Dear Editor,

We would like to thank the two reviewers for their constructive comments and suggestions, which have been fully taken into account upon manuscript revision. A point-by-point response and an accordingly updated manuscript have been uploaded.

In the following, original reviewer comments, our response, and updates on the revised manuscript are shown in **bold**, normal, and *italic*, respectively.

Kind Regards,

Jing Chen, Mikinori Kuwata

Anonymous Referee #1

General comments:

R1C0: The paper presents measurements of biomass burning aerosol hygroscopicity, both fresh and with aging. This is an important region and biome to characterize for smoke properties. The paper finds a substantial difference in kappa attributed to difference in the organic fraction hygroscopicity. The latter is related to aging and the fraction of water-soluble organic material. The paper is a well referenced manuscript and the methods appear sound. A few items need further attention before this publishable in ACP.

Response: We appreciate the reviewer for insightful comments in revising the manuscript. Our responses to reviewer's concerns are described in the following.

Major Comments on Content

R1C1: Line 6 is it agricultural development in this region? Housing, industrial? More specifics are recommended.

Response: We appreciate for the helpful comment. Over the past few decades, Indonesia has experienced rapid land use change due to development of plantations as well as agricultural activities of small farmers (Miettinen et al., 2012; Marlier et al., 2015). Especially, development of peatland has been playing an important role for wildfire, as peat becomes highly flammable after drainage of water for agricultural development. The following sentences were added to the revised manuscript for clarification.

***Page 3, Line 5:** ‘The increasing wildfire activity is associated with the recent rapid change in land use for agricultural development, including industrial plantations over peatland (Page et al., 2009; Marlier et al., 2015; Spracklen et al., 2015). Such developments are accompanied by the drainage of water of pristine peat swamp forest, making the tropical peatland susceptible to fire (Langner et al., 2007; Konecny et al., 2016).’*

R1C2: Show some data on calibration in the paper or supplementary material. This is important to give the reader confidence in the findings. The reference to the first paper is a help but some indication of these efforts is merited in the paper or supplementary material.

Response: Calibration data of HTDMA by ammonium sulfate particles were added to supplemental material of the revised manuscript to address the reviewers’ concern. Our calibration result agreed well with a literature data (Tang and Munkelwitz, 1994).

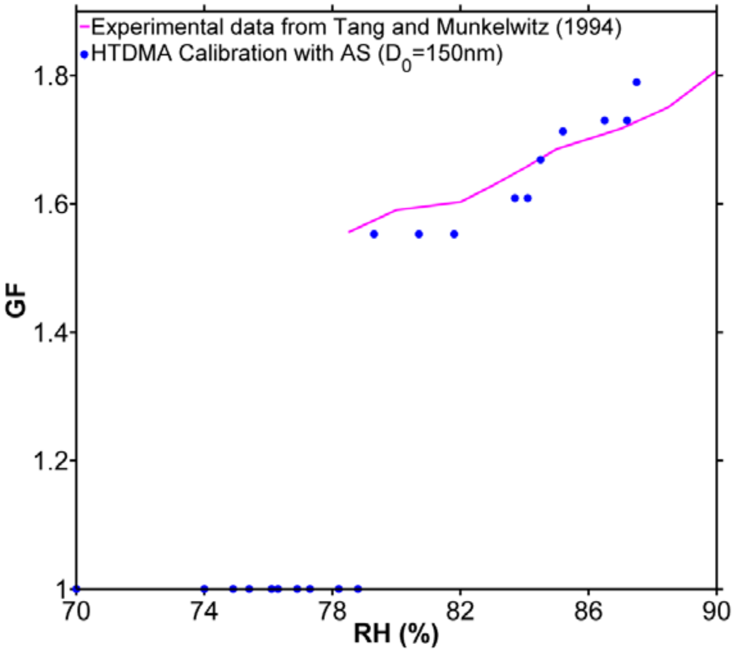

Fig. S1 *Comparison of particle diameter growth factor (GF) results derived from HTDMA calibration data for 150 nm dry ammonium sulfate (AS) particles, and experimental data (without parameterization) obtained by Tang and Munkelwitz (1994).*

Page 7, Line 9: *'… T is the absolute temperature (298 K). The HTDMA calibration results with 150 nm ammonium sulfate particles are shown in Fig. S2, demonstrating the validity of our instrument. Further details about the HTDMA are available in Chen et al. (2017).'*

R1C3: I may have missed it, but do you apply any OC to particulate organic carbon multiplier or use as measured OC? This would be good to state up front and/or in abstract.

Response: Yes, we employed an organic matter to OC ratio of 1.4 in calculating mass concentrations of total organics from OC content of the $PM_{2.5}$ filter samples, as detailed in section 4.2 (see Page 14, line 29). The derived organics mass concentration of $PM_{2.5}$ filter samples correlated well with organics quantified by the ToF-ACSM.

R1C4: Relying on the publication of a manuscript in preparation for experimental details is somewhat risky (Budisulistiorini et al.).

Response: We appreciate the reviewer for the comment. We recently submitted the corresponding manuscript, and have updated the citations in the present manuscript.

Page 7, Line 23: *'… Details about the ToF-ACSM measurements and data analysis are provided in Budisulistiorini et al. (submitted to Atmospheric Chemistry and Physics, February 2018).'*

Page 15, Line 2: *'… and the lack of EC content for the ToF-ACSM measurements (Budisulistiorini et al., submitted to Atmospheric Chemistry and Physics, February 2018).'*

Budisulistiorini, S. H., Riva, M., Williams, M., Miyakawa, T., Chen, J., Itoh, M., Surratt, J. D., and Kuwata, M.: Dominant contribution of oxygenated organic aerosol to haze particles from real-time observation at Singapore during an Indonesian wildfire event in 2015. Submitted to Atmospheric Chemistry and Physics, February 2018.

R1C5: Do you have any indication of age of the smoke aerosols that were sampled?

Response: We thank the reviewer for the helpful comments. In the revised manuscript, we added distributions of carbon emissions from wildfire (GFEDv4) as well as back trajectories of air masses arriving at Singapore. It took approximately 1~2 days for air mass transporting from the Southern part of Sumatra Island to Singapore, and 3~4 days for wildfire plumes from Central Kalimantan to arrive at Singapore.

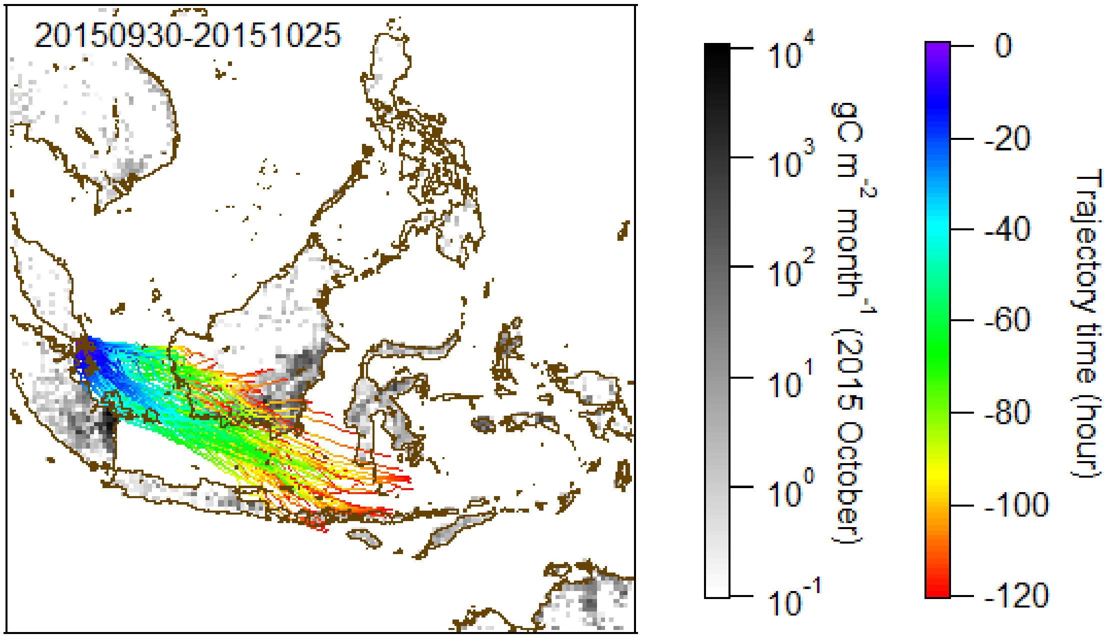

Fig. S1 *Back trajectories of air masses arriving at Singapore and monthly carbon emission from wildfires during the observation period of HTDMA measurements. The transport time of wildfire plumes is approximately 1−2 days from South Sumatra, and 3−4 days from Central Kalimantan arriving at Singapore.*

The back trajectory was calculated using the NOAA HYSPLIT model at 500 m (Kalnay et al., 1996). The altitude of the trajectories was constrained as iso-sigma. Carbon emission data was from the Global Fire Emissions Database (GFEDv4, https://daac.ornl.gov/VEGETATION/guides/fire_emissions_v4.html).

R1C6. Any characterization of the combustion characteristics of the surrounding fires (fuels, phase, etc.)? Presumably a smoldering dominated combustion situation with peat burning.

Response: Based on previous laboratory studies and field observations, Indonesian peatland fires are predominantly contributed by smoldering combustion of underground organic-rich peat soils. Vegetation burning, which could include both flaming and smoldering, also contributes to the emissions of gas and particulate matters (Field et al., 2016; Page et al., 2009; Jayaranthe et al., 2017).

Following the suggestion, these points are clarified into Sect. 2.1 of the revised manuscript, as detailed in the following.

Page 6, Line 7: *'… located approximately 8 km south. In September−October 2015, the observation site encountered severe transboundary haze pollution that was caused by recurring Indonesian peatland fires, dominated by the smoldering combustion of underground organic-rich peat soils and mixed surface vegetation burning (Field et al., 2016; Page et al., 2009; Jayaranthe et al., 2017). Particles emitted from the wildfires had experienced for approximately 1−4 days atmospheric aging process before arriving at Singapore (Fig. S1).'*

R1C7: Jayaranthe et al. (2017) on the organic carbon content and WSOC of SE Asian peatland smoke is a relevant reference to bring into your analysis.

Response: We thank the reviewer for the suggestion. Jayaranthe et al. (2017) quantified the mean WSOC/OC ratio of fresh peatland burning particles at Kalimantan in 2015 as 16 %. The value of our data in Singapore (63.6 %) is significantly higher than that reported in Jayaranthe et al. (2017), suggesting that secondary formation as well as chemical transformation of organic aerosol during atmospheric transport from Kalimantan to Singapore is important. We have added the following content into the discussion to emphasize the point.

Page 14, Line 16: *'… and maximum values of 63.6 % and 79.9 %, respectively. The mean WSOC/OC result was significantly higher than that for fresh Indonesian peat burning particles emitted from the source region (i.e., 16 %; Jayaranthe et al.,* *2017), which were demonstrated to be generally water insoluble and thus nearly non-hygroscopic (Chen et al., 2017). This result suggests that the majority of organics in the wildfire haze particles were water soluble, implying the importance of secondary formation as well as the chemical transformation of organic particles during atmospheric transport.'*

R1C8: The strength of the hygroscopic response of peat smoke organic aerosol as it ages is somewhat surprising. The assertion that wildfire haze particles are generally highly hygroscopic in the conclusion counters most of the research in the literature. Compare to the results from the Carnegie-Mellon group (e.g. Engelhart et al. 2012) or FLAME results (e.g. Carrico et al. 2010). Relevant fuels such as duff show little water uptake and only modest increases with oxidation (kappa < 0.1) for organic carbon dominated aerosol from this sourced. Commenting on this is useful.

Response: We appreciate the reviewer for the critical comment. One important difference between our observation and former laboratory studies is the time scale of chemical processing. As discussed in R1C5, it likely took 1 ~ 4 days for particles originating from peatland fires to be transported to Singapore. On the other side, laboratory experiments are typically conducted for a time scale of hours (Chang et al., 2010; Engelhart et al., 2012). Laboratory chamber experiments are conducted at a relatively lower humidity (RH < 70%) in most cases, while Southeast Asia is always highly humid. As high RH is favorable for SOA formation by particle phase chemical reactions as well as for POA aging (Lambe et al., 2011a, b, 2015), the difference in RH might be playing an important role in the difference between observation and experimental data. In addition, concentrations of other gas species such as NO_x and sulfate, those are known to influence gas and particle phase chemistry (Kang et al., 2007; Chan et al., 2009; Lambe et al., 2011a, 2015), might be different between previous laboratory experiments and field condition. Furthermore, the difference in VOCs emitted from peat burning could be different from those emitted from other types of fires (Stockwell et al., 2016).

Nevertheless, our temporal mean κ value of the OOA factor (i.e., 0.266 ± 0.184) for wildfire haze particles is still comparable to that of aged biomass burning particles (i.e., 0.2 ± 0.1, Engelhart et al., 2012). Following the reviewers' suggestion, the following description was added to the revised manuscript.

Page 15, Line 27: *'…The derived κ_{org} results are demonstrated to be comparable to previously reported κ values for bulk organics (Petters and Kreidenweis, 2007; Duplissy et al., 2011; Lathem et al., 2013; Cerully et al., 2015). Moreover, the mean κ_{OOA} value agreed well with mean κ results in previous field and laboratory studies (e.g., $\kappa = 0.25 \pm 0.06$ for biogenic OOA, Chang et al., 2010; $\kappa = 0.2 \pm 0.1$ for aged BBOA, Engelhart et al., 2012). A caveat of this comparison is the representativeness of laboratory experiments for the actual environmental conditions, including types of burnt biomasses, concentrations and types of oxidants, and aging time. As the atmospheric condition of tropical Asia is unique, a systematic study of the chemical aging process of wildfire plume for the region would be required in the future. Note that the mean κ_{OOA} was even higher than the corresponding mean κ_{HTDMA} (0.207 ± 0.093), revealing that the water uptake particularly by some highly oxygenated organics in the wildfire haze particles could be highly significant.'*

R1C9: How is RH obtained with possible temperature changes in the system? At the high RH ~ 85% of your measurements a 1degC change in temperature results in 5% change in RH. Accessing the cited Chen et al. (2017) the RH was monitored at the inlet and outlet of the humidified DMA. Could the temperature of the column have been different?

Response: In our study, RH of the humidified sheath outflow was modulated to be the target RH via PID control. For the whole humidification unit, the humidified DMA column and tubing connecting with the Nafion humidifier were wrapped well with thermal-insulation materials. There is a small temperature variance in the outer wall of the humidified DMA column (~ 0.3 °C lower in maximum) and the humidified sheath flow. The caused RH fluctuation is insignificant to the resultant GF variation, which is supported by our reasonable HTDMA calibration results with 150 nm ammonium sulfate particles (also see our response to **R1C2**).

R1C10: Related, could the diurnal variation be due to changes in sampling conditions? I find it surprising that the organic fraction hygroscopicity would change so much day to night (table 3, fig 5). More discussion as to what you attribute the changes would improve. If photochemistry and oxidation of organics is suggested is there any relationship to solar input on the days of sampling?

Response: We appreciate the reviewer for the insightful comment. The temperature of our laboratory was well-maintained by an air-conditioning system. There was no significant difference in RH of the HTDMA during daytime (85% ± 0.2 ~ 0.3%) and nighttime (85% ± 0.2 ~ 0.4%), suggesting that the diurnal variation is not caused by fluctuation in the instrumental condition.

The data in Fig. 5 is for mean GF, meaning that it includes contributions of both organics and inorganics to the bulk hygroscopic growth. As shown in Figs. 6 and 7, one of the key drivers for the diurnal variation is the enhanced sulfate fraction during the daytime (i.e., change in hygroscopicity of organics is not the only one reason for the diurnal variation of mean GF). Of course, enhanced fraction of oxygenated organics during daytime also contributed to the diurnal variation in mean GF.

The corresponding description in the manuscript was updated as follows to clarify these points.

Page 17, Line 20: *'…Variations in the fresh PBOA fraction (f_{PBOA}) were similar to those of non-peat BBOA (f_{BBOA}) (Fig. 6e), namely, there was no apparent diurnal pattern during the severe wildfire haze periods. Consequently, the distinctly enhanced mean GF during the day could be attributed to the increase in both $f_{SO4}{}^{2-}$ and $f_{OOA.}$'*

R1C11: To what do you attribute the decrease in kappa with increasing chloride and nitrate fraction? Shouldn't these be hygroscopic inorganic species that would contribute to increasing kappa? Why would kappa increase so strongly as these ion fractions approach zero?

Response: We appreciate the reviewer for pointing it out. As we can see in Fig.7, both chloride and nitrate are enriched during nighttime, while availability of these species is limited during daytime. As both ammonium nitrate and ammonium chloride tend to partition to particle phase at a high RH environment, contributions of these species are pronounced during nighttime (Aan de Brugh et al., 2012; Gong et al., 2013). On the other hand, their abundances in particle phase are limited during daytime because the corresponding RH is lower than that for nighttime. Particles tend to be more hygroscopic during daytime due to in-situ formation of sulfate. In summary, sulfate formation during daytime and diurnal variation in gas-particle partitioning of nitrate and chloride are producing the apparent anti-correlations. This point is clarified in the revised manuscript as follows.

Page 18, Line 11: *'…κ was almost independent of f_{Cl^-}, partially due to the limited availability of non-refractory chloride. These distinctly different correlations between inorganics with mean κ likely reflect the different formation mechanisms of these species. Sulfate formation occurs as the result of the photochemical process during the day, whereas diurnal variations in gas–particle partitioning are important for the mass concentration of nitrate or chloride (Aan de Brugh et al., 2012; Gong et al., 2013).'*

R1C12: A relationship in figure 9 is likely but figure 8 shows little relationship (suggest dropping this and stating no relationship found). Even without Oct 22 the relationship looks weak, r^2 of 0.2 or so?

Response: We appreciate the reviewer for the suggestion. We agree with the reviewer that the empirical correlation between κ_{org} and f_{WSOC} in Fig.8 is not that straightforward, as the correlation coefficient (R) is only 0.09. The two parameters tend to correlate more closely if not taking the Oct 22 data into account, and the R value approximates 0.51. These results suggest that the bulk WSOC fraction could still influence water uptake by wildfire haze particles, considering the potential bias in f_{WSOC} between 24h-averaged bulk $PM_{2.5}$ filter samples and real-time HTDMA measurements of 100 nm particles. In this sense, we would prefer to show the correlation plot in the manuscript; while instead, we accept the reviewer's suggestion of stating that there was little relationship between κ_{org} and f_{WSOC} based on the analysis of ambient $PM_{2.5}$ filter samples.

The manuscript was revised as follows to clarify this point.

Page 18, Line 23: *'… In general,* κ_{org} *was insignificantly correlated with* f_{WSOC}*, especially in the data on October 22.'*

Other comments on Presentation

R1C13: Overall the writing mechanics is reasonable and clear but needs further work for ACP standards. I will highlight a few passages with suggestions for better writing. I recommend further refinement with a fluent English writer to raise it to acceptable levels. Here are a few:

Response: We acknowledge the reviewer for the critical comments, which are useful in improving the impact and quality of the manuscript. We have fully revised the manuscript according to all the helpful comments and suggestions, and the updated contents can be found as stated above and elsewhere in our responses to the second reviewer's comments. The revised manuscript was sent to a professional English editing company to improve the presentation quality.

R1C14: Line 14 change to "not only in terms of hazards to human health"

Response: We have revised it accordingly.

Page 3, Line 14: *'…The recent equatorial Asian wildfire haze event in 2015 could rival the one in 1997 not only in terms of the hazards to human health but also the significant impacts on global climate …'*

R1C15: Line 16 I'm not aware of any prizes offered for poor air quality and though I'm sure the region would vie for such a title I recommend keeping magazine-like statements out of the article.

Response: We have deleted the whole sentence.

R1C16: In Figure 5 I suggest either plotting d/do or kappa an not the rainbow colors of kappa that follows the same pattern as d/do that is plotted.

Response: We have replotted Fig. 5 as below.

