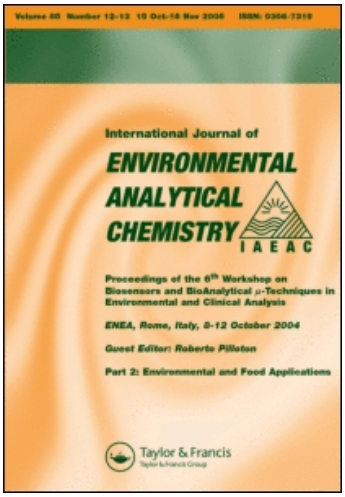

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Atmospheric Concentration of Metals and Total Suspended Particulates in the "Campo de Gibraltar" Region, Spain

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Atmospheric Concentration of Metals and Total Suspended Particulates in the "Campo de Gibraltar" Region, Spain

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Total suspended particulates (TSP) and metal concentrations were determined from October 1982 to September 1983 in the "Campo de Gibraltar", an Industrial zone where there are important residential areas. The data included in this paper provide basic information on concentrations of 13 elements (Al, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, V and Zn) in air to establish those areas where the major atmospheric levels of certain elements generally occur, to estimate the sources of such elements and to show their temporal variation.

KEY WORDS: Aerosol composition, trace elements, total suspended particulates, seasonal differences, filters, AAS, enrichment factors.

INTRODUCTION

In recent years, there has been an increasing concern to determine the atmospheric levels of elements, with particular regard to possible health hazards and environmental issues. Consequently, studies by a number of research groups around the world have produced a large amount of information concerning the distribution of trace elements in the atmosphere. However, there is little information available on

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the air in Southern Spain.[1] In this paper concentrations of TSP and 13 trace elements have been measured in air particulate samples, collected at 12 sampling sites in an industrial area in Southern Spain. The spatial and temporal variation as well as the factors which influence the levels of the elements, were also examined.

SAMPLE COLLECTION AND ANALYSIS

The aerosol particle samples were continuously collected from October 1982 to September 1983, in 12 sampling sites in the "Campo de Gibraltar" (see Figure 1). The sites were chosen to permit measurement representative of regional air quality. The selection criteria were the following:

Location on three circumferences which surround the "Campo de Gibraltar", with an average radii of 6, 8 and 10 kilometers, respectively.

Preferential location on the line East–West (prevailing winds) which passes through the most important factories (stations 3, 4, 5, 12, 11 and 9).

Location in residential areas of the "Campo de Gibraltar" Region (Algeciras, Los Barrios, San Roque and La Linea de la Concepción).

Station 2 is situated 12 kilometers from the coast and far from the industrial and urban zones.

During the sampling period, 7-day integrated samples were collected, at all sites, on Whatman 40 filters (7 cm diameter) using a low-volume ($0.83\,m^3\,h^{-1}$) sampler. In addition to the low-volume sampler, a high-volume sampler ($65\,m^3\,h^{-1}$) equipped with a glass-fiber filter was operated each day at Station 5 (representative of the studied area).

The samples collected on Whatman filters were digested in a HNO_3-$HClO_4$ mixture and analyzed by atomic absorption spectroscopy of the 13 elements of interest. The calibrations were periodically repeated to check accuracy. The concentrations of the different chemical components were obtained with reference to blank solutions. The analytical errors were nominal and varied within $\pm 10\%$. The TSP levels were measured by the weight of the glass fiber filter before and after sampling.

