

1 Measurement report: Firework impacts on air quality in Metro Manila, Philippines during the
2 2019 New Year revelry

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20 Abstract

21 Fireworks degrade air quality, reduce visibility, alter atmospheric chemistry, and cause short-
22 term adverse health effects. However, there have not been any comprehensive physicochemical
23 and optical measurements of fireworks and their associated impacts in a Southeast Asia
24 megacity, where fireworks are a regular part of the culture. Size-resolved particulate matter (PM)
25 measurements were made before, during, and after New Year 2019 at the Manila Observatory in
26 Quezon City, Philippines, as part of the Cloud, Aerosol, and Monsoon Processes Philippines
27 Experiment (CAMP²Ex). A High Spectral Resolution Lidar (HSRL) recorded a substantial
28 increase in backscattered signal associated with high aerosol loading ~440 m above the surface
29 during the peak of firework activities around 00:00 (local time). This was accompanied by PM_{2.5}
30 concentrations peaking at 383.9 $\mu\text{g m}^{-3}$. During the firework event, water-soluble ions and
31 elements, which affect particle formation, growth, and fate, were mostly in the submicrometer
32 diameter range. Total ($> 0.056 \mu\text{m}$) water-soluble bulk particle mass concentrations were
33 enriched by 5.7 times during the fireworks relative to the background (i.e., average of before and
34 after the firework). The water-soluble mass fraction of PM_{2.5} increased by 18.5% above that of
35 background values. This corresponded to increased volume fractions of inorganics which
36 increased bulk particle hygroscopicity, kappa (κ), from 0.11 (background) to 0.18 (fireworks).
37 Potassium and non-sea salt (nss) SO_4^{2-} contributed the most (70.9%) to the water-soluble mass,
38 with their mass size distributions shifting from a smaller to a larger submicrometer mode during
39 the firework event. On the other hand, mass size distributions for NO_3^- , Cl^- , and Mg^{2+} (21.1%
40 mass contribution) shifted from a supermicrometer mode to a submicrometer mode. Being both
41 uninfluenced by secondary aerosol formation and constituents of firework materials, a subset of
42 species were identified as the best firework tracer species (Cu, Ba, Sr, K^+ , Al, and Pb). Although
43 these species (excluding K^+) only contributed 2.1% of the total mass concentration of water-
44 soluble ions and elements, they exhibited the highest enrichments (6.1 to 65.2) during the
45 fireworks. Surface microscopy analysis confirmed the presence of potassium/chloride-rich cubic
46 particles along with capsule-shaped particles in firework samples. The results of this study
47 highlight how firework emissions change the physicochemical and optical properties of water-
48 soluble particles (e.g., mass size distribution, composition, hygroscopicity, and aerosol
49 backscatter), which subsequently alters the background aerosol's respirability, influence on
50 surroundings, ability to uptake gases, and viability as cloud condensation nuclei (CCN).

51 1. Introduction

52 Fireworks affect local populations through visibility reduction and increased health risks due to
53 briefly elevated particulate matter (PM) levels. Total PM mass concentrations during local
54 celebrations in the following cities exceeded the 24 h U.S. National Ambient Air Quality
55 Standard (NAAQS) for PM₁₀ of 150 µg m⁻³: Leipzig, Germany, (Wehner et al., 2000), Texas,
56 United States [U.S.], (Karnae, 2005), Montreal, Canada (Joly et al., 2010), and New Delhi, India,
57 (Mönkkönen et al., 2004). Firework emissions from at least nineteen studies have also been
58 linked to exceedance of the 24 h U.S. NAAQS limit for PM_{2.5} of 35 µg m⁻³ (Lin, 2016 and
59 references therein). Higher PM concentrations from fireworks have been reported more
60 frequently in Asia (i.e., India, China, and Taiwan) compared to Western countries (Lin, 2016;
61 Sarkar et al., 2010).

62 Health effects are of major concern during firework periods based on both short and long-term
63 exposure. For example, Diwali is a major firework festival in India, and it was shown that
64 chronic exposure to three of the most prominent tracer species (Sr, K, and Ba) translated to a 2%
65 increase in health effects based on the non-carcinogenic hazard index (Sarkar et al., 2010). On
66 the other hand, short term exposure to firework pollutants increases asthma risk, eye allergies,
67 cardiovascular and pulmonary issues, cough, and fever (Moreno et al., 2010; Singh et al., 2019;
68 Barman et al., 2008; Becker et al., 2000; Beig et al., 2013; Hirai et al., 2000). Firework pollutants
69 also impact clouds and the hydrological cycle, owing to associated aerosols serving as cloud
70 condensation nuclei (CCN) (Drewnick et al., 2006) and subsequently impacting surface
71 ecosystems after wet deposition (Wilkin et al., 2007). Although fireworks emit particles with
72 various sizes into the atmosphere, fine particles associated with PM_{2.5} are most relevant to public
73 health effects, scattering efficiency, and CCN activation (Vecchi et al., 2008; Perry, 1999).
74 Knowing the various effects of firework emissions depends on knowing their physical, chemical,
75 and optical properties.

76 Measurements of the chemical composition of firework emissions are important in order to
77 understand how they affect local air quality. The main components of fireworks are fuels (metals
78 and alloys, metalloids, and non-metals), oxidizers (nitrates, perchlorates, and chlorates), and
79 coloring agents (metal salts) (Steinhauser and Klapotke, 2010). Previous studies have relied on
80 tracer species to establish confidence in distinguishing the firework source from background air
81 and other sources (Sarkar et al., 2010). Potassium historically has been the most observable
82 tracer for fireworks emissions (Wang et al., 2007; Drewnick et al., 2006; Perry, 1999), with
83 concentrations reaching 58 µg m⁻³ during the Diwali Festival in India (Kulshrestha et al., 2004).
84 Firework color is created by metal salts such as Sr for red, Ba for green, and Cu for blue-violet,
85 all three of which have and have been found to be effective tracers of fireworks (Walsh et al.,
86 2009; Vecchi et al., 2008). Strontium in particular is an indicator of the spatial and temporal
87 extent of firework smoke plumes (Perry, 1999) because of the high prevalence of red in
88 fireworks and it is not affected by traffic emissions (Moreno et al., 2010). Other components
89 measured in the air that have been attributed to fireworks include metals (Al, Cd, Cu, Ti, Mg,
90 Mn, Ni, Zn, As, Bi, Co, Ga, Hg, Cr, Pb, Rb, Sb, P, Tl, Ag) and their salt anion counterparts (S, P,
91 Cl). Thallium makes a green flame. Potassium and Ag (as AgCNO or silver fulminate) are
92 propellants, Al is fuel, and Pb provides steady burn and is also used as an igniter for firework

93 explosions. Chromium is a catalyst for propellants, Mg is a fuel, and Mg^{2+} is a neutralizer or
94 oxygen donor (U.S. Department of Transportation, 2013). Manganese is either a fuel or oxidizer,
95 and Zn is used for sparks (Licudine et al., 2012; Martín-Alberca and García-Ruiz, 2014;
96 Shimizu, 1988; Wang et al., 2007; Ennis and Shanley, 1991). Also from fuel and oxidizer
97 combustion are species such as NO_3^- , SO_4^{2-} , and organics including oxaloacetic acid (Alpert and
98 Hopke, 1981; Barman et al., 2008; Carranza et al., 2001; Dorado et al., 2001; Drewnick et al.,
99 2006; Joly et al., 2010; Joshi et al., 2016; Kulshrestha et al., 2004; Kumar et al., 2016; Lin et al.,
100 2016; Moreno et al., 2010; Sarkar et al., 2010; Tanda et al., 2019; Thakur et al., 2010; Joshi et
101 al., 2019). Firework-derived chloride in Taiwan has been attributed to raw materials such as
102 $KClO_3$, ClO_3 , and ClO_4 with $Cl^-:Na^+$ ratios reaching approximately 3 (Tsai et al., 2012). Black
103 carbon mass concentrations during firework events can either increase due to firework emissions
104 or decrease owing to fewer vehicles on the road (Kumar et al., 2016; Yadav et al., 2019). In both
105 cases, the black carbon mass fraction decreases due to a greater contribution of other constituents
106 in firework emissions. Organic mass concentrations and mass fractions have been noted to
107 increase and decrease, respectively, with fireworks (Zhang et al., 2019). Governed largely by
108 composition, particulate hygroscopicity and solubility have also been found to be altered by
109 fireworks depending on the emitted species. Inorganic salts (K_2SO_4 , KCl) dominated the aerosol
110 hygroscopicity in Xi'an, China during fireworks (Wu et al., 2018). In the Netherlands,
111 enhancements in salt mixtures containing SO_4^{2-} , Cl^- , Mg^{2+} , and K^+ were noted to enhance
112 hygroscopicity (ten Brink et al., 2018). Copper and Mg were observed to become more soluble in
113 firework emissions in Delhi, India, while Mn, As, Ba, and Pb became less soluble (Perrino et al.,
114 2011). The water-soluble aerosol component from fireworks in Sichuan Basin (China) were
115 internally mixed and enhanced the hygroscopicity of submicrometer aerosols, especially the
116 larger particles (Yuan et al., 2020).

117 In addition to composition, a necessary aspect of characterizing impacts of firework emissions is
118 to measure aerosol size distributions within the short timeframe of an event (Joshi et al., 2019).
119 Owing to combustion during firework events, PM concentrations are dominated by particles in
120 the submicrometer range (Vecchi et al., 2008; Nicolás et al., 2009; Joshi et al., 2019; Pirker et
121 al., 2020; Do et al., 2012). Particle number concentration maxima have been noted for the
122 nucleation (0.01 to 0.02 μm) and Aitken (0.02 to 0.05 μm) modes (Yadav et al., 2019; Yuan et
123 al., 2020), in addition to both the small (0.1 to 0.5 μm) (Wehner et al., 2000; Zhang et al., 2010)
124 and large (0.5 to 1.0 μm) ends of the accumulation mode (Vecchi et al., 2008) during firework
125 events. In Nanning, China, SO_4^{2-} peaked at 0.62 μm during fireworks (Li et al., 2017). The mass
126 diameter of K^+ was 0.7 μm due to firework emissions after transport in Washington State (Perry,
127 1999). There are a few studies with observed particle mass concentration increases in the coarser
128 but still respirable ($< 10 \mu m$) mode (Tsai et al., 2011). In terms of dynamic behavior in the size
129 distributions, past work has shown a shift in number concentration from nucleation and Aitken
130 modes to the smaller end of the accumulation mode (0.1 to 0.5 μm), due to increased coagulation
131 sinks (Zhang et al., 2010). Finer temporal scale monitoring has revealed steep increases in
132 nucleation mode and Aitken mode particle concentrations associated with firework emissions
133 followed by a growth in accumulation mode particle number concentrations due to coagulation

134 (Yadav et al., 2019). An opposite shift to a smaller size distribution has been observed for certain
135 species (Mg, Al, Cu, Sr, and Ba) from the coarse mode to accumulation mode (Tanda et al.,
136 2019). Other work has shown that while there is usually a quick drop in particle concentration to
137 background values after firework events (Joly et al., 2010), elevated number concentrations of
138 accumulation mode particles are maintained for up to three hours after peak firework activity
139 (Hussein et al., 2005). New particle formation events with fireworks have also been reported in
140 Mumbai, India (Joshi et al., 2016), with enrichments of primary and secondary particles for up to
141 30 minutes after peak firework activity. Particle aging due to distance from the source and
142 meteorology alter firework emission particle concentrations (Joly et al., 2010) and size
143 distributions (Khaparde et al., 2012).

