Dear Editor,

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

Best Regards,

Jing Chen, Mikinori Kuwata

Anonymous Referee #1

General comments:

R1C0: Chen et al. use the HTDMA technique to study the water uptake properties of biomass burning particles from dried smoldering eagle fern and black wattle plants. Hygroscopic growth was correlated with chemical composition from an ACSM as well as OC/EC ratios, and WSOC content. Smoke collected on filters was extracted using water, and a liquid-liquid octanol-water extraction. Extracts are atomized and analyzed for chemical composition and hygroscopicity. One of the main findings is a correlation between f_{44} and the mean kappa observed with the HTDMA.

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

We would like to emphasize that hygroscopic properties of peat smoldering particles were quantified, in addition to those originating from combustion of peatland vegetation (e.g., fern and acacia leaves). To our knowledge, this is the first HTDMA study for particles emitted from smoldering of Indonesian peat, which is one of the most important types of biomass burning fuel. The following sentences were added to the revised manuscript to stress the point.

Page 3, Line 4: *'As one of the most important biomass burning types, the peatland fires keep smoldering for months, releasing huge amounts of greenhouse gases and fine particles to the atmosphere, impacting atmospheric radiation (Levine et al., 1999; Page et al., 2002; van der Werf et al., 2010).'*

Page 4, Line 25: *'Hygroscopic growth of various types of fresh peat burning particles, along with those originating from combustion of peatland dried plants,* *was measured using the humidified tandem differential mobility analyzer (HTDMA) for the first time.'*

R1C1: "The manuscript contains new data, collected with a valid set of techniques. The octanol-water extraction method is new. However, the direct utility of the study remains unclear. The authors do not explain the scientific value of analyzing water and octanol-water extracts. How can these be used to help understand biomass burning aerosol? Yes, products will be different in the extracts, and it may help build correlations of kappa vs f_{44} over a wider dynamic range, but beyond that, I do not see how the extracts help understanding hygroscopic growth or help improving aerosol forcing estimates as claimed in the conclusion. The authors need to explicitly make this case in the discussion of the results."

Response: We appreciate the reviewer for recognizing the validity of our experimental techniques. The 1-octanol-water partitioning method allows further classification of highly water soluble organic fraction, enabling us to tightly connect chemical composition and hygroscopic properties of biomass burning particles. In previous studies, hygroscopic growth/CCN activity of bulk material, water/methanol extracts, and solid phase extracted organic fractions in biomass burning particles were investigated. Analysis of solvent extracts provided some insights into the relevance between water uptake properties and chemical composition, yet these fractionated components still contained a wide spectrum of organic species in terms of water solubility (e.g., Psichoudaki and Pandis, 2013). Solid phase extractions allowed classification of different fractions in WSOM, yet chemical and physical significances of the separation method have been unclear.

As discussed in our previous study (Kuwata and Lee, 2017), the significance of the 1-octanol-water partitioning method is to classify water soluble organic matter into different fractions by their water solubility, which has a clear chemical meaning. To our knowledge, this study is the first application of the method for hygroscopic growth measurements.

The present study demonstrated for the first time that a highly hydrophilic fraction (A_1) is a) more hygroscopic, and b) highly oxygenated, and c) contains a smaller fraction of high-molecular weight species than bulk WSOM (A_0). Even though highly oxygenated organic fraction has been considered as highly hygroscopic due to their water solubility, there has been no experimental validation for this idea prior to this study. Therefore, the correlation of κ with f_{44} reported in this study provides a clearer idea about the relationship between water uptake properties and organic chemical compositions with different water solubility in comparison to previous studies. In addition, the relationship between molecular size of organic compounds and water solubility has never been demonstrated before, especially for a complex mixture such as biomass burning particles. In conclusion, the significance of the 1-octanol-water partitioning method is more than expanding the dynamic range for the correlation between κ and f_{44}, as the method adds a new parameter (i.e., water solubility) to characterize chemical properties of WSOM. These points are clarified and stressed in the revised manuscript, as detailed in the following.

Page 5, Line 1: *'The concurrent HTDMA and ToF-ACSM measurements were also performed for the bulk WSOM and its highly hydrophilic fraction classified with the 1-octanol-water partitioning method in terms of water solubility (Kuwata and Lee, 2017). This method provides a new angle (i.e., water solubility) to characterize chemical properties of WSOM, facilitating a more detailed* *investigation on particle water uptake property with the first application of the method in HTDMA measurements of highly hydrophilic organic fraction.'*

In previous studies, hygroscopicity/CCN activity has been related with chemical composition only corresponding to the bulk information such as f_{44} or O:C elemental ratios. Although these relationships improved our understanding on interactions between organic aerosol particles and water vapor, it has not been easy to obtain mechanistic insights on the empirical correlations. Recent development of theoretical framework for water uptake by organic aerosol particles suggests that distributions of polarity/water solubility could be an important input for detailed modeling of hygroscopic growth, although experimental verification of the idea is still challenging. The classification of WSOM by their water solubility will allow us to narrow the gap between empirical relationship and theoretical framework based on the first HTDMA measurements of highly water soluble organic fraction. These points are clarified in the revised manuscript as follows.

Page 12, Line 6: *'... biomass burning as 0.2~0.3. Our results of water uptake by organic compounds (e.g., bulk organic material, bulk WSOM, and highly hydrophilic WSOM) would be further employed to verify a theoretical framework, which uses distributions of water solubility as input parameters (Riipinen et al., 2015).'*

R1C2: "Furthermore, the correlation of kappa with f_{44} is now firmly established. Also, the water uptake properties for aerosol from predominately smoldering combustion in small burn settings is also well known to range

between 0 and 0.1 from previous studies. Repeating this type of study with more fuels adds only incrementally to the known body of literature. Perhaps the NMR functional group data could be used better for an explanatory model?*”*

Response: We thank the reviewer for the useful comment to improve the manuscript. We would like to stress that our study includes the first HTDMA measurements of bulk organic matter, bulk WSOM, and more hydrophilic WSOM fraction in different types of fresh Indonesian peatland burning particles. As far as we know, no previous HTDMA studies have conducted such intensive investigations on water uptake properties of a broad set of Indonesian peat samples, which possess different origins (e.g., Sumatra and Central Kalimantan) for various depths (i.e., surface ~ 5/10 cm, 10−20 cm, and 30−40 cm) and include different sample conditions (e.g., unburnt and disturbed). Thus, we do not consider that this study is a replication of a firmly established relationship. Rather, this study adds a critical dataset, which will serve as a base to investigate how the peatland fires influence human health, local environment, and the climate. We agree with the reviewer that repetition of existing studies would not have significant impacts. Experimental work on under-investigated yet important phenomena should never be underscored. We have added the following sentences to provide the significance of our study more clearly.

Page 17, Line 9: ‘*The last but not the least, our results can provide an experimentally validated reference for organics-dominated particle hygroscopicity, thus lowering uncertainties in current climate models and contributing to more accurate estimations of climate impacts caused by Indonesian peatland burning particles in both regional and global scales.*’

We agree with the reviewer that the empirical correlation between κ and f_{44} is already known. However, a theoretical background for the empirical relationship is still ambiguous. As stated in our response to R1C1, by relating κ to f_{44}, this study experimentally evidences the empirical assumption that more oxygenated organics generally correspond to higher water solubility, thus more hygroscopic. Our study suggests a more straightforward chemical composition-dependence, or rather solubility-dependence, of water uptake by organics than previous work. The manuscript was revised as follows to clarify this point.

Page 14, Line 19: '*Figure 8 shows a correlation of κ with f_{44} for both online (i.e., bulk organic matter) and offline (i.e., bulk WSOM and highly hydrophilic WSOM fraction) measurements of peat sampled at a burnt area (Riau-4), acacia and fern burning particles.*'

Page 14, Line 30: *'...f_{44} for the corresponding A_0 or A_1 sample are high. One notable difference of the correlation found in this work from previous studies is the inclusion of highly soluble fraction to the analysis. Although the κ - f_{44} correlations have been related to enhanced water solubility, the relationships among these three parameters (i.e., κ, f_{44}, and water solubility) have not been shown prior to this study.'*

The reviewer is right that the κ range of 0–0.1 has been commonly reported for water uptake properties of fresh smoldering biomass burning particles over the world. Considering that range of κ for pure organic compounds could vary only between 0 and 0.2 (except for oxalic acid), the variability is not negligible (Kuwata et al., 2013). In fact, the difference between $\kappa = 0$ and $\kappa = 0.1$ is physically significant, as the range includes both hydrophobic and generally hygroscopic particles. In our study, we show the corresponding κ ranges for three different particle sizes among various types of Indonesian biomasses for the first time. This enriches our understanding of the water uptake by fresh Indonesian peatland burning particles and provides a more reliable reference for climate models with consideration of the hygroscopicity of organics-dominated biomass burning particles especially in the tropical Asian regions.

As the reviewer has pointed out, NMR analysis has a great potential to improve our understanding on how different functional groups contribute to hygroscopic properties. Following descriptions were added to the revised manuscript so that the readers can qualitatively understand how the NMR data could be connected with hygroscopicity measurement.

Page 14, Line 11: *'... fern burning particles. Namely, the peat and acacia samples contain a significantly higher fraction of saturated aliphatic group (i.e., H-C; 71.7 % for peat, and 64.0 % for acacia) in comparison to that in the fern sample (38.6 %, see panel (a) of Figure S4), which readily prohibits the bulk hygroscopic growth of fresh peat burning particles. Besides, the highly polar structure (i.e., H-C-O) in the peat (6.0 %) and acacia (8.1 %) samples is distinctly lower than that in the fern sample (15.5 %, Figure S4(a)). This likely contributes to the higher WSOC fraction of fern burning particles, and the corresponding higher κ values could be related with the higher* f_{44} *and* f_{60}*.'*

R1C3: "Overall, the manuscript needs to be revised to demonstrate how the presented data advance the scientific understanding of biomass burning

aerosol (what new insight was learned and/or how it could be applied) and then re-reviewed.*”*

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.

Other comments

R1C4: pg. 8: “In all cases, narrow monodisperse distributions were observed”. This has to be evaluated against the width of a truly single component aerosol. The authors should compare the width of the distribution against some standard compound produced by atomization to support their point.

Response: We thank the reviewer for the useful comment. We have added the comparison of mean normalized particle number size distributions among five types of particles, i.e., 100 nm PSL particles (shortly, ‘PSL’) and ammonium sulfate (abbreviated as ‘AS’) during dry scans (RH < 10 %), and those observed for three types of Indonesian peatland burning particles (i.e., acacia, fern, and peat) following humidification (RH = 90 %), into the supplementary material (as displayed in Fig.S3 below).

It is obvious that the size distributions of selected 100 nm PSL and ammonium sulfate particles are monodispersed and mainly located within the size range of 90 – 120 nm. Size distributions of both peat and acacia burning particles are quite similar to those of PSL and ammonium sulfate particles, with a slightly wider size range of 90 – 130 nm. The fern burning particles tend to be more hygroscopic than peat and acacia burning particles and hence possess a wider size distribution ranging from 100 nm to 140 nm.

