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High-time resolution and size-segregated elemental composition in high-intensity pyrotechnic exposures

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HIGHLIGHTS

- ► Streaker/Dekati/PIXE are suitable to study high-intensity short-lived firework events.
- ► Fireworks related elements showed >80% elemental mass in the submicrometric region.
- ► Resuspended soil dust is an important source of atmospheric particles in these shows.

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ABSTRACT

Typical of festivals in Eastern Spain, *mascletàs* are high-intensity pyrotechnic events where thousands of firecrackers are burnt in an intense, rapid episode that generates short-lived heavy aerosol clouds. High temporal resolution and size distribution characterisation of aerosol components were performed to evaluate the effects of the brief (<30 min) and acute exposure on the spectators present. Very high concentrations of firework specific elements, especially in the fine fraction, were reached during *mascletàs*, with values of about 500 $\mu g/m^3$ for K and 300 $\mu g/m^3$ for Cl. Sr, Al, Mg, Ba, Cu, Co, Zn, and Pb concentration increase factors of more than 100 (1000 for Sr and Ba) were observed in the fine fraction with respect to background levels. Crustal origin elements, like Ca, Fe, Si, Ti, also showed an important concentration rise (∼10 times above background levels) but this is due to dust resuspension by pyrotechnic explosions. The crustal components are mainly in the coarse mode (>90% elemental mass), between 2 and 3 μm. Most firework related metals are concentrated in the submicrometric region (>80%) with a trimodal size distribution. This may be interesting to epidemiologists given the toxic effects that such fine, metal-rich particles can have on human health.

1. Introduction

In the last few years several research studies have been published in literature reporting on urban airborne particles data related to worldwide popular pyrotechnic events, such as New Year's Eve [1], national festivities [2,3], sporting championship celebrations [4], and light festivals [5,6]. Most of these published studies were carried out from pre-event to post-event pyrotechnic performances in order to evaluate urban background air quality variations usually within an hourly or daily time resolution. As a general conclusion, firework displays give rise to large (up to hundreds of $\mu g/m^3$) but transitory (up to hours or days) increases of urban atmospheric particulate matter mean levels, especially metalliferous particles (K, Mg, Ba, Cu, Sr, Al, Pb) [4]. For example, in the Indian Diwali festival, 24 h-average concentration of PM_{10} increased up to 5.7 times with respect to a normal day [7,8]; during the Lantern festival in China the rise of $PM_{2.5}$ was over 6 times the usual daily level [9]; in the Summer solstice feast in Girona (Spain) $PM_{2.5}$ daily local background doubled, from 13 $\mu g/m^3$ to 25 $\mu g/m^3$, multiplying by a factor ranging from 2 to 86 the concentrations of metals and metalloids typically emitted from fireworks [10].

During firework displays, all size ranges of atmospheric particles rise but the increase is particularly significant for fine particles [4]. As can be found in cited literature, 0.4–2.0 μm size bin is the characteristic interval related to atmospheric aerosol originating from pyrotechnic exhibitions [1,2,11]. This interval corresponds to breathable airborne particle fraction and therefore it is expected, taking into account the reported high levels of atmospheric metal, metalloid and other pollutants, that substantial human health effects can be induced by fireworks. Consequently, numerous

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Fig. 1. Location map and picture of sampling site. White arrows indicate north direction.

papers have been published describing the hazardous impact that both long-term and short-term firework events can have on human health [12–16].

Most of the studies have been designed, as mentioned before, to measure daily urban background levels of airborne fine particles by means of standard PM samplers, belonging, in many cases, to public monitoring networks, normally at considerable distances (>1 km) from sites where firework displays are launched [1,17,18]. Even though it is very common that people attending such an event can be engulfed by smoke plumes arising from pyrotechnic displays, the impact of the brief and acute exposure to these plumes on spectators standing close to an outdoor short-lived firework event is scarcely known [19,20].

This paper is focussed on aerosols generated by high-intensity pyrotechnic events, called *mascletàs*. These events take place during annual festivals in numerous cities in the Spanish south-eastern Mediterranean region (Valencian Region) (Fig. 1). Unlike usual fireworks, *mascletàs* are intended largely to stimulate the auditory system and body vibration through the strong rhythmic noise sequence produced by the burning of a type of bangers called *masclets*. The *masclet* is a powerful sound firecracker that can be burst both at ground level and at low altitude level (1.5–2.0 m). When it burns, a loud intensity detonation, light effects and abundant smoke generation are produced as a function of its composition. Thousands of *masclets* are linked by a wick forming a line (*traca*) 2 m above ground level, in rectangular or circular connected structures, and are successively burst at high speed. Furthermore, during *mascletàs*, hundreds of firework shells are also shot into the air using vertical cannons (mortars or launch tubes). They produce powerful explosions at 20–40 m high that are usually accompanied by bursts of white light and colours.

People attending these events are directly enveloped by the aerosol clouds which are produced, so our main objective in this paper is to characterise, as best as possible, the airborne particles originated by such near-ground level, short-term, high intensity outdoor firework episodes. For this purpose, we carried out a study to consider the particular characteristics of these episodes. In doing so, we determined elemental composition during *mascletàs* by means of high time resolution analysis and particle size segregation samplers.

An important methodological difference exists between our study and the majority of the studies found in the literature. In these studies the sampling point is located far away from the fireworks launching zone. As a consequence the firework aerosols are found dispersed and diluted in the atmospheric air mass. Furthermore, the local meteorological conditions can change the obtained ambient PM concentrations independently of the type of firework event. In our case, the sampling point is located very close to the launching zone, so the emission aerosol cloud is measured. It is important to remark that this different strategy affects the extrapolation of the results. It is not the same to consider emission PM concentrations than inmission concentration when human exposition are being compared. An estimation of the metallic particles dose inhaled by the people assisting to the pyrotechnic events has been calculated.