144 Meteorological and dynamic parameters such as wind speed, level of mixing (turbulent kinetic
145 energy), and mixing layer height (Lai and Brimblecombe, 2020) influence peak concentration
146 and composition of aerosols after fireworks, as well as particle residence time in the atmosphere
147 and transport to nearby regions (Vecchi et al., 2008). Although firework activities are episodic,
148 their particulate emissions, especially in the submicrometer mode (Do et al., 2012), reside in the
149 atmosphere for as long as several days to weeks (Liu et al., 1997; Lin et al., 2016; Kong et al.,
150 2015; Do et al., 2012). Dispersion of the particles under low wind speed (1 m s^{-1}) for particles
151 between 0.4 and $1 \mu\text{m}$ is estimated at 12 h (Vecchi et al., 2008) and can reach distances as far as
152 a hundred kilometers (Perry, 1999). Aitken mode and larger particles are dispersed by wind more
153 than nucleation-mode particles (Agus et al., 2008). Meteorological conditions, such as rainfall,
154 can also decrease firework particle loading in the air and relative humidity can change the
155 hygroscopicity of firework emissions (Hussein et al., 2005), thereby affecting their size and
156 radiative properties.

157 Studies on aerosol properties are limited for the rapidly developing region of Southeast Asia
158 (Tsay et al., 2013). This compounds the challenge to understand the interactions between
159 aerosols and the complex hydro-meteorological and geological environment in Southeast Asia
160 (Reid et al., 2013). Increased local and transported emissions (Hopke et al., 2008; Oanh et al.,
161 2006) in Southeast Asia add to the complexity and affect air quality in the region. Firework
162 emissions are an example of extreme and regular local emissions in Southeast Asia. Even while
163 several studies exist in the neighboring regions of East Asia (e.g., China) and South Asia (e.g.,
164 India), there currently is no in-depth analysis of the chemical, physical, and optical properties of
165 firework emissions in a Southeast Asian megacity where fireworks are culturally significant
166 (Dela Piedra, 2018). This study is additionally novel because it includes the following
167 combination of data types to investigate fireworks: size-resolved measurements (ionic/elemental
168 composition, morphology), vertically-resolved data from a High Spectral Resolution Lidar
169 (HSRL), $\text{PM}_{2.5}$, and meteorology. This work reports these data during the 2019 New Year
170 celebrations in Metro Manila, Philippines, one of the most populated cities, with 12.88 M
171 population (PSA, 2015). We address the following questions in order: (i) what are the conditions
172 of the atmosphere during the study period in relation to aerosols, and how are these affected by
173 firework emissions; (ii) what are the concentrations, mass size distributions, and morphological
174 characteristics of different elemental and ionic species specific to fireworks, and how do these

175 affect bulk aerosol hygroscopicity? The results of this work provide new data that can help
176 address how past and on-going firework emissions impact health, visibility, regional air quality,
177 and biogeochemical cycling of nutrients and contaminants in the Philippines, Southeast Asia,
178 and, more broadly, for all other cities with major firework events. It also contributes to the
179 growing body of firework research findings (Devara et al., 2015).

180

181 **2. Methods**

182 2.1 Hourly PM_{2.5} Mass Concentration

183 Hourly PM_{2.5} mass concentrations were obtained to assess the evolution of and the temporal
184 characteristics of fine particulates due to fireworks and their relation to meteorology and aerosol
185 optical properties. The hourly PM_{2.5} mass concentrations were collected at the Manila
186 Observatory, Quezon City, Philippines (14.64° N, 121.08° E, ~70 m. a. s. l.) (Fig. S1) with a beta
187 attenuation monitor (DKK-TOA Corporation) as part of the East Asia Acid Deposition
188 Monitoring Network (EANET) (Totsuka et al., 2005). The beta attenuation monitor collects
189 PM_{2.5} samples on a ribbon filter, which are irradiated with beta particles. The attenuation of the
190 beta particles through the sample and the filter is exponentially proportional to the mass loading
191 on the filter. These hourly data were then averaged over 48-hour periods coinciding with water-
192 soluble aerosol composition measurements (Section 2.5) before, during, and after the firework
193 event.

194

195 2.2 Meteorological Data

196 Rainfall, temperature, relative humidity, and wind data were collected at the Manila Observatory
197 with a Davis Vantage Pro2 Plus weather station (~90 m. a. s. l) before, during, and after the
198 firework period. Hourly precipitation accumulation and 10-min averaged temperature, relative
199 humidity, and wind were used for the analysis.

200

201 2.3 Back Trajectories

202 Three-day back trajectories with six-hour resolution were generated using the National Oceanic
203 and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Integrated
204 Trajectory (HYSPLIT) model (Rolph et al., 2017; Stein et al., 2015) using the Global Data
205 Assimilation System (GDAS) with a resolution of 1°, and vertical wind setting of "model vertical
206 velocity". To ascertain the impact of fireworks on surface particulate concentrations, back
207 trajectories were chosen to end at the beginning times of the sampling periods before, during,
208 and after the firework event. Trajectories were computed for an end point being at the Manila
209 Observatory at an altitude of 500 m because it represents the mixed layer as done in other works

210 examining surface air quality (Mora et al., 2017; Aldhaif et al., 2020; Crosbie et al., 2014;
211 Schlosser et al., 2017).

212

213 2.4 Remote Sensing

214 Vertical profiles of aerosol backscatter cross-section measured with the University of Wisconsin
215 High Spectral Resolution Lidar (HSRL) which was deployed at the Manila Observatory in
216 support of CAMP²EX. The HSRL instrument transmitting laser (Table S1) operates at 532 nm
217 with 250 mW average power and pulse repetition rate of 4 KHz. The HSRL technique measures
218 and separates the returned signal into the molecular and aerosol backscatter by using a beam
219 splitter and an iodine absorption cell filter. The separated molecular signal allows for optical
220 depth and backscatter cross section measurements in contrast to a standard backscatter lidar that
221 requires assumption related to the particulate lidar ratio (Razenkov, 2010). The HSRL also
222 measures particulate depolarization ratio, an indicator of aerosol or cloud particle shape with low
223 depolarization indicative of spherical particles while intermediate values (10%) indicate a mix of
224 spherical and nonspherical particles (Burton et al., 2014; Reid et al., 2017). HSRL data were
225 uploaded and processed at the University of Wisconsin-Madison Space Science and Engineering
226 Center server for periods before, during, and after the fireworks.

227 To verify the height values based on the vertical profiles of aerosol backscatter, the “surface-
228 attached aerosol layer” height is estimated using the maximum variance method more commonly
229 used for daytime convective boundary layer detection (Hooper and Eloranta, 1986). The height
230 detection method is limited by the complexity of the firework event case due, however, to
231 pertinent rain signals. The “surface attached aerosol layer” is derived from a 15-min moving
232 window average based on the 30-s values.

233

234 2.5 Aerosol Composition and Morphology Measurements

235 Size-speciated PM (cut-point diameters: 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, and
236 0.056 μm) was collected on Teflon substrates (PTFE membrane, 2 μm pores, 46.2 mm diameter,
237 Whatman) with two Micro-Orifice Uniform Deposition Impactor (MOUDI II 120R, MSP
238 Corporation) (Marple et al., 2014) samplers from the third floor of the main building (~85 m. a.
239 s. l) at the Manila Observatory. Sample collection for each of the three MOUDI sets lasted 48
240 hours before (13:30 December 24, 2018 to 13:30 December 26, 2018), during (14:45 December
241 31, 2018 to 14:45 January 2, 2019), and after (13:30 January 1, 2019 to 13:30 January 3, 2019)
242 firework activities. Note all times refer to local time (UTC + 8 hours). Although there were no
243 fireworks released from the sampling site, there was firework activity in the immediate vicinity
244 (~ 500 m from the sampling in all directions and all throughout the city in general). Firework
245 activity around the sampling site began around ~19:00 on 31 December 2018, peaked at 00:00 of
246 1 January 2019, and dropped drastically after. Based on PM_{2.5} data there was no evidence of
247 sustained firework activity past midnight. MOUDI samples collected before (December 24 to 26)
248 and after (January 1 to 3) the firework event (December 31 to January 2) were considered as

249 background samples. Although there is some firework activity that is expected in the evening of
250 December 24 (before the firework event), this is minimal compared to that which is the focus of
251 this study (Dela Piedra, 2018; Santos Flora et al., 2010; Roca et al., 2015). The samples were
252 covered with aluminum foil, sealed, and stored in the freezer before being shipped to the
253 University of Arizona for elemental and ionic analysis.

254 Each sample substrate was cut in half. One half of each sample was extracted in 8 mL Milli-Q
255 water (18.2 MΩcm), sonicated, and analyzed for ions (ion chromatography (IC): Thermo
256 Scientific Dionex ICS-2100 system) and elements (triple quadrupole inductively coupled plasma
257 mass spectrometer: ICP-QQQ; Agilent 8800 Series). The remaining substrate halves were stored.
258 Sample ionic and elemental concentrations were corrected by subtracting concentrations from
259 background control samples. More information about the sampling and analysis are detailed in
260 recent work (Stahl et al., 2020b). Limits of detection of the forty-one reported species are
261 summarized in Table S3. Potassium (K⁺) was reported based on ICP-QQQ measurements rather
262 than IC due to possible contamination from the KOH eluent used in the latter instrument. Non-
263 sea salt SO₄²⁻ was calculated by subtracting 0.2517 * Na⁺ from the total SO₄²⁻ concentration
264 (Prospero et al., 2003).

265 High-resolution scanning electron microscopy (SEM) combined with energy dispersive X-ray
266 analysis (EDX) was used for examining particle morphology and chemical composition on a
267 portion of the substrates collected during the firework event. Analyses were performed with a
268 Hitachi S-4800 high-resolution SEM and a Thermo Fisher Scientific Noran Six X-ray
269 Microanalysis System in the Kuiper Imaging cores at the University of Arizona. Approximately
270 1 cm² was cut from the center of substrate halves and placed on double-sided carbon tape
271 mounted on an aluminum stub. A thin layer (1.38 nm) of carbon was coated on the sample
272 surface using a Leica EM ACE600 sputter coater to improve the sample's conductivity. SEM
273 images were obtained at 15 keV and 30 keV acceleration voltages and with a 20 μA probe
274 current in high-magnification mode. The percentage contributions and the spatial distribution of
275 the elements were obtained from the EDX analysis. Carbon, F, and Al should be ignored in the
276 discussion of SEM-EDX results since C and F are present in the Teflon substrates, and the
277 sample stub is an Al-rich substrate.

278 A total of 41 water-soluble species were detected in the 48-hr size-differentiated particulate
279 samples collected before, during, and after the firework event. The total bulk mass concentration
280 is defined as the sum of the concentrations of all the measured species across the MOUDI's
281 eleven stages ($\geq 0.056 \mu\text{m}$).

282 283 2.6 Enrichment Factor Calculations

284 To identify which species are most enhanced during fireworks, enrichment values are typically
285 calculated using speciated concentrations during the fireworks relative to baseline periods
286 (Tanda et al., 2019). We calculate water-soluble mass enrichment factors for each of the forty-
287 one measured species by dividing their total bulk ($\geq 0.056 \mu\text{m}$) mass concentrations during the
288 firework event by the average of the total mass concentration of the species measured before and

289 after the firework event. Size-resolved enrichments were similarly calculated using measured
290 mass concentrations for individual MOUDI stages. In a case when the mass concentration of a
291 species during the firework event was non-zero but the mass concentrations during and after
292 were zero (e.g., succinate), half of the detection limit was used in place of zero values.

