Particulate Oxidative Burden Associated with Firework Activity

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Firework events are capable of inducing particulate matter (PM) episodes that lead to exceedances of regulatory limit values. As short-term peaks in ambient PM concentration have been associated with negative impacts on respiratory and cardiovascular health, we performed a detailed study of the consequences of firework events in London on ambient air quality and PM composition. These changes were further related to the oxidative activity of daily PM samples by assessing their capacity to drive the oxidation of physiologically important lung antioxidants including ascorbate, glutathione and urate (oxidative potential, OP). Twenty-four hour ambient PM samples were collected at the Marylebone Road sampling site in Central London over a three week period, including two major festivals celebrated with pyrotechnic events: Guy Fawkes Night and Diwali. Pyrotechnic combustion events were characterized by increased gas phase pollutants levels (NO_x and SO_2), elevated PM mass concentrations, and trace metal concentrations (specifically Sr, Mg, K, Ba, and Pb). Relationships between NO_x, benzene, and PM_{10} were used to apportion firework and traffic source fractions. A positive significant relationship was found between PM oxidative burden and individual trace metals associated with each of these apportioned source fractions. The level of exposure to each source fraction was significantly associated with the total OP. The firework contribution to PM total OP, on a unit mass basis, was greater than that associated with traffic sources: a 1 μg elevation in firework and traffic PM fraction concentration was associated with a 6.5 $\pm$ 1.5 OP^T μg^{-1} and 5.2 $\pm$ 1.4 OP^T μg^{-1} increase, respectively. In the case of glutathione depletion, firework particulate OP (3.5 $\pm$ 0.8 OP^{GSH} μg^{-1}) considerably exceeded that due to traffic particles (2.2 $\pm$ 0.8 OP^{GSH} μg^{-1}). Therefore, in light of the elevated PM concentrations caused by firework activity and the increased oxidative activity of this PM source, there is value in examining if firework derived PM is related to acute respiratory outcomes.

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Introduction

Anthropogenic emissions from firework displays are responsible for particulate matter (PM) episodes with the greatest concentrations measured in the United Kingdom (*1*). Nightly celebrations occur annually over a two to three week period to celebrate Diwali and Guy Fawkes Night during October and November. Small size pyrotechnic events (including hand-held sparklers, cherry bombs, roman candles representing British category 2 and US class 1.4G) are set off by individuals in parks and back gardens. Larger professional displays (British category 4 and US class 1.3G) also occur where pyrotechnics are projected to attain explosion heights of up to 200 m. Regardless of the type of firework ignited, the combustion products are similar: high SO_2 and NO gaseous releases (*3, 2*), dense metal-rich PM plumes with a large organic carbon component (*4*).

The firework physicochemical signature has been extensively characterized internationally: Washington State, US (*5*); California, US (*6*); Texas, US (*7*); Montreal, Canada (*8*), Hisar, Hyderabad, and Thumba, India (*10, 9, 2*); Beijing, China (*11*); Saalbach, Austria (*12*); United Kingdom (*1*); Mainz, Germany (*4*); Milan, Italy (*13*); and Valencia, Spain (*3*). These previous reports unanimously agree firework activity contributes to elevated ambient particulate metal concentrations in respirable size fraction (i.e., PM with an aerodynamic diameter of <10 μm, PM_{10}). Fireworks and related explosives account for substantial airshed emissions in the UK: 3 tonnes Cu, 10 tonnes Sr, 65 tonnes Ba, 73 tonnes Mg, and 100 tonnes K (*14*). These ambient emissions for Cu and Mg represented 6 and 8% respectively of annual atmospheric releases in the UK during 2000 (*14*). Each of these metals acts as a coloring agent and are paired with oxidizers, including nitrates, sulfates, and perchlorates. This is known as black powder and approximately 74% consists of KNO_3, 10% sulfur, and 16% carbon in the form of charcoal (*15*). Pyrotechnic displays on celebratory dates often cause PM_{10} mass concentrations to exceed 24 h limit values (50 $\mu g\ m^{-3}$) as set by the European Directive 2008/50/EC. Even though this concentration is not to be exceeded on more than 35 days annually, the UK has declared in its National Air Quality Strategy that it is inappropriate to control air quality infringements resulting from social and cultural activities, including bonfires and pyrotechnic displays (*16*).

To date only a handful of small scale studies have addressed the potential adverse health effects stemming from exposure to firework emissions. Pulmonary function monitored in nine patients (seven healthy and two with chronic respiratory disease) exposed to a six times increase in PM_{10} (110 $\mu g\ m^{-3}$ five hour experiment average which included a fifteen minute peak attaining concentrations in excess of 3.8 $mg\ m^{-3}$) from firework events was noted to cause a significant maximal midexpiratory flow rate decrease in the susceptible individuals (*17*). A potential impact on lung function was also supported by observations from a 1972 study where a 113% increase in emergency room visits by individuals with chronic respiratory disease was reported following a firework episode in Honolulu (*18*). More recently, Becker et al. (*19*) reported a near fatal and a fatal asthma exacerbation of two severely asthmatic children following exposure to elevated PM concentration from hand-held fireworks.

Despite the extensive use of fireworks to commemorate special events internationally, no literature has yet described the toxicity associated with firework PM on the respiratory system. We therefore investigated toxicologically relevant features of ambient PM collected over a three week period

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in central London during a period of intense firework activity including Diwali and Guy Fawkes Night. An oxidative potential (OP) metric was formulated for each daily PM sample based on their capacity to deplete antioxidants from a validated synthetic respiratory track lining fluid (RTLF) (*20*). The biological pertinence of this acellular model relates to the contention that inhaled PM mediates adverse health effects through the induction of oxidative stress at the air-lung interface (*21*). Generation of reactive oxygen species has been demonstrated following PM challenge in various extracellular and cellular compartments (*21*), with evidence that different components (biological material, polycyclic aromatic hydrocarbons/quinones, trace metals) can cause oxidative stress through different pathways. Thus the OP metric used in this study integrates the contribution of a range of PM components into a single biologically informative expression.

