
Metallic species in ambient air particles of Canary Islands. Soluble fraction in total suspended matter

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Especies metálicas en el medio ambiente particulado de las Islas Canarias. Fracción soluble en la materia en suspensión total

Espècies metàl·liques en partícules ambientals del medi ambient de les Illes Canàries. Fracció soluble de la matèria en suspensió total.

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RESUMEN

En el presente trabajo se cuantifican las fracciones metálicas total y soluble de la materia en suspensión total (MST), en una zona urbana de Gran Canaria. Las medidas se realizaron entre octubre de 2004 y septiembre de 2005 sobre un total de 53 muestras (4 o 5 por mes). La materia en suspensión total se recogió en filtros de fibra de vidrio usando muestreadores de alto volumen. La concentración media resultó ser $68,5 \pm 35,5 \mu\text{g}/\text{m}^3$. La MST se determinó gravimétricamente. La materia soluble en agua se extrajo mediante sonicación. Las concentraciones de los elementos metálicos se determinaron por espectrometría de emisión atómica, usando un ICP-OES. Se encontraron dos categorías de elementos de acuerdo con sus niveles de concentración: "abundantes" y "escasos". En la fracción soluble los "abundantes" fueron principalmente Na, Ca, K y Zn; entre los "escasos" predominan Cu y Ti. Se estableció la disponibilidad de todos los elementos solubles, encontrándose altos coeficientes para todos ellos y especialmente para el Mn (99,9%). A fin de identificar las fuentes para dichos elementos se usó el análisis factorial. Los resultados muestran que Al, Ca, Fe, Mg y K provienen de fuentes naturales, en tanto que Ni, Co, V, Mo, Pt, Zn, Cu, Sb y Cr son antropogénicos.

Palabras clave: Materia en suspensión, MST, especies metálicas solubles, Gran Canaria, Islas Canarias.

SUMMARY

At the present work total and water-soluble fractions of metallic species present in total suspended particulates (TSP) in an urban area of Gran Canaria (Canary Islands) were quantified. Experimental measurements were made from October 2004 to September 2005 on a total of 53 samples (4 or 5 per month). Particulate matter (TSP) was collected in fiber filters and high volume samplers. Average concentration was $68.5 \pm 35.5 \mu\text{g}/\text{m}^3$. TSP was determined gravimetrically. Water soluble fraction was extracted by sonication. Concentrations of metallic elements were analyzed by atomic emission spectrophotometry using an ICP-OES. According to their concentration levels,

two categories of elements were found: "abundant" and "scarce" elements. In water soluble, "abundant" fraction consisted mainly of Na, Ca, K and Zn; among "scarce" Cu and Ti predominate. Availability of all soluble elements was established. High coefficients for all of them (specially for Mn with 99,9%) were found. In order to identify sources of metallic species factor analysis was used. The result shows that Al, Ca, Fe, Mg, Na and K come from natural sources; Ni, Co, V, Mo, Pt, Zn, Cu, Sb and Cr from anthropogenic.

Keywords: Suspended matter, TSP, soluble metallic species, Gran Canaria, Canary Islands

RESUM

En aquest treball es quantifiquen les fraccions metàl·liques total i soluble de la matèria en suspensió total (MST), en una zona urbana de Gran Canària. Les mesures es van realitzar entre octubre de 2004 i setembre de 2005 sobre un total de 53 mostres (4 o 5 per mes). La matèria en suspensió total es va recollir en filtres de fibra de vidre utilitzant mostrejadors d'alt volum. La concentració mitjana va resultar ser $68,5 \pm 35,5 \mu\text{g}/\text{m}^3$. La MST es va determinar gravimètricament. La matèria soluble en aigua es va extreure mitjançant sonicació. Les concentracions dels elements metàl·lics es van determinar per espectrometria d'emissió atòmica, usant un ICP-OES. Es van trobar dues categories d'elements d'acord amb els seus nivells de concentració: "abundants" i "escassos". A la fracció soluble dels "abundants" es van trobar principalment Na, Ca, K i Zn, entre els "escassos" predominen Cu i Ti. Es va determinar la disponibilitat de tots els elements solubles, trobant-se coeficients alts per a tots ells i especialment per al Mn (99,9%). Per tal d'identificar les fonts per a aquests elements es va utilitzar l'anàlisi factorial. Els resultats mostren que Al, Ca, Fe, Mg i K provenen de fonts naturals, com a Ni, Co, V, Mo, Pt, Zn, Cu, Sb i Cr són antropogènics.

Paraules clau: Matèria en suspensió, MST, espècies metàl·liques solubles, Gran Canària, Illes Canàries.