293

294 2.7 Hygroscopicity Calculations

295 Hygroscopicity was calculated for particles ranging in size between 0.056 – 3.2 μm before,
296 during, and after the firework event. This size range was chosen to most closely be aligned with
297 separate measurements of $\text{PM}_{2.5}$ in the study (Section 2.1) that were used to account for the
298 remaining mass not speciated in this study. We specifically calculate values for the single
299 hygroscopicity parameter kappa, κ (Petters and Kreidenweis, 2007).

300 The water-soluble compound mass concentrations before, during, and after the firework event
301 were calculated using an ion-pairing scheme (Gysel et al., 2007) for each MOUDI stage between
302 diameters of 0.056 and 3.2 μm , and then summed to achieve a total mass concentration for each
303 compound in this size range. Black carbon mass concentrations in $\text{PM}_{2.5}$ before and after the
304 firework event were calculated based on their long-term (2001-2007) average contribution (32%)
305 to $\text{PM}_{2.5}$ mass in December and January (Cohen et al., 2009). Black carbon or elemental carbon
306 (EC) concentrations during the firework event were assumed to be the average of the black
307 carbon concentrations before and after the firework event. This was done because black carbon
308 concentrations have been observed to not increase (Santos et al., 2007) as much as organic
309 carbon (OC) (Lin, 2016), such that OC:EC mass ratios during fireworks have been observed to
310 increase. Total non-water-soluble content between 0.056 and 3.2 μm was calculated as the
311 difference between the total $\text{PM}_{2.5}$ mass concentration and the sum of the water-soluble species
312 and black carbon mass concentrations. The mass of each species was divided by its density, and
313 each of these volumes were added to quantify the volume of the measured aerosol (water-soluble
314 compounds, black carbon, and organic matter) between 0.056 and 3.2 μm . Volume fractions
315 were then computed for each species. The Zdanovskii, Stokes, and Robinson (ZSR) mixing rule
316 (Stokes and Robinson, 1966) was used to obtain the total hygroscopicity (total κ) of the mixed
317 aerosols by weighting κ values for the individual non-interacting compounds by their respective
318 volume fractions and summing linearly. Densities and κ values for the individual compounds are
319 based on those used elsewhere (AzadiAghdam et al., 2019), repeated in Table S4.

320

321 3. Results and Discussion

322 3.1 Hourly $\text{PM}_{2.5}$, Meteorological, and Transport Patterns

323 We begin with hourly $\text{PM}_{2.5}$ mass concentration results for the study period to provide context
324 for the spatio-temporal characteristics of fine particulates due to fireworks, their interaction with
325 meteorology, and effects on aerosol optical properties. Hourly $\text{PM}_{2.5}$ (Fig. 1) began to increase
326 from 44.0 $\mu\text{g m}^{-3}$ (shortly after rising above the 24-h Philippine National Ambient Air Quality

327 Guideline Value (NAAQGV) of $50.0 \mu\text{g m}^{-3}$) after 18:00 time on 31 December 2018 with the
328 beginning of firework activity and calm meteorological conditions. There was moderate (3 mm)
329 rainfall from 22:00 to 23:00 that night as the firework activity began to increase. Rain is a sink
330 for particles (Perry, 1999) and could have washed out some of the particulates in the air, thus
331 potentially causing a slight dip in the hourly $\text{PM}_{2.5}$ around midnight. $\text{PM}_{2.5}$ peaked at $383.9 \mu\text{g m}^{-3}$
332 between 01:00 to 02:00 on 1 January 2019. The $\text{PM}_{2.5}$ peak was delayed by approximately an
333 hour from the peak firework activity at midnight possibly due to rainfall, relative humidity, and
334 wind (Vecchi et al., 2008), in addition to aerosol dynamical processes requiring time for
335 secondary aerosol formation and growth (Li et al., 2017). Minimal rain (0.2 mm in an hour) with
336 high relative humidity (between $93\% \pm 4\%$ to $94\% \pm 4\%$) were conducive to aerosol growth
337 and/or secondary particle formation. High relative humidity is related to aqueous-phase oxidation
338 of SO_2 (Sun et al., 2013) and NO_2 (Cheng et al., 2014) as well as metal-catalyzed heterogeneous
339 reactions (Wang et al., 2007) to form SO_4^{2-} . Aqueous oxidation has been found to be a
340 predominant mechanism for the secondary formation of SO_4^{2-} during fireworks (Li et al., 2017),
341 in addition to promoting secondary organic aerosol formation (Wonaschuetz et al., 2012; Youn
342 et al., 2013). Light wind ($\sim 1 \text{ m s}^{-1}$) after midnight from the northeast could also have transported
343 more emissions from the populated Marikina Valley, located in the northeast, to the Manila
344 Observatory contributing to the delay of the $\text{PM}_{2.5}$ peak.

345 Particulate levels were enhanced for approximately 14 h from the beginning of the firework
346 activity (Fig. 1) during which the average $\text{PM}_{2.5}$ ($143.4 \mu\text{g m}^{-3}$) exceeded the 24 h Philippine
347 NAAQGV between 18:00 on 31 December 2018 to 08:00 on 1 January 2019. After 02:00 on 1
348 January 2019, $\text{PM}_{2.5}$ dropped quickly to $122.0 \mu\text{g m}^{-3}$ between 03:00 to 04:00 (Fig. 1). The $\text{PM}_{2.5}$
349 decrease was less pronounced after 04:00 but continued decreasing steadily along with slight rain
350 (0.4 mm in an hour) and light breeze ($1 - 2 \text{ m s}^{-1}$) from the northwest to southwest directions.
351 Firework activity in other countries have been documented to last from 2 – 6 h in a day and
352 elevated particulate levels can be maintained for up to 6 – 18 h (Thakur et al., 2010; Crespo et
353 al., 2012; Chatterjee et al., 2013; Kong et al., 2015; Tsai et al., 2012). The 48-h average $\text{PM}_{2.5}$
354 during ($49.9 \mu\text{g m}^{-3}$) the firework event was 1.9 and 3.3 times more, respectively, than before
355 ($25.8 \mu\text{g m}^{-3}$) (Fig. S2) and after ($15.2 \mu\text{g m}^{-3}$) (Fig. S3) the firework event. Two to three-fold
356 increases in PM mass concentration due to fireworks have also been observed in other countries
357 (Rao et al., 2012; Ravindra et al., 2003; Tsai et al., 2011; Shen et al., 2009). Greater increases ($>$
358 5 times) in particulate mass concentrations elsewhere were related to more intense and prolonged
359 (lasting several days) firework activity (Tian et al., 2014).

360 Three-day back trajectories for the period before the firework event were from the northeast to
361 east directions coming from the Philippine Sea (Fig. 2a). For the periods (Fig. 2b) during and
362 (Fig. 2c) after the firework event, back trajectories were from the northeast to east/northeast
363 directions. The general wind directions from the back trajectories are consistent with the
364 climatologically prevailing northeasterly monsoonal winds in December and January for the
365 Philippines (Villafuerte II et al., 2014). The origin of the air parcels did not have any major
366 emissions events that could have impacted the measurements after long-range transport. This is

367 important to note because the tracers for fireworks are also tracers for transported emissions due
368 to biomass burning (K^+) (Braun et al., 2020) and industrial activities (Cohen et al., 2009). Thus,
369 enriched particulate concentrations during the firework activity were most likely locally
370 produced. One factor impacting surface PM concentrations is the vertical structure of the lower
371 troposphere, which is addressed in the next section based on HSRL data.

372

373 3.2 Optical Aerosol Properties

374 Heavy aerosol loading at the surface was observed up to eight hours after the fireworks peak
375 (00:00) with high HSRL 532 nm backscatter cross-section and depolarization (Fig. 3a) reaching
376 ~440 m above the ground. Prior to the firework peak, the surface aerosol layer had lower
377 backscatter (before 22:00, Fig. 3a), and this cleaner condition is shown by the 16:16 local time
378 vertical profile of the aerosol backscatter (Fig. 3b). Rainfall (Fig. 1a) contributed to columns of
379 high backscatter (Fig. 3a) after 22:00 and before the firework peak with a measurable decrease in
380 the aerosol backscatter for a short time after the precipitation (23:00 and 00:00).

381 As confirmed by height detection, aerosols reached up to ~440 m (Fig 3a and b) at 00:00 (1
382 January 2019). It persisted for at least an hour then dropped to 118 ± 20 m with higher aerosol
383 backscatter retained until January 1, 2019 08:00. Some of the smoke is above the detected height
384 (i.e. 01:00).

385

386 3.3 Mass Size Distributions

387 Building on the previous results describing the general environmental conditions during the
388 study period, now we focus on the detailed size-resolved measurements. The total water-soluble
389 bulk mass concentration (Table 1) during the firework event ($16.74 \mu\text{g m}^{-3}$) was 5.71 times and
390 4.73 times higher than the total bulk mass concentrations before ($2.93 \mu\text{g m}^{-3}$) and after ($3.54 \mu\text{g}$
391 m^{-3}) the firework event, respectively. Assuming the average of the water-soluble mass
392 concentrations before and after the firework event represent background values, this translates to
393 an 80.66% increase in water-soluble mass during the firework event.

394 The firework event was associated with increased total water-soluble mass fraction (32.33%)
395 ($0.056 - 3.2 \mu\text{m}$ size range, Section 3.1) in $\text{PM}_{2.5}$ (Fig. S4) compared to before (9.90%) and after
396 (17.79%) the firework event. The water-soluble particulate mass fraction in $\text{PM}_{2.5}$ similarly
397 increased in other firework events (Yang et al., 2014). The highest total water-soluble mass
398 concentrations during the firework event were from the following ions: non-sea salt (nss) SO_4^{2-}
399 ($6.81 \mu\text{g m}^{-3}$), K^+ ($5.05 \mu\text{g m}^{-3}$), NO_3^- ($1.70 \mu\text{g m}^{-3}$), Cl^- ($1.46 \mu\text{g m}^{-3}$), Mg^{2+} ($0.37 \mu\text{g m}^{-3}$), Na^+
400 ($0.33 \mu\text{g m}^{-3}$), and Ca^{2+} ($0.30 \mu\text{g m}^{-3}$). These contributed to 95.75% of the total detected bulk
401 water-soluble mass concentration then.

402 Total water-soluble bulk mass concentration during the firework event was dominated by
403 submicrometer particles, which accounted for 77.4% of the total water-soluble bulk mass (Fig.
404 4b). Supermicrometer mass fractions were greater before (Fig. 4a) and after (Fig. 4c) the
405 firework event (43.7% and 57.5% of the water-soluble bulk mass concentration) compared to
406 during the firework event (22.6%). The increase in submicrometer mass fractions is typical with
407 firework emissions (Crespo et al., 2012; Do et al., 2012). In New York, fireworks contributed to
408 77% of PM_1 due to potassium salts and oxidized organic aerosol (Zhang et al., 2019).