Page 9, Line 12: *'In all cases, narrow monodisperse distributions were observed (see Figure S3), demonstrating that chemical compositions of particles were uniform (Gysel et al., 2007; Carrico et al., 2010).'*

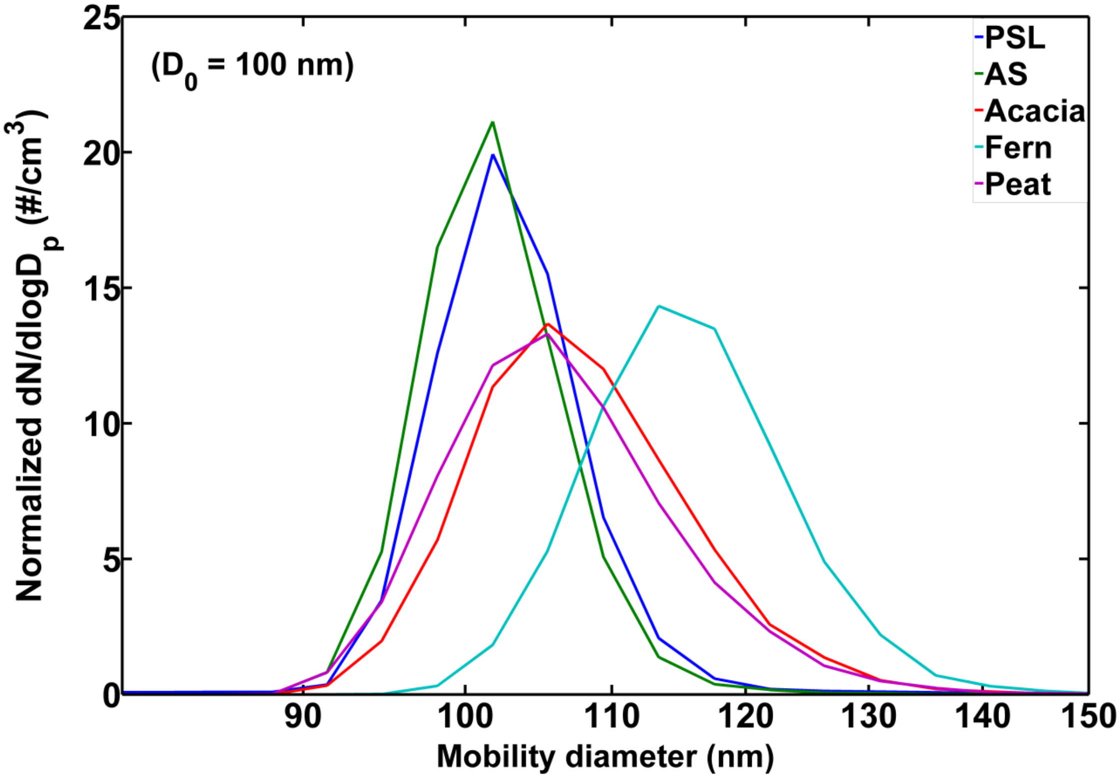

Fig. S3 *Normalized particle number size distributions of 100 nm PSL and ammonium sulfate (AS) particles under dry scans (RH < 10%), and of 100 nm peat, acacia, and fern burning particles following humidification (RH = 90%) measured with the HTDMA system.*

R1C5: pg. 10: It is unclear why Eq. (2) is provided. The data in the Table 2 appear to be calculated from the data. For a mix of compounds, the Eq. (2)

should be formulated for multiple components. Furthermore, Eq. (2) is only valid for infinitely soluble compounds. If the equation is used later, the relationship to solubility should be made clearer, especially in the context to the water and octanol extracts.

Response: We showed the equation (2), as it was employed to estimate κ from the experimental data of Asa-Awuku et al. (2008). The equation was not directly used for analysis of our data. The corresponding description was updated as follows so that the purpose of the equation will be clearer to the readers.

Page 10, Line 18: *'... temperature (298 K). The calculated κ results for our HTDMA measurements are summarized in Figure 3 and Table 2. It is worth noting that κ is related with molar volume of water soluble compounds (*M_s/ρ_s*), which is calculated from both the molecular weight (*M_s*) and density (*ρ_s*) by the following equation (Rose et al., 2008):*

$$\kappa = i_s \frac{\rho_s M_w}{\rho_w M_s}, \qquad (1)$$

where i is van't Hoff factor. This equation (2) was mainly employed to derive κ from the experimental data of Asa-Awuku et al. (2008), which has calculated the mean molar volume of WSOM extracted from biomass burning particles with a CCN measurement.'

R1C6: pg. 11: "the value of κ for acacia burning particles is similar to that was measured for WSOM extracted from a prescribed forest fire experiment in Georgia (USA) (κ = 0.10), which was estimated from a molar volume of 1.6×10^{-4} m^3 mol^{-1} (Asa-Awuku et al., 2008)." And "The κ value of biomass

burning WSOM separated by XAD-8 is estimated as 0.29, using molar volume (6.2×10^{-5} m^3 mol^{-1}) estimated from a CCN measurement by Asa-Awuku et al. (2008)." It is unclear what is meant here. Did Asa-Awuku measure water uptake or CCN and compute kappa? Did they measure (average) molecular weight and kappa is calculated from that? If so, what is the relevance? Please explain.

Response: Asa-Awuku et al. (2008) measured CCN activity, and estimated average molecular weight assuming surface tension of water and complete solubility. These values were used for the subsequent estimation of corresponding κ value. As discussed in Kuwata and Lee (2017), hydrophilic fraction separated by the 1-octanol-water partitioning method (volume ratio of 1-octanol:water = 1:1) has very similar properties as those classified by the XAD-8 column. The purpose of the description was to compare κ of hydrophilic faction of biomass burning particles measured by the present and previous studies. Following description was added to clarify this point.

Page 11, Line 23: *'...and 0.18 (fern), respectively. Although it is the first hygroscopic measurement for WSOM classified with 1-octanol-water liquid-liquid extraction technique, the value could be compared with those for hydrophilic fractions classified by XAD-8 column.'*

R1C7: pg. 12: (Lee et al., in preparation). I believe papers in preparation should not be cited in ACP articles.

Response: We have deleted the citation with the whole sentence.

Reference: Kuwata, M., and Lee, W.-C. (2017). 1-Octanol-Water Partitioning as a Classifier of Water Soluble Organic Materials: Implication for Solubility Distribution. Aerosol Sci. Technol., 51(5): 602-613.

Kuwata, M., Shao, W., Lebouteiller, R., and Martin, S. T. (2013). Classifying organic materials by oxygen-to-carbon elemental ratio to predict the activation regime of Cloud Condensation Nuclei (CCN). Atmos. Chem. Phys., 13(10): 5309-5324.

Psichoudaki, M., and Pandis, S. N. (2013). Atmospheric Aerosol Water-Soluble Organic Carbon Measurement: A Theoretical Analysis. Environ. Sci. & Technol., 47(17): 9791-9798.

Anonymous Referee #2

General comments:

R2C0: This is a very interesting study focusing on the water uptake of organic-dominated biomass burning aerosols in Indonesia. The very low hygroscopicity was attributed to the small fraction of water soluble organic matter. The authors also demonstrated the importance of biomass types in controlling the kappa and water soluble organic matter fraction and the role of highly oxygenated organic compounds in controlling aerosol hygroscopicity. Overall, it is a convincing study that may help improve our understanding on hygroscopicity of aerosol particles, especially organic aerosols. Previous work was properly referred and the paper was well written. I would recommend its publication if the authors could address a couple of minor issues listed below.

Response: We appreciate the reviewer's interest in our work and thanks for the supportive comments.

Other comments

R2C1: Based on correlations between WSOC fraction and kappa, the authors suggested the importance of WSOC fraction in determining kappa of organic aerosol particles. My question is if and how we can use the WSOC fraction and kappa of A_0 and A_1 aerosols to predict kappa, for example under the Zdanovskii, Stokes, and Robin (ZSR) assumption? Do we need additional information to improve the kappa prediction?

Response: We acknowledge the reviewer for the insightful comment. We agree with the reviewer that κ of biomass burning organic aerosol particles can be estimated using WSOC fraction (f_{WSOC}) and κ of WSOM (κ_{WSOM}) under some assumptions. These assumptions include thermodynamic approximations such as ZSR and volume additivity as well as relationships between chemical compositions of bulk and individual particles. For instance, we observed size-dependences in κ both for fresh burning and A_0 particles, suggesting that chemical composition was dependent on diameter. Although quantifications of f_{WSOC} and κ_{WSOM} provide useful insights into controlling factors of hygroscopic growth, approximations mentioned above also need to be considered for quantitative analysis. The fraction of $\mathrm{A_1}$ in $\mathrm{A_0}$ can be estimated using the approach proposed by Kuwata and Lee (2017). Even though separation of $\mathrm{A_1}$ is useful in obtaining chemical insights into how water uptake property is regulated, similar approximations still need to be applied for direct application. It is clarified in the revised manuscript as follows.

Page 15, Line 18: *'The present study demonstrates the importance of water-soluble organic fraction, which includes highly soluble one, in quantifying the hygroscopic growth of freshly emitted biomass burning particles. Addition of these different fractions could provide an accurate estimation on hygroscopic growth, which is based on theoretical background. Only size-unresolved bulk chemical data were employed for the present study. However, chemical characteristics of actual atmospheric particles could depend on both particle size and mixing state. These factors would also need to be considered in applying the laboratory data to future studies.'*

R2C2: Page 3 line 17, can the authors clarify how "hygroscopic" particles or "CCN-active" are defined here? Because a kappa of 0.02 was considered as hygroscopic while a higher kappa of 0.05 was considered as CCN inactive. Concerning the range of kappa in literature, a lower kappa of 0.01 has been reported for low-volatile biomass burning aerosol particles in Rose et al. (2008).

Reference: Rose, D., Gunthe, S. S., Su, H., Garland, R. M., Yang, H., Berghof, M., Cheng, Y. F., Wehner, B., Achtert, P., Nowak, A., Wiedensohler, A., Takegawa, N., Kondo, Y., Hu, M., Zhang, Y., Andreae, M. O., and Pöschl, U.: Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China – Part 2: Size-resolved aerosol chemical composition, diurnal cycles, and externally mixed weakly CCN-active soot particles.

Response: We appreciate the reviewer for pointing out this issue. In our original ACPD paper, we defined κ values lower than 0.01 as nearly hydrophobic under sub-saturated conditions. On the other hand, the CCN-inactive conclusion in Dusek et al.'s study (2005) was mainly drawn from the experimental result that size-resolved activation ratios of fresh Indonesian peat burning particles were generally lower than 50 % even for the measurements of large (diameter > 150 nm) particles under a high supersaturation of 1.64 %. The corresponding κ value of 0.05 for 100 nm particles was subsequently derived from the direct CCN measurements using the κ-Köhler model with an estimated critical supersaturation and an assumed surface tension equal to that of the air/pure water interface (i.e., 0.072 N m^{-1} at 25 °C). It should be noted that the actual κ value could be lower than 0.05 if surface tension of peat burning particles was lower than that for water, as organic particles with a lower surface tension are suggested to be more CCN-active (i.e., corresponding to a lower κ value) under a given supersaturation condition (Ovadnevaite et al., 2017). Nevertheless, this κ value (0.05) is still within the mean κ range (i.e., 0.02−0.06) for the 100 nm Indonesian peat burning particles as what we derived from the HTDMA measurements in this study, thus should be reliable.

In the revised manuscript, we have included the corresponding clarification into the introduction. Relevant details are provided in the discussion of hygroscopicity parameter results calculated from our laboratory measurements in Sect. 3.2.

Page 3, Line 30: *'and they were almost CCN inactive especially for particles larger than 150 nm (equivalent to $\kappa = 0.05$ for 100 nm particles, calculated with an assumed surface tension of 0.072 N m^{-1} at 25 °C) (Dusek et al., 2005).'*

Reference: Dusek, U., Frank, G. P., Helas, G., Iinuma, Y., Zeromskiene, K., Gwaze, P., Hennig, T., Massling, A., Schmid, O., Herrmann, H., Wiedensohler, A., Andreae, M. O. (2005). "Missing" cloud condensation nuclei in peat smoke. Geophys. Res. Lett., 32(11): L11802.

Ovadnevaite, J., Zuend, A., Laaksonen, A., Sanchez, K. J., Roberts, G., Ceburnis, D., Decesari, S., Rinaldi, M., Hodas, N., Facchini, M. C., Seinfeld, J. H., and O' Dowd, C. (2017). Surface tension prevails over solute effect in organic-influenced cloud droplet activation. Nature, 546(7660): 637-641.