2. Experimental

2.1. Sampling site

Alicante (38°20′43″N, 0°28′59″W) is a medium-size city (∼350,000 inhabitants) in SE Spain (Fig. 1). The city lies on the shores of the Mediterranean Sea, extended from north to south in a sloping terrain towards the sea (4%), surrounded by a number of hills and elevations. Alicante has an arid, Mediterranean climate with mild temperatures all year round (annual average of 17.8 °C) and scarce rain (336 mm/year) mostly concentrated in the autumn period. The mean daily temperatures vary from 19 °C to 30 °C in summer and from 7 °C to 17 °C in winter. Predominant wind direction is from the north-west in winter and from the south-east in summer, with a typical regime of Mediterranean Sea breezes in the latter case.

During the 2007 June festival of Alicante *Hogueras de Sant Joan* (Saint John's Bonfires) the popular sonorous and visual displays of *mascletàs* occurred in the afternoons (at 2 p.m.) from 19th to 24th, with high attendance. Different types of explosive devices were strategically situated next to and around a downtown city square (∼10,000 m^2) (Fig. 1) and ignited under computer control. Thousands of *masclets* and firecracker shells, terrestrial (75%) and aerial (25%), were burnt in a high-intensity (125 kg gunpowder), short-time (∼8 min) loud episode (average ∼80 dB$_A$). In the final minute no less than 500 powerful bangers were detonated with noise peaks up to 120 dB$_A$ and with an earthquake effect. As a

Fig. 2. White smoke cloud typically generated during Alicante Festival Mascletà.

consequence, the people (~20,000) concentrated (50 m faraway) in the streets around *mascletà* square and on numerous overlooking balconies from the surrounding apartments blocks were engulfed by dense white aerosol clouds and gasses produced throughout the event (Fig. 2). Despite the daily afternoon Mediterranean Sea breezes that favour contaminants dispersion, very intense short pollution spikes were expected. These pollution spikes are of special concern to individuals in attendance since massive increases of suspended particles (up to 1500 $\mu g/m^3$ 1-h $PM_{2.5}$) have been reported in an urban environmental exposure study during a firework episode [19].

2.2. Sampling and analysis

To assess the chemical enrichment of aerosol clouds that engulf individuals in attendance, we studied a) the fine and coarse particle hourly elemental composition and b) the particle elemental size distribution of aerosol emitted on the 19th of June *mascletà* display. For this purpose we installed the sampler instruments on a balcony situated at a height of 15 m from ground level and within 50 m from the pyrotechnic site under the influence of the plume. The samplings were carried out at different temporal resolution depending on instrument and sought results.

2.2.1. Fine and coarse particle elemental composition: streaker

The aerosol was collected during one week (June 18–24) by a “streaker” sampler (P.I.X.E. International Corporation) [21]. This device is designed to separate the fine (<2.5 μm aerodynamic diameter) and the coarse (2.5–10 μm) fractions of the aerosol. A paraffin-coated Kapton foil is used as an impaction surface for coarse particles and a Nuclepore filter as a fine particle collector. The two collecting plates are paired on a cartridge that rotates at a constant speed for a week: a circular continuous deposition of particulate matter at both stages is produced. The rotation speed during sampling (1.2 mm/h), the pumping orifice width (1.2 mm) and the beam size normally used for the subsequent PIXE (Particle-Induced X-ray Emission) analysis are such that an overall resolution of about one hour is obtained on the elemental composition of air particulate[22,23]. However it must be taken into account that we had to change the 1.2 mm nozzle with a 2 mm one to prevent filter clogging during the intense *mascletà* event; therefore, since the rotation speed of the sampler could not be changed, a little smoothing of the 1 h concentration time trends should be expected.

PIXE analyses were performed with 3 MeV protons from the 3 MV Tandetron accelerator of the LABEC laboratory of INFN in Florence, with the external beam set-up extensively described elsewhere [24,25]. The beam scanned the streak in steps corresponding to 1 h of aerosol sampling; each spot was irradiated for about 180 s with a beam intensity ranging from 20 nA to 30 nA. PIXE spectra were fitted using the GUPIX software package [26] and elemental concentrations were obtained via a calibration curve from a set of thin mono or bi-elemental standards of known surface density by Micromatter [27]. The experimental uncertainties on the elemental concentrations (ng/m^3) measured by PIXE are given by the sum of independent uncertainties on the flux measurement (about 2–3%), on certified standard sample concentrations (5%) and on peak areas. The uncertainty on peak areas includes the X-rays counting statistics and all the fitting uncertainties (background subtraction, peak overlaps, etc.). The counting statistics uncertainty may vary from few percent up to 20–30% or more when concentrations approach minimum detection limits (MDLs).

Detection limits were about 10 ng/m^3 for elements from Na to V and 1 ng/m^3 (or below) for elements from Cr to Pb. The following elements were detected: Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Ba, and Pb.

2.2.2. Particle elemental size distribution: Dekati

Particulate matter samples were collected for both the 19th June *mascletà* period (~50 min) and during a non-festival day (normal summer day, NSD), 1st July (daily average). We used a cascade small deposit area low pressure impactor (SDI, Dekati®). The sampler classifies airborne particles, from 30 nm to 10 μm, into 12 size-fraction small deposit area stages, with cut-off aerodynamic diameters (μm) of 8.50, 4.08, 2.68, 1.66, 1.06, 0.796, 0.591, 0.343, 0.231, 0.153, 0.086, and 0.045. The particles are collected on 25 mm Kapton foils with a flow rate of 11 L/min. In order to reduce particle bounce-off effects, the films were coated with apiezon.