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1. INTRODUCTION

Interest in studying atmospheric particulate matter (PM) has grown substantially in recent years, partly as a result of increasing concern about its health effects on living beings. Epidemiological studies have revealed a strong correlation between PM levels and human mortality (Baldaano et al. 2003; Lippmann et al. 2000; Maynard, 2004), the specific health effects of particulate matter depending on particle size, composition and solubility in biological fluids (Baldauf et al. 2001; Laden et al. 2000; Silbajoris et al. 2000).

Atmospheric particulate matter comprises a wide variety of metallic species the primary origin of which in urban centres of developed countries is traffic emissions, the atmosphere itself (secondary particles), marine aerosol (coarse particles), and soil and roads (resuspended dust) (Domingo 1994). Analyses of such particles can be useful towards identifying their emission sources -particularly those carried over long distances- and health impact. Recent studies on animals and *in vitro* simulated tests on the human respiratory system have suggested that the pulmonary toxicity of particulate matter is related to the presence of metallic components in it (Dye et al. 2001; Sun et al. 2001). This led the European Commission to pass a directive on air quality (Directive 2008/50/CE) setting maximum allowable concentrations of Pb, and to enforce monitoring of As, Cd, Hg and Ni concentrations (Directive 2004/107/CE), in atmospheric air. The World Health Organization (WHO) has additionally recommended monitoring V, Pt, Cr and Mn atmospheric levels (Air Quality Guidelines for Europe). The levels of metals in the platinum group (Pt, Pd and Rh mainly) have risen considerably in urban atmospheres ever since the European Union banned sales of non-catalyst cars in 1993. This has aroused great interest in their quantitation on account of their potential toxic effects (Farago et al. 2005; Ravindra et al. 2004; Whiteley et al. 2003).

Although conventional studies on metallic species present in the atmosphere have traditionally focused on quantifying their overall concentrations, there is currently a growing interest in the international scientific community in measuring their soluble fraction (SF) to assess its interactions with various ecosystems (atmosphere, hydrosphere, soil) (Morselli et al. 2000) and the ensuing toxic effects (APEG 1999; Passarini et al. 2001).

Some trace metals such as Fe, Cu, Co and Zn are known to play a central role in marine productivity (Butler 1998; Desboeufs et al. 2005; Whitfield 2002). Several studies conducted over the past two decades have shown that dry and wet deposits are two major sources -often the only sources- of these elements in some regions (Desboeufs et al. 2005; Spokes et al. 1994). Whereas the particulate fraction invariably predominates in dry deposits, it is soluble fraction that prevails in wet deposits by effect of its availability to phytoplankton (Desboeufs et al. 2005).

Dissolved trace metals are involved in the different chemical processes occurring in the atmospheric liquid phase. Thus, Fe (Farago et al. 2005; Desboeufs et al. 2005), Cu (Desboeufs et al. 2005) and Mn (Desboeufs et al. 2005) can act as catalysts for the oxidation of S (IV) in cloud water drops, their reactivity in this respect being directly proportional to their concentration in the aqueous phase.

The presence of trace metals in water drops is the exclusive result of dissolution of aerosol particles via heterogeneous chemical reactions. The outcome of the process,

and hence the composition of the soluble fraction of aerosol particles, is governed by the conditions in the drops (e.g. pH) and the nature of the particles they contain (Desboeufs et al. 1999; Desboeufs et al. 2005).

Canary Islands (Figure 1) are located northwest of Africa and frequently suffer dust episodes with origin in different zones of near continent. These clouds of dust are added to the characteristic atmospheric aerosol of each isle (area). The city of Telde is an important urban centre (population ca. 100 000) in the North-East of the Gran Canaria island. The city is under the influence of various pollution sources such as Gando Airport in the South-East, a complex including a thermal power plant and a sea water desalination plant in the North, and an industrial complex in the East. In addition, the city atmosphere contains particulate matter coming from road traffic on its streets and the nearby Las Palmas-Sur highway. These pollution sources are deteriorating the urban atmosphere of Telde and leading to an increasing number of ambulatory visits and hospital admissions due to respiratory and dermal symptoms (López Cancio et al. 2007).

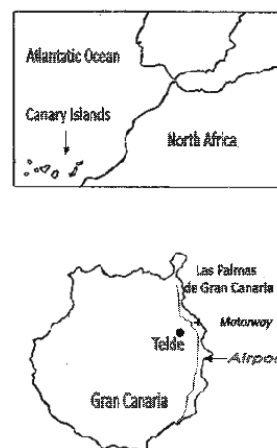


Figure 1 – Location of Telde (Gran Canaria, Spain)

This work was part of a general study on particulate matter in Telde and involved determining the average levels and availability of metallic species in the soluble fraction (SF) of total suspended matter (TSP) in its atmosphere. The knowledge of the metal load of SF is important with a view to identifying the specific metals which can be dissolved in the aqueous phase of clouds and fog, and subsequently return to the earth surface as rain or, in general, wet deposition, for eventual absorption by the human body. In addition, soluble metallic species increase the solubility of toxic organic compounds such as *n*-alkanes and polycyclic aromatic hydrocarbons -and human toxicity as a result.

