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Stubborn aerosol: why particulate mass concentrations do not drop during the wet season in Metro Manila, Philippines†

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Wet scavenging is the most important sink for particulate matter (PM) and is expected to decrease PM concentrations in the wet season. However, Metro Manila, Philippines has highly similar PM mass across seasons despite large differences in seasonal rainfall. It is important to identify factors contributing to seasonally consistent PM mass as these may be present in similar developing megacities besides Metro Manila, leading to PM accumulation and posing significant health risks. We use size-resolved aerosol composition, aerosol optical depth, and meteorological data to reveal that the seasonally consistent PM mass in Metro Manila is due to (1) opposing seasonal cycles of black carbon and water-soluble PM, (2) inefficient scavenging by short rain events (<1 h), and (3) the high frequency (50%) of these short rain events. Water-soluble PM was most sensitive to scavenging within the 0.18–1.0 μm and 1.8–5.6 μm size ranges but more clearly for rain events lasting over an hour, pointing to the importance of rain duration for efficient scavenging. We demonstrate that the presence of rain does not imply wet scavenging is taking place efficiently and rain characteristics are critical to properly estimating wet scavenging. In a changing climate, our understanding of factors such as rain duration and aerosol accumulation will become more important for guiding air quality-related policymaking and ensuring sustainable growth in developing megacities.

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Environmental significance

Wet scavenging is the most important sink for particulate matter (PM) and is expected to decrease PM concentrations during the high rainfall season. However, Metro Manila, Philippines has highly similar PM mass across seasons despite large differences in seasonal rainfall. It is important to identify factors contributing to seasonally consistent PM mass as these may be present in similar developing megacities besides Metro Manila, leading PM accumulation and posing significant health risks. This work uses a combination of size-resolved aerosol composition, meteorology, and aerosol optical depth over Metro Manila to demonstrate that the presence of rain does not imply wet scavenging is taking place efficiently and rain characteristics are critical to properly estimating wet scavenging. In a changing climate, our understanding of factors contributing to wet scavenging will become more important for guiding air quality-related policymaking and ensuring sustainable growth in developing megacities. This study motivates further research into circumstances when wet scavenging becomes inefficient, which is especially important over megacities where pollution accumulation poses serious health risks for millions of people.

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1 Introduction

Wet scavenging is the dominant particle removal mechanism in the atmosphere[1] and is an important process for global-scale scavenging of anthropogenic pollutants.[2] However, the effect of precipitation on particulate matter (PM) is dependent on several factors. Previous work associated light rain amounts (<1 h; <0.5 mm) with elevated PM and heavy rain amounts (>10 mm) with decreased PM.[3] While some studies have shown that aerosol scavenging is sensitive to rain intensity,[4] others argue that rain frequency is more important than intensity in modulating aerosol removal.[5–7] Such findings demonstrate the

complexity of wet scavenging, as characteristics of light and heavy rain remain challenging to capture for both global models[8] and satellite retrievals.[9] Since precipitation is expected to become more intense and less frequent due to climate change,[10,11] it is important to understand how these changes may affect aerosol scavenging, particularly over highly-populated environments wherein inefficient scavenging may lead to the accumulation of PM and exacerbate health risks associated with poor air quality.

Metro Manila, Philippines is a rapidly developing megacity lacking strict air quality monitoring and regulation even though there are many PM sources including vehicular, industrial, firework, and cooking emissions as well as secondary formation, based on previous source apportionment work.[12–19] Recent size-resolved measurements focusing on source apportionment showed that most of the PM mass in Metro Manila resides within the submicrometer range.[14] Though PM levels (*i.e.*, mass concentrations) are expected to be lower in the wet season (May–October) than the dry season (November–April) due to wet scavenging by precipitation, Kim Oanh *et al.*[20] revealed that PM levels in Metro Manila are remarkably consistent between wet (44 μg m^{-3}) and dry (43 μg m^{-3}) seasons, later corroborated by Simpas *et al.*[21]

Potential contributors towards the seasonally consistent PM include inefficient scavenging, seasonal emissions, and meteorological influences. Although wet scavenging is expected to be the dominant sink for PM,[2] a large fraction of rain in Metro Manila is stratiform[22] and light rain is dominant throughout northern Philippines,[23] which suggests that precipitation may not always be an efficient removal mechanism for PM. Additionally, other meteorological variables may also influence PM levels[24] and counter the effect of wet scavenging on PM (*e.g.*, hygroscopic growth facilitated by high relative humidity (RH)), resulting in sustained PM levels even in the presence of rain. Black carbon (BC) particles have been shown to catalyze sulfate formation in both laboratory[25] and *in situ* studies[26] by serving as a surface for SO_2 oxidation with NO_2 and NH_3 present at moderate RH (30–70%). Thus, BC may also play a role in sustaining PM concentrations throughout the year due to the predominance of both BC and sulfate in Metro Manila.[14]

Though this study focuses on Metro Manila, it is important to note that Metro Manila may not be unique in its seasonally consistent PM and that factors promoting such a consistency may be present in other megacities lacking adequate air quality monitoring, contributing to PM accumulation even in the presence of rain and posing major health risks. Deteriorating air quality, poor infrastructure, and worsening traffic are problems faced by megacities globally[27] such as Lagos,[28] Malaysia,[29] Jakarta,[30] Beijing,[31] and Kolkata.[32] Seasonal meteorology over several Asian megacities is influenced by the Asian monsoon.[33] For example, Chennai experiences a two-phase seasonal cycle of wet and dry seasons, has relatively consistent PM levels between seasons, and shows a clear weekday PM enhancements[34] indicative of dominant urban emissions, similar to Metro Manila.[35] It is important to identify factors leading to seasonally consistent PM mass as these may be present in similar developing megacities besides Metro Manila, promoting PM accumulation and posing significant health risks. The analysis will serve to guide air quality-related policymaking and the formulation of appropriate mitigation measures towards more sustainable development in growing megacities.

Most past *in situ* studies investigating the relationship between rain and PM focused on either chemically resolved bulk PM[36,37] or size-resolved number concentrations.[38,39] In this study, we consider both particle composition and size using size-resolved aerosol composition data collected in Metro Manila, allowing for a more comprehensive analysis of PM-rain relationships. In order to explain the occurrence of seasonally consistent PM levels, we focus on addressing the following: (1) what particle sizes and species contribute to the sustained PM during the wet season despite increased rain?; and (2) What rain characteristics may decrease scavenging efficiency during the wet season? To answer these science questions, we propose the following hypotheses: (1) submicrometer particles will be inefficiently scavenged by rain, which is largely light in intensity over Metro Manila; and (2) more conducive conditions for secondary formation will contribute to sustained PM during the wet season.

2 Methods

2.1. PM sampling

Size-resolved aerosol composition was sampled in Metro Manila, Philippines in support of the Cloud, Aerosol, and Monsoon Processes Philippines Experiment[40] ($CAMP^2Ex$) weatHEr and CompoSition Monitoring (CHECSM) campaign.[14,41] PM was measured using Micro-Orifice Uniform Deposit Impactors (MOUDIs) stationed at the Manila Observatory (MO; 14.64°N, 121.08°E; 87 m above sea level) between July 2018 and October 2019. The MO site is well-established in the literature as a well-mixed urban background site for Metro Manila emissions.[13,14,20,21] Measurements of PM at the site are representative of Metro Manila as it is located more than 100 m away from the nearest road, ensuring ample time for mixing to occur prior to sampling.