Impactor samples were chemically analysed by PIXE at the LABEC Laboratory [28]. Field blank correction was applied to all the data sets. The relative PIXE uncertainties (due to counting statistics

Table 1
Elemental 1-h concentration (ng/m^3) averaged for the whole festival week (aver), during (mas) and out (bck) of the mascletàs events for the fine and coarse fraction. The fine/coarse ratio during and out of the mascletàs events is also reported. The concentration during mascletàs has been calculated as the average of the peak values reached throughout the six episodes. The background concentration refers to the measurements carried out at times during the week when neither mascletàs peaks nor other fiesta events took place.

Element	Fine			Coarse			f/c	
	aver	mas	bck	aver	mas	bck	mas	bck
Na	1020	1440	1250	2100	1400	3700	1.0	0.3
Mg	710	7060	130	380	2300	380	3.1	0.3
Al	1960	22500	80	1770	31800	190	0.7	0.4
Si	1890	3000	430	710	3690	460	0.8	0.9
S	8670	80900	1450	950	12500	400	6.5	3.6
Cl	18700	216000	120	42300	13300	3420	16.2	0.04
K	33600	384000	250	2380	43200	240	8.9	1.0
Ca	1560	6800	390	3310	22600	1630	0.3	0.2
Ti	57	610	<7[a]	47	430	19	1.4	–
V	36	190	22	26	54	11	3.4	2.0
Cr	16	150	7	9	31	8	4.9	0.9
Mn	23	65	5	9	45	4	1.4	1.1
Fe	250	850	106	360	1900	280	0.4	0.4
Co	105	1700	<1[a]	100	2000	5	0.8	–
Ni	8	18	7	2	8	2	2.3	3.9
Cu	120	2200	12	17	180	10	12.4	1.3
Zn	50	362	8	18	80	9	4.6	0.9
As	20	80	<1[a]	3	10	<2[a]	8.0	0.9
Br	9	36	5	3	9	3	3.9	1.8
Rb	22	63	3	5	19	2	3.4	1.4
Sr	410	5750	4	40	780	10	7.4	0.4
Ba	1600	7430	<20[a]	220	750	<40[a]	9.9	–
Pb	160	1270	8	12	100	5	12.8	1.7

[a] Concentrations under experimental MDL values.

and spectrum deconvolution) typically ranged from about 1–10%, as explained in previous paragraph. The aerosol sampling in general was expected to introduce an additional relative uncertainty of about 10% [29]. The two contributions were square summed to give the overall uncertainties.

The raw elemental size distribution data of the individual SDI samples were converted into smooth distributions using the inversion code MICRON [30] and lognormal curves were then fitted to the latter, so that the elemental mass concentration, geometric mean aerodynamic diameter (GMAD) and geometric standard deviation (GSD) of the different contributing modes were obtained.

2.3. Additional measurements

Meteorological data (temperature, relative humidity, wind speed and direction) for the study period were obtained from the environmental monitoring station of Alicante University. The station is situated 3 km north of the mascletà site in a clear and well-ventilated area. Sea breezes, during festival week, blew mainly from SE, between 127° and 141°.

3. Results and discussion

3.1. Elemental concentration with one-hour temporal resolution

24-h concentration resolution is a period of time much longer than the duration of the displays so corresponding data base coming from daily sample analysis it is not adequate to assess the firework origin of different elements, especially those that could also come from sources other than fireworks (e.g. Cu from traffic). Furthermore, the individual exposure period of spectators attending short-term outdoor displays is much shorter than 24 h. For these reasons, 1-h resolution sampling is more suitable because it allows evaluating without any doubt the firework origin of the different elements and it makes possible to quantify the real exposure of spectators to short-lived fireworks plume.

The elemental hourly temporal evolution, both in the fine (<2.5 μm) and coarse (2.5–10 μm) fraction, was carried out using the Streaker device. In Table 1, the elemental 1-h concentration averaged during and out of the *mascletàs* events and over the whole festival week for the fine and coarse fraction are summarised. The fine/coarse ratio is also reported. The concentration during *mascletàs* has been calculated as the average of the peak values reached throughout the six episodes. The background concentration refers to the measurements carried out along the week in periods when *mascletà* peaks did not take place and should represent the city "normal" concentrations. The concentrations we found are higher than those found in other studies [4,10,17] and for many elements similar to the ones found by Kuhlteshta et al. and Sarkar et al. for Diwali festival [6,18] and Wang et al. for Lantern Festival [5] (our data were averaged in the same time scales used in the cited article).

As can be observed in Table 1, during the *mascletà* events the mass concentrations of most of the analysed elements show an extraordinary increase relative to background levels (especially for fine fraction). Potassium and chlorine exhibit the highest levels (384 μg/m^3 and 216 μg/m^3, respectively) and relative increases since background concentrations are multiplied by a factor higher than 1500 during these events. The concentrations of other elements related to pyrotechnic displays, like Sr, Al, Mg, Ba, Cu, Co, Zn, and Pb, are also extremely high during the *mascletàs.* In the fine fraction, increase factors with respect to background levels range from around 50 for Mg and Zn, to more than 1000 for Sr and Ba.

