Response: We thank the two reviewers for thoughtful suggestions and constructive criticism that have helped us improve our manuscript. Below we provide responses to reviewer concerns and suggestions in blue font. All changes to the manuscript can be identified in the version submitted using Track Changes.

Anonymous Referee #1

Received and published: 25 November 2020

In this study, most contents are spent on describing the data without enough discussion. There was no new information on the method development and conclusion. The suggestions are as follows:

Response: Thank you for your blunt evaluation but we want to also remind the reviewer that according to ACPD, a Measurement Report aims to do the following: "Measurement reports present substantial new results from measurements of atmospheric properties and processes from field and laboratory experiments. Analysis of the measurements may include model results and conclusions of more limited scope than in research articles." We fit into this category as we report substantial new results from field measurements of aerosols over Metro Manila (satisfying the first sentence in the quotation above). Further, we discuss the results and reach a series of conclusions (satisfying the second sentence in the quotation above). If there is any concern that the conclusions are of limited scope, that is fine and not an issue as that is partly the nature of Measurement Reports based on the quotation above.

1. Fireworks have been widely studied all over the world. Although the studies in the Southeast Asian are not so much, the authors must tell us the difference with other regions and the significance of studying fireworks in this region.

Response: Thank you for this comment. China (East Asia) and India (South Asia) where most of the other firework studies have been done are not part of Southeast Asia (SEA) that includes Cambodia, Laos, Myanmar (Burma), Peninsular Malaysia, Thailand, Vietnam, Brunei, East Malaysia, East Timor, Indonesia, Philippines, Singapore, and a small part of India. East Asia and South Asia have different meteorological conditions and geology as compared to SEA. SEA has a unique hydrometeorological condition (high moisture) and geology (islands and mainland) and as such complicates the study of aerosols in the area. Aerosol studies in SEA are generally limited. An extreme event such as New Year with fireworks adds to the complexity and there are scarce studies on this. More specifically, there are no size-speciated chemical analysis as well as optical properties of firework emissions in Manila. Results of this work can improve understanding of the local impacts on health and the environment, which currently are still lacking. Several sentences and sources were added to the introduction about these. Here is the added text:

"Studies on the properties of aerosols in general in South East Asia (Tsay et al., 2013) which is one of the rapidly developing regions in Asia are limited. This compounds the challenge to understand the interactions between aerosols and the complex hydro-meteorological and geological environment in South East Asia (Reid et al., 2013). Increased local and transported emissions (Hopke et al., 2008; Oanh et al., 2006) in South East Asia adds to the complexity and affects air quality in the region. Firework emissions are an example of extreme and regular local emissions in South East Asia. And even while several studies exist in the neighboring regions of East Asia and South Asia, there currently is no in-depth analysis of the chemical, physical, and optical properties of firework emissions in a South East Asian megacity where fireworks are culturally significant. Studies on the impacts on health and the general environment due to firework emissions in South East Asia are as scarce."

2. There are too many questions that the manuscript wants to address. Please combine some of them, so that the aims of this work can be better understood.

Response: Thank you for this note, we have condensed the questions to two major questions:

"We address the following questions in order: (i) what are the conditions of the atmosphere during the study period in relation to aerosols, and how are these affected by firework emissions?; and (ii) what are the concentrations, mass size distributions, and morphological characteristics of different elemental and ionic species specific to fireworks, and how do these affect bulk aerosol hygroscopicity?"

3. Why the carbon fractions were not detected in this work? The manuscript said that "Although fireworks emit extensive amounts of inorganic species, the calculated κ values were still relatively low because the background air is dominated by organics and black carbon, which are relatively hydrophobic species: : :". Carbon fractions accounted for high percentages of PM, and they are important product of fireworks as reported in many literatures. In addition, the carbon aerosol is critical for studying the optical properties and hygroscopicity, which are important parts of this work. Thus, it is a big problem if the carbon fractions were not detected.

Response: We were not able to analyze both for elemental and organic carbon because of the need for separate analysis which was not available at that time. We used related literature on a study done in a nearby site to estimate the ratio of elemental carbon in the samples. An issue was insufficient substrate surface area to do all of the various types of analyses possible. We cut the substrates into portions for the different types of analyses we report in the paper and there was insufficient sample left for more detailed carbon analysis.

4. Many results were reported in this work. However, the explanation and the discussion are lacked. And the relationships among data from different methods must be discussed.

Response: Thanks for this note, hopefully the condensed conclusions and rearranged sentences helped to address the connection between the data, analysis, and implications.

5. The size distribution of chemical compositions can be very useful to study the PM properties, but related discussion is unabundant. And the influence of size distribution of chemical compositions on the optical properties and hygroscopicity must be studied.

Response: We have added text to address the implications of the composition results for optical and hygroscopic properties:

"Higher concentrations of secondary particles, which in this study is in the accumulation mode, from fireworks are related to increased mass extinction efficiency and therefore decreased visibility (Jiang et al., 2014) as was observed. The increased water-soluble fraction, especially in the submicrometer mode, during firework events coincides with elevated particle hygroscopicity which is related to CCN activity (Drewnick et al., 2006) at smaller diameters (Yuan et al., 2020) and which can be part of a future study."

6. More evidences (such as fire plots) should be provided and combined to get conclusion.

Response: We are not fully sure what the reviewer is referring to here as the suggestion is vague to us. We feel that we have reported our measurement data effectively and comprehensively already. We have tried to improve our conclusions, as also mentioned in response to the next comment. Extending the analysis is beyond the scope of this work as this is just a Measurement Report where we report special data for a specific region; more extensive analysis and discussion would warrant a regular article submission which is not what our intention is at this point.

7. The conclusion should be rewritten. The conclusion now just listed some results of the data. The logical relationship of results must be analyzed and more deeper conclusion must be summarized.

Response: Thank you for this note. We have rewritten the conclusion to address the two major science questions in the introduction. We reordered the sentences also to give the context of the work and connect the analysis and results better and more fluidly.

8. The results about compositions have been widely reported, and no new information is provided in this work. The size distribution may be an interesting topic, but it was not studied abundantly in the discussion and no conclusion about it is provided.

Response: We believe the novelty of this work is the "combination" of different datasets used to characterize firework emissions in a critically important (and highly populated area) without a detailed firework study in the peer-reviewed literature yet. We respectfully disagree that we did not study the size distribution behavior as that is the foundation of our analysis (i.e., the MOUDI data). We have addressed this comment thought by adding some more discussion and improved conclusions.

Anonymous Referee #2

Received and published: 2 December 2020

Statement:

This article investigates firework pollution during the 2019 New Year celebrations in Manila, Philippines. It takes a comprehensive approach of investigating the emissions and aftermath of the fireworks from a number of angles, including atmospheric composition, meteorological conditions, transport, and growth/decay of particles. It also investigates changes to atmospheric properties as a result of New Year celebrations. There are several measurements taken during this observation period that are unique to this study.

The authors provide an analysis of pollutants, including particulate matter, metals, and toxins. Further, the article includes particle mode analysis. Concentrations of many pollutants, metals and toxins increased dramatically during the celebrations. Some of these dispersed within a few minutes whereas others stayed longer. Some of the observed compounds decreased during the New Year, which is either attributed to interactions with firework emissions or is attributed to the decrease of normal-day human activity, such as traffic. The study also shows that the chemical behavior of the atmosphere, e.g. particle hygroscopicity, can be altered by firework emissions.

Some of the content, especially in the Results and Discussion section, is rather choppy and needs to be restructured. There are numerous comparisons with other cities without much context explained. Some of the content in the Results and Discussion should be moved to the Introduction or Methods sections, noted in the specific comments below.

The results and conclusions of the article include a blend of scientific and detailed technical observations. Consequently, this feels like it is somewhere in between ACP and ACP Measurement Reports. I would suggest revisions to either make the paper more scientific in nature to submit to ACP, or focus on the new and unique measurements and keep it in ACP Measurement Reports. Should the authors decide to keep the article in ACP Measurement Reports with revisions, I would gladly re-review the article.

Response: Thank you for the thoughtful feedback. We have kept the paper as a Measurement Report and made the necessary revisions to address both reviewer comments, and hope this version is viewed as improved by this reviewer.

Major comments:

The article feels a bit choppy. It jumps from one subject or result to another without necessarily any coherent transition. A few examples are noted in "Specific comments" below. With some revisions to connect different points together, I think this article would flow much better.

The abstract states, "there have not been any comprehensive physicochemical and optical measurements of fireworks and their associated impacts in a Southeast Asia megacity." A similar statement is made in the Introduction. This statement seems a bit bold and also vague and contradictory to the fact that several other studies of firework celebrations in China and India are cited. Perhaps the authors don't consider China and India to be Southeast Asia, but regardless, this statement needs to be more clear. For example, which measurements have never been done before, and which are new in this study and not in the other cited studies? Is this the first study of its kind in the Philippines?

Response: Thank you for this comment. Yes, China (East Asia) and India (South Asia) are not part of South East Asia (Cambodia, Laos, Myanmar (Burma), Peninsular Malaysia, Thailand, Vietnam, Brunei, East Malaysia, East Timor, Indonesia, Philippines, Singapore, and small part of India). We add text to clarify studies in Southeast Asia (SEA) are limited (this is the first to our knowledge for the Philippines in the peer-reviewed literature) and that India and China are not considered part of SEA:

"Studies on the properties of aerosols in general in South East Asia (Tsay et al., 2013) which is one of the rapidly developing regions in Asia are limited. This compounds the challenge to understand the interactions between aerosols and the complex hydro-meteorological and geological environment in South East Asia (Reid et al., 2013). Increased local and transported emissions (Hopke et al., 2008; Oanh et al., 2006) in South East Asia adds to the complexity and affects air quality in the region. Firework emissions are an example of extreme and regular local emissions in South East Asia. And even while several studies exist in the neighboring regions of East Asia and South Asia, there currently is no in-depth analysis of the chemical, physical, and optical properties of firework emissions in a South East Asian megacity where fireworks are culturally significant. Studies on the impacts on health and the general environment due to firework emissions in South East Asia are as scarce."

We also clarify what is unique about our study in terms of our technical approach. We specifically use a wide blend of datasets which are not commonly used altogether to study fireworks, including size-resolved aerosol measurements (e.g.. ionic/elemental composition, morphology), HSRL-2, $PM_{2.5}$ and meteorology). The following text was added:

"And even while several studies exist in the neighboring regions of East Asia and South Asia, there currently is no in-depth analysis of the chemical, physical, and optical properties of firework emissions in a South East Asian megacity where fireworks are culturally significant.

This study is novel because it includes, for the first time aerosol data during fireworks, including size-resolved measurements (e.g. ionic/elemental composition, morphology), HSRL-2, $PM_{2.5}$ and meteorology."

There are many measurements and results here, and not all of them are linked or compared to each other. This contributes to the choppiness of the paper, and there could be more description of how the different observations and results relate to each other.

Response: We try to reduce the so-called choppiness by adding more transition statements between the different types of analyses we present. We also try to harmonize the results and observations better, especially in the conclusions. Here are examples of transition sentences we have now in the draft:

"We begin with hourly $PM_{2.5}$ mass concentration results for the study period to provide context for the spatio-temporal characteristics of fine particulates due to fireworks, their interaction with meteorology, and effects on aerosol optical properties."

"One factor impacting surface PM concentrations is the vertical structure of the lower troposphere, which is addressed in the next section based on HSRL data."

"Building on the previous results describing the general environmental conditions during the study period, now we focus on the detailed size-resolved measurements. "

"Here we more closely examine how much concentrations of species changed during the firework event. "

The conclusion mostly reiterates the results in bullet point form. This needs to be more concise, with only key findings pointed out. Then the conclusion needs to include more relevance to the aerosol measurement science and/or the greater scientific community and public.

Response: We revised conclusions and it has fewer bullets. We tried to make it more concise with only the most important findings. We also tried to emphasize its relevance to broader themes.

This article was submitted to ACP Measurement Reports. In general, there is alignment with the aims of this journal in terms of measurements of various compounds in Manila, which is a new location for such study. This study also contributes new types of measurements. However, the questions in lines 149-155 are more broadly scientific in nature, and the results and conclusions package these results into a more scientific format, similar to other studies on the effects of firework pollution. At the same time, the scientific conclusions are minimal, and focus is very local and not focused on the bigger scientific aims of ACP. In its current form, the content and nature of this article feels somewhere in between ACP and ACP Measurement Reports and not focused on one or the other.