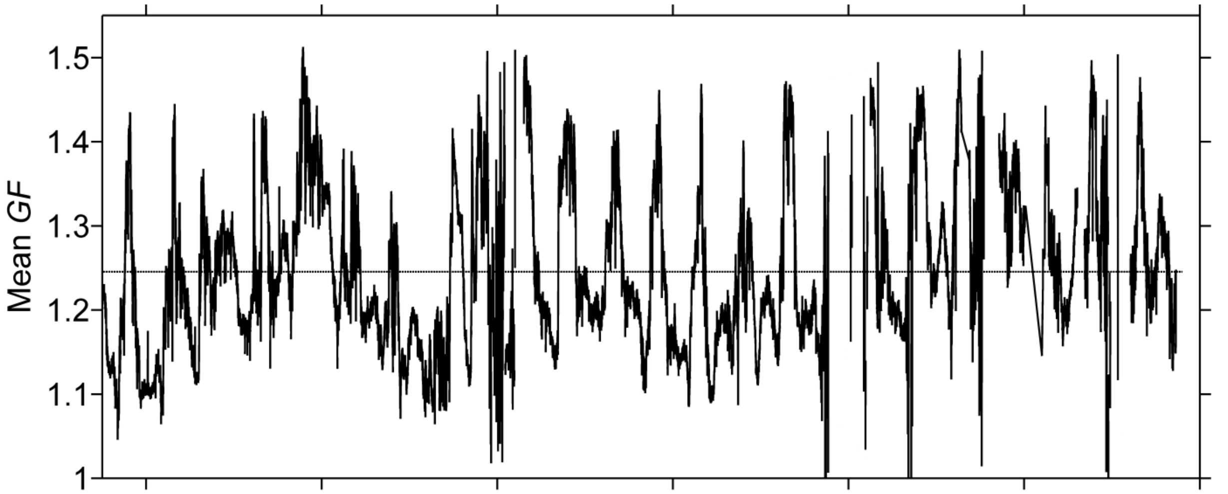

Fig.5 *Time series of the volume-weighted mean particle diameter growth factor (GF) derived from HTDMA measurements (date format: Month/Day, 2015). The black dashed line stands for the temporal mean GF averaged over the entire observation period.*

R1C17: The traces in figure 6 are somewhat difficult to distinguish."

Reference: Chemical characterization of fine particulate matter emitted by peat fires in Central Kalimantan, Indonesia, during the 2015 El Niño, Jayarathne et al. (2017) ACP.

Cloud condensation nuclei activity of fresh primary and aged biomass burning aerosol, G. J. Engelhart, Atmos. Chem. Phys., 12, 7285–7293, 2012, www.atmos-chemphys.net/12/7285/2012/doi:10.5194/acp-12-7285-2012

Response: We appreciate the reviewer for the comment. We have updated Figure 6 as below, where the four OA factors (previously displayed in subfigure (d)) were separately plotted in panels (d-e) to distinguish each other more clearly.

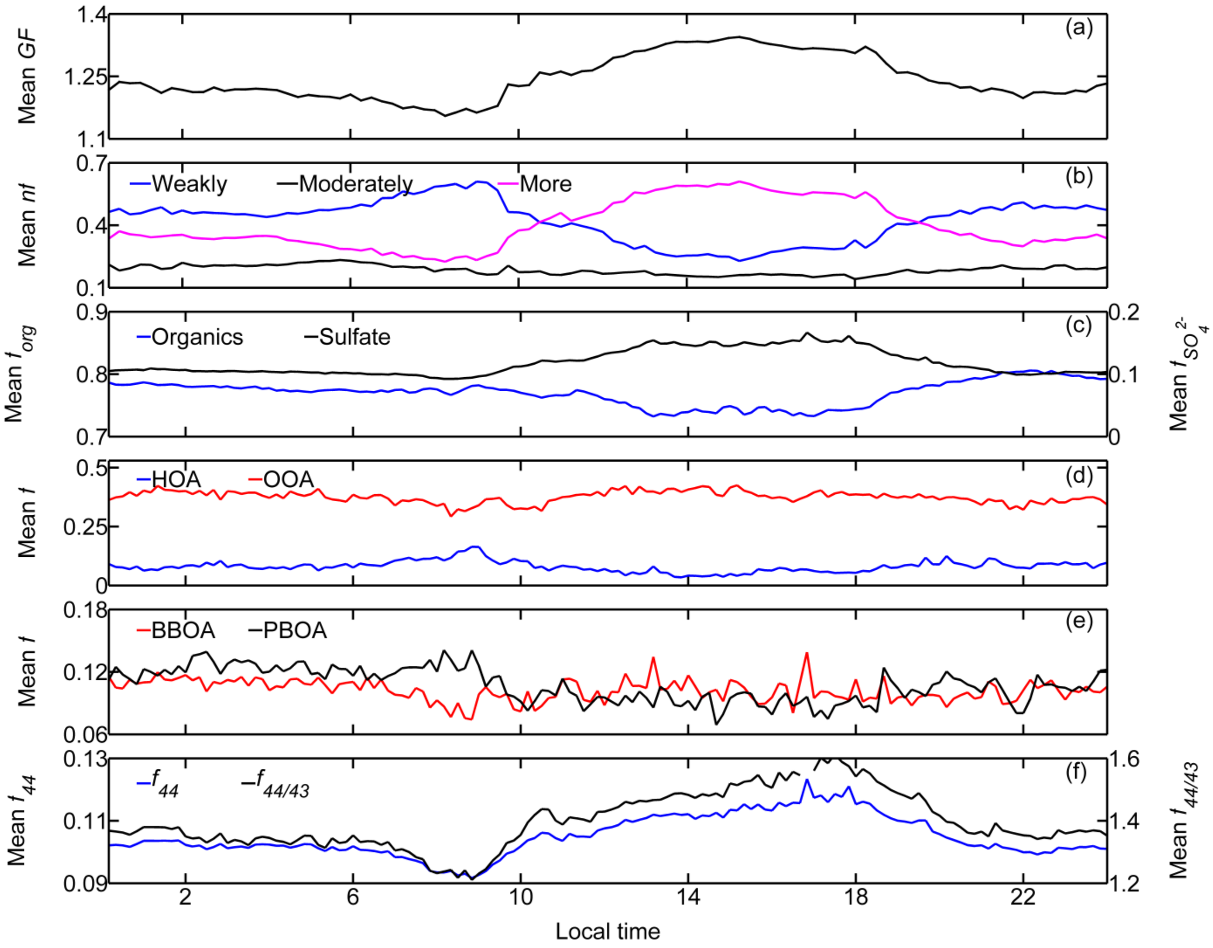

Fig.6 *Temporal averaged (10−24 October 2015) diurnal variations of (a) the mean GF, (b) number fraction (nf) of the three hygroscopic modes, (c) mass fraction of the two main components in NR-PM*$_1$*, i.e., organics (*f_{org}*) and sulfate (*$f_{SO4^{2-}}$*), (d-e) mass fraction of the ME2-resolved four OA factors in NR-PM*$_1$ *(i.e.,* f_{HOA}*,* f_{OOA}*,* f_{BBOA}*, and* f_{PBOA}*), and (f) mean* f_{44} *and* $f_{44/43}$ *of organics in NR-PM*$_1$ *(local time, LT).*

Pronounced diurnal patterns were observed for the mean GF, number fractions of both weakly and more hygroscopic modes, f_{44}*,* $f_{44/43}$*, and mass fractions of organics and sulfate as well as HOA and OOA.* nf_{more}*,* $f_{SO4^{2-}}$*,* f_{44}*,* $f_{44/43}$*, and* f_{OOA} *showed variations similar to that of the mean GF, whereas contrasting diurnal patterns were found for* nf_{weakly}*,* f_{org}*, and* f_{HOA}*.*

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Anonymous Referee #2

General comments:

R2C0: This manuscript describes an aerosol dataset collected in Singapore during a period in October, 2015 when the region was impacted by high concentrations of smoke particles. Though I have some concerns with the analysis, I support eventual publication in ACP in part because the region and this particle source are understudied. But major revisions would be required first. In addition to the concerns identified below, the writing would need to be improved prior to publication. The mistakes are too numerous to identify in this review.

Response: We appreciate the reviewer's supportive comments. We have organized the following responses to address the reviewer's concerns and revised the manuscript thoroughly. The revised manuscript was sent to a professional English editing company to correct any grammatical issues.

Other comments

R2C1: A general concern I have with the manuscript is that it lacks a description of the meteorological and chemical setting that readers would need to understand the data. There is a brief mention of the location of the sampling site relative to a road and a petrochemical complex, but no discussion about whether and when those sources would be upwind. There is also no discussion of the typical transport time of the smoke prior to arrival at the sampling site. And to put the smoke-impacted measurements into context,

there needs to be some data and discussion of the typical concentration and composition at the site.

Response:

We thank the reviewer for the helpful comments. In the revised manuscript, we added distributions of carbon emissions from wildfire (GFEDv4) as well as back trajectories of air masses arriving at Singapore. It took approximately 1~2 days for air mass transporting from the Southern part of Sumatra Island to Singapore, and 3~4 days for wildfire plumes from Central Kalimantan to arrive at Singapore.

The highway and petrochemical complex are located at south of the observation site. As shown in Fig. S1, the air masses were arriving at Singapore from Southeast. Although we do not have the local meteorological data, it is likely that the sampling site was influenced by these emission sources.

The above information on meteorological condition and chemical characteristics associated with our observations has been clarified in the revised manuscript as follows.

Page 6, Line 7: *'…located approximately 8 km south. In September−October 2015, the observation site encountered severe transboundary haze pollution that was caused by recurring Indonesian peatland fires, dominated by the smoldering combustion of underground organic-rich peat soils and mixed surface vegetation burning (Field et al., 2016; Page et al., 2009; Jayaranthe et al., 2017). Particles emitted from the wildfires had experienced for approximately 1−4 days atmospheric aging process before arriving at Singapore (Fig. S1).'*

R2C2: Line 20 (and later): There is no discussion about the disconnect between the single size at which g was measured (100 nm) and the larger particles that dominate the composition measured by the ACSM. There is a mention that the number size distribution is dominated by particles in the 50 – 200 nm size range, but the number distribution is irrelevant. It seems likely that the diurnal variations in g would not be as important for particles near the mass median size of the distribution. So then the composition should be comparatively constant and the variation between it and g introduces scatter to the inferred hygroscopicity parameters. It also seems likely that much of the sulfate will be in >100 nm particles if it forms in cloud. So then it is questionable how much direct impact it has on g.

Response: We appreciate the reviewer for pointing out this issue. We selected 100 nm particles for the present study, as the diameter is close to the mode diameter for number size distribution. We agree with the reviewer that the mode diameter for mass size distribution (~ 300 nm) was much larger than 100 nm, as shown in **Fig. S4**. This value is comparable to those in previous haze events in Singapore (Balasubramanian et al., 2003; See et al., 2006).

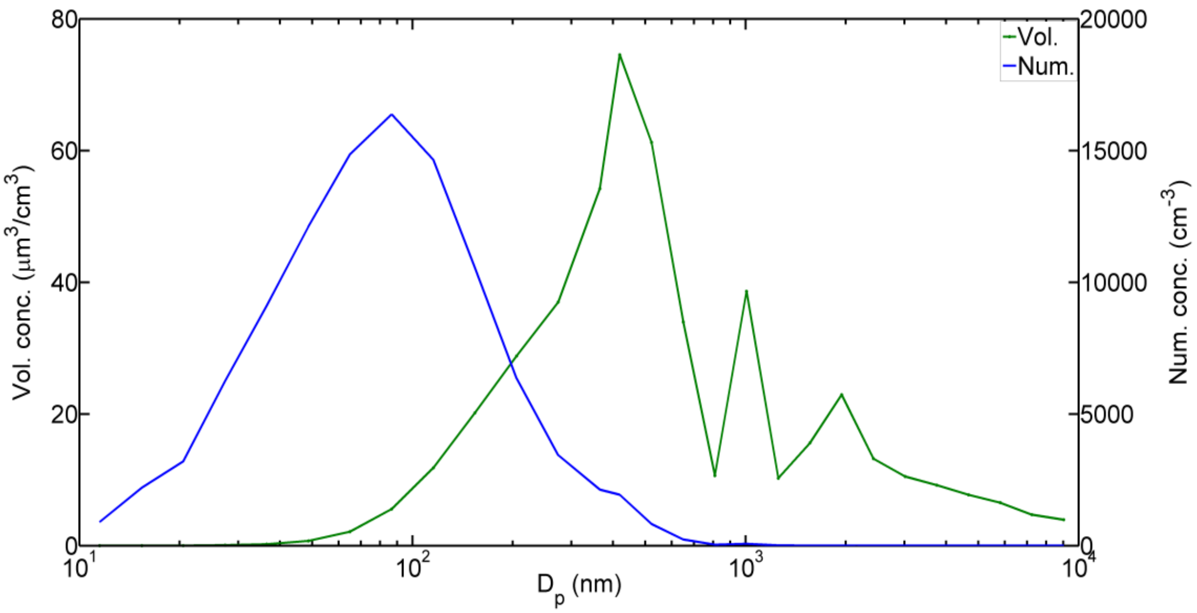


Fig. S2 *Mean particle number (Num.) and volume (Vol.) size distributions over the entire wildfire haze observation period. Submicron particles with 200 nm < D_p < 1 μm dominate the particle volume concentration, while 30−200 nm particles are the major contributor to the particle number concentration.*

In the revised manuscript, we have included the corresponding clarification.

Page 13, Line 4: *'…whereas particles larger than 600 nm accounted for a minor fraction (less than 4.0 % on average; Fig. S4 and Fig. S5). This result suggests that in Singapore, the wildfire haze particles were predominantly contributed by submicron particles, in line with the corresponding chemical characteristics obtained in previous studies (Balasubramanian et al., 2003; See et al., 2006).'*

R2C3: I am unfamiliar with the characteristics of PBOA. Is it reliably separated from BBOA? Could variation in fuel type or burning characteristics cause shifts in attribution between the two types? And what is known about the solubility of peat burning primary particles? I ask because it could influence the fraction of soluble species in solution at the 85% RH in the

HTDMA. These points should be added to the manuscript and not simply provided in a response.

Response: We thank the reviewer for the comments. The details about the ME-2 analysis are available in our recent manuscript, which was submitted to ACP (Budisulistiorini et al., submitted). Briefly, the mass spectrum of PBOA factor is almost identical to the mass spectra for peat burning particles in laboratory data, as the initial guess was provided from our experimental data (Budisulistiorini et al., 2017). Mass spectra of peat burning particles, which are significantly different from those emitted from combustion of other types of biomass, are only slightly influenced by smoldering condition, as demonstrated by Kuwata et al. (2017). The contributions of PBOA and BBOA factors exhibit different patterns in time series, suggesting that they can be separated well (Budisulistiorini et al., submitted). We agree with the reviewer that a unique solution does not exist for such a factor analysis, causing ambiguity in interpretation of data. This point is clarified in the revised manuscript as follow.

Page 7, Line 19: *'… Four specific types of OA were identified: hydrocarbon-like OA (HOA), peat burning OA (PBOA), non-peat biomass burning OA (briefly BBOA), and oxygenated OA (OOA). The HOA factor was mainly contributed by primary sources, such as the combustion emissions from fossil fuel (e.g., related to traffic, shipping, and industrial use), excluding the influence of biomass burning. The PBOA and BBOA factors were well separated. Details about the ToF-ACSM measurements and data analysis are provided in Budisulistiorini et al. (submitted to Atmospheric Chemistry and Physics, February 2018).'*

The mean hygroscopicity parameter κ of freshly emitted peat burning particles is approximately 0.04, which is limited by availability of water soluble organic compounds (WSOC/OC = 0.03) (Chen et al., 2017; Relevant details were also provided in our response to **R1C7**.). The result demonstrates that PBOA can practically be considered as nearly non-hygroscopic.

In the revised manuscript, we have included the corresponding clarification.

Page 14, Line 16: *'… and maximum values of 63.6 % and 79.9 %, respectively. The mean WSOC/OC result was significantly higher than that for fresh Indonesian peat burning particles emitted from the source region (i.e., 16 %; Jayaranthe et al., 2017), which were demonstrated to be generally water insoluble and thus nearly non-hygroscopic (Chen et al., 2017). This result suggests that the majority of organics in the wildfire haze particles were water soluble, implying the importance of secondary formation as well as the chemical transformation of organic particles during atmospheric transport.'*

R2C4: Page 8, line 13: The OPS does not measure aerodynamic size.

Response: The reviewer is right. We have revised it to optical size.

R2C5: Page 9, Line 3: The only g distribution provided is the study average shown in Figure 1. The separation of particles into the three g categories implies that the distributions were generally multimodal. I don't doubt that, but it should be shown. Perhaps a few example distributions could be included in a supplemental document.

Response: We thank the reviewer for the suggestion. We have added an example of normalized particle size distributions (in the period of 1−7 Oct 2015) after humidification at 85 % RH into the supplementary material. Accordingly, we have updated the manuscript as follows.

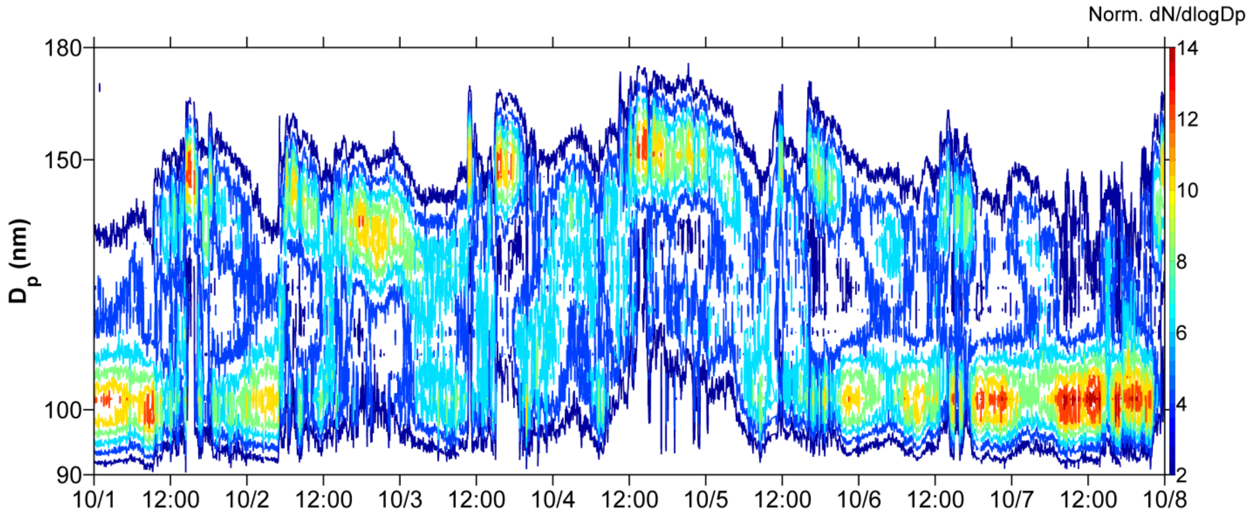


Fig. S3 *An example (1−7 Oct 2015) of the HTDMA data at RH = 85% for D_0 = 100 nm particles. Temporal variation of normalized particle number size distributions (i.e., Norm. dN/dlogD_p) is shown, with every 12 hours interval.*

Page 9, Line 8: *'… hygroscopic properties at RH = 85 % (temporal variation of the multimodal size distribution patterns are shown in Fig. S3 of the supplementary material), facilitating the analysis of heterogeneity of particle chemical composition.'*

R2C6: Page 9, line 14: I think "More" would be a better word here. Highly to me implies much higher g than 1.27. Especially when those with g < 1.15 are "Nearly non-hygroscopic"; that's a large change in type over a small change in g.

Response: We agree with the reviewer. In the revised manuscript, we have replaced the 'highly hygroscopic' by 'more hygroscopic'.

Page 9, Line 19: *'(3) More hygroscopic particles ($\kappa \geq 0.2$; $g \geq 1.27$): Aerosol particles contain inorganic salts as well as some more hygroscopic organic species such as …'*

R2C7: Page 10, line 9: Those are not salts.

Response: We thank the reviewer for the comment. We have changed it into 'inorganic constitutes'.

Page 10, Line 13: *'…The subscript SNA represents the three major inorganic constituents of sulfate, nitrate, and ammonium;'*

R2C8: Page 10, line 12: Is sea salt expected to be important at the site? Unless operated at a high temperature the ACSM would not see it.

Response: Previous study on wildfire haze in Singapore demonstrated that sea salt (e.g., Na^+, Cl^-, approximately 1% ~ 3%) was much less abundant than organics (30 ~ 40%) or sulfate (~ 20%) (Balasubramanian et al., 2003; See et al., 2006). We added the following sentence in the main text to address the point.

Page 10, Line 17: *'…Other materials, such as sea salt and crustal elements, were demonstrated to be neglected because they are relatively scarce in submicron wildfire haze particles in Southeast Asia (Balasubramanian et al., 2003; Keywood et al., 2003; See et al., 2006; Stockwell et al., 2016).'*

R2C9: Page 10, line 21: The second sentence in this paragraph needs to be rewritten.

Response: We have rephrased it as below.

Page 11, Line 1: *'The mass fraction is taken as the first-order approximation of the volume fraction, based on the hypothesis that the bulk particle density is similar to the densities of individual compounds when volume additivity is assumed …'*

R2C10: Page 11, line 15: I can't understand why the authors chose to assume that both BBOA and PBOA have kappas of 0.0. Even if they are low, why not use best estimates of the values instead of just arbitrarily setting them to 0. Because they are not actually completely non-hygroscopic, the result will be an erroneous sensitivity of kappa_OOA to the organic type fractions. This needs to be changed in the revision.

Response: We thank the reviewer for the suggestion. In the revised manuscript, we used the values of κ, those were obtained in our previous laboratory study (κ_{PBOA} = 0.04, κ_{BBOA} = 0.06, Chen et al., 2017). The revised manuscript was updated accordingly, as detailed below.