2. EXPERIMENTAL

2.1. Sampling and analysis

Experimental tests were performed from October 2004 to September 2005. A total of 53 samples (4 or 5 per month) were collected for analysis; on Monday, on Tuesday and so on. Atmospheric particulate matter (TSP), was collected onto Whatman GF/A 20 x 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 ending

at 24 h and started at 8:00 am. The sample collector was placed 10 m above ground level on the roof of two public buildings at Telde: "Ayuntamiento" (28° 00' 48"N, 15° 24' 52.50" W) and "Casa de la Cultura" (27° 59' 54.98" N; 15° 24' 49.41" W); the first under the influence of thermal power and water treatment plants emissions, and the second in an area open to different influences such the airport and the motorway Las Palmas-Sur. 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 (Omar et al. 2002; Voutsas et al. 2002). Total metallic fraction was achieved by treatment of filters with nitric and hydrochloric acids according to the Beyer modified method (López Cancio et al. 2008). The concentration of total suspended particulates (TSP) was determined gravimetrically by weighing the filters prior to and after collecting samples using an analytical balance with a reading precision of $\pm 10 \mu\text{g}$. 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 $\mu\text{S/cm}$ under sonication in a Bransonic 2510 apparatus for 60 min (Voutsas et al. 2002; López Cancio et al. 2008; Chandra et al. 2002). The extracts thus obtained were filtered and stored in polypropylene bottles with 2% HNO_3 at 4 °C until analysis. All chemicals used were analytical reagent-grade. Metal elements (Al, Sb, As, Ba, Cd, Ca, Zn, Co, Cu, Cr, Sc, Sn, Fe, Mg, Mn, Mo, Ni, Pd, Pt, Pb, K, Rh, Na, Ti and V) were determined by atomic emission spectrophotometry using an ICP-OES, Perkin Elmer 3200 DV instrument.

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. Particulate matter

The concentration of total suspended matter (TSP) ranged from 22.0 to 225.5 $\mu\text{g}/\text{m}^3$ (average 68.5 $\mu\text{g}/\text{m}^3$). The highest levels (67% greater than the mean for the studied period) were recorded in October 1982 and undoubtedly resulted from the "calima" episode (clouds of dust) of October 7 that year. TSP levels are also typically high in February, May and July, when there are usually additional inputs of African air. Some studies (Omar et al. 2002; Voutsas et al. 2002) have shown that the Canary Islands are under the influence of African dust inputs, which occur at low altitudes in winter and high altitudes in summer. Thus, invasive air masses come from the Sahara in summer and the Sahel region in winter (López Cancio et al. 2008).

3.2. Metallic species

A total of 23 of the 25 elements studied were detected. The Sn and Pd concentrations fell beyond the detection capabilities of the instrument. The average concentration

of metals was 14.76 $\mu\text{g}/\text{m}^3$ and accounted for 21.5% of TSP. The average concentrations (Table I) were used to classify the metallic species present in the atmosphere of Telde into "abundant elements" (Na, Ca, K, Ba, Mg, Zn, Al and Fe) and "scarce elements" (Ti, Cu, Mn, Pb, V, Cr, Ni, As, Sb, Co, Mo, Pt, Sc, Rh and Cd). The abundant elements jointly accounted for 99.8% of all metallic TSP. Based on these results, if one assumes Ba, Ca, Na, Al, Zn, Fe and K to be present as BaCO_3 , CaCO_3 , NaCl, Al_2O_3 , ZnO, Fe_2O_3 and K_2O (Chandra et al. 2002), then these series of elements accounted for 48% by weight of TSP in combination.

The levels of the abundant elements were lower than those previously reported for Las Palmas de Gran Canaria (Spain) (Rodríguez 1999) and Lahore (Pakistan), but exceeded those for Taichung (Taiwan) (Querol et al. 2002), Birmingham (England) (Torres et al. 2001), TelShikmona (Israel) (Macías Ortega 2002), Beijing (China) (Harrison et al. 1997) and Islamabad (Pakistan) (Fang et al. 2003). This was especially true with Na, Ca, K and Ba, which can be ascribed to the former two elements coming largely from natural sources (marine breeze and soil), and also to the scant precipitation and nearness to the ocean of the city of Telde. On the other hand, the levels of scarce elements were very low and well below those reported for the previous cities except Beijing. It should be noted that the Pb concentrations were lower than all others -again, that of Beijing excepted-, which testifies to the good quality of the atmosphere in Telde.

