



Metallic species in atmospheric particulate matter in Las Palmas de Gran Canaria

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ABSTRACT

In this work, we quantified the total, water-soluble and insoluble fractions of 12 metallic species (Na, Ca, K, Mg, Fe, Zn, Cr, Ni, Cu, Cd, Pb and Mn) present in total suspended particulates (TSP) in an urban area with heavy traffic (about 80 000 vehicles/day) of Las Palmas de Gran Canaria (Canary Islands). Experimental measurements were made from July to December 2003 on a total of 42 samples (7 per month). Particulate matter (TSP) was collected in fiber filters and high volume samplers. PM₁₀ levels were estimated assuming the PM₁₀ fraction is about 70% of all TSP. Total fractions were determined gravimetrically. Water-soluble fraction was extracted by sonication. Concentrations of metallic elements were analyzed by flame atomic absorption spectrophotometer. Temporal changes in the concentrations of the target elements were examined and a multivariate approach used to identify the primary sources for each species. Mean value for TSP is 71.92 μg/m³. The water-soluble fraction consisted mainly of Na, Ca, Mg, and K. The insoluble fraction contained higher concentrations of all elements than the soluble except Na. In the water-soluble fraction, Na, K, Ca and Mg were found to come mainly from natural sources; Cr, Pb, Cd, Ni, Zn and Cu from anthropogenic sources.

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1. Introduction

Atmospheric pollutants in general, and suspended particulates in particular, can have adverse effects on health [1–5] and deleterious consequences on the environment [6]. Its specific effects depend largely on the size of particles, their contents in toxic species and their solubility in biological fluids [7–10].

Total suspended particulates (TSP) in the atmosphere of urban areas in developed countries encompasses a variety of metallic species coming from traffic exhaust, secondary particles formed in the atmosphere, and coarse particles from marine aerosol or resuspended soil and road dust [11]. Examining the incidence of such species can help to identify their sources, the way total suspended matter is transported over long distances and last, but not least, their effects on human health. The results of recent tests on animals and others simulating the human respiratory system *in vitro* suggest that the presence of metallic components in atmospheric particulate matter is directly correlated with its pulmonary toxicity [12–14]. In fact, because lead is known to be toxic, its tolerated atmospheric levels have been regulated for some time now. More recently, the European Union has proposed that atmospheric levels of As, Cd, Hg and Ni should

also be monitored with a view to their eventual regulation [15].

While conventional tests on metallic species in the atmosphere have largely focused on determining total concentrations, a growing interest currently exists in the international scientific community in quantifying the water-soluble and insoluble fractions of such species with a view of elucidating their interactions with various ecosystems including the atmosphere, hydrosphere and soils [16,17], and also any deleterious effects of such interactions [18–20]. Soluble metallic species can be toxic to both the cells onto which they deposit and those in their neighbourhood; by contrast, insoluble species exert their cytotoxic effects by direct contact with cells or phagocytosis via alveolar macrophages [21–26].

The fact that road traffic constitutes the primary source of metallic particles in many urban areas prompted us to study the contents in soluble and insoluble metallic species of the atmosphere of a district in the city of Las Palmas de Gran Canaria currently under heavy traffic for which no such data had previously been reported.

2. Experimental

2.1. Sampling and analysis

Experimental tests were performed from July to December 2003. A total of 42 samples (7 per month) were collected for analy-

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sis; 6 on Monday, 6 on Tuesday and so on. Atmospheric particulate matter was collected onto Whatman GF/A 20 cm × 25 cm fiberglass filters using a high-vol pumping System (CAV-P; MCV, Collbato, Spain) at a flow-rate of 50 m³/h. Each sampling period lasted 24 h and started at 8:00 a.m. The sample collector was placed 10 m above ground level on the roof of a public building in the vicinity of Bravo Murillo (28°06'28"N, 15°25'13"W) a downtown street in the city of Las Palmas de Gran Canaria (Fig. 1) with heavy traffic (80 000 vehicles/day during the sampling period) [27]. The street runs normal to a neighbouring coastal highway which constitutes an additional source of anthropogenic particulates swept by the sea breeze in the sampling zone. Winds during the sampling period were predominantly from the NE. Because fiberglass filters are hygroscopic, they were carefully equilibrated in desiccator for 48 h prior to and after collecting samples in order to examine the influence of moisture and ensure accurate measurements of particulates [28–30]. The concentration of TSP was determined gravimetrically by weighing the filters prior to and after collecting samples using an analytical balance with a reading precision of ±10 µg. The water-soluble fraction was determined by previously extracting the mass retained on one side of each filter with 50 ml of bidistilled water of 8–10 µΩ/cm under sonication in a Bransonic 2510 apparatus for 60 min [30,31]. The extracts thus obtained were filtered and stored in polypropylene bottles at 4 °C until analysis. All chemicals used were analytical reagent-grade. Metal elements (Na, Ca, K, Mg, Fe, Zn, Cr, Ni, Cu, Cd, Pb and Mn) were determined by atomic absorption spectrophotometry on a PerkinElmer 2380 dual-beam instrument equipped with a deuterium corrector, using hollow-cathode lamps as light sources and an air-acetylene flame.