Water Uptake by Fresh Indonesian Peat Burning Particles is Limited by Water Soluble Organic Matter

Jing Chen[1, *], Sri Hapsari Budisulistiorini[1], Masayuki Itoh[2], Wen-Chien Lee[1, 3], Takuma Miyakawa[4], Yuichi Komazaki[4], LiuDongQing Yang[1], and Mikinori Kuwata[1, 2, *]

[1] {Earth Observatory of Singapore, Nanyang Technological University, Singapore}

[2] {Center for Southeast Asian Studies, Kyoto University, Japan}

[3] {Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore}

[4] {Research and Development Center for Global Change, Japan Agency for Marine-Earth Science and Technology, Japan}

* Correspondence to: chen.jing@ntu.edu.sg; kuwata@ntu.edu.sg

Abstract

The relationship between hygroscopic properties and chemical characteristics of Indonesian biomass burning (BB) particles, which are dominantly generated from peatland fires, was investigated using the humidified tandem differential mobility analyzer. In addition to peat, acacia (a popular species at plantation) and fern (a pioneering species after disturbance by fire) were used for experiments. Fresh Indonesian peat burning particles are almost non-hygroscopic (mean hygroscopicity parameter, $\kappa < 0.06$) due to predominant contribution of water-insoluble organics. The range of κ spans from $\kappa = 0.02-0.04$ (dry diameter = 100 nm, hereinafter) for Riau peat burning particles, while that for Central Kalimantan ranges from $\kappa = 0.05-0.06$. Fern combustion particles are more hygroscopic ($\kappa = 0.08$), whereas the acacia burning particles have a mediate κ value (0.04). These results suggest that κ is significantly dependent on biomass types. This variance in κ is partially determined by fractions of water soluble organic carbon (WSOC), as demonstrated by a correlation analysis ($R = 0.65$). κ of water soluble organic matter is also quantified, incorporating the 1-octanol-water partitioning method. κ values for the water extracts are high, especially for peat burning particles (A_0 (a whole part of water-soluble fraction): $\kappa = 0.18$, A_1 (highly water-soluble fraction): $\kappa = 0.30$). This result stresses the importance of both WSOC fraction and κ of water soluble fraction in determining hygroscopicity of organic aerosol particles. Values of κ correlate positively ($R = 0.89$) with fraction of *m/z* 44 ion signal quantified using a mass spectrometric technique, demonstrating the importance of highly oxygenated organic compounds to the water uptake by Indonesian BB particles. These results provide an experimentally validated reference for hygroscopicity of organics-dominated particles, thus contributing to more accurate estimation of~~can be further utilized for investigating~~ environmental and climatic impacts ~~of~~ driven by Indonesian BB particles in both regional and global scales.

1. Introduction

In Southeast Asia, tropical peatland fires, which occur by combustion of both peat and vegetation, have become frequent during the last few decades (van der Werf et al., 2010; Reddington et al., 2014; Marlier et al., 2015; Spracklen et al., 2015; Stockwell et al., 2016). As one of the most important biomass burning types, t~~T~~he peatland fires keep smoldering for months, releasing huge amounts of greenhouse gases and fine particles to the atmosphere, impacting ~~the~~ atmospheric radiation (Levine et al., 1999; Page et al., 2002; van der Werf et al., 2010). In addition, the peatland burning particles cause transboundary air pollution, influencing visibility and human health (Kunii et al., 2002; Wang et al., 2004; Marlier et al., 2013; Crippa et al., 2016; Koplitz et al., 2016). These regional and global climate impacts have been commonly evaluated using different models (e.g., large eddy simulation (LES) and global climate models (GCMs)) but with large uncertainties likely due to the inaccurate estimation of cloud condensation nuclei (CCN) number concentration and subsequent cloud formation and precipitation processes (Mircea et al., 2005; Rose et al., 2010; Bougiatioti et al., 2016). One of the essential uncertainty contributors to the complex aerosol-cloud-precipitation interactions is~~are~~ ~~closely related with~~ water uptake properties of peatland burning particles, as water vapor alters aerosol physical and chemical characteristics, such as particle diameter.

Water uptake properties of biomass burning particles, including those emitted from peatlands, have been explored in laboratory through measurements of hygroscopic growth and CCN activity (Chand et al., 2005; Dusek et al., 2005; Day et al., 2006; Petters et al., 2009; Carrico et al., 2010; Dusek et al, 2011). In general, freshly emitted biomass burning particles have been found to be hygroscopic. For instance, the reported range of hygroscopicity parameter, κ, which serves as a metric for water uptake properties, varies from weakly (κ = 0.02) to highly hygroscopic (κ = 0.80) (Day et al., 2006; Petters and Kreidenweis, 2008; Petters et al., 2009; Carrico et al., 2010). A field observation of water uptake properties of Indonesian biomass burning plumes also demonstrated that these particles are hygroscopic, with a median hygroscopic growth in light scattering (f(RH)) of 1.65 between 20% and 80% relative humidity (RH) (Gras et al., 1999). On the other hand, freshly emitted Indonesian peat burning particles generated in a laboratory were suggested to be non-hygroscopic with respect to quite a low f(RH) = 1.05 at 90% RH (Chand et al., 2005), and they were almost CCN inactive especially for particles larger than 150 nm (equivalent to $\kappa = 0.05$ for 100 nm particles, calculated with an assumed surface tension of 0.072 N $\mathrm{m^{-1}}$ at 25 °C) (Dusek et al., 2005). The uniqueness of water uptake property of freshly emitted Indonesian peatland burning particles as well as the discrepancy between the previously reported laboratory and field data need to be consistently understood based on their chemical compositions for accurate evaluation on the environmental impacts.

Chemical composition of biomass burning particles, including these from Indonesian peatland fires, is dominated by a complex mixture of organic species (Jimenez et al., 2009; Ng et al., 2010; Cubison et al., 2011; Stockwell et al., 2016). The complexity in chemical composition inhibits understanding their water uptake properties at molecular levels (Asa-Awuku et al., 2008; Psichoudaki and Pandis, 2013; Riipinen et al., 2015). To overcome this difficulty, classification of organic compounds using multiple solvents (Carrico et al., 2008; Polidori et al., 2008; Chen et al., 2016), liquid-liquid extraction using 1-octanol and water (Kuwata and Lee, 2017), and solid phase extraction (Asa-Awuku et al., 2008) has been conducted. Functional group analysis of segregated organic matter has also been demonstrated as a strong tool to characterize complex mixture of organic compounds (Chen et al., 2016). For instance, chemical characteristics of water soluble organic matter (WSOM) have been intensively investigated, revealing that WSOM is predominantly consisted of levoglucosan-like species, carboxylic acids, aldehydes, ketones, aliphatic alcohols, and polyacids (Decesari et al., 2000; Peng et al., 2001; Suzuki et al., 2001; Mayol-Bracero et al., 2002; Chan et al., 2005; Psichoudaki and Pandis, 2013). Recently, the important roles of functional groups on water uptake properties were also investigated by both theoretical and experimental approaches (Suda et al., 2014; Petters et al., 2016).

In this study, hygroscopic growth of Indonesian peatland burning particles was investigated in a series of laboratory experiments to understand the relationships between water uptake properties and chemical characteristics. Hygroscopic growth of various types of fresh peat~~/biomass~~ burning particles, along with those originating from combustion of peatland dried plants, was measured using the humidified tandem differential mobility analyzer (HTDMA) ~~(Massling et al., 2003; Gysel et al., 2004; Carrico et al., 2008, 2010; Dusek et al., 2011)~~ for the first time. Chemical characterization was also conducted using the Aerodyne Time of Flight-Aerosol Chemical Speciation Monitor (ToF-ACSM). In addition, ratios of water soluble organic carbon (WSOC) to organic carbon (OC) were quantified. The concurrent HTDMA and ToF-ACSM measurements were also ~~conducted~~ performed for the bulk WSOM ~~fraction~~and its highly hydrophilic fraction classified with the 1-octanol-water partitioning method in terms of water solubility (Kuwata and Lee, 2017). ~~Furthermore, WSOM was fractionated by the 1-octanol-water partitioning method, providing data on hydrophilic fraction (Kuwata and Lee, 2017).~~ This method provides a new angle (i.e., water solubility) to characterize chemical properties of WSOM, facilitating a more detailed investigation on particle water uptake property with the first application of the method in HTDMA measurements of highly hydrophilic organic fraction. These data were synergistically combined to provide a detailed picture on water uptake properties of freshly emitted Indonesian peatland burning particles.

2. Experiment

2.1. Combustion setup

Figure 1(a) shows the experimental setup. Peat and biomass samples were collected at peatlands in Riau and Central Kalimantan provinces in Indonesia (Table 1). The sampling sites include both burnt and undisturbed forest areas. In this region, peatland fire frequently reoccurs, and vast areas are experiencing regeneration of vegetation after fire events. The peat samples were segregated for different sampling depths, as detailed in Table 1. Two other types of biomasses from Riau, including *pteridium aquilinum* (called as fern here) and leaves of *acacia mangium* (abbreviated as acacia), were also employed for the experiment. Fern is one of the major pioneer species after peatland fires (Aswin et al., 2004). Acacia is one of the representative trees for plantations over drained peatland. Both acacia and fern samples were dried at ambient temperature after sampling. Further detailed information on the biomass samples is available in Budisulistiorini et al. (2017).

The biomass samples were used without desiccation. Approximately 1.0 g of biomass sample was combusted in a sealed 100 L stainless steel container using a crucible, which was heated at 350 °C by a ribbon heater, thermocouple, and PID controller (Kuwata et al., 2017). The target heating temperature was normally achieved within 2 − 3 min. Visual inspection confirmed that the combustion condition was mostly smoldering, consistent with a previous report (Usup et al., 2004). Particle-free air was continuously supplied to the container. Excess amount of particle-free air was released to the laboratory, allowing conducting the experiments at room pressure. Particles generated by the burning experiments were diluted by a two-stage dilution system. Size distributions of biomass burning particles were measured using the Scanning Mobility Particle Sizer (SMPS, TSI Inc.). The measurement range of the SMPS was set as 14.6 − 685.4 nm, and time resolution was 3-min. Chemical compositions of particles were quantified using the Aerodyne ToF-ACSM (Fröhlich et al., 2013), while water uptake property was measured using the HTDMA (Massling et al., 2003, 2007; Duplissy et al., 2009). Online instruments such as SMPS, ToF-ACSM, and HTDMA were all operated following the dilution. Each combustion experiment lasted for ~ 1 h. Detailed descriptions about the ToF-ACSM and HTDMA are provided in the following sections.

Two filter samples were also collected simultaneously for each of the experiments. Particles were collected onto two 47 mm diameter filters housed in stainless steel filter holders (BGI Inc.) for half an hour at flowrates of 5.0 lpm. Teflon filters (0.2 µm pore size, Fluoropore™, Sigma Aldrich) were used for WSOM samples, while quartz filter samples were employed for carbon analysis by the thermal-optical method. The collected samples were stored under refrigeration at −20 °C until analysis.

2.2. Extraction and nebulization of WSOM

Filter samples were extracted using approximately 20 ml of ultrapure water (Type I) by sonicating them for 30-min at room temperature. The resulting solutions were filtered through 0.2 µm PTFE syringe filters (514-0070, VWR), yielding water extracts (denoted as A_0, i.e., a whole part of or bulk water-soluble fraction). An aliquot of A_0 was mixed with the same volume (5 ml) of 1-octanol (Wako first grade, Wako) using a separatory funnel for classification by 1-octanol-water extraction (Valvani et al., 1981). The aqueous phase following the 1-octanol-water extraction is denoted as A_1 (slightly less than 5 ml), corresponding to the highly water-soluble fraction. Details of the extraction method are provided in Kuwata and Lee (2017).

The aqueous solutions were nebulized using a glass nebulizer. A mass flow controller (MC-20 SLPM-D, Alicat Scientific, Inc.) was used to regulate the flow rate (3.5 lpm) of particle-free air supplied to the nebulizer. Following nebulization, the sample was desiccated by a diffusion dryer (Model 42000, Brechtel Manufacturing, Inc.) filled with silica gel (Chameleon 83000.360, VWR International). The desiccated particles were measured using the HTDMA, ToF-ACSM, and SMPS. The analysis of A_0 and A_1 were conducted only for peat (sampled from a burnt area, Riau-4), acacia, and fern samples.