Table I – Statistics of concentrations of total metallic elements (TSP) in Telde during the study.
a – 'Abundant' elements (in $\mu\text{g}/\text{m}^3$)

	Ma	Me	Mg	σ	CV (%)	Min	Max	RIC	P 90%
Na	7.755	7.231	7.202	3.317	42.8	3.634	18.710	3.793	11.800
Ca	2.290	2.079	2.040	1.231	53.7	0.852	7.627	1.370	3.384
K	1.181	1.073	1.125	0.475	40.2	0.458	3.845	0.214	1.512
Ba	1.101	1.042	1.069	0.358	32.5	0.808	2.963	0.112	1.148
Mg	0.685	0.650	0.624	0.307	44.8	0.210	1.718	0.334	1.202
Zn	0.656	0.613	0.636	0.211	32.2	0.460	1.663	0.084	0.732
Al	0.588	0.538	0.514	0.348	59.1	0.215	1.968	0.328	1.037
Fe	0.475	0.421	0.418	0.254	53.4	0.100	1.515	0.292	0.811

b – 'Scarce' elements (in ng/m^3)

	Ma	Me	Mg	σ	CV (%)	Min	Max	RIC	P 90%
Ti	14.470	10.250	10.270	13.660	94.4	1.506	80.610	13.810	24.530
Cu	6.040	4.700	4.946	5.044	83.5	0.944	30.950	2.928	8.803
Mn	2.819	2.482	2.364	1.833	65.0	0.605	10.020	1.987	4.747
Pb	2.353	1.905	2.089	1.270	54.0	0.843	7.561	1.552	3.953
V	1.073	0.877	0.725	0.900	83.9	0.016	4.550	0.980	2.085
Cr	0.702	0.411	0.530	0.684	97.5	0.229	2.985	0.341	1.817
Ni	0.643	0.533	0.491	0.506	78.6	0.087	2.977	0.589	1.197
As	0.145	0.126	0.113	0.092	63.8	0.005	0.509	0.106	0.256
Sb	0.104	0.093	0.091	0.057	54.3	0.026	0.290	0.065	0.180
Co	0.055	0.044	0.039	0.048	86.1	0.005	0.243	0.052	0.108
Mo	0.033	0.025	0.021	0.027	81.3	0.001	0.120	0.028	0.076
Pt	0.031	0.017	0.016	0.050	161.3	N.D.	0.250	0.025	0.046
Cd	0.011	0.003	0.002	0.038	332.8	N.D.	0.194	0.005	0.013
Rh	0.010	0.005	0.004	0.013	135.7	0.001	0.062	0.006	0.020
Sc	0.009	0.007	0.007	0.011	111.1	N.D.	0.028	0.004	0.016

Ma: Arithmetic mean, Me: Median, Mg: Geometric mean, σ : Standard deviation, CV: Coefficient of Variation, Min: Minimum value, Max: Maximum Value, RIC: Interquartile range, P90%: 90th percentile.

3.3. Soluble fraction

The average total concentration of SF was 11.73 $\mu\text{g}/\text{m}^3$ and accounted for 79.5% of all metal content. This value is nearly twice higher than that reported for Las Palmas de Gran Canaria (LPGC) in 2002 (Rodríguez 1999), 6.84 $\mu\text{g}/\text{m}^3$, despite the similarity of their TSP values (71.9 $\mu\text{g}/\text{m}^3$ for LPGC and 68.5 $\mu\text{g}/\text{m}^3$ for Telde). The difference suggests the presence of some singular emission source in Telde or a disparate contribution of emission sources to its atmospheric aerosol.

Table II - Statistics of concentrations of soluble metallic elements (TSP) in Telde during the study.
a - 'Abundant' elements (in $\mu\text{g}/\text{m}^3$)

	Ma	Me	Mg	σ	CV (%)	Min	Max	RIC	P 90%
Na	6.421	6.108	6.134	2.015	31.4	3.572	11.804	2.850	9.975
Ca	2.169	1.939	1.907	1.229	56.7	0.774	7.338	1.363	3.212
K	1.146	1.035	1.088	0.482	42.0	0.460	3.857	0.229	1.352
Zn	0.576	0.549	0.559	0.180	31.3	0.390	1.468	0.099	0.657
Mg	0.521	0.483	0.465	0.253	48.6	0.112	1.348	0.311	0.884
Al	0.429	0.392	0.377	0.246	57.3	0.139	1.518	0.241	0.668
Ba	0.252	0.207	0.216	0.195	77.5	0.111	1.021	0.087	0.301
Fe	0.201	0.185	0.179	0.098	48.6	0.040	0.571	0.126	0.307

b - 'Scarce' elements (in ng/m^3)