(Sect. 3.3) Page 11, Line 21: *'… where v_i stands for the volume fraction of component i in all the organics.*

Water uptake by a mixed particle is largely driven by the relative abundance of more or less hygroscopic component, and it is more sensitive to uncertainties in *the hygroscopicity of more hygroscopic compounds than that of less hygroscopic compounds (Gysel et al., 2007). Hydrocarbon (-like) OA is known to be almost non-hygroscopic, leading to the estimation that the* κ *value of HOA is 0 (Gysel et al., 2007; Gunthe et al., 2009; Chang, et al., 2010). Water uptake by freshly emitted biomass burning particles is generally limited, especially compared with OOA (Carrico et al., 2010; Chang et al., 2010; Chen et al., 2017). Based on our previously measured* κ *results of fresh Indonesian peatland burning particles, an overall mean value of* $\kappa_{PBOA} = 0.04$ *was used for the fresh PBOA factor, and* $\kappa_{BBOA} = 0.06$ *was applied for the non-peat BBOA factor with mixed vegetation burning mainly of acacia and fern species (Chen et al., 2017). Under these assumptions,* κ_{OOA} *can be calculated by the following equation:*

$$\kappa_{OOA} = (\kappa_{org} - \kappa_{PBOA} \cdot \upsilon_{PBOA} - \kappa_{BBOA} \cdot \upsilon_{BBOA}) / \upsilon_{OOA} . \quad (5)$$

The density of OOA/PBOA/BBOA is required to calculate $\upsilon_{OOA}/\upsilon_{PBOA}/\upsilon_{BBOA}$ *using the ME-2 resolved corresponding mass concentration combined with the total volume concentration of the bulk OA derived from the ToF-ACSM observed OA mass. The density of oxygenated organics was assumed to be 1.50 g cm*$^{-3}$ *(as summarized in Table 1), which is a typical value for carboxylic and multifunctional organic acids (Saxena et al., 1995; Peng et al., 2001; Gysel et al., 2004; Carrico et al., 2010; Ogawa et al., 2016). According to the reported average density for common dry smoke particles (i.e., 1.20 − 1.40 g cm*$^{-3}$*, Reid et al., 2005), and considering the dominance of non-refractory organic material in fresh Indonesian peatland burning particles (Budisulistiorini et al., 2017), the densities of PBOA and non-peat BBOA were assumed to be 1.10 and 1.20 g cm*$^{-3}$*, respectively. Detailed information on the parameters utilized for the* κ_{org} *calculation is provided in Table 1.'*

(Sect. 4.3) Page 15, Line 25: *'…The mean κ_{org} (0.157 ± 0.108) was lower than the mean κ_{OOA} (0.266 ± 0.184), as the whole organic fraction normally contains both non-hygroscopic and hygroscopic organics. The derived κ_{org} results are demonstrated to be comparable to previously reported κ values for bulk organics (Petters and Kreidenweis, 2007; Duplissy et al., 2011; Lathem et al., 2013; Cerully et al., 2015). Moreover, the mean κ_{OOA} value agreed well with mean κ results in previous field and laboratory studies (e.g., $\kappa = 0.25 \pm 0.06$ for biogenic OOA, Chang et al., 2010; $\kappa = 0.2 \pm 0.1$ for aged BBOA, Engelhart et al., 2012). A caveat of this comparison is the representativeness of laboratory experiments for the actual environmental conditions, including types of burnt biomasses, concentrations and types of oxidants, and aging time. As the atmospheric condition of tropical Asia is unique, a systematic study of the chemical aging process of wildfire plume for the region would be required in the future. Note that the mean κ_{OOA} was even higher than the corresponding mean κ_{HTDMA} (0.207 ± 0.093), revealing that the water uptake particularly by some highly oxygenated organics in the wildfire haze particles could be highly significant.'*

(Sect. 4.4) Page 16, Line 16: *'Similarly, the daytime mean κ_{org} and κ_{OOA} were 0.200 ± 0.104 and 0.323 ± 0.177, respectively, whereas the nighttime mean values were 0.103 ± 0.086 (κ_{org}) and 0.186 ± 0.177 (κ_{OOA}) (Table 3). These mean κ values were 19.2 % lower (κ_{org}) and 30.8 % higher (κ_{OOA}) than the concurrently measured mean κ_{HTDMA} result of 0.247 ± 0.096 (daytime), whereas they were 35.9 % lower (κ_{org}) and 16.3 % higher (κ_{OOA}) than that of 0.160 ± 0.063 (nighttime).'*

R2C11: Page 12, line 21: I agree that most of wildfire haze mass will be submicron, but that can't be asserted based on the number concentration as

the authors do. At a minimum the supermicron volume fraction should be used for this conclusion.

Response: We appreciate the reviewer for the helpful suggestion. We have calculated the total particle volume concentrations of PM_1 and PM_{10}, and corresponding volume fraction of PM_1 to PM_{10} (as displayed in **Fig. S5**). The mean submicron volume fraction is higher than 0.7, revealing the dominance of submicron particles in total particle mass of wildfire haze particles in Singapore.

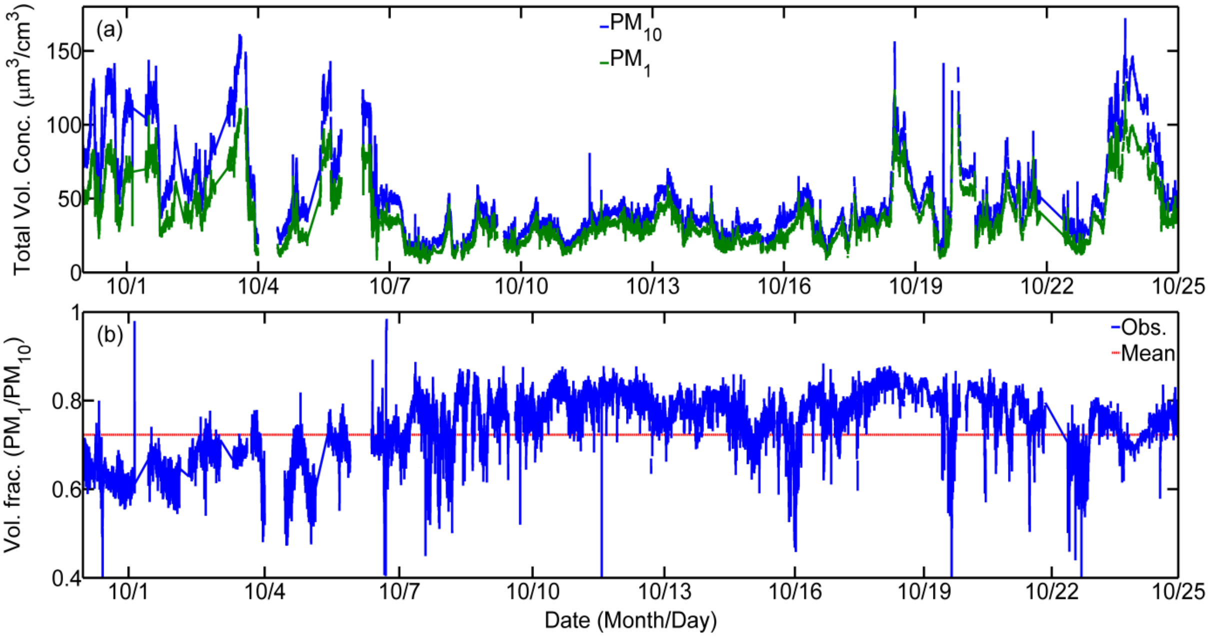


Fig. S5 (a) Time series of total particle volume concentration (Vol. Conc.) for PM_1 and PM_{10}. (b) The corresponding volume fraction (Vol. frac.) of PM_1 to PM_{10} calculated from the combined particle size distribution data observed with NanoScan SMPS and OPS. The red line represents the mean level (approximately 72.3 %) averaged over the entire wildfire haze period. This suggests the predominant role of submicron particles in total particle mass.

Accordingly, we have updated the corresponding content in Sect. 4.1 of the manuscript as below.

Page 13, Line 4: *'…whereas particles larger than 600 nm accounted for a minor fraction (less than 4.0 % on average; Fig. S4 and Fig. S5). This result suggests that in Singapore, the wildfire haze particles were predominantly contributed by submicron particles, in line with the corresponding chemical characteristics obtained in previous studies (Balasubramanian et al., 2003; See et al., 2006).'*

R2C12: Page 12, lines 25 and 26: dN/dlogDp is not the same as number concentration.

Response: We appreciate the reviewer for the comment. We have updated the sentence as below.

Page 13, Line 9: *'Figure 2b shows the mean diurnal cycle of particle number size distribution. The growth of ultrafine particles was typically observed in the afternoon. The* $dN/dlogD_p$ *higher than* 1.5×10^4 cm^{-3} *was commonly observed in the 50–200 nm particle size range, while the* $dN/dlogD_p$ *of super micron particles seldom exceeded* 1.0×10^3 cm^{-3}*.'*

R2C13: Page 13, line 1: The authors note that traffic emissions may be important but take no steps to correct for the impact in their analysis. Should periods when winds are from the road and when traffic is heavy be excluded? The novelty of this dataset is obviously the wildfire haze and anything local is an interference.

Response: We appreciate the reviewer for pointing out this issue. We agree that HOA and EC are likely dominantly emitted from traffic or other types of industrial combustion processes around the observation site. Contributions of these unavoidable locally emitted species were minimal (e.g., HOA/OA < 0.1; Budisulistiorini et al., submitted), suggesting that the dominant fraction of observed aerosol was from wildfire. As the contributions of locally emitted species are likely limited, no data point was excluded from the analysis.

We have included the corresponding clarification into the revised manuscript.

Page 7, Line 19: *'Four specific types of OA were identified: hydrocarbon-like OA (HOA), peat burning OA (PBOA), non-peat biomass burning OA (briefly BBOA), and oxygenated OA (OOA). The HOA factor was mainly contributed by primary sources, such as the combustion emissions from fossil fuel (e.g., related to traffic, shipping, and industrial use), excluding the influence of biomass burning. The PBOA and BBOA factors were well separated. Details about the ToF-ACSM measurements and data analysis are provided in Budisulistiorini et al. (submitted to Atmospheric Chemistry and Physics, February 2018).'*

Page 11, Line 21: *'… where υ_i stands for the volume fraction of component i in all the organics.*

Water uptake by a mixed particle is largely driven by the relative abundance of more or less hygroscopic component, and it is more sensitive to uncertainties in the hygroscopicity of more hygroscopic compounds than that of less hygroscopic compounds (Gysel et al., 2007). Hydrocarbon (-like) OA is known to be almost non-hygroscopic, leading to the estimation that the κ value of HOA is 0 (Gysel et al., 2007; Gunthe et al., 2009; Chang, et al., 2010).'

R2C14: Page 13, line 22: Add non-refractory in front of each instance of chloride.

Response: We have updated the corresponding contents accordingly.

Page 14, Line 6: *'The mass concentration of non-refractory chloride was almost negligible …'*

Page 18, Line 12: *'… partially due to the limited availability of non-refractory chloride.'*

R2C15: Page 14, line 2: Related to the above comment about the assumption that only the OOA contributed to hygroscopicity, the fraction of the organic mass that was water soluble was quite high (average 64%, max 80%). How frequently was this higher than the fraction of organics categorized as OOA?

Response: The reviewer is right that the mean WSOC/OC ratio is approximately 63.6 % for the $PM_{2.5}$ filter samples collected on 8 specific days. Correspondingly, the mass fraction of WSOC in $PM_{2.5}$ ranges from 17.6–30.2 % (as displayed in Fig.4 and Fig.8), with a mean value of 25.3 %. On average, OOA accounts for 36.0 % of mass in NR-PM_1 (f_{OOA}) during the entire wildfire observation period. Although we need to be careful about comparing $PM_{2.5}$ and NR-PM_1 data because of the difference in their size ranges, this mean f_{OOA} value is quite comparable to the mean fraction of WSOC in $PM_{2.5}$ mass.

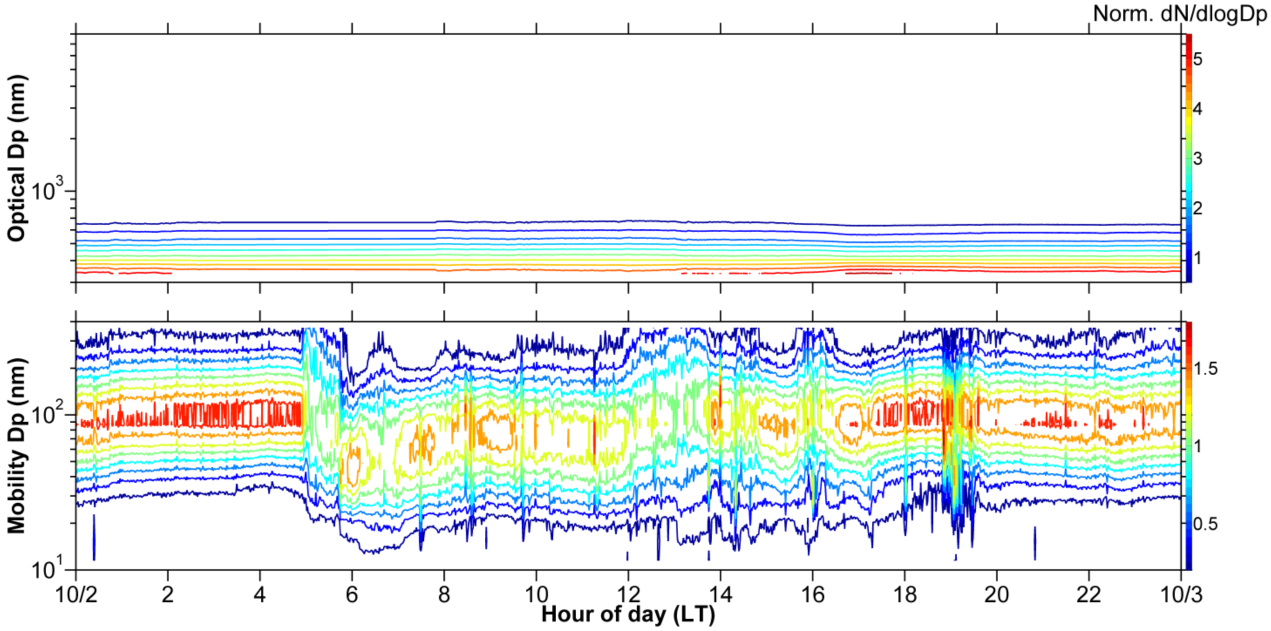
R2C16: Page 14, line 7: Is it surprising that there is much less K than SO_4?

Response: Previous observation data at Singapore during similar wildfire events demonstrated that SO_4^{2-} is much more abundant than K^+. For instance, the mass fraction of SO_4^{2-} was found to be approximately 20%, while that for K^+ was around 3% (Balasubramanian et al., 2003; See et al., 2006). So, we do not consider that the observed concentration values of K^+ and SO_4^{2-} are surprising.

R2C17: Page 14, line 26: Somewhere in the paper there needs to be a conceptual explanation of what is responsible for the observed mix of HOA, PBOA, BBOA, and OOA. Do the authors believe that closer to the source measurements would show mostly PBOA and BBOA and that aging is responsible for the conversion to OOA? (the transport timescale issue mentioned above is relevant here). Is the daily variation thought to be mostly due to photochemical processing or could it also be daily variation in fire characteristics? And is it thought that the changes are due to processing of the existing particles or production of SOA from gas phase emissions from the fires? The one example size distribution time series presented does not seem to indicate particles are growing, but rather the size is about constant and only the concentration changes. Do the time series on other days look like that as well? And if so, what is responsible?

Response: We thank the reviewer for the comment. We think that PBOA and BBOA factors will dominate the contributions to OA at a vicinity of the source region. The OOA factor, which is much more oxygenated than any types of POAs, should be associated with both aging of primary organic particles and secondary formation processes (Stockwell et al., 2016). As the observation is located far from the source regions (1~4 days), diurnal variation in fire characteristics (if any) would not directly influence that of our observation data directly. Considering these conditions, we think that the diurnal variation of OOA factor is mainly caused by *in-situ* photochemical processing of primary particles and/or secondary formation from VOC precursors, rather than by the daily variation in fire characteristics.

The size distribution displayed in Fig. 2(b) actually demonstrates the mean diurnal variation of particle number size distribution. Growth of ultrafine particles during afternoon period is evident in the figure. It is also evident in data on 2 October 2015, which is shown in the following figure.



We added the following sentence to the revised manuscript to stress the point.

Page 13, Line 9: *'Figure 2b shows the mean diurnal cycle of particle number size distribution. The growth of ultrafine particles was typically observed in the afternoon.'*

R2C18: Page 17, line 15: NO_3 was a small contributor to the overall mass. It seems pointless to note that variations in that small contribution had little effect on kappa.

Response: We appreciate the reviewer for the comment. We have updated the corresponding description in a following way.

Page 18, Line 9: *'… There was no clear correlation between κ and f_{NO3^-}, implying that the small amount of nitrate had an insignificant contribution to the variability in κ of wildfire haze particles.'*

R2C19: Figure 3: I would like to be able to see whether organic mass and sulfate mass are correlated. But with the use of the same y-scale for both in (a) that is not possible.

Response: We have provided the correlation plots of organics mass concentration vs. sulfate mass concentration (both with and without the data for the extremely pollution episode in the evening of 19 October 2015 till the noon time of the next day) into supplementary material. The corresponding correlation coefficients are $R = 0.49$ (without) and 0.62 (with), respectively, suggesting that both of the two chemical species could be from the peatland fires in Indonesia.

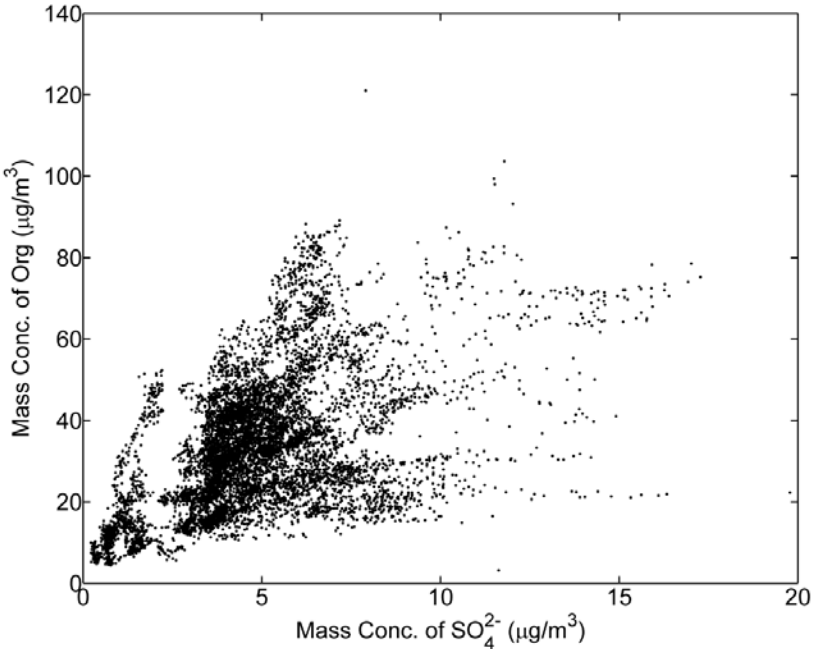


Fig. S6 *Correlation between mass concentration of organics and that of sulfate (R = 0.49), without the data measured during the extremely pollution episode in the evening of 19 October 2015 till the noon time of 20 October 2015.*

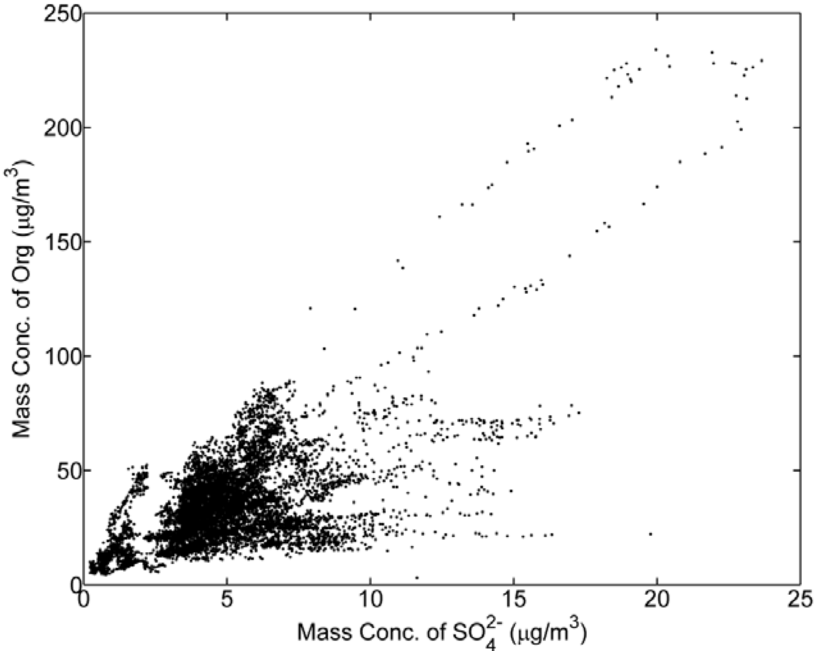


Fig. S7 *Correlation between mass concentration of organics and that of sulfate (R = 0.62) during the entire wildfire haze observation period.*

R2C20: Figure 6: Specify date.