Complete details of the sampling methodology and analysis are described elsewhere[42] with a brief summary provided here. The MOUDI sampled PM over approximately 48 hour periods at least once every week at the following aerodynamic cutpoint diameters: 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.10, 0.056 μm. Aqueous extracts of collected substrates using ultrapure water were subsequently analyzed for ions by ion chromatography (IC; Thermo Scientific Dionex ICS-2100 system) and for elements by triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ; Agilent 8800 Series). MOUDI species concentrations have relative uncertainties of <20%.[42] The water-soluble component of PM (hereafter PM-WS) was calculated as the total mass concentration of speciated ions (nitrate, maleate, magnesium, phthalate, sodium, calcium, pyruvate, succinate, adipate, oxalate, MSA, TMA/DEA, ammonium, sulfate, chloride, and DMA) and elements (Mo, Ni, Ti, Fe, Al, Cr, Tl, Zn, V, Cs, K, Zr, Sr, Nb, Ba, Y, Cu, As, Rb, Mn, Se, Ag, Co, Sn, Pb, Cd, and Hf). Black carbon (BC) was analyzed with a multi-wavelength

absorption black carbon instrument (MABI; Australian Nuclear Science and Technology Organization) at a wavelength of 870 nm for consistency with previous work.[14] Note that PM-WS does not include BC due to the less frequent measurements of BC. Gravimetric mass was measured by a Sartorius ME5-F microbalance (sensitivity: ± 1 μg). Full details of the measurements are provided in the data descriptor.[42]

A total of 54 MOUDI sets measured ionic and elemental concentrations while 11 sets measured gravimetric mass and BC. In this study, we define the wet (dry) season as May–October (November–April), corresponding roughly to the two phases of the Asian monsoon as established in previous studies.[23,43–47] As a result, we have 32 (22) MOUDI sets measuring PM-WS and 8 (3) MOUDI sets measuring gravimetric mass and BC for the wet (dry) season. Note that 23 out of 32 MOUDI sets during the wet season were influenced by rain.

Although 65 MOUDI sets (11 of them with gravimetric and BC data) may be seen as a limited sample size, the MOUDI dataset is the first time to our knowledge that size- and chemically-resolved measurements of PM have been collected in Metro Manila at such a frequency (at least once and up to three times per week) and duration (16 months with coverage of both monsoon seasons). Thus, findings from this dataset are a valuable contribution to the characterization and understanding of mechanisms that govern a relatively understudied but rapidly developing region of the world.

2.2. Meteorological data

Meteorological data (2010–2020) were collected at 5 min resolution by a Davis Vantage Pro2™ Plus automatic weather station (AWS) on the rooftop of the Manila Observatory (90 m above sea level). The data was quality-screened for meteorological values within acceptable ranges based on previous criteria.[22] To compare the meteorological data and MOUDI sets more directly, meteorological data was averaged between the start and end times of each MOUDI set except for precipitation which was accumulated per MOUDI set. Missing values such as those from maintenance periods were replaced with measurements from two nearby AWS stations (2 km and 5 km away). A complete description of the syncing of AWS data to the MOUDI sets is provided elsewhere.[35]

Rain events are defined as consecutive timestamps with non-zero rain amounts. For each rain event, we calculated rain amount (total rain amount during each rain event), rate (mean rain rate during each rain event), and duration (number of hours). For the MOUDI analysis, these characteristics were either summed or averaged per MOUDI set (*e.g.*, if three rain events occurred during a single MOUDI set (48 hours), their respective rain amounts and duration were added while their intensities were averaged).

2.3. AERONET data

To complement the long-term AWS data with a proxy of aerosol loading, we used Level 2 aerosol optical depth (AOD; 500 nm) data collected by the NASA AErosol RObotic NETwork (AERONET)[48] photometer on the rooftop of the Manila Observatory. The AOD data has a reported uncertainty of <0.02.[49,50] In order to quantify the response of AOD to rain event characteristics, we calculated the percent difference between AOD averaged three hours after (*i.e.*, after the end of the rain event until three hours later) and three hours before each rain event, termed ΔAOD (unit: %). If two rain events occurred with less than one hour between them, we considered the two as a single rain event. We use a percent difference in AOD in order to normalize for differing AOD values between rain events and to isolate the effect of wet scavenging by rainfall. The use of percent differences also accounts for the natural variability in sources over long time periods. Varying the averaging window between two and six hours reveals that the overall trends are robust to the width of the AOD averaging window. There was a total of 51 rain events across wet and dry seasons between 2010–2019 with useable AERONET data before and after the event (29 during the wet season between 2012–2019). The strict filtering down to 51 rain events was necessary to reduce possibility of confounding effects (*e.g.*, immediately consecutive rain events) in order to capture the full impact of wet scavenging on PM. We note that although AERONET and MOUDI data span different timescales (10 years and 16 months, respectively), both sources of data are robust and reveal very similar results, providing further confidence in our conclusions.

2.4. Curve-fitting

To provide a more quantitative description of the relationships between aerosol variables (AOD and PM concentration) and meteorology, we performed curve-fitting based on a simple exponential decay function $y = be^{-ax}$ where x is the meteorological variable (*e.g.*, rain duration), y is the aerosol variable (*e.g.*, PM concentration), and a and b depend on aerosol characteristics. This can be linearized such that a and $\ln(b)$ are interpretable as the slope and intercept, respectively. When fitting curves involving ΔAOD, an offset (c), defined as the absolute value of the minimum ΔAOD, was added to all ΔAOD values prior to curve-fitting to account for the non-negative constraints of exponential decay functions. After obtaining the curve-fit parameters (a, b), the offset was subtracted to revert ΔAOD values back to their original range. To quantify the goodness-of-fit of the resulting curves, we use scatter index (SI) which is the root mean squared error (RMSE) divided by the mean ΔAOD (with offset) or PM concentrations and has been used in previous work on error quantification.[51–53]

3 Results & discussion

3.1. Consistent PM across wet and dry seasons

The seasonal consistency in PM observed by Kim Oanh *et al.*[20] motivates the question of what factors contribute to this feature, with possibilities including inefficient wet scavenging and enhanced secondary production during the wet season. The average gravimetric mass is nearly identical across seasons for both PM_1 and PM_{10} size ranges (Fig. 1), corroborating previous work in Metro Manila.[20,21] The consistent gravimetric mass is explained by the opposing seasonal trends in PM-WS and BC