	Ma	Me	Mg	σ	CV (%)	Min	Max	RIC	P 90%
Cu	5.466	4.492	4.587	4.048	74.1	0.944	23.605	2.755	8.585
Ti	5.273	4.500	4.264	3.604	68.4	1.007	19.008	4.505	9.206
Mn	2.815	2.474	2.361	1.836	65.2	0.608	10.084	1.984	4.710
Pb	1.445	1.221	1.222	0.835	57.8	0.271	3.928	1.073	2.823
V	0.803	0.475	0.463	0.852	106.1	0.016	4.387	0.931	1.521
Ni	0.520	0.374	0.383	0.445	85.6	0.053	2.590	0.441	1.068
Cr	0.359	0.235	0.285	0.349	97.2	0.124	2.293	0.193	0.652
As	0.102	0.092	0.067	0.076	74.4	0.001	0.320	0.090	0.205
Sb	0.061	0.056	0.049	0.037	60.4	0.008	0.156	0.056	0.113
Co	0.054	0.044	0.039	0.045	82.5	0.005	0.224	0.052	0.106
Pt	0.030	0.017	0.015	0.050	169.6	N.D.	0.250	0.026	0.044
Mo	0.020	0.017	0.015	0.013	65.2	0.001	0.065	0.013	0.038
Rh	0.009	0.005	0.004	0.013	140.3	0.001	0.039	0.010	0.030
Cd	0.006	0.005	0.005	0.003	61.2	N.D.	0.014	0.003	0.012
Sc	0.004	0.003	0.003	0.004	104.2	0.001	0.025	0.003	0.008

Ma: Arithmetic mean, Me: Median, Mg: Geometric mean, σ : Standard deviation, CV: Coefficient of Variation, Min: Minimum value, Max: Maximum Value, RIC: Interquartile range, P90%: 90th percentile.
N.D.: Not detected

Table II shows the elements contained in SF alongside their statistics (central tendency, dispersion, and maximum and minimum values). Sodium was the predominant metal in SF; in fact, it accounted for 54% of the total metal soluble mass (99% consisting of major elements) (Table II). Sodium was followed by Ca, which accounted for only 19%; K (10%) and Zn (5%). Na, Ca and K species jointly accounted for 83.0% of SF. These results are lower than others previously reported by some authors. Thus, Wang (Herut et al. 2001) studied urban aerosols in the Nanking region (China) and found the soluble fraction to be dominated (93%) by Na, Ca and K. This was also the case in other cities such as Kofu (Japan) (Okuda et al. 2004) and Tirupati (India) (Wang et al. 2002). A similar result -as a consequence of not all elements being determined- was also reported for LPGC in 2002 (Rodríguez 1999). The remainder species (Zn, Mg, Al, Ba and Fe) jointly accounted

for 17% of SF; their distribution is shown in Figure 3, with 29% corresponding to Zn, 26% to Mg, 22% to Al, 13% to Ba and 10% to Fe.

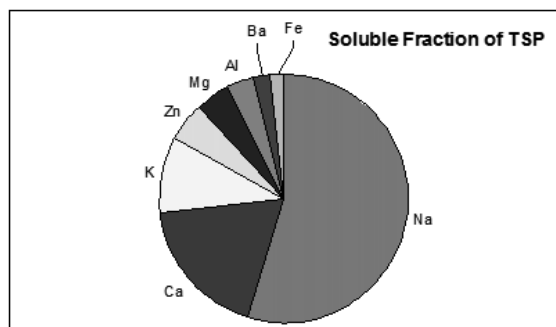


Figure 2 - 'Abundant' metallic elements in the soluble fraction of the TSP in Telde.

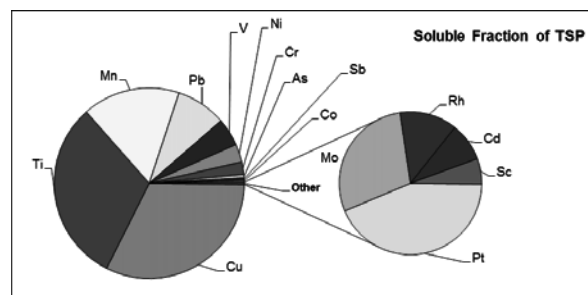


Figure 3 - 'Scarce' metallic elements in the soluble fraction of the TSP in Telde.

Populational stability in the abundant elements was generally good judging by their coefficients of variation. Stability was maximal for Zn and Na (CV = 0.31) and minimal for Ba (0.78). The relatively low variability observed suggests that the abundant elements are usual components of the local aerosol and that the oscillations in their concentrations are largely caused by weather changes.