In Fig. 3a–c we show the concentrations (μg/m^3) of (a) K, Cl, S (fine fraction); (b) Al, Ba, Sr (fine fraction); and (c) Ca (fine and coarse fraction) registered during the whole *Hogueras* week. As can be seen from the figures, the high time resolution allows us to follow the rapid evolution of the pollutant concentration due to the short-time daily events. All the reported elements had very sharp peaks on the time of *mascletàs* burning. They also showed a quick decrease after the events due to high dispersion capability of the atmosphere favoured by sea breeze and thermal convective processes. A similar time pattern is also presented by Mg, Si, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Br, Rb, Ba, and Pb. Most of these elements were already identified

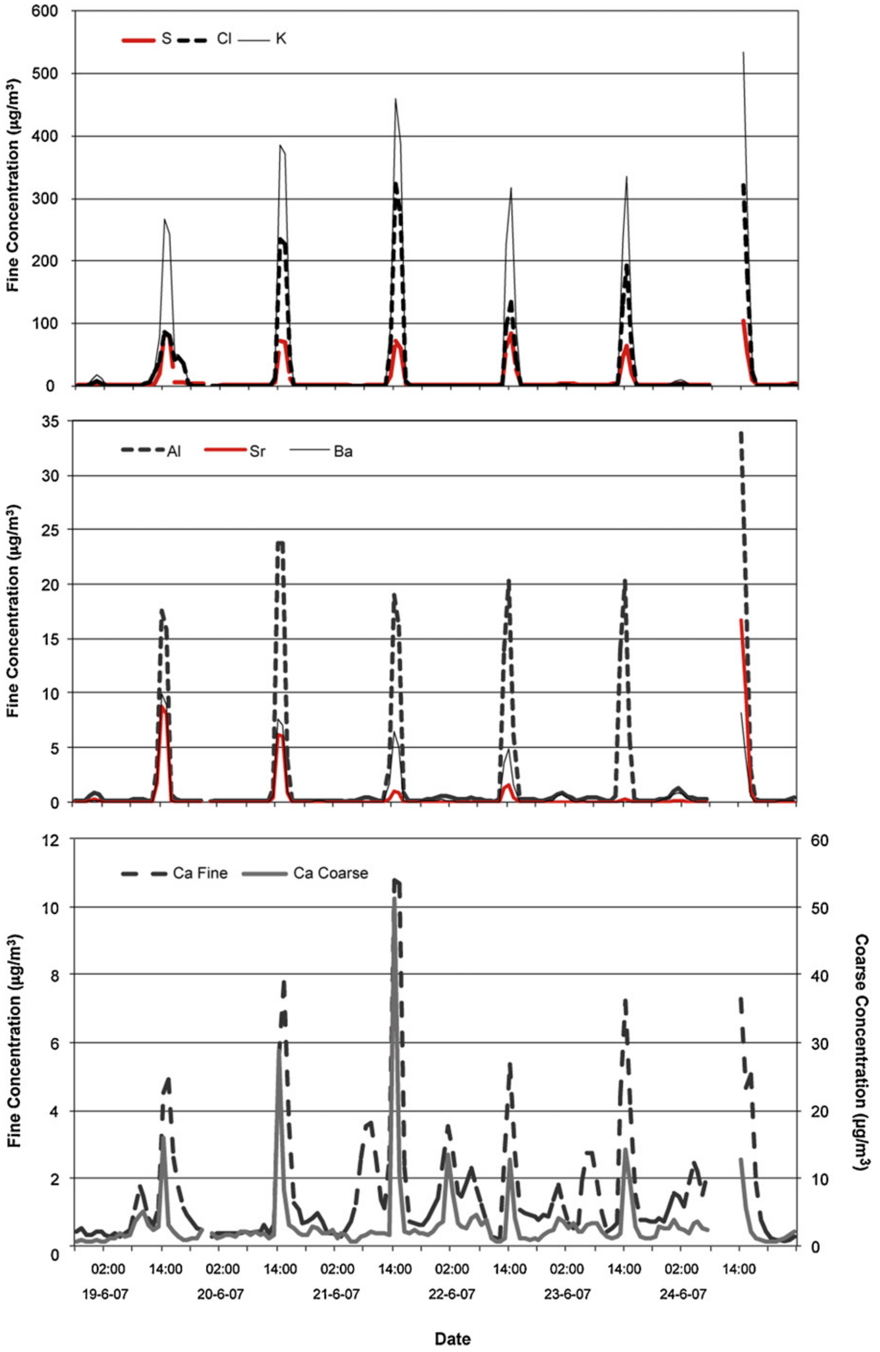

Fig. 3. Hourly time trends of fine K, Cl, S (a); fine Al, Sr, Ba (b); fine and coarse Ca (c). The lack of data during some hours on June 24th was due to a power black-out.

in literature as tracers of firework emissions. However, it is clear that the different nature of *mascletàs* respect to standard fireworks may vary enormously the ratio of metals in the heterogeneous and dense aerosol they produce.

Fig. 3a shows the temporal pattern of K, Cl and S concentrations in the fine fraction. Levels measured inside the plume in our study were roughly of the same order of magnitude as those found by Drewnick et al. and Joly et al. [1,19] and far higher than those found by Dutcher et al. [11] which refers to indoor particulate. These elements originate from gunpowder combustion [11], still the principal component of actual pyrotechnic devices. Pyrotechnic process basically consists in an oxidation–reduction reaction between an oxygen source (oxidant), typically potassium nitrate or perchlorate, and some reducing agents (fuel), classically charcoal and sulphur but also other components like binders, metal powders or smoke generating agents added to the aforementioned substances in order to reach the desired pyrotechnic performances [11,31].

Dutcher et al. [11] reported that gunpowder, typically composed of 74.0% KNO_3, 10.4% S, and 15.6% C by mass, shows an ambient air K/S mass ratio after fireworks, practically equivalent the theoretically determined value, 2.76. In contrast, the measured ambient average K/S mass ratio found in this study was much higher, about 5.0, not far that obtained by Croteau et al. (5.73) in a close-monitored pyrotechnic event [20]. Furthermore, the ambient K/Cl mass ratio obtained (between 1.1 and 3.1 along *mascletà* week) indicates that *mascletà* episodes released into the atmosphere large quantities of chlorine together with potassium in the fine fraction. These results seem related to the use of potassium perchlorate, a

Table 2
Geometric mean aerodynamic diameter (GMAD, μm), associated geometric standard deviation (GSD, μm) and relative mode concentration (RMC) of the detected modes for investigated elements of the Mascletà samples.

