Effect of fireworks events on urban background trace metal aerosol concentrations: is the cocktail worth the show?

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ABSTRACT

We report on the effect of a major firework event on urban background atmospheric PM_{2.5} chemistry, using 24-hour data collected over eight weeks at two sites in Girona, Spain. The firework pollution episode (*Sant Joan* fiesta on 23rd June 2008) measured in city centre parkland increased local background PM_{2.5} concentrations as follows: Sr (x86), K (x26), Ba (x11), Co (x9), Pb (x7), Cu (x5), Zn (x4), Bi (x4), Mg (x4), Rb (x4), Sb (x3), P (x3), Ga (x2), Mn (x2), As (x2), Ti (x2) and (SO₄²⁻) (x2). Marked increases in these elements were also measured outside the park as the pollution cloud drifted over the city centre, and levels of some metals remained elevated above background for days after the event as a reservoir of metalliferous dust persisted within the urban area. Transient high-PM pollution episodes are a proven health hazard, made worse in the case of firework combustion because many of the elements released are both toxic and finely respirable, and because displays commonly take place in an already polluted urban atmosphere.

Keywords: Fireworks smoke emissions, urban background PM_{2.5}, air pollution.

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1. Introduction

The polluting nature of the smoke plumes arising from firework displays has recently received considerable scientific attention, with published studies reporting mainly on specific events such as Independence Day in the USA [1], European World Cup football celebrations [2], Lantern festival in China [3], Diwali in India [4], Las Fallas in Spain [5], and New Year's Day [e.g. 6]. The smoke plumes arising from such events can raise atmospheric particulate matter (PM) levels from tens to thousands of $\mu\text{g m}^{-3}$ [7], with most particles being fine (1-2 μm) and therefore potentially respirable [1]. The chemistry of these plumes is complex, but is always characterised by a high metal content due to presence of K in the black powder propellant and a range of other metals/metalloids used as oxidisers, stabilisers, and to add colour and other special effects.

The inhalation of smoke loaded with metalliferous particles small enough to enter the lung alveoli causes negative health effects in humans [e.g. 8], especially among vulnerable individuals such as asthmatics [9]. However, demonstrating toxicological responses to the inhalation of fireworks smoke is hampered by a continuing lack of detail about the exact nature of the inorganic chemical cocktail being inhaled. Most publications to date have published only partial chemical analyses, and/or have measured materials also contaminated by sources other than fireworks. Furthermore, focussing only on the specific fireworks event fails to provide the longer term context of urban atmospheric PM chemistry normally present in a given urban area. In this short communication we summarise new chemical data from filters collected daily over a seven-week period prior to a major summer fireworks festival in Mediterranean Spain (*Sant Joan*), and compare them with data collected during and one week after the event. The primary aim of the study was to characterise the concentrations and chemistry of urban background levels of $\text{PM}_{2.5}$ in Girona, compare these with more traffic-polluted sites within the city, and to identify unusual spikes in air pollution such as, in this case, a fireworks festival. Our data include analyses of trace elements (using ICP-AES and ICP-MS) in 107 24hr filter samples: such a comprehensive database on the effect of fireworks emissions on urban background atmospheric chemistry has not previously been published.