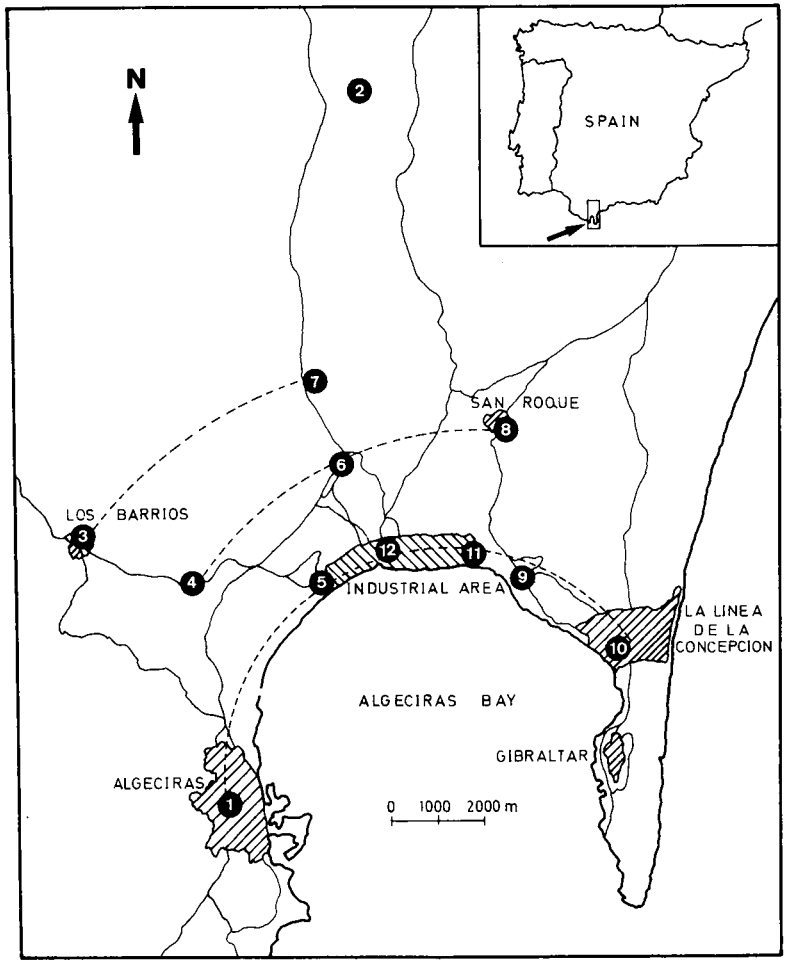

Figure 1 Location of sampling stations.

RESULTS AND DISCUSSION

Total suspended particulate (TSP)

The monthly mean and standard deviation of TSP levels measured at Station 5 are shown in Table I. One can observe that the TSP does not fluctuate substantially during the year.

Table I Monthly averages and standard deviation of TSP levels in Station 5 ($\mu g\,m^{-3}$)

Month	Range	Mean	Standard deviation
October 82	21– 82	54.3	21.3
November 82	20– 90	65.6	17.2
December 82	28– 68	44.7	11.3
January 83	26–287	82.9	58.9
February 83	20–213	63.9	45.4
March 83	33–120	74.2	30.1
April 83	14–136	64.9	35.4
May 83	22– 72	48.5	16.5
June 83	53–124	84.9	29.2
July 83	53– 86	61.8	9.8
August 83	70–110	82.3	13.0
September 83	49–138	82.2	21.0

To study the effects of the weather patterns on TSP levels, Table II shows these levels and meteorological parameters on selected days when TSP levels of $100\,\mu g\,m^{-3}$ was surpassed. The data in Table II show that the rain reduces the TSP levels (note that none of the cases included in Table II correspond to rainy periods).

The highest TSP levels are usually produced during periods with easterly winds, which should not be surprising, if we bear in mind that under these conditions Station 5 is specially affected by emissions from the industrial area.

To compare the TSP levels obtained in this paper, with the Spanish, EEC and USA air quality standards (AQS), Table III indicates in brackets the number of cases in which the AQS have been surpassed.

It can be observed that the TSP levels in the "Campo de Gibraltar" are notably inferior to the Spanish and EEC AQS. According to the USA legislation, the TSP levels found surpass the secondary AQS (level of air quality which the Administrator judges necessary to protect the public welfare), however the primary AQS is only surpassed on one occasion (level of air quality which the Administrator judges are necessary, with an adequate margin of safety, to protect the public health).

