



Short communication

Characterisation of particulate exposure during fireworks displays

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ABSTRACT

Little is known about the level and content of exposure to fine particles (PM_{2.5}) among persons who attend fireworks displays and those who live nearby. An evaluation of the levels of PM_{2.5} and their elemental content was carried out during the nine launches of the 2007 Montréal International Fireworks Competition. For each event, a prediction of the location of the firework plume was obtained from the Canadian Meteorological Centre (CMC) of the Meteorological Service of Canada. PM_{2.5} was measured continuously with a photometer (Sidepak™, TSI) within the predicted plume location ("predicted sites"), and integrated samples were collected using portable personal samplers. An additional sampler was located on a nearby roof ("fixed site"). The elemental composition of the collected PM_{2.5} samples from the "predicted sites" was determined using both a non-destructive energy dispersive ED-XRF method and an ICP-MS method with a near-total microwave-assisted acid digestion. The elemental composition of the "fixed site" samples was determined by the ICP-MS with the near-total digestion method. The highest PM_{2.5} levels reached nearly 10 000 µg m⁻³, roughly 1000 times background levels. Elements such as K, Cl, Al, Mg and Ti were markedly higher in plume-exposed filters. This study shows that 1) persons in the plume and in close proximity to the launch site may be exposed to extremely high levels of PM_{2.5} for the duration of the display and, 2) that the plume contains specific elements for which little is known of their acute cardio-respiratory toxicity.

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1. Introduction

Outdoor ambient fine particulate levels are known to increase with fireworks displays. During the Indian Diwali festival, which last for a few days, daily levels of PM₁₀ (particles with diameters less than 10 µm) were shown to increase 2–6 times the usual daily levels (e.g. Barman et al., 2008; Ravindra et al., 2003). Following short-term displays, such as during National celebrations, increases in fine particles have also been reported. For example, Vecchi et al. (2008) reported an increase in PM₁₀ of 33.6 µg m⁻³, due to

fireworks displays, with a 4 h time resolution; Perry (1995) found an 18.5 µg m⁻¹ increase in PM_{2.5} averaged over 24 h.

Unusually high levels of a number of trace elements, such as Ti, S, Cl, Mg, K, Sr, Ba, C, Ca, Al, Cu, Pb, have been measured in outdoor ambient fine particles following both day-long celebrations (e.g. Indian Diwali festival, Spanish Las Fallas celebration) and after short-term displays (Kim and Hopke, 2008; Vecchi et al., 2008; Moreno et al., 2007; Kulshrestha et al., 2004; Rössli et al., 2001; Perry, 1995). Some of these elements, namely C, K and S, originate from black powder combustion (Perry, 1995), whereas others such as Sr have been suggested as being particularly characteristic of fireworks aerosols (Walsh et al., 2009; Vecchi et al., 2008).

Notwithstanding this literature, little is known about the exposure of spectators attending short-term outdoor displays despite the fact that they are more common. Most studies that measured outdoor ambient fine particles during short-term displays, sampled either air at fixed monitoring sites located on

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roofs of buildings or at remote monitoring sites (e.g. Vecchi et al., 2008; Drewnick et al., 2006; Perry, 1995), and not at the breathing height where people attend displays. Furthermore, levels have usually been measured over periods of time much longer than the duration of the displays and thus over periods of time much longer than the individual's exposure period (e.g. Walsh et al., 2009; Rööslä et al., 2001; Perry, 1995).

The present study was thus performed to quantify the levels and elemental composition of the exposure of individuals attending short-term displays during the 2007 International Fireworks Competition in Montréal.

2. Methods

2.1. Design and particulate measurement sites

The 2007 Montréal International Fireworks Competition consisted of 9 fireworks displays in June and July. Each display started at 22:00 and lasted from 30 to 45 min, with test shots occurring for a few minutes preceding each event. On the morning of each event, the day's weather forecast was used to predict the most likely plume location, based on the Canadian Meteorological Centre (CMC)'s short range LaGrangian particle dispersion model. This approach was used to maximize the particulate exposure of the collection team going to the "predicted site" on each fireworks display of the competition. All the "predicted sites" were situated within 500–2000 m from the "launch site" (Ste-Hélène Island in the St. Lawrence River just off Montréal, Qc.) and were occupied by numerous spectators. A "fixed site" situated on the roof of a building in Longueuil, Qc. (immediately South of Montréal) at a height of 10 m from ground level and a distance of 1100 m from the "launch site" was used for all launches.