Element	Accumulation mode			Intermediate mode			Coarse mode		
	GMAD	GSD	RMC	GMAD	GSD	RMC	GMAD	GSD	RMC
Mg	0.22	1.87	0.62	0.85	1.84	0.31	3.356	1.53	0.08
Al	0.21	1.68	0.18				2.10	2.11	0.82
Si	0.14	1.88	0.13				2.13	2.27	0.87
S	0.19	1.50	0.41	0.67	1.62	0.49	2.978	1.53	0.10
Cl	0.19	1.47	0.44	0.61	1.53	0.53	2.378	1.26	0.03
K	0.19	1.51	0.44	0.65	1.60	0.50	2.75	1.45	0.07
Ca	0.16	1.72	0.05				2.49	2.13	0.95
Ti							2.32	2.17	1.00
V	0.34	2.75	1.00						
Cr	0.50	3.35	1.00						
Mn	0.32	2.63	0.69				2.15	2.43	0.31
Fe	0.284	1.40	0.14	1.13	1.46	0.42	3.39	1.41	0.44
Co	0.319	1.18	0.06	1.03	1.37	0.43	3.24	1.47	0.51
Cu	0.24	1.63	0.60	0.64	1.45	0.37	2.9	1.35	0.04
Zn	0.30	2.36	0.95				3.34	1.47	0.05
As	0.34	2.23	0.96				3.46	1.73	0.04
Rb	0.404	2.52	1.00						
Sr	0.24	1.65	0.61	0.69	1.41	0.37	2.719	1.25	0.02
Ba	0.197	1.61	0.58	0.604	1.57	0.38	2.955	1.38	0.05

more powerful oxidiser, when intense daylight flashes and pronounced noise effects are required, as occurred in *mascletàs* [32]. So, $KClO_4$ appears to be a major source of the K found in *mascletà* PM fractions. It is common the use of an excess of oxidisers in the composition of the fireworks mixture in order to assure a complete combustion. In this case, some of the potassium perchlorate could remain without reacting into aerosol cloud after the explosions. That would imply an additional harmful effect for the people attending the *mascletàs* given the high toxicity of ClO_4^- ion on humans [33]

Moreover, taking into account the elevated chlorine concentration found during the events and the urban pollution background of Alicante, organic chlorides perhaps should also be formed after mascletàs increasing still further the harmful effects.

In addition, it was found that the K/S mass ratio is almost inversely proportional to K/Cl mass ratio, (Pearson correlation, $R^2 = 0.96$) indicating a competition for potassium between S and Cl as a function of availability of these elements resulting from chemical composition of daily employed pyrotechnic devices.

In the coarse fraction the concentrations obtained for these elements were far lower than those found in fine fraction (average fine/coarse ratios during mascletà were 8.9; 16.2; 6.5 for K, Cl and S, respectively). S concentrations of coarse fraction were higher than in the fine fraction, with an average Cl/S mass ratio of 1.2 as compared to 2.6 for the fine fraction. It has to be noted that in background conditions, Cl was mainly in the coarse fraction and showed a time pattern very similar to that of Na, pointing to a common origin which is sea-salt aerosol source. Furthermore, the average K/S ratio was, in this case, close to 2.8, indicating a lower influence of mascletà generated Cl in the coarse fraction. In addition, a weak correlation ($R^2 < 0.4$) between K/S and K/Cl mass ratios was found which also suggests different sources for these elements.

In Fig. 3b the temporal evolution of other elements related with crackers and fireworks activity, namely Al, Sr, and Ba, are presented. Aluminium is used as a common constituent for fuel, alone or together with magnesium (which indeed is correlated to Al for *mascletà* episodes: $R^2 \sim 0.80$) as the alloy magnalium (50:50 MgAl) to produce sparks and flash effects [34]. During *mascletà* periods the concentrations of Al reached values in the fine fraction of about 35 $\mu g/m^3$ and 45 $\mu g/m^3$ in the coarse one, two order of magnitude higher than background values (<0.2 $\mu g/m^3$ in all cases). Barium and strontium salts are used as colour agents, imparting a red or green colour, respectively, to firework displays. They are also important for stabilising fireworks and barium nitrates or chlorates as oxidiser too [4,10]. Sr and Ba, elements with still lower background concentrations (<10 ng/m^3), reached concentration peaks during *mascletàs* up to 16 and 10 $\mu g/m^3$ in the fine fraction, respectively, and about 1.5 $\mu g/m^3$ in the coarse fraction. The concentration of Sr and Ba found in the generated *mascletà* plume is not constant for each festival day because, as already mentioned, the composition of the released particulate matter depends on specific type of pyrotechnic device used. For example, during the 23rd June *mascletà*, there were a small contribution to fine fraction from Sr and negligible from Ba, while in the next day Sr and Ba concentrations increased up to 16 and 8 $\mu g/m^3$, respectively.

Similar patterns, with peaks every day at 2 p.m., are shown by Mg (maximum concentrations for the fine and the coarse fraction, respectively, 10 and 4 $\mu g/m^3$), V (0.4 and 0.06 $\mu g/m^3$), Mn (0.1 and 0.07 $\mu g/m^3$), Cu (7 and 0.3 $\mu g/m^3$), Zn (0.7 and 0.1 $\mu g/m^3$), Br (0.1 and 0.01 $\mu g/m^3$), Rb (0.08 and 0.02 $\mu g/m^3$). A few elements are present only in some *mascletà* events: Cr (maximum concentrations for the fine and the coarse fraction, respectively, 0.16 and 0.05 $\mu g/m^3$), As (0.17 and 0.01 $\mu g/m^3$), Pb (5 and 0.2 μ g/m^3), and Co (1.8 and 6 μ g/m^3).