Response: Diurnal variations in this figure are averaged over the entire observation period (10−24 October 2015). We have added the time period into the caption of Figure 6 for clarification.

Caption of Figure 6*: ‘**Fig.6** Temporal averaged (10−24 October 2015) diurnal variations of…’*

R2C21: Figure 9: Clarify what “averaged diurnal” means.

Response: “averaged diurnal” represents that the diurnal results for each day were further averaged over the period when both the HTDMA and ToF-ACSM data were available (i.e., 10−24 October 2015). We have changed it into ‘mean diurnal’ and added the corresponding information to the caption of Fig.9 for clarification.

Caption of Figure 9*: ‘Relationships between the mean diurnal κ_{org} results vs. (a) f_{44} and (b) $f_{44/43}$ in NR-PM$_1$ haze particles. Mean diurnal here represents that the diurnal results for each day were further averaged over the overlapping observation period, i.e., with both HTDMA and ToF-ACSM measurements taken from 10−24 October 2015.’*

Reference:

Balasubramanian, R., Qian, W. -B., Decesari, S., Facchini, M. C. and Fuzzi, S. (2003). Comprehensive characterization of $PM_{2.5}$ aerosols in Singapore, J. Geophys. Res., 108(D16), 4523.

Budisulistiorini S. H., Riva, M., Williams, M., Chen, J., Itoh, M., Surratt, J. D., Kuwata, M. (2017). Light-absorbing brown carbon aerosol constituents from combustion of Indonesian peat and biomass, Environ. Sci. & Technol., 51, 4415-4423.

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Chen, J., Budisulistiorini, S. H., Itoh, M., Lee, W.-C., Miyakawa, T., Komazaki, Y., Yang, L., Kuwata, M. (2017). Water uptake by fresh Indonesian peat burning particles is limited by water soluble organic matter. Atmos. Chem. Phys., 17, 11591-11604.

Kuwata, M., Kai, F. M., Yang, L., Itoh, M., Gunawan, H., and Harvey, C. F. (2017). Temperature and Burning History Affect Emissions of Greenhouse Gasses and Aerosol Particles from Tropical Peatland Fire. J. Geophys. Res. Atmos., 121, 1281-1292.

See, S. W., Balasubramanian, R., and Wang, W. (2006). A study of the physical, chemical, and optical properties of ambient aerosol particles in Southeast Asia during hazy and nonhazy days, J. Geophys. Res. Atmos., 111(D10S08).

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Secondary aerosol formation promotes water uptake by organic-rich wildfire haze particles in Equatorial Asia

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Abstract

The diameter growth factor (*GF*) of 100 nm haze particles at 85 % relative humidity and their chemical characteristics were simultaneously monitored at Singapore in October 2015 during a pervasive wildfire haze episode that was caused by peatland burning in Indonesia. Non-refractory submicron particles (NR-PM_1) were dominated by organics (approximating 77.1 % in total mass), whereas sulfate was the most abundant inorganic constituent (11.7 % on average). A statistical analysis of the organic mass spectra showed that most organics (36.0 % of NR-PM_1 mass) were highly oxygenated. Diurnal variations of *GF*, number fractions of highly hygroscopic mode particles, mass fractions of sulfate, and mass fractions of oxygenated organics (OOA) synchronized well, peaking during daytime. The mean hygroscopicity parameter (κ) of the haze particles was 0.189 ± 0.087, and the mean κ values of organics were 0.157 ± 0.108 (κ_{org}, bulk organics) and 0.266 ± 0.184 (κ_{OOA}, OOA), demonstrating the important roles of both sulfate and highly oxygenated organics in the hygroscopic growth of organics-dominated wildfire haze particles. κ_{org} correlated with the water-soluble organic fraction insignificantly, but it positively correlated with f_{44} (fraction of the ion fragment at *m/z* 44 in total organics) ($R = 0.70$), implying the oxygenation degree of organics could be more critical for the water uptake of organic compounds. These results suggest the importance of secondary formation of both inorganic and organic species in promoting the hygroscopic growth of wildfire haze particles. Further detailed size-resolved as well as molecular-level chemical information about organics is necessary for the profound exploration of water uptake by wildfire haze particles in Equatorial Asia.

1. Introduction

In the last few decades, wildfire haze has periodically raged throughout equatorial Asian countries (Page et al., 2002; van der Werf et al., 2010; Field et al., 2016; Koplitz et al., 2016), resulting in billions of dollars of economic losses as well as thousands of premature deaths (Johnston et al., 2012; Marlier et al., 2013). The increasing wildfire activity is associated with the recent rapid change in land use for agricultural development, including industrial plantations over peatland (Page et al., 2009; Marlier et al., 2015; Spracklen et al., 2015). Such developments are accompanied by the drainage of water of pristine peat swamp forest, making the tropical peatland susceptible to fire (Langner et al., 2007; Konecny et al., 2016). The occurrence of peatland fires is closely related to El Niño-induced droughts (Page et al., 2002; Field et al., 2016). Enhanced peatland fires have been observed during intense El Niño years, including 1997, 2006, and 2015 (Page et al., 2002; van der Werf et al., 2010; Stockwell et al., 2016). In 1997, the peatland fire was of global concern, as the total carbon emission was estimated to equal 13−40 % of the year's annual global carbon emission from fossil fuels (Page et al., 2002). The recent equatorial Asian wildfire haze event in 2015 could rival the one in 1997 not only in terms of the hazards to human health but also the significant impacts on global climate (Crippa et al, 2016; Field et al., 2016; Huijnen et al., 2016; Koplitz et al., 2016; Stockwell et al., 2016). ~~In fact, if there were a prize for the worst air pollution disasters of the century, the 2015 equatorial Asian haze event would likely be nominated (Crippa et al, 2016; Stockwell et al., 2016).~~ During September−October 2015, thick smoke from peatland fires blanketed Equatorial Asia and released huge amounts of organic material and fine particulate matter (particulate matter of aerodynamic diameter below 2.5 μm, $PM_{2.5}$) (Crippa et al, 2016; Koplitz et al., 2016), which is the leading cause of global air-pollution-related mortality (Kunii et al., 2002; World Health Organization, 2009; Johnston et al., 2012; Marlier et al., 2013; Lelieveld et al., 2015).

A previous study on the peatland fire event in 1997 has reported that the wildfire haze particles resulted in dramatic cooling effects on the atmospheric radiative budget, especially over the source region of Indonesia (−150 W m^{-2}) and the tropical Indian Ocean (−10 W m^{-2}) (Duncan et al., 2003). In addition to the subsequently affected shallow warm clouds and deep convection processes, the resultant abnormal rainfall in adjacent tropical region and the extra-tropics was also confirmed by both satellite observations and model simulations (Rosenfeld, 1999). These studies demonstrate the importance of investigating aerosol-cloud-precipitation interactions of Indonesian wildfire haze particles, including water uptake properties of aerosol particles.

Previous studies on water uptake properties of aerosol particles stemmed from Indonesian peatland fires are controversial. On one hand, laboratory studies have demonstrated that fresh Indonesian peat burning particles are weakly hygroscopic and almost inactive as cloud condensation nuclei (CCN) (Chand et al., 2005; Dusek et al., 2005; Chen et al., 2017). On the other hand, a field observation showed that the wildfire haze particles were highly hygroscopic during the 1997 Indonesian peatland fires (Gras et al., 1999). Such discrepancies impede reliable evaluations of the effects on regional and global climate changes driven by Indonesian wildfire haze particles (Lin et al., 2013; Reid et al., 2013). The cause of the discrepancies needs to be understood quantitatively in comparison with the chemical composition of particles.

Aerosol particles emitted from wildfires are a mixture of inorganic and organic compounds, which complicates their water uptake properties (Carrico et al., 2008, 2010; Petters et al., 2009; Hallar et al., 2013; Lathem et al., 2013). Water uptake properties of inorganic salts, such as ammonium sulfate and ammonium nitrate, are well known, yet the hygroscopic behavior of organic compounds or organic-inorganic mixtures is still difficult to predict due to the complex chemical composition of organics and the associated distinct affinity for water of a specific chemical constituent (Saxena et al., 1995; Gysel et al., 2004; Dinar et al., 2007; Petters and Kreidenweis, 2007; Carrico et al., 2010; Kristensen et al., 2012; Marsh et al., 2017). For instance, experimental and modeling studies have shown that the water uptake by water-soluble matter is governed by the inorganic fraction, whereas the hygroscopic properties of inorganics can be altered substantially by the presence of organics (Saxena et al., 1995; Dick et al., 2000). In general, with the increase in the organic fraction, the water uptake by wildfire particles has presented an overall decreasing trend (Mircea et al., 2005; Carrico et al., 2010), evidencing the high sensitivity of particle water uptake to organic fractions. The high sensitivity to organic fractions has been observed, as inorganic species are much more hygroscopic than most organic compounds. However, the roles of inorganic and organic species in water uptake by Indonesian peatland burning particles have rarely been investigated (Dusek et al., 2005; Chen et al., 2017).

Water uptake properties of organic compounds have also been demonstrated to be important especially when the chemical composition of aerosol particles is dominated by organics. Such cases have been frequently observed in particles emitted from wildfires (Petters et al., 2009; Carrico et al., 2010; Cubison et al., 2011; Hallar et al., 2013; Chen et al., 2017). Both theoretical and experimental studies demonstrated that water-soluble organic matter (WSOM) plays the key role in determining the water uptake by organic compounds (Peng et al., 2001; Gysel et al., 2004; Petters and Kreidenweis, 2007; Carrico et al., 2008; Petters et al., 2009; Lathem et al., 2013; Chen et al., 2017). For instance, freshly emitted peat burning particles are known to contain a small fraction of WSOM, which explains their limited hygroscopicity (Chen et al., 2017). Chemical aging and oxidation of organic compounds in both gas and particle phases could alter the water uptake properties of aerosol particles in a wildfire plume (Gras et al., 1999; Petters et al., 2009; Rose et al., 2010; Cubison et al., 2011). These chemical processes in the atmosphere enhance the fractions of highly oxygenated organics and polar species, which are typically water soluble (Duplissy et al., 2008, 2011; Jimenez et al., 2009; Chang et al., 2010; Massoli et al., 2010; Cubison et al., 2011; Cerully et al., 2015). Although such chemical transformation and corresponding changes in hygroscopicity have been observed in wildfire particles in both the laboratory and the field (Petters et al., 2009; Massoli et al., 2010; Rose et al., 2010; Cubison et al., 2011; Duplissy et al., 2011), the importance of these processes for water uptake properties has never been investigated for peatland burning particles in the equatorial Asian region.

In this work, we investigated the relationships between water uptake properties and the chemical composition of aerosol particles in a tropical peatland fire haze in October 2015 by conducting atmospheric observations in Singapore. We quantified water uptake properties using the Humidified Tandem Differential Mobility Analyzer (HTDMA). In parallel, particle chemical composition was characterized in real-time using the Aerodyne Time of Flight-Aerosol Chemical Speciation Monitor (ToF-ACSM). Furthermore, water-soluble organic carbon (WSOC) and elemental carbon (EC) contents were quantified by an off-line analysis of ambient $PM_{2.5}$ filter samples. The data from these measurements were combined to explore how the water uptake properties of tropical peatland burning particles are regulated.

2. Observation

2.1. Field Campaign

The field observation was conducted at the campus of Nanyang Technological University (NTU), Singapore (1°20′41″ N, 103°40′53″ E) during October 2015. The campus is located 20 km away from the city center, and it is surrounded by a secondary tropical forest and grassland. The site is located 0.8 km away from a highway, and a petrochemical complex (Jurong Island) is located approximately 8 km south. In September–October 2015, the observation site encountered severe transboundary haze pollution that was caused by recurring Indonesian peatland fires, dominated by the smoldering combustion of underground organic-rich peat soils and mixed surface vegetation burning (Field et al., 2016; Page et al., 2009; Jayaranthe et al., 2017). Particles emitted from the wildfires had experienced for approximately 1–4 days atmospheric aging process before arriving at Singapore (Fig. S1).

The observation was performed in an air-conditioned room, with the room temperature maintained at 22 °C. A cyclone (URG-2000-30EN $PM_{2.5}$, URG) was employed for ambient aerosol sampling at a flow rate of 16.67 L min^{-1}. The inlet was fixed on the rooftop, which was located approximately 10 m above the ground. The sample air was split into several flows for measurements with different instruments after drying by diffusion dryers (the relative humidity, RH, of the sample flow was below 30 %). During the observation, particle number size distribution, chemical composition, and hygroscopic growth were monitored.

2.2. Particle water uptake measurements

Water uptake properties were measured using the HTDMA system (Chen et al., 2017). Briefly, the sampled particles were desiccated using a diffusion dryer (Model 42000, Brechtel Manufacturing, Inc.), and the resulting dry polydisperse particles were classified by the first differential mobility analyzer (DMA, Model 3081, TSI Inc.). The DMA selects particles of a specific mobility diameter (D_0), which was fixed at 100 nm during the observation. The classified particles were humidified to RH = 85 % using nafion tubings (MD-110-12S-4, Perma Pure) operated under a controlled RH condition. The particle residence time in the humidifier was approximately 10 seconds. The variation in RH was ± 0.5 % (peak to peak). The resulting size distribution of humidified particles was measured by the second DMA coupled with a condensation particle counter (CPC, Model 3775, TSI Inc.). The diameter growth factor parameter, *g*, which is defined as the ratio of the particle diameter after humidification at a conditioned *RH* ($D_p(RH)$) to the initial dry size (D_0) (i.e., $g = D_P(RH)/D_0$), was calculated from the HTDMA data. Hygroscopicity parameter, κ, was derived from the corresponding *g* at a given *RH* and D_0 using the following equation (Petters and Kreidenweis, 2007):

$$\kappa = (g^3 - 1)\cdot\left(\frac{1}{RH}\cdot\exp\left(\frac{4\sigma_{s/a}\cdot M_w}{\rho_w\cdot R\cdot T\cdot D_0\cdot g}\right)-1\right), \tag{1}$$

where $\sigma_{s/a}$ is the surface tension of the solution/air interface (0.0718 N m^{-1} at 25 °C), M_w and ρ_w are the molecular weight (0.018 kg mol^{-1}) and density of water (1×10^3 kg m^{-3}), respectively; *R* is the universal gas constant (8.31 J K^{-1} mol^{-1}), and *T* is the absolute temperature (298 K). The HTDMA calibration results with 150 nm ammonium sulfate particles are shown in Fig. S2, demonstrating the validity of our instrument. Further details about the HTDMA are available in Chen et al. (2017).

2.3. Aerosol chemical analysis

The ToF-ACSM (Aerodyne Inc.) was utilized to measure the chemical composition of non-refractory submicron particles (NR-PM_1), including organics (OA), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and chloride (Cl^-) (Fröhlich et al., 2013). The ToF-ACSM sampled particles that were desiccated by a nafion tubing. The organic mass spectra measured by the ToF-ACSM were analyzed in detail using the Multilinear Engine (ME-2 solver) software (Canonaco et al., 2013). Four specific types of OA were identified: hydrocarbon-like OA (HOA), peat burning OA (PBOA), non-peat biomass burning OA (briefly BBOA), and oxygenated OA (OOA). The HOA factor was mainly contributed by primary sources, such as the combustion emissions from fossil fuel (e.g., related to traffic, shipping, and industrial use), excluding the influence of biomass burning. The PBOA and BBOA factors were well separated. Details about the ToF-ACSM measurements and data analysis are provided in Budisulistiorini et al. (submitted to Atmospheric Chemistry and Physics, February 2018).

$PM_{2.5}$ filter samples for chemical analysis were also collected using filter holders (BGI Inc.). The samples were collected for 24 hours using 47 mm (diameter) quartz-fiber filters. The sampling started/ended at 08:00 local time (LT). The collected samples were analyzed for bulk OC, EC, and WSOC. All the quartz-fiber filters were prebaked at 900 ºC for 3 hours before sampling, after which they were stored in a refrigerator (−20 °C) until analysis. For each sampling, a back-up quartz-fiber filter was used to account for the potential influence of gas phase organic components on the particulate organics collected on the front quartz-fiber filter (Turpin et al., 1994). The method assumes that all the particulate OC is collected by the front filter, while the gas phase OC is collected equally on both front and back filters. Subtraction of the OC loading on the back filter (i.e., gas phase OC) from that on the front one allows quantification of particulate OC (i.e., corrected OC).

Concentrations of OC and EC were determined by thermal-optical reflectance analysis (Chow et al., 1993) using the Sunset Laboratory OC/EC Analyzer, following the IMPROVE-A protocol. WSOC was quantified with the Sievers 800 Total Organic Carbon (TOC) Analyzer following extraction of part of a filter sample (8 mm φ) by 10 ml of HPLC-grade water. An orbital shaker was operated for 21 hours for the extraction, and the subsequent solutions were filtered with syringe filters (pore size of 0.2 μm).

2.4. Particle number size distribution

Particle number size distributions were measured using a NanoScan SMPS Nanoparticle Sizer (NanoScan-SMPS, Model 3910, TSI Inc.) and an Optical Particle Sizer (OPS, Model 3330, TSI Inc.). The detected particle sizes ranged from 11.5−365.2 nm (NanoScan-SMPS) in mobility size and 0.3−10 μm (OPS) in optical size. Both instruments sampled particles desiccated by a diffusion dryer (Model 42000, Brechtel Manufacturing, Inc.). The time resolution of both instruments was 1 minute.

3. HTDMA data analysis

3.1. Classification of three hygroscopic modes

Figure 1 shows the HTDMA data averaged over the entire observation period. The mean normalized particle size distribution after humidification at 85 % *RH* has spanned a few different modes, reflecting mixing states of ambient wildfire haze particles observed at Singapore (Bougiatioti et al., 2016; Ogawa et al., 2016). For particles in a specific hygroscopic mode, *i*, with $g_{1,i} < GF < g_{2,i}$, the number fraction of this mode (nf_i) was derived from measured probability density function of *g* (i.e., $c(g, D_0)$) as $nf_i = \int_{g_{1,i}}^{g_{2,i}} c(\mathrm{g}, \mathrm{D}_0)\, dg$. The corresponding mean *GF* ($g_{mean,i}$) was calculated from $g_{mean,i} = \frac{1}{nf_i} \int_{g_{1,i}}^{g_{2,i}} g\, c(\mathrm{g}, \mathrm{D}_0)\, dg$ (Gysel et al., 2009). The equivalent values of κ for mode *i* were obtained from $g_{mean,i}$ using Eq. (1).

The observed 100 nm dry particles were categorized into the following three groups based on their hygroscopic properties at $RH = 85\ \%$ (temporal variation of the multimodal size distribution patterns are shown in Fig. S3 of the supplementary material), facilitating the analysis of heterogeneity of particle chemical composition:

(1) Nearly non-hygroscopic or weakly hygroscopic particles ($0 \leq \kappa < 0.1$; $g < 1.15$): Particles are predominantly composed of black carbon (BC) and non-polar hydrocarbon-like organic compounds (Peng et al., 2001; Gysel et al., 2007; Kreidenweis et al., 2008).

(2) Moderately hygroscopic particles ($0.1 \leq \kappa < 0.2$; $1.15 \leq g < 1.27$): They could contain hygroscopic organics (e.g., carboxylic acids and levoglucosan) and/or mixtures of non-/less and more hydrophilic compounds (e.g., BC, fatty acids, and/or humic-like substances mixed with ammonium sulfate or levoglucosan-like species) (Peng et al., 2001; Chan and Chan., 2003; Gysel et al., 2004, 2007; Chan et al., 2005; Petters and Kreidenweis, 2007);

(3) More hygroscopic particles ($\kappa \geq 0.2$; $g \geq 1.27$): Aerosol particles contain inorganic salts as well as some more hygroscopic organic species such as multifunctional organic acids (Peng et al., 2001; Carrico et al., 2008; Duplissy et al., 2011; Ogawa et al., 2016).

In addition, the volume-weighted mean growth factor, *GF*, was also calculated using $c(g, D_0)$ (Gysel et al., 2009):

$$GF = \left(\int_0^{\infty} g^3 \cdot c(\mathrm{g}, \mathrm{D}_0) \cdot dg\right)^{1/3} . \tag{2}$$

GF was employed to calculate the mean values of κ, which facilitated the comparison with chemical composition of aerosol particles.

