Metallic Species In Ambient Air Particles. PM10

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Especies metálicas en la materia particulada del aire. PM10

Especies metàl·liques en el material particulat de l'aire. PM 10

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RESUMEN

En el presente trabajo se cuantificaron las especies metálicas del material particulado (PM10) presente en un área urbana de la isla de Gran Canaria. Las medidas experimentales fueron realizadas desde octubre de 2004 a septiembre de 2005 con un total de 53 muestras (4 o 5 por mes). La PM10 se recogió en filtros de fibra de vidrio utilizando muestreadores de alto volumen. La concentración promedio fue de 32,6 ± 19,6 µg/m^3. La PM10 se determinó gravimétricamente. Las concentraciones de elementos metálicos fueron analizadas por espectrofotometría de emisión atómica utilizando un ICP-OES. Se encontraron dos categorías de elementos: "escasos" y "abundantes". Los elementos examinados fueron caracterizados según su origen en emisiones naturales o antropogénicas en base a factores de enriquecimiento. El análisis factorial de la composición elemental se utilizó también para identificar diferentes tipos de fuentes de contaminación posibles.

Palabras clave: Materia particulada, PM10, especies metálicas, Islas Canarias, transporte a grandes distancias.

SUMMARY

In the present work metallic species of particulate matter (PM10) present in an urban area of Gran Canaria Island were quantified. Experimental measurements were carried out from October 2004 to September 2005 with a total of 53 samples (4 or 5 per month). PM10 was collected in fiber filters using high volume samplers. The average concentration was 32,6 ± 19,6 µg/m^3. PM10 was determined gravimetrically. Concentrations of metallic elements were analized by atomic emission spectrophotometry using an ICP-OES. Two categories of elements were found: "abundant" and "scarce". The examined elements were characterized according to their origin from natural or anthropogenic emissions on the basis of enrichment factors. Factor analysis of elemental composition pattern was also used to identify possible pollution source-types.

Keywords: Particulate matter, PM10, metallic species, Canary Islands, long transport.

RESUM

En el present treball es van quantificar les especies metàlliques del material particulat (PM10) presents en una àrea urbana de l'illa de Gran Canària. Les mides experimentals van ser realitzades des d'octubre de 2004 a setembre de 2005 amb un total de 53 mostres (4 ó 5 per mes). La PM10 es va recollir en filtres de fibra de vidre utilitzant mostrejadors d'alt volum. La concentració mitjana va ser de 32,6 ± 19,6 µg/m3. La PM10 es va determinar gravimètricament. Les concentracions d'elements metàl·lics van ser analitzats per espectrofotometria d'emissió atòmica utilitzant un ICP-OES. Es van trobar dues categories d'elements: "escassos" i "abundants". Els elements examinats van ser caracteritzats segon el seu origen en emissions naturals o antropogèniques basant-se en els factors d'enriquiment. L'anàlisi factorial de la composició elemental es va utilitzar també per identificar diferents tipus de fonts de contaminació possibles.

Mots clau: Material particulat; PM10; especies metàl·liques; illes Canàries; transport a grans distancies.

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1. INTRODUCTION

Epidemiological studies of atmospheric particulate matter (PM) have unequivocally established a high correlation between PM concentrations and human mortality (Baldasano et al., 2003; Mallone et al. 2011; Gupta et al., 2012). The effects of PM on human health depend on particle size, composition and solubility in biological fluids (Silbajoris et al., 2000; Tchepel and Dias, 2011; Balbay et al., 2012; Hoek et al., 2012).