Materials and Methods

Sampling Site Description. Sampling was conducted at the Marylebone Road kerbside site in central London, UK. Details of sampling site have been previously reported (*22*). Given the proximity of the sampling site to traffic emissions, considerable PM and gas species contribution from traffic sources was found. Fireworks and bonfires were ignited across the city during the sampling period by individuals and at large-scale organized public displays. Large-scale organized events commenced after dusk and extended for approximately 30 min on November second (8 displays), third (17 displays), fourth (4 displays), fifth (6 displays), ninth (2 displays), and 10th (2 displays), 2007. The number of firework incidences reported to the London Fire Brigade was used as a surrogate measure of firework displays ignited by individuals. A total of 2427 incidences were logged in the inner London Boroughs over the first ten days of November 2007, significantly greater than the outer Boroughs (1720) (*23*). Specifically in the London Borough of Westminster, an inner city borough in which the Marylebone Road sampling site is located, 99 firework related incidences occurred with 26 of these events reported in the immediate Marylebone area (*23*). An indication of the number of bonfires lit by individuals was also estimated using London Fire Brigade statistics: 262 incidences of runaway bonfires, recorded as secondary fires (nonproperty location fires free of injury), were logged on November 5, 2007, representing the highest number of calls during the year (*23*).

Instrumentation. PM with an aerodynamic diameter between 1 and 10 μm (PM_{1-10}) was collected on polyurethane foams (PUFs) using the Airborne Sample Analysis Platform (Thermo ASAP) located on the roof of the monitoring station at the Marylebone Road site. Foams were exposed for 24 h periods at 200 L min^{-1}. PUFs were changed daily at 9:30GMT for samples collected between October 24, 2007 and November 6, 2007 and at 15:00GMT November 7, 2007 to November 13, 2007. PM collected on these foams was used for trace metal analysis and assessment of PM oxidative potential.

Ambient PM_{10} mass concentrations were measured by the UK Automatic Urban and Rural Network at the Marylebone Road sampling site using a Tapered Element Oscillating Microbalance (TEOM) with 15 min resolution. In addition, gaseous pollutant concentrations (SO_2, NO, NO_2) and meteorological parameters (temperature, wind direction, and wind speed) were measured on an equivalent time basis. Ambient benzene concentrations were measured at an hourly resolution by Defra's Automatic Hydrocarbon Monitoring Network using a Perkin-Elmer Online system. This consisted of an ATD400, sampling onto a carbon impregnated trap at −30 °C for 40 min every hour and an Autosystem XL gas chromatograph with a PLOT column and flame ionization detector.

Chemicals and Chelex Water Preparation. All water, unless otherwise stated, was deionized and ultrafiltered using an Elga-stat filtration system. All chemicals used were obtained from Sigma Chemical Company Ltd. and were of analytical grade. Ultrapure Chelex100 resin treated water was utilized to eliminate background metal contamination when assessing oxidative potential (*20*).

Sample Preparation. PM_{1-10} samples collected on PUFs were extracted in a 5% high pressure liquid chromatography (HPLC)-grade methanol prepared in Chelex resin treated ultrapure water, pH 7.0 to achieve a final PM concentration of 150 μg mL^{-1}. To ensure PM suspensions were homogeneous, resuspension was performed using a probe sonicator (MSE Soniprep150, 23 kHz, generator with a titanium probe) operated at an amplitude of 15 μm for 30 s. Further details are provided in the Supporting Information regarding the extraction efficiency of the PUFs and comparison to hourly PM_{1-10} mass concentrations measurements. Interexperimental positive (residual oil fly ash) and negative (M120, carbon black) PM control samples were also resuspended using the same procedure. Compositional details of the residual oil fly ash (*24, 25*) and M120 (*27, 26*) control particles have been published previously.

Assessment of Oxidative Potential. The oxidative potential of PM was assessed *in vitro* by measuring the depletion of antioxidants by standardized concentrations of resuspended particulate in a synthetic RTLF. This chemical model contained physiologically relevant concentrations (200 μM) of urate (UA), ascorbate (AA), and glutathione (GSH) adjusted to pH 7.0 and incubated at 37 °C with equal mass concentrations of PM samples (50 μg mL^{-1}) for four hours. Briefly, AA and UA concentrations were determined using reverse phase HPLC with electrochemical detection (Jones Chromatography, Hengoed, Wales). Total glutathione (GSx) and glutathione disulfide (GSSG) concentrations were determined with the GSSG-reductase-5,5′-dithio-bis(2-nitrobenzoic acid) (DNTB) recycling assay. Subtracting two times the measured GSSG from the GSx concentration yielded GSH. Further information regarding antioxidant measurements have been described elsewhere (*28*). The Supporting Information contains details describing the calculation method of the AA and GSH OP metrics.

Total PM Metal Analysis. An aqua regia solution was prepared in Chelex-100 resin treated water. This digestion media was added to the resuspended PM solution such that final concentrations of 2.8% HNO_3, 5.1% HCl, and 7.5 μg mL^{-1} PM were achieved. Samples were digested in a microwave system (Mars 240/50) for 30 min at 180 °C on full power (1600W). Following digestion, samples were further diluted with Chelex-100 resin treated water to attain a final acid and PM concentration of ca. 1.9% HNO_3, 3.4% HCl, and 5 μg mL^{-1} PM. Concentrations of K, Ca, Mg, Fe, Cu, Zn, Sr, V, Ba, and Pb in solution were determined using inductively coupled plasma mass spectrometry (ELAN DRC ICP-MS, MSF008). Dilutions of a certified multielement standard solution (VI CertiPUR Merck, Lot. No.OC529648) were used for calibration. Six NIST 1648a Urban PM control samples and water blanks were run in addition to samples; 3σ of the water blank elemental concentrations were used to establish minimum detection limits.