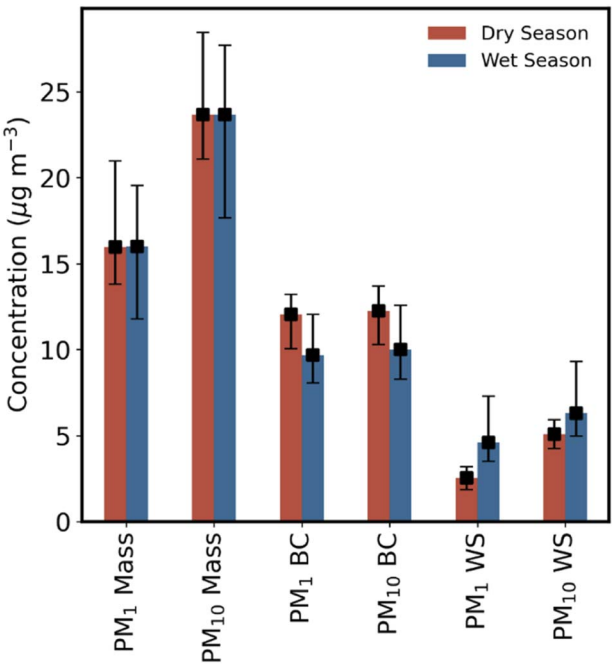

Fig. 1 Seasonal medians of gravimetric mass, black carbon (BC), and total water-soluble species (PM-WS) for PM_1 and PM_{10} size ranges. Wet (dry) season is defined as May to October (November to April). PM-WS was measured for 32 (22) sets during the wet (dry) season; gravimetric mass and BC were measured for 8 (3) MOUDI sets during the wet (dry) season. Lower and upper ends of error bars represent the 25th and 75th percentile concentrations, respectively.

(Fig. 1): while BC was higher during the dry season, PM-WS was higher during the wet season. Combined, these two major components of total PM result in seasonally consistent gravimetric mass. We assume gravimetric mass to be mainly composed of BC and PM-WS with the unaccounted fraction attributable to non-BC and non-water-soluble components of PM that were not measurable by IC or ICP-QQQ. Since BC is relatively inert, its main sink is wet scavenging.[54] While the increased BC in the dry season is expected due to the lower levels of rainfall and therefore precipitation scavenging, the increased PM-WS in the wet season is initially counter-intuitive. Since scavenging efficiency is composition-dependent[6,55] and PM-WS in Metro Manila is mostly composed of sulfate and ammonium,[14] PM-WS is expected to be susceptible to wet scavenging and should have lower levels during the wet season. This interesting seasonal feature is the focus of the analysis in this study as the enhancement in PM-WS is enough to offset the reduced BC concentrations in the wet season.

We considered if seasonal differences in PM in Metro Manila could arise from emissions that exhibit seasonal cycles. However, seasonal differences in meteorology may be seen as the chief driver of seasonal trends in PM due to the following reasons: (1) sampling was conducted within Metro Manila with the main PM sources including vehicular emissions, industry, cooking, sea salt, and waste processing,[12–19] which are consistent throughout the year given the tropical urban setting; (2) urban emissions are expected to be consistent throughout the year as Metro Manila has a tropical climate with relatively stable year-round temperatures (primarily between 25–30 °C),[35] thus emissions from heating or cooling remain consistent throughout the year; and (3) although the Philippines does receive long-range transport from East Asia and the Maritime Continent,[13,35,40,56–58] Metro Manila itself is largely insulated by mountains and ocean from these sources. Previous work has shown that the long-range transport of PM to the Philippines is naturally transient and PM levels return to normal values after episodes of long-range transport.[58] Since peaks in PM related to transport are both occasional and transient, a seasonal PM average measured within Metro Manila will mainly reflect local emissions, which are consistent throughout the year. This is in contrast to cities such as Delhi, India which are situated close to biomass burning areas and experience seasonal cycles in emissions as a result.[59] Besides wet scavenging, we do not discount the presence of other factors that may affect seasonal PM averages. Although the MOUDI dataset is rich in both size- and chemically-resolved information, the determination of causation in the observed relationships in this study is a natural limitation, and future work is encouraged to employ high-resolution modeling to isolate contributions of different factors to total PM.

Seasonal differences in the size distributions of gravimetric mass (Fig. 2a) revealed that submicrometer concentrations were slightly higher in the dry season, especially between 0.18–0.32 μm, while supermicrometer concentrations were slightly higher during the wet season, notably between 1.8–5.6 μm. A wet season enhancement is observed for gravimetric mass between 0.32–1.0 μm (Fig. 2a). Aged aerosol particles from secondary processes have been identified as the most important source of PM in this size range;[14] thus, gravimetric mass in this size range may be enhanced due to more conducive meteorological conditions for secondary aerosol processing in the wet season, which have been shown to be a factor in Metro Manila (*i.e.*, higher RH, lower boundary layer height).[35]

A lack of significant wet season enhancement in typical supermicrometer aerosol tracers (*e.g.*, sodium, calcium) (Fig. S1d and f†) suggests that the supermicrometer peak in gravimetric mass during the wet season (Fig. 2a) is largely unaccounted for by the species measured in this study. After considering contributions from PM-WS and BC, an average of 27.1% of PM_{10} gravimetric mass remained unaccounted for, reflecting a similar result in Cruz *et al.*,[14] while an average of only 6.8% was unaccounted for in the PM_1 range. This suggests that there exists a supermicrometer mode component of total gravimetric mass that cannot be fully explained by the MOUDI data (*i.e.*, water-soluble species and BC). One possible source for the enhanced supermicrometer mode are particles that are relatively water-insoluble (*i.e.*, not detected by IC/ICP-QQQ analyses) and do not contain BC (*i.e.*, not detected by the MABI). The investigation of this possibility and its source is left to future work.

BC and PM-WS (Fig. 2b and c) experienced the greatest seasonal changes in the submicrometer range. The heightened PM_1-WS concentrations during the wet season are well-explained by similar wet season enhancements of PM_1 sulfate

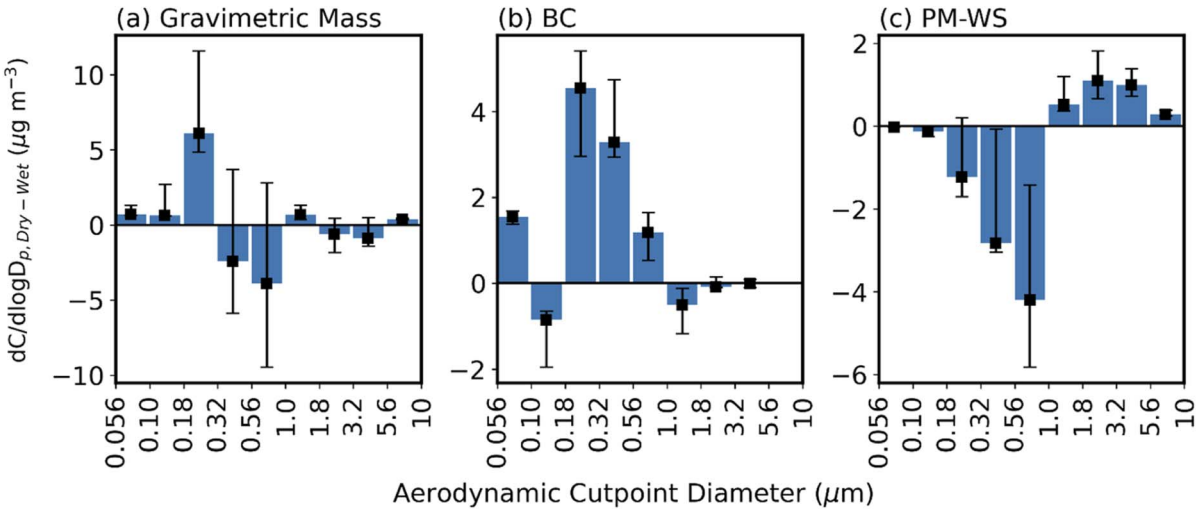

Fig. 2 Size-resolved differences in seasonal median concentrations (dry minus wet) of (a) gravimetric mass, (b) black carbon (BC), and (c) total water-soluble species (PM-WS). A positive (negative) value indicates higher dry (wet) season concentrations. Lower (upper) ends of error bars represent the differences in 25th (75th) percentile concentrations between seasons.