PM10 has aroused much interest in the recent years given that its adverse effects on the heart and lungs are better correlated with human morbidity and mortality than those of any other type of particulate matter (Gomiscek et al., 2004; Abu-Allaban et al., 2007; Kocak et al., 2007; Shandilya et al., 2007; Lazaridis et al., 2008; Van Zelm et al., 2008; Hoek et al., 2012; Tchepel and Dias, 2011). PM10 comprises a variety of metal species that are originated mainly from urban centres in developed countries, traffic emissions, secondary particles forming in the atmosphere and coarse particles in marine aerosol, and resuspended ground and road dust (López Cancio et al. 2008). Animal studies simulating human respiratory system *in vivo* have suggested a correlation between lung toxicity and metal components in atmospheric particulate matter (Dye et al., 2001; Sun et al., 2001). This has led the European Commission to issue a directive on air quality, Directive 2008/50/CE, establishing allowed limits for Pb concentrations and requiring the monitoring of the atmospheric concentrations of As, Cd, Hg and Ni in Directive 2004/107/CE. World Health Organization additionally recommends monitoring V, Pt, Cr and Mn levels (Air Quality Guidelines, 2000). There has been a widespread increase in the concentrations of metals in the platinum group (particularly Pd, Rh and Pt) in urban atmospheres ever since sales of non-catalyst cars were banned in the European Union in 1993. This has aroused interest in quantifying such concentrations by virtue of the well-known toxic effects of these metals and, especially, platinum, which is an active component of automobile catalysts (Whiteley and Murray, 2003; Ravindra et al., 2004; Farago et al., 2005; Osornio-Vargas et al., 2011). Canary Islands, by its geographical position, receive local and external influences from Africa, the Middle East and Europe. However, local sources and topography exert significant influence on the final aerosol.

The city of Telde is an important urban centre (population *ca.* 100 000) in the NW of the Gran Canaria island that is under the influence of various local pollution sources including Gando Airport (SW), a complex including a thermal power and a seawater purification plant (N), and an industrial complex (E) with paper and cardboard recycling industries, glass recycling, gas processing, ... In addition, the city is under the impact of particulate matter from traffic (exhaust emissions, tyre and brake wear) from both its streets and the nearby GC-1 motorway. The local and external sources are deteriorating the city atmosphere and leading to an increasing number of outpatient visits and hospital admissions for respiratory and dermal diseases, especially among children (López Cancio et al., 2007).

In this work, we studied the levels of metal components in the particulate matter fraction PM10 in the city of Telde.

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; alternating different days of the week, sometimes a Monday, sometimes on a Tuesday and so on. Atmospheric particulate matter (PM10), 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 m^3/h. Each sampling period lasted 24 h and started at 8:00 am.

Two sample collectors were placed 10 m above ground level on the roof of two public buildings at Telde: "Ayuntamiento" (28º 00' 48"N, 15º 24' 52.50" W) and "Casa de la Cultura" (27º 59' 54.98" N; 15º 24' 49.41" W); the first under the influence of thermal power and water treatment plants emissions, and the second in an area opened to different influences such the airport and the motorway GC-1.

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. Total metallic fraction was achieved by treatment filters with nitric and hydrochloric acids according to the Beyer modified method (López Cancio et al., 2008). PM10 concentration of was determined gravimetrically by weighing the filters prior to and after collecting samples using an analytical balance with a reading precision of ±10 µg.

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 the one described for the field samples. The results indicated that the ranges of recovery efficiencies were varied between a 94% and 103%.

3. RESULTS AND DISCUSSION

3.1. Concentration of particulate matter (PM10)

PM10 suspended matter levels ranged from 11.5 to 136.2 µg/m^3. The average, 32.6 µg/m^3, was 82% of the annual limit set by EU Directive 2008/50/CE (Directive 2008/50/CE). The highest concentrations, which were 3.18 times higher than the average for the sampling period, were recorded in October 2004 and due to a haze episode occurred on the seventh day of the month. Concentrations were also high in February 2005, again by effect of inputs of African air, which are a common occurrence in the Canary Islands in summer and winter (Torres et al., 2001; Querol et al., 2002). The concentrations recorded in Telde exceeded those of rural areas such as Monegrera (Spain) (Artiñano et al., 2001); were similar to those of large cities such as Singapore (Baldasano et al., 2003), London (UK) (Baldasano et al., 2003) and Madrid (Spain) (Querol, 1999); higher than those of Melbourne (Australia) (Baldasano et al., 2003); and lower than those of Las Palmas (Canary islands) (Ma-

cías, 2002), L'Hospitalet (Spain) (Querol et al., 2001), Milan (Italy) and Seville (Spain) (Baldasano et al., 2003).