Results and Discussion

Air Mass Origin. The dominating parameters influencing the concentration of PM species measured at the Marylebone Road sampling site were local and regional emissions. Pyrotechnic and biomass burning (in the form of Guy Fawkes Night celebratory bonfires) were known to occur locally but

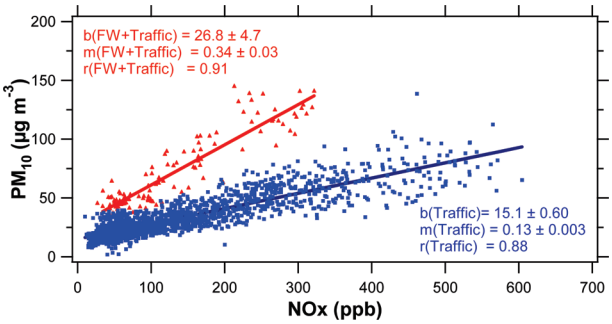

FIGURE 1. Relationship between 15 min mean NO_x and PM_{10} mass concentrations for the entire campaign period. The fraction of PM_{10} derived from vehicle sources is colored in blue squares. Red triangular markers indicate the PM attributed to firework and bonfire events as estimated by NO_x concentrations.

also took place across the United Kingdom, likely contributing to an elevated regional PM background level. The relevance of each combustion event, local or regional, to the sampling site was influenced by varying wind patterns. However, proximity of the known firework events to the sampling site and PM_{10} episode timings implicated local London combustion events with the observed PM episodes. A single large-scale firework event (the Lord Mayor Show) occurred at 18:30GMT on November 10, 2007 along the River Thames (3 km southeast of the sampling site) but did not result in a PM_{10} episode at Marylebone Road. Meteorological data obtained from Heathrow Airport indicated winds were from the northwest inhibiting the firework plume from reaching the sampling site. In contrast, firework activity on November 3 and 9, 2007 (at locations north and northwest of Marylebone Road) enhanced the magnitude of measured PM_{10} concentration given the sampled air mass on these days originated from the north and northwest, respectively. The highest PM_{10} concentrations measured during the campaign, however, occurred on the early morning of November 5, 2007 and were associated with an air mass which traveled through London from the northeast. Unlike all other discussed events, the latter period was dominated by high pressure conditions with near stagnant wind speeds (1.24 ± 0.44 m s^{-1}) which limited PM dispersion.

Nitrogen Oxides (NO_x) and PM_{10} Relationship. A relationship between NO_x and PM_{10} mass concentration was used to determine the fraction of PM_{10} attributable to differing combustion contributions (Figure 1) (*29, 30*). Complete regression source apportionment details are described in the Supporting Information. Briefly, this regression analysis segregated the data set into two groups to represent pyrotechnics/bonfires and traffic (*31*) and traffic alone (including vehicular tail pipe emissions, road dust resuspension, and tire and brake pad wear) sources such that each group was characterized by distinct PM_{10}-NO_x slope. The former mass concentration grouping corresponded to (i) periods of organized firework-bonfire displays, November 3, 2007; (ii) Guy Fawkes Night, November 4 and 5, 2007; (iii) Diwali, November 9, 2007. Parallel NO_x increases with firework activity have been identified previously (*2, 32*) and were suggested to originate from the black powder KNO_3 component (*4*). Allan et al. (*33*) evaluated the contribution of biomass combustion sources to regional NO_x concentrations during the REPARTEE 2 campaign (October 16, 2007-November 9, 2007) which overlapped with the current study: a high resolution time-of-flight Aerosol Mass Spectrometer (AMS) was operated at the Regent's Park urban background site (further site details are provided in the Supporting Information). The AMS measured $PM_{2.5}$ total organics concentrations were deconvolved using Positive Matrix Factorization into four factors profiling different source attributions: oxygenated organic aerosol, cooking organic aerosol, solid fuel organic aerosol (SFOA), and hydrocarbon-like organic aerosol (HOA). A univariate linear regression between HOA and NO_x was performed in additional to a bilinear fit including both HOA and SFOA factors with NO_x. This latter approach did not yield improved Pearson r-values compared to univariate regression results. The authors concluded that despite the NO_x emissions from solid fuel combustion, on the regional scale during REPARTEE 2, traffic dominated NO_x emissions relative to solid fuel combustion in central London as more local sources were present. Thus, the enhanced rate of PM_{10} emission relative to NO_x identified via the regression analysis in the current study is likely isolated to pyrotechnic combustion sources and not from bonfire or other solid fuel combustion emissions.

The validity of assigning the lower PM_{10}-NO_x slope to traffic-related emissions was evaluated by considering two week periods void of firework and bonfire activity before and after the campaign (October 9-24, 2007 and November 15-28, 2007). A similar traffic PM_{10}-NO_x relationship was found for these periods (slope 0.14 μg m^{-3} ppb^{-1}; y-intercept 19 μg m^{-3}; $r = 0.81$; $p < 0.001$; $N = 2695$) as during the campaign (slope 0.13 μg m^{-3} ppb^{-1}; y-intercept 15 μg m^{-3}; $r = 0.87$; $p < 0.001$; $N = 1817$).

The uncertainty of traffic and firework/bonfire apportioned PM_{10} fractions were determined as the combined uncertainties of each input variable derived in accordance with the ISO Guide to the expression of uncertainty in measurement (GUM) (*34*). Calculation details are provided in the Supporting Information. The average uncertainty for 15 min resolution firework apportioned PM_{10} mass concentrations was 3.7 μg m^{-3}. For the 15 min averaged traffic PM_{10} fraction the uncertainty on mass concentrations was estimated as 1.5 μg m^{-3}.