2.3. HTDMA

Hygroscopic growth of particles was measured using the HTDMA (Massling et al., 2003, 2007; Duplissy et al., 2009; Gysel et al., 2009). The HTDMA system consists of three major components: 1) the first DMA (TSI Inc. Model 3081) to select monodisperse particles of a specific diameter, 2) the humidification unit for hydrating the classified particles at a target RH, and 3) the second DMA (TSI Inc. Model 3081) and a condensation particle counter (CPC, TSI Inc. Model 3775) to detect humidified size distributions (Figure S1).

Aerosol particles were dried using a diffusion dryer (Model 42000, Brechtel Manufacturing, Inc.), and introduced to the first DMA at a flow rate of 0.3 lpm. The first DMA selected 50, 100, and 200 nm particles. Both the first and second DMAs were operated at sheath-to-sample flow ratios of 10:1. The resulting monodisperse particles were exposed to a predefined RH environment using two Nafion membrane tubes (Permapure Inc. Model MD-110-12S-4) in series. The target RH, which was set at 90%, was regulated by controlling the flow ratio of humidified and dry air flows via a PID controlling software (National Instruments Inc. Labview). The particle residence time between the humidifier and the second DMA was approximately 10 seconds. The RH-controlled humid air was used as the sheath flow for the second DMA. The RH and temperature of the second DMA were continuously monitored at both the sample inlet and sheath outlet using two capacitive RH and temperature probes (Rotronic Inc. Hygroclip HC2-S). The RH differences between the sample and sheath flows were less than 2%. RH of humidified sample air was slightly higher than that of the sheath outflow for the setup shown in Figure S1.

The operating conditions of the DMAs were checked using 100 ± 3 nm polystyrene latex particles (PSL, Thermo Scientific Inc., Cat. No.: 3100A). Hygroscopic growth of particles in the HTDMA was calibrated by measuring growth factor (g), which is defined as a diameter ratio of humidified (D(RH)) and dry particles (D_0) ($g = (D(RH)/D_0$), of ammonium sulfate particles.

The measured value of g at RH = 85% was 1.71 (D_0 = 150 nm), which is comparable to a literature data (g = 1.69) (Tang and Munkelwitz, 1994). The stability of detected RH of the HTDMA system was within ± 1.0% RH (peak-to-peak) for the target RH of 90% (see Figure S2). A volume mean growth factor (GF) was calculated using measured probability density function of g (i.e., $c(g, D_0)$) as $GF = (\int_0^\infty g^3 c(g, D_0) dg)^{1/3}$.

2.4. Chemical characterization

The Aerodyne ToF-ACSM was utilized to measure chemical compositions of non-refractory submicron particles (NR-PM_1) (Fröhlich et al., 2013). Five specific chemical components, including organic matter (OM), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and chloride (Cl^-), were quantitatively detected (Allan et al., 2003), with a time resolution of 3-min.

Bulk OC, elemental carbon (EC), and WSOC contents were also analyzed for 10 samples (Table 3) using quartz-fiber filter samples (47 mm in diameter). All the quartz-fiber filters were prebaked at 900 ºC for 3 h before sampling. The filter samples were stored in a refrigerator (−20 °C) until analysis. For each sampling, a back-up quartz-fiber filter was used to account for potential influence of adsorption of gas phase organic components (Turpin et al., 1994). OC loading on the back-up filter was subtracted from that on the front filter to estimate particulate OC (i.e., corrected OC).

OC and EC were analyzed by thermal-optical reflectance analysis (Chow et al., 1993) using a Sunset Laboratory OC/EC Analyzer, following the IMPROVE-A protocol. WSOC was quantified with a Sievers 800 Total Organic Carbon (TOC) Analyzer after extraction of biomass burning filter samples by water. A portion (8 mm φ) of each WSOC sample was extracted using 10 ml of HPLC-grade water. The samples were shaken by an orbital shaker for 21 h. The extracted sample solutions were filtered with syringe filters (pore size of 0.2 µm) prior to injection to the TOC analyzer. The particulate WSOC of peat burning particles was also corrected following the similar procedure to that of particulate OC.

3. Results and discussion

Both the HTDMA and chemical analysis data are summarized in Table 2 and 3. The ToF-ACSM and OC/EC data (Table 3) demonstrate that chemical composition of submicron biomass burning particles is dominated by organic species, accounting for approximately 99% in mass (Budisulistiorini et al., 2017). Contributions of other species, including inorganic ionic species and EC, were minimal. In the following, the relationships between hygroscopic property and chemical characteristics of organic species are discussed.

3.1. Hygroscopic growth factor

Figure 2 shows normalized particle number size distributions of peat sampled from a burnt area (Riau-4), acacia leaves, and fern burning particles following hygroscopic growth at RH = 90% (D_0 = 100 nm). The data shown in Figure 2 include both online (a) and offline ((b): A_0, and (c): A_1)) measurements. In all cases, narrow monodisperse distributions were observed (see Figure S3), demonstrating that chemical compositions of particles were uniform (Gysel et al., 2007; Carrico et al., 2010). For online measurements, diameter change induced by hygroscopic growth was minimal for the peat and acacia burning particles (g = 1.05 ~ 1.09), while diameter of fern burning particles significantly increased following exposure to high RH (g = 1.17). The variation in hygroscopic properties is attributed to differences in organic chemical composition, as these biomass burning particles contain negligible fractions of inorganic ionic species (Budisulistiorini et al., 2017).

Table 2 summarizes all the values of GF. Values of GF for most of peat samples from burnt peatland in Riau were less than 1.1. Sampling depths of peat did not significantly affect GF. There was no clear size-dependence of GF. For instance, GF values of particles from combustion of peat at drained and burnt areas in Riau were 1.07 ± 0.04 (D_0 = 50 nm), 1.06 ± 0.02 (D_0 = 100 nm), and 1.07 ± 0.02 (D_0 = 200 nm). Particles emitted from the undisturbed forest area in Riau (i.e., Riau-Zam) were more hygroscopic (GF = 1.11 for D_0 = 100 nm) than those generated from other samples from Riau, while GF of particles emitted by combustion of a peat sample from the secondary forest in Riau (i.e., Riau-SF) was very similar to those from Riau peat samples from burnt areas (i.e., Riau-1~4). The similarity is probably due to the short distance between the two sampling sites (less than 10 km). Particles emitted from peat samples collected at Central Kalimantan (i.e., C.K.-DB and C.K.-DF) were relatively more hygroscopic (GF > 1.11) than those from Riau.

Hygroscopic growth of bulk water-soluble fraction (A_0) is much more significant than those of the online measurements. Specifically, the mean diameter growth factors were 1.34 (peat sampled from a burnt area, Riau-4), 1.23, (acacia), and 1.28 (fern) for 100 nm particles. The significant hygroscopic growth of A_0 from peat burning particles could be due to high water uptake by the highly water-soluble fraction, A_1 (GF = 1.50). The GFs of A_1 for acacia and fern burning particles were 1.42 and 1.33, respectively. Although water uptake by fresh peat burning particles was much less than those of vegetation burning particles, the water soluble fraction of peat burning particles was the most hygroscopic. This result stresses the importance of understanding hygroscopic properties of WSOM as well as WSOC fraction in total OC.

3.2. Hygroscopicity parameter (*κ*)

Hygroscopicity parameter (κ) was calculated using the κ–Köhler theory (Petters and Kreidenweis, 2007):

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

where $\sigma_{s/a}$ is the surface tension of the solution/air interface (0.0718 N m^{-1} at 25 °C), Mw is the molecular weight of water (18 g mol^{-1}), ρ_w is the density of water (1.0 g cm^{-3}), R is the universal gas constant (8.31 J K^{-1} mol^{-1}) and T is temperature (298 K). The calculated κ results for our HTDMA measurements are summarized in Figure 3 and Table 2. It is worth noting that κ is related with molar volume of water soluble compounds (M_s/ρ_s), which is calculated from both the molecular weight (M_s) and density (ρ_s) by the following equation (Rose et al., 2008):

$$\kappa = i_s \frac{\rho_s M_w}{\rho_w M_s}, \tag{2}$$

where i is van't Hoff factor. This equation (2) was mainly employed to derive κ from the experimental data of Asa-Awuku et al. (2008), which has calculated the mean molar volume of WSOM extracted from biomass burning particles with a CCN measurement.

The range of κ for peat burning particles in Riau (sampled from burnt areas) is 0.02 to 0.04, while that for Central Kalimantan samples is 0.05 to 0.06 (100 nm). These values may be compared with CCN activity of peat burning particles reported by Dusek et al. (2005). Based on the experimental data by Dusek et al. (2005), the critical supersaturation for CCN activation of Indonesian peat burning particles is derived as 0.53% for 100 nm particles. This value can be converted to κ of 0.05, which is very similar to the values summarized in Figure 3 and Table 2. The consistently low values of κ suggest that water uptake by freshly emitted peat burning particles is minimal. The range of κ observed for acacia and fern burning particles ($\kappa = 0.04-0.08$) is comparable to that observed for less hygroscopic mode by previous laboratory experiments on biomass burning particles (Carrico et al., 2010).

The values of κ observed for water extracts (A_0) span from 0.11 (acacia, 100 nm) to 0.18 (peat sampled from a burnt area, Riau-4, 100 nm) (Figure 4 and Table 2). The κ value for peat burning particles (A_0) is significantly higher than those emitted from the acacia and fern leaves, highlighting the importance of understanding hygroscopicity of WSOM as well as water soluble fraction in quantitatively understanding water uptake properties. The value of κ for acacia burning particles is similar to that was measured for WSOM extracted from a prescribed forest fire experiment in Georgia (USA) ($\kappa = 0.10$), which was estimated from a molar volume of 1.6×10^{-4} m^3 mol^{-1} (Asa-Awuku et al., 2008).

The κ values for A_1 are higher than those for A_0. Namely, κ observed for A_1 were 0.30 (peat sampled from a burnt area, Riau-4), 0.24 (acacia), and 0.18 (fern), respectively. Although it is the first hygroscopic measurement for WSOM classified with 1-octanol-water liquid-liquid extraction technique, the value could be compared with those for hydrophilic fractions classified by XAD-8 column. Kuwata and Lee (2017) demonstrated that classification of WSOM by XAD-8 column, which is one of the most frequently used materials for solid phase extraction of WSOM, has a strong relationship with 1-octanol-water partitioning coefficient (K_{OW}). Namely, XAD-8 column selectively traps hydrophobic chemical species in WSOM, which tend to partition to 1-octanol phase ($K_{OW} > 1$). Thus, hydrophilic fraction separated by XAD-8 is dominantly composed of chemical species, which has $K_{OW} < 1$. The WSOM in A_1 is also dominantly composed of organic compounds with lower values of K_{OW} ($K_{OW} < 1$), suggesting that A_1 and WSOM classified by XAD-8 are comparable. The κ value of biomass burning WSOM separated by XAD-8 is estimated as 0.29, using molar volume (6.2×10^{-5} m^3 mol^{-1}) estimated from a CCN measurement by Asa-Awuku et al. (2008). The comparison provides a typical range of κ for hydrophilic ($K_{OW} < 1$) fraction of WSOM emitted from biomass burning as 0.2~0.3. Our results of water uptake by organic compounds (e.g., bulk organic material, bulk WSOM, and highly hydrophilic WSOM) would be further employed to verify a theoretical framework, which uses distributions of water solubility as input parameters (Riipinen et al., 2015).

3.3. κ (online) and WSOC/OC

WSOC/OC ratios of Indonesian peat and vegetation burning particles are summarized in Table 3. In general, WSOC/OC ratios for peat burning particles from the burnt area in Riau are small, ranging from 0.93% to 1.80%. Particles emitted from combustion of peat collected in other areas tend to contain higher fractions of WSOC (WSOC/OC = 2.03−6.08%). The variability in WSOC/OC ratio could be due to differences in chemical composition of peat sampled at different areas (Hikmatullah and Sukarman, 2014). These values are an order of magnitude lower than the experimental data by Iinuma et al. (2007), which reported WSOC/OC ratio for Indonesian peat burning particles from South Sumatra as 39%. The significant difference in WSOC/OC ratio could be stemmed from the variations in chemical compositions of peat as well as combustion conditions. Both a systematic laboratory experiment and chemical analysis of freshly emitted peat burning particles are needed to address the difference in the data. The WSOC fractions for acacia and fern burning particles were relatively higher (WSOC/OC = 3.42−6.56%) than those from peat combustion.