and ammonium (Fig. S1a and b†). Higher PM_1 sulfate and ammonium concentrations may point to meteorological conditions during the wet season that are conducive for secondary production (*e.g.*, higher RH, lower boundary layer height[35]) despite increased rain. Lower boundary layer heights over Metro Manila in the wet season[35] may also increase surface PM concentrations, which may also contribute to sustained wet season PM-WS; however, the lack of a similar enhancement in BC suggests boundary layer height may not be an important factor for explaining the seasonal consistency in gravimetric mass. Additionally, due to BC's high contribution to total PM in Metro Manila,[14] BC-catalyzed sulfate formation may also serve as an important contributor to sulfate concentrations.[25,26]

In summary, total PM mass was consistent across seasons due to opposing seasonal cycles of BC and PM-WS concentrations. While BC is generally higher in the dry season, PM-WS concentrations are higher in the wet season. The largest seasonal enhancements in BC and PM-WS occur in the submicrometer range, suggestive of the contributions of secondary formation[14] due to conducive meteorology (*i.e.*, high RH).

3.2. Relationships between PM and rain duration

Compared to rain amount (*i.e.*, accumulated rain during event) and rain intensity (*i.e.*, mean rain rate during event) (Fig. S2†), rain duration showed the clearest relationships with AOD and PM_1-WS (Fig. 3a and b), suggestive of wet scavenging, and is thus the focus of this section. Rain events with duration less than one hour are generally associated with heightened AOD after the event, perhaps due to RH-related effects on AOD,[60] while rain events longer than one hour tend towards lower AOD afterwards (Fig. 3a). Similarly, MOUDI sets with mean rain durations over one hour have notably lower concentrations of PM_1-WS (Fig. 3b), sulfate (Fig. S3a†), and ammonium (Fig. S3b†). This suggests that one hour may serve as a rough threshold for efficient wet scavenging.

To provide long-term context for rain in the sampling area, a multi-year characterization of rain duration during the wet season (2010–2020) revealed that 50% of rain events last less than one hour (Fig. 3c). Furthermore, rain has been shown to be mostly light in intensity over Metro Manila[22] and over the island of Luzon (northern Philippines) where Metro Manila is located (0–2.5 mm h^{-1}).[23] Considering the trends in Fig. 3a and b, the predominance of light and short rain events and their inefficient scavenging may be partly why PM-WS is higher in the wet season than the dry season. This is supported by Sun *et al.*[3] who showed that light rain (<1 h and <0.5 mm) did not scavenge PM efficiently. In addition to inefficient wet scavenging, we also note that elevated RH (Fig. S4†) and lower boundary layer heights[35] during the wet season in Metro Manila may also counteract scavenging by creating conducive conditions for secondary production of sulfate and ammonium. Besides sulfate and ammonium, secondary production is an important source of several species such as organic acids;[61] however, PM_1-WS in Manila is composed largely of sulfate (58% of PM_1-WS mass, on average) and ammonium (28%), which are much more abundant than other secondarily produced species such as organic acids (2%). Note that we focus on PM_1 because most of the PM mass resides within this range in Metro Manila based on previous source apportionment work.[14]

Stratifying Fig. 3a by rain rate reveals specific rain characteristics under which AOD can increase or decrease (Fig. 4). Note that in Fig. 4 we included data from the dry season to increase the number of data points for stratification; however, the inclusion of dry season data did not change the overall trends. We use percent differences in AOD rather than absolute differences in AOD to isolate the impact of each rain event on AOD while accounting for the confounding factor of pre-rain AOD levels which will naturally vary between rain events. Note that the use of percent differences also accounts for possible variability in sources over different time periods.

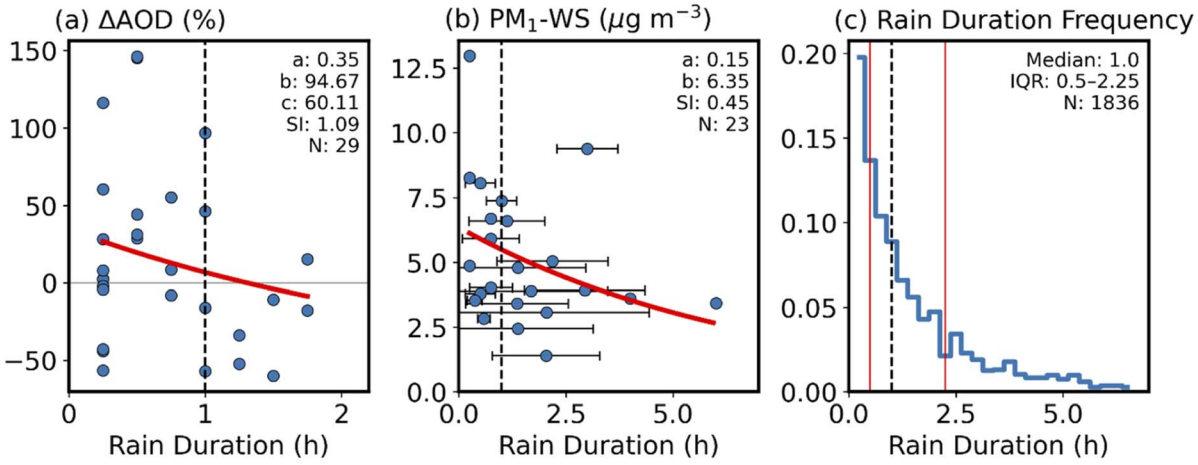

Fig. 3 Scatterplots of the (a) percent difference in AOD before and after rain events (ΔAOD; %; 2012–2019). (b) MOUDI total water-soluble species (PM_1-WS; μg m^{-3}; 2018–2019) as a function of rain duration (hours). (c) Histogram of rain duration (2010–2020). Rain duration in (b) refers to the mean duration of all rain events during each MOUDI set with error bars along the *x*-axis representing one standard deviation. Note that points in (b) without error bars consist of single rain events. The black dashed vertical lines in (a–c) mark the median rain duration based on (c). In (c), the red lines represent the 25th–75th percentile range (interquartile range, IQR). Number of data points per panel (*N*) is provided. Only data from the wet season were plotted (May–October). Curve-fitting for (a and b) is described in Section 2.4.