When interpreting temporal traffic PM_{10} source fraction fluctuations (Figure 2), it is useful to note that the Marylebone Road site is located on the south side of the carriageway in a street canyon such that a vortex is created at sufficiently high wind speeds coming perpendicular to the street (*22, 35, 36*). Consequently, strong southerly winds and those flowing parallel to the street yield increased PM concentrations. Two scenarios may result from northerly wind depending on wind speed: high velocities will cause air recirculation leading to the lowest contribution of local traffic emissions to the site, while low wind speeds enable local traffic emissions to be measured directly and thus the highest PM concentrations. During the campaign, northerly winds were associated with near-stagnant wind conditions (<1 m s^{-1}). Consequentially the maximum traffic component PM_{10} concentration measured was 16.3 ± 14.2 μg m^{-3} (33 ± 26% of the total PM_{10} mass concentration) on average during these periods. In contrast, the lowest concentrations of this source fraction (5.1 ± 7.8 μg m^{-3} or 15 ± 14% of the total PM_{10} mass concentration) were measured when higher wind speeds induced the microscale recirculation effect within this street canyon.

The firework PM component was isolated to episodes which were rapidly dispersed with only acute air quality degradations. These celebratory combustion events included (i) November 3, 2007 19:45GMT - November 4, 2007 3:45GMT (15.7 ± 5.1 μg m^{-3} PM_{10} average), (ii) November 4, 2007 18:15GMT - November 5, 2007 5:00GMT (44.3 ± 17.6 μg m^{-3}), and (iii) November 9, 2007 20:45−23:45GMT (49.9 ± 10.0 μg m^{-3}). This source fraction represented 33 ± 9%, 41 ± 13%, and 60 ± 5% of these total PM_{10} mass concentrations for each of the noted periods.

To further elucidate differences between these two combustion processes and other possible contributing anthropogenic emissions, PM_{1-10} chemical characteristics, PM number concentration, and gaseous SO_2 fluctuations were

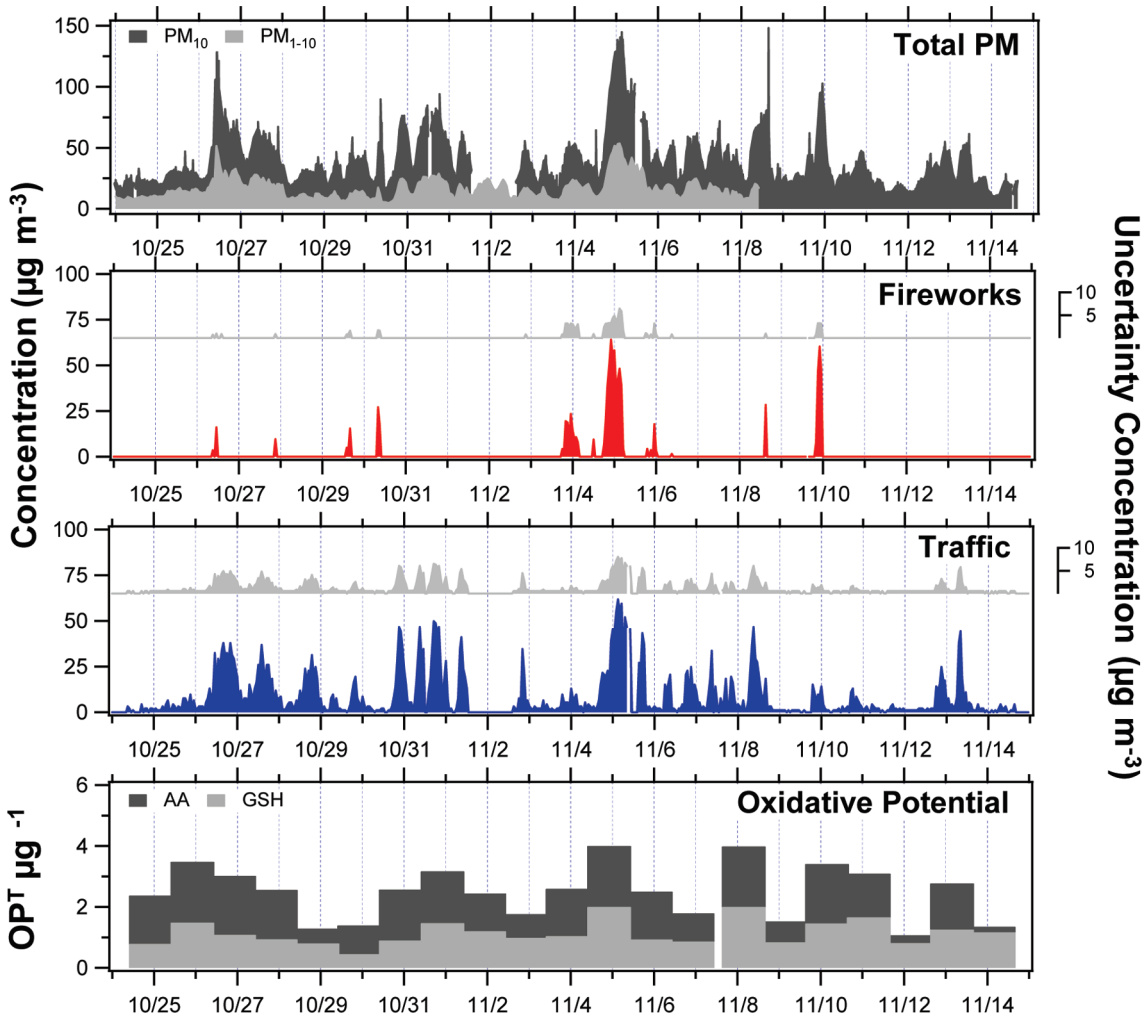

FIGURE 2. Time series of (i) PM_{10} mass concentrations measured by the TEOM (1 h average) and PM_{1-10} mass concentrations estimated by merged SMPS-APS measurements (1 h average). One hour resolution source apportioned PM_{10} firework-bonfire (ii) and traffic (iii) fractions (left axis) with the associated uncertainty for each fraction colored in light gray (right axis). Twenty-four hour averaged PM_{1-10} ascorbate (AA, light gray) and glutathione (GSH, dark gray) oxidative potential per unit mass.

assessed; the latter two are described in the Supporting Information.