From the website of ACP Measurement Reports: **Measurement reports** present substantial new results from measurements of atmospheric properties and processes from field and laboratory experiments. Analysis of the measurements may include model results and conclusions of more limited scope than in research articles.

Although this study might be the first of its kind in the Philippines, the results are expected and not necessarily new with respect to the many existing publications related to air pollution from firework celebrations. The article needs more emphasis on the aspects of the study that can be considered as “substantial new results.”

Therefore, I would suggest the paper be revised as one of the following:

• Revise the overall nature of the paper to focus more on the scientific and societal contribution of the study, and then submit the paper to the main ACP journal. In particular, include more in-depth scientific answers to the scientific questions asked in lines 149-155.

Additionally, scientific results could, for example, include: How do the results of this study help scientists, policymakers and the general public in not just the Philippines but around the world, and how can these results be used to improve air quality during the New Year in the future?

• Revise to focus more on the aerosol technology, specifically the measurements that are new and unique. There also needs to be more elaboration to how this contributes to the aerosol measurement community. With such revision, this would better align with the aims of ACP Measurement Reports.

Response: We respond to the string of suggestions above all at once here because the string relates to the same theme of whether this paper is a Measurement Report or not. We originally intended for it to be a Measurement Report and still stand by this idea with the submitted draft. We break down each of the 2 sentences from the ACP website about what a Measurement Report is and we justify why our previous version and the revised version fit into this category:

*“**Measurement reports** present substantial new results from measurements of atmospheric properties and processes from field and laboratory experiments.”: We indeed present new and valuable data and results about atmospheric properties from field measurements. There should be no question about this hopefully.*

“Analysis of the measurements may include model results and conclusions of more limited scope than in research articles.”: We analyze the measurement data and present results and conclusions. They may arguably be more limited in scope that research articles because they may be mostly specific to the Philippines region. But again, the limitation of this study having been done in one site is why we originally even considered that this would eventually be placed into a Measurement Report category. We don’t feel (like the reviewer said) that we need especially high focus on “aerosol technology” as we aren’t focused on a methods/instrument paper (otherwise that would be a AMT submission). If we put in too much discussion and comparisons with other regions, we do not feel that hurts the paper but instead makes it stronger, especially for a Measurement Report type of paper.

As an example of what could be revised, the article throws in comparisons with various other cities around the world in with the results/discussion. This shows promise for good scientific content. In its current form, however, these comparisons cause the article to feel choppy. What is the relevance of these comparisons? What do these comparisons to other cities contribute to either aerosol technology and/or to the general scientific community and public? These comparisons could be elaborated and made more scientific.

Response: We have addressed these by moving some of the comparisons to the Introduction for better flow and background information before getting into the results. Examples of the text now are as follows:

"In Nanning, China, SO_4^{2-} peaked at 0.62 µm during fireworks (Li et al., 2017). The mass diameter of K^+ was 0.7 µm due to firework emissions after transport in Washington State (Perry, 1999)." This sentence was moved from the discussion of results and now appears in the introduction section in the paragraph on size distributions.

"Inorganic salts (K_2SO_4, KCl) dominated the aerosol hygroscopicity in Xi'an, China during fireworks (Wu et al., 2018). In the Netherlands, enhancements in salt mixtures containing SO_4^{2-}, Cl^-, Mg^{2+}, and K^+ were noted to enhance hygroscopicity (ten Brink et al., 2018)." This sentence was also removed from the discussion of the results and moved to the introduction section on composition.

One thing that really stood out to me is the toxins, especially lead. This brings to mind a hypothetical question: Could it be possible to use this study to make an argument to policymakers to forbid the use of these toxins or find alternatives to these toxins in fireworks? Although such recommendation might be outside the scope of this specific Measurement Report, elaboration on the seriousness of lead and other toxins in fireworks, which were clearly observed in Manila, could be emphasized more – this could make the paper into a stronger contribution to the scientific community and general public, and it could make the conclusions much stronger.

Response: Excellent suggestion, thank you. We have included a phrase on the hazardous effect of Pb to health in the conclusion. We also add mention to a very recently published paper on lead in the Metro Manila region (Gonzalez et al., 2021). Here is our added text:

"The presence of Pb in the firework emissions exacerbates the presence of submicrometer Pb in Metro Manila (Gonzalez et al., 2021)."

I would also suggest making a timeseries figure with these metals and toxins, not just a before/during/after figure.

Response: This is currently not possible because we only have three data points in time (accumulated sample of 2 days for before, during and after) for each metal and toxin. We hope we understood what you meant. Had we obtained more data at better than 2 day time resolution, this would have been an excellent addition.

Specific comments:

Title: The plural of "Fireworks" plus the second noun "impacts" is not correct English. It should say any of the following: "Firework impacts" or "Impacts of fireworks" or possessive "Fireworks' impacts".

Response: Thank you, we removed the "s" tailing Firework. Now the title reads… "Firework impacts"…

Lines 54-59: Listing these specific numbers from cities around the world is not necessary, and giving these numbers does not add any significance to the article. The two sentences following this are sufficient for this paragraph.

Response: We removed the specific numbers from the text but kept the list of cities and then combined that with the following sentence:

"Total PM mass concentrations during local celebrations in different cities: Leipzig, Germany, (Wehner et al., 2000), Texas, United States [U.S.], (Karnae, 2005), Montreal, Canada (Joly et al., 2010), and New Delhi, India, (Mönkkönen et al., 2004) exceeded the 24 h U.S. National Ambient Air Quality Standard (NAAQS) for PM_{10} of 150 µg m^{-3}."

Line 64: "India where" should be "India, and"

Response: We replaced to "India, and"…

Lines 161-163: This sentence doesn't make sense, and it is irrelevant to the article. This topic is not discussed anywhere in the article.

Response: Ok, we deleted that sentence.

Lines 207-214: The sentence beginning with "Although" through the sentence ending with "study" do not belong in this paragraph. This is introductory material, not methods.

Response: We needed to include that sentence because locally there is also firework activity on December 24 which is included in the date of the background sample (before) used for the New Year firework sampling (December 31 to January 2). We included the dates for the before, after, and during samples in the sentence before for context.

Line 211: The sentence, "There was limited firework after midnight" needs to be more specific and clear – what does "limited" mean, and with respect to what, specifically?

Response: We changed the preceding sentence:

"Firework activity around the sampling site began around ~19:00 on December 31, 2018, peaked at 00:00 of 1 January 2019, and dropped drastically after. Based on $PM_{2.5}$ data there was no evidence of sustained firework activity past midnight."

Section 2.7 "Back Trajectories" should be moved to after section 2.2 "Meteorological Data" for better flow of related content and to be consistent with the order in which results are presented.

Response: Thank you for this note, we reordered the section and moved Back Trajectories to section 2.3 and reordered the sections that came after. We also edited in-line text that may have been affected by this reordering.

Line 293-295: This first sentence should be in the introduction or methods section, not results.

Response: Thank you for this, we deleted this first sentence in the results and added the following to the first sentence of the Methods section "the evolution of and the":

"Hourly $PM_{2.5}$ mass concentrations were obtained to assess the evolution of and the temporal characteristics of fine particulates due to fireworks and their relation to meteorology and aerosol optical properties."

Lines 325-329: The last two sentences in this paragraph jump back to talking about fireworks in other countries, which was already stated in the introduction and are now redundant. These two sentences could be deleted. Alternatively, if the intention is to make a scientific comparison of Manila in 2019 to other cities, then this needs to be elaborated, and the comparison needs to be done in more scientific detail.

Response: The last two sentences were revised. The first sentence was revised to emphasize that the results are comparable to past studies, and that greater increases (second sentence) have been observed where there were more firework activity in general (Chinese New Year, more intense and prolonged, lasting several days)). The edited two sentences follow:

"Two to three-fold increases in PM mass concentration due to fireworks has also been observed in previous work in other countries (Rao et al., 2012; Ravindra et al., 2003; Tsai et al., 2011; Shen et al., 2009). Greater increases (> 5 times) in particulate mass concentrations elsewhere were related to more intense and prolonged "(lasting several days)" firework activity (Tian et al., 2014)"

Lines 330-332: This first sentence was already stated in the methods sections and is redundant here.

Response: We removed this first sentence from the results and added the following to the methods section for context: "To ascertain the impact of fireworks on the surface particulate concentrations,…"

Lines 353-358: Again, this is jumping back to methods. Only the last three sentences in this paragraph are the results.

Response: We moved these sentences to the methods section and edited appropriately. Here is what it looks like in the methods section:

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

Lines 364-367: These first two sentences are also describing methods of calculation as opposed to results.

Response: We moved these sentences to the methods section (2.5 Aerosol Composition and Morphology Measurements).

Lines 393-394: Again, this jumps back-and-forth from showing results to comparing to another city. If this kind of comparison is desired, then another sentence or two describing the relevance and greater context of this should be added. This should be in a separate paragraph rather than squeezed in the middle of a paragraph reporting numerical results.

Response: We were doing the comparison in order to suggest possible mechanisms for the slightly larger sulfate particle size during fireworks. The Li article makes a suggestion that it is because sulfate is formed secondarily during the fireworks and that particle aging contributes also to growth. We moved the information about the size to the introduction. Then we moved the other sentences in the noted line numbers to another paragraph after the discussion of K^+ results.

Lines 404-405: This is another comparison to a different city that doesn't quite fit in between reporting numerical results from Manila.

Response: We moved the size info of the different city to the introduction.

Lines 429-433: Here is another comparison to a different location, this time Taiwan. Here, though, the relevance is better explained, and it flows better than these comparisons in other places in the manuscript, but then the following sentence beginning with "The lack of increased sea salt" jumps back to results/discussion in Manila. I would suggest the comparison to Taiwan be moved to a separate paragraph.

Response: Thank you for this note, and for the appreciation… we moved the note on the Taiwan results to the introduction as there was only one sentence about this and would have been insufficient for another paragraph.

Lines 485-486: "Lead is highly toxic and thus regulated (Moreno et al., 2010) as its occurrence in fireworks is not ideal." – I would say it's more than just "not ideal;" it sounds like a serious health hazard to me.

Response: We have changed the wording to "serious health hazard"

Lines 570-573: This is again a place where the text jumps into comparisons with specific other cities. The relevance and context needs to be elaborated a bit more. Figure 3: Why does this figure use UTC when the other figures use local time? Then there is unnecessary text in the middle of (a) stating that 16UTC is midnight local time. I would suggest using local time because the study is with respect to the New Year (centered around 00:00) and to be consistent with other figures.

Response: Thank you, we moved the note on the different countries to the introduction. We changed the time units to local time instead of UTC for Figure 3.

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

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Abstract

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

1. Introduction

Fireworks affect local populations through visibility reduction and increased health risks due to briefly elevated particulate matter (PM) levels. Total PM mass concentrations during local celebrations in the followingdifferent cities exceeded the 24 h U.S. National Ambient Air Quality Standard (NAAQS) for PM_{10} of 150 µg m^{-3}: have reached up to 235 µg m^{-3} (Leipzig, Germany,) (Wehner et al., 2000), 700 µg m^{-3} (Texas, United States [U.S.],.]) (Karnae, 2005), 1,510 µg m^{-3} (Montreal, Canada) (Joly et al., 2010), and 2,582 µg m^{-3} (New Delhi, India,) (Mönkkönen et al., 2004). These levels exceed the 24 h U.S. National Ambient Air Quality Standard (NAAQS) for PM_{10} of 150 µg m^{-3}. Firework emissions from at least nineteen studies have also been linked to exceedance of the 24 h U.S. NAAQS limit for $PM_{2.5}$ of 35 µg m^{-3} (Lin, 2016 and references therein). Higher PM concentrations from fireworks have been reported more frequently in Asia (i.e., India, China, and Taiwan) compared to Western countries (Lin, 2016; Sarkar et al., 2010).