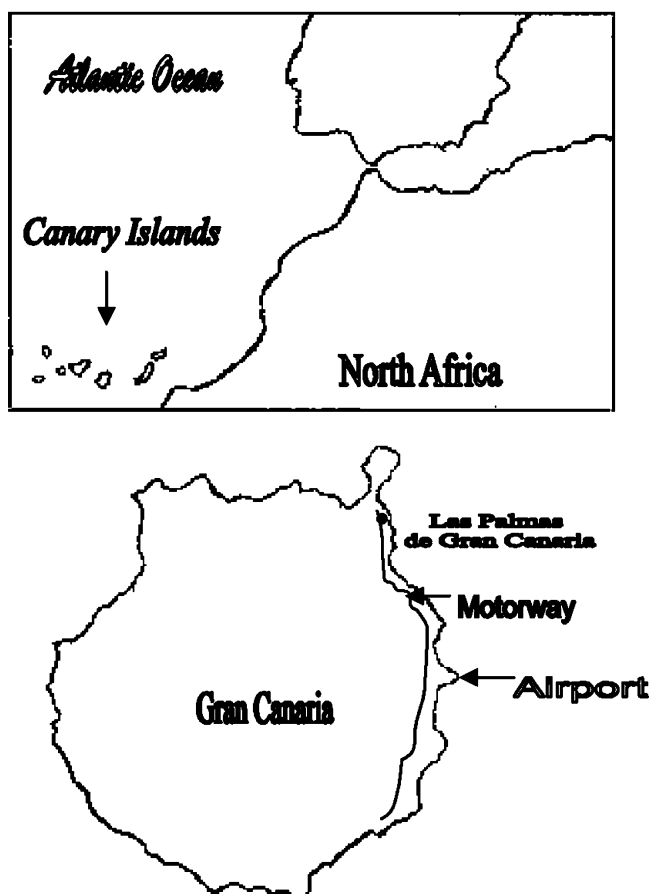


Fig. 1. Location of Las Palmas de Gran Canaria, Spain.

The blank test background contamination was routinely monitored by using operational blanks (unexposed filters) which were processed simultaneously with field samples. Background contamination of metals was accounted for by subtracting field blank values from the concentrations. All samples were analyzed by spiking with a known amount of metal to calculate recovery efficiencies. The analytical procedure for the recovery test was the same as that described for the field samples. The results indicated that the ranges of recovery efficiencies were varied between 94 and 103%.

3. Results and discussion

3.1. Total particulate concentration

The concentration of total suspended matter, as TSP, ranged from 27.86 to 146.47 µg/m³ and averaged at 71.92 ± 28.40 µg/m³. The highest concentrations, which exceeded the averages by 20%, were recorded in September (84.20 µg/m³) and November (85.91 µg/m³) by effect of the strong influence of dust from the nearby African continent.

Several studies [32–35] have shown that the Canary Islands receive inputs of such dust mainly at low heights in winter (from the Sahara desert) and high ones in summer (from the Sahel region), but also that inputs reach the islands in other season as well [36].

Based on the concentrations obtained in this study, the increased levels found in autumn can be ascribed to an inflow of air masses from both regions during this season (especially in October and November, but also, occasionally, in December). The autumn episodes are shorter (2–5 days), but stronger, than those of other seasons.

Because the European Commission set tolerated limits for TSP smaller than 10 µm in size (PM₁₀) in its latest directive on air quality [37], we believed it of interest to estimate the PM₁₀ levels in the atmosphere of the study area. Based on the results of various studies on particulate aerosol [38,39] we assumed the <10-µm particle fraction to account for about 70% of all TSP; under such conditions, the average PM₁₀ concentration was calculated to 50.34 ± 7.95 µg/m³, which is 25% higher than the limit set in the above-mentioned EC directive. The directive additionally establishes the maximum tolerated number of days during which the average particulate concentration may exceed a given limit. In the least restrictive regulation, which came into force in 2005, the limit was 35 days and the maximum tolerated concentration was 50 µg/m³. Therefore, this level should never be exceeded for more than 9.6% of the year; in the study area, however, the limit was exceeded in 40.5% of the days during the sampling period.

3.2. Metallic species: concentrations and sources

Table 1 shows the average total concentration of each metallic species in addition to those in the soluble and insoluble fractions. The right-most column in the table shows the percent solubility with respect to the whole.

3.2.1. Total metallic species

As can be seen, metallic species in this fraction fell into three distinct groups depending on their concentrations. Thus, Na and Ca were the most abundant elements, with a concentration of 6.72 and 4.62 µg/m³, respectively, followed by Fe, K, Zn and Mg (with concentrations from 1.33 µg/m³ for Zn to 1.58 µg/m³ for K), and, finally, Cu, Mn, Cr, Ni, Pb and Cd, all at much lower concentrations than the previous ones. Also, Cu was present at much higher concentrations than all other elements in the third group – more than twice higher than those for the next – and Cd was the least abundant element in it, with 0.001 µg/m³.