Table II TSP and meteorological parameters on selected days when TSP level of $100\,\mu g\,m^{-3}$ was surpassed

Day	TSP ($\mu g\,m^{-3}$)	Wind direction	Wind speed ($Km\,h^{-1}$)	Rainfall (mm)
19-I-83	186	WSW	19.1	—
20-I	287	E	30.4	—
21-I	169	E	38.0	TR
26-I	106	E	37.3	—
31-I	110	SW	21.2	—
2-II	213	W, E	29.8	—
3-II	191	E	48.2	TR
10-II	110	WNW	22.1	—
3-III	101	E	37.6	—
4-III	102	E	50.6	—
7-III	120	E	58.7	—
9-III	113	E	22.1	—
11-III	104	ENE, E	13.7	—
12-III	106	NE, E	13.0	—
13-III	107	ENE, E	19.8	—
14-III	109	ENE, E, WSW	14.6	—
15-III	107	W	33.4	—
12-IV	116	SW, E	26.7	—
14-IV	124	E	43.6	—
15-IV	136	E	56.0	TR
8-VI	105	WSW, SW, E	21.9	—
10-VI	108	E, ENE	19.6	—
11-VI	112	W, SW	11.1	—
12-VI	114	WSW, SW	20.0	—
13-VI	124	WSW, SW	20.2	—
14-VI	105	E	22.2	—
15-VI	118	E	25.6	—
17-VI	104	E	14.3	—
2-VIII	102	E, ENE	11.9	—
3-VIII	110	E	22.1	—
4-VIII	104	E	29.5	—
5-VIII	101	E	31.5	—
16-IX	113	SW	18.5	—
22-IX	103	ESE, SE, ENE, E	25.0	—
23-IX	138	ENE, E	28.9	—
26-IX	107	WSW, E	10.7	—
27-IX	114	ENE, E	22.8	—

Table III Ambient air quality standards (AQS) for total suspended particulate ($\mu g\,m^{-3}$). The number in brackets indicate the number of cases in which the AQS have been surpassed.

Country/State	AQS		Averaging time
Spain	300 (0)		24 h
	202 (0)		Monthly (arithmetic mean)
	130 (0)		Annual (arithmetic mean)
EEC	150 (0)		Annual (arithmetic mean)
	300 (0)		Annual (95th percentile)
USA[a]	*Primary*	*Secondary*	
	260 (1)	150 (5)	24 h
	75 (0)	60 (1)	Annual (geometric mean)

[a]Maximum 24 h concentration not to be exceeded by more than once a year.

Table IV Comparison of measured TSP with other works

Sampling location	Range	Mean	Reference no.
Present work	14–287	68	–
Taberna (Spain)	49–207	92	1
Denver (USA)	25–216	104	2
Chicago (USA)	32–244	76	3
San Francisco (USA)	43–120	88	4
Jerusalem (Israel)	36–176	69	5
Indian sub-continent	24– 52	40	6
Taiwan (China)	85–400	210	7
Vancouver (Canada)	22–182	77	8
Zagreb (Yugoslavia)	19–579	140	8

In Table IV the annual mean TSP in the "Campo de Gibraltar" is compared with levels recorded at other sites throughout the world. It can be observed that the mean values are generally in agreement with those reported in other works.

Aerosol elemental concentration

The average annual concentrations at the different stations are shown in Figure 2. Generally, the higher concentrations of Cr, Fe, Mn, Mg and Na can be observed in samples from stations 10 and 5. This is not surprising if we bear in mind that the mentioned stations