The fraction of scarce elements was dominated by Cu and Ti (Table II, Figure 3), which jointly accounted for 63%. These two were followed by Mn, Pb, V, Ni, As, Sb and Co, with a combined contribution of 36%. Finally, five elements were present at minimal concentrations (0.24%), namely: Pt (44%), Mo (29%), Rh (13%), Cd (9%) and Sc (6%).

The populational stability of the scarce elements was quite low. Thus, Pt, Rh, V, Sc and Cr had coefficients of variation as high as 170, 140, 106, 104 and 87%, respectively. This instability was especially outstanding in V and Rh, the interquartile range (differences between the 75 and 25 percentiles) exceeding their respective arithmetic means. The least unstable populations were those of Pb and Sb, with a coefficient of variation of 58 and 60, respectively. The instability in the contents of these elements can be ascribed to the action of various pollution sources.

In order to check whether the above-described changes were due to the typical mobile emission sources of the area (i.e. car traffic), the mean concentrations for the weekdays were compared with those for the weekends (Saturday and Sunday). The concentrations and their changes (positive or negative depending on whether they rose or fell during weekends) are shown in Table III, which includes the amount of metal present per TSP unit mass. As can be

seen, metal levels tended to decrease during the weekend. Some elements (Ti, Sb, Al, Fe, Ca, Pb, Mo, Sc) exhibited large changes in relation to others (Fe, Ca, Pb). Still others (Ba, Zn, Na and Ni) changed by less than 10%, possibly because they were scarcely affected by the reduced traffic at weekends. Surprisingly, however, there was a very large increase in the levels of Rh (150%), a large one in those of Cr (39.8%) and fairly small ones (13–25%) in those of Cd, As and V. The most outstanding result was the increase in soluble Rh, suggests some influence of remote emission sources being favoured by the decreased urban activity in the city centre during the weekend.

Table III - Percentage change in geometric mean concentrations of the soluble fraction of the metallic elements in TSP.

	ng/m ³		Variation (%)	µg/g		Variation (%)
	Weekdays	Weekend		Weekdays	Weekend	
Al	431	261	-39,4	6 288	5 121	-18,6
Ba	213	226	6,1	3 108	4 434	42,7
Ca	2153	1370	-36,4	31 412	26 879	-14,4
Zn	569	533	-6,3	8 302	10 457	26,0
Fe	203	127	-37,4	2 962	2 492	-15,9
Mg	487	411	-15,6	7 105	8 064	13,5
K	1135	972	-14,4	16 560	19 070	15,2
Na	6111	6196	1,4	89 160	12 1562	36,3
Sb	0,054	0,039	-27,8	0,788	0,765	-2,9
As	0,073	0,054	-26,0	1,065	1,059	-0,5
Cd	0,004	0,005	25,0	0,058	0,098	68,1
Co	0,037	0,045	21,6	0,540	0,883	63,6
Cu	4,586	4,589	0,1	66,910	90,033	34,6
Cr	0,263	0,356	35,4	3,837	6,985	82,0
Sc	0,003	0,002	-33,3	0,044	0,039	-10,4
Mn	2,798	1,485	-46,9	40,823	29,135	-28,6
Mo	0,017	0,011	-35,3	0,248	0,216	-13,0
Ni	0,384	0,383	-0,3	5,603	7,514	34,1
Pt	0,016	0,012	-25,0	0,234	0,235	0,4
Pb	1,399	0,844	-39,7	20,411	16,559	-18,9
Rh	0,005	0,003	40,0	0,073	0,059	-0,2
Ti	4,909	2,903	-40,9	71,622	56,955	-20,5
V	0,466	0,455	-2,4	6,799	8,927	31,3

The data of Table III seemingly confirm the potential influence of remote emission sources. As can be seen, many metallic species exhibited an increased proportion in suspended matter during the weekend as a result, among others, of particle sweeping from remote areas -there were three calima episodes at weekends during the studied period.

3.4. Availability

As noted earlier, trace metals play a major role in the processes occurring in the atmospheric liquid phase, their effects depending on the concentration levels they reach in it. It is therefore essential to identify the particular elements in TSP that can be easily recovered as SF in order to assess their immediacy of action (availability) in the en-

vironment. Table IV shows the metal concentration levels in TSP and SF, and their ratio (TSP/SF). Such a ratio, labelled R, was designated "availability coefficient". As can be seen from the table, all elements were readily soluble in water (particularly Mn, 99.9% of which was in environmentally available form). Also, a number of elements (Co, K, Pt, Ca, Cu, Rh and Zn) were more than 80% soluble. Interestingly, the soluble elements included some highly toxic species for living beings (As, Cr, Ni, Pb and V) which might therefore have an adverse impact on health.