It is should be stressed that the average mass concentration of all the reported elements (except S, Cl and K) in the fine fraction during *mascletà* was about 17 $\mu g/m^3$ and reached values as high as 34 $\mu g/m^3$, to be compared to a value of 0.03 $\mu g/m^3$ during the background period. In Fig. 3c, the temporal evolution of Ca concentrations in both fractions, fine and coarse, is shown. A higher increase in the coarse fraction than in the fine one during the events is evident. This temporal pattern is very similar for most of the elements of crustal origin like Fe, Si, Ti, etc. The fine/coarse ratios (see Table 1) for Si were 0.8 and 0.9 respectively for mascletà and background period, for Ca 0.2 and 0.3, for Fe 0.4 and for Ti 0.4 (Ti was below mdl in normal days in the fine fraction), while for most of the other elements increases of at least a factor 2 (up to more than 10) in the *mascletà* respect to the background period. In sharp contrast to what seen for the elements reported in Fig. 3a and b, the ratio between the concentration of these 4 crustal elements during the *mascletà* and during the background period was nearly constant (for Ti the difference is due to two days when there was some contribution by fireworks, see below). Finally, the enrichment factors (EF), calculated using Si as reference element and the crustal composition given by Mason and Moore [35], are close to 1, both during the *mascletà* and the background period, except Ca with a

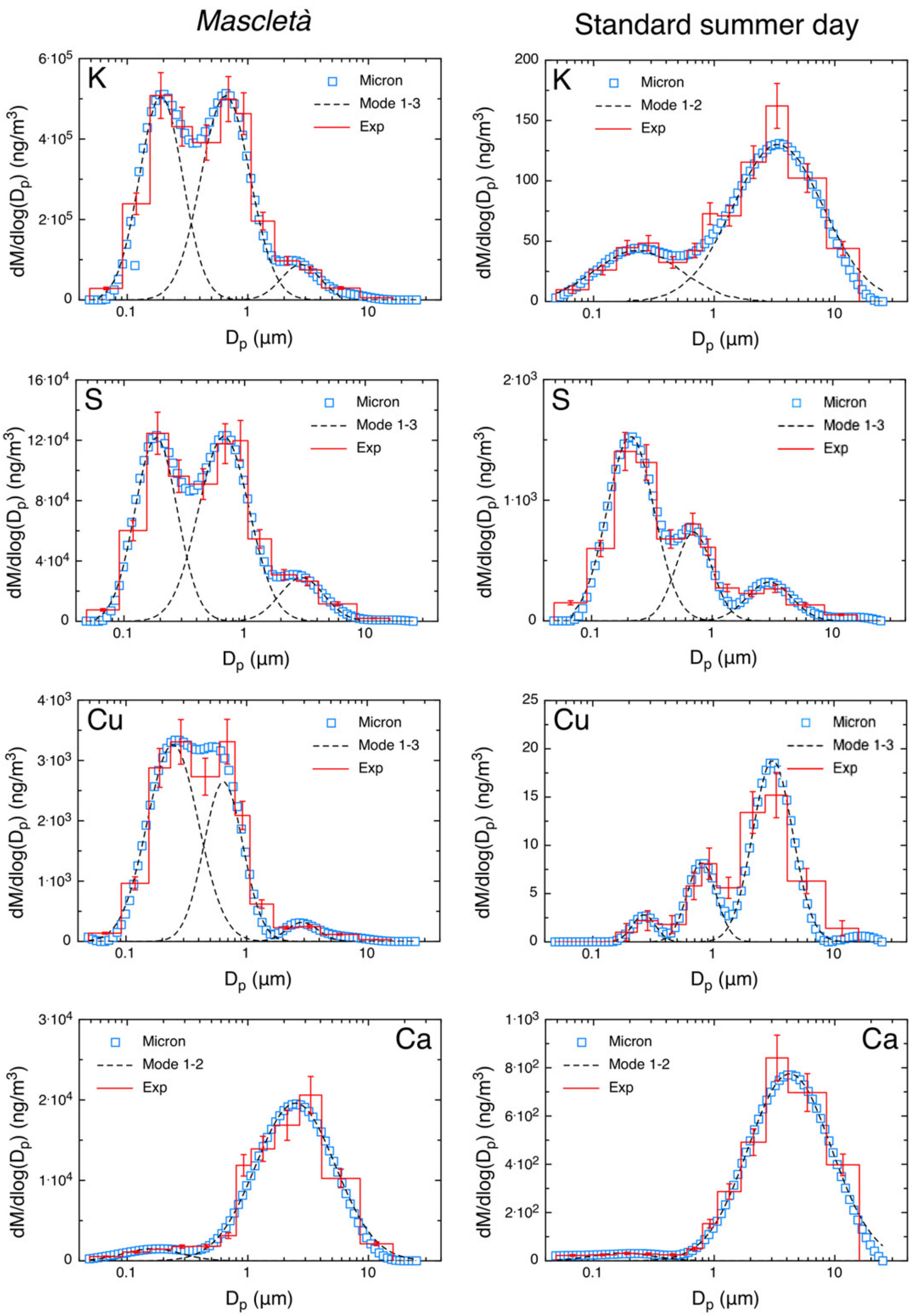

Fig. 4. Mass-size distribution for Mascletà and "Normal summer day" for typical gunpowder bulk elements (K, S), for a pyrotechnic origin element (Cu) and for a crustal origin element (Ca). The histogram gives the raw size distribution, the inverted distribution is indicated by the square symbols, and the smooth dashed lines represent the lognormal fits.

higher EF, but it is known that Alicante soil is Ca enriched [36,37]. For example, EF were: Al 1.2, Ca 21, Ti 2.1, Fe 2.8 Sr 13.2 during normal period; during mascletà we obtain Al 28, Ca 31, Ti 5.9, Fe 2.4, Sr 126. So it is evident the difference between elements like Fe, Ca or Ti (with the problem discussed above) and other elements produced also by fireworks like Al or Sr. Therefore, the concentration increase seems not to be due to the combustion products but to the resuspension of crustal origin material deposited on the ground where the explosions take place. A confirm of this hypothesis could come from further studies on the of U/Ra ratio in isolated particles by AMS as reported by Steinhauser and Musilek [38].