Table 1Metallic concentration (ng/m³) of total, soluble and insoluble fractions in the TSP of Bravo Murillo

Element	X_t	X_s	X_i	X_s/X_t (%)
Na	$(6.72 \pm 2.52) \times 10^3$	4.65×10^3	2.07×10^3	69.19
Ca	$(4.62 \pm 2.25) \times 10^3$	1.17×10^3	3.45×10^3	25.31
K	$(1.58 \pm 0.32) \times 10^3$	0.42×10^3	1.16×10^3	26.65
Mg	$(1.478 \pm 0.77) \times 10^3$	0.53×10^3	0.95	35.91
Fe	$(1.44 \pm 0.57) \times 10^3$	3.94	1.44×10^3	0.27
Zn	$(1.33 \pm 0.37) \times 10^3$	54.36	1.28×10^3	4.08
Cr	26.99 ± 6.84	1.44	25.55	5.34
Ni	18.94 ± 12.00	1.89	17.05	9.98
Cu	62.19 ± 15.70	2.39	59.80	3.84
Cd	1.29 ± 2.32	0.02	1.27	1.55
Pb	13.92 ± 4.35	2.08	11.84	14.94
Mn	27.16 ± 15.40	3.69	23.47	13.59

These results reflect the presence of metallic species at much higher concentrations than those in atmospheric aerosol in many urban areas of the world [40–44]. Worth special note are the concentrations of the elements in the former two groups (*viz.*, Na, K, Ca, Mg, Fe and Zn), which are much higher than those recorded in other cities such as Birmingham (England) and Coimbra (Portugal) [40]. By exception, the concentrations measured in Birmingham [40] amounted to 1.05 µg/m³ for Na and 0.21 µg/m³ for Ca. The concentrations of the other elements were generally very similar to those for Coimbra, but lower than those for Lahore (Pakistan) [40] and Cartagena (Spain) [41]. Worth special note is the low concentration of Pb (0.014 µg/m³), particularly in relation to those for Birmingham (0.091 µg/m³) and Coimbra (0.31 µg/m³) [40], and also for Cartagena (0.33 µg/m³) [41] a result of the use on unleaded gasoline in the EC since 2000.

These results provide an indication of the significance of each source to the aerosol composition in the studied city. Thus, Na is typically present in coastal atmospheres, which it reaches from marine aerosol. On the other hand, Ca can come from mechanical attrition processes (*e.g.* surface and soil erosion) and also from building materials containing this element.

3.2.2. Soluble fraction

The metallic species in this fraction also fell in three groups according to concentration. The first comprised Na and Ca. Na in this fraction accounted for 70% of all Na, which appears to confirm its marine origin. On the other hand, Ca in this fraction accounted for only 25% of the total concentration of this element, so it must come from slightly soluble salts (oxide and sulphate mainly) of anthropogenic origin. The second group comprised K and Mg, which were present at moderate concentrations (*viz.*, 27 and 36%, respectively, of their total levels). It should be noted that the first two groups accounted jointly for 99% of the whole soluble fraction. The other elements (Fe, Cr, Ni, Cu, Pb, Mn and Cd) constituted the third group; all were present at much lower concentrations and in the form of slightly soluble species accounting for variable proportions of their total amounts from 15% for Pb to only 0.27% for Fe.

The results for these fractions are essentially similar to those previously reported by other authors. Thus, Wang et al. [45] found the soluble fraction of Chinese aerosols to consist predominantly (95%) of three of our four species (*viz.*, Na, Ca and K). This was also the case with other cities such as Kofu in Japan [46] or Tirupati in India [47].

Table 2 shows the statistical figures of merit of the metal concentrations in the soluble fraction, in ng/m³.

The concentrations of Zn varied markedly among samples. Thus, Zn was the sole studied element the standard deviation for which invariably exceeded its average concentration. In fact, this metal was detected at levels from 0.002 to 0.26 µg/m³.

Table 2Central trend (ng/m³) and dispersion of soluble metallic aerosols

Element	Mean	S.D.	IQR
Na	4.65×10^3	2.10×10^3	2.21×10^3
Ca	1.17×10^3	0.44×10^3	0.61×10^3
K	0.42×10^3	0.16×10^3	0.22×10^3
Mg	0.53×10^3	0.24×10^3	0.27×10^3
Fe	3.94	2.72	2.89
Zn	54.36	71.32	71.72
Cr	1.44	0.47	0.41
Ni	1.89	1.44	1.64
Cu	2.39	1.70	0.83
Cd	0.02	0.09	0.00
Pb	2.08	1.19	2.06
Mn	3.69	2.31	3.26

IQR: interquartile range.

The Ni, Pb, Mn and Cu concentrations were also highly variable, albeit to a lesser extent than those of Zn. Such variability suggests that they come from specific sources possibly related to human activities (*e.g.* industries, car traffic) or are contained in resuspended dust produced by such activities.

The decreased variability in the concentrations of the other studied elements suggest that they are typical components of the local aerosol and regularly present in it, so changes in their concentrations are very probably dictated by the particular weather conditions. In order to confirm whether the variability was due to mobile sources typical of the area (*i.e.* car traffic in Bravo Murillo and neighbouring streets), we calculated the geometric means of the metallic concentrations for weekdays and weekends. The results are shown in Table 3 together with the percent changes, which were deemed positive or negative depending on whether levels decreased or increased. In addition, the table shows the amounts of metals, in micrograms, present per gram of particulate matter.