2.2. PM_{2.5} sampling

PM_{2.5} samples were collected with a large URG cyclone sampler on 90 mm Zefluor® filters at ~55 lpm at the "fixed site". Sampling at the "predicted sites" was conducted with a smaller URG cyclone sampler on 47 mm Teflo® filters at 10 lpm. Collection with the URG samplers at both the "predicted" and "fixed" sites was performed for 60 min. Field blank filters were recovered on every day of sampling for both URG samplers. The Teflo® filters were weighed before and after sample collection using a Mettler Microbalance (MT-5, Mettler-Toledo Inc., Hightstown, NJ) under controlled relative humidity (45 ± 5%) and temperature (23 ± 3 °C) conditions; Zefluor® filters were not weighed due to the unavailability of a balance that could accommodate their large size. In addition, PM_{2.5} levels were also measured continuously with a Sidepack™ (photometer) at the "predicted sites".

2.3. Chemical analysis

The elemental composition of the PM_{2.5} samples from the "predicted site" was determined by both ED-XRF and ICP-MS with a near-total microwave-assisted acid digestion. The samples collected at "fixed sites" were determined only by ICP-MS after the near-total microwave-assisted acid digestion.

A Jordan Valley EX-6600 AF dispersive X-ray spectrometer equipped with a 400 watt Rhodium target tube was used for the analysis of 22 elements (Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Cl, Zn, Se, Br, Rb, Sr, Cd, Sn, Ni, Cs, Ba, Pb). Following the measurement process, data treatment was performed to correct results for background signal, spectral interferences, and X-ray signal loss due to absorption by the sample mass. Micromatter® standard reference samples were used for the quantitative calibration of the system. Calibration

was checked by analyzing NIST standards (SRM 1832 and SRM 1833). Blank filters were used for background subtraction. The detection limits were in the range of 1–15 ng m⁻³. Experimental overall uncertainties were in the range of 5–35%.

All ICP-MS measurements were performed using an Agilent Technologies 7500c ICP-MS system (Agilent Technologies, Wilmington, DE, USA), equipped with an octopole collision/reaction system (ORS), a Babington nebulizer, a Peltier cooled (2 °C) quartz Scott-type double pass spray chamber and an Agilent I-AS integrated autosampler. The ICP-MS ChemStation software (Agilent Technologies, Inc.) was used to control all instrument operations including tuning, data acquisition, and data analysis. ICP-MS measurements were performed in semiquant (SemiQ) mode (Chen et al., 2008) with a 100 µg l⁻¹ multi-element calibration standard used for calibration. Before the daily analysis, the instrument was tuned in both normal and reaction cell mode in terms of sensitivity, interference levels and resolution, using a tuning solution that contains 10 µg l⁻¹ of Li, Y, Tl, Ce and Co in 2% (v/v) HNO₃. Internal standardization with 1 mg l⁻¹ solution of ⁴⁵Sc, ⁸⁹Y, ¹¹⁵In, and ¹⁶⁵Ho was used to correct for the instrumental drifts and nonspectral interferences. The internal standard was added on line and was automatically mixed with the sample solution before being introduced into the nebulizer.

A closed vessel microwave-assisted reaction system (MARS 5, CEM Corporation, Matthews, NC) was used for near-total digestion of samples prior to ICP-MS measurements for 20 metals (Ag, Al, As, Ba, Be, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sb, Sn, Sr, Ti, V, Zn) (Celo et al., 2005). The PM_{2.5} laden filters were digested using 40% (v/v) HNO₃, following a two-step digestion program (Celo et al., 2005). The precision and accuracy of the analysis were checked by analyzing standard reference materials prepared in the same way as the digested samples, spikes and duplicates. The detection limits were in the range 0.02–4 ng m⁻³. The overall uncertainties for determined trace metals were in the range 10–25%.

2.4. Statistical analysis

Elements with values below the limits of detection (LOD) were set at half the LOD for each element. Elements showing less than 4 out of 9 readings above the LOD were discarded. The discarded elements were all from the ED-XRF analysis.

A hierarchical cluster analysis, using Ward's method and the Euclidian squared distance of the elemental proportions of each filter, was used to classify them into "Exposed" and "Non-exposed" filters. The elemental proportions of each filter, with respect to their total mass, were calculated with the ICP-MS values. This filter classification approach was used to remove any ambiguity as to whether the filters had been exposed or not.