3.2. Metallic species

Twenty-two of the 25 elements studied were detected in the studied samples (only the concentrations of Sn, Pd and Cd invariably fell below the detection limits of the methodology used). The total average concentration of metallic species was 9.34 μg/m^3 and accounted for 63.3% of the metal fraction in total suspended particles (TSP) (López Cancio, 2013). The average concentrations, shown in Table I, were used to classify the studied elements as "abundant" (Na, Ca, Ba, K, Zn, Mg, Al and Fe) or "scarce" (Ti, Cu, Pb, Mn, V, Ni, Cr, As, Sb, Mo, Pt, Rh, Cd and Sc). The "abundant" elements in combination accounted for 99.9% of all PM10.

Table I – Statistics of concentrations of total metallic elements (PM_{10}) in Telde during the study

a - 'Abundant' elements (in μg/m^3)

	Ma	Me	Mg	σ	CV (%)	Min	Max	RIC	P 90%
Na	4.799	4.565	4.415	1.971	41.1	1.511	10.860	2.219	7.516
Ca	1.154	0.953	1.034	0.748	64.8	0.586	4.518	0.421	1.454
Ba	1.035	0.985	1.010	0.333	32.2	0.808	3.383	0.116	1.110
K	0.864	0.816	0.836	0.284	32.9	0.578	2.598	0.143	1.049
Zn	0.604	0.577	0.591	0.177	29.3	0.460	1.820	0.085	0.666
Mg	0.360	0.345	0.334	0.153	42.5	0.135	0.871	0.176	0.564
Al	0.287	0.238	0.256	0.191	66.5	0.148	1.337	0.095	0.424
Fe	0.229	0.203	0.204	0.129	56.6	0.083	0.884	0.110	0.396

b – 'Scarce' elements (in ng/m^3)

	Ma	Me	Mg	σ	CV (%)	Min	Max	RIC	P 90%
Ti	4.518	3.315	3.524	3.924	86.8	0.959	18.390	2.585	8.191
Cu	2.024	1.814	1.899	0.763	37.7	0.937	4.349	0.969	2.969
Pb	1.737	1.251	1.122	2.278	131.2	0.138	16.020	1.247	0.761
Mn	1.100	0.872	0.883	0.919	83.6	0.097	6.183	0.636	1.897
V	0.697	0.543	0.469	0.606	87.0	0.035	2.580	0.683	1.543
Ni	0.436	0.372	0.335	0.331	75.9	0.049	1.764	0.372	0.819
Cr	0.312	0.294	0.284	0.147	47.0	0.126	0.815	0.183	0.521
As	0.136	0.105	0.091	0.119	87.9	0.011	0.437	0.149	0.312
Sb	0.087	0.083	0.066	0.063	72.3	0.002	0.407	0.071	0.151
Mo	0.022	0.020	0.016	0.015	68.9	N.D.	0.086	0.021	0.040
Pt	0.018	0.017	0.012	0.012	69.4	0.001	0.045	0.016	0.036
Rh	0.008	0.008	0.007	0.005	57.8	N.D.	0.019	0.006	0.016
Cd	0.007	0.006	0.005	0.004	66.8	N.D.	0.024	0.005	0.012
Sc	0.005	0.001	0.002	0.007	157.8	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. N.D.: Not Detected

Enrichment factors. The contribution of anthropogenic emissions to the presence of metallic species in the atmosphere of Telde was estimated by calculating the so-called "enrichment factor" (EF) for each element with reference to Sc and the earth crust composition proposed by Taylor and McLennan (1985). The choice of scandium as the reference element was dictated by its low volatility and lack of industrial applications (Voutsa et al., 2002). By convention, the concentrations in the upper layer of the earth crust are preferred to those for the area concerned because the latter is difficult to obtain. The fact that the literature abounds with data relative to Al and Fe led us to also include them in Table II.

Table II – Enrichment factors of metallic elements under study.