An estimate of the resuspended soil dust concentration during masclètas can be calculated considering the crustal elements as oxides [39]. Since we have discussed above that Al, K and Sr are produced by fireworks (indeed they showed high enrichment factors), only the natural fraction of Al, K and Sr (their concentration divided by their enrichment factor) was included in the crustal matter calculation. The sum of the fine and coarse resuspended soil dust concentration varied from 44 μg/m^3 to 130 μg/m^3, while the background concentration is normally less than 10 μg/m^3.

3.2. Elemental mass-size distribution

In order to measure the aerosol elemental mass-size distributions during *mascletà* and to compare them with those on a “normal summer day” (NSD), 12-stages Dekati cascade impactor was used. The following PIXE analysis provided raw concentration-size data (mass per stage and per m^3) for the elements Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, As, Br, Sr, Ba and Pb. From the obtained results we observe significant changes both in concentrations as well as in modal distributions of investigated elements.

To obtain more quantitative results, the raw size distribution data were converted into smooth size distributions by means of the inversion code MICRON [40] to reveal the modal structure of the aerosol more accurately than would be the case if using the discrete distributions only. Lognormal curves were then fitted to the inverted smooth distributions, so that the elemental mass concentration, geometric mean aerodynamic diameter (GMAD) and geometric standard deviation (GSD) of the different contributing modes were obtained. For the *Mascletà* samples, these parameters for the firework related elements are reported in Table 2.

Fig. 4 shows the raw data, the MICRON inversions and the lognormal fits for K, S, Cu and Ca both in the *mascletà* and in the NSD samples. It can be clearly seen from Fig. 4 that mode mass concentrations increased in general throughout *mascletàs*, depending on element and mode. For K, S, and Cu different types of distribution profiles, on *mascletàs* and on NSD, were also obtained.

On *mascletà* the distribution for typical gunpowder bulk elements, K, S (Fig. 4), is trimodal, with a coarse mode (with GMAD 2.4–3 μm, GSD 1.3–1.5 μm and RMC < 10%), and two separate submicrometer-sized submodes, one with GMAD 0.19 μm, GSD ~ 1.5 μm and RMC ~ 40% and the intermediate one with GMAD ~ 0.65 μm, GSD ~ 1.6 μm and RMC ~ 50%. Therefore, all these elements presented higher concentrations in the submicrometer size bins. Correlation coefficients between different pairs of these elements for each diameter bin have been calculated to quantify the correspondences among their elemental mass-size distributions. The determination coefficients R^2 between K and Cl and between K and S during *mascletàs* were 0.98 and 0.99, respectively. A good correlation was observed for all the size bins, with more Cl associated to K in the submicrometer fraction and more S related to K in the coarse one.

For NSD, completely different mass-size distribution pattern for K was found. It showed relative high concentrations in the coarse mode but with far lower intensity with respect to *mascletà* event. Sulphur presented a different behaviour, as can be also seen in Fig. 4. The distribution profiles both on NSD and during *mascletàs* were trimodal, with an equivalent GMAD in all cases. A similar concentration increase of about two orders of magnitude is produced approximately in all sizes bins.

Most of the other firework related elements (Mg, Cr, Cu (Fig. 4), Zn, As Sr, Pb, Rb, Ba), are characterised by a trimodal size distribution, with the accumulation mode (GMAD ~ 0.2–0.3 μm) as the dominant one with RMC between 50% and 100%. For some of those elements (Mg, Cu (Fig. 4), Zn, Pb, and Ba) also the intermediate mode (GMAD ~ 0.6–0.8 μm) is important (RMC 30–50%). In fact, Ba, Sr, Cu and Pb, specific indicators of pyrotechnic events, raised their accumulation mode concentrations from <10 ng/m^3 up to 1 μg/m^3 (Pb, Cu) and 10 μg/m^3 (Ba, Sr). It has to be noted the sharp difference of the pattern of NSD Sr, whose low concentration levels are limited exclusively to the coarse mode. Other elements showed similar behaviour but with a relative lower concentration in general and particularly in the coarse mode. Anthropogenic compounds like V, Zn, Ni, As are found in this group with levels above that of normal anthropogenic sources approximately in two orders of magnitude. Mg shows a similar pattern, but with a relative lower concentration in general and particularly in the coarse mode. An exception is constituted by Co, whose mass is concentrated in two modes with GSD ~ 1 and 3.2 μm.

In Fig. 4 the mass distribution for a typical crustal element, Ca, is shown. During *mascletàs* crustal elements (Ca, Mg, Si, Mn, Ti and Fe) show two main modes: with GMAD of 2–3 μm (containing more than 90% of the elemental mass) and with GMAD of about 0.14–0.3 μm (containing the remaining elemental mass, lower than 10%). Typical GSDs of the modes were ∼2 and 1.3–1.8 μm, respectively. Their size distribution patterns remain quite similar on NSD, but with a remarkable concentration decrease. This fact, together with the strong correlation between the typical crustal elements distributions (i.e., Si, Ca, Ti, and Fe resulted in correlation coefficients above 0.9) and the enrichment factors [35] for all the size bins close to 1 (similar to the values derived for the whole coarse size fraction in the streaker samples) hint to a common main source for these elements. The increase in the concentration is probably due to resuspension of soil material, consequence of massive ground explosions throughout the pyrotechnic event, already noted from the streaker data.