3. Results

Sampling was successful at all sampling sites, on all fireworks dates, and a total of 18 filters (9 Zefluor®, 9 Teflo®) were collected.

Fig. 1 presents the Sidepak® continuous PM_{2.5} levels measured on the 9 Montréal 2007 fireworks displays at breathing height at the "predicted sites". As can be observed in Fig. 1, PM_{2.5} within the fireworks plume can reach sustained levels above 1000 µg m⁻³ for a period of about 45 min (duration of each display) with peaks reaching 10 000 µg m⁻³. Such high levels were reached when measurements were directly taken in the plume (refer to black lines in Fig. 1). Lower levels were measured when the samples were taken at the edge or outside the main path of the plume. It is customary for fireworks crews to perform test shots of a single pyrotechnic device at a time before the actual event; when

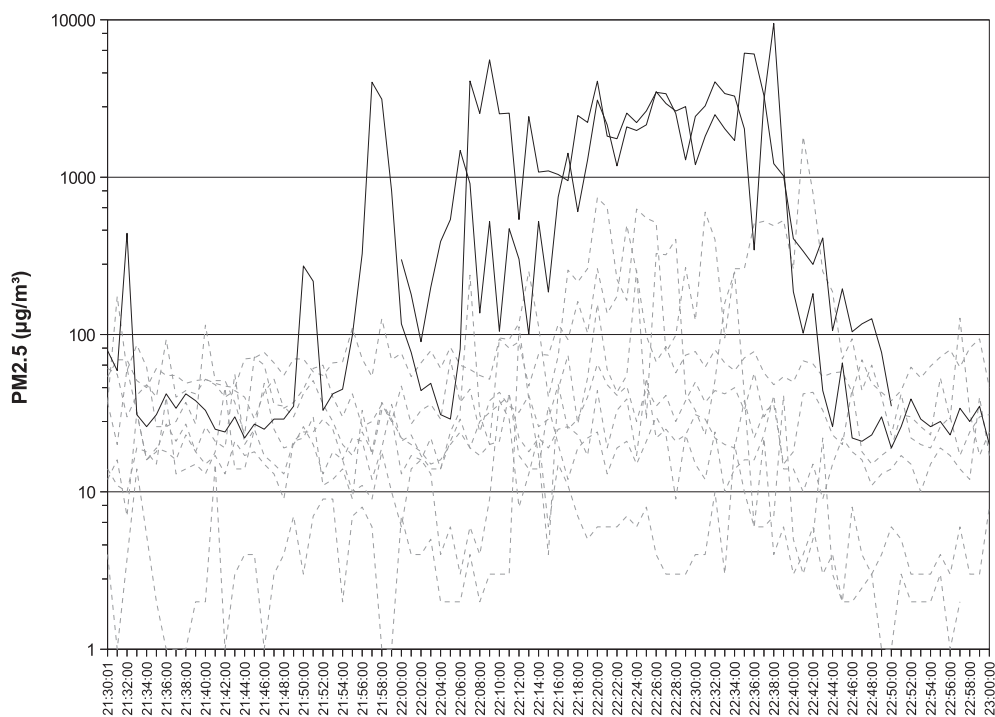


Fig. 1. Sidepack™ (photometer) PM_{2.5} levels measured at all 9 locations predicted to receive the smoke plume during the summer 2007 Montréal international fireworks competition. In black are the two highest data series obtained when measurements were taken directly in the plume. Displays started at 10 PM and ended at 10 h 30 PM.

sampling occurred directly downwind, these test shots registered in our data as the peaks that can be seen before 22 h (event start).

The mass concentration levels for the breathing height filters collected at the “predicted sites” ranged from 15 to 1510 $\mu\text{g m}^{-3}$. At one of the “predicted site” locations where people attend the fireworks (the Jacques-Cartier bridge), the highest levels were measured some 10 m above the ground. Sidepak™ minute concentration levels, integrated mathematically over the duration of the sampling time (1 h), showed results similar to gravimetric results (8–1450 $\mu\text{g m}^{-3}$). The sum of metal mass concentration levels, measured by ICP-MS, ranged from <1 to 51 $\mu\text{g m}^{-3}$. For those filters from the “predicted sites”, which were weighed, the total metal mass always accounted for less than 4.5% of the total mass of particles in the filters.