As can be seen, some elements (specifically, Na, K, Mg, Fe and Cd) were scarcely affected by the reduction in car traffic and urban activities at weekends and point out that element could derive from natural sources. Surprisingly, however, the Cu, Ni, Cr and Pb concentrations rose slightly (14–18%), and the Zn concentrations much more markedly (70%), during holidays and weekends. This suggests an influence of remote emission sources. Based on the data of Table 3 (in mg metal/g particulate), all species studied exhibited increased proportions in suspended matter at weekends. Overall, these results suggest that the observed changes were caused by clouds of African dusts—of which there were three episodes at weekends.

3.2.3. Insoluble fraction

As can be seen in Table 1, all studied elements but Na exhibited higher concentrations in the insoluble fraction than in the soluble one. The elements at the two solubility extremes were Fe (0.3%) and Cd (1.5%).

The studied species fell into three groups that coincided with those for the soluble fraction. Ca, as the major species, accounted for 32.9% of the insoluble fraction, followed by Na (20%). The high value for Na could be associated with the presence of insoluble native feldspar in Gran Canaria [48]. These two species were followed by another four in similar proportions, namely Fe (14%), Zn (12%), K (11%) and Mg (9%). The remaining species (Cr, Ni, Cu, Cd, Pb and Mn) were present in much lower proportions and accounted for 1.3% of the fraction as a whole. Fig. 2 shows the distribution of species in the third group. As can be seen, Cu was by far the most abundant among them, with 43%, all other metals but Cd (1%) being at concentrations from 9% for Pb to 18% for Cr.

Table 4 shows the statistical figures of merit for the insoluble fraction. Note the high variability in the concentration of Mg,

Table 3
Percent variation of the geometric means of the concentrations of the metallic elements in the soluble fraction

	ng/m ³			µg/g		
	Weekdays	Weekend	% of variation	Weekdays	Weekend	% of variation
Ca	1.21×10^3	0.88×10^3	27.7	16.19×10^3	$17.08 \cdot 10^3$	-5.2
Mg	0.48×10^3	0.48×10^3	0.2	6.45×10^3	$9.39 \cdot 10^3$	-31.3
K	0.40×10^3	0.39×10^3	4.4	5.39×10^3	$7.52 \cdot 10^3$	-28.3
Na	4.40×10^3	4.08×10^3	7.3	58.83×10^3	$79.52 \cdot 10^3$	-26.0
Fe	3.0	3.5	-5.6	42.5	66.0	-35.6
Zn	16.0	52.7	-69.9	211	$1.03 \cdot 10^3$	-79.4
Cr	1.0	1.5	-15.0	17.4	29.7	-41.4
Ni	1.5	1.8	-14.6	20.1	33.2	-33.3
Cu	1.9	2.3	-17.8	25.5	45.1	-43.4
Cd	0.4	0.4	0.0	5.4	6.2	-13.3
Pb	1.5	1.8	-18.0	20.1	35.8	-43.8
Mn	3.2	2.6	18.9	43.1	50.8	-15.2

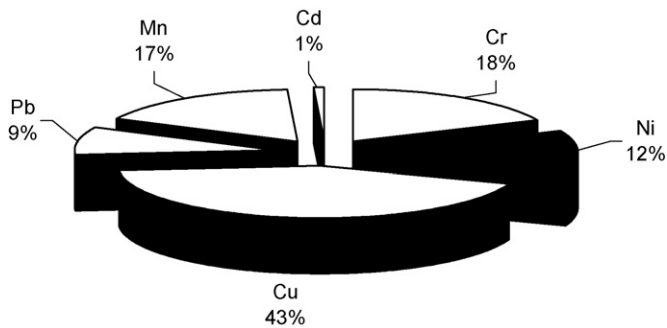


Fig. 2. Percent of metallic species of third group in the insoluble fraction at Bravo Murillo.

which was the sole species with an interquartile range exceeding its arithmetic mean. There were also substantial variations in the concentrations of Na, Ca, Ni and Mn, but only small differences in those of Cu, Zn, Cr, K and, to a lesser extent, Fe. This suggests that the latter elements might be less markedly influenced by remote sources and come largely from the typical sources of the study area. On the other hand, the former elements appear to be subjected to a strong influence of the weather conditions (especially through the sweeping of particulates in areas far from Bravo Murillo street).