At low rain rates (Fig. 4a), shorter rain durations were associated with highly variable effects on AOD, with most points falling within the range of −50% and +50%. Longer rain durations exceeding 30 minutes were associated with more consistent decreases in post-rain AOD even if rain rate was low. At moderate rain rates (Fig. 4b), AOD tends to increase slightly post-rain, perhaps due to the enhanced moisture provided by moderate rain leading to higher AOD.[60] When rain durations exceed one hour, this enhancement in AOD is less pronounced. At high rain rates (Fig. 4c), we observe the clearest dependence of AOD on rain duration. For longer (shorter) rain events, a large decrease (increase) in AOD is observed post-rain. We hypothesize that this is due to the initial supply of moisture by shorter rain events that enhances AOD post-rain, but AOD is reduced after longer rain events wherein aerosol scavenging is more efficient. The enhancement of AOD after short rain events may be due to a combination of the following reasons: (1) intense rain supplies the necessary moisture for hygroscopic growth,[60] (2) intense rain causes a disturbance at the surface and a resuspension of aerosol,[62] and (3) shorter rain events may not scavenge aerosol particles efficiently. The overall trends in AOD reflect the findings from the MOUDI data (Fig. 3b), which further suggests more efficient aerosol removal occurs with longer rain events.

As precipitation is expected to become more intense and less frequent due to climate change,[10,11] it is possible that rain events

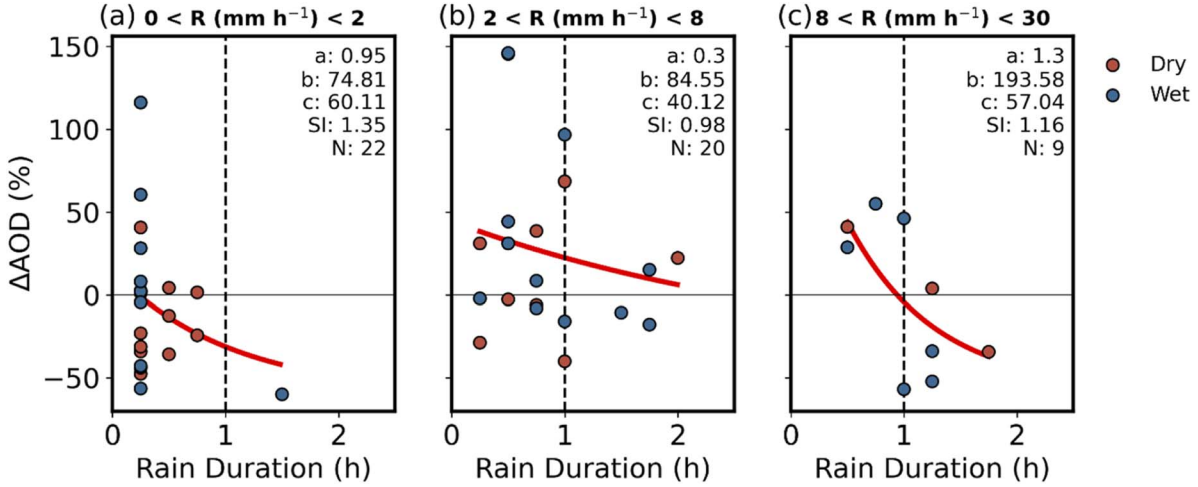

Fig. 4 Scatterplots of the percent difference in AOD post-rain event (ΔAOD; %) as a function of rain duration (hours) and colored by season. Data are stratified by rain rate (*R*; mm h^{-1}): (a) $0 < R < 2$, (b) $2 < R < 8$, (c) $8 < R < 30$. Wet (dry) season is defined as May to October (November to April). Number of data points per panel (*N*) is provided. The black dashed vertical lines mark the median rain duration based on Fig. 3c. Curve-fitting was performed as in Fig. 3a (see Section 2.4).

will shorten in duration, which may reduce wet scavenging efficiency and contribute to PM accumulation in other megacities besides Metro Manila. We do note that the relationship between precipitation intensity–frequency–duration is complex,[7,63] pointing to the importance of understanding aerosol-rain relationships in a warming world.[5]

In summary, rain events longer than one hour were associated with decreases in PM_1-WS and AOD. AOD tended to increase (decrease) after rain events shorter (longer) than one hour in duration, a trend that was more apparent at higher rain rates (>2 mm h^{-1}). A long-term characterization of rain duration revealed that during the wet season 50% of rain events last less than one hour. This finding, in addition to the insensitivity of PM-WS to shorter rain events, implies that inefficient scavenging occurs approximately half the time in Metro Manila and explains how total PM mass can remain elevated during the wet season.

3.3. Relationships of size-resolved PM and meteorology

In order to explore how aerosol size distributions change as a function of rain duration, we analyze size-resolved aerosol composition grouped by rain duration. Note that adjustments to the rain duration categories in Fig. 5 and S5† resulted in the same general conclusions. For rain events lasting less than one hour, PM-WS is bimodal (Fig. 5a), peaking at 0.56–1.0 μm and 1.8–3.2 μm. Rain events longer than one hour are associated with lower PM-WS concentrations (Fig. 5a) particularly between 0.18–1.0 μm and 1.8–5.6 μm, suggestive of more scavenging on an absolute mass basis within these size ranges by long rain events. The PM-WS supermicrometer mode peak experienced a relatively large decrease (~50%), likely due to the high hygroscopicity of species that compose most of the speciated supermicrometer mode mass (*i.e.*, nitrate, sodium, calcium, chloride; Fig. S5†). Based on previous source apportionment work,[14] sodium and chloride (calcium) in Metro Manila mostly originate from sea salt (dust) while nitrate was sourced from HNO_3 partitioning onto sea salt particles.[64] Dust[65] and sea salt[66,67] are efficiently removed by wet scavenging, which explains the large concentration drop in response to higher duration precipitation.

Both sulfate (Fig. 5b) and ammonium (Fig. 5c) tend to decrease when rain duration exceeds one hour similar to PM-WS; however, ammonium experienced a relatively larger decrease within the 0.32–0.56 μm range wherein concentrations dropped as much as ~30% (~1 μg m^{-3}) in response to longer rain durations. This is explainable by the higher scavenging efficiency of ammonium compared to sulfate.[68,69] We emphasize that, although most of the PM-WS mass (Fig. 5a) is composed of hygroscopic species (*i.e.*, sulfate, ammonium), PM-WS is largely unresponsive to rain events shorter than one hour (*i.e.*, the division of samples into more rain duration groups (not shown) reflects the patterns shown in Fig. 5). This result supports our previous analysis (Section 3.2) where we demonstrated that rain durations shorter than one hour tend to be inefficient at aerosol scavenging.