3.2. Effective κ of organic compounds (κ_{org})

Water uptake properties of organic compounds were estimated using the Zdanovskii–Stokes–Robinson (ZSR) mixing rule, employing the observed values of κ and chemical composition as input parameters. The ZSR mixing rule assumes that water uptake by a mixture of materials is additive of the water content retained by each chemical species (Stokes and Robinson, 1966). The rule also assumes that the volume change in the mixing of species within individual particles is almost negligible (Brechtel and Kreidenweis, 2000, Gysel et al., 2007; Petters and Kreidenweis, 2007):

$$\begin{aligned}&\kappa = \sum_i \kappa_i \cdot \varepsilon_i = \kappa_{SNA} \cdot \varepsilon_{SNA} + \kappa_{org} \cdot \varepsilon_{org} + \kappa_{EC} \cdot \varepsilon_{EC} \\ &\Leftrightarrow \kappa_{org} = \frac{\kappa - \kappa_{SNA} \cdot \varepsilon_{SNA} - \kappa_{EC} \cdot \varepsilon_{EC}}{\varepsilon_{org}} \end{aligned}, \qquad (3)$$

where κ_i and ε_i stand for the hygroscopicity parameter and the volume fraction of a specific component *i* in dry particles, respectively. The subscript *SNA* represents the three major inorganic constituents of sulfate, nitrate, and ammonium; *org* denotes organic species; *EC* indicates elemental carbon.

Sulfate, ammonium, and nitrate were considered for inorganics, the majority of which were contributed by sulfate (see Table 2). Other materials, such as sea salt and crustal elements, were demonstrated to be neglected because they are relatively scarce in submicron wildfire haze particles in Southeast Asia (Balasubramanian et al., 2003; Keywood et al., 2003; See et al., 2006; Stockwell et al., 2016). Almost all the sulfate and nitrate were neutralized by ammonia, and these three most abundant inorganic constituents were combined and assumed as ammonium sulfate (i.e., $\varepsilon_{SNA} = \varepsilon_{SO4} + \varepsilon_{NO3} + \varepsilon_{NH4} \approx \varepsilon_{AS}$). Thus, the value of κ_{SNA} was considered to approximate the κ value of ammonium sulfate under the condition when sulfate dominates inorganics (Gunthe et al., 2009; Chang et al., 2010; Ogawa et al., 2016). The elemental carbon (EC) is known as non-hygroscopic (i.e., $\kappa_{EC} \approx 0$).

Values of densities are required to compute ε_i from observed mass fractions. The mass fraction is taken as the first-order approximation of the volume fraction, based on the hypothesis that the bulk particle density is similar to the densities of individual compounds when volume additivity is assumed (Kreidenweis et al., 2008; Gunthe et al., 2009; Hallquist et al., 2009). This hypothesis has been demonstrated to be acceptable when particles are composed primarily of organics and sulfate (Cross et al., 2007; King et al., 2007). The densities of ammonium sulfate and EC were assumed to be 1.77 g cm^{-3} and 1.80 g cm^{-3}, respectively (Park et al., 2004; Bond and Bergstrom, 2006). The density of organics is known to vary depending on their elemental composition (Kuwata et al., 2012). The value was assumed as 1.40 g cm^{-3}, which is a typical value for ambient organic aerosols (Hallquist et al., 2009).

The EC mass fraction of approximately 10.0 % in submicron wildfire haze particles was utilized according to the time-averaged EC content in ambient $PM_{2.5}$ filter samples (see Table 2). This assumption was based on the preconditions that the wildfire haze particles were homogeneously mixed in varied sizes and that there was no significant difference between BC and EC.

3.3. κ of oxygenated organic compounds (κ_{OOA})

As described in Sect. 2.3, organics were numerically segregated to HOA, PBOA, BBOA, and OOA. The value of κ_{org} can be calculated by a linear combination of contributions from segregated fractions (Petters and Kreidenweis, 2007; Chang et al., 2010):

$$\kappa_{org} = \upsilon_{HOA} \cdot \kappa_{HOA} + \upsilon_{PBOA} \cdot \kappa_{PBOA} + \upsilon_{BBOA} \cdot \kappa_{BBOA} + \upsilon_{OOA} \cdot \kappa_{OOA}, \qquad (4)$$

where υ_i stands for the volume fraction of component *i* in all the organics.

Water uptake by a mixed particle is largely driven by the relative abundance of more or less hygroscopic component, and it is more sensitive to uncertainties in the hygroscopicity of more hygroscopic compounds than that of less hygroscopic compounds (Gysel et al., 2007). Hydrocarbon (-like) OA is known to be almost non-hygroscopic, leading to the estimation that the κ value of HOA is 0 (Gysel et al., 2007; Gunthe et al., 2009; Chang, et al., 2010). Water uptake by freshly emitted biomass burning particles is generally limited, especially compared with OOA (Carrico et al., 2010; Chang et al., 2010; Chen et al., 2017). Based on our previously measured κ results of fresh Indonesian peatland burning particles, an overall mean value of κ_{PBOA} = 0.04 was used for the fresh PBOA factor, and κ_{BBOA} = 0.06 was applied for the non-peat BBOA factor with mixed vegetation burning mainly of acacia and fern species (Chen et al., 2017). Under these assumptions, κ_{OOA} can be calculated by the following equation:

$$\kappa_{OOA} = (\kappa_{org} - \kappa_{PBOA} \cdot \upsilon_{PBOA} - \kappa_{BBOA} \cdot \upsilon_{BBOA}) / \upsilon_{OOA} . \quad (5)$$

The density of OOA/PBOA/BBOA is required to calculate $\upsilon_{OOA}/\upsilon_{PBOA}/\upsilon_{BBOA}$ using the ME-2 resolved corresponding mass concentration combined with the total volume concentration of the bulk OA derived from the ToF-ACSM observed OA mass. The density of oxygenated organics was assumed to be 1.50 g cm^{-3} (as summarized in Table 1), which is a typical value for carboxylic and multifunctional organic acids (Saxena et al., 1995; Peng et al., 2001; Gysel et al., 2004; Carrico et al., 2010; Ogawa et al., 2016). According to the reported average density for common dry smoke particles (i.e., 1.20 − 1.40 g cm^{-3}; Reid et al., 2005), and considering the dominance of non-refractory organic material in fresh Indonesian peatland burning particles (Budisulistiorini et al., 2017), the densities of PBOA and non-peat BBOA were assumed to be 1.10 and 1.20 g cm^{-3}, respectively. Detailed information on the parameters utilized for the κ_{org} calculation is provided in Table 1.

4. Results

In this section, aerosol number size distribution (Figure 2), chemical composition (Figures 3 and 4), and hygroscopic properties of aerosol particles (Figure 5) are described in addition to diurnal variations in these data (Figure 6).

4.1 Number size distribution of wildfire haze particles

Figure 2a displays the time-averaged particle size distribution within the entire size range of 11.5 nm−10 µm measured by NanoScan-SMPS combined with OPS. The NanoScan-SMPS data were used for the fine particles (11.5–365.2 nm), and the overlapped size range of the OPS (338 nm size bin) was excluded from the analysis. The data in the remaining OPS size range

(419 nm–10 μm) were combined with the fine particle data. The temporal average size distribution presented a unimodal structure, in which the number mode diameter was located around 100 nm. Particles in the range of 30–200 nm dominated the total particle number concentration, whereas particles larger than 600 nm accounted for a minor fraction (less than 4.0 % on average; Fig. S4 and Fig. S5). This result suggests that in Singapore, the wildfire haze particles were predominantly contributed by submicron particles, in line with the corresponding chemical characteristics obtained in previous studies (Balasubramanian et al., 2003; See et al., 2006).

Figure 2b shows the mean diurnal cycle of particle number size distribution. The growth of ultrafine particles was typically observed in the afternoon. The dN/dlogD$_p$ higher than 1.5 × 10^4 cm^{-3} was commonly observed in the 50–200 nm particle size range, while the dN/dlogD$_p$ of super micron particles seldom exceeded 1.0 × 10^3 cm^{-3}. The particle number concentration was high from 08:00–09:00 LT in the morning. The concentration increased again in the afternoon (about 14:00 LT), which lasted until midnight. The high concentration periods could have been caused by local traffic emissions and by secondary formation processes. Diurnal variations were also observed in the number concentrations of all particles.

Figure 2c depicts the mean diurnal variations of the corresponding total particle number and volume concentrations. The total number concentration started to increase after 07:00 LT until around 10:00 LT, and it reached the highest level after 14:00 LT. The particle number concentration was higher than 1.5 × 10^4 cm^{-3} before 19:00 LT. After that, the number concentration decreased gradually, reaching 1.2 × 10^4 cm^{-3} at midnight. Correspondingly, the aerosol volume concentration was higher than 50.0 μm^3 cm^{-3} during the day. The volume concentration decreased during the night, although it was still higher than 45.0 μm^3 cm^{-3}. These results demonstrate that the aerosol loading was significantly high during the period of pollution caused by wildfire haze.

4.2 Chemical characteristics of wildfire haze particles

Figures 3a-b show the time series of both the mass concentrations and the corresponding mass fractions of organics, sulfate, nitrate, ammonium, and chloride (expressed as f_{org}, $f_{SO_4^{2-}}$, $f_{NO_3^-}$, $f_{NH_4^+}$, and f_{Cl^-}, respectively) in NR-PM$_1$ quantified by the ToF-ACSM. The average mass loading of NR-PM_1 was as high as 44.7 ± 24.5 μg m^{-3}, confirming the severity of the pervasive wildfire haze. During the observation period, organics were always the most abundant compounds in NR-PM_1 (34.8 ± 20.7 μg m^{-3}). The mass concentration of organics was higher than 50.0 μg m^{-3} in many cases, and it occasionally exceeded 100.0 μg m^{-3}. On average, organics accounted for the highest mass fraction of 77.1 %, followed by sulfate (11.7 %), ammonium (6.4 %), and nitrate (4.2 %). The mass concentration of non-refractory chloride was almost negligible (0.6 % of the total mass). These results demonstrate that the submicron wildfire haze particles were predominantly composed of organics.

Table 2 summarizes the mass concentrations of all the analyzed inorganic ionic species in the $PM_{2.5}$ filter samples. The corresponding data for carbonaceous fractions are presented in Fig. 4. Overall, the mass fraction of EC varied from 4.4 % to 15.8 % with a mean value of 10.8 %. OC occupied 30.4–50.7 % of the total $PM_{2.5}$ mass concentration, and the mean fraction was 43.0 %. The WSOC fraction was in the range of 17.6–30.2 % with the mean level of 26.7 %. Correspondingly, the water-insoluble OC (WISOC) content was calculated to be 6.1–20.5 % with the mean fraction of 16.3 %. The WSOC/OC ratios were consistently higher than 50.0 % with a mean and maximum values of 63.6 % and 79.9 %, respectively. The mean WSOC/OC value was significantly higher than that for fresh Indonesian peat burning particles emitted from the source region (i.e., 16 %; Jayaranthe et al., 2017), which were demonstrated to be generally water insoluble and thus nearly non-hygroscopic (Chen et al., 2017). This result suggests that the majority of organics in the wildfire haze particles were water soluble, implying the importance of secondary formation as well as the chemical transformation of organic particles during atmospheric transport. Inorganic ions were less abundant and less variable than the organics were. On average, the inorganics accounted for 30.5 % of the $PM_{2.5}$ mass loading with the mean contributions of 0.6 % by Cl^-, 2.6 % by NO_3^-, 17.2 % by SO_4^{2-}, 0.4 % by Na^+, 8.1 % by NH_4^+, 0.8 % by K^+, 0.1 % by Mg^{2+}, and 0.7 % by Ca^{2+}. Sulfate, ammonium, and nitrate were the most abundant inorganic components. More than half of the inorganics was contributed by sulfate. These results show that the wildfire haze particles were dominated by organics especially water-soluble species. Mass concentrations of organics measured by the $PM_{2.5}$ filter samples and by the ToF-ACSM agreed well when the organics/OC ratio was assumed to be 1.4 (slope = 1.07; R^2 = 0.91) (Reid et al., 2005; Hallquist et al., 2009; Levin et al., 2010). The total mass concentrations of aerosol particles quantified by the filter samples and the ToF-ACSM also correlated well (R^2 =

0.96). The mass loading of the $PM_{2.5}$ filter samples was approximately 30 % higher than that of the ToF-ACSM results, likely because of the difference in particle size range and the lack of EC content for the ToF-ACSM measurements (Budisulistiorini et al., submitted to Atmospheric Chemistry and Physics, February 2018).

Figure 3c shows the mean mass spectra of organics averaged over the observation period. Ion signals at *m/z* 43 (most likely $C_2H_3O^+$) and *m/z* 44 (CO_2^+) were prominent, accounting for 7.5 % and 10.5 % of the total organics mass spectrum. The predominant signal of *m/z* 44 indicates that organic compounds in wildfire haze particles were highly oxygenated. High-molecular weight organic signals with $m/z > 100$ possessed an abundance of 13.3 %. The marker ions for biomass burning particles, such as *m/z* 60 (mostly $C_2H_4O_2^+$) and *m/z* 73 (mainly $C_3H_5O_2^+$), which originating in levoglucosan-like species (e.g., levoglucosan, mannosan, and galactosan) were also clearly observed (Cubison et al., 2011).

Figures 6d-e show the mean contributions of four organic components classified by the ME-2 method, including HOA (8.8 % of $NR\text{-}PM_1$ mass), PBOA (10.4 %), BBOA (10.0 %), and OOA (36.0 %). The primary organics originating from biomass burning (i.e., PBOA and BBOA) accounted for 20.4 %. OOA was the dominant type of organics during the wildfire haze episodes.

4.3 Hygroscopic properties of wildfire haze particles

Figure 5 displays the time series of the mean *GF* data as well as the corresponding values of κ during the entire observation period. The mean values of *GF* varied between 0.98 and 1.52 with the average of 1.25 ± 0.09. *GF* values larger than 1.40 were normally observed in the after noon. The variation in the corresponding κ results ranged from 0.004−0.475, and the average κ value was 0.189 ± 0.087. Table 3 summarizes the mean κ results for organics (cf. Sect.3.2, with EC considered), which were calculated using the HTDMA and ToF-ACSM measurements during the overlapping observation period from 10−24 October 2015. The HTDMA-derived bulk κ results averaged over the same overlapping period were defined as κ_{HTDMA}. The mean κ_{org} (0.157 ± 0.108) was lower than the mean κ_{OOA} (0.266 ± 0.184), as the whole organic fraction normally contains both non-hygroscopic and hygroscopic organics. The derived κ_{org} results are demonstrated to be comparable to previously reported κ values for bulk organics (Petters and Kreidenweis, 2007; Duplissy et al., 2011; Lathem et al., 2013; Cerully et al., 2015). Moreover, the mean κ_{OOA} value agreed well with mean κ results in previous field and laboratory studies (e.g., $\kappa = 0.25 \pm 0.06$ for biogenic OOA, Chang et al., 2010; $\kappa = 0.2 \pm 0.1$ for aged BBOA, Engelhart et al., 2012). A caveat of this comparison is the representativeness of laboratory experiments for the actual environmental conditions, including types of burnt biomasses, concentrations and types of oxidants, and aging time. As the atmospheric condition of tropical Asia is unique, a systematic study of the chemical aging process of wildfire plume for the region would be required in the future. Note that the mean κ_{OOA} was even higher than the corresponding mean κ_{HTDMA} (0.207 ± 0.093), revealing that the water uptake particularly by some highly oxygenated organics in the wildfire haze particles could be highly significant.

4.4 Diurnal variations of hygroscopic properties and chemical composition

GF exhibited a clear pattern of diurnal variation (Fig. 6a). Higher *GF* values were observed during the daytime (*GF* = 1.27 ± 0.05 for 08:00–20:00 LT). However, the values were lower in the early morning and at night (1.23 ± 0.05 for 20:00–08:00 LT). The corresponding mean bulk κ results averaged over the entire observation period were 0.213 ± 0.051 for the daytime and 0.172 ± 0.043 for nighttime.

Similarly, the daytime mean κ_{org} and κ_{OOA} were 0.200 ± 0.104 and 0.323 ± 0.177, respectively, whereas the nighttime mean values were 0.103 ± 0.086 (κ_{org}) and 0.186 ± 0.177 (κ_{OOA}) (Table 3). These mean κ values were 19.2 % lower (κ_{org}) and 30.8 % higher (κ_{OOA}) than the concurrently measured mean κ_{HTDMA} result of 0.247 ± 0.096 (daytime), whereas they were 35.9 % lower (κ_{org}) and 16.3 % higher (κ_{OOA}) than that of 0.160 ± 0.063 (nighttime). A more significant discrepancy between κ_{org} and κ_{HTDMA} was observed at night, whereas a larger difference between κ_{OOA} and κ_{HTDMA} occurred during the day, which was likely due to the greatly inhibited oxidation processes of organic compounds in the evening in contrast to the enhanced situations during the day. This correlation could be visually observed in the corresponding diurnal patterns of both mean *GF* and OA factors, as the fraction of OOA was demonstrated as a moderately good indicator of the hygroscopicity of organics (Ogawa et al., 2016).

The observed variation in *GF* was predominantly caused by diurnal variations in the probability distribution of *g* (Fig. 6b). Specifically, the number fractions of the highly hygroscopic mode particles were low in the early morning and evening ($nf_{highly} < 0.3$), and higher during the afternoon (approaching the highest level of 0.6 around 15:00 LT). The value was positively correlated with *GF* (R = 0.97). The number fraction of the weakly hygroscopic particles was opposite that of the highly hygroscopic particles, and it was negatively correlated with the mean *GF* ($R = -0.95$). There was no clear diurnal variation in the number fraction of the moderately hygroscopic mode particles (stable around 0.2). These results suggest that the water uptake by wildfire haze particles is closely related to the fractions of weakly and highly hygroscopic mode particles. The mean *g* values for each mode were 1.05 ± 0.02 for weakly, 1.21 ± 0.01 for moderately, and 1.40 ± 0.05 for highly hygroscopic particles. The average values for *nf* were 0.42 ± 0.18 for weakly, 0.18 ± 0.07 for moderately, and 0.40 ± 0.20 for highly hygroscopic particles (Table 4).

The diurnal variation in hygroscopic properties coincided with that in chemical compositions (Fig. 6c). The mean *GF* correlated well with $f_{SO4}{}^{2-}$, suggesting the primary role of $f_{SO4}{}^{2-}$ in governing the water uptake by wildfire haze particles. The enhancement of $f_{SO4}{}^{2-}$ accompanied decreased f_{org}. Variations in the chemical composition of organics also correlated well with the water uptake properties. The fraction of signal intensity at *m/z* 44 (f_{44}), which is considered as a marker ion for the degree of oxidation (Duplissy et al., 2011; Ng et al., 2011; Ogawa et al., 2016), was also high during the day, which was similar to the case of the mean *GF* and $f_{SO4}{}^{2-}$. A similar pattern was also observed in f_{OOA}, whereas that in HOA was the opposite (Fig. 6d). For instance, f_{HOA} was the highest during the morning rush hours, and it subsequently decreased throughout the day. Variations in the fresh PBOA fraction (f_{PBOA}) were similar to those of non-peat BBOA (f_{BBOA}) (Fig. 6e), namely, there was no apparent diurnal pattern during the severe wildfire haze periods. Consequently, the distinctly enhanced mean *GF* during the day could be attributed to the increase in both $f_{SO4}{}^{2-}$ and f_{OOA}.

The diurnal variations in the organic composition were caused by the enhanced f_{OOA} during the day, which accompanied decreases in f_{HOA}. In general, highly oxygenated organic compounds are highly hygroscopic due to their water solubility, qualitatively explaining the similarities in the diurnal variations among mean *GF*, f_{OOA}, and f_{44} (Duplissy et al., 2011; Zhao et al., 2015; Ogawa et al., 2016). The relationship between the particle hygroscopicity and the degree of oxidation of organics will be discussed in detail in Sect. 5.2.

5. Discussion

5.1 Chemical composition dependences of water uptake by wildfire haze particles

Figure 7 depicts the relationships between κ and the mass fractions of both inorganic and organic species in NR-PM$_1$ in the data obtained during the day and at night. κ and $f_{SO4}{}^{2-}$ were positively correlated, demonstrating that sulfate was the most important compound in governing water uptake by 100 nm wildfire haze particles due to its high hygroscopicity. Similarly, κ was positively related to $f_{NH4}{}^{+}$, as it is the counter cation of sulfate. In contrast, κ was negatively correlated with f_{org}, as organics are less hygroscopic than inorganic salts are. There was no clear correlation between κ and $f_{NO3}{}^{-}$, implying that the small amount of nitrate had an insignificant contribution to the variability in κ of wildfire haze particles. κ was almost independent of $f_{Cl}{}^{-}$, partially due to the limited availability of non-refractory chloride. These distinctly different correlations between inorganics with mean κ likely reflect the different formation mechanisms of these species. Sulfate formation occurs as the result of the photochemical process during the day, whereas diurnal variations in gas–particle partitioning are important for the mass concentration of nitrate or chloride (Aan de Brugh et al., 2012; Gong et al., 2013).

The correlation between κ and f_{org} was relatively scattered. For instance, κ varied from 0.10 to 0.40 when f_{org} was 0.7, signifying that factors other than f_{org} could influence the water uptake. The variability in the chemical characteristics of organics might have played a role in the scattering of the data (Fig. 6d-f).