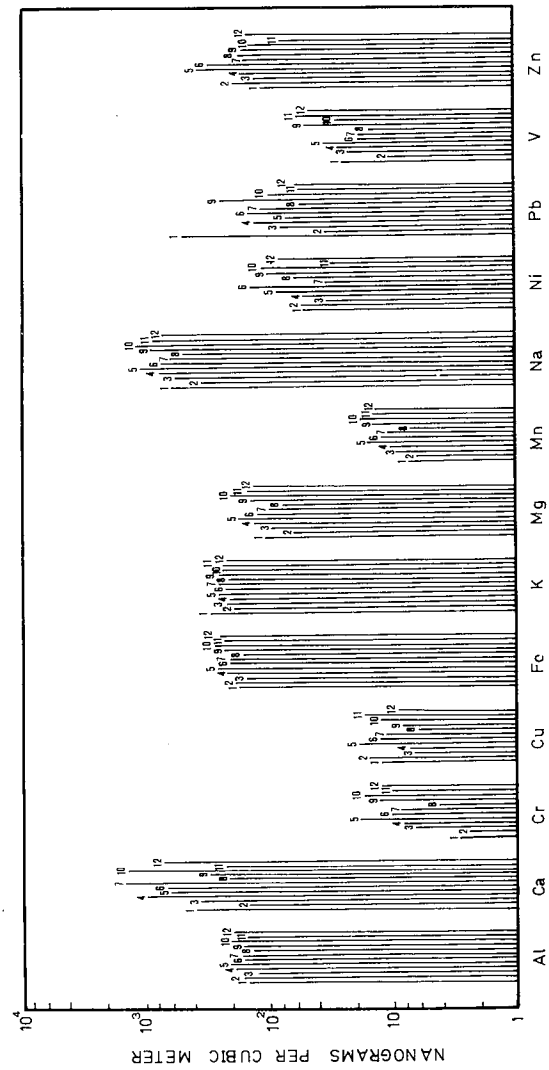

Figure 2 Average annual elemental concentrations at the different stations of the network.

are situated close to the coast, at both ends of the industrial area, and under its contaminating action by effect of the wind.

The greatest concentration of V are found at stations 11, 9, 12 and 5, which should not be surprising, bearing in mind that close to these stations, an important oil-fired power plant has been installed. This supports the suggestion[9–10] that the major source of V is the combustion of fuel oil.

The sampling stations situated in zones with greater vehicular traffic (stations 1 and 9) present the greatest concentration of Pb, since vehicles constitute the major source of lead in the atmosphere.

At Stations 5 and 6, the highest concentrations of Zn have been observed, confirming statements by Hopke *et al.*[9] and Thurston *et al.*[11] which indicate that the refuse incineration constitutes the main source of this element.

The concentrations of Al, Fe and K, do not present major differences between the samples obtained at each station. This is consistent with the assumption that these elements originate from soil resuspension particles.[12–13]

The highest Na and Mg concentrations appear at stations situated close to the coast, which is in agreement with the suggestion made by various authors[13–14] which indicates that the marine aerosol constitutes the major source of these elements.

Station 2 (background) usually shows the lowest concentrations of the elements measured, especially those of anthropogenic or marine origin (Na, Mg, Pb, V, etc).

Enrichment factors

A method which is becoming popular for identifying the elements that are enriched in the atmosphere as compared with average soil material is that of calculating an enrichment factor (EF).[15–16] The advantage of this method is the reduced uncertainty in the interpretation of results compared to the interpretation of absolute concentrations (affected by factors such as wind speed and direction, rain, distance from the source, etc). The EF is the result of a double normalization technique where the ratio of a given element to a reference element in the suspended particulate matter is compared to the same ratio for average soil material. The reference element, Al, is chosen for normalization because of its low volatility, it is one of the

main constituents of the soil and lacks the anthropogenic sources. Thus, the EF is calculated as:

$$EF = \frac{(X/Al)\ \text{aerosol}}{(X/Al)\ \text{soil}}$$

where X is the concentration of the element of interest.

Enrichment factors for elements in airborne particulate at the "Campo de Gibraltar" are shown in Figure 3. Elements that show low enrichment factors include Al, Fe, Cr, K and Mn. This suggests a predominantly natural source (soil dust). For elements that are usually associated with anthropogenic emission and are potentially toxic, such as V, Ni, Cu, Pb and Zn, the enrichment factors were in the range of 30–250.