The hierarchical cluster analysis classified 8 filters out of 18 as “Exposed” to the fireworks smoke plume. Fig. 2 presents the elemental composition in particulate matter of “Exposed” and “Non-exposed” filters. In this figure, ED-XRF measurements are presented only for elements not measured by ICP-MS. Those elements measured which showed a noticeable increase in exposed filters were: K, Cl, Al, Mg, and Ti (Fig. 2). Measurements of these elements were also always above the LOD of the ICP-MS and ED-XRF methods in exposed filters. Results below the LOD occurred more often in non-exposed filters. Elemental levels on field blank filters were either below or close to the LOD and always much lower than the exposed filters (data not shown).

4. Discussion

This study documents particulate exposure of spectators to outdoor fireworks displays. It shows that spectators and residents in the fireworks plume, and less than 2 km from the launch, may be exposed to levels as high as 10 000 $\mu\text{g m}^{-3}$ of fine particles for a very short period of time. Levels can be sustained above

1000 $\mu\text{g PM}_{2.5} \text{ m}^{-3}$ during a display (i.e. about 45 min). The particles emitted during fireworks displays contain unusually high levels of specific elements. The PM_{2.5} exposure levels measured over 1 h during fireworks displays in Montréal can be up to 50 times the urban mean annual hourly concentration (<20 $\mu\text{g m}^{-3}$) and more than 10 times the maximal hourly concentration ($\sim 120 \mu\text{g m}^{-3}$).

The high PM_{2.5} levels drop rapidly to background levels ($\sim 10\text{--}40 \mu\text{g m}^{-3}$) once the display is over. Given that fireworks last for a short period of time, it is important to integrate the data over an hour to most precisely estimate personal exposure. It is worth mentioning that while levels at measurement sites located in proximity to the fireworks launch pad (<2 km) drop quickly after the event, the emitted particles remain in the atmosphere for a longer period of time and travel in space, according to meteorological conditions. At a fixed ambient monitoring site located 14 km downwind from the launch site, levels more than five times the urban mean annual hourly concentration ($\sim 10 \mu\text{g PM}_{2.5} \text{ m}^{-3}$) have been measured (C. Gagnon, City of Montréal, fall 2000, personal communication).

Compared to other studies where ambient outdoor particles were measured during fireworks displays, levels measured in the plume in our study were roughly one order of magnitude higher. For example, fine particulate levels (PM₁₀) measured by Vecchi et al. (2008) over 4 h, reached a maximum of less than 70 $\mu\text{g m}^{-3}$ during the celebrations for the win of the 2006 FIFA World Cup. Hourly total particulate levels reported by Moreno et al. (2007), following a six day National celebration, reached a maximum level of 180 $\mu\text{g m}^{-3}$. Differences observed between studies are due to the distance of the measurements from the launch site, to the height of the measurement, the duration of sampling and, to whether or not the measurements took place directly in the plume. Vecchi et al. (2008) for instance took measurements at a fixed site on the roof of a University building, about 3 km from the fireworks launch site and the duration of sampling was 4 h. Moreno et al. (2007) sampled