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

Measurements of the chemical composition of firework emissions are important in order to understand how they affect local air quality. The main components of fireworks are fuels (metals and alloys, metalloids, and non-metals), oxidizers (nitrates, perchlorates, and chlorates), and coloring agents (metal salts) (Steinhauser and Klapotke, 2010). Previous studies have relied on tracer species to establish confidence in distinguishing the firework source from background air and other sources (Sarkar et al., 2010). Potassium historically has been the most observable tracer for fireworks emissions (Wang et al., 2007; Drewnick et al., 2006; Perry, 1999), with concentrations reaching 58 µg m^{-3} during the Diwali Festival in India (Kulshrestha et al., 2004). Firework color is created by metal salts such as Sr for red, Ba for green, and Cu for blue, all three of which have and have been found to be effective tracers of fireworks (Walsh et al., 2009; Vecchi et al., 2008). Strontium in particular is an indicator of the spatial and temporal extent of firework smoke plumes (Perry, 1999) because of the high prevalence of red in fireworks and it is not affected by traffic emissions (Moreno et al., 2010). Other components measured in the air that have been attributed to fireworks include metals (such as Al, Cd, Cu, Ti, Mg, Mn, Ni, Zn, As, Bi, Co, Ga, Hg, Cr, Pb, Rb, Sb, P) and their salt anion counterparts (S, P, Cl).) and other trace metals

(As, Bi, Co, Ga, Hg, Cr, Pb, Rb, Sb, and P). Also from fuel and oxidizer combustion are species such as NO_3^-, SO_4^{2-}, and organics including oxaloacetic acid (Alpert and Hopke, 1981; Barman et al., 2008; Carranza et al., 2001; Dorado et al., 2001; Drewnick et al., 2006; Joly et al., 2010; Joshi et al., 2016; Kulshrestha et al., 2004; Kumar et al., 2016; Lin et al., 2016; Moreno et al., 2010; Sarkar et al., 2010; Tanda et al., 2019; Thakur et al., 2010; Joshi et al., 2019). Firework-derived chloride in Taiwan has been attributed to raw materials such as $KClO_3$, ClO_3, and ClO_4 with $Cl^-:Na^+$ ratios reaching approximately 3 (Tsai et al., 2012). Black carbon mass concentrations during firework events can either increase due to firework emissions or decrease owing to fewer vehicles on the road (Kumar et al., 2016; Yadav et al., 2019). In both cases, the black carbon mass fraction decreases due to a greater contribution of other constituents in firework emissions. Organic mass concentrations and mass fractions have been noted to increase and decrease, respectively, with fireworks (Zhang et al., 2019). Governed largely by composition, particulate hygroscopicity and solubility have also been found to be altered by fireworks depending on the emitted species. Inorganic salts (K_2SO_4, KCl) dominated the aerosol hygroscopicity in Xi'an, China during fireworks (Wu et al., 2018). In the Netherlands, enhancements in salt mixtures containing SO_4^{2-}, Cl^-, Mg^{2+}, and K^+ were noted to enhance hygroscopicity (ten Brink et al., 2018). Copper and Mg were observed to become more soluble in firework emissions in Delhi, India, while Mn, As, Ba, and Pb became less soluble (Perrino et al., 2011). The water-soluble aerosol component from fireworks in Sichuan Basin (China) were internally mixed and enhanced the hygroscopicity of submicrometer aerosols, especially the larger particles (Yuan et al., 2020).

In addition to composition, a necessary aspect of characterizing impacts of firework emissions is to measure aerosol size distributions within the short timeframe of an event (Joshi et al., 2019). Owing to combustion during firework events, PM concentrations are dominated by particles in the submicrometer range (Vecchi et al., 2008; Nicolás et al., 2009; Joshi et al., 2019; Pirker et al., 2020; Do et al., 2012). Particle number concentration maxima have been noted for the nucleation (0.01 to 0.02 µm) and Aitken (0.02 to 0.05 µm) modes (Yadav et al., 2019; Yuan et al., 2020), in addition to both the small (0.1 to 0.5 µm) (Wehner et al., 2000; Zhang et al., 2010) and large (0.5 to 1.0 µm) ends of the accumulation mode (Vecchi et al., 2008) during firework events. In Nanning, China, SO_4^{2-} peaked at 0.62 µm during fireworks (Li et al., 2017). The mass diameter of K^+ was 0.7 µm due to firework emissions after transport in Washington State (Perry, 1999). There are a few studies with observed particle mass concentration increases in the coarser but still respirable (< 10 µm) mode (Tsai et al., 2011). In terms of dynamic behavior in the size distributions, past work has shown a shift in number concentration from nucleation and Aitken modes to the smaller end of the accumulation mode (0.1 to 0.5 µm), due to increased coagulation sinks (Zhang et al., 2010). Finer temporal scale monitoring has revealed steep increases in nucleation mode and Aitken mode particle concentrations associated with firework emissions followed by a growth in accumulation mode particle number concentrations due to coagulation (Yadav et al., 2019). An opposite shift to a smaller size distribution has been observed for certain species (Mg, Al, Cu, Sr, and Ba) from the coarse mode to accumulation mode (Tanda et al., 2019). Other work has shown that while there is usually a quick drop in particle concentration to background values after firework events (Joly et al., 2010), elevated number concentrations of accumulation mode particles are maintained for up to three hours after peak firework activity (Hussein et al., 2005). New particle formation events with fireworks have also been reported in Mumbai, India (Joshi et al., 2016), with enrichments of primary and secondary particles for up to 30 minutes after peak firework activity. Particle aging due to distance from the source and meteorology alter firework emission particle concentrations (Joly et al., 2010) and size distributions (Khaparde et al., 2012).

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

Studies on aerosol properties are limited for the rapidly developing region of Southeast Asia (Tsay et al., 2013). This compounds the challenge to understand the interactions between aerosols and the complex hydro-meteorological and geological environment in Southeast Asia (Reid et al., 2013). Increased local and transported emissions (Hopke et al., 2008; Oanh et al., 2006) in Southeast Asia add to the complexity and affect air quality in the region. Firework emissions are an example of extreme and regular local emissions in Southeast Asia. Even while several studies exist in the neighboring regions of East Asia (e.g., China) and South Asia (e.g., India), thereThere currently is no in-depth analysis of the chemical, physical, and optical properties of firework emissions in a Southeast Asian megacity where fireworks are culturally significant. This study is additionally novel because it includes the following combination of data types to investigate fireworks: size-resolved measurements (ionic/elemental composition, morphology), vertically-resolved data from a High Spectral Resolution Lidar (HSRL), $PM_{2.5}$, and meteorology. This work reports these data on size-resolved aerosol characteristics during the 2019 New Year celebrations in Metro Manila, Philippines, one of the most populated cities, with 12.88 M population (PSA, 2015).), in Southeast Asia. We address the following questions in order: (i) what areis the conditions of the atmospheremeteorological backdrop during the study period in relation to aerosols, and how are these affected by $PM_{2.5}$ levels; (ii) what is the effect of the firework emissions?; (ii on optical properties of aerosols?; (iii) what are the concentrations, and mass size distributions, and morphologicaldistribution characteristics of different elemental and ionic species specific to fireworks, and how do these affect bulk?; (iv) what are the most enhanced tracers in firework emissions?; (v) what are the size-resolved morphological characteristics of firework aerosols?; (vi) how does aerosol hygroscopicity? respond to firework emissions? The results of this work provide new data that can help address how past and on-going firework emissions impact health, visibility, regional air quality, and biogeochemical cycling of nutrients and contaminants in the Philippines, Southeast Asia, and, more broadly, for all other cities with major firework events. It also contributes to the growing body of firework research findings (Devara et al., 2015)., with a unique feature of this work being the combination of multiple data products, including surface-based lidar retrievals and size-resolved composition and morphology analyses. Firework events are widespread episodes that can also be used to expose and ultimately resolve differences between satellite and surface data (Williams et al., 2005; Kumar et al., 2016).

2. Methods

2.1 Hourly $PM_{2.5}$ Mass Concentration

Hourly $PM_{2.5}$ mass concentrations were obtained to assess the evolution of and the temporal characteristics of fine particulates due to fireworks and their relation to meteorology and aerosol optical properties. The hourly $PM_{2.5}$ mass concentrations were collected at the Manila Observatory, Quezon City, Philippines (14.64° N, 121.08° E, ~70 m. a. s. l.) (Fig. S1) with a beta attenuation monitor (DKK-TOA Corporation) as part of the East Asia Acid Deposition Monitoring Network (EANET) (Totsuka et al., 2005). The beta attenuation monitor collects $PM_{2.5}$ samples on a ribbon filter, which are irradiated with beta particles. The attenuation of the beta particles through the sample and the filter is exponentially proportional to the mass loading on the filter. These hourly data were then averaged over 48-hour periods coinciding with water-soluble aerosol composition measurements (Section 2.54) before, during, and after the firework event.

2.2 Meteorological Data

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

2.3 Back Trajectories

Three-day back trajectories with six-hour resolution were generated using the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Rolph et al., 2017; Stein et al., 2015) using the Global Data Assimilation System (GDAS) with a resolution of 1°, and vertical wind setting of "model vertical velocity". To ascertain the impact of fireworks on surface particulate concentrations, back trajectories were chosen to end at the beginning times of the sampling periods before, during, and after the firework event. Trajectories were computed for an end point being at the Manila Observatory at an altitude of 500 m because it represents the mixed layer as done in other works examining surface air quality (Mora et al., 2017; Aldhaif et al., 2020; Crosbie et al., 2014; Schlosser et al., 2017).

2.43 Remote Sensing

Vertical profiles of aerosol backscatter cross-section measured with the University of Wisconsin High Spectral Resolution Lidar (HSRL) which was deployed at the Manila Observatory in support of CAMP^{2}EX. The HSRL instrument transmitting laser (Table S1) operates at 532 nm with 250 mW average power and pulse repetition rate of 4 KHz. The HSRL technique measures and separates the returned signal into the molecular and aerosol backscatter by using a beam splitter and an iodine absorption cell filter. The separated molecular signal allows for optical depth and backscatter cross section measurements in contrast to a standard backscatter lidar that requires assumption related to the particulate lidar ratio (Razenkov, 2010). The HSRL also measures particulate depolarization ratio, an indicator of aerosol or cloud particle shape with low depolarization indicative of spherical particles while intermediate values (10%) indicate a mix of spherical and nonspherical particles (Burton et al., 2014; Reid et al., 2017). HSRL data were uploaded and processed at the University of Wisconsin-Madison Space Science and Engineering Center server for periods before, during, and after the fireworks.

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

2.54 Aerosol Composition and Morphology Measurements

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 0.056 µm) was collected on Teflon substrates (PTFE membrane, 2 µm pores, 46.2 mm diameter, Whatman) with two Micro-Orifice Uniform Deposition Impactor (MOUDI II 120R, MSP Corporation) (Marple et al., 2014) samplers from the third floor of the main building (~85 m. a. s. l) at the Manila Observatory. Sample collection for each of the three MOUDI sets lasted 48 hours before (13:30 December 24, 2018 to 13:30 December 26, 2018), during (14:45 December 31, 2018 to 14:45 January 2, 2019), and after (13:30 January 1, 2019 to 13:30 January 3, 2019) firework activities. Note all times refer to local time (UT + 8 hours). Although there were no fireworks released from the sampling site, there was firework activity in the immediate vicinity (~ 500 m from the sampling in all directions and all throughout the city in general). Firework activity around the sampling site began around ~19:00 on 31 December ~~31,~~ 2018,~~ and~~ peaked at 00:00 of 1 January 2019, and dropped drastically after. Based on $PM_{2.5}$ data there~~). There~~ was no evidence of sustained~~limited~~ firework activity past~~after~~ midnight. MOUDI samples collected before (December 24 to 26) and after (January 1 to 3) the firework event (December 31 to January 2) were considered as background samples. Although there is some firework activity that is expected in the evening of December 24 (before the firework event), this is minimal compared to that which is the focus of this study. The samples were covered with aluminum foil, sealed, and stored in the freezer before being shipped to the University of Arizona for elemental and ionic analysis.

Each sample substrate was cut in half. One half of each sample was extracted in 8 mL Milli-Q water (18.2 MΩcm), sonicated, and analyzed for ions (ion chromatography (IC): Thermo Scientific Dionex ICS-2100 system) and elements (triple quadrupole inductively coupled plasma mass spectrometer: ICP-QQQ; Agilent 8800 Series). The remaining substrate halves were stored. Sample ionic and elemental concentrations were corrected by subtracting concentrations from background control samples. More information about the sampling and analysis are detailed in recent work (Stahl et al., 2020b). Limits of detection of the forty-one reported species are summarized in Table S3. Potassium (K^+) was reported based on ICP-QQQ measurements rather than IC due to possible contamination from the KOH eluent used in the latter instrument. Non-sea salt SO_4^{2-} was calculated by subtracting 0.2517 * Na^+ from the total SO_4^{2-} concentration (Prospero et al., 2003).

