devices. The source sampling apparatus are described by Watson.[4]

Table III summarizes results of CEB on the 144 samples. NO_3^-, NH_4^+ and SO_4^{2-} have not been included in this table because their major source is secondary aerosols. As a measure of the quality of the fits, we calculated the predicted/observed ratio for each element in CEB. As shown in Table III, most of the elements have a ratio close to 1. The elements most poorly fitted are Cr, Ni and Fe, which seems to be due to the contribution of a metallurgical company not included in the CEB.

Table IV summarizes the major sources of each element in the "Campo de Gibraltar". As might be expected, a majority of the V and Ni are associated with the oil component, while most of the Na and Cl^- are contributed by the marine aerosol. The major sources of Mg are marine aerosol and the combustion of residual fuel oil (the Mg is used as an additive in installations of fuel oil). The soil component dominates the crustal element impacts (Al, Fe, Cr and Mn).

Average total deposition contributions from the various sources as indicated by the CEB are shown in Table V. The total deposition

Table III Average results of chemical element balances of 144 samples from the "Campo de Gibraltar"

Element	Predicted contributions. $\mu g\,m^{-2}\,d^{-1}$					Total, $\mu g\,m^{-2}\,d^{-1}$		Predicted/ observed
	Soil	Sea-salt	Fuel oil	Refuse	Limestone	Predicted	Observed	
				Elements used in fitting				
Al	4,484.4	[a]	68.4	189.0	858.1	5,600	5,600	1.0
Na	487.6	14,654.7	418.6	343.1	146.0	16,050	16,050	1.0
V	8.0	[a]	904.0	[a]	[a]	912	912	1.0
Zn	8.0	[a]	53.4	880.6	[a]	942	942	1.0
Ca	1,790.6	554.2	225.2	220.5	12,469.5	15,260	15,260	1.0
				Remaining elements				
Fe	3,157.0	[a]	101.7	85.8	434.4	3,770	5,400	0.7
Cr	40.0	[a]	3.3	7.0	[b]	50	110	0.5
Pb	32.0	[a]	8.3	40.3	[a]	81	118	0.7
Mn	48.0	[a]	5.0	10.5	14.2	78	99	0.8
Ni	16.0	[a]	198.5	1.8	[a]	216	311	0.7
Mg	255.8	1,850.6	440.3	159.3	170.9	2,877	2,520	1.1
Cl^-	8.0	25,847.6	618.8	651.1	106.8	27,232	29,450	0.9
K	1,223.0	526.1	21.7	155.8	188.7	2,115	1,940	1.1

[a] Negligible.
[b] Unknown.

Table IV Major sources of elements in atmospheric deposition of the "Campo de Gibraltar"

Components	Element for which component is major source
Marine	Na, Cl^-
Soil	Al, Fe, Mn, Cr
Oil	V, Ni
Refuse	Zn
Limestone	Ca
Soil and marine	K
Soil and refuse	Pb
Marine and oil	Mg

Table V Average contributions of atmospheric deposition matter from various sources in the "Campo de Gibraltar"

Source	Predicted contribution ($mg\,m^{-2}\,d^{-1}$)	Percentage
Soil	75.9	30.7
Marine	47.0	19.0
Oil	16.7	6.8
Refuse	17.5	7.1
Limestone	35.6	14.4
Total primary aerosol predicted	192.7	78.0
Average value of total atmospheric deposition	247.0	
Unidentified deposition	54.3	

contributions are calculated from the CEB with knowledge of the concentration of a prominent element in particulate material from each source.

As a whole, the five sources used in the resolution account for about 193 $mg\,m^{-2}\,d^{-1}$ of total atmospheric deposition while measure values are about 247 $mg\,m^{-2}\,d^{-1}$ during the sampling period. Thus, we account for about 80 per cent of the total atmospheric deposition with primary aerosols.