As with the soluble fraction, we discriminated the species concentrations obtained during weekdays on the one hand, and weekends and holidays on the other. Fig. 3 shows the geometric means obtained. Unlike the soluble fraction, Ni, Cu and Fe in the insoluble fraction were found at higher concentration levels on weekdays especially Fe, which exhibited concentrations up to 33% higher than at holidays and weekends. As in the soluble fraction, Mn and Ca also exhibited increased concentrations on weekdays; however, the percent differences in the two fractions were virtu-

Table 4
Central trend (ng/m³) and dispersion of insoluble metallic aerosols

Element	Mean	S.D.	IQR
Na	2.07×10^3	1.43×10^3	1.21×10^3
Ca	3.45×10^3	2.20×10^3	1.77×10^3
K	1.16×10^3	0.32×10^3	0.45×10^3
Mg	0.95×10^3	0.65×10^3	1.20×10^3
Fe	1.44×10^3	0.56×10^3	0.84×10^3
Zn	1.28×10^3	0.34×10^3	0.44×10^3
Cr	25.55	6.81	8.56
Ni	17.05	12.51	11.96
Cu	59.80	16.21	20.59
Cd	1.27	2.23	2.13
Pb	11.84	5.53	7.46
Mn	23.47	15.60	11.35

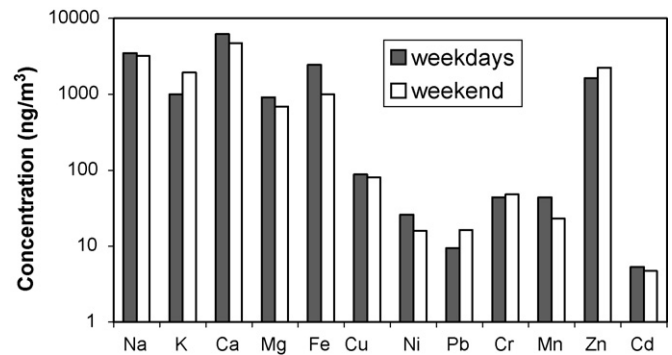


Fig. 3. Geometric mean concentrations of insoluble metallic aerosol on weekdays and weekend.

ally identical for Ca, but not for Mn the concentrations of which rose by 41% in the insoluble fraction versus only 19% in the soluble one. On the other hand, Zn predominated at weekends in the soluble fraction, but exhibited very similar concentrations throughout the week in the insoluble fraction. Finally, Pb was found at increased levels during weekends in both fractions.

3.3. Temporal variations

3.3.1. Soluble fraction

Figs. 4–8 show the variation of the concentrations of the studied elements during the summer (July–September) and autumn (October–December). As can be seen in Figs. 4 and 5, Na, K, Ca and Mg generally exhibited higher mean concentrations (considering all season) in summer than in autumn, the difference ranging from 4.14% for Na to 32.8% for Mg. Also, the four elements exhibited markedly decreased concentrations in December as the likely result of the abundant rainfall during that month.

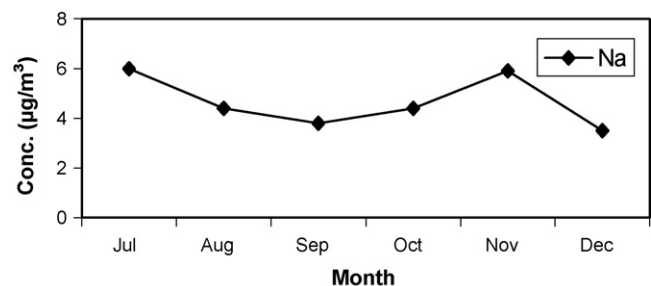


Fig. 4. Monthly variation of Na-soluble concentrations.

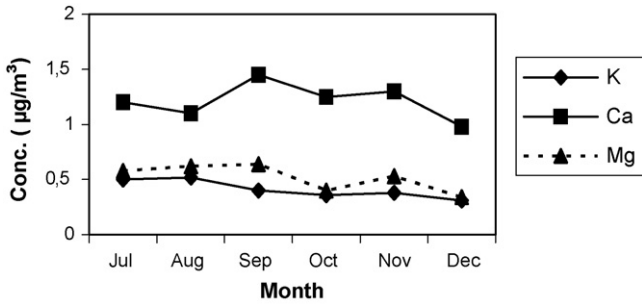


Fig. 5. Monthly variation of K-Ca-Mg-soluble concentrations.

As can be seen in Fig. 6, the Ni, Mn and Pb concentrations peaked in autumn – the period of greatest urban activity – the differences, however, varied between elements: 12.7% for Mn, 41.45% for Ni and 39.02% for Pb. These metals exhibited increasing concentrations throughout the sampling period that were not affected by rainfall, possibly as a result of their small size facilitating persistence in suspension, and hindering removal from atmospheric aerosol as a

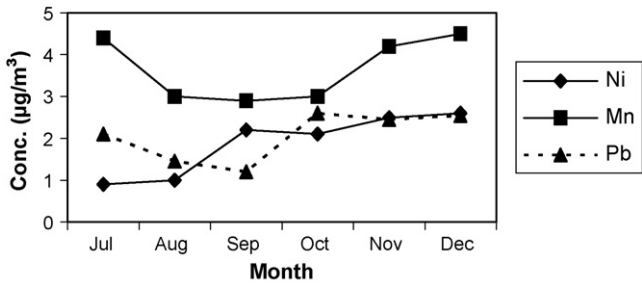


Fig. 6. Monthly variation of Ni-Mn-Pb-soluble concentrations.

