Atmospheric Environment 178 (2018) 101–108

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Low hygroscopicity of ambient fresh carbonaceous aerosols from pyrotechnics smoke

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ARTICLE INFO

Keywords:
Fireworks smoke
Ultrafine particles
Fine mode aerosols
Carbonaceous aerosols
Photoacoustic extinctiometer (PAX)
Nephelometer
Hygroscopicity

ABSTRACT

Pyrotechnics (fireworks) displays are common for many cultures worldwide, with Independence Day celebrations occurring annually on July 4th as the most notable in the U.S. Given an episodic nature, fireworks aerosol properties are poorly characterized. Here we report observations of optical properties of fresh smoke emissions from Independence Day fireworks smoke sampled at Los Alamos National Laboratory, New Mexico U.S.A. on 4–5 July 2016. Aerosol optical properties were measured with a photoacoustic extinctiometer (PAX, DMT, Inc., Model 870 nm) at low RH < 30% and a humidity controlled nephelometry system (Ecotech, Inc., 450 nm Aurora). 'Dry' light scattering coefficient (σ_{sp}) increased from background < 15 Mm^{-1} reaching 120 Mm^{-1} (450 nm) as a 2-min event peak, while the absorption coefficient increased from background of 0.5–4.4 Mm^{-1} (870 nm). The event peak occurred at 00:35 on 5 July 2016, ~3 h after local fireworks events, and decreased to background by 04:00 on 5 July 2016, showing well mixed aerosol properties. A notable result is that the aerosol hygroscopic response, as characterized by the ratio of wet to dry light scattering or *f*(RH = 85%), declined to 1.02 at the peak fireworks influence from a background ~1.7. Strong wavelength dependence of light scattering with Ångström exponent ~2.2 throughout the event showed a size distribution dominated by sub-micrometer particles. Likewise, single scattering albedo at 870 nm remained constant throughout the event with $\omega = 0.86 \pm 0.03$, indicating light absorbing carbon, though not dominant, was mixed with organic carbon. Subsequent laboratory testing with ground-level sparklers showed that pyrotechnics smoke can generate a strong hygroscopic response, however. As confirmed with chemical analysis, the chemistry of the fireworks was key to defining the hygroscopic response. Sparkler smoke was dominated by salt species such as hygroscopic potassium chloride while it lacked the black powder explosives in aerial fireworks that contribute organic and elemental carbon to its non-hygroscopic smoke.

1. Introduction

1.1. Particulate material ($PM_{2.5}$) and its air quality impacts

Particulate material, particularly the fine fraction, has important impacts on atmospheric chemistry and optics. Particulate matter with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$) is a specific parameter of interest to human health, atmospheric visibility, and climate. $PM_{2.5}$ has primary and secondary sources; it is responsible for substantial atmospheric light extinction, penetrates deeply into the human lungs, and is a source of cloud condensation nuclei. Traditionally in the U.S., the regulatory focus has been on $PM_{2.5}$ as the basis for human health impacts (Pope and Dockery, 2006). Recently, interest has also developed in D_p < 1 μm (PM_1) and ultrafine particles (D_p < 100 nm) which often dominate number concentrations freshly emitted from combustion sources (Carrico et al., 2016a); the European Union currently has regulatory statutes addressing ultrafine particles. The sources of these particles are diverse and include many anthropogenic contributions, largely from combustion sources, as well as from new particle formation from natural and anthropogenic precursors. Here we examine the microphysical properties of 2–3 h old smoke from the combustion of pyrotechnics (fireworks) associated with the U.S. Independence Day celebration in 2016.

1.2. Fireworks emissions and air quality

Fireworks displays are common globally across many cultures, associated with select secular and religious events. Emissions from fireworks represent a distinct though transient impact on local to regional air quality. In the U.S., the most important fireworks event is

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https://doi.org/10.1016/j.atmosenv.2018.01.024
Received 27 June 2017; Received in revised form 28 December 2017; Accepted 13 January 2018
Available online 31 January 2018
1352-2310/

Independence Day on July 4th, with 75% of professional and 90% of retail fireworks sales associated with the event according to the American Pyrotechnics Association (APA). Moreover, fireworks sales have increased from 41 to 285 million pounds of fireworks from 1980 to 2015 in the U.S. alone (APA data). In 2015, revenues from consumer sales were $0.76 billion vs. $0.34 billion for display fireworks (APA data). Thus, the emissions in the U.S. are distributed beyond major professional displays and likely track population density among other factors. Differences are expected as a function of height, as consumer fireworks are closer to ground level vs. those in professional displays.

Gas-phase and particle emissions from fireworks may differ substantially from those from fuels combustion. For example, ozone formation can be impacted by fireworks, as they can serve as a direct formation mechanism for ozone in addition to emission of precursors (Attri et al., 2001). Some studies have shown some elevated NO_x while other studies have shown negligible impacts on NO_x and ozone (Mandal et al., 2012; Parkhi et al., 2016). Due to its oxidative capacity fireworks smoke has been implicated as a health risk for acute cardio-respiratory effects (Godri et al., 2010).