2. Methodology

50 Filter samples for this study were collected during a monitoring campaign in May-June 2008 from two
 51 locations in the city of Girona (population 96,000) in NE Spain, including an urban background and a more
 52 traffic-polluted site in the city centre. The traffic site lies in the southern city centre (*Escola Musica*
 53 41°58'69"N/2°49'31"E: adjacent to the busy main road feeding north into the centre) whereas the
 54 background site lies in urban parkland (*Parc Migdia* 41°58'10"N/2°49'28"E) 350 metres to the SE (150°).
 55 Data from both stations were obtained from 5 May to 30 June 2008, with 24-h PM_{2.5} sampling being carried
 56 out by means of MCV CAV-A and DIGITEL DH80 high volume samplers (30 m³ h⁻¹) equipped with quartz
 57 fibre filters (Munktell). Filters were treated and analyzed following the procedure described by Pey et al.
 58 [10]. This is based on the daily sampling of PM and subsequent analysis of major and trace elements by ICP-
 59 AES and ICP-MS (of acidic digestions of 1/2 of each filter), soluble anions and cations by ion
 60 chromatography, ammonium by colorimetry-FIA (water leached, 1/4 of each filter) and carbon by thermo-
 61 optical methods. Contents of Si and CO₃²⁻ were indirectly determined from the contents of Al, Ca and Mg,
 62 on the basis of prior experimental equations (2Al₂O₃=SiO₂; 1.5Ca+2.5Mg=CO₃²⁻). Blank field filters were
 63 used for every stock purchased for sampling and analyzed in the same batches of their respective filter
 64 samples. The corresponding blank concentrations were subtracted for each sample. For analysis control,
 65 reference material NIST 1633b was added to a fraction of a blank filter to check the accuracy of the analysis
 66 of the acidic digestions. The individual uncertainty of daily measurements due to analytical techniques was
 67 estimated following the method described by Amato et al. [11] and expressed as % (interquartile range) of
 68 specie concentration (Table 1). An estimate of Detection Limit (DL) was performed for the j^{th} analyte based
 69 on the following formula:

$$DL^j = \frac{\sqrt{\sigma_0^{2j} + \sigma_{BLK}^{2j}}}{V}$$

71 which combines estimates of the two uncertainties linked to the instrument σ_0 (ICP-MS, ICP-AES, HPLC
 72 etc.) and the blank subtraction σ_{BLK} [12]; V is an average value of air volume sampled in 24 hours.
 73 Additional measurements were made every 15 minutes for SO₂ (ultraviolet fluorescence), and atmospheric
 74 conditions (wind velocity and direction, precipitation, relative humidity and ambient temperature) were
 75 supplied by the local site in the meteorological network of the Generalitat of Catalonia.

76 3. Results

77 The *Sant Joan* fireworks fiesta is celebrated late in the evening of 23rd June, and is recorded on an hourly
78 scale by our SO₂ data at *Parc Migdia* which show a sudden rise after 20:00 to a transient peak at 22:00 UTC
79 time (from 2.0 to 6.8 µg m⁻³), followed by rapid subsidence to background levels after midnight (Fig. 1
80 inset). In contrast, neither aerosol nitrate nor ammonium levels were significantly affected by fireworks
81 combustion, as also noted in previous works during New Year celebrations in Germany [6]. Mass
82 concentrations of PM_{2.5} (averaged over 24 hours) rose from 14 µg m⁻³ on the 22nd June to 25 µg m⁻³ on the
83 23rd June. The influence of fireworks on the PM content of filter samples for 23rd June in *Parc Migdia* is
84 clear: they are unusually rich in metals, with K, Ba, Mg, Sr, Cu, Pb, Sn, Al, Bi, and Ga all rising suddenly to
85 their highest value during the 7 week sampling campaign. The elemental increases relative to pre-fireworks
86 background levels measured over the preceding 6 weeks are, in decreasing order, Sr (x86), K (x26), Ba
87 (x11), Co (x9), Pb (x7), Cu (x5), Zn (x4), Bi (x4), Mg (x4), Rb (x4), Sb (x3), P (x3), Ga (x2), Mn (x2), As
88 (x2), Ti (x2) and (SO₄²⁻) (x2).

89 Fig. 1 illustrates the scale of the fireworks metals peak at *Parc Migdia* on 23rd June, using five metals
90 which best define the event, namely Sr, K, Mg, Cu and Pb. Interestingly, ambient concentrations of these and
91 other metals during the week after the firework show do not fall back to pre-fireworks background levels but
92 instead remain relatively elevated (Fig. 1). During this time the weather in Girona remained very hot and dry,
93 with above average PM_{2.5} concentrations (except after an early morning storm on 27th June). This
94 observation of a post-fireworks concentration anomaly suggests that the transient but intense smoke event on
95 the 23rd June created a reservoir of metalliferous particles which continued to contaminate the area days after
96 the initial pollution episode. We envisage much of this reservoir as fine metalliferous PM attached to surface
97 deposited particles later subject to daytime resuspension by wind, traffic and other activities. Further study is
98 needed to ascertain for how long this “reservoir effect” can be detected within an urban area.