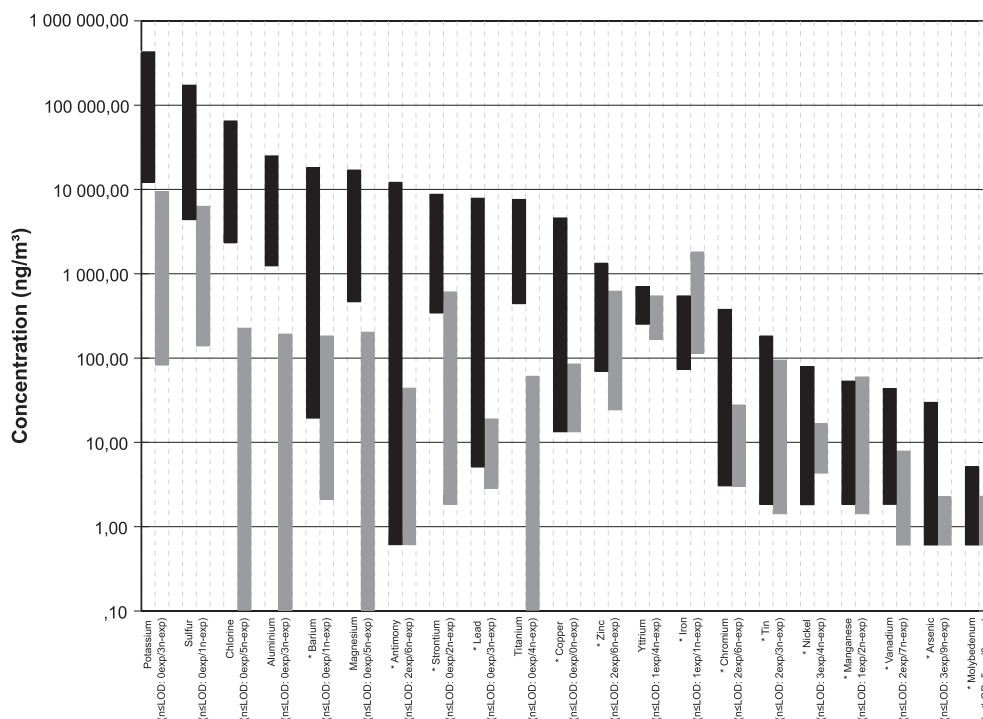


Fig. 2. Maximum and minimum elemental composition in particulate matter of “Exposed” and “Non-exposed” filters during the 2007 International Montréal Competition. The black boxes represent the exposed filters while the grey boxes represent the non-exposed filters. Levels of elements with an “*” were measured with ICP-MS on filters from both “fixed” and “predicted” sites; other elements were measured by ED-XRF on filters from the predicted sites. ED-XRF measurements are presented only for elements not measured by ICP-MS. In all cases, elements showing less than 4 readings above the LOD were discarded. The discarded elements were all from the ED-XRF analysis.

closer to the launch sites (i.e. 1 km) and on an hourly basis but measurements were again taken on building roofs, not in the breathing zone of people attending the displays. Breathing height may, however, be at building height such as in our study where thousands of people attend fireworks on a bridge.

During the displays that we measured, the elements showing the most noticeable increases, at both the “fixed” site and for “personal measurements” (at the “predicted sites”), were K (range non-exposed and exposed filters: [0–9.4 $\mu\text{g m}^{-3}$] and [12.3–434.1 $\mu\text{g m}^{-3}$] respectively), Cl (range non-exposed and exposed filters: [0–0.3 $\mu\text{g m}^{-3}$] and [2.3–65.3 $\mu\text{g m}^{-3}$]), Al (range non-exposed and exposed filters: [0–0.2 $\mu\text{g m}^{-3}$] and [1.2–25.3 $\mu\text{g m}^{-3}$]), Mg (range non-exposed and exposed filters: [0–0.2 $\mu\text{g m}^{-3}$] and [0.5–17.1 $\mu\text{g m}^{-3}$]) and Ti (range non-exposed and exposed filters: [0–0 $\mu\text{g m}^{-3}$] and [0.4–7.7 $\mu\text{g m}^{-3}$] respectively). Ba, Sr, Pb, S, Cu also showed important increases but levels of “exposed” filters slightly overlapped with those of “non-exposed” filters. High levels of these trace elements have been reported following both day-long celebrations and short-term displays (e.g. Vecchi et al., 2008; Moreno et al., 2007; Perry, 1995). Although others have suggested that Sr is particularly characteristic of fireworks aerosols (Walsh et al., 2009; Vecchi et al., 2008) we observed overlap in the Sr concentrations between “exposed” and “non-exposed” filters as well as a greater increase in other elements (see above).

Little is known about the health effects of sub-daily peaks of ambient fine particles. Most studies on the acute health effects of exposure to ambient fine particles have considered daily exposure levels (U.S. EPA, 2004). Furthermore, to our knowledge, very few studies, namely Bach et al., 1972 and Hirai et al., 2000, have reported on the effects of fireworks particulate emissions. Evidence suggests though that inhalation of fumes containing high levels of specific elements such as chlorine can cause mucosal irritation and acute respiratory distress syndrome (Babu et al., 2008). Further

studies are needed to document the health effects of peaks of fine particles, especially in persons with pre-existing diseases such as asthma and cardiovascular diseases. Furthermore, studies are needed to document exposure to species of the elements emitted by fireworks and to assess the toxicity of particles of various chemical compositions in inhaled fireworks smoke such as those containing high levels of Al and Ti.

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