Trace Metals. The temporal fluctuations of PM_{1-10} Sr, K, Mg, Ba, and Pb concentrations were found to be similar; the maximum concentration measured for all these metals was for the 24-h sample collected over November 4 to 5, 2007, representing a period of intense pyrotechnic activity (Figure 3-A). An additional rise was observed for the 24-h November 9 to 10, 2007 p.m. sample, also corresponding with a firework combustion period. No significant concentration changes during these celebratory periods were found for metals predominately associated with vehicular nontail pipe emissions (Figure 3-B). Despite the elevated Cu firework emission factors estimated by Passant et al. (*14*), no Cu concentrations increases were found during periods of known firework activity. Ba concentrations reflected firework and traffic emission fluctuations, where the latter was the result of brake pad abrasion (*37, 38*). Following PM size distribution results presented in the Supporting Information, the authors acknowledge that the sampled size fraction (PM_{1-10}) does not represent the total metal concentration associated with firework activity. As instrumentation available for daily PM filter sampling was limited to the 1 and 10 μm cut points, the reported firework PM parameters measured were therefore underestimated given that much of the PM derived from pyrotechnic combustion events was found below 1 μm.

Trace metal enrichment factors were determined for 24-h PM_{1-10} samples collected on November 4−5, 2007 and October 28−29, 2007 relative to the November 13−14, 2007 sample (Figure 4). Pyrotechnic combustion related emissions were sampled during the former as predicted from source apportionment results and the occasion of city-wide organized firework displays. In contrast, the latter two samples were primarily subject to continuous traffic emissions given the lack of apportioned firework PM component in parallel with no organized firework events. The sample collected over Guy Fawkes Night celebrations was associated with large increases of firework combustion derived trace metals. The enrichment factor calculated for the nonfirework period maintained approximately unit values for trace metals without a vehicular source. Ba, Sr, and Pb sustained the largest increases (28-, 25-, and 19-fold, respectively) on the pyrotechnic date considered. However, Ba, unlike Sr and Pb, was also associated with an increase factor of 1.4 on the nonfirework days reflective of a traffic emission contribution.

All of the measured trace metals had the potential of originating from either pyrotechnic or urban sources. To determine the elemental composition associated specifically with firework derived PM, bivariate correlations were performed with Sr and the other measured trace metals. The strongest correlation ($p < 0.0001$, $N = 21$) existed between K ($r = 0.98$), Pb ($r = 0.96$), Ba ($r = 0.92$), and Mg ($r = 0.73$)

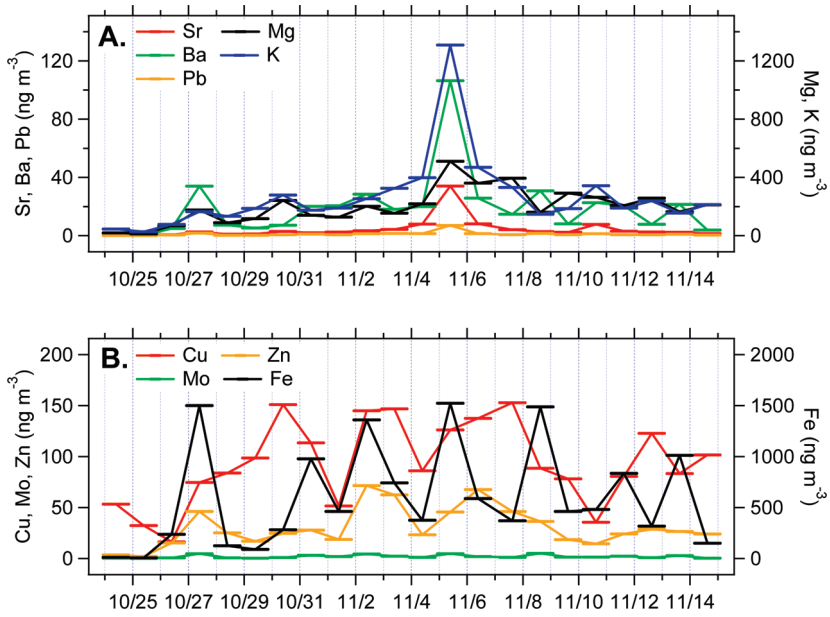

FIGURE 3. Twenty-four hour averaged PM_{1-10} concentrations for metals attributable (A; Sr, Ba, Pb, Mg, K) and not attributable (B; Cu, Mo, Zn, Fe) to firework combustion emissions.

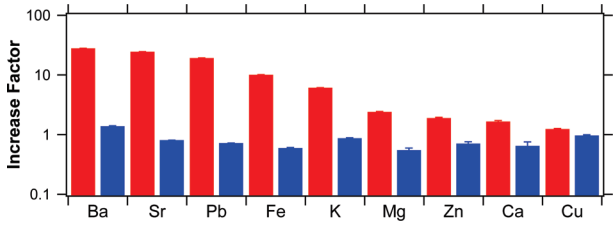

FIGURE 4. Ratio of trace metal concentrations as measured for PM samples run on (1) October 28, 2007 9:30 GMT - October 29, 2007 9:30 GMT (no fireworks events, blue bars) and (2) November 4, 2007 9:30 GMT - November 5, 2007 9:30 GMT (firework events, red bars) to PM samples collected between November 13, 2007 15:00 GMT - November 14, 2007 15:00 GMT.

confirming the elemental firework composition described by previous studies with the exception of Cu (*3, 5*). A weaker significant association was identified with Fe concentrations ($r = 0.43$, $p = 0.05$). No correlation was established between Sr with Ca, Cu, and Zn despite reported use of these species in fireworks as orange ($CaCO_3$, $CaCl_2$, $CaSO_4 \bullet xH_2O$), blue ($CuCO_3$, $CuSO_4 \bullet 5H_2O$, CuCl), and white (ZnO) coloring, respectively (*39*).