99 During the fireworks event light winds blew the main body of the dispersing smoke plume generally
100 northwards over the city centre. The distinctive metalliferous fingerprint of fireworks emissions at the *Escola*
101 *Musica* site was therefore again obvious, but with correspondingly reduced concentrations and a slightly
102 different chemical mix. Once again pronounced increases were shown by Sr (x71), Ba (x6), Pb (x5), Bi (x4)

103 although K levels dropped considerably (from x26 at *Parc Migdia* to x13 at *Escola Musica*), presumably due
104 to less intense levels of black powder smoke close to ground level. Table 1 compares metal aerosol
105 concentrations at the two monitoring sites averaging the 24-hour values before, during and after the
106 fireworks event.

107 The data from *Escola Musica* again show a post-fireworks aftermath of continued contamination,
108 although as this site was less of a main focus of firework activity the effect is weaker (Table 1). Furthermore,
109 there is a more obvious PM contribution from road vehicles at *Escola Musica*, as reflected by higher levels
110 of background pre- and post-fireworks metals such as Ba, Zn, Cu, and Sb concentrations (Table 1), these
111 elements being well established tracers not only for fireworks events but also for other anthropogenic
112 emissions such as those from road traffic [13 and references therein]. The usefulness of these four metals in
113 highlighting fireworks events is therefore somewhat compromised in sites with heavy traffic. In contrast, the
114 element Sr is not only an excellent tracer for fireworks emissions, but also is unaffected by high traffic flows,
115 with similar pre-fireworks background concentrations at both *Parc Migdia* and *Escola Musica* (Table 1).

116 In general, and with the obvious exception of 23rd June, background levels of trace metals at the two
117 monitoring sites are controlled primarily by weather conditions and traffic density. Ambient PM
118 concentration reach peaks during dry, mid-week periods and fall to prominent troughs during rainy spells,
119 especially if these coincide with weekends. The first four rainy periods during this summer campaign period
120 occurred at weekends, when daytime traffic flows were at their lowest, and each of these periods is
121 correspondingly marked by a prominent fall in PM concentrations. In contrast, the weekly PM maxima over
122 this period consistently occurred between Tuesday and Thursday under dry conditions. Fig. 2 illustrates how
123 trace metals record this fluctuation in PM concentrations, comparing levels of Sb and Sn, two trace metals
124 with contrasting behaviours with respect to fireworks emissions. The obvious exception to a generally
125 concordant pattern between Sb and Sn occurs over the *Sant Joan* fiesta, when Sb levels more than triple their
126 pre-fireworks average whereas Sn levels, unaffected by fireworks, stay well below their average (Table 1;
127 Fig. 2). Fig. 2 therefore demonstrates that although contaminants such as Sb derive from mixed sources (in
128 this case traffic and fireworks), comparing this metalloid with trace elements not present in fireworks (in this
129 case Sn) can be a useful way to identifying a fireworks event. Overviewing the chemistry of both sites leads

us to conclude that the best firework elemental tracers in our study were Sr, K, SO_4^{2-} , Pb, and Bi, with Ba, Zn, Cu, and Sb also clearly showing firework peaks additional to those associated with traffic.