5.2 Relationship between the hygroscopicity and chemical composition of organics

Table 2 summarizes the κ_{org} and κ_{OOA} results averaged over the same PM$_{2.5}$ filter sampling periods. Figure 8 illustrates the relationship between κ_{org} and f_{WSOC}. In general, κ_{org} was insignificantly correlated with f_{WSOC}, especially in the data on October 22. The relatively high value of f_{44} (0.11) on October 22 might have caused the deviation. These results indicate that the oxygenation degree of organics could predominate over the WSOC fraction regarding the hygroscopic growth of organic-rich wildfire haze particles.

Figure 9 depicts the relationships between κ_{org} and f_{44} as well as κ_{org} and f_{44}/f_{43}. The daily average data were utilized. Although the data were scattered, a positive correlation between κ_{org} and f_{44} was observed (R = 0.70). The signal of m/z 44 (mostly CO_2^+) is known to originate in highly oxidized organic functional groups, such as dicarboxylic acids and acyl peroxides (Aiken et al., 2008). These highly oxygenated functional groups contribute to promoting hygroscopicity by enhancing water solubility (Topping et al., 2005; Cubison et al., 2006; Hallquist et al., 2009; Duplissy et al., 2011; Psichoudaki and Pandis, 2013; Suda et al., 2014; Riipinen et al., 2015; Ogawa et al., 2016; Petters et al., 2016; Marsh et al., 2017). κ_{org} and f_{44}/f_{43} also presented a similar trend to that of κ_{org} and f_{44}. The correlations shown in Figure 9 clearly demonstrate the important role of oxygenation degree in the water uptake properties of organic compounds in wildfire haze particles.

During the day, organic particles tend to be highly oxidized because of the oxidation of primary organic aerosol as well as the formation of secondary organic aerosol from volatile organic compounds (Ng et al., 2010 − see Fig. 6; Zhao et al., 2016). The chemical evolution processes of organic aerosol particles need to be better understood to enhance quantitative predictions of water uptake by wildfire haze particles (Kroll and Seinfeld, 2008; Riipinen et al., 2011; Winkler et al., 2012; Ehn et al., 2014). The evolution process could induce alternations in size dependence of chemical composition, and in the mixing state (Chakrabarty et al., 2006; Zhao et al., 2015). To address these unanswered questions, further knowledge about size- and mixing state-dependent chemical composition as well as the molecular-level chemical characteristics of Indonesian wildfire haze particles are required.

6. Conclusions

In September−October 2015, Indonesian wildfire-induced transboundary haze pollution spread throughout Southeast Asia, affecting both environment and climate dramatically and ravaging public health and the economy seriously. As a downwind receptor city, Singapore experienced pervasive wildfire haze events. In this study, we simultaneously measured the hygroscopic growth factor (*GF*) and the chemical composition of ambient wildfire haze particles in Singapore, with the aim of providing comprehensive insights into the linkages between water uptake and particle chemical composition as well as secondary aerosol formation.

High aerosol loading of non-refractory submicron particles (NR-PM_1, occasionally exceeding 100.0 μg m^{-3}) was frequently observed, stressing the severity of the 2015 wildfire haze pollution. The NR-PM_1 particles are predominantly composed of organics (OA, approximately 77.1 % on average) and sulfate dominates the inorganic constituents (about 11.7 %). Chemical analyses of NR-PM_1 indicate the ubiquity and dominance of oxygenated species in organics, in line with the most intense ion signals at m/z 44 (mostly CO_2^+, f_{44} = 10.5 % in total OA mass) and m/z 43 (most likely $C_2H_3O^+$, f_{43} = 7.5 % on average). Moreover, a major fraction of organics is water soluble, as signified by the high water-soluble organic carbon fraction in ambient $PM_{2.5}$ filter samples (26.7 % of the total $PM_{2.5}$ mass).

Wildfire haze particles are generally highly hygroscopic. The hygroscopicity parameter, κ, of 100 nm particles varied between 0.004 and 0.475, with a mean κ value of 0.189 ± 0.087. The derived mean κ results of organics were 0.157 ± 0.108 (κ_{org}, bulk organics) and 0.266 ± 0.184 (κ_{OOA}, oxygenated organic fraction), which are comparable to previously reported values of organic compounds (Petters and Kreidenweis, 2007; Duplissy et al., 2011; Lathem et al., 2013; Cerully et al., 2015). These results highlight the difference in κ between wildfire haze particles and fresh Indonesian peat burning particles, which are intrinsically non-hygroscopic due to the rather limited water-soluble organic fraction (Chen et al., 2017). The *GF* data showed a notable diurnal variation that usually peaked during the day. This variation was identical to the diurnal pattern of the number fraction of highly hygroscopic mode particles, and it accompanied the opposite fluctuation of the number fraction of weakly hygroscopic mode particles. These results imply the chemical composition dependence of particle hygroscopicity, as supported by the positive correlation of κ with the mass fraction of sulfate but its inverse relation to the mass fraction of organics. In addition to the governing influence of sulfate, κ of the haze particles was promoted by the water uptake of organics. Although κ_{org} was loosely related to the water-soluble organic fraction, a positive correlation between κ_{org} and f_{44} was shown (R = 0.70). This denotes that the oxygenation degree of organics may play an important role in water uptake especially by organic-rich haze particles.

To the best of our knowledge, this could be the first reported field measurements of water uptake by wildfire haze particles in Equatorial Asia. The results suggest that formation of secondary aerosol particles, including both inorganics and organics, is key in addressing the variability of reported results about the hygroscopic properties of aerosol particles originating from Indonesian peatland fires. Further quantitative studies on size-dependent chemical composition and detailed chemical analyses at molecular levels are needed to deepen our understanding of the water uptake by particles stemmed from Indonesian wildfires.

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Table 1. Summary of the hygroscopicity parameters (κ) and material densities of different chemical constituents utilized in the theoretical κ calculation with chemical data.

Chemical compounds	**Hygroscopicity parameter, κ**	**Density (10^3 kg/m^3)**
SNA[†]	0.59	1.77
EC	0	1.80
PBOA	0.04^{ζ}	1.10
BBOA	0.06^{ζ}	1.20
OOA	$\kappa_{OOA}{}^{*}$	1.50
Bulk OA	$\kappa_{org}{}^{*}$	1.40

[†] *SNA* includes all the sulfate, nitrate, and ammonium in submicron wildfire haze particles.

[ζ] κ values were assumed according to the mean κ results derived from laboratory studies (Chen et al., 2017).

* κ_{OOA} and κ_{org} were derived from ambient water uptake measurements and chemical data, in combination of the given parameters in Table 1, using the simplified algorithm introduced in Sects. 3.3 and 3.2.

Table 2. Summary of the averaged chemical characteristics of the 24 h $PM_{2.5}$ filter samples collected during 2015 haze events and the accordingly calculated mean κ results of organics (RH = 85 %).

Sampling date	**Cl^- (μg/m^3)**	**NO_3^- (μg/m^3)**	**SO_4^{2-} (μg/m^3)**	**Na^+ (μg/m^3)**	**NH_4^+ (μg/m^3)**	**K^+ (μg/m^3)**	**Mg^{2+} (μg/m^3)**	**Ca^{2+} (μg/m^3)**
Oct-14	0.64	2.40	10.21	0.20	4.93	0.62	0.05	0.55
Oct-15	0.38	1.72	10.51	0.18	4.63	0.60	0.03	0.50
Oct-16	0.27	1.62	9.01	0.25	4.03	0.48	0.08	0.65
Oct-19	0.65	2.39	15.90	0.20	7.99	0.58	0.03	0.41
Oct-20	0.24	1.09	10.22	0.31	4.33	0.51	0.05	0.48
Oct-21	0.19	0.83	7.95	0.23	3.15	0.51	0.08	0.52
Oct-22	0.23	0.80	9.71	0.29	3.78	0.38	0.08	0.50
Oct-23	0.56	2.65	15.92	0.18	9.13	0.70	0.005	0.25
Average	0.40	1.69	11.18	0.23	5.25	0.55	0.05	0.48

Table 2. (continued)

Sampling date	**f_{inorg}* (%)**	**$f_{SO_4^{2-}}$ (%)**	**f_{EC} (%)**	***WSOC/OC* (%)**	**Mean κ**	**Mean κ_{org}† (D_0 = 100 nm)**	**Mean κ_{OOA}†**
Oct-14	42.1	21.9	15.3	79.9	0.114	0.030	0.054
Oct-15	41.1	23.3	11.1	64.8	0.202	0.118	0.185
Oct-16	28.6	15.7	11.7	66.4	0.161	0.133	0.256
Oct-19	26.6	15.0	5.9	60.2	0.265	0.229	0.450
Oct-20	30.3	18.0	11.3	61.5	0.271	0.236	0.443
Oct-21	26.4	15.6	11.0	56.9	0.193	0.148	0.283

Oct-22	42.9	26.4	15.8	59.5	0.265	0.212	0.376
Oct-23	24.6	13.3	4.4	59.6	0.217	0.184	0.337
Average	30.5	17.2	10.8	63.6	0.211	0.161	0.298

* The subscript $_{inorg}$ stands for all the inorganic species; hence, f_{inorg} is the mass fraction of inorganic particles in the $PM_{2.5}$ filter sample. All the ionic data are provided with the mean mass concentration (µg/m^3).

[†] The mean κ results of organics were calculated assuming 10.0 % elemental carbon (EC) in total mass (see Sect.3.2).

Table 3. Derived mean κ values of organics with consideration of 10.0 % *EC* mass fraction in total NR-PM$_1$, as well as the mean κ results for HTDMA measurements conducted within the overlapped ToF-ACSM observation period of 10–24 October 2015 (i.e., κ_{HTDMA}).

	Mean κ (mean ± SD)		
	Overall	**Daytime**	**Nighttime**
κ_{org}	0.157 ± 0.108	0.200 ± 0.104	0.103 ± 0.086
κ_{OOA}	0.266 ± 0.184	0.323 ± 0.177	0.186 ± 0.177
κ_{HTDMA}	0.207 ± 0.093	0.247 ± 0.096	0.160 ± 0.063

Table 4. The temporally mean number fraction (*nf*), volume-weighted mean diameter growth factor (*GF*), and κ results (mean ± SD) of 100 nm wildfire haze particles in the three different hygroscopicity ranges at 85 % *RH*.

Hygroscopic mode	***nf***	***GF***	κ
Weakly ($g < 1.15$)	0.42 ± 0.18	1.05 ± 0.02	0.030 ± 0.013
Moderately ($1.15 \le g < 1.27$)	0.18 ± 0.07	1.21 ± 0.01	0.151 ± 0.005
More ($1.27 \le g < 1.85$)	0.40 ± 0.20	1.40 ± 0.05	0.343 ± 0.054
Bulk mean	*n/a*	1.25 ± 0.09	0.189 ± 0.087

n/a: not applicable.

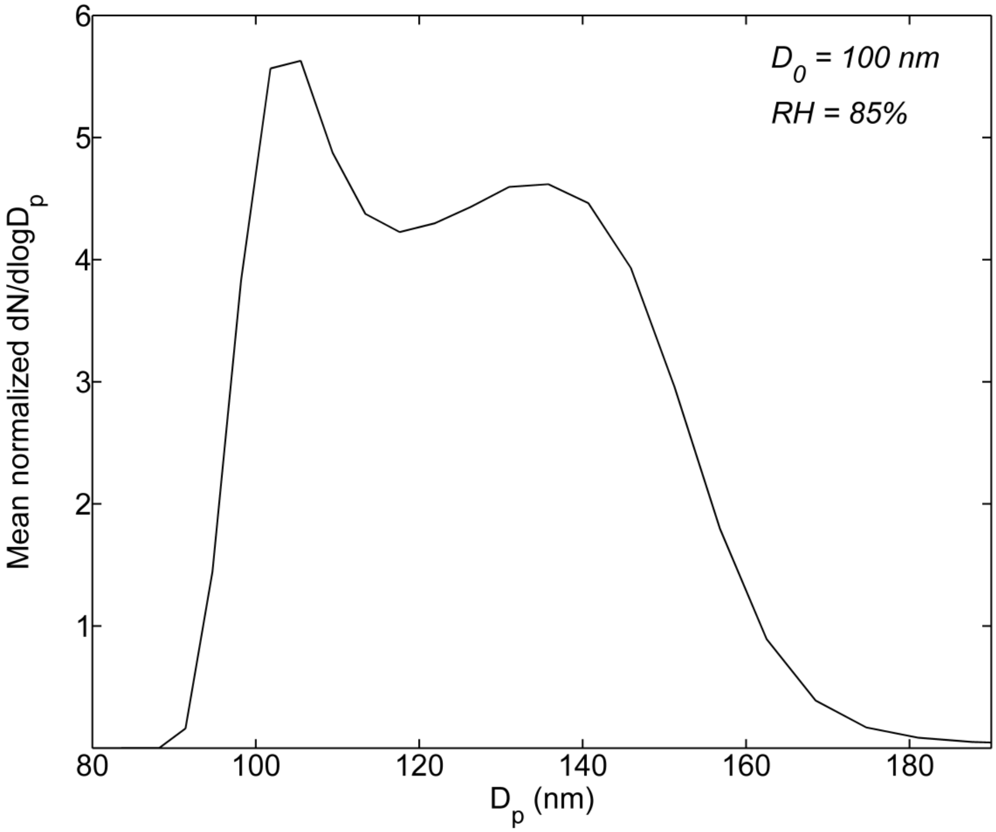

Fig. 1 Normalized particle number size distribution ((dN/dlogDp)/N) after humidification averaged over the entire haze observation period.

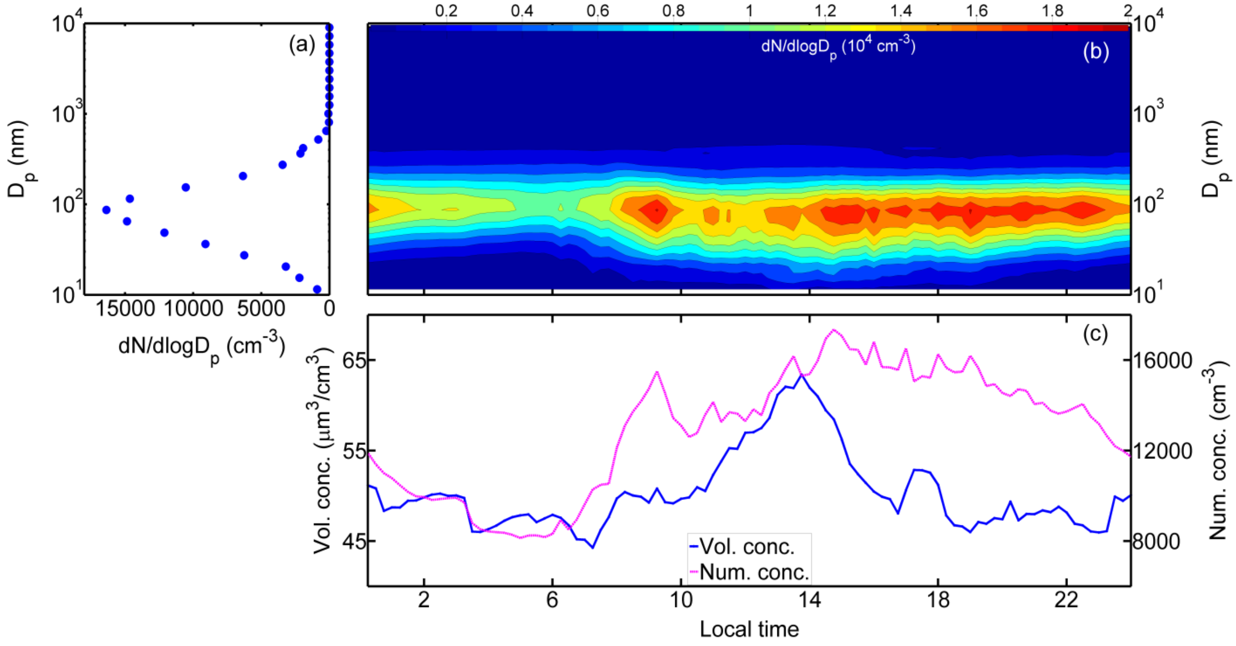

Fig. 2 (a) The mean particle number size distribution (dN/dlogD$_p$, cm^{-3}) during the ambient wildfire haze observations as well as the mean diurnal variations of (b) particle size distribution, (c) number concentration (Num. conc., cm^{-3}, denoted by the magenta solid line), and volume concentration (Vol. conc., μm^3/cm^3, as the blue line displayed) measured with NanoScan-SMPS (11.5−365.2 nm) and OPS (419 nm–10 μm) (local time, LT).

High aerosol loading was commonly observed during the transboundary wildfire haze. Submicron particles in the size range of 30−200 nm dominated the total number concentration of wildfire haze particles.

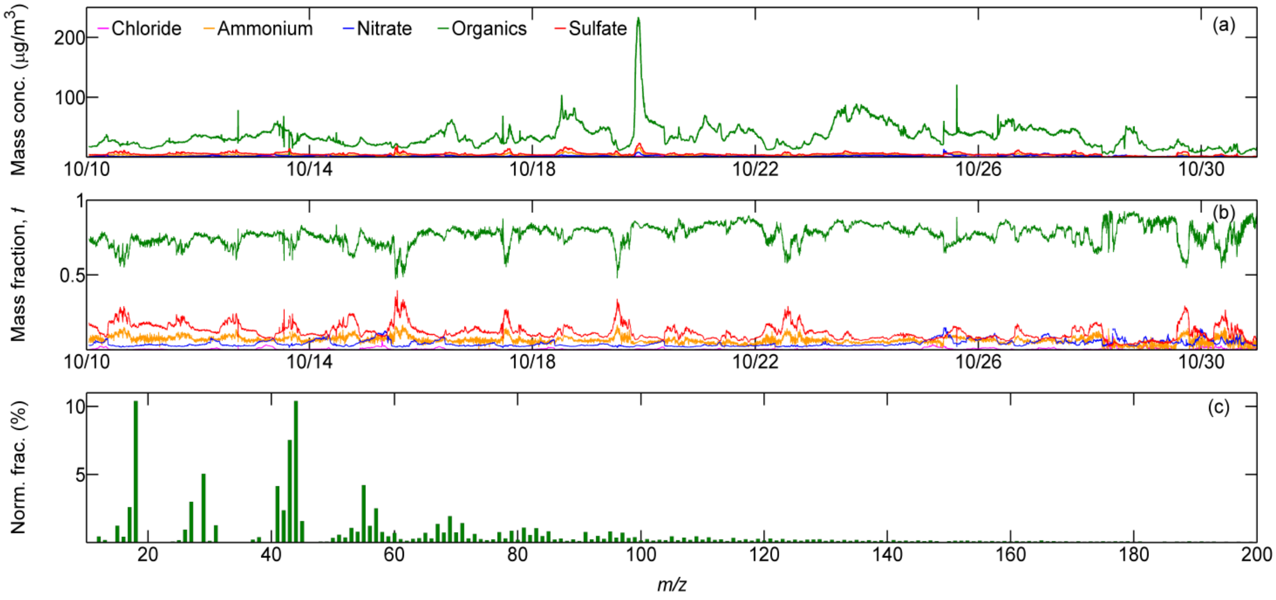

Fig. 3 Time series of (a) mass concentration (Mass conc., $\mu g/m^3$) and (b) corresponding mass fraction, *f*, of the five specific chemical species in NR-PM_1 measured by ToF-ACSM (abscissa shows the observation dates in October 2015 in the date format of month/day). (c) Temporally averaged OA mass spectra for submicron wildfire haze particles, displayed with the normalized ion fraction (Norm. frac., %) of each ion fragment.

Wildfire haze particles were predominantly composed of organics. Ion signals (*m/z*) from oxygenated organics (e.g., *m/z* 43, 44) were prominent, while intensities of ions for hydrocarbon-like organic compounds (e.g., *m/z* 41, 55, 57) and biomass burning tracers (e.g., *m/z* 60, 73) were relatively less intense. See the text for details.