High-resolution scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX) was used for examining particle morphology and chemical composition on a portion of the substrates collected during the firework event. Analyses were performed with a Hitachi S-4800 high-resolution SEM and a Thermo Fisher Scientific Noran Six X-ray Microanalysis System in the Kuiper Imaging cores at the University of Arizona. Approximately 1 cm^2 was cut from the center of substrate halves and placed on double-sided carbon tape mounted on an aluminum stub. A thin layer (1.38 nm) of carbon was coated on the sample surface using a Leica EM ACE600 sputter coater to improve the sample's conductivity. SEM images were obtained at 15 keV and 30 keV acceleration voltages and with a 20 µA probe current in high-magnification mode. The percentage contributions and the spatial distribution of the elements were obtained from the EDX analysis. Carbon, F, and Al should be ignored in the discussion of SEM-EDX results since C and F are present in the Teflon substrates, and the sample stub is an Al-rich substrate.

A total of 41 water-soluble species were detected in the 48-hr size-differentiated particulate samples collected before, during, and after the firework event. The total bulk mass concentration is defined as the sum of the concentrations of all the measured species across the MOUDI's eleven stages (≥ 0.056 µm).

2.6~~5~~ Enrichment Factor Calculations

To identify which species are most enhanced during fireworks, enrichment values are typically calculated using speciated concentrations during the fireworks relative to baseline periods (Tanda et al., 2019). We calculate water-soluble mass enrichment factors for each of the forty-one measured species by dividing their total bulk (≥ 0.056 μm) mass concentrations during the firework event by the average of the total mass concentration of the species measured before and after the firework event. Size-resolved enrichments were similarly calculated using measured mass concentrations for individual MOUDI stages. In a case when the mass concentration of a species during the firework event was non-zero but the mass concentrations during and after were zero (e.g., succinate), half of the detection limit was used in place of zero values.

2.7~~6~~ Hygroscopicity Calculations

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

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

~~2.7 Back Trajectories~~

~~Three-day back trajectories with six-hour resolution were generated using the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Rolph et al., 2017; Stein et al., 2015) using the Global Data Assimilation System (GDAS) with a resolution of 1°, and vertical wind setting of "model vertical velocity". Back trajectories were chosen to end at the beginning times of the sampling periods before, during, and after the firework event. Trajectories were computed for an end point being at the Manila Observatory at an altitude of 500 m because it represents the mixed layer as done in other works examining surface air quality (Mora et al., 2017; Aldhaif et al., 2020; Crosbie et al., 2014; Schlosser et al., 2017).~~

3. Results and Discussion

3.1 Hourly $PM_{2.5}$, Meteorological, and Transport Patterns

We begin with hourly ~~Temporal analysis of~~ $PM_{2.5}$ mass concentration results for the study period to provide context for the spatio-temporal characteristics of fine particulates due to fireworks, their interaction with ~~and~~ meteorology, and effects on aerosol optical properties. Hourly $PM_{2.5}$ (Fig. 1)~~1) can help in understanding how the enhanced particulate concentrations detected at the Manila Observatory during the fireworks evolved and were influenced by meteorology. Hourly PM2.5~~ began to increase from 44.0 μg m^{-3} (shortly after rising above the 24-h Philippine National Ambient Air Quality Guideline Value (NAAQGV) of 50.0 μg m^{-3}) after 18:00 time on 31 December 2018 with the beginning of firework activity and calm meteorological conditions. There was moderate (3 mm) rainfall from 22:00 to 23:00 that night as the firework activity began to increase. Rain is a sink for particles (Perry, 1999) and could have washed out some of the particulates in the air, thus potentially causing a slight dip in the hourly $PM_{2.5}$ around midnight. $PM_{2.5}$ peaked at 383.9 μg m^{-3} between 01:00 to 02:00 on 1 January 2019. The $PM_{2.5}$ peak was delayed by approximately an hour from the peak firework activity at midnight possibly due to rainfall, relative humidity, and wind (Vecchi et al., 2008), in addition to aerosol dynamical processes requiring time for secondary aerosol formation and growth (Li et al., 2017). Minimal rain (0.2 mm in an hour) with high relative humidity (between 93% ± 4% to 94% ± 4%) were conducive to aerosol growth and/or secondary particle formation. High relative humidity is related to aqueous-phase oxidation of SO_2 (Sun et al., 2013) and NO_2 (Cheng et al., 2014) as well as metal-catalyzed heterogeneous reactions (Wang et al., 2007) to form SO_4^{2-}. Aqueous oxidation has been found to be a predominant mechanism for the secondary formation of SO_4^{2-} during fireworks (Li et al., 2017), in addition to promoting secondary organic aerosol formation (Wonaschuetz et al., 2012; Youn et al., 2013). Light wind (~1 m s^{-1}) after midnight from the northeast could also have transported more emissions from the populated Marikina Valley, located in the northeast, to the Manila Observatory contributing to the delay of the $PM_{2.5}$ peak.

Particulate levels were enhanced for approximately 14 h from the beginning of the firework activity (Fig. 1) during which the average $PM_{2.5}$ (143.4 μg m^{-3}) exceeded the 24 h Philippine

NAAQGV between 18:00 on 31 December 2018 to 08:00 on 1 January 2019. After 02:00 on 1 January 2019, $PM_{2.5}$ dropped quickly to 122.0 µg m^{-3} between 03:00 to 04:00 (Fig. 1). The $PM_{2.5}$ decrease was less pronounced after 04:00 but continued decreasing steadily along with slight rain (0.4 mm in an hour) and light breeze (1 – 2 m s^{-1}) from the northwest to southwest directions. Firework activity in other countries have been documented to last from 2 – 6 h in a day and elevated particulate levels can be maintained for up to 6 – 18 h (Thakur et al., 2010; Crespo et al., 2012; Chatterjee et al., 2013; Kong et al., 2015; Tsai et al., 2012). The 48-h average $PM_{2.5}$ during (49.9 µg m^{-3}) the firework event was 1.9 and 3.3 times more, respectively, than before (25.8 µg m^{-3}) (Fig. S2) and after (15.2 µg m^{-3}) (Fig. S3) the firework event. Two~~Previous work in other countries has shown two~~ to three-fold increases in PM mass concentration due to fireworks have also been observed in other countries (Rao et al., 2012; Ravindra et al., 2003; Tsai et al., 2011; Shen et al., 2009). Greater increases (> 5 times) in particulate mass concentrations~~levels~~ elsewhere were related to more intense and prolonged (lasting several days) firework activity (Tian et al., 2014).

~~Air parcel trajectories arriving at the Manila Observatory during the sampling periods before, during, and after the firework event were assessed to ascertain the impact of fireworks on the enhanced particulate concentrations.~~ Three-day back trajectories for the period before the firework event were from the northeast to east directions coming from the Philippine Sea (Fig. 2a). For the periods (Fig. 2b) during and (Fig. 2c) after the firework event, back trajectories were from the northeast to east/northeast directions. The general wind directions from the back trajectories are consistent with the climatologically prevailing northeasterly monsoonal winds in December and January for the Philippines (Villafuerte II et al., 2014). The origin of the air parcels did not have any major emissions events that could have impacted the measurements after long-range transport. This is important to note because the tracers for fireworks are also tracers for transported emissions due to biomass burning (K^+) (Braun et al., 2020) and industrial activities (Cohen et al., 2009). Thus, enriched particulate concentrations during the firework activity were most likely locally produced. One factor impacting surface PM concentrations is the vertical structure of the lower troposphere, which is addressed in the next section based on HSRL data.

3.2 Optical Aerosol Properties

Heavy aerosol loading at the surface was observed up to eight hours after the fireworks peak (00:00~~16 UTC, 12 AM local time~~) with high HSRL 532 nm backscatter cross-section and depolarization (Fig. 3a) reaching ~440 m above the ground. Prior to the firework peak, the surface aerosol layer had lower backscatter (before 22:00~~14 UTC~~, Fig. 3a), and this cleaner condition is shown by the 16~~08~~:16 local time~~UTC~~ vertical profile of the aerosol backscatter (Fig. 3b). Rainfall (Fig. 1a) contributed to columns of high backscatter (Fig. 3a) after 22:00~~14 UTC~~ and before the firework peak with a measurable decrease in the aerosol backscatter for a short time after the precipitation (23~~15~~:00 and ~~16:~~00:00~~ UTC~~).

~~To verify the height values (Fig. 3b), the "surface-attached aerosol layer" height is estimated using the maximum variance method more commonly used for daytime convective boundary layer detection (Hooper and Eloranta, 1986). The method is also limited by the complexity of the case due to pertinent rain signals for this event. The "surface attached aerosol layer" (Fig. 3a) is derived from a 15-min moving window average based on the 30-s values shown with a thin black line.~~ As confirmed by ~~the~~ height detection, aerosols reached up to ~440 m (Fig 3a and b) at 00:00 (1 January 2019).~~on 16 UTC (31 December 2018).~~ It persisted for at least an hour then dropped to 118 ± 20 m with higher aerosol backscatter retained until January 1, 2019 08:00~~0 UTC~~. Some of the smoke is above the detected height (i.e. 01:00~~17 UTC~~).

3.3 Mass Size Distributions

Building on ~~A total of 41 water-soluble species were detected in~~ the previous results describing the general environmental conditions~~48-hr size-differentiated particulate samples collected before,~~ during~~, and after the firework event. The total bulk mass concentration is defined as~~ the study period, now we focus on~~sum of~~ the detailed size-resolved measurements.~~concentrations of all the measured species across the MOUDI's eleven stages (≥ 0.056 μm).~~ The total water-soluble bulk mass concentration (Table 1) during the firework event (16.74 μg m^{-3}) was 5.71 times and 4.73 times higher than the total bulk mass concentrations before (2.93 μg m^{-3}) and after (3.54 μg m^{-3}) the firework event, respectively. Assuming the average of the water-soluble mass concentrations before and after the firework event represent background values, this translates to an 80.66% increase in water-soluble mass during the firework event.

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

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

Non-sea salt SO_4^{2-} had the highest contribution (40.7%) to total water-soluble bulk mass concentration during the firework event (Table 1). Sulfate exhibited a shift in its mass size distribution to a slightly larger size during firework activity (Fig. 4b). During the firework event, 87.13 % of the nss-SO_4^{2-} was in the 0.32 μm to 1.8 μm size fraction. Before and after the firework event, 87.28% and 85.14% of the nss-SO_4^{2-} mass concentration, respectively, was distributed in a finer size fraction (0.18 μm to 1 μm) (Fig. 4a and 4c). For context, SO_4^{2-} peaked at 0.62 μm during fireworks in Nanning, China (Li et al., 2017). Firework emissions include gases like SO_2 which undergo aqueous uptake and oxidation onto particles to form SO_4^{2-}. Furthermore, enhanced secondary formation is aided by metals emitted during fireworks that help convert SO_2 to SO_4^{2-} (Feng et al., 2012; Wang et al., 2007). Non-sea salt SO_4^{2-} had the highest contribution (40.7%) to total water-soluble bulk mass concentration during the firework event (Table 1). Sulfate exhibited a shift in its mass size distribution to a slightly larger size during firework activity (Fig. 4b). During the firework event, 87.13 % of the nss-SO_4^{2-} was in the 0.32 μm to 1.8 μm size fraction. Before and after the firework event, 87.28% and 85.14% of the nss-SO_4^{2-} mass concentration, respectively, was distributed in a finer size fraction (0.18 μm to 1 μm) (Fig. 4a and 4c).

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

This is comparable to the mass diameter (0.7 μm) due to firework emissions after transport in Washington State (Perry, 1999). The shift in the mass size distribution of K^+ and nss-SO_4^{2-} can be due to the removal of nucleation-mode particles as a result of increased coagulation in the accumulation mode (Zhang et al., 2010). Relatively larger SO_4^{2-} particles can also be due to secondary sources rather than primary sources, and aging could have also contributed to particle growth as has been suggested for firework particles in Nanning, China (Li et al., 2017). Firework emissions include gases like SO_2 which undergo aqueous uptake and oxidation onto particles to form SO_4^{2-}. Furthermore, enhanced secondary formation is aided by metals emitted during fireworks that help convert SO_2 to SO_4^{2-} (Feng et al., 2012; Wang et al., 2007).