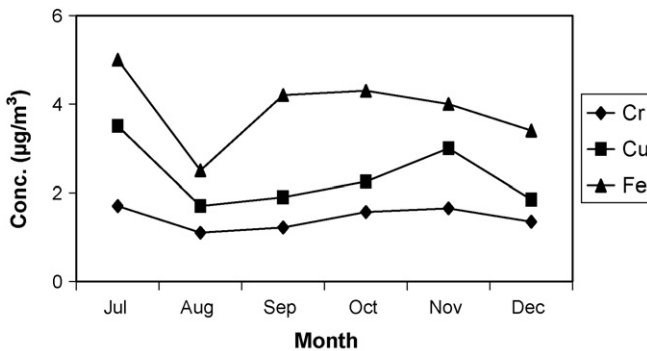


Fig. 7. Monthly variation of Cr-Cu-Fe-soluble concentrations.

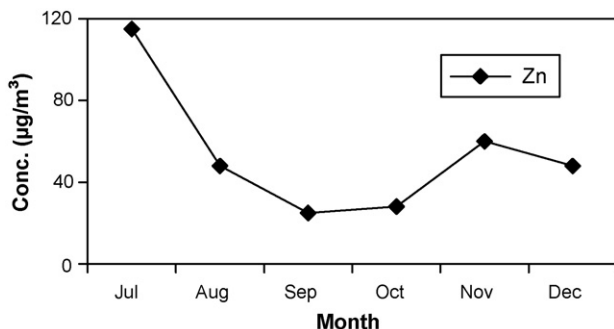


Fig. 8. Monthly variation of Zn-soluble concentrations.

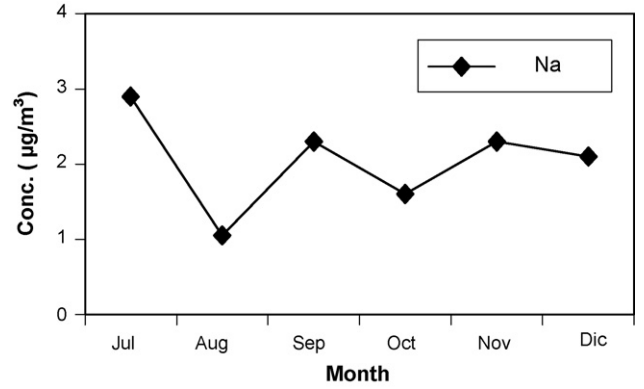


Fig. 9. Monthly variation of Na-insoluble concentrations.

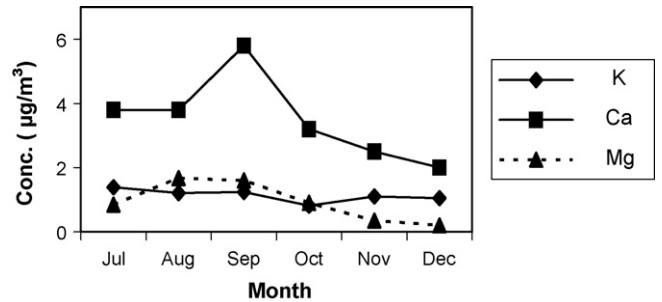


Fig. 10. Monthly variation of K-Ca-Mg-insoluble concentrations.

result, over longer periods. The lowest levels of these elements were found in summer (August or September).

As can be seen in Figs. 7 and 8, the concentrations of Cr, Cu, Fe and Zn were maximal in July, and minimal in August and September. However, Cr and Cu exhibited higher average concentrations in autumn than in summer, the difference amounting to 13.01% for Cr and being very small for Cu. On the other hand, Fe and Zn had higher averages in summer, the difference being 1.76% for Fe and 29.24% for Zn—the latter was found at very high levels in July.

Finally, Cd departed markedly from the other studied elements. In fact, its concentrations fell below the detection limit of the instrument except in all months but July.

3.3.2. Insoluble fraction

Figs. 9–13 show the monthly variation of the arithmetic means of the element concentrations. As can be seen in Fig. 9, the Na concentration remained virtually constant in both seasons – the difference was only 3.63% – which is consistent with its natural marine origin.

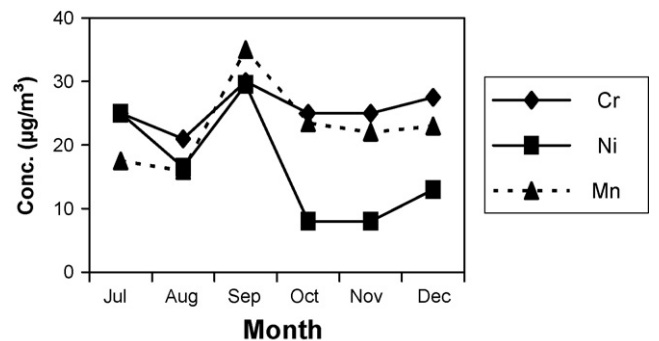


Fig. 11. Monthly variation of Cr-Ni-Mn-insoluble concentrations.