4. Discussion and conclusions

Most previous publications dealing with atmospheric PM emissions from fireworks have emphasised Sr, Ba, and K as especially typical tracers of firework emissions. With regard to other metals and metalloids there is less agreement, with different papers variously identifying some combination of Cu, Ti, Al, Ni, Cr, Zn, Cd, Mg, Co, Pb, Bi, and As [1-7, 14-16]. It is clear that different fireworks vary enormously in the cocktail of metals they contain. Although K, as the black powder fuel and combined with S, is dominant, the main “special effects” trace additive can include a variety of other metals such as Al, Cu, Ti, or even Pb [17]. The case of Pb is of especially interest, given the high toxicity of this metal, as it is one of the few metals/metalloids for which legal atmospheric concentration limits exist (along with As, Hg, Ni, and Cd), although only for PM_{10} rather than $\text{PM}_{2.5}$. Despite this awareness, it is clear that in many countries any legal requirement for avoiding use of Pb in fireworks manufacture and combustion is being thwarted by imports from manufacturing countries less concerned with potential health implications. Some fireworks continue to contain Pb levels measurable in decigrams [17], and the effect of this on the chemistry of the resulting combustion plume is obvious. In both this current study in Girona, as well as in our study of Las Fallas smoke clouds in Valencia [5], Pb was a prominent component of the firework pollution plume, with average daily levels in Girona rising an order of magnitude higher following the display.

Despite the lack of legal controls on PM emissions emanating from firework combustion, the severity of the impact of such events on urban background atmospheric chemistry provides reasonable cause for concern [18]. There is already abundant published evidence that short-lived fluctuations in pollutants can induce changes in both lung and heart function [8, 19-23]. Asthma symptoms, perhaps the most obvious risk factor, have been linked to one-hour PM_{10} and NO_2 concentrations rising from background values of $20\text{--}30\ \mu\text{g m}^{-3}$ to brief peaks at $40\text{--}70\ \mu\text{g m}^{-3}$ [24]. Similarly, 1-hour exposure to elevated traffic levels has been associated with the onset of myocardial infarction [25], and hourly increases in $\text{PM}_{2.5}$ linked to myocardial ischaemia [26]. In the specific case of fireworks emissions it is the metalliferous component of atmospheric aerosols which is additionally implicated in negative health effects, not only with acute responses but also in their

possible contribution to long term degenerative conditions such as Parkinson's and Alzheimer's diseases [e.g. 27-28]. Presumably, those most immediately at risk from exposure to dense smoke clouds are people already debilitated by pre-existing illness, notably severe asthma or coronary heart disease, but the metalliferous and highly respirable nature of fireworks emissions makes them *per se* hazardous to the general population.

Finally, we emphasise that it is the additional burden of smoke emissions on already contaminated urban air which makes many fireworks events especially polluting. In the case of Girona, a fireworks event lasting an hour or two contributed to raising the daily average PM_{2.5} mass from 13 µg m⁻³ on 22nd June to 25 µg m⁻³ on 23rd June. City centre concentrations of metals and metalloids such as Pb, Co, Ni, Zn, As, Al all increased markedly due to the fireworks display. All of these elements are listed in the Comprehensive Environmental Response, Compensation and Liabilities Act (CERCLA) Priority List of Hazardous Substances published by the US Agency for Toxic Substances and Disease Registry. The health effects of inhaling such a concentrated and complex chemical cocktail of different toxic substances in the form of micron sized particles remain unknown. Furthermore, our observation of a continued "reservoir effect" enhancement of ambient metal PM levels persisting for days after the fireworks event indicates that the effect on urban background PM is less transient than might be supposed.

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Figure and table captions

Fig. 1. Daily concentrations of Sr (x2), Mg, Cu, Pb and K (÷10) at Parc Migdia urban background monitoring station, Girona. The prominent fireworks-related peak on 23rd June is followed by an aftermath of elevated levels compared to pre-fireworks background. Inset: hourly SO₂ levels registered on the 23rd of June.

Fig. 2. Concentrations of the trace metals Sb and Sn in ambient air at Parc Migdia (Parc, urban background) and Escola Musica (EM, heavy traffic) monitoring sites in Girona. The repeated pattern of higher weekday and lower weekend levels is overprinted by cleansing rainfall (grey) events. During the *Sant Joan* fireworks event on 23 June Sb concentrations rise anomalously, exceeding those of Sn, making Sb a useful fireworks marker.