Nitrate, Cl^-, and Mg^{2+} mass size distributions all exhibited pronounced peaks in the submicrometer range during the firework event (Fig. 5). The mass sum concentration of the aforementioned ions peaked (46.39% of the total mass concentration of the three species) between 0.56 and 1.0 μm. On the other hand, their mode appeared between 1.8 and 3.2 μm before and after the firework event (33.02% and 32.91% of the total mass concentration of the three species, respectively) (Fig. 5). Nitrate, Cl^-, and Mg^{2+} are emitted during fireworks (Zhang et al., 2017) as finer-sized submicrometer particles (Tsai et al., 2011) compared to background conditions when these species are mostly associated with coarser supermicrometer particles (AzadiAghdam et al., 2019; Cruz et al., 2019; Hilario et al., 2020). Nitrate can also be formed secondarily (Yang et al., 2014) from firework emissions. Firework emissions are associated with lower NO_3^-:SO_4^{2-} ratios (Feng et al., 2012) compared to days dominated by mobile sources (Arimoto et al., 1996) due to different formation mechanisms (Tian et al., 2014). Consistent with the literature, low NO_3^-:SO_4^2 ratios were also observed during the firework event (before: 0.79, during: 0.25, after: 0.82). A low NO_3^-:SO_4^{2-} ratio is related to decreased pH of the particles (Cao et al., 2020), which may impact not just air quality and health but also nearby waterbodies where the particles may deposit. It is important to note that background supermicrometer Cl^- and Mg^{2+} in Manila are most likely associated with sea salt while background supermicrometer NO_3^- possibly in the form of $NaNO_3$ (de Leeuw et al., 2001) or NH_4NO_3 likely stems from partitioning of nitric acid gas onto surfaces (de Leeuw et al., 2001) of coarse particles such as sea salt and dust (AzadiAghdam et al., 2019; Cruz et al., 2019). The Cl^-:Na^+ mass ratio during the firework event increased to 4.44 (from 0.69 and 1.08 before and after, respectively) and was higher than the typical Cl^-:Na^+ ratio in seawater of 1.81 (Braun et al., 2017). These ratio results confirm that the increase in Cl^- concentrations during the firework event is not driven by sea salt but instead linked to firework emissions.~~These ratio results confirm that the increase in Cl^- concentrations during the firework event is not driven by sea salt but instead linked to firework emissions such as what was shown during Taiwan's lantern festival with Cl^-:Na^+ ratios reaching approximately 3 owing to raw materials in fireworks such as $KClO_3$, ClO_3, and ClO_4 (Tsai et al., 2012).~~ The lack of increased sea salt influence during the firework event, which is not to be expected, is further confirmed by relatively small changes in the amount of observed Na^+, as will be discussed subsequently.

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

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

3.4 Enriched Tracers in Firework Emissions

Here we more closely examine how much concentrations of species changed during the firework event. Bulk mass concentrations of eighteen of the forty-one measured species were enriched during the firework event by more than two times compared to the average of their bulk mass concentrations before and after the firework event (Fig. 5). Enrichments for Cu (65.2), Sr (24.4), 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 highest (> 5) among the species measured (Fig.5). Potassium and nss-SO_4^{2-} together contributed to 70.9% of the total measured species during the firework event (Table 1). However, Cu, Sr, succinate, Ba, Al, Pb, and maleate contributed a total of only 2.1~~14~~% to the total measured species mass concentration. This reinforces the importance of looking at enrichments rather than absolute mass concentrations for identifying which aerosol constituents are firework tracers. Tracer metals in firework emissions were previously shown to contribute a small fraction (~<2%) to total PM mass (Jiang et al., 2014).

Of the eighteen species with observed enrichments exceeding two (Fig. 5), only those which are firework components and that are uninfluenced by secondary formation are considered tracers. The identified fourteen firework tracers based on these criteria are as follows: Cu, Sr, Ba, K^+, Al, Pb, Mg^{2+}, Cr, Tl, Cl^-, Mn, Rb, Zn, and Ag. Copper gives the blue-violet color of fireworks, Sr gives the red color, Ba and Tl makes the green flame, and Rb gives a purple color. Potassium and Ag (as AgCNO or silver fulminate) are propellants, Al is fuel, and Pb provides steady burn and is also used as an igniter for firework explosions. Chromium is a catalyst for propellants, Mg is a fuel, and Mg^{2+} is a neutralizer or oxygen donor (U.S. Department of Transportation, 2013). Manganese is either a fuel or oxidizer, and Zn is used for sparks (Licudine et al., 2012; Martín-Alberca and García-Ruiz, 2014; Shimizu, 1988; Wang et al., 2007; Ennis and Shanley, 1991). Metals are usually in the form of Cl^- salts in fireworks (Wang et al., 2007). In this study, the enrichment of Cl^- during the firework event was found to be 3.7. Some of the identified tracer metals are regulated and their detection is of concern. Magnesium is not recommended as a firework component because it is sensitive to heat and can easily ignite in storage (Do et al., 2012). Lead is highly toxic and thus regulated (Moreno et al., 2010) as its occurrence in fireworks is a serious health hazard.~~not ideal.~~ Although SO_4^{2-}, maleate (fuel), and NO_3^- (oxidant) were also enriched more than two times during the firework event and are also firework components (Zhang et al., 2019), they can be formed secondarily via gas-to-particle conversion processes (Yang et al., 2014) and are not considered as firework tracers. Succinate is likewise formed secondarily and is not considered a firework tracer (Wang et al., 2007). The identified firework tracers with the highest enrichments (>5) (excluding K^+), including Cu, Sr, Ba, Al, and Pb, together contributed 2.1% to the total measured species mass concentration during the firework event (Table 1).

Size-resolved enrichments (Fig. 65) were highest in the submicrometer range for most measured species. This is consistent with past studies such as in Italy (Vecchi et al., 2008), Taiwan (Do et al., 2012), and Spain (Crespo et al., 2012) where elemental concentrations due to pyrotechnics increased in the submicrometer mode. The peak size differentiated enrichments of the first five firework tracers Sr (45.08), Ba (57.82), K^+ (48.70), Al (18.75), and Pb (69.07) were in the 1.0 – 1.8 μm size range. Copper (49.85) peaked between 0.56 – 1.0 μm because it did not have valid data for diameters exceeding 1.0 μm. Strontium and Ba had very high enrichments (254.40 and 195.84) from 0.1 – 0.18 μm due to very low concentrations before and after the firework event in that size range. Enrichments of up to ~1000 (Crespo et al., 2012) for Sr and Ba have been observed due to pyrotechnics, and both are known firework tracers (Kong et al., 2015).

The size-resolved enrichments of other notable species (Fig. 65 and Fig. S6) peaked at specific 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 (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 – 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 (6.63, 0.32 – 0.56 μm), Co (17.94, 0.56 – 1.0 μm), and methanesulfonate (MSA) (6.66, 0.56 – 1.0 μm). Among all the measured water-soluble species, Cl^- had the highest size-resolved enrichment, followed by Sr, Ba, K^+, Pb, and Cu. This is expected because inorganic salts comprise an enormous percentage of firework emissions (Martín-Alberca et al., 2016).

3.5 SEM-EDX

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

The chemical composition of the blank Teflon substrate (Fig. 7a) was examined first by EDX to determine the background signals before the actual samples were analyzed. The color intensity of the element maps (Fig. S7) relates the concentration of the analyzed element relative to the backscattered electron image (gray-scale) of the sample. The background substrate was dominated by C, F, and Al (bright yellow, bright blue, and bright blue-green, respectively, in Fig. S7-a1/a2/a3). Metallic elements were distributed in each of the five featured SEM images. Molybdenum and K were present in all of the substrate stages (bright red in Fig. S7-b3/b4/c3/c8/d7/d8/e6/e7/f6/f9). Other metals were also found in the different stages such as K, Mg, Al, Ru, Pd, Ba, Hf, and Tl. The identified heavy metals in the particles are commonly used in firework as fuel components, colorants, and oxidants (Singh et al., 2019). Potassium, Mg, Al, Ba, and Tl are in the group of firework tracers that were already identified (Section 3.4 and Fig. 5) to have mass bulk concentration enrichments exceeding two. Molybdenum exhibited a reduced mass bulk concentration enrichment of 1.93 (Fig. 5), but had size-resolved enrichments between 1.21 and 4.15 (Fig. 6) in the substrate cut-outs analyzed for EDX. The cube-shaped feature in the 0.56 – 1.0 µm substrate appears to be KCl because of the high color density of K and Cl in the elemental maps (bright red and bright blue-green in Fig. S7-f6/f8) and because the shape of KCl is cubic (Pirker et al., 2020). The crystal-shaped rectangle in the 0.32 – 0.56 µm range appears to be enriched by Cl (bright blue-green in Fig. S7-d6). The same applies to the capsule-shaped particle in 0.56 – 1.0 µm image (bright blue-green in Fig. S7-e5). The chloride ion (Cl^-) is a component of metal salts, usually in the form of ClO_4^- or ClO_3^- (Tian et al., 2014) used to color fireworks (Shimizu, 1988).

These results of the sampled portions of the substrate stages are consistent with the results of the size-resolved submicrometer enrichments measured by IC and ICP-QQQ (Section 3.4) for Mo, K, Mg, Al, Ba, and Tl. Molybdenum was brightest red in the 0.32 – 0.56 µm image (Fig. S7-d8), consistent with the highest enrichments (4.15 in Fig. 6) for that size range. Potassium was brightest red in the 0.56 – 1.0 µm image (Fig. S7-e6/f6), consistent with highest enrichments (33.04 in Fig. 6). Magnesium was brightest yellow from 0.32 – 1.0 µm (Fig. S7-d4/e3/f4), consistent with highest enrichments (9.50 and 11.58 in Fig. 6). Aluminum had a high signal in the blank Teflon substrate but also was brightest blue-green (Fig. S7-d5/e4/f5) in between 0.32 – 1.0 µm in the sample during the firework event, consistent with highest enrichments (9.22 and 13.32 in Fig. 6). Barium was detected by EDX between 0.56 – 1.0 µm (Fig. S7-f11 where its enrichment was 12.39 (Fig. 6). Thallium was detected between 0.56 and 1.0 µm (Fig. S7-f13) by EDX, where its enrichment was highest (18.12 in Fig. 76) as detected by ICP-QQQ. The submicrometer metal salts due to fireworks can uptake water at high humidity (ten Brink et al., 2018).

3.6 Hygroscopicity Analysis

As fireworks alter the chemical profile of ambient PM, we estimate how aerosol hygroscopicity responded during fireworks relative to periods before and after. For reference, typical κ values range from 0.1 to 0.5 for diverse air mass types such as urban, marine, biogenic, biomass burning, and free troposphere (Dusek et al., 2010; Hersey et al., 2013; Shingler et al., 2016;

Shinozuka et al., 2009). AzadiAghdam et al. (2019) reported size-resolved values ranging from 0.02 to 0.31 using data from the same field site in Metro Manila but for a different time period and without any firework influence (July – December 2018). They found the highest values to be coincident with MOUDI stages with most sea salt influence (3.2 – 5.6 μm).

For this study, a bulk κ value is reported for the size range between 0.056 – 3.2 μm as noted in Section 2.76, and subsequent references to composition data are for this size range. Kappa was enhanced during the firework event (0.18) compared to before (0.11), due mostly to increased contributions from K_2SO_4 and $Mg(NO_3)_2$ (Fig. 8a). More specifically, the volume fractions of K_2SO_4 and $Mg(NO_3)_2$ increased from 0.01 to 0.10 and 0.01 to 0.03, respectively (Fig. 8b). For context, inorganic salts (K_2SO_4, KCl) dominated the aerosol hygroscopicity in Xi'an, China during fireworks (Wu et al., 2018). In the Netherlands, enhancements in salt mixtures containing SO_4^{2-}, Cl^-, Mg^{2+}, and K^+ were noted to enhance hygroscopicity (ten Brink et al., 2018). Notable reductions in volume fraction during the firework event were for $NaNO_3$ (0.01 to 0.00), black carbon (0.26 to 0.12), and $(NH4)_2SO_4$ (0.02 to 0.01) (Fig. 8b). All three species are not associated with primary firework emissions. Although $NaNO_3$ and $(NH4)_2SO_4$ are hygroscopic, their decreased volume fractions happened alongside a decreased volume fraction of non-hygroscopic black carbon and increased volume fractions of the firework-related and hygroscopic K_2SO_4 and $Mg(NO_3)_2$, which increased bulk aerosol hygroscopicity during the firework event.