Figure 5 compares κ and WSOC/OC ratios. κ and WSOC/OC correlate to some extent (R = 0.65), although the variation ranges for both variables are small. Fern burning particles contain significantly higher fraction of WSOM than other samples, providing an explanation for higher κ value for fern burning particles. Nevertheless, the correlation between these two parameters is not tight. This result suggests that other factors, such as chemical composition and hygroscopic property of water soluble fraction, should also be considered to quantitatively understand water uptake property.

3.4. *κ* and OM mass spectra

Figure 6 shows the ToF-ACSM mass spectra for online, A_0, and A_1 particles, including those from peat (sampled at a burnt area, Riau-4), acacia and fern burning. The online mass spectra have intense signals at *m/z* 41 ($C_3H_5^+$), 43 (most likely $C_3H_7^+$), 55 ($C_4H_7^+$) and 57 ($C_4H_9^+$), suggesting that these particles are highly hydrogenated (Canagaratna et al., 2015). On the other hand, fractions of ions at *m/z* 44 (f_{44}, mostly CO_2^+) are limited ($f_{44} < 0.02$), especially for peat burning particles. This result signifies that the freshly emitted Indonesian biomass burning particles, especially those from peat, are not highly oxygenated (Ng et al., 2011). This is in accordance with a previous study, which showed that f_{44} values for primary hydrocarbon-like organic compounds are usually less than 0.05 (Ng et al., 2011). In addition, *m/z* 60 and *m/z* 73 (mainly from $C_2H_4O_2^+$ and $C_3H_5O_2^+$, respectively), marker ions of levoglucosan-like species (a tracer for cellulose in biomass burning particles) (Simoneit et al., 1999; Cubison et al., 2011), were especially pronounced for fern burning particles.~~ These results are also supported by functional group analysis by proton nuclear magnetic resonance (^{1}H NMR) technique, which contains strong signals originated from levoglucosan-like species (Lee et al., in preparation).~~

The mass spectra of A_0 are significantly different from those of online measurements. The most abundant ion in the mass spectra of A_0 is *m/z* 44. Hydrocarbon peaks, such as *m/z* 41, 43, 55, and 57, are still significant, yet less abundant than those of the online measurements. In addition, contributions of *m/z* 60 and 73 are also enhanced. These results consistently support the idea that A_0 fraction is highly oxygenated. Especially, A_0 fraction for peat burning particles is much more oxidized than those of fern and acacia samples.

The mass spectra of A_1 from acacia and fern burning show that the A_1 fraction is more oxidized than A_0, as indicated by higher values of f_{44}. For instance, f_{44} of A_1 from fern burning particles is 0.08, while that of A_0 is 0.05. Another notable characteristic of A_1 mass spectra is the smaller fraction of high molecular weight (HMW) ions, which is observed for the region of *m/z* > 100. The HMW fractions (f_{HMW}) for A_0 and A_1 are 15.8% and 16.0% (peat sampled at a burnt area, Riau-4), 21.8% and 11.6% (acacia), and 17.4% and 8.2% (fern), which are significantly lower than the corresponding values for online measurements (Table 3). These results suggest that A_1 contains lower fractions of high molecular weight species, although decomposition during ionization process makes the estimation of actual contributions of these compounds difficult.

Figure 7 displays f_{44}, f_{60}, and mean κ for different types of Indonesian biomass burning particles. The data points in Figure 7 distribute to two different regions. Low f_{44} and f_{60} values are observed for particles emitted from Sumatran peat burning (i.e., Riau-1, -2, -3, -4). The f_{44} of acacia burning particles is slightly higher but f_{60} is low. By contrast, distinctly higher f_{44} and f_{60} are observed for fern, undisturbed peat (Riau), and peat (Central Kalimantan) burning particles. This is also in accordance with the proton nuclear magnetic resonance (^{1}H NMR) ~~^{1}H NMR~~ analysis, which suggests that functional group distributions of peat and acacia burning particles are significantly different from that emitted from fern burning particles. Namely, the peat and acacia samples contain a significantly higher fraction of saturated aliphatic group (i.e., H-C; 71.7 % for peat, and 64.0 % for acacia) in comparison to that of the fern sample (38.6 %, see panel (a) of Figure S4), which readily prohibits the bulk hygroscopic growth of fresh peat burning particles. Besides, the highly polar structure (i.e., H-C-O) in the peat (6.0 %) and acacia (8.1 %) samples is distinctly lower than that in the fern sample (15.5 %, Figure ~~S3~~S4(a)). This likely contributes to t~~T~~he higher WSOC fraction ~~and κ~~ of fern burning particles, and the corresponding higher κ values could be related with the higher f_{44} and f_{60}.

Figure 8 shows a ~~correlates~~ correlation of κ with f_{44} for both online (i.e., bulk organic matter) and offline (i.e., bulk WSOM and highly hydrophilic WSOM fraction) measurements of peat sampled at a burnt area (Riau-4), acacia and fern burning particles. Similar correlations for all the biomass burning samples are displayed in Figure ~~S4~~ S5 of the supplementary material. The correlation of these two variables is represented as $\kappa = 2.31 \times f_{44} + 0.02$ (R = 0.89). The slope is very close to that reported for the relationship between the hygroscopicity of organics (κ_{org}) and f_{44} ($\kappa_{org} = 2.2 \times f_{44} - 0.13$, Duplissy et al., 2011). The correlation demonstrates that the degree of oxidation, which is represented by f_{44}, is the key controlling parameter in determining hygroscopicity of Indonesian peatland burning particles. As discussed above, f_{44} of peat burning particles (Riau-4) is extremely small (Table 3). Minimal water uptake by peat burning particles (Riau-4) could be associated with low water-soluble fraction (Table 3), considering that both κ and f_{44} for the corresponding A_0 or A_1 sample are high. One notable difference of the correlation found in this work from previous studies is the inclusion of highly soluble fraction to the analysis. Although the κ - f_{44} correlations have been related to enhanced water solubility, the relationships among these three parameters (i.e., κ, f_{44}, and water solubility) have not been shown prior to this study.

The correlation shown in Figure 8 has a significant divergence, especially at the region for high f_{44} and κ values (upper right corner of the figure), suggesting that degree of oxidation is not the only one parameter, which controls water uptake property. Especially, comparison of A_0 and A_1 for peat burning particles highlights the limitation of correlating f_{44} and κ. The values of f_{44} for these two fractions are almost the same, while κ for A_1 is significantly higher than that for A_0. As discussed in section 3.2, the difference of A_0 and A_1 could be related to that of hydrophobic and hydrophilic WSOM separated by XAD-8 (Graber and Rudich, 2006; Sullivan and Weber, 2006). The hydrophobic fraction separated by XAD-8 is typically considered as humic-like substances (HULIS), which has high molecular weight (e.g., fulvic and humic acids, Gysel et al., 2004; Graber and Rudich, 2006; Fan et al., 2013). These results suggest that quantification of HULIS as well as evaluation of their water uptake property will be important for understanding hygroscopicity of biomass burning particles, including those emitted from Indonesian peatland fires.

The present study demonstrates the importance of water-soluble organic fraction, which includes highly soluble one, in quantifying the hygroscopic growth of freshly emitted biomass burning particles. Addition of these different water-soluble organic fractions could provide an accurate estimation on hygroscopic growth, which is based on theoretical background. Only size-unresolved bulk chemical data were employed for the present study. However, chemical characteristics of actual atmospheric particles could depend on both particle size and mixing state. These factors would also need to be considered in applying the laboratory data to future studies.

4. Conclusions

Hygroscopic growth of freshly emitted Indonesian biomass burning particles was investigated in laboratory using the humidified tandem differential mobility analyzer (RH = 90%). The biomass samples included peat, fern, and acacia leaves collected at Riau and Central Kalimantan in Indonesia. Hygroscopicity was measured for the freshly emitted particles (online), bulk water-soluble fraction (A_0), and highly water-soluble fraction (i.e., fraction with lower K_{OW} values) classified by the 1-octanol-water partitioning method (A_1). Hygroscopicity parameter κ was derived from the growth factor data. Chemical compositions of these particles were also quantified using both online and offline techniques.

Hygroscopicity of fresh Indonesian peat burning particles is highly dependent on the origin and condition (e.g., pristine and disturbed) of peat. Particles emitted from combustion of disturbed peat in Riau were nearly non-hygroscopic (mean $\kappa = 0.02-0.04$), while those from undisturbed areas were more hygroscopic ($\kappa = 0.03-0.05$). Particles emitted from Central Kalimantan peat samples were generally more hygroscopic ($\kappa = 0.05-0.06$) than those from Riau. For biomass samples, acacia burning particles were slightly hygroscopic ($\kappa = 0.03-0.04$), and fern burning particles were the most hygroscopic ($\kappa = 0.04-0.09$) among all samples. These values loosely correlated with ratio of WSOC to OC ($R = 0.65$). This result suggests that WSOC fraction could play an important role in determining κ, yet other factors, such as difference in hygroscopicity of slightly and highly water-soluble fractions, should also be considered.

Hygroscopicity data of A_0 and A_1 fractions were significantly different from those of online measurements. The values of κ for A_0 were 0.17−0.20 (Riau disturbed peat), 0.09−0.14 (acacia), and 0.10−0.16 (fern). These values were even higher for A_1 ($\kappa = 0.26-0.31$ for Riau disturbed peat, $\kappa = 0.19-0.24$ for acacia, and $\kappa = 0.16-0.20$ for fern). These results demonstrate that the low hygroscopicity of Riau peat burning particles (online) is due to small water soluble fraction.

The variation in κ was related with aerosol mass spectra of organics. f_{44}, which is an indicator for degree of oxygenation, correlated well with κ ($R = 0.89$), demonstrating that oxygenated functional groups are important for water uptake. In addition, comparison of A_0 and A_1 data suggested the importance of high molecular weight species, such as humic-like substances, in determining the magnitude of hygroscopicity for water soluble fraction.

Our experimental results are consistent with previous laboratory studies, which reported insignificant water uptake by fresh Indonesian peat burning particle (Chand et al., 2005; Dusek et al, 2005). On the contrary, Gras et al. (1999) showed that particles observed in wildfire plume from Kalimantan were hygroscopic. The differences between field observation and laboratory experiments could be caused by atmospheric processes (e.g., secondary formation and chemical aging of particles), and likely resulted from the differences of burnt materials, their origins and combustion conditions in practical situations as well. In the future, observations of both chemical composition and hygroscopic growth of particles emitted from peatland fires need to be conducted both at vicinity and downstream regions to address the question. The last but not the least, our results can provide an experimentally validated reference for organics-dominated particle hygroscopicity, thus lowering uncertainties in current climate models and contributing to more accurate estimations of climate impacts caused by Indonesian peatland burning particles in both regional and global scales.~~results obtained from this work can be further developed and applied for modeling studies, improving estimation of aerosol radiative forcing introduced by Indonesian peat burning particles in both regional and global scales.~~

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References

Allan, J. D., Jimenez, J. L., Williams, P. I., Alfarra, M. R., Bower, K. N., Jayne, J. T., Coe, H., Worsnop, D. R. (2003). Quantitative sampling using an Aerodyne aerosol mass spectrometer 1. Techniques of data interpretation and error analysis. J. Geophys. Res. Atmos., 108: 4090.

Asa-Awuku, A., Sullivan, A. P., Hennigan, C. J., Weber, R. J., Nenes, A. (2008). Investigation of molar volume and surfactant characteristics of water-soluble organic compounds in biomass burning aerosol. Atmos. Chem. Phys., 8: 799-812.