Element	CCT (ppm)	Ma (μg/m^3)	EF_{Sc}	EF_{Al}	EF_{Fe}
Na	28 900	4.80	365	47	25.3
Ca	30 000	1.15	85	11	5.8
Ba	550	1.04	4 140	527	287.8
K	28 000	0.86	68	9	4.7
Zn	71	0.60	18 715	2 382	1 286.0
Mg	13 300	0.36	60	8	4.1
Al	80 400	0.29	8	1	0.55
Fe	35 000	0.23	14	2	1
Ti	3 000	4.52×10^{-3}	3	0.42	0.23
Cu	25	2.02×10^{-3}	178	23	12.3
Pb	20	1.74×10^{-3}	191	24	13.2
Mn	600	1.10×10^{-3}	4	0.5	0.28
V	60	0.70×10^{-3}	26	3	1.78
Ni	20	0.44×10^{-3}	48	6	3.35
Cr	35	0.31×10^{-3}	20	3	1.35
As	1.5	0.14×10^{-3}	205	26	14.2
Sb	0.2	0.09×10^{-3}	990	126	68.5
Mo	1.5	0.022×10^{-3}	32	4	2.23
Pt	0.01	0.018×10^{-3}	3 960	499	2.74
Rh	0.005	0.008×10^{-3}	3 520	444	244
Cd	0.098	0.007×10^{-3}	157	19.8	10.9
Sc	11	0.005×10^{-3}	1	0.1	0.069

CCT: Earth's Crust Concentration. Ma: Average concentration in Telde. EF_{Sc}: Enrichment factor with respect to scandium. EF_{Al}: Enrichment factor with respect to aluminum. EF_{Fe}: Enrichment factor with respect to iron

Zinc, with EF = 18 700, appears as the most anthropogenic element among those studied; in fact, its EF strongly exceeded those for the Brocken/Harz Mountains (Central Germany) (Plessov et al., 2001) and the Mediterranean coast of Israel (Herut et al., 2001), with 4 560 and 1 148, respectively. Zinc is an essential element and it is known to come from emission sources such as brake and tyre wear (Weckwerth, 2001) or soot from diesel engines, as well as dust clouds swept by the wind from heavily industrial areas in Europe, Northern Africa and the Middle East. Extremely high levels of Zn in Telde suggest that most of this metal comes from long transported sources.

Zinc was followed in importance with Ba, Pt and Rh, with EF values from 1 000 to 10 000. Barium comes from the same sources as Zn and presents high potential of long-range transportation. Pt and Rh, as noted earlier, result from the growing use of car catalyst. The high levels of Ba, Pt and Rh in the atmosphere of Telde also suggest a significant influence of long-range atmospheric transport from remote environments.

The previous elements were followed by Sb, Na, As, Pb, Cu and Cd, with EF values from 100 to 1 000. Cu, Pb and Cd appear enriched in the atmosphere of Telde. The three elements come from diesel combustion (Lewandowsky et al., 2008), brake wear and waste incinerators, among other anthropogenic sources (Lim et al., 2010). High values for Pb after its use was banned in many countries as an additive point to incinerators as the largest source of lead. As and Sb, originating from road traffic (Hsu et al., 2004; Moreno et al., 2006), were also enriched. The levels of Na

were consistent with its continuous presence in local aerosol. Previous elements other than sodium appear to come from distant sources.
Seven other elements (Ca, K, Mg, Ni, Mo, V and Cr) were the least enriched of all. The first three come mainly from natural sources (Ca and K come with African dust clouds that regularly visit the islands. Magnesium comes from marine aerosol around us) and the other four come from road traffic (Moreno et al., 2006; Sánchez et al., 2007). Finally, Al, Mn and Ti were not enriched.
Identification of sources. The data of Table III were subjected to factor analysis in order to establish potential correlations between the different elements and the PM10 fraction, as well as to identify their emission sources and compare them with those of TSP. The first five factors accounted for 78% of the total variance. The first included Fe, Mn, Al, Ca, Mg, Ti and PM10, all with high coefficients. Therefore, this factor encompassed elements of natural origin and was referred to as the "earth crust factor" in studying the major elements (Déniz, 2010), all of which were slightly to markedly enriched.
The second factor ("mix factor") comprised the elements Zn, Ba, Pt, K and Sc. As confirmed by their high EF values, the former three were essentially anthropogenic and from long transport (Déniz, 2010). Furthermore, the potassium naturally occurring, long distance comes, too.
The third factor comprised Cd, Sb, Cu and Pb, and coincided largely with factor 3 of TSP, which was ascribed to road traffic (Déniz, 2010). The EF values for these elements confirmed their anthropogenic origin (traffic road, mainly).
The fourth factor comprised Ni and V, both essentially coming from combustion processes and highly similar to the "industrial factor" in TSP (Déniz, 2010). These elements were less markedly enriched and come from road traffic as well.
Finally, the fifth factor consisted exclusively of Rh, which was strongly enriched. These two results, together, suggest the presence of possibly a remote source from which they are swept to the Canary Islands by the wind (Rauch et al., 2005).