Oxidative Potential. Bivariate correlations were conducted with the bulk PM mass and trace metals for the ascorbate and glutathione dependent OP components on a unit mass basis. Individual metals, representative of the source apportioned firework and traffic PM fractions, were all found to be positively associated the OP parameters. A combination of the combustion derived metals were correlated with OP^{GSH} μg^{-1} related to both traffic (Ba, $r = 0.62$, $p = 0.003$; Mo, $r = 0.57$, $p = 0.007$; Fe $r = 0.57$, $p = 0.01$; Cu) and firework (Pb, $r = 0.54$, $p = 0.01$; Sr, $r = 0.48$, $p = 0.03$) emissions. However only traffic emissions related metals were significantly associated with OP^{AA} μg^{-1}: Mo ($r = 0.48$, $p = 0.03$), Fe ($r = 0.47$, $p = 0.03$) and Ba ($r = 0.46$, $p = 0.04$). A subset of the measured trace metals (Zn, Ca, Cu) lacked an association with antioxidant depletion. The oxidative loss of antioxidants from the synthetic RTLF model is sensitive only to intrinsic redox active PM constituents: redox active metals and quinones. With the exception of Fe and Pb, the contribution of the trace metals noted in the bivariate correlation analysis to reactive oxygen species production, and thus AA and GSH depletion, has not been reported in the literature. These species probably represent surrogates of constituents with intrinsic redox active properties which were not quantified.

A heterogeneous panel of metals, representing different source fractions, were found to be predictor/surrogate measures of OP^{AA} μg^{-1} and OP^{GSH} μg^{-1}; the former was related to traffic and the latter was associated with both traffic and firework related combustion products. Consideration of the individual trace metals in a multivariate regression method was not feasible as the colinearity of the metal concentrations would confound results. Multivariate regressions were instead performed between the ascorbate, glutathione, and total OP $(\mu g\, PM_{1-10})^{-1}$ metrics and apportioned PM_{10} source fractions such that OP dose effects were estimated for an increase of each PM source fraction in the ambient airshed. The PM_{10}(traffic), PM_{10}(firework), and PM_{10}(other) fractions were averaged to a 24-h periods to correspond with the ASAP PUF PM_{1-10} sampling intervals. As only transient firework concentrations were measured during the campaign, the validity of averaged daily firework PM_{10} concentrations was assessed based on the number of 15 min measurements included in the 24 h average. For averaging periods comprised of only a single firework concentration measurement ($N = 5$), the timing of the episode was evaluated to avoid inclusion of misclassified firework data points; this possibility is acknowledged given the limitations in the methodology employed to segregated traffic from traffic+firework measurements (Figure 1). For these firework events isolated to a 15 min averaged period, the authors dismiss the likelihood that measurements which occurred during the late morning hours (October 26, 2007 9:00 and November 6, 2007 9:30GMT) were in fact derived from a firework source and were excluded from the regression analysis. A further restraint on the regression analysis was caused by the significant negative correlation ($r = 0.63$, $p = 0.002$) between the PM_{10}(traffic) and PM_{10}(other) fractions, arising as an artifact of the definition of PM_{10}(other) (Equation S10). Consequently, the PM_{10}(other) fraction was excluded from the regression analysis, and the predicted mean contribution of this fraction to each OP metric was calculated from the traffic and firework regression coefficients.

Significance was sustained at the 95% confidence level for all OP metrics when a multivariate model was constructed to explain the measured variance (Table 1). The plot of

TABLE 1. Multivariate Regression Analysis of OP μg^{-1} (Ascorbate, Glutathione, and Total) with PM_{10} Traffic and Firework Fractions[a]

	PM source fraction	explanatory variable			model	
metric	(μg (μg PM_{10})$^{-1}$)	B	SE	p-value	r	p-value
OP^{AA} ug^{-1}	traffic	3.1	1.2	0.05	0.79	0.05
	firework	3.1	1.3	0.05		
	constant	0.4	0.4	0.30		
OP^{GSH} ug^{-1}	traffic	2.2	0.8	0.03	0.89	0.008
	firework	3.5	0.8	0.005		
	constant	0.2	0.2	0.36		
OP^{T} ug^{-1}	traffic	5.2	1.4	0.01	0.90	0.006
	firework	6.5	1.5	0.005		
	constant	0.6	0.4	0.18		

[a] B-values indicate the estimated change in OP μg^{-1} for an increase in 1 μg of each apportioned source fraction. The associated standard errors (SE) for regression coefficients and each model are also presented.

regression residuals against standardized predicted values exhibited random scatter around the zero line for all three OP metric models. The fireworks PM factor was implicated with the greatest increase in OP^{GSH} μg^{-1} and OP^{T} μg^{-1} for each 1 μg dose (GSH: 3.5 ± 0.8 μg^{-1}, $p = 0.005$; Total: 6.5 ± 1.5 μg^{-1}, $p = 0.005$) compared to the traffic fraction (GSH: 2.2 ± 0.8 μg^{-1}, $p = 0.03$; Total: 5.2 ± 1.4 μg^{-1}, $p = 0.01$). Therefore, the firework PM contributed more substantially per unit mass to the PM OP in this acellular model than the traffic related PM_{10} component. Moreover, the predicted oxidative burden associated with the PM_{10}(other) fraction was 0.51 μg^{-1} and 0.96 μg^{-1} for the glutathione and total OP models, respectively. This suggested the bulk of the oxidative activity of the particles was related to the traffic and pyrotechnic sources. In contrast to the GSH and total OP metrics, the oxidative burden associated with the traffic and firework PM_{10} fractions was equivalent (3.1 ± 1.2 μg^{-1}, $p = 0.05$) in the OP^{AA} μg^{-1} regression model. These results further highlight that depletion of each antioxidant is sensitive to a heterogeneous panel of metals. The OP predicted to be derived from the PM_{10}(other) source fraction for the case of ascorbate related oxidative activity was low (0.44 μg^{-1}) compared to the traffic and firework sources, similar to the glutathione and total OP results. It is also important to note when interpreting these results that the reported oxidative potential, in particular for the firework component, was underpredicted: the lower cut point (1 μm) of the sampled size fraction prevented collection of the entire firework PM size distribution as described in the Supporting Information.