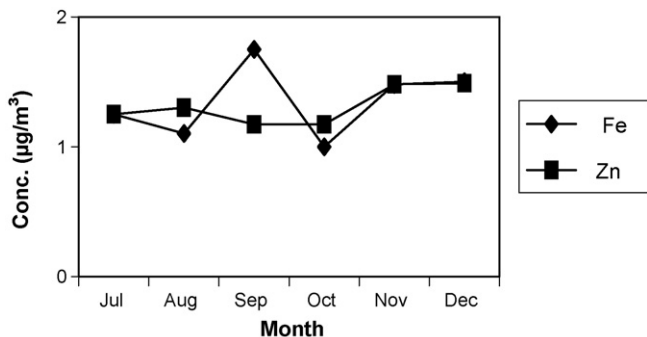


Fig. 12. Monthly variation of Fe-Zn-insoluble concentrations.

On the other hand, Ca, Mg and K were detected at higher concentrations in summer, the differences between both seasons amounting to 43% for Ca, 64.5% for Mg, and 21.85% for K (Fig. 10). Ca exhibited a strong peak in September, and Mg similar peak concentrations in August and September.

As can be seen in Figs. 11 and 12, the Cr, Ni, Mn, Fe and Zn concentrations peaked in summer (specifically, and except for Zn, in September); however, differences between the two seasons were only slight. The autumn levels of these elements were thus lower than their summer levels, but the differences between means were quite small (*viz.*, 3.47% for Cr, 3.80% for Mn, 5.64% for Fe and 11.1% for Zn). Zn exhibited its highest levels in November and December, and its lowest ones in September and October.

The average Pb and Cu concentrations in this fraction (Fig. 13) were higher in summer than in autumn, the difference amounting to being 12.1%. However, Cu exhibited its lowest levels in July and its highest ones in September, in addition to intermediate levels during the autumn months. The average concentrations of Pb exceeded $0.001 \mu\text{g}/\text{m}^3$ and remained virtually unchanged in both seasons with slightly higher values in the summer.

Again, Cd departed from the behaviour of the other elements. Thus, its concentrations fell below the detection limit of the instrument throughout the autumn and averaged at only $0.003 \mu\text{g}/\text{m}^3$ during the summer.

3.4. Identification of sources

In this work, we used the multivariate analysis technique known as factor analysis to establish correlations between the 12 variables studied (*viz.*, the concentrations of Na, K, Ca, Mg, Fe, Cu, Ni, Pb, Cr, Mn, Zn and Cd) and identify their emission sources. Our study excluded those factors with eigenvalues smaller than unity [49,50], all others being subjected to a Varimax orthogonal transformation. We used the ratios of the element concentrations to TSP as inputs [51].

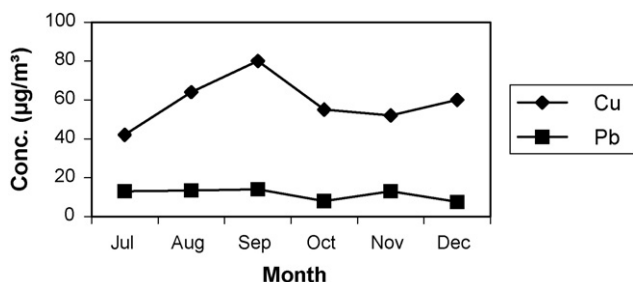


Fig. 13. Monthly variation of Cu-Pb-insoluble concentrations.

3.4.1. Soluble fraction

Table 5 shows the factor matrix obtained by applying the orthogonal transformation to the data for this fraction. As can be seen, five factors had eigenvalues greater than unity and accounted jointly for 79.95% of the overall variance. As can be seen, the first factor, which accounted for 32.42% of the variance, included Zn, Mn, Fe and Cu, all with high coefficients. Zn and Cu came virtually exclusively from anthropogenic sources. Zn has been used as a tracer to identify various types of industries [52]; on the other hand, Cu in urban atmospheres comes mainly from diesel fuel exhaust [53–55]. Their occurring in combination with Fe and Mn, two typically natural elements, also suggests anthropogenic local influences; both metals have been cited to originate from the burning of oils and fuels [56–58]. In addition, Fe can originate by abrasion of car brake drums [59]. Interestingly, this element appeared in three of the five factors (F1, F2 and F4), which is typical of elements coming from multiple sources [60].

The second factor included Ca and Mg with high coefficients, and Fe with somewhat lower ones. The former two can be assigned a natural origin as both are constituents of sand in the Canary Islands (calcite (CaCO_3) and dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)) and in the nearby African continent, as well as local marine aerosol. The presence of Fe can be assigned to natural sources.

The third factor, which accounted for 11.54% of the variance, included Na, K and Mg, in order of decreasing significance; all were of natural – but marine – origin. Na comes mainly from marine breeze while K is usually of terrestrial origin (soil, biomass burning, waste ashing) and has been associated to Na in coastal atmospheres [40,58]. In our case, we should also consider particulates swept from the Sahara and Sahel deserts across the ocean, the major constituents of which are K and Mg [61]. Therefore, the third factor is strongly related to natural emission sources.

The fourth factor, which accounted for 8.99% of the variance, included Cr, Pb and Fe. Until the year 2000, Pb came mainly from automobile exhaust. The fact that these three elements clustered in this component suggests that they come mainly from road traffic (exhaust gases and resuspended dust).