4. CONCLUSIONS

Concentration of atmospheric particulate matter (PM10) in Gran Canaria Island during twelve months has been established. The concentration ranged from 15.5 and 136.2 μg/m^3 with an average concentration of 32.6 μg/m^3.
A total of 22 metallic elements were divided into two groups: "abundant" (Na, Ca, Ba, K, Zn, Mg, Al y Fe) and "scarce" (Ti, Cu, Pb, Mn, V, Ni, Cr, As, Sb, Mo, Pt, Rh, Cd y Sc) according to their concentrations.
Zn, Ba, Pt y Rh have high enrichment factors suggesting the predominance of anthropogenic sources. Vehicle emissions, industrial processes and road dust are their major source-types affecting the local atmosphere. The high value for Zn (18 700) suggests the action of transportation from distant sources. High values of Pt and Rh show the direct influence of automobile catalysts and also come from long distance.
In order to identify sources contaminants, a factor analysis is applied. Five factors are found, 'crust' essentially natural constituted by Fe, Mn, Al, Ca, Mg and Ti. 'Traffic', 'industrial' and 'mix' that comprend Cd, Sb, Cu, Pb, Ni, V, Zn, Ba, K, Pt and Sc. There is an 'Rh' factor which confirms the influence of distant sources.

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

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Aluminum	**0,912418**	0,3391268	0,02024163	-0,00363888	0,01839977
Antimony	-0,00319544	0,07631151	**0,8706309**	-0,02949705	-0,08757699
Arsenic	0,1429162	0,5457237	0,06516524	-0,03888831	-0,09364521
Barium	0,09887834	**0,9456271**	-0,1196966	0,1349353	-0,1171885
Cadmium	-0,150541	0,2503608	**0,9617515**	-0,1701265	0,4642102
Calcium	**0,8758026**	0,2012783	0,02563876	0,1282508	0,1241491
Zinc	0,1381474	**0,961138**	-0,02687929	0,1810611	-0,2210744
Copper	0,2497371	-0,09270314	**0,7335024**	0,2976244	-0,4788143
Chromium	0,4161259	0,1503386	0,05951058	0,337417	-0,0204875
Scandium	0,3378548	**0,8246151**	0,04118955	-0,1315649	0,3540726
Iron	**0,9444657**	0,1883793	0,09447595	0,03968953	-0,1690579
Magnesium	**0,7442478**	0,152006	-0,1204389	0,1855346	0,3656152
Manganese	**0,9396836**	0,2586441	0,05121243	-0,00496285	-0,05292466
Molybdenum	0,2484419	0,0230265	0,3633895	0,4812716	0,00493241
Nickel	-0,0078843	-0,04405812	-0,04977415	**0,9029902**	0,1509758
Platinum	0,3899265	**0,8740226**	0,065881	-0,2612616	0,2234187
Lead	0,08152741	-0,03507713	**0,906684**	0,05915515	0,2376928
Potassium	0,2749313	**0,9166996**	0,3274639	0,00152705	-0,1109882
Rhodium	0,1010709	-0,2469717	0,3939595	0,3687962	**0,9686362**
Sodium	0,3021766	0,5550578	-0,09600883	0,219549	0,284181
Titanium	**0,6596407**	0,3289732	0,04033803	-0,06264356	-0,1854507
Vanadium	0,07296313	0,05225356	-0,02749529	**0,9911582**	0,02756812
PM10	**0,9230313**	0,03378516	0,09285141	0,1180506	0,1307963
Eigenvalue	8,465069	3,737424	3,232365	2,280879	1,807281
% of Variance	34,051	15,034	13,002	9,175	7,27

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