Table IV - Availability coefficient (R) of 'scarce' elements in the soluble fraction (FS) of the TSP in Telde.

Element	In TSP (ng/m ³)	In FS (ng/m ³)	R (FS/TSP) %
Cu	6,040	5,466	90,5
Ti	14,470	5,273	36,4
Mn	2,819	2,815	99,9
Pb	2,353	1,445	61,4
V	1,073	0,803	74,8
Ni	0,643	0,520	80,9
Cr	0,702	0,359	51,1
As	0,145	0,102	70,3
Sb	0,104	0,061	58,7
Co	0,055	0,054	98,2
Pt	0,031	0,030	96,8
Mo	0,033	0,020	60,6
Rh	0,010	0,009	90,0
Cd	0,011	0,006	54,5
Sc	0,009	0,004	44,4

Table V - Ratios of the Mg, Ca and K with respect to Na in the soluble fraction of aerosol and sea water.

	Aerosol in Telde	Sea water
Mg/Na	0,078	0,120
Ca/Na	0,288	0,038
K/Na	0,160	0,036

3.5. Influence of marine aerosol

The influence of Telde's nearness to the sea on its major atmospheric aerosol components (Na, Mg, Ca and K) was assessed from the concentration ratio of each element to sodium, which was used as reference on the assumption that it came entirely from the sea. The ratios obtained are listed in Table V. As can be seen, the Ca/Na and K/Na ratios were relatively high, which suggests the influence of terrestrial sources on the soluble components of the atmospheric aerosol. Also, the Ca and K contents in the atmospheric aerosol were nearly 8 and more than 4 times higher, respectively, than those in the marine aerosol. This is unsurprising if one considers their presence in African calima, which reaches the Canary Islands very often (López Cancio et al. 2008).

3.6. Identification of sources

Potential relationships between the studied trace elements and total suspended matter were established, and emission sources identified, by subjecting the results to factor analysis. This is a multivariate methodology formulating

Table VI – Factor Loadings (Varimax normalized). Extraction: Principal components

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aluminum	0,9747897	-0,02681007	0,03141991	0,06189775	0,01480602
Barium	-0,0318553	-0,09059257	0,7493476	0,1446325	-0,02693095
Calcium	0,8858523	0,04786628	-0,1477198	0,1830016	-0,1248151
Zinc	0,09155849	0,09741029	0,8932921	0,03598489	-0,06424506
Iron	0,9355242	0,124138	0,00982847	0,1065548	0,1714261
Magnesium	0,5019095	0,1031668	-0,3389879	0,7155696	0,1152638
Potassium	0,2828379	0,1439798	0,4296597	0,5473874	0,02026674
Sodium	0,07820565	0,01515181	0,1152756	0,9210645	-0,00623152
Antimony	0,09094716	0,226453	0,09810858	0,2594251	0,5902247
Arsenic	0,5713274	0,2750999	0,2078914	-0,04229117	-0,1282862
Cadmium	0,1318896	0,1346428	-0,3185856	0,09727584	-0,07068546
Cobalt	0,06151459	0,8733803	0,01164821	0,1326928	0,02812882
Copper	0,1831997	0,1685937	-0,0545729	-0,1054164	0,6804592
Chromium	-0,02788433	0,07664311	0,1430582	0,02686043	-0,5414973
Scandium	0,3225975	0,00801169	-0,384285	0,05327537	-0,619428
Manganese	0,9821106	0,02028905	-0,1200555	-0,05132401	0,01954817
Molybdenum	0,319776	0,7520853	-0,04742729	-0,04941967	0,1134425
Nickel	-0,05733084	0,9070183	-0,05295176	0,1705484	0,1840081
Platinum	-0,00752141	0,7710036	0,08623027	-0,3282369	0,00027925
Lead	0,6150594	-0,07515868	-0,03660486	0,2354583	0,4572151
Rhodium	-0,1353579	-0,02996156	0,488705	0,437107	-0,4075772
Titanium	0,8007223	-0,07766622	0,1227063	0,04232834	0,3079697
Vanadium	-0,09388523	0,8699631	-0,1818591	0,1624732	-0,05890864
TSP	0,8786186	0,02743546	-0,2842168	0,2138576	-0,00747981
Eigenvalue	6,916603	3,675919	2,637885	1,980887	1,708399
% of variance	28,664	15,234	10,932	8,209	7,08

relationships between actual variables in terms of a small number of hypothetical variables called “factors” that are relatively independent and easy to interpret but cannot be directly observed. The analysis was performed on element contents and TSP.