In conclusion, this study highlighted distinctions between ambient PM and gas phase species resulting from firework or traffic activity. Furthermore, ambient PM_{10} concentrations were deconvolved into source apportioned fractions which were coupled with measurements of particulate oxidative burden. The *in vitro* PM total OP per unit mass associated with pyrotechnic activity was shown to be significantly greater than that associated with traffic derived PM emissions. From the current study it was not clear if the measured pyrotechnic PM trace metals were the drivers for the measured OP or simply represent surrogates for some unmeasured components. Thus, the authors recommend further examination of a possible relationship between firework exposure and acute respiratory outcomes.

Acknowledgments

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Appendix A

AA	ascorbate
ASAP	airborne sample analysis platform
GSH	reduced glutathione
HPLC	high pressure liquid chromatography
ICP-MS	inductively coupled plasma mass spectrometry
NO_x	nitrogen oxides
OP	oxidative potential
$OP^{T}m^{-3}$	total particulate oxidative burden per cubic meter of sampled air
$OP^{T}\mu g^{-1}$	total particulate oxidative burden per unit mass PM
$OP^{AA}\mu g^{-1}$	particulate OP with respect to AA depletion per unit mass PM
$OP^{GSH}\mu g^{-1}$	particulate OP with respect to GSH depletion per unit mass PM
PM	particulate matter
PM_{10}	particulate matter with an aerodynamic diameter of 10 μm
PM_{1-10}	particulate matter with an aerodynamic diameter between 1 and 10 μm
PUF	polyurethane foams
RTLF	respiratory tract lining fluid
TEOM	tapered element oscillating microbalance

Supporting Information Available

The supplemental methodology details the instrumentation employed for continuous size distribution measurements, sampling location, campaign period, and source apportionment uncertainty calculations. Additional results are included discussing temporal variation of PM physical (size distributed PM number and mass concentrations) and gaseous pollutant (SO_2) characteristics. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Clark, H. New directions. Light blue touch paper and retire. *Atmos. Environ.* **1997**, *31*, 2893–2894.
(2) Ravindra, K.; Mor, S.; Kaushik, C. P. Short-term variation in air quality associated with firework events: A case study. *J. Environ. Monit.* **2003**, *5*, 260–264.
(3) Moreno, T.; Querol, X.; Alastuey, A.; Cruz Minguillón, M.; Pey, J.; Rodriguez, S.; Vicente Miró, J.; Felis, C.; Gibbons, W. Recreational atmospheric pollution episodes: Inhalable metalliferous particles from firework displays. *Atmos. Environ.* **2007**, *41*, 913–922.
(4) Drewnick, F.; Hings, S. S.; Curtius, J.; Eerdekens, G.; Williams, J. Measurement of fine particulate and gas-phase species during the New Year's fireworks 2005 in Mainz, Germany. *Atmos. Environ.* **2006**, *40*, 4316–4327.
(5) Perry, K. D. Effects of outdoor pyrotechnic displays on the regional air quality of western Washington State. *J. Air Waste Manage. Assoc.* **1999**, *49*, 146–155.
(6) Liu, D. Y.; Rutherford, D.; Kinsey, M.; Prather, K. A. Real-Time Monitoring of Pyrotechnically Derived Aerosol Particles in the Troposphere. *Anal. Chem.* **1997**, *69*, 1808–1814.
(7) Dutcher, D. D.; Perry, K. D.; Cahill, T. A.; Copeland, S. A. Effects of indoor pyrotechnic displays on the air quality in the Houston astrodome. *J. Air Waste Manage. Assoc.* **1999**, *49*, 156–160.
(8) Joly, A.; Smargiassi, A.; Kosatsky, T.; Fournier, M.; Dabek-Zlotorzynska, E.; Celo, V.; Mathieu, D.; Servranckx, R.; D'amours, R.; Malo, A.; et al. Characterisation of particulate exposure during fireworks displays. *Atmos. Environ.* 2010.
(9) Kulshrestha, U. C.; Nageswara Rao, T.; Azhaguvel, S.; Kulshrestha, M. J. Emissions and accumulation of metals in the atmosphere due to crackers and sparkles during Diwali festival in India. *Atmos. Environ.* **2004**, *38*, 4421–4425.
(10) Babu, S. S.; Moorthy, K. K. Anthropogenic impact on aerosol black carbon mass concentration at a tropical coastal station: A case study. *Curr. Sci.* **2001**, *81*, 1208–1214.
(11) Wang, Y.; Zhuang, G.; Xu, C.; An, Z. The air pollution caused by the burning of fireworks during the lantern festival in Beijing. *Atmos. Environ.* **2007**, *41*, 417–431.