409 Non-sea salt SO_4^{2-} had the highest contribution (40.7%) to total water-soluble bulk mass
410 concentration during the firework event (Table 1). Sulfate exhibited a shift in its mass size
411 distribution to a slightly larger size during firework activity (Fig. 4b). During the firework event,
412 87.13 % of the nss- SO_4^{2-} was in the 0.32 μm to 1.8 μm size fraction. Before and after the
413 firework event, 87.28% and 85.14% of the nss- SO_4^{2-} mass concentration, respectively, was
414 distributed in a finer size fraction (0.18 μm to 1 μm) (Fig. 4a and 4c).

415 Potassium contributed 30.19% to the total water-soluble mass concentration during the firework
416 event (Table 1), presumably in the form of KNO_3 . This compound is associated with black
417 powder used as a propellant (Li et al., 2017). Potassium's mass concentration distribution
418 similarly shifted to a slightly larger size during the firework event (Figure 4b). Most (87.6%) of
419 the bulk K^+ mass concentration during the firework event was between 0.32 and 1.8 μm ,
420 compared to 85.4% and 79.4% between 0.18 and 1 μm before and after the firework event,
421 respectively (Fig. 4a and 4c).

422 The shift in the mass size distribution of K^+ and nss- SO_4^{2-} can be due to the removal of
423 nucleation-mode particles as a result of increased coagulation in the accumulation mode (Zhang
424 et al., 2010). Relatively larger SO_4^{2-} particles can also be due to secondary sources rather than
425 primary sources, and aging could have also contributed to particle growth as has been suggested
426 for firework particles in Nanning, China (Li et al., 2017). Firework emissions include gases like
427 SO_2 which undergo aqueous uptake and oxidation onto particles to form SO_4^{2-} . Furthermore,
428 enhanced secondary formation is aided by metals emitted during fireworks that help convert SO_2
429 to SO_4^{2-} (Feng et al., 2012; Wang et al., 2007).

430 Nitrate, Cl^- , and Mg^{2+} mass size distributions all exhibited pronounced peaks in the
431 submicrometer range during the firework event (Fig. 5). The mass sum concentration of the
432 aforementioned ions peaked (46.39% of the total mass concentration of the three species)
433 between 0.56 and 1.0 μm . On the other hand, their mode appeared between 1.8 and 3.2 μm
434 before and after the firework event (33.02% and 32.91% of the total mass concentration of the
435 three species, respectively) (Fig. 5). Nitrate, Cl^- , and Mg^{2+} are emitted during fireworks (Zhang et
436 al., 2017) as finer-sized submicrometer particles (Tsai et al., 2011) compared to background
437 conditions when these species are mostly associated with coarser supermicrometer particles
438 (AzadiAghdam et al., 2019; Cruz et al., 2019; Hilario et al., 2020). Nitrate can also be formed
439 secondarily (Yang et al., 2014) from firework emissions. Firework emissions are associated with
440 lower $NO_3^-:SO_4^{2-}$ ratios (Feng et al., 2012) compared to days dominated by mobile sources

441 (Arimoto et al., 1996) due to different formation mechanisms (Tian et al., 2014). Consistent with
442 the literature, low $\text{NO}_3^-:\text{SO}_4^{2-}$ ratios were also observed during the firework event (before: 0.79,
443 during: 0.25, after: 0.82). A low $\text{NO}_3^-:\text{SO}_4^{2-}$ ratio is related to decreased pH of the particles (Cao
444 et al., 2020), which may impact not just air quality and health but also nearby waterbodies where
445 the particles may deposit. It is important to note that background supermicrometer Cl^- and Mg^{2+}
446 in Manila are most likely associated with sea salt while background supermicrometer NO_3^-
447 possibly in the form of NaNO_3 (de Leeuw et al., 2001) or NH_4NO_3 likely stems from partitioning
448 of nitric acid gas onto surfaces (de Leeuw et al., 2001) of coarse particles such as sea salt and
449 dust (AzadiAghdam et al., 2019; Cruz et al., 2019). The $\text{Cl}^-:\text{Na}^+$ mass ratio during the firework
450 event increased to 4.44 (from 0.69 and 1.08 before and after, respectively) and was higher than
451 the typical $\text{Cl}^-:\text{Na}^+$ ratio in seawater of 1.81 (Braun et al., 2017). These ratio results confirm that
452 the increase in Cl^- concentrations during the firework event is not driven by sea salt but instead
453 linked to firework emissions. The lack of increased sea salt influence during the firework event,
454 which is not to be expected, is further confirmed by relatively small changes in the amount of
455 observed Na^+ , as will be discussed subsequently.

456 The Na^+ , Ca^{2+} , and NH_4^+ mass size distributions peak in the supermicrometer range (1.8 to 3.2
457 μm) (Figure S5) and total mass concentrations (Table 1) varied minimally, relative to the earlier
458 mentioned species, before ($0.33 \mu\text{g m}^{-3}$, $0.21 \mu\text{g m}^{-3}$, $0.21 \mu\text{g m}^{-3}$, respectively), during ($0.33 \mu\text{g}$
459 m^{-3} , $0.30 \mu\text{g m}^{-3}$, $0.19 \mu\text{g m}^{-3}$) and after ($0.53 \mu\text{g m}^{-3}$, $0.38 \mu\text{g m}^{-3}$, $0.28 \mu\text{g m}^{-3}$) the firework
460 event. The minimal change in NH_4^+ mass concentration is most likely due to little or no variation
461 of its precursor gas (e.g., NH_3) due to firework activities and the fact that firework materials are
462 commonly composed of K-rich salts rather than NH_4^+ salts (Zhang et al., 2019). The latter seems
463 probable because the K:S mass ratios of 2.75 and 2.71, observed from 0.18 – 0.32 μm and 0.32 –
464 0.56 μm , respectively, during the firework event suggests a firework-related source of K and S.
465 This ratio is similar to the K:S ratio of 2.75 (Dutcher et al., 1999) of “black powder” (Perry,
466 1999), a type of pyrotechnic comprised of K and S.

467 The mass size distribution for the sum of the rest of the species (“others” in Fig. 4) shifted from
468 having a peak at the smaller end of the accumulation mode (0.18 – 0.32 μm) before and after the
469 firework event to larger sizes in the accumulation mode (0.56 – 1.0 μm) during the firework
470 event. The shift in mode to slightly larger particles during the firework event may be due to
471 increased coagulation sinks (Zhang et al., 2010) and secondary production (Retama et al., 2019).
472 An additional coarse peak (3.2 – 5.6 μm) observed after the firework event is mainly attributed
473 to sea salt constituents (e.g., Cl^- , Na^+) and likely unrelated to firework emissions aging and
474 processing. The mass contribution of the “others” to the total measured water-soluble mass
475 concentration decreased during the firework event to 4.3% from 12.5% before and 11.6% after
476 the firework event due to the prevalence of the ionic species (nss-SO_4^{2-} , K^+ , NO_3^- , Cl^- , Mg^{2+} , Na^+ ,
477 Ca^{2+} , and NH_4^+) discussed earlier (Table 1).

478

479 3.4 Enriched Tracers in Firework Emissions

480 Here we more closely examine how much concentrations of species changed during the firework
481 event. Bulk mass concentrations of eighteen of the forty-one measured species were enriched
482 during the firework event by more than two times compared to the average of their bulk mass
483 concentrations before and after the firework event (Fig. 5). Enrichments for Cu (65.2), Sr (24.4),
484 succinate (19.4), Ba (18.2), K^+ (16.3), $nss-SO_4^{2-}$ (9.8), Al (6.9), Pb (6.1), and maleate (5.3) were
485 highest (> 5) among the species measured (Fig.5). Potassium and $nss-SO_4^{2-}$ together contributed
486 to 70.9% of the total measured species during the firework event (Table 1). However, Cu, Sr,
487 succinate, Ba, Al, Pb, and maleate contributed a total of only 2.1% to the total measured species
488 mass concentration. This reinforces the importance of looking at enrichments rather than
489 absolute mass concentrations for identifying which aerosol constituents are firework tracers.
490 Tracer metals in firework emissions were previously shown to contribute a small fraction
491 ($\sim < 2\%$) to total PM mass (Jiang et al., 2014).

492 Of the eighteen species with observed enrichments exceeding two (Fig. 5), only those which are
493 firework components and that are uninfluenced by secondary formation are considered tracers.
494 The identified fourteen firework tracers based on these criteria are as follows: Cu, Sr, Ba, K^+ , Al,
495 Pb, Mg^{2+} , Cr, Tl, Cl^- , Mn, Rb, Zn, and Ag. Metals are usually in the form of Cl^- salts in fireworks
496 (Wang et al., 2007). In this study, the enrichment of Cl^- during the firework event was found to
497 be 3.7. Some of the identified tracer metals are regulated and their detection is of concern.
498 Magnesium is not recommended as a firework component because it is sensitive to heat and can
499 easily ignite in storage (Do et al., 2012). Lead is highly toxic and thus regulated (Moreno et al.,
500 2010) as its occurrence in fireworks is a serious health hazard. Although SO_4^{2-} , maleate (fuel),
501 and NO_3^- (oxidant) were also enriched more than two times during the firework event and are
502 also firework components (Zhang et al., 2019), they can be formed secondarily via gas-to-
503 particle conversion processes (Yang et al., 2014) and are not considered as firework tracers.
504 Succinate is likewise formed secondarily and is not considered a firework tracer (Wang et al.,
505 2007). The identified firework tracers with the highest enrichments (> 5) (excluding K^+),
506 including Cu, Sr, Ba, Al, and Pb, together contributed 2.1% to the total measured species mass
507 concentration during the firework event (Table 1).

508 Size-resolved enrichments (Fig. 6) were highest in the submicrometer range for most measured
509 species. This is consistent with past studies such as in Italy (Vecchi et al., 2008), Taiwan (Do et
510 al., 2012), and Spain (Crespo et al., 2012) where elemental concentrations due to pyrotechnics
511 increased in the submicrometer mode. The peak size differentiated enrichments of the first five
512 firework tracers Sr (45.08), Ba (57.82), K^+ (48.70), Al (18.75), and Pb (69.07) were in the 1.0 –
513 1.8 μm size range. Copper (49.85) peaked between 0.56 – 1.0 μm because it did not have valid
514 data for diameters exceeding 1.0 μm . Strontium and Ba had very high enrichments (254.40 and
515 195.84) from 0.1 – 0.18 μm due to very low concentrations before and after the firework event in
516 that size range. Enrichments of up to ~ 1000 (Crespo et al., 2012) for Sr and Ba have been
517 observed due to pyrotechnics, and both are known firework tracers (Kong et al., 2015).

518 The size-resolved enrichments of other notable species (Fig. 6 and Fig. S6) peaked at specific
519 size ranges between 0.32 – 1.8 μm : Mg^{2+} (18.93, 0.056 – 0.1 μm), Cr (14.37, 1.0 – 1.8 μm), Tl

520 (18.12, 0.56 – 1.0 μm), Cl^- (170.94, 0.32 – 0.56 μm), Mn (6.29, 1.0 – 1.8 μm), Rb (6.87, 1.0 –
521 1.8 μm), NO_3^- (7.26, 0.56 – 1.0 μm), Cs (6.28, 1.0 – 1.8 μm), Mo (4.15, 0.32 – 0.56 μm), Ti
522 (6.63, 0.32 – 0.56 μm), Co (17.94, 0.56 – 1.0 μm), and methanesulfonate (MSA) (6.66, 0.56 –
523 1.0 μm). Among all the measured water-soluble species, Cl^- had the highest size-resolved
524 enrichment, followed by Sr, Ba, K^+ , Pb, and Cu. This is expected because inorganic salts
525 comprise an enormous percentage of firework emissions (Martín-Alberca et al., 2016).