The first factor, which explained 28.7% of the total variance, encompassed Mn, Al, Fe, Ca, Ti and TSP with high coefficients, and Pb, As and Mg with somewhat lower coefficients. Therefore, this variable related several elements and TSP, so it was designated “earth crust” factor; in fact, the elements in TSP came from sources including a natural component accounting for their oscillations in parallel with TSP. Metals such as Al, Ca, Fe and Mg are usually assumed to come from the earth crust (Kyotani et al. 2002; Mouli et al. 2003). In urban environments, however, Fe originates mainly from traffic-related human sources such as lubricant oil burning (Mouli et al. 2003; Hsu et al. 2004; Kulshrestha et al. 2009) and brake abrasion (Mouli et al. 2003).

The second factor explained 15.2% of the variance and encompassed Ni, Co and V with high coefficients, and Mo and Pt with somewhat lower, but still high coefficients. Nearly all these elements came from combustion processes or resuspended road dust (Mouli et al. 2003). This variable, which seemingly reflected the influence of the nearby airport and water desalination plant, was designated “industrial” factor.

The third factor accounted for 11% of the total variance and contained Zn and Ba. Barium (particularly in the form of poorly soluble salts such as carbonates and sulphates) is usually associated to terrestrial sources but comes in part from human sources such as car traffic in urban locations (Kyotani et al. 2002; Karar et al. 2006). Zinc is virtually exclusively associated to anthropogenic sources such as traffic and combustion residues of urban waste ashers; in fact, it has been used as a tracer of some types of industries (Shandilya et al. 2007). This variable was designated the “mixed”.

Factor 4 explained 8.2% of the variance and encompassed Na, Mg and K. Sodium usually comes from marine breeze and potassium from terrestrial sources –the latter, however, has often been found associated with the former in coastal atmospheres (Torres et al. 2001; Kyotani et al. 2002; Wang et al. 2006). The presence of Mg in this group can also be ascribed to its association with Na (Kyotani et al. 2002), and also to the sweeping of particles containing high proportions of Mg and K crossing over the Atlantic from the Sahara and Sahel deserts (Wang et al. 2002). Therefore, this variable was markedly natural and thus called the “marine”.

Finally, factor 5 accounted for 7.1% of the total variance and comprised Cu, Sc, Sb and Cr, all of which except the first were of essentially terrestrial origin: the city atmosphere (Kyotani et al. 2002; Mouli et al. 2003; Hsu et al.

2004; Kulshrestha et al. 2009; Karar et al. 2006; Shandilya et al. 2007; Wang et al. 2006; Marcazzan et al. 2001). Consequently, it was designated the "traffic" factor.

4. CONCLUSIONS

Concentration of atmosphere particulate matter (TSP) in Gran Canaria (Canary Islands) during twelve months has been established. The concentration ranged from 22.0 to 225.5 $\mu\text{g}/\text{m}^3$ with an average concentration of 68.5 $\mu\text{g}/\text{m}^3$. A total of 23 metallic elements divided into two groups: "abundant" (Na, K, Ca, Ba, Mg, Zn, Al and Fe) and "scarce" (Ti, Cu, Mn, Pb, V, Cr, Ni, As, Sb, Co, Mo, Pt, Sc, Rh and Cd) according to their concentrations have been quantified. Concentrations of "abundant" metallic elements were higher than those previously reported for other urban areas in the world; this was especially true for Na, Ca, K y Ba. The contribution of the first group to metal fraction is predominant (99.8%).

Soluble fraction constitutes the 21.5% of TSP and 79.5% of metal fraction. All elements contained in the metal fraction are present in the soluble, although in a different order of concentrations. In this fraction, Na, Ca and K constitute 83.0%, result lower than those found in other areas. Between "scarce" elements predominate Cu and Ti.

A temporal study to try to find an explanation to the variability of observed concentrations was carried out. Locating an increase in the concentration of Rh during the weekends that we have tried to explain the influence of emission sources far from the study area

Availability of soluble elements, represented by availability coefficient is generally high. Mn presents the higher with a 99.9%. Co, K, Pt, Ca, Cu, Rh and Zn present also high coefficients (over 80%). Taking into account that As, Cr, Ni, Pb and V present high toxicity to humans, one might expect from its high availability increased risk for them

The marine influence into the aerosol is established using ratios with respect Na into marine water concentration. An enrichment of 8 for Ca and more than 4 for K was found. Probably due to africans "calimas" that affects Canary Islands.

In order to identify sources contaminants, factor analysis is applied. Five factors are found "crust" and "marine" essentially natural constituted by Mn, Al, Fe, Ca, Ti, Pb, As, Mg, Na, Mg, K. "industrial" and "traffic" that comprehend Ni, Co, V, Mo, Pt, Cu, Sb and Cr basically anthropogenic. And "mixed" that includes natural as Ba and anthropogenic as Zn.

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