(12) Steinhauser, G.; Sterba, J. H.; Foster, M.; Grass, F. Heavy metals from pyrotechnics in New Years Eve snow. *Atmos. Environ.* **2008**, *42*, 8616–8622.
(13) Vecchi, R.; Bernardoni, V.; Cricchio, D.; D'Alessandro, A.; Fermo, P.; Lucarelli, F.; Nava, S.; Piazzalunga, A.; Valli, G. The impact of fireworks on airborne particles. *Atmos. Environ.* **2008**, *42*, 1121–1132.
(14) Passant, N. *Emission factors programme task 1: summary of simple desk studies*, DEFRA: London, United Kingdom, 2003.
(15) Ellern, H. *Modern Pyrotechnics:Fundelmentals of Applied Physical Pyrochemistry*; Chemical Pub. Co.: New York, NY, 1961.
(16) Department of the Environment *The United Kingdom National Air Quality Strategy*; Department of the Environment and the Scottish Office; 1997.
(17) Merrill Smith, R.; Dinh, V. D. Changes in forced expiratory flow due to air pollution from fireworks. Preliminary report. *Environ. Res.* **1975**, *9*, 321–331.
(18) Bach, W.; Dickinson, L.; Weiner, B.; Costello, G. Some adverse health effects due to air pollution from fireworks. *Hawaii Med. J.* **1972**, *31*, 459–465.
(19) Becker, J. M.; Iskandrian, S.; Conkling, J. Fatal and near-fatal asthma in children exposed to fireworks. *Ann. Allergy Asthma Immunol.* **2000**, *85*, 512–513.
(20) Mudway, I. S.; Stenfors, N.; Duggan, S. T.; Roxborough, H.; Zielinski, H.; Marklund, S. L.; Blomberg, A.; Frew, A. J.; Sandstrom, T.; Kelly, F. J. An in vitro and in vivo investigation of the effects of diesel exhaust on human airway lining fluid antioxidants. *Arch. Biochem. Biophys.* **2004**, *423*, 200–212.
(21) Li, N.; Hao, M.; Phalen, R. F.; Hinds, W. C.; Nel, A. E. Particulate air pollutants and asthma: A paradigm for the role of oxidative stress in PM-induced adverse health effects. *Clin. Immunol.* **2003**, *109*, 250–265.
(22) Charron, A.; Harrison, R. M. Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere. *Atmos. Environ.* **2003**, *37*, 4109–4119.
(23) London Community Safety Partnership. *Halloween and fireworks in London - 2007*, London, United Kingdom, 2007.
(24) Costa, D. L.; Dreher, K. L. Bioavailable transition metals in particulate matter mediate cardiopulmonary injury in healthy and compromised animal models. *Environ. Health Perspect.* **1997**, *105 Suppl 5*, 1053–1060.
(25) Dreher, K. L.; Jaskot, R. H.; Lehmann, J. R.; Richards, J. H.; McGee, J. K.; Ghio, A. J.; Costa, D. L. Soluble transition metals mediate residual oil fly ash induced acute lung injury. *J. Toxicol. Environ. Health, Part A* **1997**, *50*, 285–305.
(26) Zielinski, H.; Mudway, I. S.; Bérubé, K. A.; Murphy, S.; Richards, R.; Kelly, F. J. Modeling the interactions of particulates with epithelial lining fluid antioxidants. *Am. J. Physiol. Lung Cell. Mol. Physiol.* **1999**, *277*, L719–L726.
(27) Miller, C. A.; Linak, W. P.; King, C.; Wendt, J. O. L. Fine particle emissions from heavy fuel oil combustion in a firetube package boiler. *Combust. Sci. Technol.* **1998**, *134*, 477–502.
(28) Godri, K. J.; Harrison, R. M.; Evans, T.; Baker, T.; Dunster, C.; Mudway, I. S.; Kelly, F. J. Increased oxidative burden associated with the traffic component of ambient particulate matter at roadside and urban background schools sites in Greater London. *Part. Fibre Toxicol.* 2010.
(29) Fuller, G. W.; Green, D. Evidence for increasing concentrations of primary PM10 in London. *Atmos. Environ.* **2006**, *40*, 6134–6145.
(30) Harrison, R.; Deacon, A.; Jones, M.; Appleby, R. Sources and processes affecting concentrations of PM10 and PM2.5 particulate matter in Birmingham (U.K.). *Atmos. Environ.* **1997**, *31*, 4117.
(31) Glasius, M.; Ketzel, M.; Wåhlin, P.; Jensen, B.; Mønster, J.; Berkowicz, R.; Palmgren, F. Impact of wood combustion on particle levels in a residential area in Denmark. *Atmos. Environ.* **2006**, *40*, 7115–7124.
(32) Wehner, B.; Wiedensohler, A.; Heintzenberg, J. Submicrometer aerosol size distributions and mass concentration of the Millennium fireworks 2000 in Leipzig, Germany. *J. Aerosol Sci.* **2000**, *31*, 1489–1493.
(33) Allan, J. D.; Williams, P. I.; Morgan, W. T.; Martin, C. L.; Flynn, M. J.; Lee, J.; Nemitz, E.; Phillips, G. J.; Gallagher, M. W.; Coe, H. Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities. *Atmos. Chem. Phys.* **2010**, *10*, 647–668.
(34) International Organisation for Standardisation. *Guide to the Expression of Uncertainty in Measurement (GUM)*; ISO: Geneva, 1995.
(35) Charron, A.; Harrison, R. M. Fine (PM2.5) and coarse (PM2.5−10) particulate matter on a heavily trafficked London highway: Sources and processes. *Environ. Sci. Technol.* **2005**, *39*, 7768–7776.
(36) Scaperdas, A.; Covile, R. N. Assessing the representativeness of monitoring data from an urban intersection site in central London, UK. *Atmos. Environ.* **1999**, *33*, 661–674.
(37) Boulter, P. G. *A review of emission factors and models for road vehicle non-exhaust particulate matter*, TRL Limited: Wokingham, United Kingdom, 2006.
(38) Gietl, J. K.; Lawrence, R. G.; Thorpe, A. J.; Harrison, R. M. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmos. Environ.* **2010**, *44*, 141–146.
(39) Steinhauser, G.; Klapötke, T. M. Green" pyrotechnics: A chemists' challenge. *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347.

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