1.3. Particulate material properties from fireworks smoke

Nearly universally, observations show elevated PM and particularly ultrafine and accumulation mode particles associated with emissions from fireworks. They are a substantial though short-lived source of fine mode particulate material ($PM_{2.5}$) including trace metal species (Drewnick et al., 2006; Moreno et al., 2007). One of the most comprehensive fireworks-related studies examined a network of 315 U.S. ambient aerosol monitoring stations over multiple years (Seidel and Birnbaum, 2015). Observations showed recurrent, though short-lived (< 0.5 days), impacts associated with U.S. Independence Day fireworks at urban U.S. monitoring stations (Seidel and Birnbaum, 2015). For example, the study found average hourly $PM_{2.5}$ concentrations elevated by 21 μg/m^3 during the hour from 19:00–20:00, with a 42% average increase in 24-h $PM_{2.5}$ concentrations compared to proximate days.

The chemical composition of fireworks is relevant for the resulting smoke properties. The primary composition of fireworks' black powder charge is graphitic carbon, potassium nitrate, and elemental sulfur in varying proportions (Russell, 2000). The black powder is use as a propellant and explosive charge for aerial fireworks, and the products of combustion include potassium compounds (Russell, 2000). There are various emitter compounds, mainly metals, including iron oxides, aluminum, titanium and potassium compounds for coloration. For example, the primary colorants for yellow coloration are sodium salts (Russell, 2000). Nonetheless, organic carbon (OC) species are often the dominant chemical contributor in ambient fireworks observations (Jiang et al., 2015; Tsai et al., 2012).

1.4. Southeast Asia studies of fireworks emission characteristics

The origin of fireworks traces to East Asia, and the Asian continent has a long history in religious and secular festivals (Russell, 2000). Numerous recent studies have examined the significance of fireworks to air quality in south and East Asia, and most notably India, Taiwan, and China (Chen et al., 2016). Several studies have examined fireworks in India particularly as related to the annual Diwali Festival (Kumar et al., 2016; Nasir and Brahmaiah, 2015). One of the worst smog events in India occurred in New Delhi, India in early November 2016 with $PM_{2.5}$ concentrations exceeding the instrument upper limit of 999 μg/m^3. It is still under investigation, but it was estimated that 60–70% contributions from fireworks smoke (https://phys.org/news/2016-10-delhi-toxic-smog-diwali-festival.html). As a result, the Supreme Court of India banned the sale of fireworks in 2017, though the air quality impacts were still very significant during the Diwali festival of 2017 (https://phys.org/news/2017-10-delhi-toxic-haze-diwali-fireworks.html).

1.5. Optical properties of fireworks aerosols

Many of the measurements of fireworks smoke impacted aerosols have focused on $PM_{2.5}$ mass concentrations and chemical speciation. However, a small number of studies investigated aerosol optical properties of fireworks smoke. The general observations are a fine mode dominance of PM properties and elevated single scattering albedo (ω, the ratio of light scattering to extinction) during impacted time periods (Devara et al., 2015). In part due to their transitory impacts, data in the literature is lacking on the extent, duration, and characteristics—particularly optical properties—of emissions from fireworks. The intent of this study is to report observations of freshly emitted fireworks generated smoke including optical properties, and in particular, aerosol hygroscopic response as related to the U.S. Independence Day fireworks on 4–5 July 2016.

2. Experimental details

2.1. Sampling site

Measurements were conducted in summer 2016 at Technical Area-51 at Los Alamos National Laboratory (LANL) (Fig. 2) located at 35.850° N 106.272° W at an elevation of 2149 m ASL. The LANL study was focused on laboratory biomass burning emissions, yet it also provided a unique opportunity to examine ambient fireworks influenced ambient smoke properties. We conducted follow-up laboratory experiments with commercially available sparklers using the same measurement techniques. The following section describes the measurements and experimental quality assurance efforts. Carrico et al. (2016b) gives more details on the experimental methods and results for laboratory combustion of biomass fuels.

The nearest meteorological measurements were ~3 km due north at Los Alamos Municipal Airport (WBAN:93091) which is located at 35.881° N 106.276° W at an elevation of 2184 m ASL (Fig. 2). Local wind direction and speed are reported on a 30-min average basis and were examined to determine atmospheric transport and source regions. Furthermore, NOAA Hysplit backtrajectory analyses were conducted at the LANL sampling site and the Los Alamos Municipal Airport sites (Rolph, 2017; Stein et al., 2015).

Nearby local municipal fireworks displays included White Rock, NM display which was 8.8 km ESE of the LANL sampling site (288° vector from White Rock to LANL site). A public display of fireworks was ignited at Overlook Park in White Rock, NM, for an hour beginning at approximately 21:00 on the evening of 4 July 2016. A public display occurred in Jemez Springs approximately 40 km to the west-southwest of Los Alamos at the same time. Additionally, there were no fewer than six municipal fireworks displays within 200 km of Los Alamos on the evening of 4 July 2016 with unknown contributions including Santa Fe, NM (38 km to the SE), Albuquerque (80 km SSW), Rio Rancho (80 km SSW), Las Vegas (100 km ESE), Grants (163 km WSW), and Farmington (190 km WNW).

2.2. Measurement methods

An aerosol sample inlet extended above roof level of the LANL building at a height of approximately 5-m above ground level. A laminar sample flow of 6 lpm was drawn through a 6.5 mm OD copper tubing, and the aerosol instruments sampled the flow undiluted. Due to the length and pressure drop through the ambient inlet line, no further sample conditioning or size cut was introduced before measurement instrumentation. Combustion sources, particularly with flaming combustion, produce size distributions shifted toward smaller (D_p ~ 50 nm) more absorbing particles whereas smoldering fires produce larger though still predominantly sub-μm particles (D_p ~ 200 nm) with high ω (Carrico et al., 2016a). As discussed later, measured wavelength dependence of light scattering (as demonstrated by the unitless Ångström