526

527 3.5 SEM-EDX

528 In addition to size-resolved species concentrations, the morphology of particles is important with
529 regard to their optical properties, hygroscopicity, and their transport behavior. Five SEM
530 images from the different stages (0.18 – 1 μm) of the MOUDI sampler with possible firework
531 influence are highlighted (Fig. 7). There were signs of nano-scale aggregation that were chain-
532 like and reminiscent of soot particles from pyrolysis and combustion (Pirker et al., 2020; Pósfai
533 et al., 2003; D’Anna, 2015) in all of the images, and especially distinct in the 0.1 – 0.18 μm (Fig.
534 4b) and 0.18 – 0.32 μm (Fig.7c) stages. Images for larger sizes revealed relatively larger particles
535 appearing as a translucent crystal-shaped rectangle in the 0.32 – 0.56 μm image (Fig. 7d), in
536 addition to a capsule-shaped particle (Fig. 7e) and a cubic-shaped particle (Fig. 7f) in the two
537 0.56 – 1.0 μm images. The presence of such non-spherical shapes including chain aggregates
538 points to the potential for particle collapse and shrinking associated with humidified conditions
539 as noted in past work (Shingler et al., 2016 and references therein).

540 The chemical composition of the blank Teflon substrate (Fig. 7a) was examined first by EDX to
541 determine the background signals before the actual samples were analyzed. The color intensity of
542 the element maps (Fig. S7) relates the concentration of the analyzed element relative to the
543 backscattered electron image (gray-scale) of the sample. The background substrate was
544 dominated by C, F, and Al (bright yellow, bright blue, and bright blue-green, respectively, in Fig.
545 S7-a1/a2/a3). Metallic elements were distributed in each of the five featured SEM images.
546 Molybdenum and K were present in all of the substrate stages (bright red in Fig. S7-
547 b3/b4/c3/c8/d7/d8/e6/e7/f6/f9). Other metals were also found in the different stages such as K,
548 Mg, Al, Ru, Pd, Ba, Hf, and Tl. The identified heavy metals in the particles are commonly used
549 in firework as fuel components, colorants, and oxidants (Singh et al., 2019). Potassium, Mg, Al,
550 Ba, and Tl are in the group of firework tracers that were already identified (Section 3.4 and Fig.
551 5) to have mass bulk concentration enrichments exceeding two. Molybdenum exhibited a
552 reduced mass bulk concentration enrichment of 1.93 (Fig. 5), but had size-resolved enrichments
553 between 1.21 and 4.15 (Fig. 6) in the substrate cut-outs analyzed for EDX. The cube-shaped
554 feature in the 0.56 – 1.0 μm substrate appears to be KCl because of the high color density of K
555 and Cl in the elemental maps (bright red and bright blue-green in Fig. S7-f6/f8) and because the
556 shape of KCl is cubic (Pirker et al., 2020). The crystal-shaped rectangle in the 0.32 – 0.56 μm
557 range appears to be enriched by Cl (bright blue-green in Fig. S7-d6). The same applies to the
558 capsule-shaped particle in 0.56 – 1.0 μm image (bright blue-green in Fig. S7-e5). The chloride

559 ion (Cl^-) is a component of metal salts, usually in the form of ClO_4^- or ClO_3^- (Tian et al., 2014)
560 used to color fireworks (Shimizu, 1988).

561 These results of the sampled portions of the substrate stages are consistent with the results of the
562 size-resolved submicrometer enrichments measured by IC and ICP-QQQ (Section 3.4) for Mo,
563 K, Mg, Al, Ba, and Tl. Molybdenum was brightest red in the $0.32 - 0.56 \mu\text{m}$ image (Fig. S7-d8),
564 consistent with the highest enrichments (4.15 in Fig. 6) for that size range. Potassium was
565 brightest red in the $0.56 - 1.0 \mu\text{m}$ image (Fig. S7-e6/f6), consistent with highest enrichments
566 (33.04 in Fig. 6). Magnesium was brightest yellow from $0.32 - 1.0 \mu\text{m}$ (Fig. S7-d4/e3/f4),
567 consistent with highest enrichments (9.50 and 11.58 in Fig. 6). Aluminum had a high signal in
568 the blank Teflon substrate but also was brightest blue-green (Fig. S7-d5/e4/f5) in between $0.32 -$
569 $1.0 \mu\text{m}$ in the sample during the firework event, consistent with highest enrichments (9.22 and
570 13.32 in Fig. 6). Barium was detected by EDX between $0.56 - 1.0 \mu\text{m}$ (Fig. S7-f11 where its
571 enrichment was 12.39 (Fig. 6). Thallium was detected between 0.56 and $1.0 \mu\text{m}$ (Fig. S7-f13) by
572 EDX, where its enrichment was highest (18.12 in Fig. 7) as detected by ICP-QQQ. The
573 submicrometer metal salts due to fireworks can uptake water at high humidity (ten Brink et al.,
574 2018).

575

576 3.6 Hygroscopicity Analysis

577 As fireworks alter the chemical profile of ambient PM, we estimate how aerosol hygroscopicity
578 responded during fireworks relative to periods before and after. For reference, typical κ values
579 range from 0.1 to 0.5 for diverse air mass types such as urban, marine, biogenic, biomass
580 burning, and free troposphere (Dusek et al., 2010; Hersey et al., 2013; Shingler et al., 2016;
581 Shinzuka et al., 2009). AzadiAghdam et al. (2019) reported size-resolved values ranging from
582 0.02 to 0.31 using data from the same field site in Metro Manila but for a different time period
583 and without any firework influence (July – December 2018). They found the highest values to be
584 coincident with MOUDI stages with most sea salt influence ($3.2 - 5.6 \mu\text{m}$).

585 For this study, a bulk κ value is reported for the size range between $0.056 - 3.2 \mu\text{m}$ as noted in
586 Section 2.7, and subsequent references to composition data are for this size range. Kappa was
587 enhanced during the firework event (0.18) compared to before (0.11), due mostly to increased
588 contributions from K_2SO_4 and $\text{Mg}(\text{NO}_3)_2$ (Fig. 8a). This is expected because based on the ZSR
589 mixing rule (Stokes and Robinson, 1966) the bulk hygroscopicity (κ) is dependent on the sum of
590 the κ values for individual non-interacting compounds weighted by their respective volume
591 fractions. More specifically, the volume fractions of K_2SO_4 and $\text{Mg}(\text{NO}_3)_2$ increased from 0.01
592 to 0.10 and 0.01 to 0.03, respectively (Fig. 8b). Notable reductions in volume fraction during the
593 firework event were for NaNO_3 (0.01 to 0.00), black carbon (0.26 to 0.12), and $(\text{NH}_4)_2\text{SO}_4$ (0.02
594 to 0.01) (Fig. 8b). All three species are not associated with primary firework emissions. Although
595 NaNO_3 and $(\text{NH}_4)_2\text{SO}_4$ are hygroscopic, their decreased volume fractions happened alongside a
596 decreased volume fraction of non-hygroscopic black carbon and increased volume fractions of

597 the firework-related and hygroscopic K_2SO_4 and $Mg(NO_3)_2$, which increased bulk aerosol
598 hygroscopicity during the firework event.

599 Kappa decreased to an intermediate value after the firework event (0.15) (Fig. 8a); this value
600 exceeds that from before the fireworks owing partly to more sea salt influence that was unrelated
601 to fireworks. The change in volume fraction of sea salt from before and during fireworks (0.01)
602 to after the fireworks (0.03) (Fig. 8b) translated to an increase of 0.03 in bulk κ (Fig. 8a) from
603 before to after the firework event. Although fireworks emit extensive amounts of inorganic
604 species, the calculated κ values were still relatively low because the background air is dominated
605 by organics and black carbon, which are relatively hydrophobic species (Table S4) (Cohen et al.,
606 2009; Oanh et al., 2006; Cruz et al., 2019).

607

608 **4. Conclusion**

609 This study reports on important aerosol characteristics measured during the 2019 New Year
610 fireworks in Metro Manila. Notable results of this work, following the order of questions raised
611 at the end of Section 1, are as follows:

- 612 • Firework activities caused significant enhancement of $PM_{2.5}$ reaching a maximum of
613 $383.9 \mu g m^{-3}$ between 01:00 to 02:00 on 1 January 2019. Surface aerosol loading
614 increased over a period of eight hours during the firework event, coincident with peak
615 $PM_{2.5}$ levels. The heaviest aerosol layer measured by the HSRL lidar was observed for at
616 least an hour, and reached ~ 440 m above the surface, after which the aerosol layer
617 dropped to 118 ± 20 m. Aerosol backscatter during the firework activity decreased
618 noticeably for short periods after rainfall. Besides rainfall, wind, and relative humidity
619 also possibly contributed to washout, local dispersion, and secondary formation of
620 particles, respectively. There was no significant influence from long-range transport to
621 the sampling site, confirming that the sample data was most representative of the local
622 nature of particulate enhancements observed during the firework event.
- 623 • The firework event enhanced bulk concentrations of water-soluble aerosol species,
624 especially in the submicrometer range. Mass size distributions of the water-soluble
625 species shifted to slightly larger accumulation-mode sizes most likely due to increased
626 coagulation sinks and secondary formation. Potassium and $nss-SO_4^{2-}$ were the major
627 water-soluble contributors. Cubic and capsule-shaped Cl^- -rich particles were prominent in
628 submicrometer particles collected during the firework event, suggesting the presence of
629 KCl . Inorganic species including Cu, Sr, Ba, K^+ , Al, Pb, Mg^{2+} , Cr, Tl, Cl^- , Mn, Rb, Zn,
630 and Ag were enriched more than two times by mass during the firework event as
631 compared to before and after the event. While the most enriched inorganic firework
632 tracers, including Cu, Sr, Ba, Al, and Pb (excluding K^+), comprised only 2.1% of the total
633 water-soluble mass, their contribution is significant because they support findings that the
634 samples represent firework emissions. The increased volume fractions of inorganics

635 increased aerosol hygroscopicity (κ) between 0.056 and 3.2 μm from 0.11 (before the
636 fireworks) to 0.18 during the firework event.

637 Fireworks caused unhealthy levels of $\text{PM}_{2.5}$ that exceeded the Philippine ($50.0 \mu\text{g m}^{-3}$), U.S.
638 ($35.0 \mu\text{g m}^{-3}$), and World Health Organization (WHO, $25.0 \mu\text{g m}^{-3}$) standards for $\text{PM}_{2.5}$ over 24
639 hours. The brief but sharply enhanced concentrations of water-soluble species in the
640 submicrometer size range, especially for K^+ and SO_4^{2-} , have implications for both public health
641 and the environment, the former of which is owing to how smaller particles can penetrate more
642 deeply into the human respiratory system. Some of the components detected during the fireworks
643 were submicrometer Pb and Mg^{2+} , which is of concern because these are banned substances due
644 to their being health and fire hazards, respectively. The presence of Pb in the firework emissions
645 exacerbates the presence of submicrometer Pb in Metro Manila (Gonzalez et al., 2021). The
646 results show the opportunity that improved quality and management of fireworks can have for
647 better local air quality.