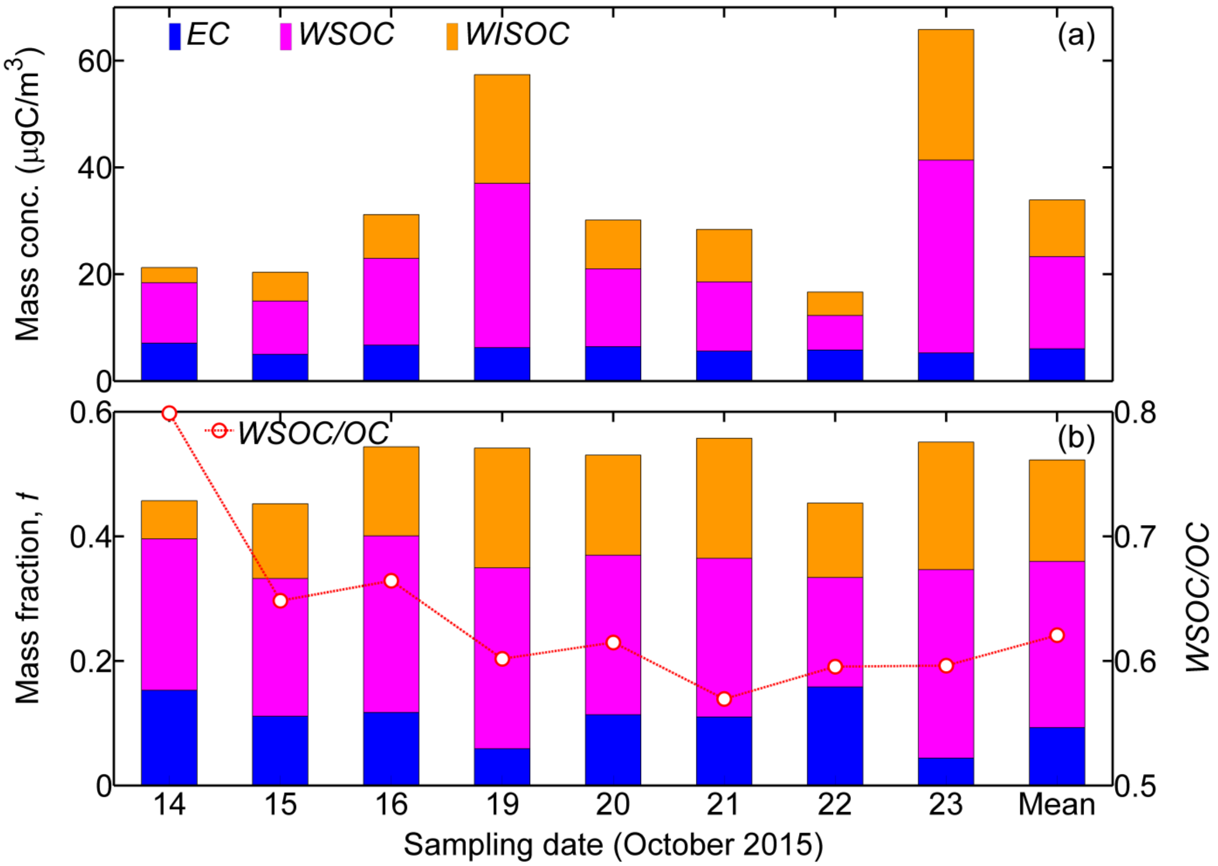

Fig. 4 (a) Mass concentration (Mass conc., μgC/m^3) and (b) corresponding mass fraction, *f*, of the carbon contents including *EC*, *WSOC*, and water-insoluble *OC* (*WISOC*) in $PM_{2.5}$ filter samples. The *WSOC/OC* ratio is also displayed by the scattered dots in panel (b). All the corresponding temporal mean results are shown as “Mean”.

The *WSOC* fraction was exclusively higher than that of *WISOC* or *EC*, highlighting the dominance of *WSOC* in the carbon content of $PM_{2.5}$ filter samples. In general, the *EC* fraction fluctuated around 10.0 % of the total $PM_{2.5}$ mass.

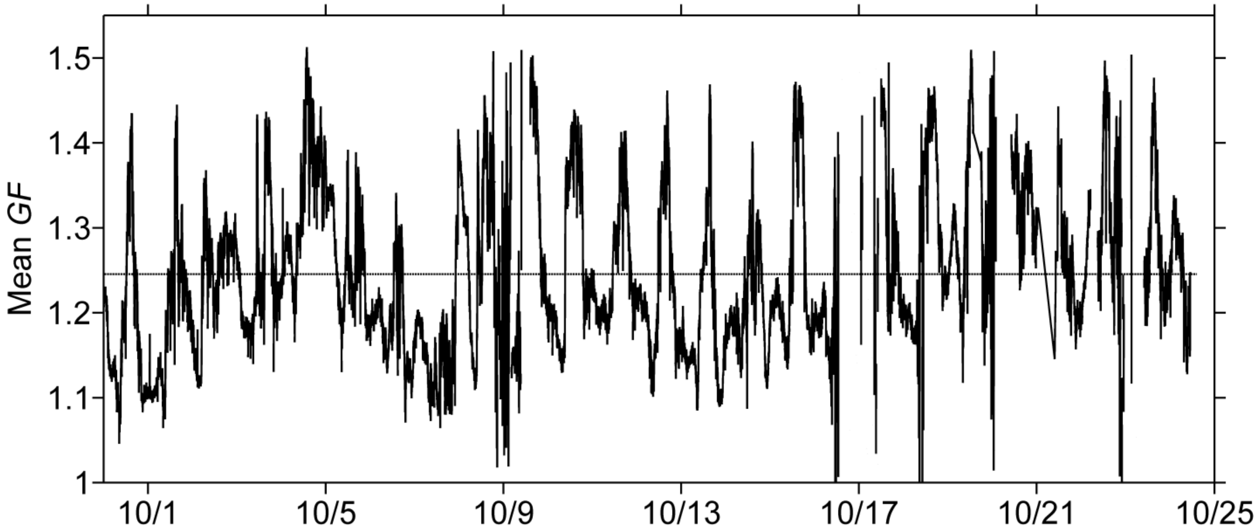

Fig. 5 Time series of the volume-weighted mean particle diameter growth factor (*GF*) derived from HTDMA measurements (date format: month/day, 2015)~~, colored with the corresponding mean hygroscopicity parameter, *κ*~~. The black dashed line stands for the temporal mean *GF* averaged over the entire observation period.

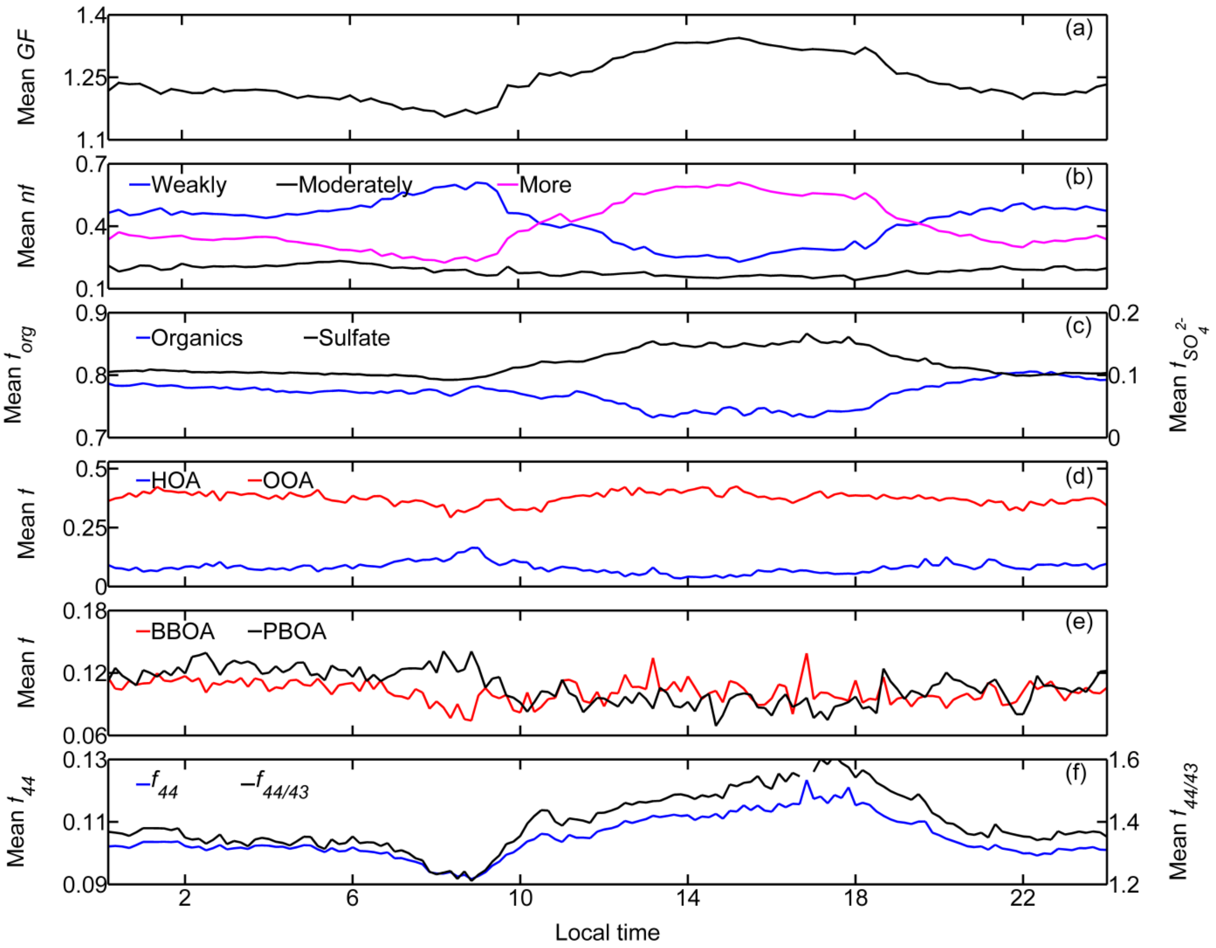

Fig. 6 Temporal averaged (10−24 October 2015) diurnal variations of (a) the mean *GF*, (b) number fraction (*nf*) of the three hygroscopic modes, (c) mass fraction of the two main components in NR-PM$_1$, i.e., organics (f_{org}) and sulfate ($f_{SO4}{}^{2-}$), (d-e) mass fraction of the ME2-resolved four OA factors in NR-PM$_1$ (i.e., f_{HOA}, f_{OOA}, f_{BBOA}, and f_{PBOA}), and (f) mean f_{44} and $f_{44/43}$ of organics in NR-PM$_1$ (local time, LT).

Pronounced diurnal patterns were observed for the mean *GF*, number fractions of both weakly and more hygroscopic modes, f_{44}, $f_{44/43}$, and mass fractions of organics and sulfate as well as HOA and OOA; nf_{more}, $f_{SO4}{}^{2-}$, f_{44}, $f_{44/43}$, and f_{OOA} showed variations similar to that of the mean *GF*, whereas contrasting diurnal patterns were found for nf_{weakly}, f_{org}, and f_{HOA}.

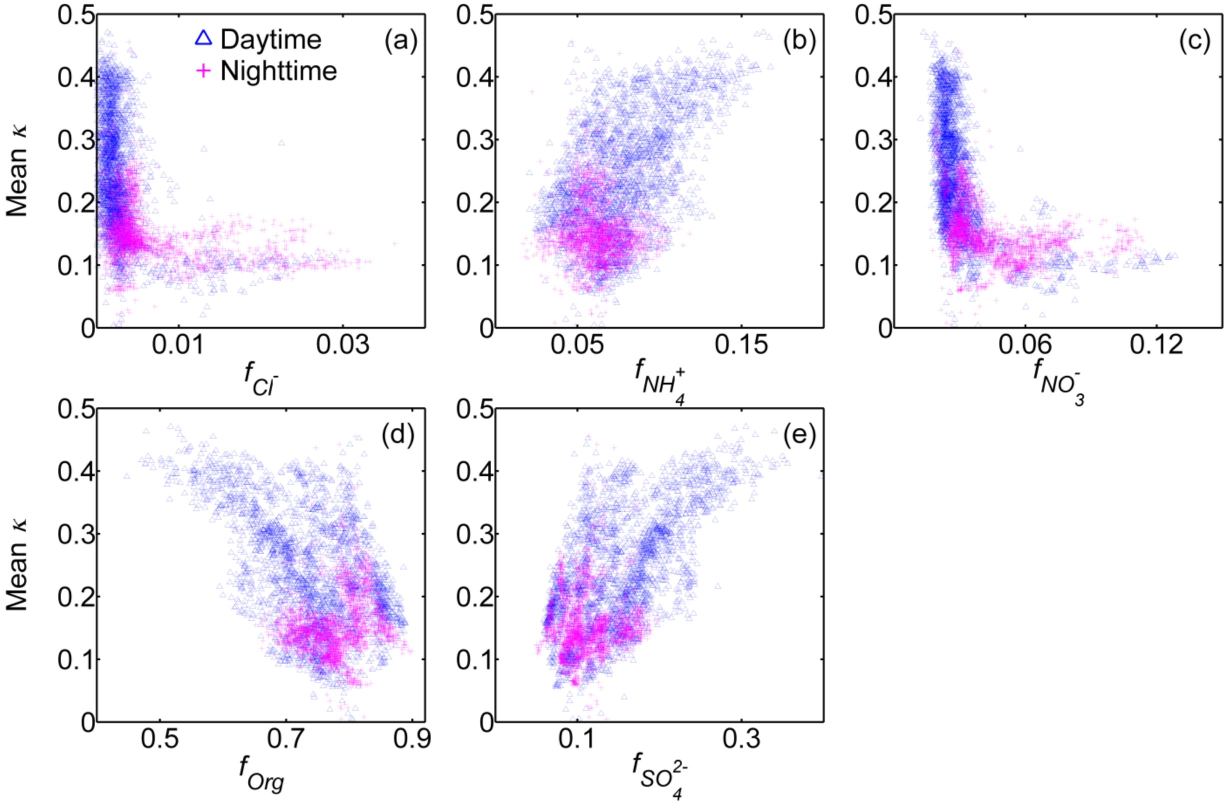

Fig. 7 Relationships between the mean *κ* results (100 nm) and the mass fractions of the five non-refractory chemical compositions of submicron wildfire haze particles.

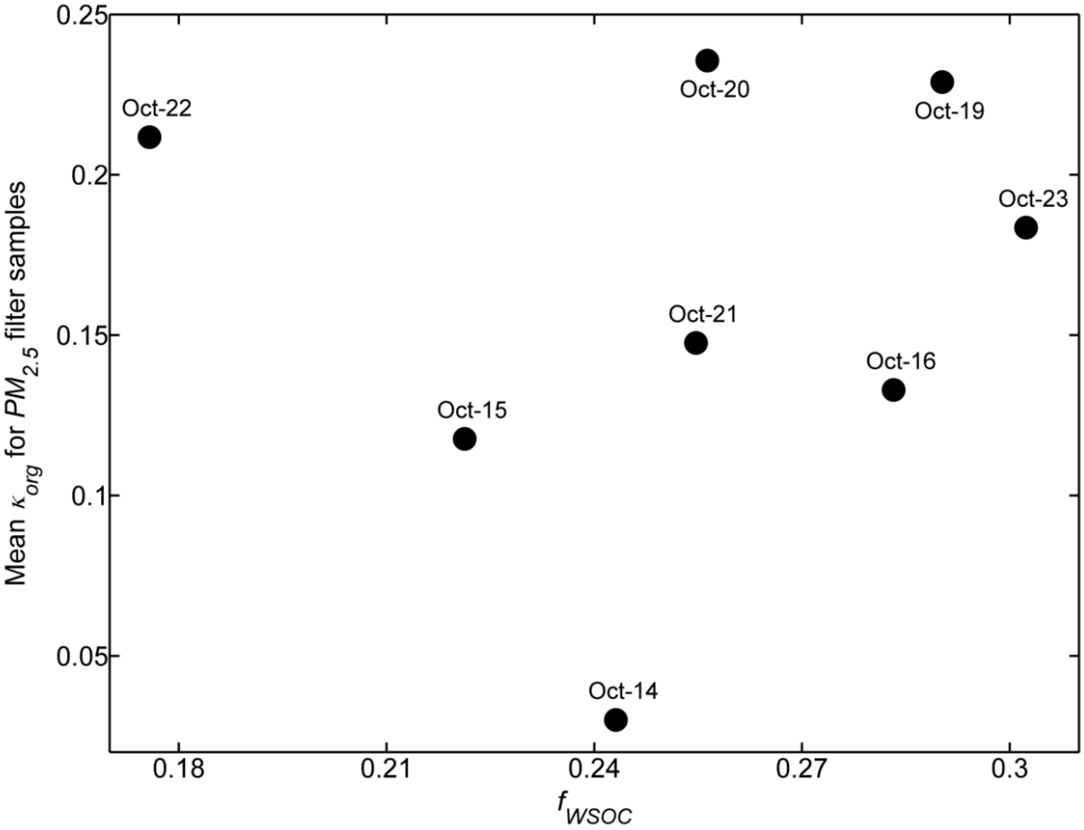

Fig. 8 Correlation between the mean κ of organics (κ_{org}, with 10.0 % *EC* mass fraction considered in the κ calculation) and the mean *WSOC* fraction (f_{WSOC}) of $PM_{2.5}$ filter samples.

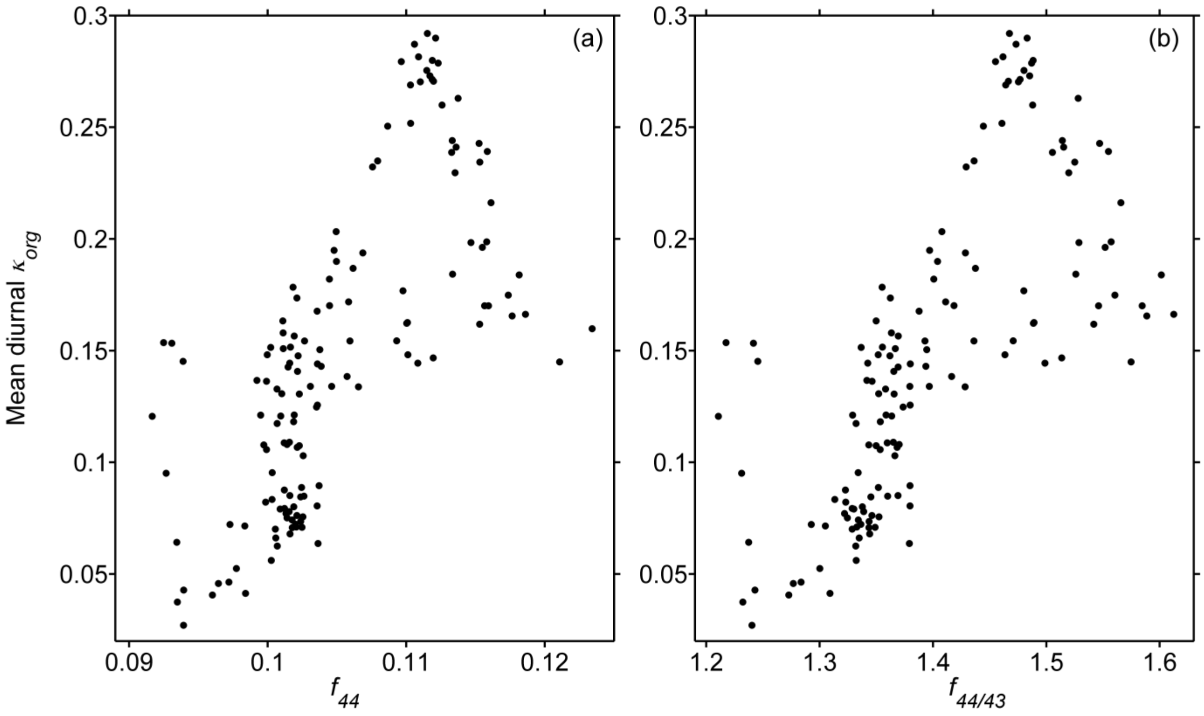

Fig. 9 Relationships between the mean diurnal κ_{org} results vs. (a) f_{44} and (b) $f_{44/43}$ in NR-PM$_1$ haze particles. Mean diurnal here represents that the diurnal results for each day were further averaged over the overlapping observation period, i.e., with both HTDMA and ToF-ACSM measurements taken from 10−24 October 2015.

Supplementary Information

Secondary aerosol formation promotes water uptake by organic-rich wildfire haze particles in Equatorial Asia

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S1. Back trajectories and carbon emission from wildfires

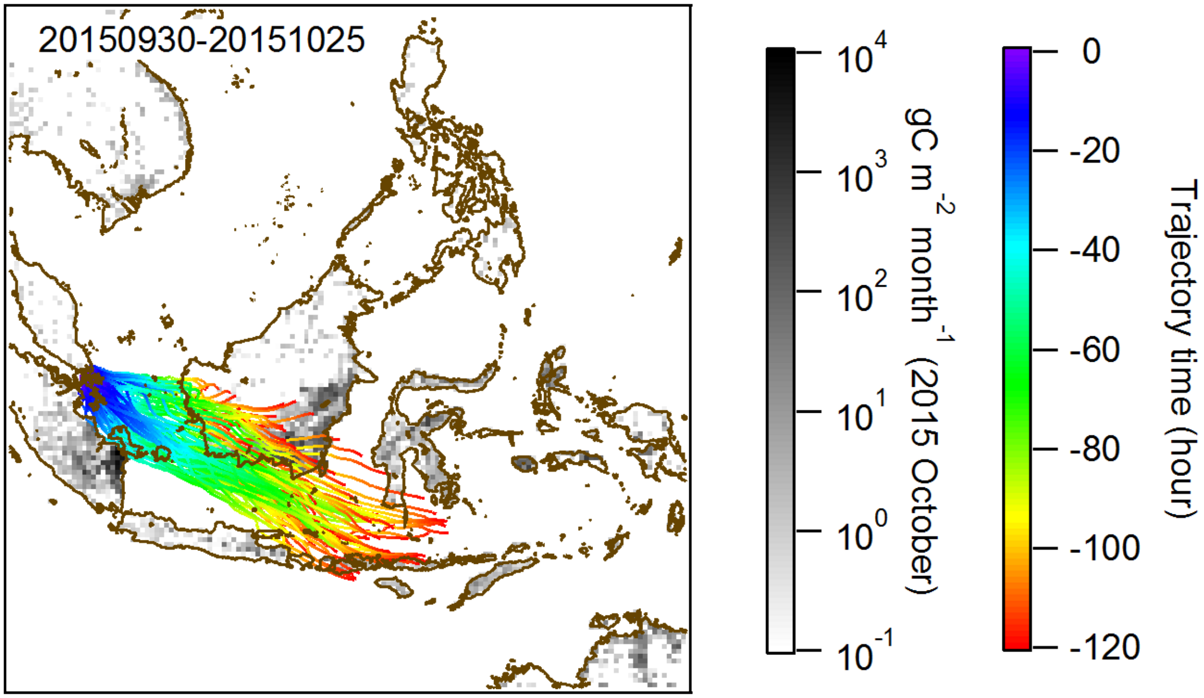

Fig. S1 Back trajectories of air masses arriving at Singapore and monthly carbon emission from wildfires during the observation period of HTDMA measurements. The transport time of wildfire plumes is approximately 1−2 days from South Sumatra, and 3−4 days from Central Kalimantan arriving at Singapore.