Aswin, U., Hashimoto, Y., Takahashi, H., and Hayasaka, H. (2004). Combustion and thermal characteristics of peat fire in tropical peatland in Central Kalimantan, Indonesia. Tropics, 14: 1-19.

Bougiatioti, A., Bezantakos, S., Stavroulas, I., Kalivitis, N., Kokkalis, P., Biskos, G., Mihalopoulos, N., Papayannis, A., and Nenes, A. (2016). Biomass-burning impact on CCN number, hygroscopicity and cloud formation during summertime in the eastern Mediterranean. Atmos. Chem. Phys., 16: 7389-7409.

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.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R. (2015). Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications. Atmos. Chem. Phys., 15: 253-272.

Carrico, C. M., Petters, M. D., Kreidenweis, S. M., Sullivan, A. P., McMeeking, G. R., Levin, E. J. T., Engling, G., Malm, W. C., and Collett Jr., J. L. (2010). Water uptake and chemical composition of fresh aerosols generated in open burning of biomass. Atmos. Chem. Phys., 10: 5165–5178.

Carrico, C. M., Petters, M. D., Kreidenweis, S. M., Collett Jr., J. L., Engling, G., Malm, W. C. (2008). Aerosol hygroscopicity and cloud droplet activation of extracts of filters from biomass burning experiments. J. Geophys. Res. Atmos., 113: D08206.

Chan, M. N., Choi, M. Y., Ng, N. L., Chan, C. K. (2005). Hygroscopicity of Water-Soluble Organic Compounds in Atmospheric Aerosols: Amino Acids and Biomass Burning Derived Organic Species. Environ. Sci. & Technol., 39: 1555-1562.

Chand, D., Schmid, O., Gwaze, P., Parmar, R. S., Helas, G., Zeromskiene, K., Wiedensohler, A., Massling, A., Andreae, M. O. (2005). Laboratory measurements of smoke optical properties from the burning of Indonesian peat and other types of biomass. Geophys. Res. Lett., 32: L12819.

Chen, Q., Ikemori, F., Higo, H., Asakawa, D., and Mochida, M. (2016). Chemical Structural Characteristics of HULIS and Other Fractionated Organic Matter in Urban Aerosols: Results from Mass Spectral and FT-IR Analysis. Environ. Sci. & Technol., 50, 1721-1730.

Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G. (1993): The DRI Thermal/Optical Reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies, Atmos. Environ., 27A, 1185–1201.

Crippa, P., Castruccio, S., Archer-Nicholls, S., Lebron, G. B., Kuwata, M., Thota, A., Sumin, S., Butt, E., Wiedinmyer, C., Spracklen, D. V. (2016). Population exposure to hazardous air quality due to the 2015 fires in Equatorial Asia. Sci. Rep., 6: 37074.

Cubison, M. J., Ortega, A. M., Hayes, P. L., Farmer, D. K., Day, D., Lechner, M. J., Brune, W. H., Apel, E., Diskin, G. S., Fisher, J. A., Fuelberg, H. E., Hecobian, A., Knapp, D. J., Mikoviny, T., Riemer, D., Sachse, G. W., Sessions, W., Weber, R. J., Weinheimer, A. J., Wisthaler, A., Jimenez, J. L. (2011). Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies. Atmos. Chem. Phys., 11: 12049-12064.

Day, D. E., Hand, J. L., Carrico, C. M., Engling, G., Malm, W. C. (2006). Humidification factors from laboratory studies of fresh smoke from biomass fuels. J. Geophys. Res. Atmos., 111, D22202.

Decesari, S., Facchini, M. C., Fuzzi, S., Tagliavini, E. (2000). Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach. J. Geophys. Res. Atmos., 105: 1481-1489.

Duplissy, J., DeCarlo, P. F., Dommen, J., Alfarra, M. R., Metzger, A., Barmpadimos, I., Prevot, A. S. H., Weingartner, E., Tritscher, T., Gysel, M., Aiken, A. C., Jimenez, J. L., Canagaratna, M. R., Worsnop, D. R., Collins, D. R., Tomlinson, J., Baltensperger, U. (2011). Relating hygroscopicity and composition of organic aerosol particulate matter. Atmos. Chem. Phys., 11: 1155-1165.

Duplissy, J., Gysel, M., Sjogren, S., Meyer, N., Good, N., Kammermann, L., Michaud, V., Weigel, R., Martins dos Santos, S., Gruening, C., Villani, P., Laj, P., Sellegri, K., Metzger, A., McFiggans, G. B., Wehrle, G., Richter, R., Dommen, J., Ristovski, Z., Baltensperger, U., Weingartner, E. (2009). Intercomparison study of six HTDMAs: results and recommendations. Atmos. Meas. Tech., 2: 363–378.

Dusek, U., Frank, G. P., Helas, G., Iinuma, Y., Zeromskiene, K., Gwaze, P., Hennig, T., Massling, A., Schmid, O., Herrmann, H., Wiedensohler, A., Andreae, M. O. (2005). “Missing” cloud condensation nuclei in peat smoke. Geophys. Res. Lett., 32: L11802.

Dusek, U., Frank, G. P., Massling, A., Zeromskiene, K., Iinuma, Y., Schmid, O., Helas, G., Hennig, T., Wiedensohler, A., Andreae, M. O. (2011). Water uptake by biomass burning aerosol at sub- and supersaturated conditions: closure studies and implications for the role of organics. Atmos. Chem. Phys., 11: 9519-9532.

Fan, X., Song, J., Peng, P. (2013). Comparative study for separation of atmospheric humic-like substance (HULIS) by ENVI-18, HLB, XAD-8 and DEAE sorbents: Elemental composition, FT-IR, ^{1}H NMR and off-line thermochemolysis with tetramethylammonium hydroxide (TMAH). Chemosphere, 93: 1710-1719.

Fröhlich, R., Cubison, M. J., Slowik, J. G., Bukowiecki, N., Prévôt, A. S. H., Baltensperger, U., Schneider, J., Kimmel, J. R., Gonin, M., Rohner, U., Worsnop, D. R., Jayne, J. T. (2013). The ToF-ACSM: a portable aerosol chemical speciation monitor with TOFMS detection. Atmos. Meas. Tech., 6: 3225-3241.

Graber, E. R., and Rudich, Y. (2006). Atmospheric HULIS: How humic-like are they? A comprehensive and critical review. Atmos. Chem. Phys. 6: 729-753.

Graham, B., Mayol-Bracero, O. L., Guyon, P., Roberts, G. C., Decesari, S., Facchini, M. C., Artaxo, P., Maenhaut, W., Köll, P., Andreae, M. O. (2002). Water-soluble organic compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and GC-MS. J. Geophys. Res. Atmos., 107: 8047.

Gras, J. L., Jensen, J. B., Okada, K., Ikegami, M., Zaizen, Y., Makino, Y. (1999). Some optical properties of smoke aerosol in Indonesia and tropical Australia. Geophys. Res. Lett., 26: 1393-1396.

Gysel, M., Crosier, J., Topping, D. O., Whitehead, J. D., Bower, K. N., Cubison, M. J., Williams, P. I., Flynn, M. J., McFiggans, G. B., Coe, H. (2007). Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2. Atmos. Chem. Phys., 7: 6131-6144.

Gysel, M., McFiggans, G. B., Coe, H. (2009). Inversion of tandem differential mobility analyser (TDMA) measurements. J. Aerosol Sci., 40: 134-151.

Gysel, M., Weingartner, E., Nyeki, S., Paulsen, D., Baltensperger, U., Galambos, I., Kiss, G. (2004). Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol. Atmos. Chem. Phys., 4(1): 35-50.

Hawkins, L. N. and Russell, L. M. (2010). Oxidation of ketone groups in transported biomass burning aerosol from the 2008 Northern California Lightning Series fires, Atmos. Environ., 44, 4142-4154.

Hikmatullah and Sukarman. (2014). Physical and Chemical Properties of Cultivated Peat Soils in Four Trial Sites of ICCTF in Kalimantan and Sumatra, Indonesia. J. Trop Soils, 19: 131-141.

Iinuma, Y., Brüggemann, E., Gnauk, T., Müller, K., Andreae, M. O., Helas, G., Parmar, R., and Herrmann, H. (2007), Source characterization of biomass burning particles: The combustion of selected European conifers, African hardwood, savanna grass, and German and Indonesian peat, J. Geophys. Res., 112, D08209.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y, Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., Worsnop, D. R. (2009). Evolution of Organic Aerosols in the Atmosphere. Science, 326: 1525-1529.

Koplitz, S. N., Mickley, L. J., Marlier, M. E., Buonocore, J. J., Kim, P. S., Liu T., Sulprizio, M. P., DeFries, R. S., Jacob, D. J., Schwartz, J., Pongsiri, M., Myers, S. S. (2016). Public health impacts of the severe haze in Equatorial Asia in September–October 2015: demonstration of a new framework for informing fire management strategies to reduce downwind smoke exposure. Environ. Res. Lett., 11: 094023.

Kunii, O., Kanagawa, S., Yajima, I., Hisamatsu, Y., Yamamura, S., Amagai, T., Ismail, Ir T. S. (2002). The 1997 Haze Disaster in Indonesia: Its Air Quality and Health Effects. Archives of Environmental Health: An International Journal, 57: 16-22.

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.

Kuwata, M. and Lee, W.-C. (2017). 1-Octanol-Water Partitioning as a Classifier of Water Soluble Organic Materials: Implication for Solubility Distribution. Aerosol Sci. Technol., 51: 602-613.

Levine, J. S. (1999). The 1997 fires in Kalimantan and Sumatra, Indonesia: Gaseous and particulate emissions. Geophys. Res. Lett., 26: 815-818.

Marlier, M. E., DeFries, R. S., Voulgarakis, A., Kinney, P. L., Randerson, J. T., Shindell, D. T., Chen, Y., Faluvegi, G. (2013). El Niño and health risks from landscape fire emissions in southeast Asia. Nat. Clim. Change, 3: 131-136.

Marlier, M. E., DeFries, R. S., Kim, P. S., Gaveau, D. L. A., Koplitz, S. N., Jacob, D. J., Mickley, L. J., Margono, B. A., Myers., S. S. (2015). Fire emissions and regional air quality impacts from fires in oil palm, timber, and logging concessions in Indonesia. Environ. Res. Lett., 10: 085005.

Massling, A., Leinert, S., Wiedensohler, A., Covert, D. (2007). Hygroscopic growth of sub-micrometer and one-micrometer aerosol particles measured during ACE-Asia. Atmos. Chem. Phys., 7: 3249-3259.

Massling, A., Wiedensohler, A., Busch, B., Neusüß, C., Quinn, P., Bates, T., and Covert, D. (2003). Hygroscopic properties of different aerosol types over the Atlantic and Indian Oceans, Atmos. Chem. Phys., 3, 1377-1397.

Mayol-Bracero, O. L., Guyon, P., Graham, B., Roberts, G., Andreae, M. O., Decesari, S., Facchini, M. C., Fuzzi, S., Artaxo, P. (2002). Water-soluble organic compounds in biomass burning aerosols over Amazonia 2. Apportionment of the chemical composition and importance of the polyacidic fraction. J. Geophys. Res. Atmos., 107: 8291.

Mircea, M., Facchini, M. C., Decesari, S., Cavalli, F., Emblico, L., Fuzzi, S., Vestin, A., Rissler, J., Swietlicki, E., Frank, G., Andreae, M. O., Maenhaut, W., Rudich, Y., and Artaxo, P. (2005). Importance of the organic aerosol fraction for modeling aerosol hygroscopic growth and activation: a case study in the Amazon Basin. Atmos. Chem. Phys., 5: 3111-3126.

Mochida, M. and Kawamura, K. (2004). Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles. J. Geophys. Res. Atmos., 109, D21202.

Narukawa, M., Kawamura, K., Takeuchi, N., Nakajima, T. (1999). Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires. Geophys. Res. Lett., 26: 3101-3104.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R. (2011). Changes in organic aerosol composition with aging inferred from aerosol mass spectra. Atmos. Chem. Phys., 11: 6465-6474.