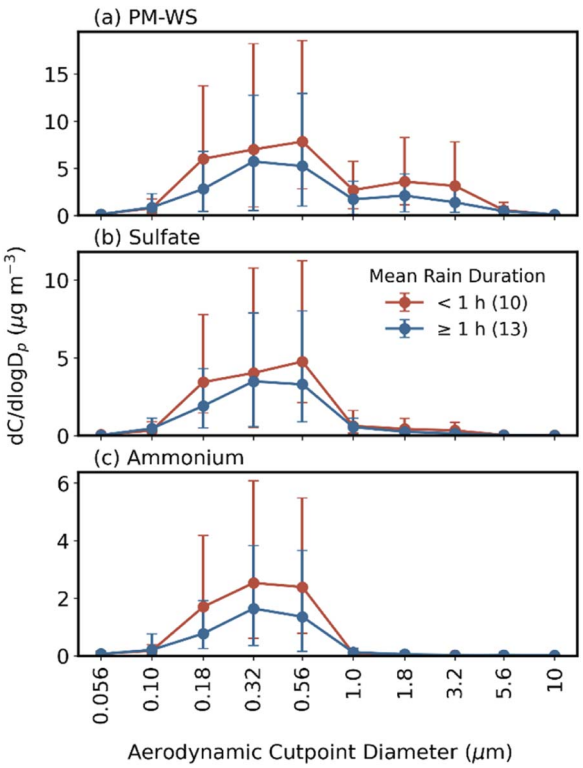

Fig. 5 Size distributions of median (a) total water-soluble species (PM-WS), (b) sulfate, and (c) ammonium grouped by mean rain duration during each MOUDI set. Only data from the wet season were plotted (May–Oct). Note that *y*-axis limits are not the same across panels. The number of MOUDI sets per grouping is provided in parentheses in the legend. Lower and upper ends of error bars represent the 25th and 75th percentile concentrations, respectively.

4 Summary and conclusions

As wet scavenging is the main aerosol sink, its characterization is important for modeling aerosol lifecycle and guiding air quality-related policymaking in megacities that may be susceptible to pollution accumulation despite the presence of rain. It is generally expected that PM mass concentrations during the wet season will be lower than those during the dry season. However, previous work observed seasonally consistent PM in Metro Manila, Philippines. Using a rich dataset of size-resolved aerosol composition, meteorology, and AOD retrieved by AERONET, the following major conclusions are reached:

(1) Consistent PM concentrations across wet and dry seasons are due to opposite-phase seasonal cycles of BC and PM-WS concentrations. While BC is generally higher in the dry season, PM-WS concentrations are higher in the wet season. The largest seasonal enhancements in BC and PM-WS occur in the submicrometer range, pointing to the role of anthropogenic emissions and secondary formation. Heightened PM-WS concentrations during the wet season are largely due to submicrometer sulfate and ammonium. Wet season enhancements are at least partially attributable to favorable conditions (*e.g.*, high RH) for secondary formation and hygroscopic growth.

(2) The presence of rain does not imply wet scavenging is taking place efficiently. The characteristics of rain are critical to estimating wet scavenging. Rain events longer than one hour were associated with decreases in PM_1-WS and AOD. AOD

tended to increase (decrease) after rain events shorter (longer) than one hour in duration, a trend that was more apparent at high rain rates. A long-term characterization of rain duration revealed that 50% of rain events during the wet season last less than one hour. This finding, in addition to the insensitivity of PM-WS to shorter rain events, implies that inefficient scavenging may occur approximately half the time in Metro Manila and explains how gravimetric mass remains elevated during the wet season.

(3) Size-resolved composition grouped by rain duration revealed the sensitivity of major PM-WS components (sulfate and ammonium) to rain events longer than one hour. On an absolute mass basis, the size ranges 0.18–1.0 μm and 1.8–5.6 μm were the most sensitive to wet scavenging *via* longer rain events. Notably, ammonium experienced a large decrease (up to ~30%) in response to rain events exceeding one hour. Though most PM-WS mass resides in the submicrometer range, the clear decrease in PM-WS concentrations in response to longer rain events indicates the importance of composition in explaining wet scavenging trends.

With the expectation of more intense, less frequent precipitation due to climate change,[10,11] changes in rain duration with increasing temperatures may result in inefficient wet scavenging over megacities aside from Metro Manila and contribute to the accumulation of PM and degradation of air quality. Thus, further work is needed to better understand factors leading to inefficient aerosol scavenging as well as the potential influence of these factors in other parts of the world. Future work is encouraged to: (1) examine size-resolved composition data at higher temporal resolution to further characterize PM responses to rain, (2) investigate the influence of Metro Manila's large BC contributions (26.9% of total mass[14]) on aerosol hygroscopicity, scavenging efficiency, and sulfate formation, (3) analyze speciated size distributions in response to different raindrop size distributions, (4) compare aerosol & meteorological data in other megacities to assess the prevalence of inefficient wet scavenging and to build more statistics on these relationships, and (5) high-resolution modeling to further explore causation behind the observed relationships between PM and meteorology in this study.

Author contributions

Formal analysis, visualization, writing – original draft: MRAH.

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Data curation: PAB, GB, RAB, MOC, MTC, GRL, ABM, PCP, JBS, CS, JRY, AS.

Conflicts of interest

There are no conflicts to declare.

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References

1 J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*, John Wiley & Sons, Inc, New Jersey, Third., 2016.
2 C. Textor, M. Schulz, S. Guibert, S. Kinne, Y. Balkanski, S. Bauer, T. Berntsen, T. Berglen, O. Boucher, M. Chin, F. Dentener, T. Diehl, R. Easter, H. Feichter, D. Fillmore, S. Ghan, P. Ginoux, S. Gong, A. Grini, J. Hendricks, L. Horowitz, P. Huang, I. Isaksen, I. Iversen, S. Kloster, D. Koch, A. Kirkevåg, J. E. Kristjansson, M. Krol, A. Lauer, J. F. Lamarque, X. Liu, V. Montanaro, G. Myhre, J. Penner, G. Pitari, S. Reddy, Ø. Seland, P. Stier, T. Takemura and X. Tie, *Atmos. Chem. Phys.*, 2006, **6**, 1777–1813.
3 Y. Sun, C. Zhao, Y. Su, Z. Ma, J. Li, H. Letu, Y. Yang and H. Fan, *Earth Space Sci.*, 2019, **6**, 1915–1925.
4 X. Zhao, Y. Sun, C. Zhao and H. Jiang, *Atmosphere*, 2020, **11**, 906.
5 Y. Wang, W. Xia, X. Liu, S. Xie, W. Lin, Q. Tang, H.-Y. Ma, Y. Jiang, B. Wang and G. J. Zhang, *Nat. Geosci.*, 2021, **14**, 72–76.
6 Y. Wang, W. Xia and G. J. Zhang, *Atmos. Chem. Phys. Discuss.*, 2021, 1–33.
7 P. Hou, S. Wu, J. L. McCarty and Y. Gao, *Atmos. Chem. Phys.*, 2018, **18**, 8173–8182.
8 L. Zhang, P. Wu, T. Zhou, M. J. Roberts and R. Schiemann, *Atmos. Sci. Lett.*, 2016, **17**, 646–657.
9 H. Chen, B. Yong, Y. Shen, J. Liu, Y. Hong and J. Zhang, *J. Hydrol.*, 2020, **581**, 124376.
10 K. E. Trenberth, *Clim. Res.*, 2011, **47**, 123–138.
11 K. E. Trenberth, A. Dai, R. M. Rasmussen and D. B. Parsons, *Bull. Am. Meteorol. Soc.*, 2003, **84**, 1205–1218.
12 M. AzadiAghdam, R. A. Braun, E.-L. Edwards, P. A. Bañaga, M. T. Cruz, G. Betito, M. O. Cambaliza, H. Dadashazar, G. R. Lorenzo, L. Ma, A. B. MacDonald, P. Nguyen, J. B. Simpas, C. Stahl and A. Sorooshian, *Atmos. Environ.*, 2019, **216**, 116922.
13 R. A. Braun, M. A. Aghdam, P. A. Bañaga, G. Betito, M. O. Cambaliza, M. T. Cruz, G. R. Lorenzo, A. B. MacDonald, J. B. Simpas, C. Stahl and A. Sorooshian, *Atmos. Chem. Phys.*, 2020, **20**, 2387–2405.
14 M. T. Cruz, P. A. Bañaga, G. Betito, R. A. Braun, C. Stahl, M. A. Aghdam, M. O. Cambaliza, H. Dadashazar, M. R. Hilario, G. R. Lorenzo, L. Ma, A. B. MacDonald, P. C. Pabroa, J. R. Yee, J. B. Simpas and A. Sorooshian, *Atmos. Chem. Phys.*, 2019, **19**, 10675–10696.