The back trajectory was calculated using the NOAA HYSPLIT model at 500 m (Kalnay et al., 1996). The altitude of the trajectories was constrained as iso-sigma. Carbon emission data was from the Global Fire Emissions Database (GFEDv4, https://daac.ornl.gov/VEGETATION/guides/fire_emissions_v4.html).

S2. HTDMA calibration results with 150 nm ammonium sulfate particles

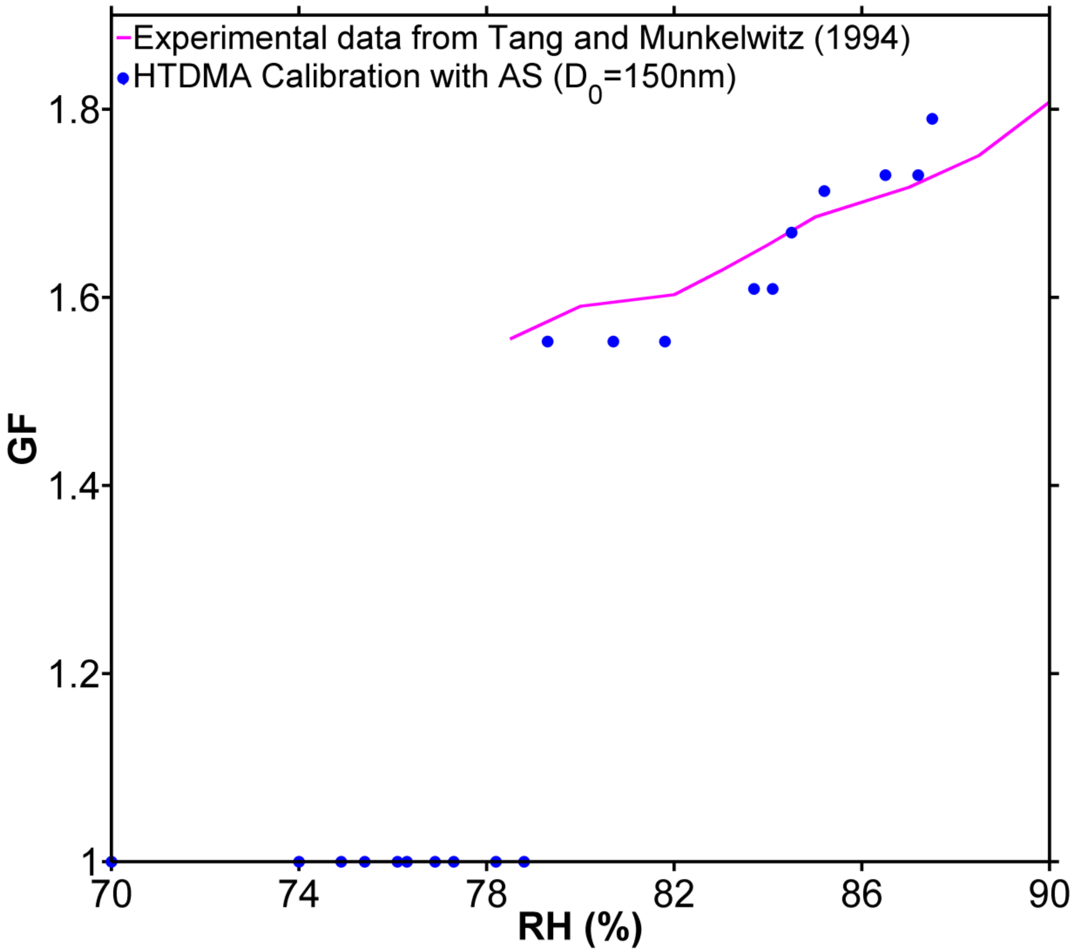

Fig. S2 Comparison of particle diameter growth factor (GF) results derived from the HTDMA calibration data for 150 nm dry ammonium sulfate (AS) particles, and experimental data (without parameterization) obtained by Tang and Munkelwitz (1994).

S3. An example of normalized particle number size distributions of 100 nm particles after humidification at 85 % RH measured using the HTDMA system

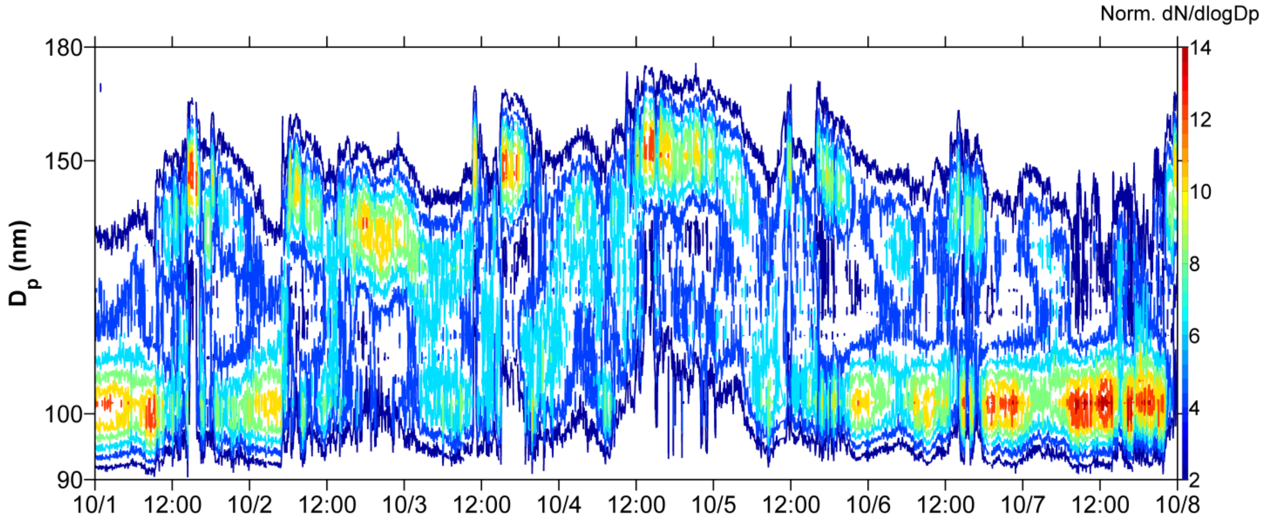

Fig. S3 An example (1−7 Oct 2015) of the HTDMA data at RH = 85% for D_0 = 100 nm particles. Temporal variation of normalized particle number size distributions (i.e., Norm. dN/dlogD$_p$) is shown, with every 12 hours interval.

S4. Mean particle number and volume size distributions

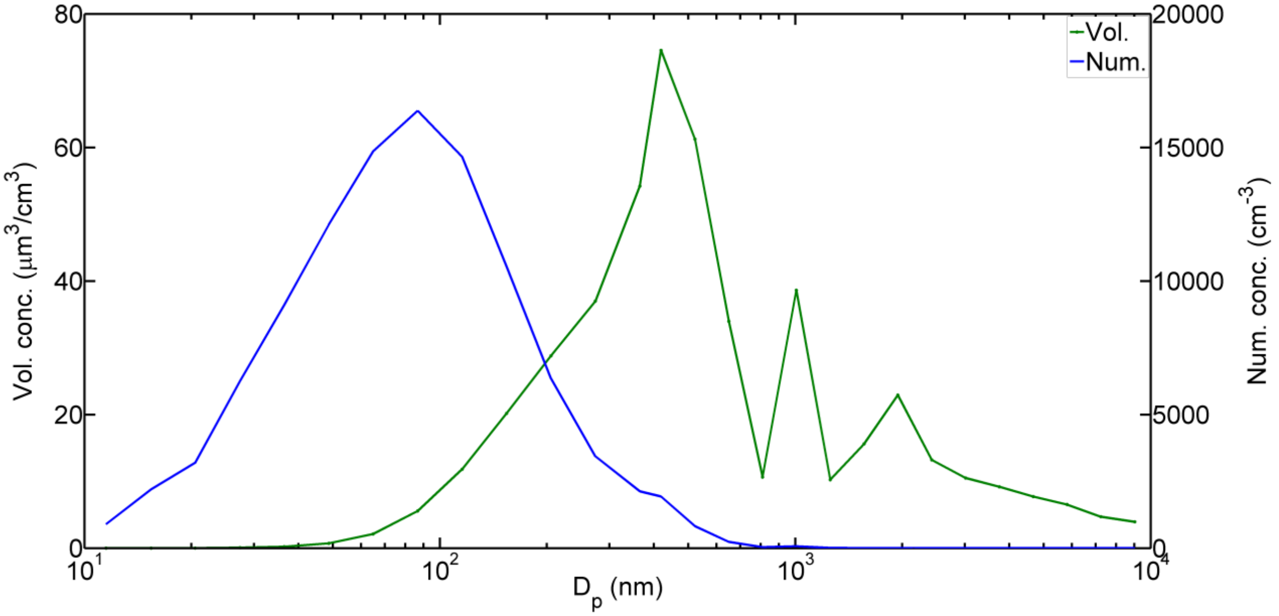

Fig. S4 Mean particle number (Num.) and volume (Vol.) size distributions over the entire wildfire haze observation period. Submicron particles with 200 nm < D_p < 1 μm dominate the particle volume concentration, while 30−200 nm particles are the major contributor to the particle number concentration.

S5. Time series of total particle volume concentrations for PM$_1$ and PM$_{10}$ measured during the wildfire haze periods

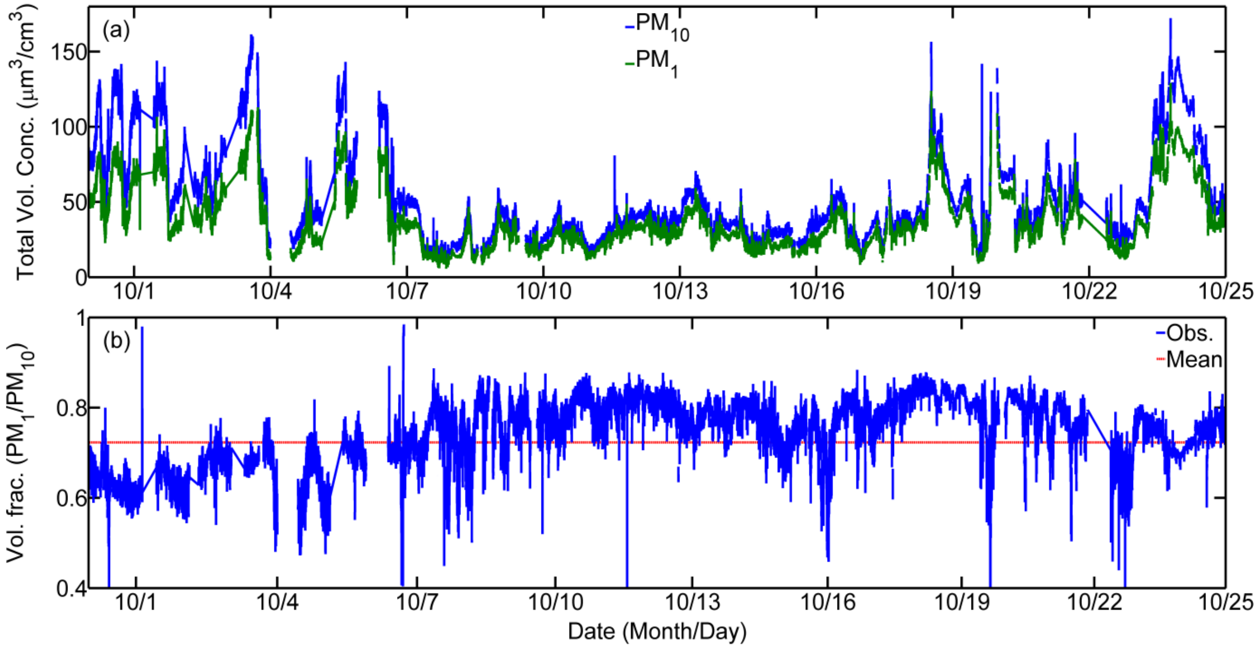

Fig. S5 (a) Time series of total particle volume concentrations (Vol. Conc.) for PM$_1$ and PM$_{10}$. (b) The corresponding volume fraction (Vol. frac.) of PM$_1$ to PM$_{10}$ calculated from the combined particle size distribution. The data from the NanoScan SMPS and OPS were used for the analysis. The red line represents the mean level (approximately 72.3 %) averaged over the entire observation period. This result suggests the predominant role of submicron particles in total particle mass.

S6. Correlations between the mass concentration of organics and that of sulfate

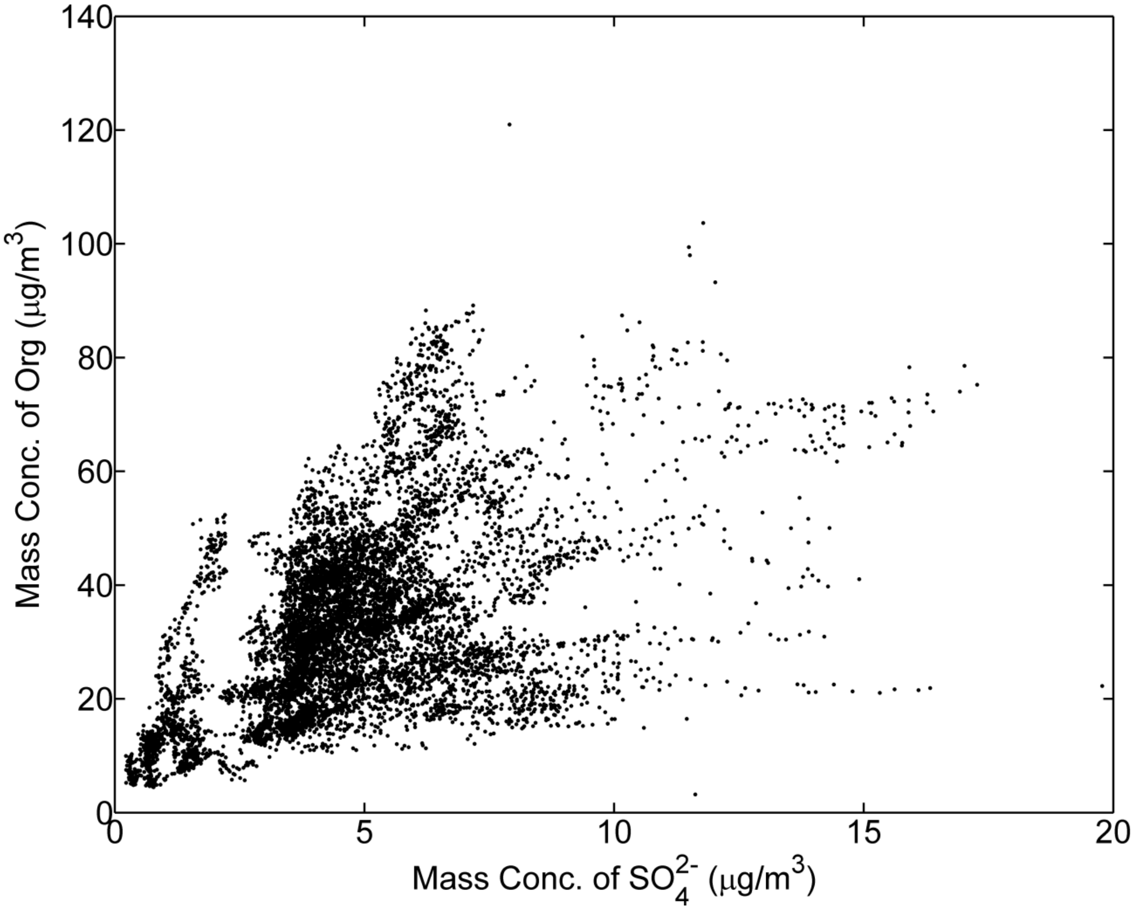

Fig. S6 Correlation between mass concentration of organics and that of sulfate (*R* = 0.49), without the data measured during the extremely pollution episode in the evening of 19 October 2015 till the noon time of 20 October 2015.

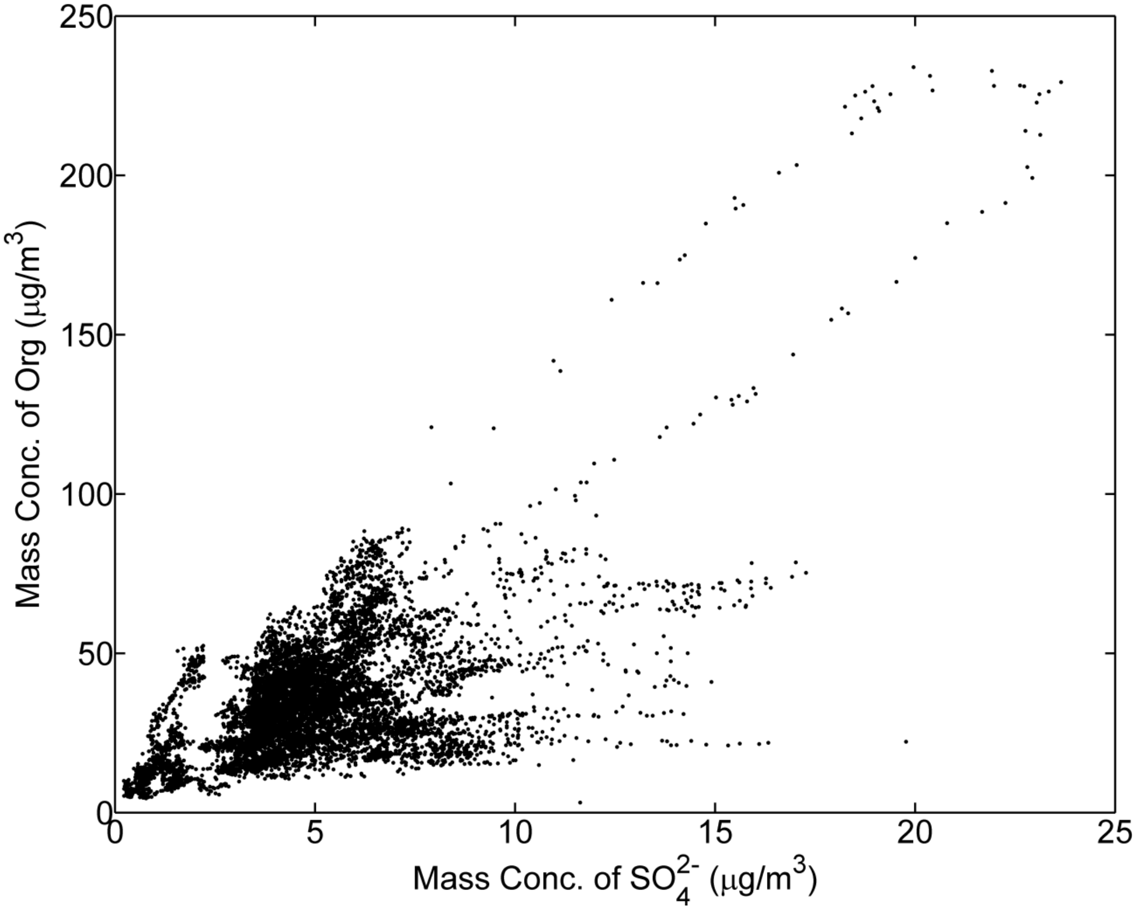

Fig. S7 Correlation between mass concentration of organics and that of sulfate (*R* = 0.62) during the entire wildfire haze observation period.

References:

Kalnay et al. (1996). The NCEP/NCAR 40-year reanalysis project, Bull. Amer. Meteor. Soc., 77, 437-470.

Tang, I. N. and H. R. Munkelwitz (1994). Water activities, densities, and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance. J. Geophys. Res. Atmos., 99(D9): 18801-18808.