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prevot, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R. (2010). Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 10, 4625-4641.

Page, S. E., Siegert, F., Rieley, J. O., Boehm, H.-D. V., Jaya, A., Limin, S. (2002). The amount of carbon released from peat and forest fires in Indonesia during 1997. Nature, 420: 61-65.

Peng, C., Chan, M. N., and Chan, C. K. (2001). The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, Environ. Sci. & Technol., 35, 4495-4501.

Petters, M. D., Carrico, C. M., Kreidenweis, S. M., Prenni, A. J., DeMott, P. J., Collett Jr., J. L., and Moosmuller, H. (2009). Cloud condensation nucleation activity of biomass burning aerosol. J. Geophys. Res. Atmos., 114, D22205.

Petters, M. D., and Kreidenweis, S. M. (2007). A single parameter representation of hygroscopic growth and cloud condensation nucleus activity. Atmos. Chem. Phys., 7: 1961-1971.

Petters, M. D., and Kreidenweis, S. M. (2008). A single parameter representation of hygroscopic growth and cloud condensation nucleus activity − Part 2: Including solubility. Atmos. Chem. Phys., 8: 6273-6279.

Petters, M. D., Kreidenweis, S. M., Ziemann, P. J. (2016). Prediction of cloud condensation nuclei activity for organic compounds using functional group contribution methods. Geosci. Model Dev., 9: 111-124.

Polidori, A., Turpin, B. J., Davidson, C. I., Rodenburg, L. A., and Maimone, F. (2008). Organic $PM_{2.5}$: Fractionation by Polarity, FTIR Spectroscopy, and OM/OC Ratio for the Pittsburgh Aerosol. Aerosol Sci. & Technol. 42: 233-246.

Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., and Ming, Y. (2001). The effects of low molecular weight dicarboxylic acids on cloud formation. J. Phys. Chem. A, 105:11240-11248.

Prenni, A. J., DeMott, P. J., Sullivan, A. P., Sullivan, R. C., Kreidenweis, S. M., Rogers, D. C. (2012). Biomass burning as a potential source for atmospheric ice nuclei: Western wildfires and prescribed burns. Geophys. Res. Lett., 39, L11805.

Psichoudaki, M. and Pandis, S. N. (2013). Atmospheric Aerosol Water-Soluble Organic Carbon Measurement: A Theoretical Analysis. Environ. Sci. & Technol., 47: 9791-9798.

Reddington, C. L., Yoshioka, M., Balasubramanian, R., Ridley, D., Toh, Y. Y., Arnold, S. R., Spracklen, D. V. (2014). Contribution of vegetation and peat fires to particulate air pollution in Southeast Asia. Environ. Res. Lett., 9: 094006.

Riipinen, I., Rastak, N., Pandis, S. N. (2015). Connecting the solubility and CCN activation of complex organic aerosols: a theoretical study using solubility distributions. Atmos. Chem. Phys., 15: 6305-6322.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Pöschl, U. (2008). Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment. Atmos. Chem. Phys., 8: 1153-1179.

Rose, D., Nowak, A., Achtert, P., Wiedensohler, A., Hu, M., Shao, M., Zhang, Y., Andreae, M. O., and Pöschl, U. (2010). Cloud condensation nuclei in polluted air and biomass burning smoke near the mega-city Guangzhou, China – Part 1: Size-resolved measurements and implications for the modeling of aerosol particle hygroscopicity and CCN activity. Atmos. Chem. Phys., 10: 3365-3383.

Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., Cass, G. R. (1999). Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos. Environ., 33: 173-182.

Spracklen, D.V., Reddington C. L., and Gaveau, D. L. A. (2015). Industrial concessions, fires and air pollution in Equatorial Asia. Environ. Res. Lett., 10: 091001.

Stockwell, C. E., Jayarathne, T., Cochrane, M. A., Ryan, K. C., Putra, E. I., Saharjo, B. H., Nurhayati, A. D., Albar, I., Blake, D. R., Simpson, I. J., Stone, E. A., Yokelson, R. J. (2016). Field measurements of trace gases and aerosols emitted by peat fires in Central Kalimantan, Indonesia, during the 2015 El Nino. Atmos. Chem. Phys., 16: 11711-11732.

Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J. (2015). Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry. Atmos. Chem. Phys., 15: 845-865.

Suda, S. R., Petters, M. D., Yeh, G. K., Strollo, C., Matsunaga, A., Faulhaber, A., Ziemann, P. J., Prenni, A. J., Carrico, C. M., Sullivan, R. C., Kreidenweis, S. M. (2014). Influence of Functional Groups on Organic Aerosol Cloud Condensation Nucleus Activity. Environ. Sci. & Technol., 48: 10182-10190.

Sullivan, A. P., and Weber, R. J. (2006), Chemical characterization of the ambient organic aerosol soluble in water: 1. Isolation of hydrophobic and hydrophilic fractions with a XAD-8 resin, J. Geophys. Res., 111, D05314.

Sullivan, R. C., Moore, M. J. K., Petters, M. D., Kreidenweis, S. M., Roberts, G. C., Prather, K. A. (2009). Effect of chemical mixing state on the hygroscopicity and cloud nucleation properties of calcium mineral dust particles. Atmos. Chem. Phys., 9: 3303-3316.

Suzuki, Y., Kawakami, M., and Akasaka, K. (2001). ^{1}H NMR Application for Characterizing Water-Soluble Organic Compounds in Urban Atmospheric Particles. Environ. Sci. & Technol., 35: 2656-2664.

Tagliavini, E., Moretti, F., Decesari, S., Facchini, M. C., Fuzzi, S., Maenhaut, W. (2006). Functional group analysis by H NMR/chemical derivatization for the characterization of organic aerosol from the SMOCC field campaign. Atmos. Chem. Phys., 6: 1003-1019.

Takegawa, N., Miyakawa, T., Kawamura, K., and Kondo, Y. (2007). Contribution of selected dicarboxylic and w-oxocarboxylic acids in ambient aerosol to the m/z 44 signal of an Aerodyne aerosol mass spectrometer, Aerosol Sci. Technol., 41, 418-437.

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

Turpin, B. J., Hering, S. V., and Huntzicker, J. J. (1994). Investigation of organic aerosol sampling artifacts in the Los Angeles Basin, Atmos. Environ., 28, 3061-3071.

Usup A., Hashimoto, Y., Takahashi, H., and Hayasaka, H. (2004). Combustion and thermal characteristics of peat fire in tropical peatland in Central Kalimantan, Indonesia. Tropics, 14: 1-19.

van der Werf, G.R., Randerson, J. T., Giglio, L., Collatz, G. J., Mu, M., Kasibhatla, P. S., Morton, D. C., DeFries, R. S., Jin, Y., van Leeuwen, T. T. (2010). Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997−2009). Atmos. Chem. Phys., 10: 11707-11735.

Valvani, S. C., Yalkowsky, S. H., and Roseman, T. J. (1981). Solubility and partitioning IV: Aqueous solubility and octanol-water partition coefficients of liquid nonelectrolytes. J. Pharmaceutical Sci., 70: 502-507.

Wang, Y., Field, R. D., Roswintiarti, O. (2004). Trends in atmospheric haze induced by peat fires in Sumatra Island, Indonesia and El Niño phenomenon from 1973 to 2003. Geophys. Res. Lett., 31: L04103.

Yustiawati, Kihara, Y., Sazawa, K., Kuramitz, H., Kurasaki, M., Saito, T., Hosokawa, T., Syawal, M. S., Wulandari, L., Hendri, I., Tanaka, S. (2015). Effects of peat fires on the characteristics of humic acid extracted from peat soil in Central Kalimantan, Indonesia. Environ. Sci. & Pollut. Res., 22: 2384-2395.

Table 1. Summary of Indonesian peat and biomasses used for the laboratory combustion experiments. Samples 9, 15, and 16 were also used for offline experiments of their aqueous extracts (A_0 and A_1).

Exp. No.	**Sample name**	**Sample depth (cm)**	**Type /Species**	**Location**	**Description**
1	Riau-1	Surface ~ 10	Peat	Riau, Sumatra	D&B* peatland
2	Riau-1.1	10−20	Peat	Riau, Sumatra	D&B* peatland
3	Riau-1.2	30−40	Peat	Riau, Sumatra	D&B* peatland
4	Riau-2	Surface ~ 10	Peat	Riau, Sumatra	D&B* peatland
5	Riau-2.1	10−20	Peat	Riau, Sumatra	D&B* peatland
6	Riau-2.2	30−40	Peat	Riau, Sumatra	D&B* peatland
7	Riau-3	Surface ~ 10	Peat	Riau, Sumatra	D&B* peatland
8	Riau-3.1	10−20	Peat	Riau, Sumatra	D&B* peatland
9	**Riau-4****	**Surface ~ 10**	**Peat**	**Riau, Sumatra**	**D&B* peatland**
10	Riau-4.1	10−20	Peat	Riau, Sumatra	D&B* peatland
11	Riau-SF	Surface ~ 5	Peat	Riau, Sumatra	Secondary forest
12	Riau-Zam	Surface ~ 5	Peat	Riau, Sumatra	Undisturbed peat forest
13	C.K.-DF	Surface ~ 5	Peat	Palangkaraya, Central Kalimantan	D&UB# peat forest
14	C.K.-DB	Surface ~ 5	Peat	Palangkaraya, Central Kalimantan	D&B* peat forest
15	**acacia****	**N/A**	**Acacia mangium**	**Riau, Sumatra**	**Dried leaves**
16	**fern****	**N/A**	**Pteridium aquilinum**	**Riau, Sumatra**	**Dried leaves**

* D&B stands for the drained and burnt condition.

D&UB represents the drained but unburnt case.

** Teflon filter samples were collected during online combustion experiments.

Table 2. Volume weighted mean GF and κ values (average ± 1 standard deviation, S.D.) of different types of Indonesian peat and biomasses. The results of their aqueous extracts (*A_0* and *A_1*) are also shown.

Sample name			**Mean GF (RH = 90%)**			**Mean κ (RH = 90%)**		
			50 nm	**100 nm**	**200 nm**	**50 nm**	**100 nm**	**200 nm**
Online	**Sumatra**	Riau-1	1.17 ± 0.07	1.09 ± 0.06	1.04 ± 0.01	0.089 ± 0.042	0.039 ± 0.028	0.016 ± 0.002
		Riau-1.1	1.15 ± 0.06	1.05 ± 0.01	1.04 ± 0.01	0.080 ± 0.036	0.021 ± 0.005	0.014 ± 0.002
		Riau-1.2	1.00 ± 0.002	1.08 ± 0.04	1.06 ± 0.01	0.001 ± 0.001	0.036 ± 0.017	0.025 ± 0.002
		Riau-2	–	1.07 ± 0.01	1.12 ± 0.06	–	0.029 ± 0.005	0.052 ± 0.032
		Riau-2.1	1.06 ± 0.04	1.06 ± 0.01	1.06 ± 0.01	0.029 ± 0.019	0.023 ± 0.005	0.024 ± 0.005
		Riau-2.2	1.05 ± 0.02	1.09 ± 0.02	1.10 ± 0.02	0.024 ± 0.010	0.037 ± 0.009	0.042 ± 0.009
		Riau-3	1.07 ± 0.04	1.05 ± 0.01	1.08 ± 0.01	0.035 ± 0.022	0.022 ± 0.006	0.033 ± 0.006
		Riau-3.1	1.05 ± 0.02	1.05 ± 0.02	1.08 ± 0.01	0.024 ± 0.012	0.022 ± 0.010	0.031 ± 0.006
		Riau-4	1.04 ± 0.01	1.08 ± 0.01	1.05 ± 0.002	0.017 ± 0.003	0.034 ± 0.003	0.019 ± 0.001
		Riau-4.1	1.07 ± 0.10	0.99 ± 0.01	1.02 ± 0.01	0.059 ± 0.063	N/A	0.007 ± 0.003
	(Burnt peatland)	**Riau D&B**[#]	1.07 ± 0.04	1.06 ± 0.02	1.07 ± 0.02	0.040 ± 0.023	0.029 ± 0.010	0.026 ± 0.007
	(Secondary forest)	Riau-SF	1.04 ± 0.05	1.07 ± 0.004	1.09 ± 0.01	0.025 ± 0.028	0.028 ± 0.002	0.034 ± 0.003
	(Undisturbed area)	Riau-Zam	1.10 ± 0.07	1.11 ± 0.04	1.08 ± 0.004	0.053 ± 0.038	0.048 ± 0.017	0.032 ± 0.002
	Kalimantan	C.K.-DF	1.11 ± 0.06	1.13 ± 0.01	1.11 ± 0.01	0.057 ± 0.033	0.058 ± 0.005	0.046 ± 0.004
		C.K.-DB	1.11 ± 0.05	1.12 ± 0.02	1.13 ± 0.01	0.055 ± 0.028	0.054 ± 0.011	0.056 ± 0.005
		acacia	1.05 ± 0.01	1.09 ± 0.01	1.09 ± 0.01	0.026 ± 0.005	0.039 ± 0.006	0.037 ± 0.006
		fern	1.08 ± 0.02	1.17 ± 0.02	1.20 ± 0.03	0.039 ± 0.011	0.078 ± 0.010	0.088 ± 0.014