Table 1. Concentrations, detection limits and uncertainty of selected elements at the Parc Migdia and Escola Musica monitoring sites before, during and after the *Sant Joan* fireworks event. See text for details.

Figure 1

Figure 2

	Parc Migdia			Escola Musica				
	Before	During	After	Before	During	After		
	05/05- -22/06	23/06	24/06- -30/06	05/05- -22/06	23/06	24/06- -30/06	DL ($\mu\text{g m}^{-3}$)	uncertainty (%)
$\mu\text{g m}^{-3}$								
PM _{2.5}	16.3	25.3	22.1	22.1	30.8	20.1		
OM+EC	5.7	7.9	7.3	13.6	11.9	14.4	0.58558	15-20
CO ₃ ²⁻	0.3	0.3	0.5	0.5	0.4	0.5	0.06008	4-5
SiO ₂	2.1	2.7	2.1	1.9	2.1	1.9	0.11739	3-4
Al ₂ O ₃	0.7	0.9	0.7	0.6	0.7	0.6	0.03913	3-4
Ca	0.2	0.2	0.3	0.3	0.3	0.3	0.04005	4-5
Fe	0.1	0.1	0.1	0.1	0.1	0.2	0.02017	3-4
K	0.1	2.6	0.2	0.1	1.3	0.2	0.02075	3-4
Na	0.2	0.2	0.2	0.3	0.3	0.4	0.10293	4-6
Mg	<0.1	0.2	0.1	0.1	0.2	0.1	0.01697	3-5
SO ₄ ²⁻	2.5	5.7	3.7	2.8	5.5	4.0	0.12572	5
NO ₃ ⁻	0.4	0.2	0.1	0.5	0.1	0.1	0.07476	6-15
Cl ⁻	0.3	0.3	0.4	0.3	0.4	0.4	0.18700	15-28
NH ₄ ⁺	1.0	0.8	1.3	1.0	1.5	1.4	0.01793	14
ng m^{-3}								
P	10.3	26.9	25.7	15.2	15.8	23.8	0.00579	3-4
Ti	10.3	15.5	16.0	8.6	14.0	13.0	0.00218	3-4
V	4.1	4.5	3.7	3.8	4.6	3.8	0.00020	4
Mn	3.9	7.2	5.3	4.3	5.4	5.3	0.00079	4-6
Co	0.1	0.9	0.1	0.2	0.2	0.1	0.00004	5-6
Ni	2.9	3.2	3.1	3.6	4.5	3.6	0.00118	5
Cu	4.0	20.2	5.1	12.8	17.5	11.5	0.00278	4
Zn	18.3	71.3	64.3	39.8	74.6	86.8	0.03073	7-10
Ga	0.1	0.2	0.1	0.1	0.1	0.1	0.00004	8-10
Ge	1.1	1.1	0.9	0.8	0.9	0.7	0.00057	9-12
As	0.3	0.6	0.3	0.3	0.6	0.4	0.00007	4-5
Se	0.3	0.2	0.3	0.2	0.1	0.3	0.00008	4-5
Rb	0.2	0.8	0.4	0.3	0.6	0.4	0.00005	5-7
Sr	1.4	120.5	2.1	1.5	106.8	2.1	0.00043	6-8
Cd	0.1	0.2	0.1	0.1	0.2	0.2	0.00009	7-9
Sn	0.9	1.2	1.1	1.4	1.4	1.6	0.00201	4-5
Sb	0.4	1.4	0.7	0.9	1.7	1.0	0.00010	4-5
Ba	29.4	321.7	131.0	47.0	261.1	165.3	0.03708	10-18
La	0.2	0.3	0.2	0.2	0.2	0.2	0.00013	6-8
Ce	0.6	0.7	0.5	0.4	0.5	0.5	0.00032	6-7
Pb	4.2	29.1	4.9	4.4	22.8	5.8	0.00060	4
Bi	0.1	0.4	0.1	0.1	0.4	0.1	0.00004	6-10

Table 1