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

4. Conclusion

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

- Firework $PM_{2.5}$ was significantly enhanced during firework activities caused significant enhancement of $PM_{2.5}$ reaching a maximum of 383.9 μg m^{-3} between 01:00 to 02:00 on 1 January 2019. RainfallSurface aerosol loading increased over a period of eight hours during the firework event, coincident with peak $PM_{2.5}$ levels. The heaviest aerosol layer measured by the HSRL lidar was observed for at least an hour, and reached ~440 m above the surface, after which the aerosol layer dropped to 118 ± 20 m. Aerosol backscatter during the firework activity decreased noticeably for short periods after rainfall. Besides rainfall, wind, and relative humidity also possibly contributed to washout, local dispersion, and secondary formation of particles, respectively. ~~A noticeable decrease in aerosol backscatter was measured by the HSRL lidar for short periods after the rain fall.~~ There was no significant influence from long-range transport to the sampling site, confirming that the sample data was most representative of the local nature of particulate enhancements observed during the firework event.

- ~~Surface aerosol loading increased over a period of eight hours during the firework event, coincident with peak $PM_{2.5}$ levels.~~ The firework event enhanced bulk~~The heaviest aerosol layer was observed for at least an hour, and reached ~440 m above the surface, after which the aerosol layer dropped to 118 ± 20 m.~~
- ~~Bulk~~ concentrations of water-soluble aerosol species, ~~were enhanced~~ especially in the submicrometer range. Mass size distributions of the ~~mode during the firework event along with increased~~ water-soluble species ~~mass fractions in $PM_{2.5}$. Potassium and nss-SO_4^{2-} were the major contributors. Mass size distributions~~ shifted to slightly larger accumulation-mode sizes most likely due to increased coagulation sinks and secondary formation. Potassium and nss-SO_4^{2-} were the major water-soluble contributors. Cubic and capsule-shaped Cl^--rich particles were prominent in submicrometer particles collected during the firework event, suggesting the presence of KCl. Inorganic species including
- ~~Components of inorganic salts such as~~ Cu, Sr, Ba, K^+, Al, Pb, Mg^{2+}, Cr, Tl, Cl^-, Mn, Rb, Zn, and Ag were enriched more than two times by mass during the firework event as compared to before and after the event. While the most enriched inorganic firework tracers, including Cu, Sr, Ba, Al, and Pb ~~Even while they~~ (excluding K^+), ~~$^+$)~~ comprised only 2.1~~88~~% of the total water-soluble mass, their contribution is significant because they support ~~the~~ findings that the samples represent firework emissions. The increased volume fractions of inorganics increased aerosol ~~, and especially since some of the components like Pb and Mg^{2+} are banned substances.~~
- ~~Cubic and capsule-shaped Cl^--rich particles, suggesting the presence of KCl, were prominent in submicrometer particles collected during the firework event.~~
- ~~Aerosol~~ hygroscopicity (κ) between 0.056 and 3.2 μm ~~increased~~ from 0.11 (before the fireworks) to 0.18 during the firework event. ~~due to the increased volume fractions of inorganics.~~
-

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

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

Data availability

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

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

Author Contributions

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

Competing Interests

The authors declare that they have no conflict of interest.

Acknowledgements

The authors acknowledge support from NASA grant 80NSSC18K0148 in support of the NASA $CAMP^2Ex$ project. R. A. Braun acknowledges support from the ARCS Foundation. M. T. Cruz acknowledges support from the Philippine Department of Science and Technology's ASTHRD

Program. A. B. MacDonald acknowledges support from the Mexican National Council for Science and Technology (CONACYT). We acknowledge Agilent Technologies for their support and Shane Snyder's laboratories for ICP-QQQ data. We thank the Department of Environment and Natural Resources Environmental Management Bureau (DENR-EMB) Central Office Air Quality Management Section in the Philippines and the Air Center for Air Pollution Research in Japan of EANET for the hourly $PM_{2.5}$ data. The tradition of sampling the New Year air quality in Metro Manila was instilled by Fr. Dan McNamara, SJ, Fr. Jett Villarin, SJ, and Gemma Narisma, and for this we are grateful.

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Table 1: Summary of total and speciated concentrations before, during, and after the firework event. Species are divided based on units (Total to Zn: µg 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-SO_4^{2-}	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
NO_3^-	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
Mg^{2+}	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
Ca^{2+}	0.21	0.30	0.38	**V**	0.32	0.14	0.30
NH_4^+	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

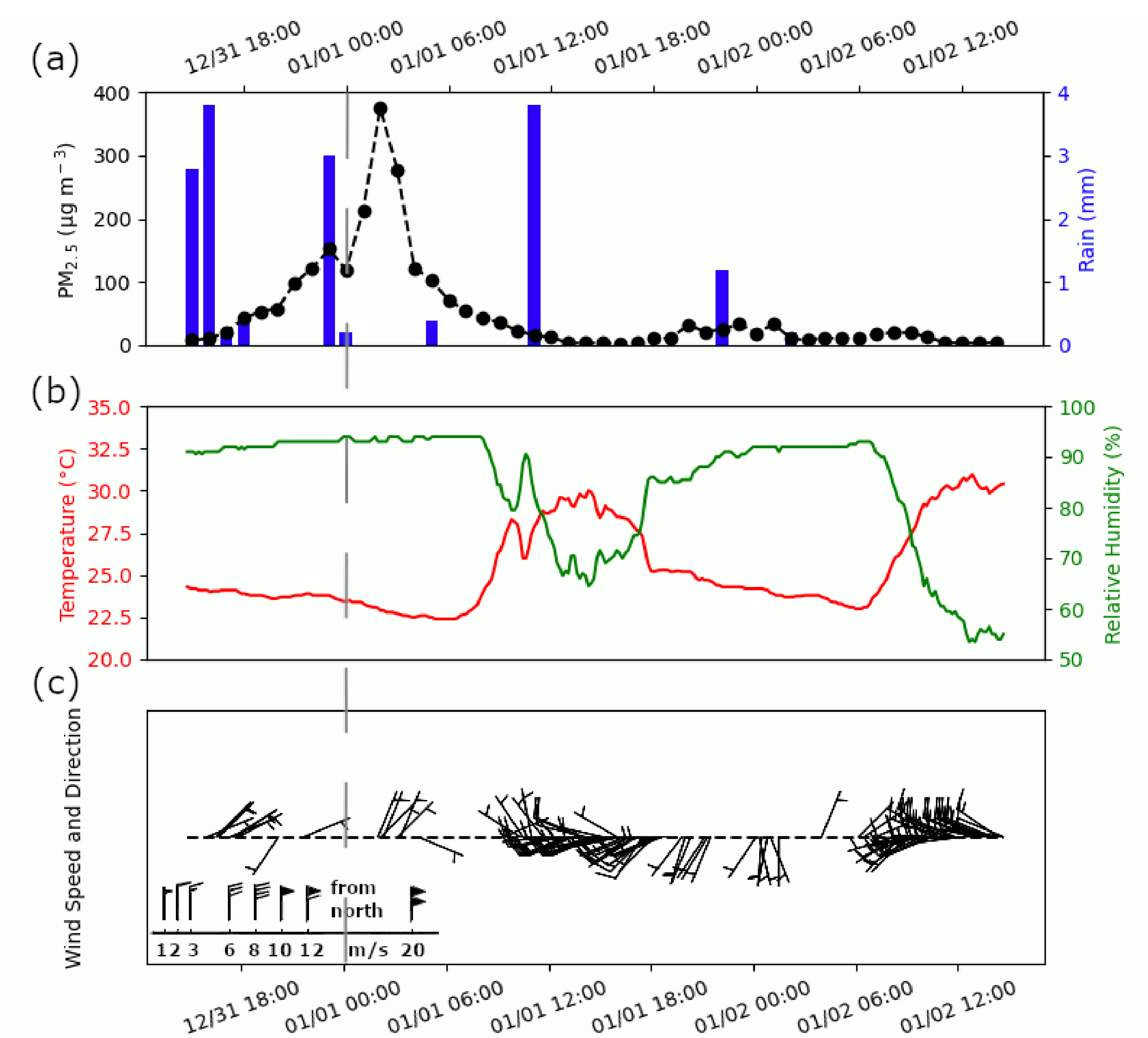


Figure 1: (a) $PM_{2.5}$ mass concentrations and rain accumulation at hourly resolution (local time, dashed vertical line indicates midnight) as measured from the Manila Observatory main building third floor rooftop (~88 m.a.s.l.) at the same period as the MOUDI size-speciated samples during the firework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

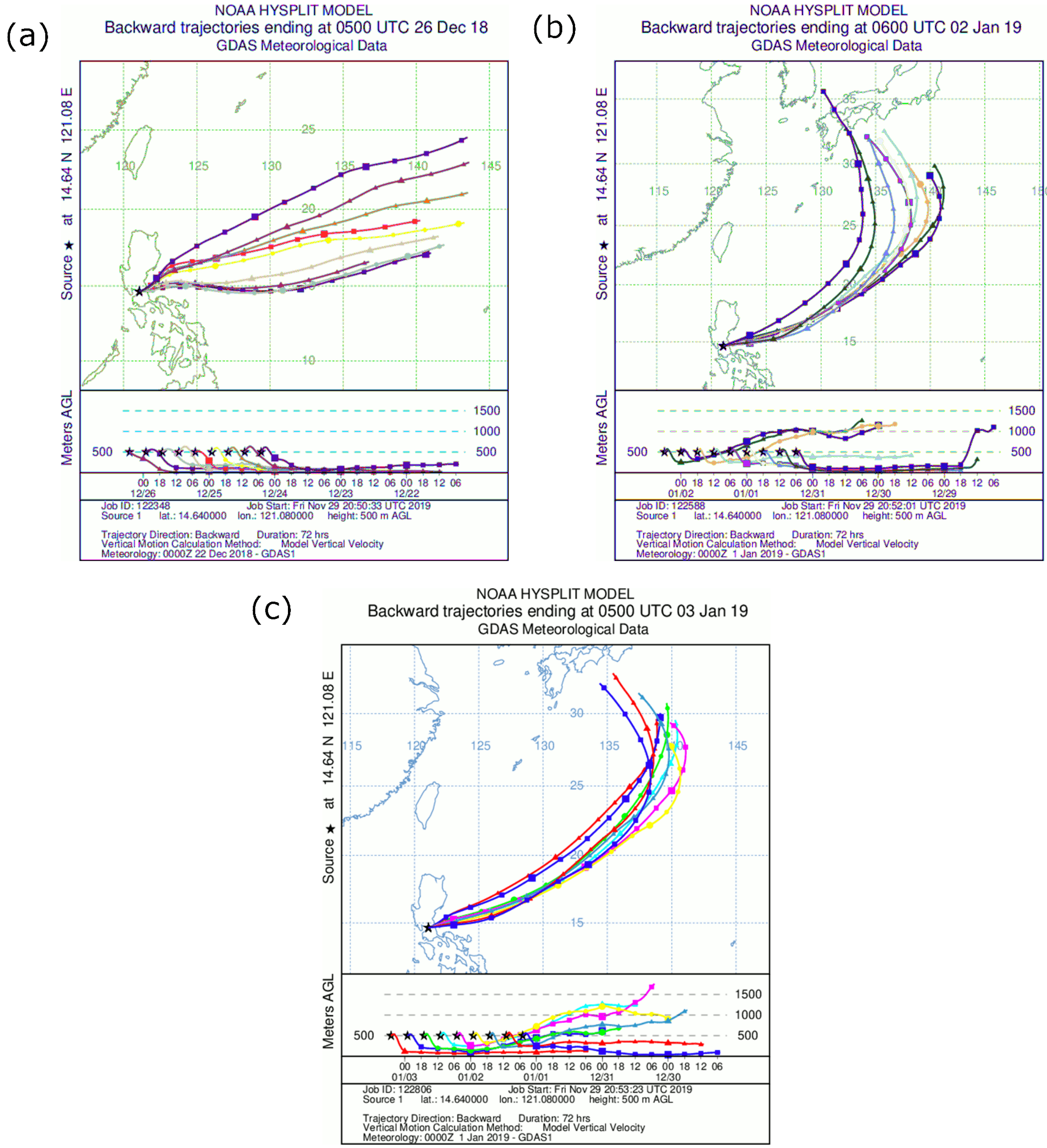
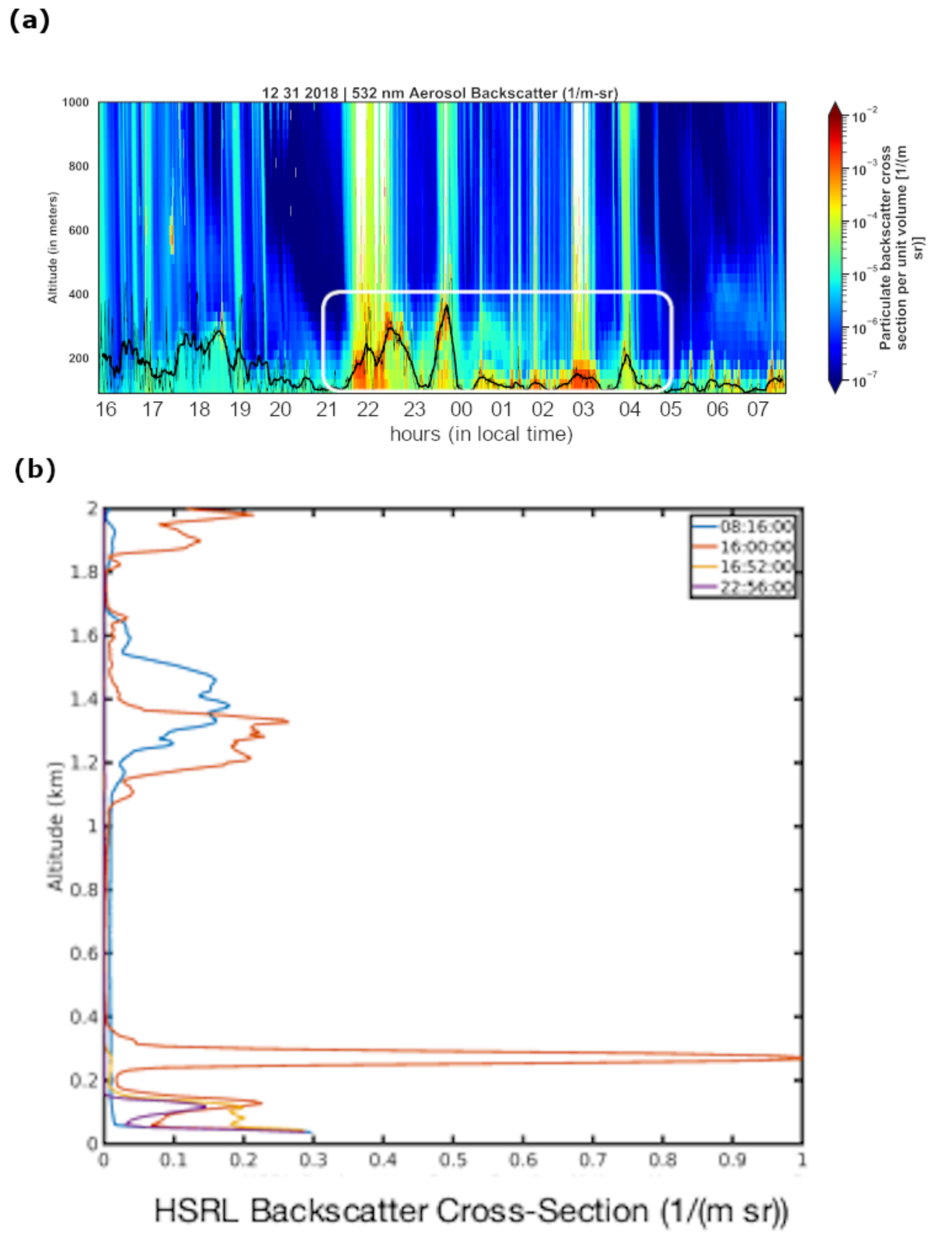