Statistical and temporal variation assessments of data

The results of the correlation coefficient are shown in Table V. A significant correlation was found between elements which have a

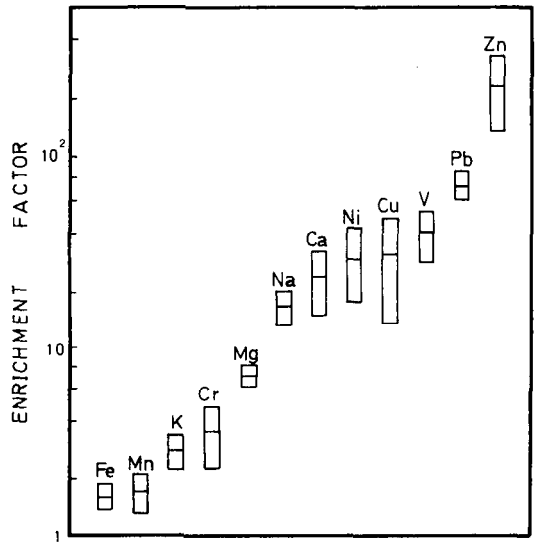

Figure 3 Enrichment factors. The vertical bars represent the standard deviation; the horizontal dashes represent the arithmetic mean.

Table V Correlation coefficients matrix using 144 sample data sets

Al	1.00												
Ca	0.01	1.00											
Cr	0.69	0.00	1.00										
Cu	−0.03	0.77	−0.10	1.00									
Fe	0.91	0.34	0.65	0.27	1.00								
K	0.51	0.64	0.52	0.56	0.67	1.00							
Mg	0.67	0.18	0.53	0.29	0.74	0.46	1.00						
Mn	0.70	0.28	0.72	0.30	0.82	0.62	0.72	1.00					
Na	0.47	0.33	0.38	0.52	0.59	0.62	0.85	0.69	1.00				
Ni	0.06	0.40	0.07	0.34	0.27	0.34	0.39	0.58	0.61	1.00			
Pb	0.19	0.51	0.30	0.65	0.35	0.67	0.39	0.58	0.57	0.43	1.00		
V	0.58	0.37	0.27	0.20	0.58	0.52	0.51	0.51	0.46	0.52	0.31	1.00	
Zn	−0.05	−0.38	0.08	0.54	−0.14	−0.33	−0.15	−0.12	−0.07	−0.27	−0.44	0.23	1.00
	Al	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	V	Zn

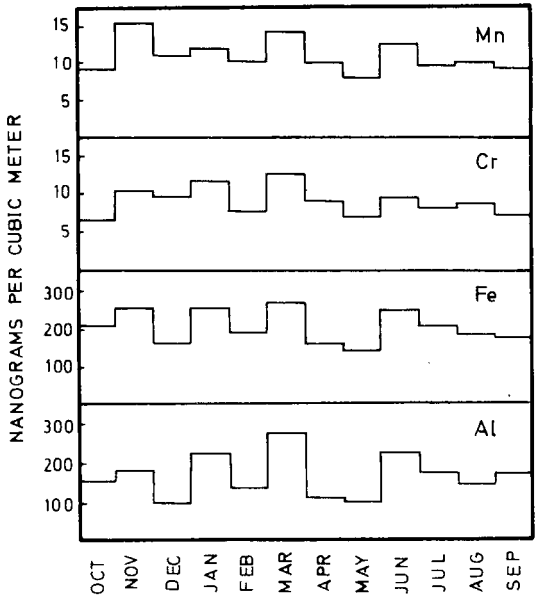

Figure 4 Temporal variation of Al, Fe, Cr and Mn concentrations (average at all stations).

common source as is the case for Al, Fe, Cr and Mn (soil dust) or amongst Na and Mg (marine aerosol). These correlations may allow the reduction of the number of determinations necessary if a permanent network was established and the measurement of the most simple ones.