15 M. E. Gonzalez, C. Stahl, M. T. Cruz, P. A. Bañaga, G. Betito, R. A. Braun, M. Azadi Aghdam, M. O. Cambaliza, G. R. Lorenzo, A. B. MacDonald, J. B. Simpas, J. Csavina, A. E. Sáez, E. Betterton and A. Sorooshian, *Atmos. Pollut. Res.*, 2021, **12**, 352–361.
16 S. Kecorius, L. Madueño, E. Vallar, H. Alas, G. Betito, W. Birmili, M. O. Cambaliza, G. Catipay, M. Gonzaga-Cayetano, M. C. Galvez, G. Lorenzo, T. Müller, J. B. Simpas, E. G. Tamayo and A. Wiedensohler, *Atmos. Environ.*, 2017, **170**, 169–183.
17 G. R. Lorenzo, P. A. Bañaga, M. O. Cambaliza, M. T. Cruz, M. AzadiAghdam, A. Arellano, G. Betito, R. Braun, A. F. Corral, H. Dadashazar, E.-L. Edwards, E. Eloranta, R. Holz, G. Leung, L. Ma, A. B. MacDonald, J. S. Reid, J. B. Simpas, C. Stahl, S. M. Visaga and A. Sorooshian, *Atmos. Chem. Phys.*, 2021, **21**, 6155–6173.
18 L. Madueño, S. Kecorius, W. Birmili, T. Müller, J. Simpas, E. Vallar, M. C. Galvez, M. Cayetano and A. Wiedensohler, *Atmosphere*, 2019, **10**, 603.
19 C. Stahl, M. T. Cruz, P. A. Bañaga, G. Betito, R. A. Braun, M. A. Aghdam, M. O. Cambaliza, G. R. Lorenzo, A. B. MacDonald, M. R. A. Hilario, P. C. Pabroa, J. R. Yee, J. B. Simpas and A. Sorooshian, *Atmos. Chem. Phys.*, 2020, **20**, 15907–15935.
20 N. T. Kim Oanh, N. Upadhyay, Y.-H. Zhuang, Z.-P. Hao, D. V. S. Murthy, P. Lestari, J. T. Villarin, K. Chengchua, H. X. Co and N. T. Dung, *Atmos. Environ.*, 2006, **40**, 3367–3380.
21 J. B. Simpas, G. R. H. Lorenzo and M. T. Cruz, in *Improving Air Quality in Asian Developing Countries: Compilation of Research Findings*, Vietnam Publishing House of Natural Resources, Environment and Cartography, Vietnam, 2014.
22 E. N. Bañares, G. T. T. Narisma, J. B. B. Simpas, F. T. Cruz, G. R. H. Lorenzo, M. O. L. Cambaliza and R. C. Coronel, *Atmos. Res.*, 2021, **258**, 105646.
23 M. R. A. Hilario, L. M. Olaguera, G. T. Narisma and J. Matsumoto, *Asia-Pacific Journal of Atmospheric Sciences*, 2020, **57**, 573–585.
24 A. P. K. Tai, L. J. Mickley and D. J. Jacob, *Atmos. Environ.*, 2010, **44**, 3976–3984.
25 F. Zhang, Y. Wang, J. Peng, L. Chen, Y. Sun, L. Duan, X. Ge, Y. Li, J. Zhao, C. Liu, X. Zhang, G. Zhang, Y. Pan, Y. Wang, A. L. Zhang, Y. Ji, G. Wang, M. Hu, M. J. Molina and R. Zhang, *Proc. Natl. Acad. Sci. U. S. A.*, 2020, **117**, 3960–3966.
26 G. Zhang, Y. Fu, X. Peng, W. Sun, Z. Shi, W. Song, W. Hu, D. Chen, X. Lian, L. Li, M. Tang, X. Wang and X. Bi, *J. Geophys. Res.: Atmos.*, 2021, e2021JD035226.
27 L. T. Molina, *Faraday Discuss.*, 2021, **226**, 9–52.
28 L. Croitoru, J. C. Chang and A. Kelly, *The Cost of Air Pollution in Lagos*, World Bank, Washington, DC, 2020.
29 S. N. Brohi, T. R. Pillai, D. Asirvatham, D. Ludlow and J. Bushell, *IOP Conf. Ser. Earth Environ. Sci.*, 2018, **167**, 012015.
30 A. A. Yusuf and B. P. Resosudarmo, *Ecol. Econ.*, 2009, **68**, 1398–1407.
31 P. Zhao and H. Hu, *Cities*, 2019, **92**, 164–174.
32 D. Mukherjee and S. Mitra, *Transportation in Developing Economies*, 2019, **5**, 6.
33 B. Wang, *The Asian Monsoon*, Springer Science & Business Media, 2006.
34 Y. Chen, O. Wild, L. Conibear, L. Ran, J. He, L. Wang and Y. Wang, *Atmos. Environ.: X*, 2020, **5**, 100052.
35 M. R. A. Hilario, M. T. Cruz, P. A. Bañaga, G. Betito, R. A. Braun, C. Stahl, M. O. Cambaliza, G. R. Lorenzo, A. B. MacDonald, M. AzadiAghdam, P. C. Pabroa, J. R. Yee, J. B. Simpas and A. Sorooshian, *J. Geophys. Res.: Atmos.*, 2020, **125**, 13.
36 B. Ge, D. Xu, O. Wild, X. Yao, J. Wang, X. Chen, Q. Tan, X. Pan and Z. Wang, *Atmos. Chem. Phys.*, 2021, **21**, 9441–9454.
37 D. Xu, B. Ge, Z. Wang, Y. Sun, Y. Chen, D. Ji, T. Yang, Z. Ma, N. Cheng, J. Hao and X. Yao, *Environ. Pollut.*, 2017, **230**, 963–973.
38 C. Blanco-Alegre, A. I. Calvo, A. Castro, F. Oduber, E. Alonso-Blanco and R. Fraile, *Environ. Pollut.*, 2021, **285**, 117371.
39 S. Licen, S. Cozzutto and P. Barbieri, *Aerosol Air Qual. Res.*, 2020, **20**, 800–809.
40 M. R. A. Hilario, E. Crosbie, M. Shook, J. S. Reid, M. O. L. Cambaliza, J. B. B. Simpas, L. Ziemba, J. P. DiGangi, G. S. Diskin, P. Nguyen, F. J. Turk, E. Winstead, C. E. Robinson, J. Wang, J. Zhang, Y. Wang, S. Yoon, J. Flynn, S. L. Alvarez, A. Behrangi and A. Sorooshian, *Atmos. Chem. Phys.*, 2021, **21**, 3777–3802.
41 M. AzadiAghdam, R. A. Braun, E.-L. Edwards, P. A. Bañaga, M. T. Cruz, G. Betito, M. O. Cambaliza, H. Dadashazar, G. R. Lorenzo, L. Ma, A. B. MacDonald, P. Nguyen, J. B. Simpas, C. Stahl and A. Sorooshian, *Atmos. Environ.*, 2019, **216**, 116922.
42 C. Stahl, M. T. Cruz, P. A. Bañaga, G. Betito, R. A. Braun, M. A. Aghdam, M. O. Cambaliza, G. R. Lorenzo, A. B. MacDonald, P. C. Pabroa, J. R. Yee, J. B. Simpas and A. Sorooshian, *Sci. Data*, 2020, **7**, 128.
43 F. T. Cruz, G. T. Narisma, M. Q. Villafuerte, K. U. Cheng Chua and L. M. Olaguera, *Atmos. Res.*, 2013, **122**, 609–616.
44 J. Matsumoto, L. M. P. Olaguera, D. Nguyen-Le, H. Kubota and M. Q. Villafuerte, *Int. J. Climatol.*, 2020, **40**, 4843–4857.
45 I. Akasaka, *Int. J. Climatol.*, 2010, **30**, 1301–1314.
46 I. Akasaka, W. Morishima and T. Mikami, *Int. J. Climatol.*, 2007, **27**, 715–725.
47 L. M. Olaguera, J. Matsumoto, H. Kubota, T. Inoue, E. O. Cayanan and F. D. Hilario, *Atmosphere*, 2018, **9**, 464.
48 B. N. Holben, T. F. Eck, I. Slutsker, D. Tanré, J. P. Buis, A. Setzer, E. Vermote, J. A. Reagan, Y. J. Kaufman, T. Nakajima, F. Lavenu, I. Jankowiak and A. Smirnov, *Remote Sens. Environ.*, 1998, **66**, 1–16.
49 O. Dubovik, B. Holben, T. F. Eck, A. Smirnov, Y. J. Kaufman, M. D. King, D. Tanré and I. Slutsker, *J. Atmos. Sci.*, 2002, **59**, 590–608.
50 T. F. Eck, B. N. Holben, J. S. Reid, O. Dubovik, A. Smirnov, N. T. O'Neill, I. Slutsker and S. Kinne, *J. Geophys. Res.*, 1999, **104**, 31333–31349.
51 J. J. Williams and L. S. Esteves, *Adv. Civ. Eng.*, 2017, **2017**, e5251902.