Figure 2: Three-day back trajectories with 6-h resolution for the periods (a) before, (b) during, and (c) after the firework event, ending at the point of the Manila Observatory at 500 m.


(a)
12 31 2018 | 532 nm Aerosol Backscatter (1/m-sr)
Altitude (in meters)
1000
800
600
400
200
16 17 18 19 20 21 22 23 00 01 02 03 04 05 06 07
hours (in local time)
Particulate backscatter cross section per unit volume [1/(m sr)]
(b)
Altitude (km)
08:16:00
16:00:00
16:52:00
22:56:00
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
HSRL Backscatter Cross-Section (1/(m sr))

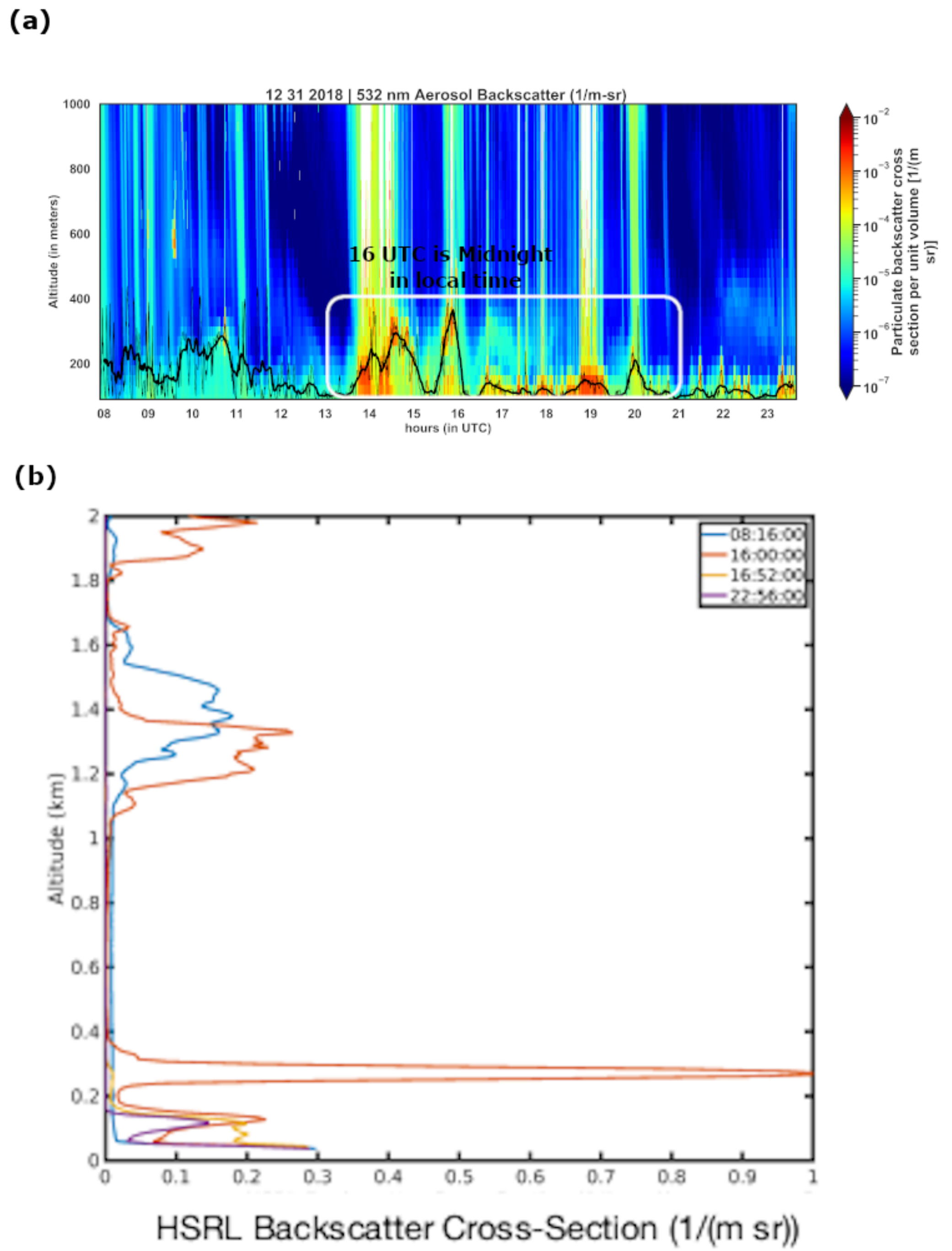


Figure 3: (a) Time series of the aerosol backscatter vertical profile from the High Spectral Resolution Layer (HSRL). The time shown is Universal Time (UT) and local time is UT + 8 hours. The times circled by the white oval correspond to the peak of aerosol backscatter in the mixing layer due to firework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

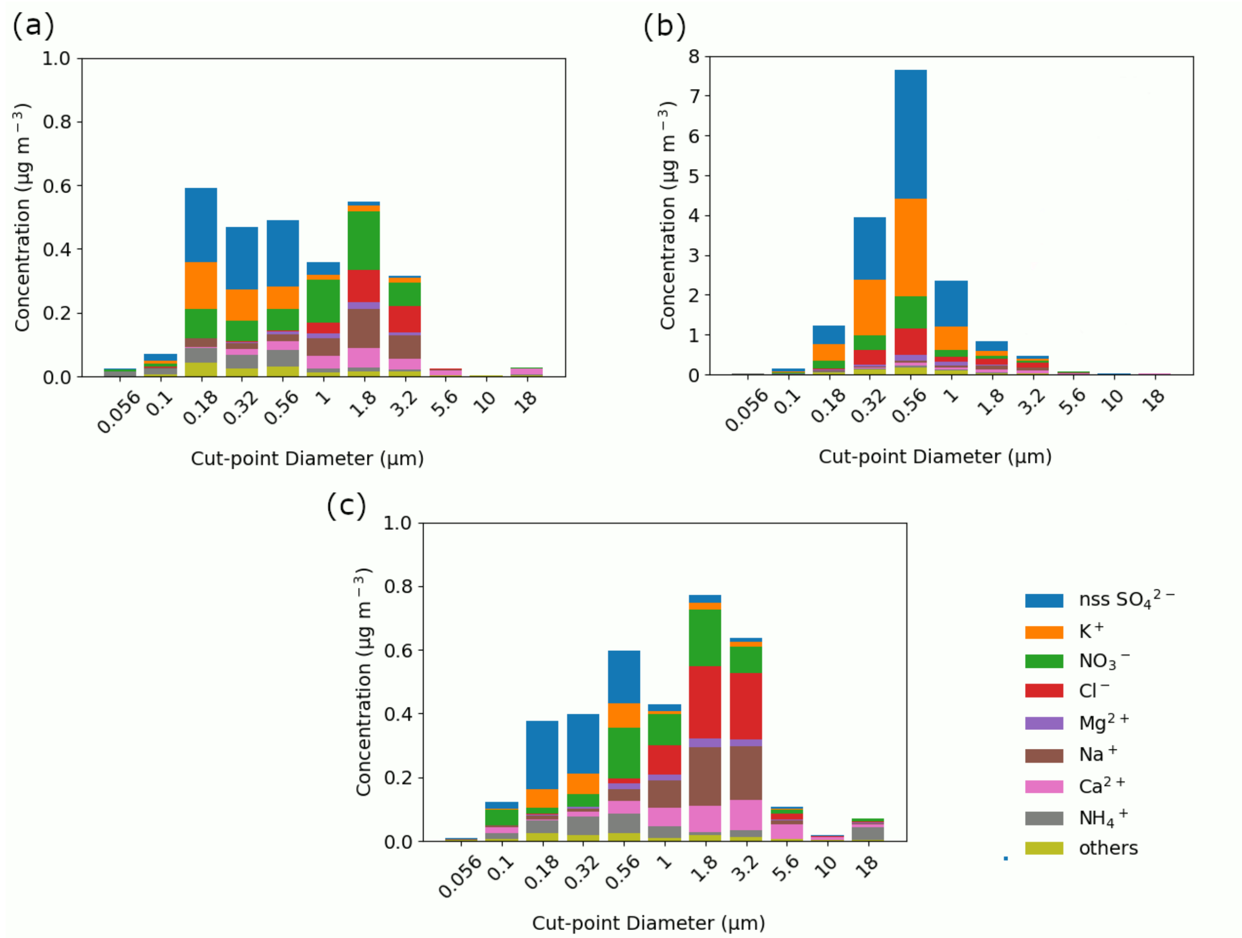


Figure 4: Speciated mass size distributions of the major aerosol constituents measured (a) before, (b) during, and (c) after the firework event. Table 1 lists the bulk (≥ 0.056 μm) mass concentrations of these ions and elements, including those labeled here as "others" (Ba, oxalate, Cu, Al, Sr, Zn, succinate, 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).