It should be noted that the elements of anthropogenic origin, Zn, Pb, V, etc., present low correlation coefficients, in most cases, since they originate from different sources.

In Figures 4, 5 and 6, the monthly mean variations of selected elements are plotted. One can see from Figure 4, that the temporal variations of Al, Fe, Cr and Mn are similar, suggesting that all originate from a common source. Similar features were noticed in the case of Mg and Na (Figure 5). Finally, in Figure 6, it can be observed that the temporal variations of the elements represented are not generally similar. These findings are consistent with what was previously indicated about the different anthropogenic sources of these elements (vehicles, incinerators, etc).

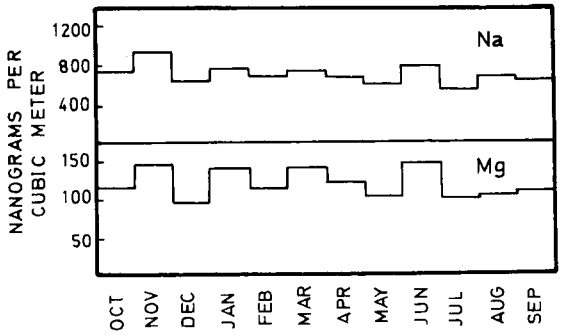

Figure 5 Temporal variation of Mg and Na concentrations (average at all stations).

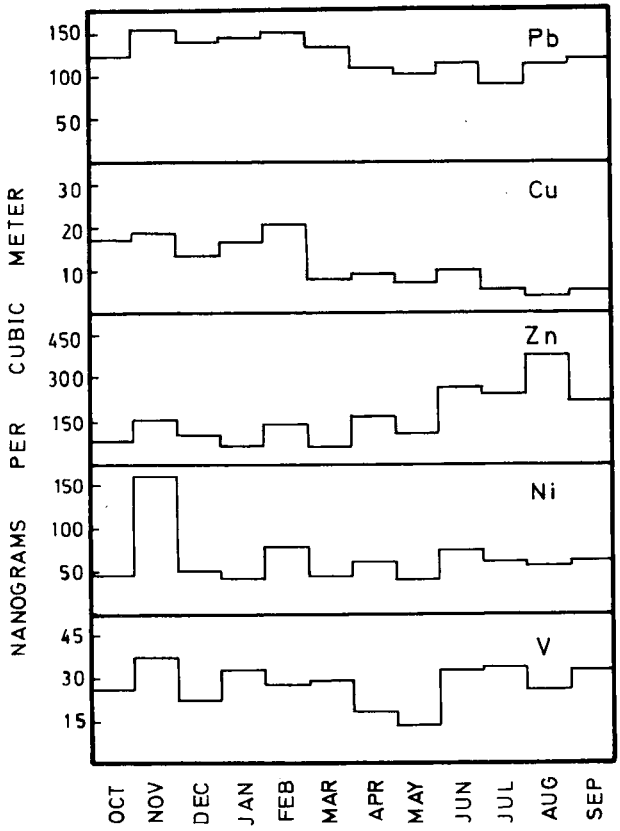

Figure 6 Temporal variation of V, Ni, Zn, Cu and Pb concentrations (average at all stations).

CONCLUSIONS

Examination of the aerosol particles data in the "Campo de Gibraltar" Region has led to the following general conclusions.

The TSP levels are notably inferior to the Spanish and EEC air quality standards.

On the basis of enrichment factors, temporal variation and correlation analysis, a soil-derived group of elements was identified (Al, Fe, Cr, K and Mn). A large majority of the V, Ni, Cu, Pb and Zn concentrations present in the "Campo de Gibraltar" is of anthropogenic origin.

Spatial variations in the concentrations of certain elements were observed. The highest levels of these elements were found in the following locations: Pb at the stations situated in zones with major circulation, V at stations close to an oil-fired power plant, Zn near incinerators and Na and Mg at stations situated close to the coast.

The most abundant elements were those commonly associated with soil and marine aerosol.

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