52 R. M. Campos and C. Guedes Soares, *Ocean Eng.*, 2016, **112**, 320–334.
53 S. Abdalla, P. A. E. M. Janssen and J.-R. Bidlot, *Mar. Geodes.*, 2011, **34**, 393–406.
54 N. Moteki, Y. Kondo, N. Oshima, N. Takegawa, M. Koike, K. Kita, H. Matsui and M. Kajino, *Geophys. Res. Lett.*, 2012, **39**, L13802.
55 S. Izhar, T. Gupta and A. K. Panday, *Atmos. Res.*, 2020, **235**, 104767.
56 J. S. Reid, E. J. Hyer, R. S. Johnson, B. N. Holben, R. J. Yokelson, J. Zhang, J. R. Campbell, S. A. Christopher, L. Di Girolamo, L. Giglio, R. E. Holz, C. Kearney, J. Miettinen, E. A. Reid, F. J. Turk, J. Wang, P. Xian, G. Zhao, R. Balasubramanian, B. N. Chew, S. Janjai, N. Lagrosas, P. Lestari, N.-H. Lin, M. Mahmud, A. X. Nguyen, B. Norris, N. T. K. Oanh, M. Oo, S. V. Salinas, E. J. Welton and S. C. Liew, *Atmos. Res.*, 2013, **122**, 403–468.
57 J. S. Reid, P. Xian, E. J. Hyer, M. K. Flatau, E. M. Ramirez, F. J. Turk, C. R. Sampson, C. Zhang, E. M. Fukada and E. D. Maloney, *Atmos. Chem. Phys.*, 2012, **12**, 2117–2147.
58 M. R. A. Hilario, M. T. Cruz, M. O. L. Cambaliza, J. S. Reid, P. Xian, J. B. Simpas, N. D. Lagrosas, S. N. Y. Uy, S. Cliff and Y. Zhao, *Atmos. Chem. Phys.*, 2020, **20**, 1255–1276.
59 S. Bikkina, A. Andersson, E. N. Kirillova, H. Holmstrand, S. Tiwari, A. K. Srivastava, D. S. Bisht and Ö. Gustafsson, *Nat. Sustain.*, 2019, **2**, 200–205.
60 C. Zheng, C. Zhao, Y. Zhu, Y. Wang, X. Shi, X. Wu, T. Chen, F. Wu and Y. Qiu, *Atmos. Chem. Phys.*, 2017, **17**, 13473–13489.
61 A. Hodzic, P. S. Kasibhatla, D. S. Jo, C. D. Cappa, J. L. Jimenez, S. Madronich and R. J. Park, *Atmos. Chem. Phys.*, 2016, **16**, 7917–7941.
62 Y. S. Joung and C. R. Buie, *Nat. Commun.*, 2015, **6**, 6083.
63 P. Hosseinzadehtalaei, H. Tabari and P. Willems, *J. Hydrol.*, 2020, **590**, 125249.
64 G. Prabhakar, A. Sorooshian, E. Toffol, A. F. Arellano and E. A. Betterton, *Atmos. Environ.*, 2014, **92**, 339–347.
65 P. Ginoux, M. Chin, I. Tegen, J. M. Prospero, B. Holben, O. Dubovik and S.-J. Lin, *J. Geophys. Res.: Atmos.*, 2001, **106**, 20255–20273.
66 D. M. Murphy, K. D. Froyd, H. Bian, C. A. Brock, J. E. Dibb, J. P. DiGangi, G. Diskin, M. Dollner, A. Kupc, E. M. Scheuer, G. P. Schill, B. Weinzierl, C. J. Williamson and P. Yu, *Atmos. Chem. Phys.*, 2019, **19**, 4093–4104.
67 J. S. Schlosser, H. Dadashazar, E.-L. Edwards, A. H. Mardi, G. Prabhakar, C. Stahl, H. H. Jonsson and A. Sorooshian, *J. Geophys. Res.: Atmos.*, 2020, **125**, e2019JD032346.
68 S. Gilardoni, P. Massoli, L. Giulianelli, M. Rinaldi, M. Paglione, F. Pollini, C. Lanconelli, V. Poluzzi, S. Carbone, R. Hillamo, L. M. Russell, M. C. Facchini and S. Fuzzi, *Atmos. Chem. Phys.*, 2014, **14**, 6967–6981.
69 A. Kasper-Giebl, M. F. Kalina and H. Puxbaum, *Atmos. Environ.*, 1999, **33**, 895–906.