Soil is the dominant source of primary total deposition, yielding a mass concentration 1.6 times as great as the closest competitor, marine aerosol.

CONCLUSIONS

In this paper, the factor analysis has been used as a qualitative technique to identify the major sources of total deposition in the "Campo de Gibraltar". With regard to these sources, CEB has been applied to determine the relative contribution of such sources.

The results of the factorial analysis and the CEB suggest that the major primary sources of total deposition in the "Campo de Gibraltar" are: soil dust, marine aerosol, fuel oil and refuse combustion and limestone. As a whole, the five sources account for about 80 per cent of measured total deposition and most elements are reasonably well fitted.

Soil is the dominant source of total deposition (31%) and also of Al, Fe, Mn and Cr. Next is marine aerosol (19%), which is the main source of Na and Cl^-, and limestone (14%) which is the main source of Ca. In spite of its small contribution to the total atmospheric deposition, the combustion of fuel oil constitutes the major source of V and Ni.

It should be noted that the contribution of natural sources (soil and marine aerosol) account for about 50 per cent of the total deposition.

References

1. G. E. Gordon, *Environmental Science and Technology* **14,** 792 (1980).
2. G. S. Kowalczyk, G. E. Gordon and S. W. Rheingrover, *Environmental Science and Technology* **16,** 79 (1982).
3. S. Budiansky, *Environmental Science and Technology* **14,** 370 (1980).
4. J. G. Watson, Jr., Ph.D. Dissertation, Oregon Graduate Center, Beaverton, OR (1979).
5. J. G. Watson, Jr. *et al.*, EPA-600/2-81-039, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1981).
6. J. G. Watson, Jr. *Journal of the Air Pollution Control Association* **34,** 619 (1984).
7. J. E. Core, EPA-450/4-81-061a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (1981).
8. J. A. Cooper and J. G. Watson, Jr., *Journal of the Air Pollution Control Association* **30,** 1116 (1980).
9. R. C. Henry, C. W. Lewis, Ph. K. Hopke and H. J. Williamson, *Atmospheric Environment* **18,** 1507 (1984).
10. M. S. Miller, S. K. Friedlander and G. M. Hidy, *Journal of the Colloid Interface Science* **39,** 165 (1972).

11. S. K. Friedlander, *Environmental Science and Technology* **7,** 235 (1973).
12. D. H. Lowenthal and K. Rahn, *Atmospheric Environment* **19,** 2011 (1985).
13. Ch. K. Liu, B. A. Roscoe, K. G. Severin and Ph. K. Hopke, *American Industrial Hygiene Association Journal* **43,** 314 (1982).
14. N. Z. Heidam, *Atmospheric Environment* **18,** 1507 (1981).
15. G. D. Thurston and J. D. Spengler, *Atmospheric Environment* **19,** 9 (1985).
16. British Standards Institution, *Methods for the Measurement of Air Pollution.* Part 1, London (1969).
17. W. J. Dixon and M. B. Brown, *BMDP Biomedical Computer Programs,* University of California Press (1979).
18. Ph. K. Hopke *et al.*, *Atmospheric Environment* **10,** 1015 (1976).
19. R. K. Stevens *et al.*, *Atmospheric Environment* **18,** 261 (1984).
20. M. T. Kleinman, M. Eisenbud, M. Lippmann and T. J. Kneip, *Environment International* **4,** 53 (1980).
21. S. H. Cadle, R. J. Countess and N. A. Kelly, *Atmospheric Environment* **16,** 2501 (1982).
22. R. L. Tanner, *Atmospheric Environment* **16,** 2935 (1982).
23. P. A. Sheff, R. A. Wadden and R. J. Allen, *Environmental Science and Technology* **18,** 923 (1984).
24. G. S. Kowalczyk, C. E. Choquette and G. E. Gordon, *Atmospheric Environment* **12,** 1143 (1978).
25. F. D. Gatz, *Atmospheric Environment* **9,** 1 (1975).