The fifth factor accounted for 8.68% of the variance and included Cd and Ni, which are also markedly anthropogenic in origin.

Finally, the following five elements were distributed among several factors: Mg (F2 and F3), Fe (F1, F2 and F4), Cr (F3 and F4), Cu (F1 and F4) and Pb (F2 and F4). This suggests that they come from multiple sources.

3.4.2. Insoluble fraction

The analysis of the concentration data for the insoluble fraction provided four principal factors that accounted jointly for 79.70% of the overall variance. Table 6 shows the factor matrix obtained

Table 5
Rotated factor matrix for metallic species of soluble TSP

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Ca	0.060	0.936	0.123	0.067	-0.020
Mg	-0.037	0.793	0.493	0.161	0.016
K	0.154	0.149	0.826	0.046	-0.073
Na	-0.010	0.178	0.841	0.199	0.184
Fe	0.557	0.454	-0.119	0.497	0.098
Zn	0.911	0.103	0.130	0.086	0.162
Cr	-0.010	-0.051	0.318	0.838	0.063
Ni	0.200	-0.032	0.101	0.058	-0.777
Cu	0.819	0.061	0.102	0.453	0.012
Cd	0.253	-0.050	0.220	0.026	0.730
Pb	0.210	0.369	-0.001	0.701	-0.175
Mn	0.879	-0.083	0.009	-0.129	-0.189

Correlation coefficients higher than 0.45 are in bold.

Table 6
Rotated factor matrix for metallic species of insoluble TSP

	Factor 1	Factor 2	Factor 3	Factor 4
Ca	0.524	0.324	0.041	0.644
Mg	0.827	0.231	−0.019	0.324
K	0.629	0.152	0.616	0.285
Na	0.035	0.049	0.917	0.175
Fe	0.285	0.836	0.122	0.004
Zn	0.667	0.025	0.639	−0.051
Cr	0.664	0.258	0.489	−0.071
Ni	0.313	0.441	0.393	0.270
Cu	0.748	0.491	0.288	0.068
Cd	0.108	0.056	0.188	0.906
Pb	0.780	−0.113	0.119	0.218
Mn	−0.083	0.879	−0.013	0.156

Correlation coefficients higher than 0.45 are in bold.

by orthogonal transformation of the data. The first factor, which accounted for 43.38% of the variance, included Ca, Mg, K, Zn, Cu and Pb. The presence of Pb can be assigned to emissions from road traffic. The association of Pb and Zn is not unusual as the latter element is being increasingly used as a potential identifier for automobile emissions instead of Pb—the levels of which have dropped to extremely low, near-zero levels as the use of leaded gasoline has rapidly declined [40,62]. Surprisingly, there seems to be no contribution of road traffic to the other elements under this factor. In fact, K and Ca are among the most abundant metals in exhaust from catalyst-equipped vehicles [63]. Also, as noted earlier, Cu and Mg in urban atmospheres come largely from diesel exhaust.

The second factor included Fe and Mn, which suggests a natural origin for both. These two elements occurred mainly under F1, however. Although both usually come from various sources, they originate largely from natural ones [59]. Therefore, this factor must be primarily associated with such sources.

Na occurred mainly under the third factor, which accounted for 9.70% of the variance, in association with K and Zn. Its association with K has been explained and documented above, and is suggestive of a marine origin for both. The additional presence of Zn, an element of typically anthropogenic origin, with a substantial coefficient (0.639) suggests that it might come in part from areas near the coast or under the influence of marine breezes, or even result from tyre wear [64,65] on the Las Palmas-Sur highway.

Once the previous factors were associated to specific emission sources, the elements present in more than one were examined. Thus, K, Cr and Zn were associated to F1 and F3; Cu to F1 and F2; Ca to F1, F2 and F4; and Ni to all five. Therefore, the ambient concentrations of the different trace metals are strongly influenced by changes in wind direction in the study area. This warrants considering the potential influence of weather-related variables in future studies and sampling further areas in the city under rather disparate conditions in order to confirm some hypotheses formulated in this section.

4. Conclusions

The concentration of TSP ranged from 27.86 to 146.47 $\mu\text{g}/\text{m}^3$ and averaged at $71.92 \pm 28.40 \mu\text{g}/\text{m}^3$. PM_{10} levels were estimated to be $50.34 \pm 7.95 \mu\text{g}/\text{m}^3$, which is 25% higher than the tolerated limit established by European regulations.

The total concentrations of metallic elements were higher than those previously reported for other urban areas in the world; this was especially so for Na, K, Ca, Mg, Fe and Zn.

In the soluble fraction, Na, K, Ca and Mg were found to come mainly from natural sources; Cr, Pb, Cd, Ni, Zn and Cu from anthropogenic sources; and Fe and Mn from both.

In the insoluble fraction, Ca, Mg, K, Zn, Cu and Pb were mainly associated to anthropogenic sources (particularly automobile fuels and catalysts); also, a number of elements were associated to various sources, which suggests a substantial local influence of the wind direction.

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