648 Higher concentrations of secondary particles in the accumulation mode from fireworks are
649 related to increased mass extinction efficiency and therefore decreased visibility (Jiang et al.,
650 2014), as was observed in this study. The increased water-soluble fraction, especially in the
651 submicrometer mode, during firework events coincides with elevated particle hygroscopicity,
652 which is related to CCN activity (Drewnick et al., 2006) at smaller diameters (Yuan et al., 2020),
653 with implications that can be better assessed in a future study. The atmospheric environment in
654 Southeast Asia, coupled with increasing emissions and extreme sources such as fireworks, offers
655 a unique field laboratory for the study of aerosol aqueous processes.

656

657 **Data availability**

658 High Spectral Resolution Lidar data collected at Manila Observatory can be found at:
659 (University of Wisconsin Lidar Group) http://hsrl.ssec.wisc.edu/by_site/30/custom_rti/

660 Size-resolved aerosols data collected at Manila Observatory can be found at: (Stahl et al., 2020a)
661 on figshare as well as on the NASA data repository at
662 DOI:10.5067/Suborbital/CAMP2EX2018/DATA001.

663

664 **Author Contributions**

665 MTC, MOC, JBS, RAB, ABM, CS, and AS designed the experiments. All coauthors carried out
666 various aspects of the data collection. MTC, EE, SV, RH, GL, LM, CS, and AS conducted
667 analysis and interpretation of the data. EE, LM, SV, RH, GL, and AS prepared the manuscript
668 with contributions from the coauthors.

669

670 **Competing Interests**

671 The authors declare that they have no conflict of interest.

672

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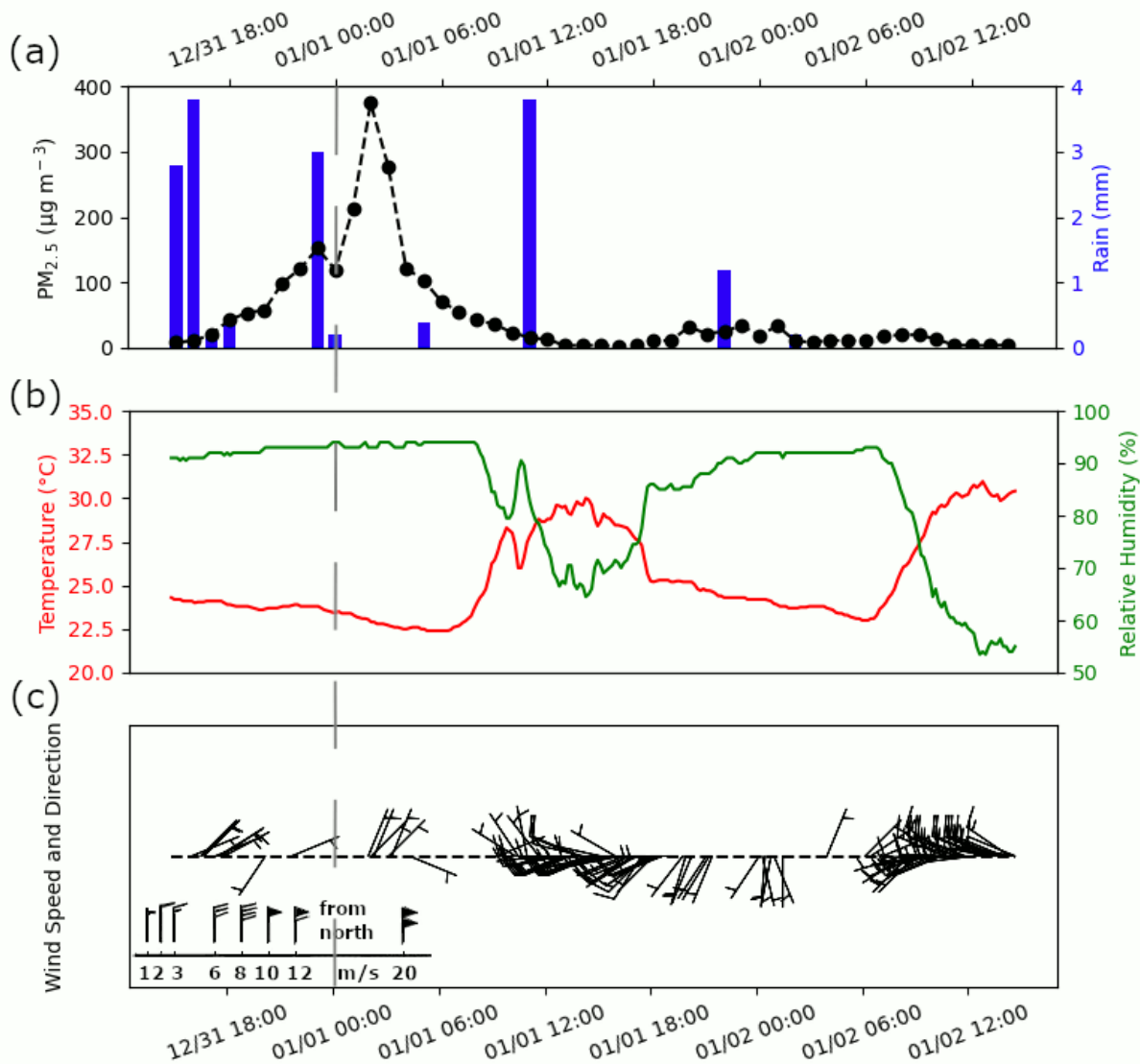
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1015 **Table 1:** Summary of total and speciated concentrations before, during, and after the firework
 1016 event. Species are divided based on units (Total to Zn: $\mu\text{g m}^{-3}$; succinate to Se: ng m^{-3}).

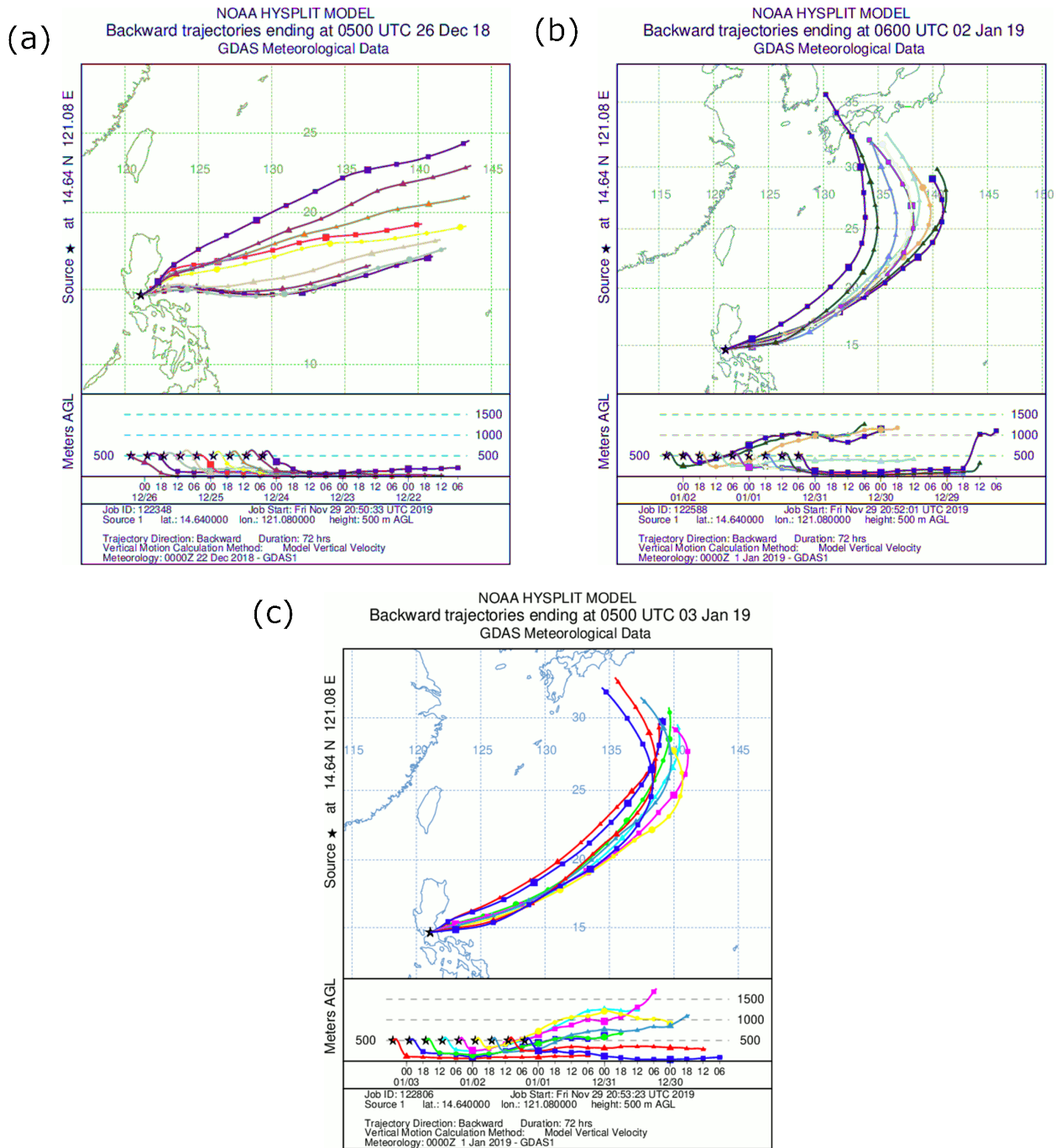
| Species | Total Concentration | | | Species | Total Concentration | | |
|----------------------------------------|---------------------|----------|----------|------------|---------------------|----------|----------|
| | Before | During | After | | Before | During | After |
| TOTAL | 2.93 | 16.74 | 3.54 | MSA | 4.44 | 3.22 | 2.43 |
| nss-SO₄²⁻ | 0.73 | 6.81 | 0.66 | Mn | 0.88 | 2.97 | 1.03 |
| K⁺ | 0.37 | 5.05 | 0.25 | Rb | 0.62 | 1.24 | 0.25 |
| NO₃⁻ | 0.64 | 1.70 | 0.65 | Cr | 0.16 | 1.01 | 0.29 |
| Cl⁻ | 0.23 | 1.46 | 0.57 | As | 0.60 | 0.71 | 0.38 |
| Mg²⁺ | 0.06 | 0.37 | 0.10 | Ni | 0.41 | 0.46 | 0.99 |
| Na⁺ | 0.33 | 0.33 | 0.53 | Ti | 0.10 | 0.27 | 0.24 |
| Ca²⁺ | 0.21 | 0.30 | 0.38 | V | 0.32 | 0.14 | 0.30 |
| NH₄⁺ | 0.21 | 0.19 | 0.28 | Mo | 0.05 | 0.10 | 0.06 |
| Ba | 0.01 | 0.17 | 0.01 | Cd | 0.11 | 0.10 | 0.13 |
| oxalate | 0.10 | 0.12 | 0.06 | Co | 0.05 | 0.05 | 0.05 |
| Cu | 2.48E-04 | 6.89E-02 | 1.86E-03 | Cs | 0.02 | 0.02 | 0.01 |
| Al | 4.53E-03 | 0.05 | 0.01 | Ag | 0.02 | 0.02 | 4.00E-04 |
| Sr | 1.27E-03 | 4.65E-02 | 2.54E-03 | Tl | 0.01 | 0.02 | 1.80E-03 |
| Zn | 0.01 | 0.02 | 0.01 | Zr | 0.01 | 0.01 | 0.03 |
| succinate | 0.98 | 9.51 | 0 | Sn | 0.01 | 6.69E-04 | 0.03 |
| Pb | 1.68 | 8.33 | 1.03 | Y | 2.16E-04 | 4.56E-04 | 2.44E-03 |
| phthalate | 12.82 | 5.36 | 5.59 | Nb | 2.28E-04 | 1.59E-04 | 3.00E-04 |
| adipate | 5.35 | 4.83 | 11.73 | Hf | 0 | 0 | 2.18E-04 |
| maleate | 1.54 | 4.12 | 0 | Hg | 1.03E-03 | 0 | 0 |
| Fe | 2.91 | 3.47 | 7.32 | Se | 5.76 | 0 | 0 |