Some differences for some crustal elements like Al, Mg were observed. We have seen in the previous section that they also originated from fireworks; together with a coarse mode similar to the one present in NSD, a strong accumulation mode (maximum at about 0.3 μm) was present, due to the pyrotechnic event.

4. Conclusions

This paper shows an experimental procedure to study the time evolution and size distribution of aerosol elements emitted into the atmosphere by high-intensity pyrotechnic events. The procedure was carried out during the *Mascletàs*, daily events typical of festivals in eastern Spain. The coupling of 1-h resolution sampling followed by PIXE analysis of *mascletà* collected aerosols have proven to be a powerful methodology to monitor the temporal trend of aerosol elemental concentration, both in the fine and the coarse fraction. *Mascletàs* combustion generates heavy aerosol clouds which contain a complex mixture of different metals and other components. Extremely high concentrations in the fine fraction with values of about 384 μg/m^3 for K and 216 μg/m^3 for Cl were reached during *mascletàs*. Increase factors of more than 1500 relating to background levels were found for these firework specific elements.

Other elements related to pyrotechnic displays like Al, Mg, Cu, Co, Zn, and Pb also presented a large rise, with increase factors above 100, mainly in the fine fraction in comparison to their normal values. In the particular case of Sr and Ba, factors up to ∼1000 were observed. The concentrations found in generated *mascletà* plumes were not constant due to variability of gunpowder composition and pyrotechnic devices used to attain specific firework effects.

A few elements were present only in some *mascletà* events: Cr, As, Pb and Co. It is to be noted that these metals are dangerous elements because of their toxicity, especially As and Pb [41,42], and their use in pyrotechnic devices are forbidden by law in the European Union. Nevertheless, as stated in the bibliography [3], pyrotechnic materials can be imported from countries with more permissive legislation resulting in sporadic atmospheric toxic discharge as we observed in our study. In our case, in some *mascletàs*, As and Pb reached concentrations of up to 0.17 and 5 μg/m^3 respectively, two and three orders of magnitude above background levels. Such very high concentrations in a short time in a place where thousands of people are gathered may be of concern, particularly for people who suffer from chronic respiratory health problems, cardiovascular disease, etc.

Ambient concentration increase was also observed for most of the elements of crustal origin, like Ca, Fe, Si, Ti. This is due to the resuspension, produced by pyrotechnic device explosions, of material already deposited on the ground. Such an important contribution of the resuspended soil dust (~10 times above background levels) has to be taken into account as a source of particulate matter in these types of events.

We also compared the aerosol elemental size distribution related to *mascletà* events with the corresponding elemental size distribution of a normal summer day (NSD). While as expected the crustal components are mainly in the coarse mode with two main modes, all the firework related elements (except Co) are more concentrated in the submicrometric region (>80% elemental mass) with a trimodal size distribution for *mascletà* events. This information may be useful to epidemiologists given the harmful effects of metallic particles on human health [43–46]. With regards to a NSD, firework associated elements were generally evident in relative high concentrations in the coarse mode but with far lower intensity. The size distribution patterns remained quite similar for crustal elements but with a remarkable concentration decrease that confirms *mascletà* resuspension processes.

A preliminary approach to quantify the elemental mass dose received by individuals due to smoke plume during mascletàs was attempted. The calculation was made for Pb. This element was chosen as it is one of the metals which appear in greatest concentration during mascletàs (despite its prohibition in pyrotechnic use). Moreover, given that it is one of the metals whose harmful effects have been most studied during recent decades [43,44], the result of the calculation can be compared with bibliographic data.

$$\text{Dose can be calculated as}: D_{\text{Pb}} = \text{CPbmas} \times \text{IR} \times \text{ED} \times \text{DF}$$

where CPbmas = mascletà fine fraction Pb concentration (μgPb air m^{-3}); IR = human inhalation rate (air m^3 min^{-1}); ED = exposure duration (min mascletà$^{-1}$); DF = deposition factor (as a fraction of Pb mass inhaled) [47].

Since the mascletà episode lasted approximately 8 min, we assumed that *CPbmas*, at least (as a minimum), was equal to fine fraction Pb 1-h concentration, i.e. ~1.3 μgPb air m^{-3} (Table 1). Although natural breathing patterns have variable inhalation rates, we used the average breathing pattern in adults at rest, typically 8.5×10^{-3} air m^3 min^{-1} [47]. Moreover, there were several factors, like the length of time people spent at the mascletà site or the distance to launching site, that caused variation in ED of spectators. It could be estimated minimum 8 min mascletà$^{-1}$. In addition, as stated by Kin and Hu [47], in healthy adults DF varied from 0.12 to 0.25 and from 0.26 to 0.68 for aerosol particles with 1 μm and 3 μm in diameter, respectively, depending on the breathing pattern applied. We used the lowest 1 μm DF value (0.12) to obtain a minimum Pb dose, $D_{\text{Pb}} \cong 10$ ngPb individual^{-1} mascletá$^{-1}$. It is important to stress that this result is only an estimation of the actual dose in terms of mass of Pb in the aerosol fine fraction (1 μm) deposited in the airway per person and mascletà. Calculations can be applied to other metallic elements analysed in the pyrotechnic aerosol. Additional harmful effects would be expected if overall metallic elemental dose is considered. The number of people that are typically exposed to these high metallic PM concentration levels during the mascletàs can be estimated by taking into account the characteristics of the square from where the fireworks are launched and the position of the people around it. The direction of the breeze was largely from the SE sector (120–140°). Under these conditions, the pyrotechnic plume impacts on only a third of the total surface of the square (~0.3×10^{-2} km^2). If we assume that there are 3 spectators per square metre, an average of 9000 spectators would be directly affected by the impact of the aerosol plume during each mascletà. This would represent 2–3% of the entire Alicante population, although it should be noted that tens of thousands of tourists visit the city during *Las Hogueras de San Juan*.

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