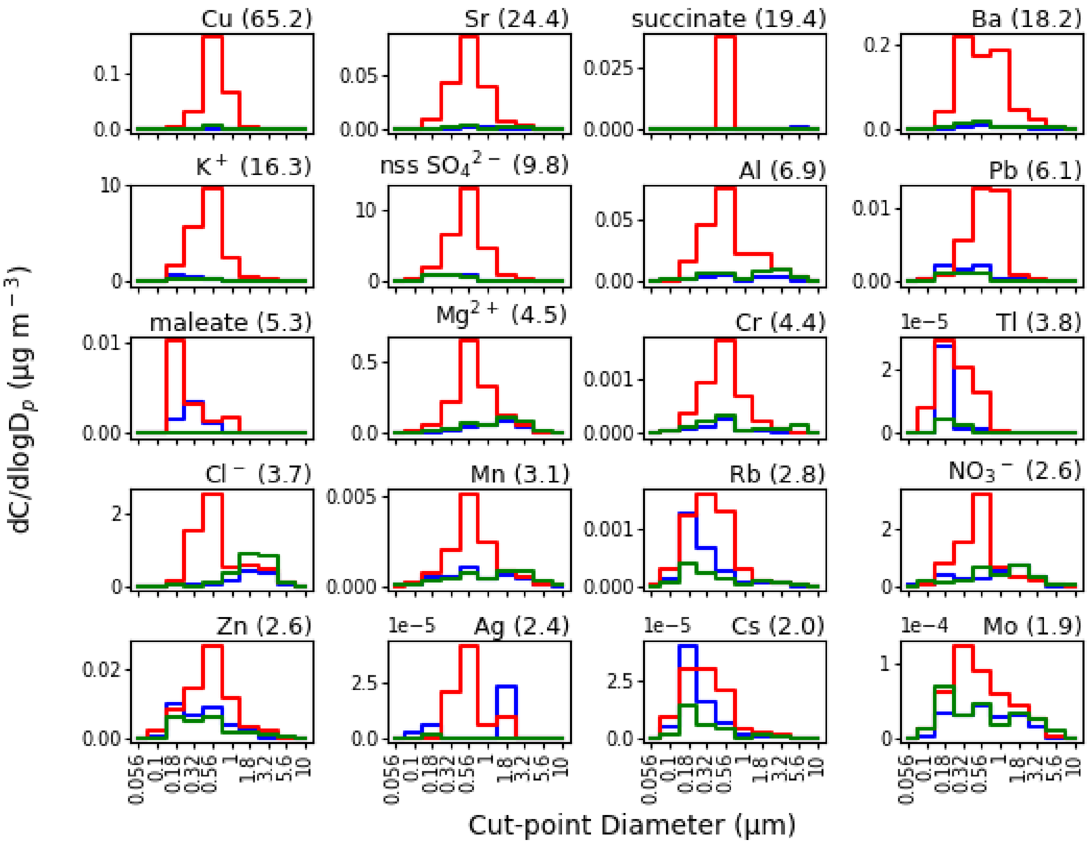


Figure 5: Speciated mass size distributions before (blue line), during (red line), and after (green line) the firework event. Next to species labels are bulk (≥ 0.056 µm) mass concentration enrichment values due to the firework event; species are shown with enrichments ≥ 1.9. Figure S5 shows similar results for all other species.

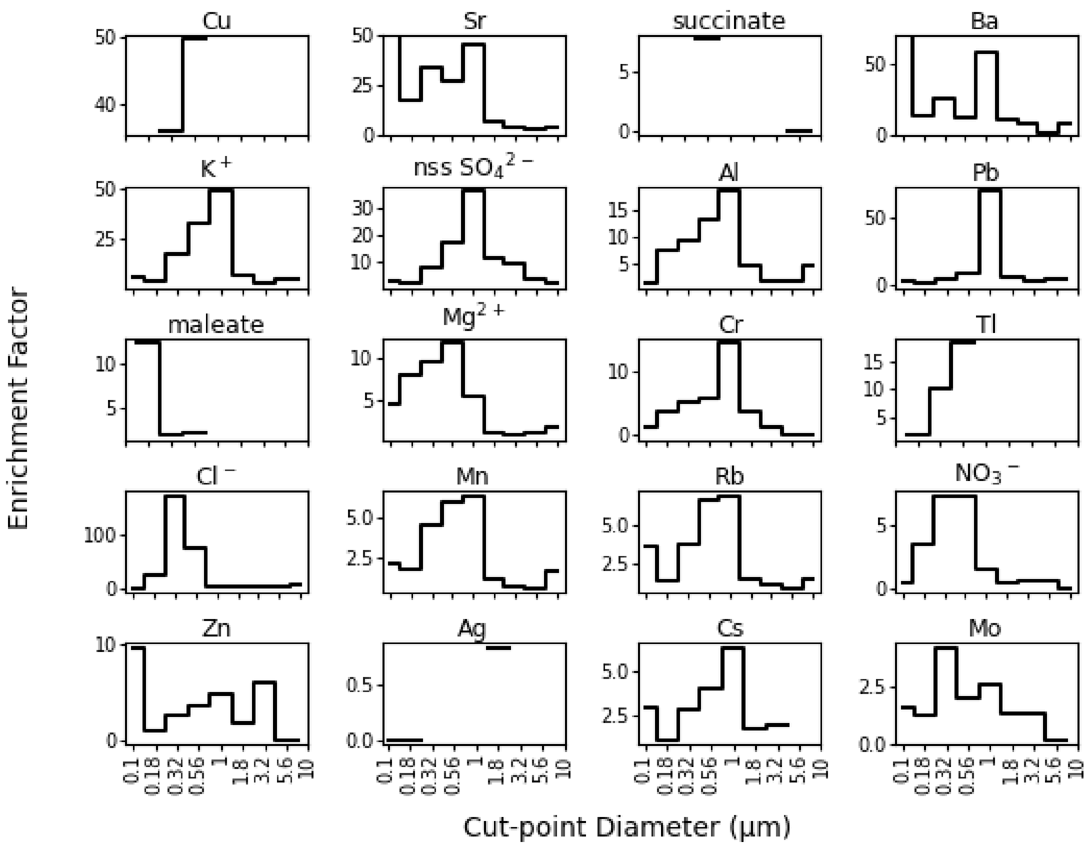


Figure 6: Size-resolved enrichments for individual firework tracer species in order of decreasing total bulk mass concentration enrichment (species from Fig. 5). Cut-point diameters with no valid data are left blank. The y-axis of Sr and Ba are truncated to more easily show enrichments in the larger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

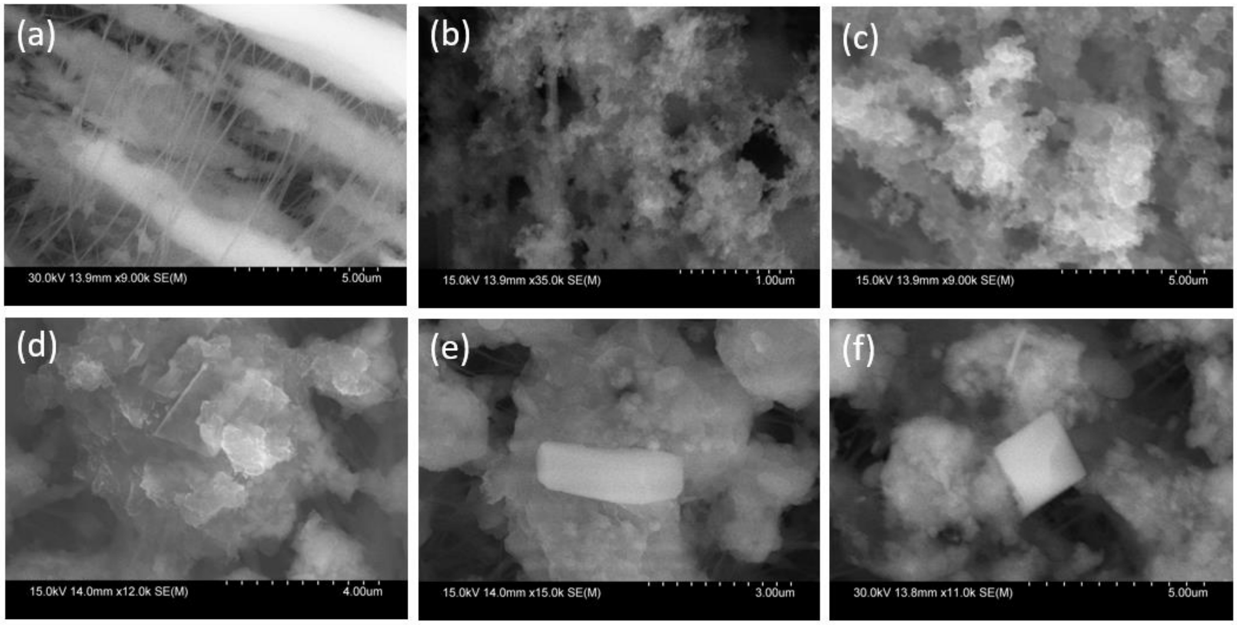


Figure 7: Scanning electron microscope (SEM) images of (a) a blank PTFE (Teflon) substrate and (b-f) particles in different diameter ranges with firework influence: (b) 0.1 – 0.18 µm, (c) 0.18 – 0.32 µm, (d) 0.32 – 0.56 µm, (e-f) 0.56 – 1.0 µm.

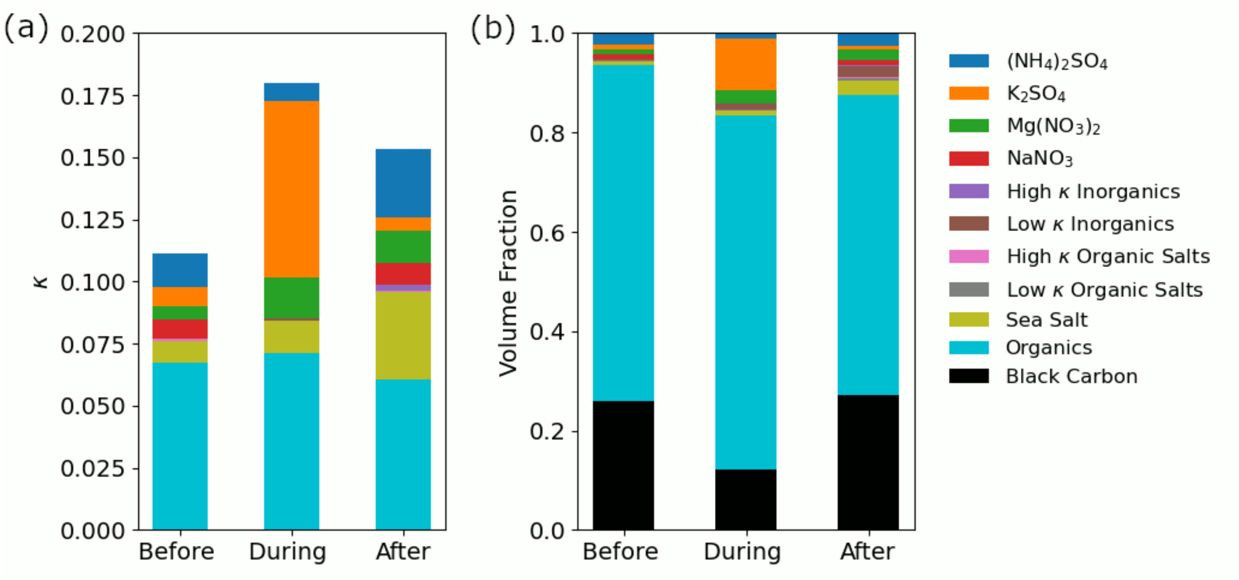


Figure 8: (a) Kappa (κ) values for the aerosol fraction between 0.056 – 3.2 µm before, during, and after the firework event. The speciated contributions to the overall κ values (represented by the colors) are categorized based on the classes of compounds in the legend following past work (AzadiAghdam et al., 2019). Ammonium sulfate, K_2SO_4, $Mg(NO_3)_2$, and $NaNO_3$ are high κ inorganics but are plotted separately because of their large contributions. The speciated contributions were calculated by multiplying the volume fraction of each compound class by its intrinsic κ value (Table S4).