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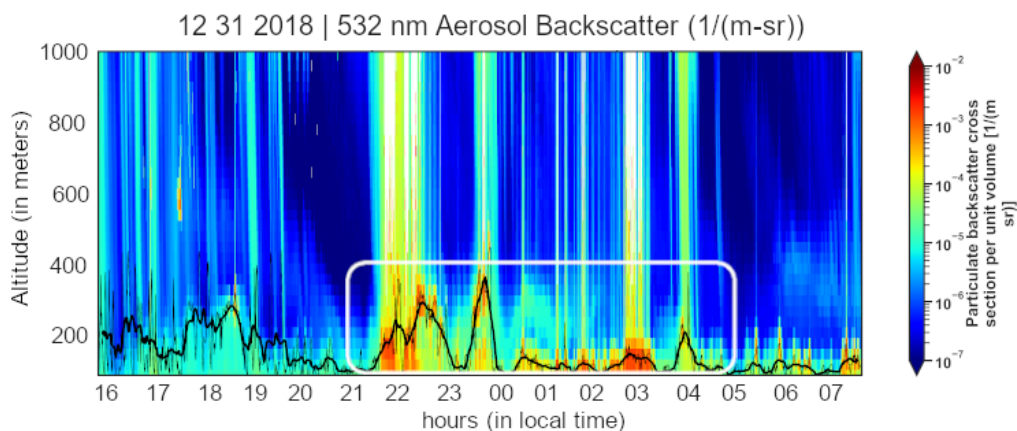
1019 **Figure 1:** (a) PM_{2.5} mass concentrations and rain accumulation at hourly resolution (local time,
 1020 dashed vertical line indicates midnight) as measured from the Manila Observatory main building
 1021 third floor rooftop (~88 m.a.s.l.) at the same period as the MOUDI size-specified samples during
 1022 the firework event. Ten-minute averaged values of (b) temperature and relative humidity, in
 1023 addition to (c) wind speed and direction. The wind barb legend in (c) shows how flags are added
 1024 to the staff with increasing wind speed and in the direction where the wind comes from. Figures
 1025 S2 and S3 show the hourly PM_{2.5} mass concentrations and ten-minute meteorological data before
 1026 and after the firework event, respectively.



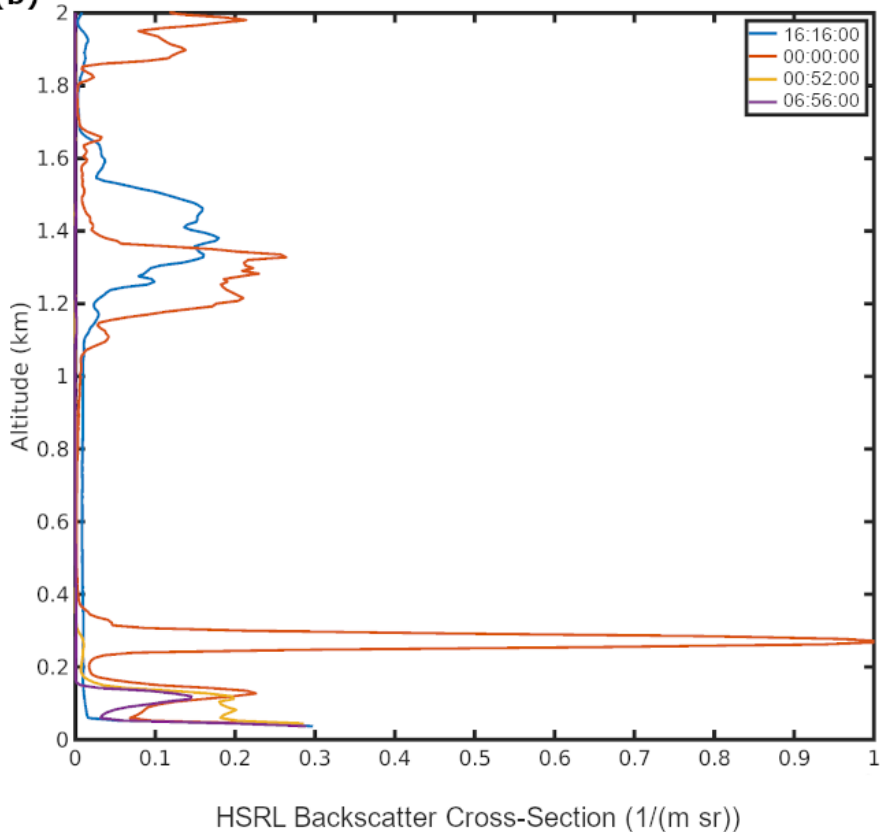
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1028 **Figure 2:** Three-day back trajectories with 6-h resolution for the periods (a) before, (b) during,
1029 and (c) after the firework event, ending at the point of the Manila Observatory at 500 m.

(a)



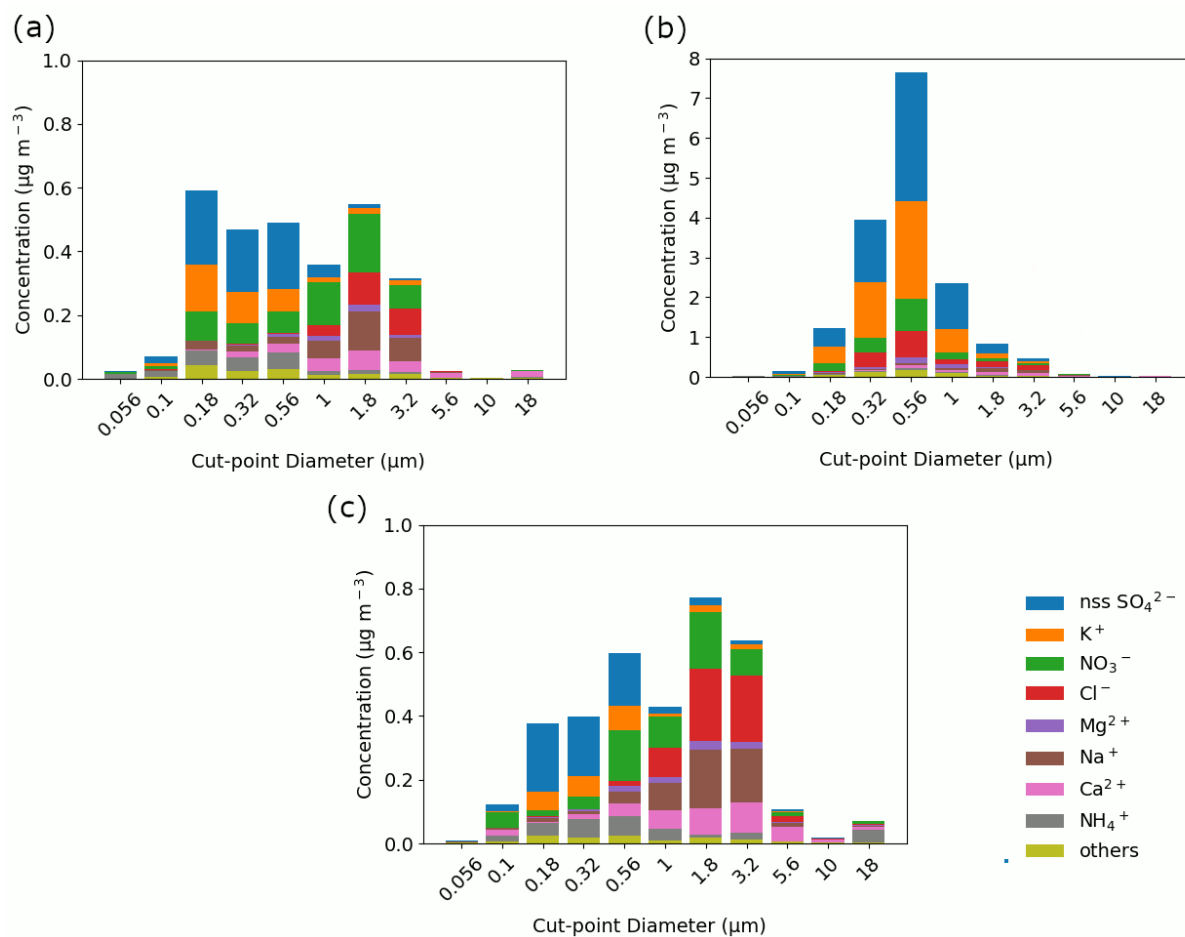
(b)



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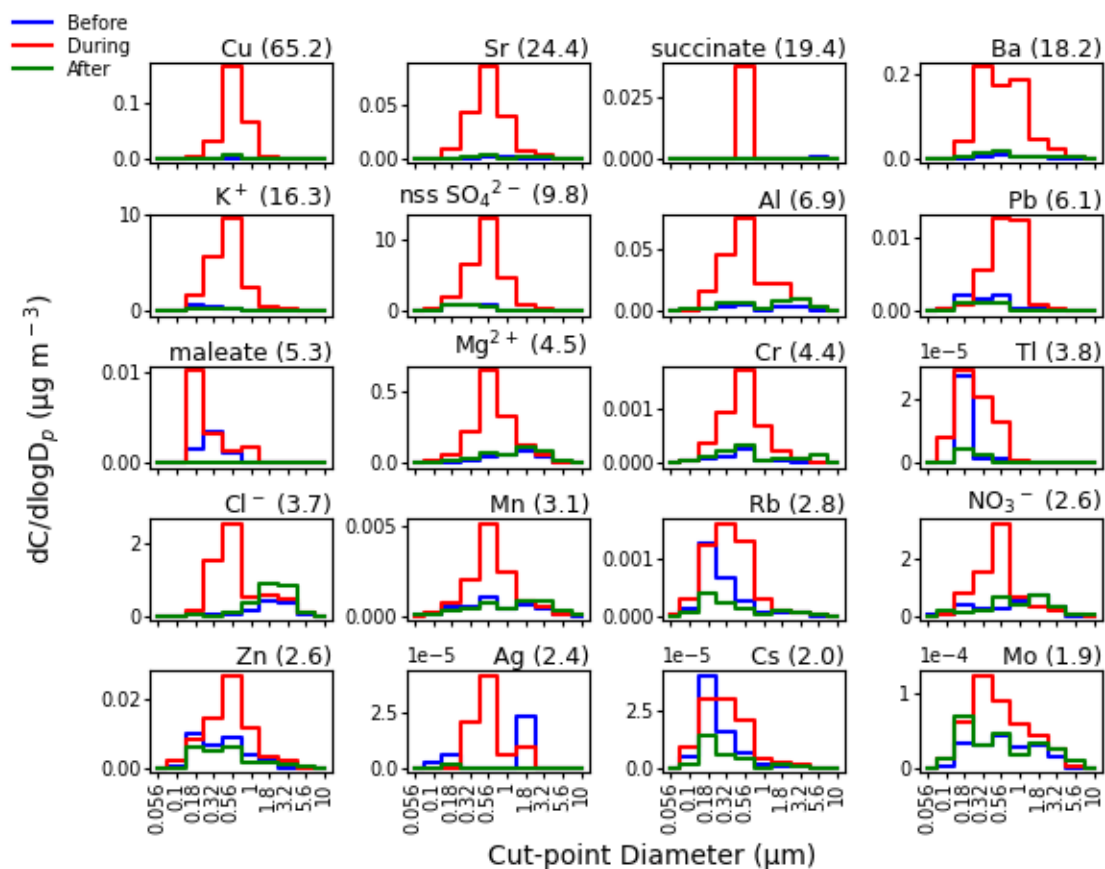
1031 **Figure 3:** (a) Time series of the aerosol backscatter vertical profile from the High Spectral
1032 Resolution Layer (HSRL). The time shown is Universal Time (UT) and local time is UT + 8
1033 hours. The times circled by the white oval correspond to the peak of aerosol backscatter in the
1034 mixing layer due to firework activity. The approximate surface-attached aerosol layer height is
1035 shown as a thick black line. It is derived from a 30-min moving window average based on the 1-
1036 min values shown in thin black line (b) Vertical profiles of aerosol back-scatter at specific UT
1037 times of interest before, during, and after the fireworks.

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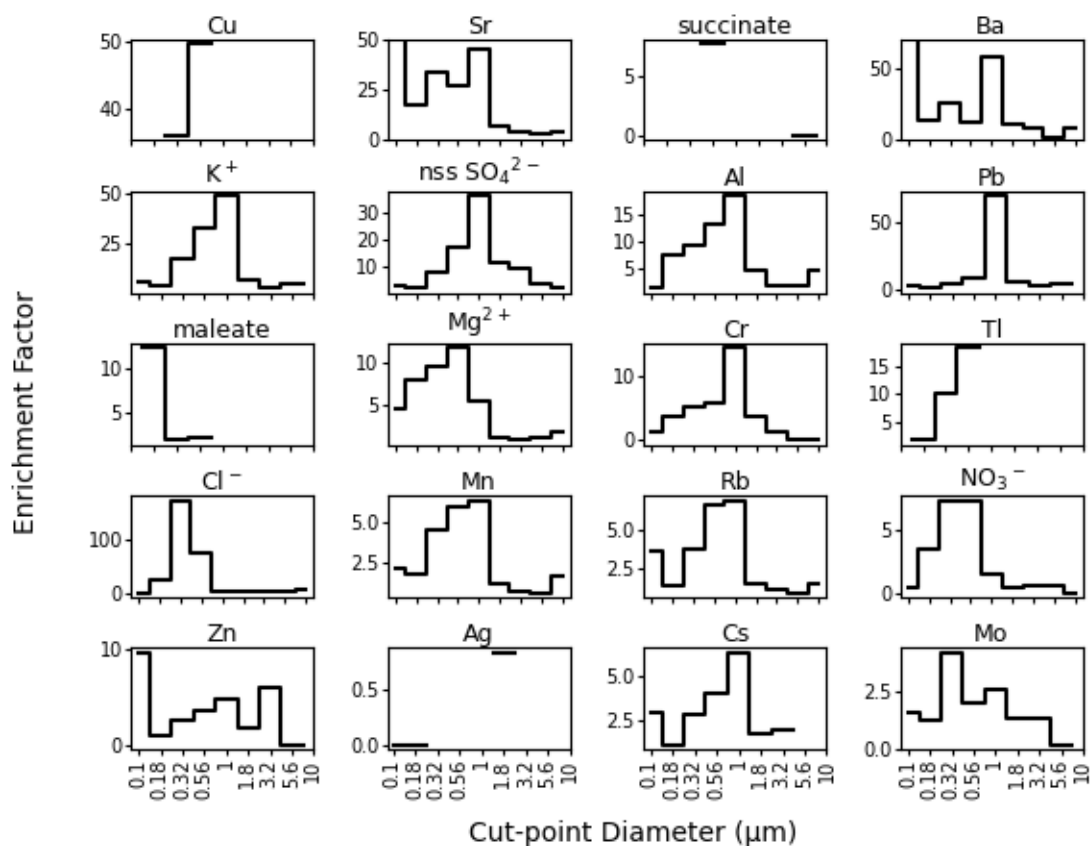
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Figure 4: Speciated mass size distributions of the major aerosol constituents measured (a) before, (b) during, and (c) after the firework event. Table 1 lists the bulk ($\geq 0.056 \mu\text{m}$) mass concentrations of these ions and elements, including those labeled here as “others” (Ba, oxalate, Cu, Al, Sr, Zn, succinate, Pb, phthalate, adipate, maleate, Fe, MSA, Mn, Rb, Cr, As, Ni, Ti, V, Mo, Cd, Co, Cs, Ag, Tl, Zr, Sn, Y, Nb, Hf, Hg, and Se).

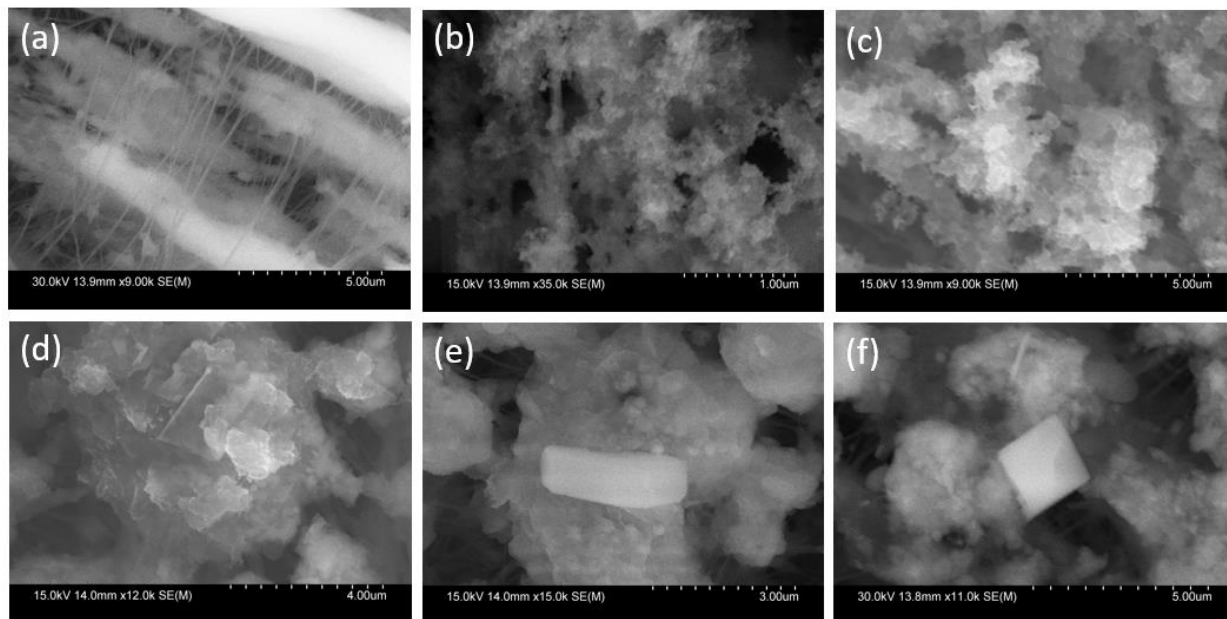


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1047 **Figure 5:** Speciated mass size distributions before (blue line), during (red line), and after (green line)
 1048 the firework event. Next to species labels are bulk ($\geq 0.056 \mu\text{m}$) mass concentration
 1049 enrichment values due to the firework event; species are shown with enrichments ≥ 1.9 . Figure S5
 1050 shows similar results for all other species.

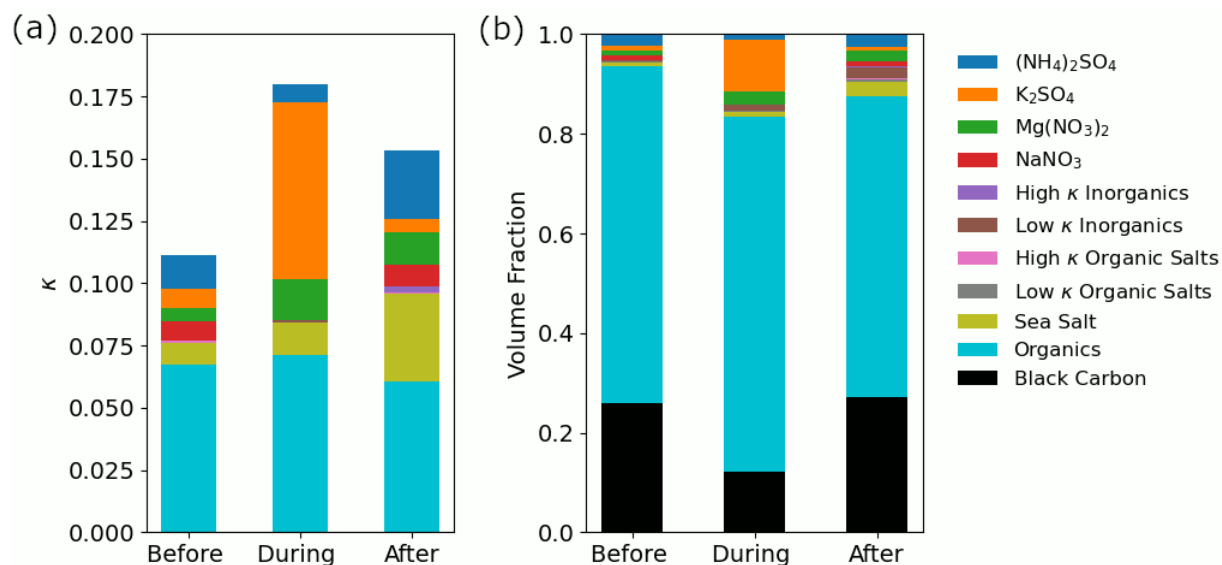


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 1052 **Figure 6:** Size-resolved enrichments for individual firework tracer species in order of decreasing
 1053 total bulk mass concentration enrichment (species from Fig. 5). Cut-point diameters with no
 1054 valid data are left blank. The y-axis of Sr and Ba are truncated to more easily show enrichments
 1055 in the larger size fractions. Figure S6 shows similar results for all other species.



1056

1057 **Figure 7:** Scanning electron microscope (SEM) images of (a) a blank PTFE (Teflon) substrate
1058 and (b-f) particles in different diameter ranges with firework influence: (b) 0.1 – 0.18 μm, (c)
1059 0.18 – 0.32 μm, (d) 0.32 – 0.56 μm, (e-f) 0.56 – 1.0 μm.



1060

1061 **Figure 8:** (a) Kappa (κ) values for the aerosol fraction between 0.056 – 3.2 μm before, during,
 1062 and after the firework event. The speciated contributions to the overall κ values (represented by
 1063 the colors) are categorized based on the classes of compounds in the legend following past work
 1064 (AzadiAghdam et al., 2019). Ammonium sulfate, K_2SO_4 , $\text{Mg}(\text{NO}_3)_2$, and NaNO_3 are high κ
 1065 inorganics but are plotted separately because of their large contributions. The speciated
 1066 contributions were calculated by multiplying the (b) volume fraction of each compound class by
 1067 its intrinsic κ value (Table S4).