Aqueous extracts: A_0 (the water extracts), A_1 (the 1-octanol water extracts)

Sample name			**Mean GF (RH = 90%)**			**Mean κ (RH = 90%)**		
			50 nm	**100 nm**	**200 nm**	**50 nm**	**100 nm**	**200 nm**
Offline	A_0	**peat***	1.29 ± 0.05	1.34 ± 0.06	1.38 ± 0.09	0.168 ± 0.039	0.179 ± 0.038	0.198 ± 0.058
		acacia	1.17 ± 0.03	1.23 ± 0.04	1.28 ± 0.05	0.090 ± 0.019	0.110 ± 0.025	0.135 ± 0.027
		fern	1.18 ± 0.03	1.28 ± 0.03	1.32 ± 0.05	0.100 ± 0.016	0.141 ± 0.020	0.157 ± 0.031
	A_1	**peat***	1.47 ± 0.06	1.50 ± 0.09	1.47 ± 0.11	0.311 ± 0.052	0.302 ± 0.074	0.262 ± 0.083
		acacia	1.32 ± 0.04	1.42 ± 0.03	1.44 ± 0.07	0.195 ± 0.027	0.237 ± 0.023	0.239 ± 0.049
		fern	1.28 ± 0.04	1.33 ± 0.05	1.39 ± 0.05	0.162 ± 0.026	0.177 ± 0.034	0.205 ± 0.038

− Data are unavailable due to low particle number concentration.

Riau D&B represents the averages of all the D&B peat samples collected from different depths of the Sumatran peatlands (i.e., samples used for **Exp. 1-10** in Table 1).

* **Peat** in Table 2 refers to the Riau-4 sample collected from burnt peatlands in Sumatra (see Sect.2 for details).

Table 3. Summary of chemical characteristics of different types of Indonesian peat and biomass burning particles.

Sample name		Mean κ (100 nm)	f_{44} (%)	f_{HMW} (%)	OC (mg C)	EC (mg C)	WSOC/OC (%)
Sumatra	Riau-1	0.039	0.4	42.9	12.69	0.13	0.93
	Riau-2	0.029	0.7	26.9	14.08	0.12	1.80
	Riau-3	0.022	0.7	31.7	13.58	0.13	1.63
	Riau-4	0.034	0.5	29.0	18.86	0.13	1.51
	Riau-SF	0.028	1.7	21.1	7.64	0.07	4.15
	Riau-Zam	0.048	1.6	23.8	2.58	0.03	6.08
Kalimantan	C.K.-DF	0.058	2.0	19.5	5.58	0.05	4.16
	C.K.-DB	0.054	1.9	19.3	7.51	0.05	2.03
	acacia	0.039	1.1	27.0	14.61	0.05	3.42
	fern	0.078	1.9	21.5	13.34	0.07	6.56
A0	**peat***	0.179	9.5	15.8	N/A	N/A	N/A
	acacia	0.110	4.7	21.8	N/A	N/A	N/A
	fern	0.141	5.2	17.4	N/A	N/A	N/A
A1	**peat***	0.302	9.3	16.0	N/A	N/A	N/A
	acacia	0.237	6.6	11.6	N/A	N/A	N/A
	fern	0.177	7.9	8.2	N/A	N/A	N/A

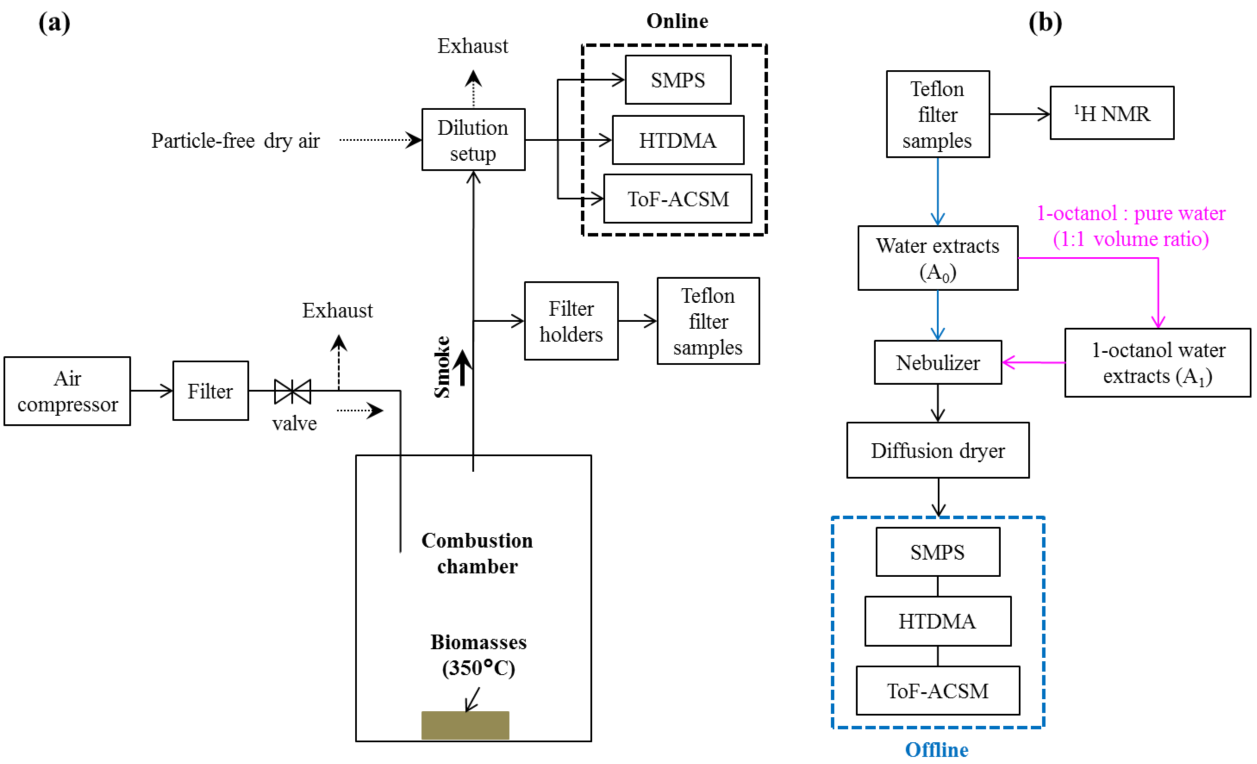

Fig. 1 Schematic diagrams of the laboratory experimental setups.

(a) The experimental setup for combustion experiment and subsequent online measurements, and (b) experimental setup for offline measurements of water extracts (A_0, blue arrows) and 1-octanol water extracts (A_1, magenta arrows) from the filter samples.

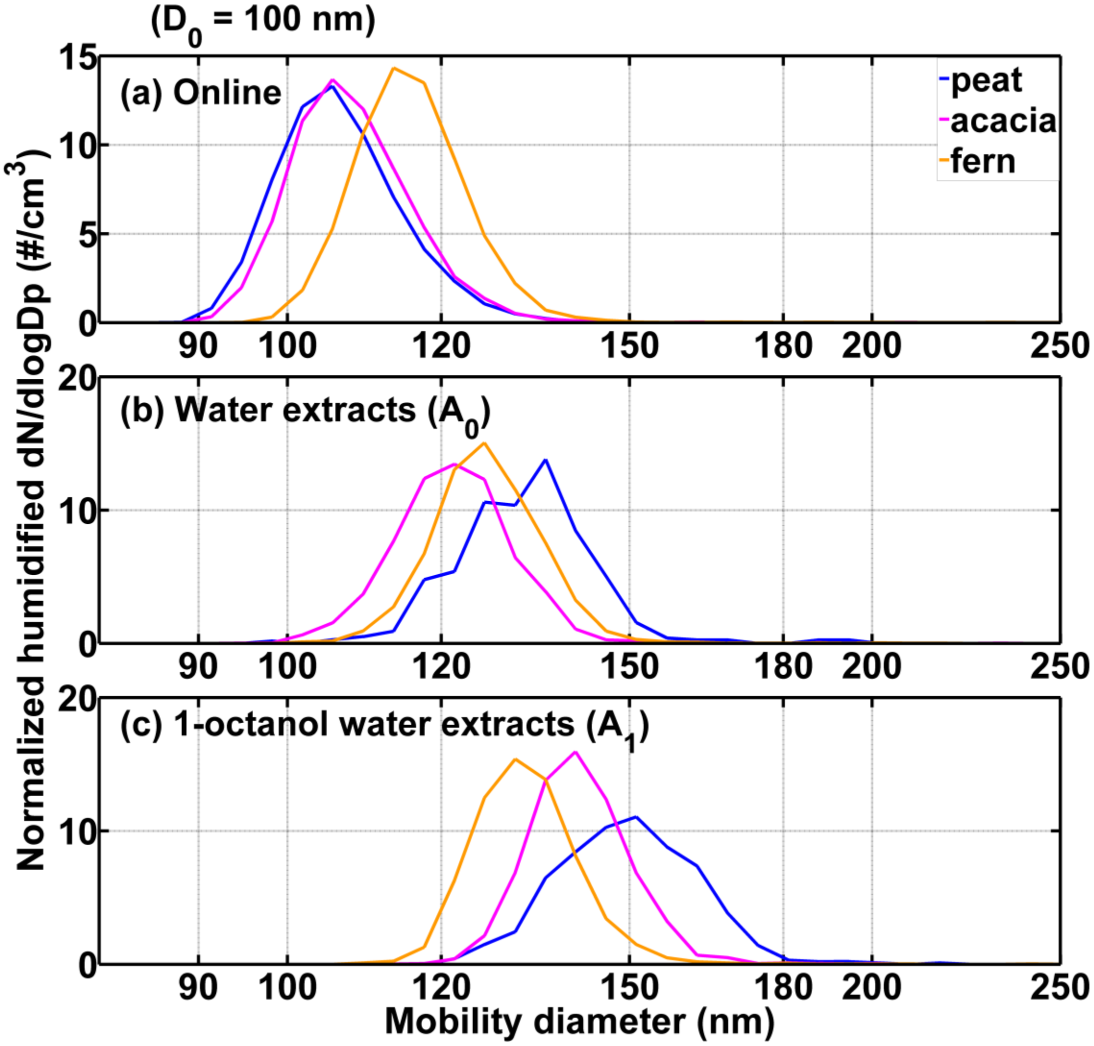

Fig.2 Normalized number size distributions measured by the HTDMA (D_0 = 100 nm; RH = 90%) of peat, fern and acacia burning particles. (a) online data, (b) A_0, and (c) A_1. For online data, peat burning particles are nearly non-hygroscopic, while fern burning particles are more hygroscopic. Aqueous extracts of peat burning particles are the most hygroscopic among the three types of biomasses. The x-axis is on a logarithmic scale.

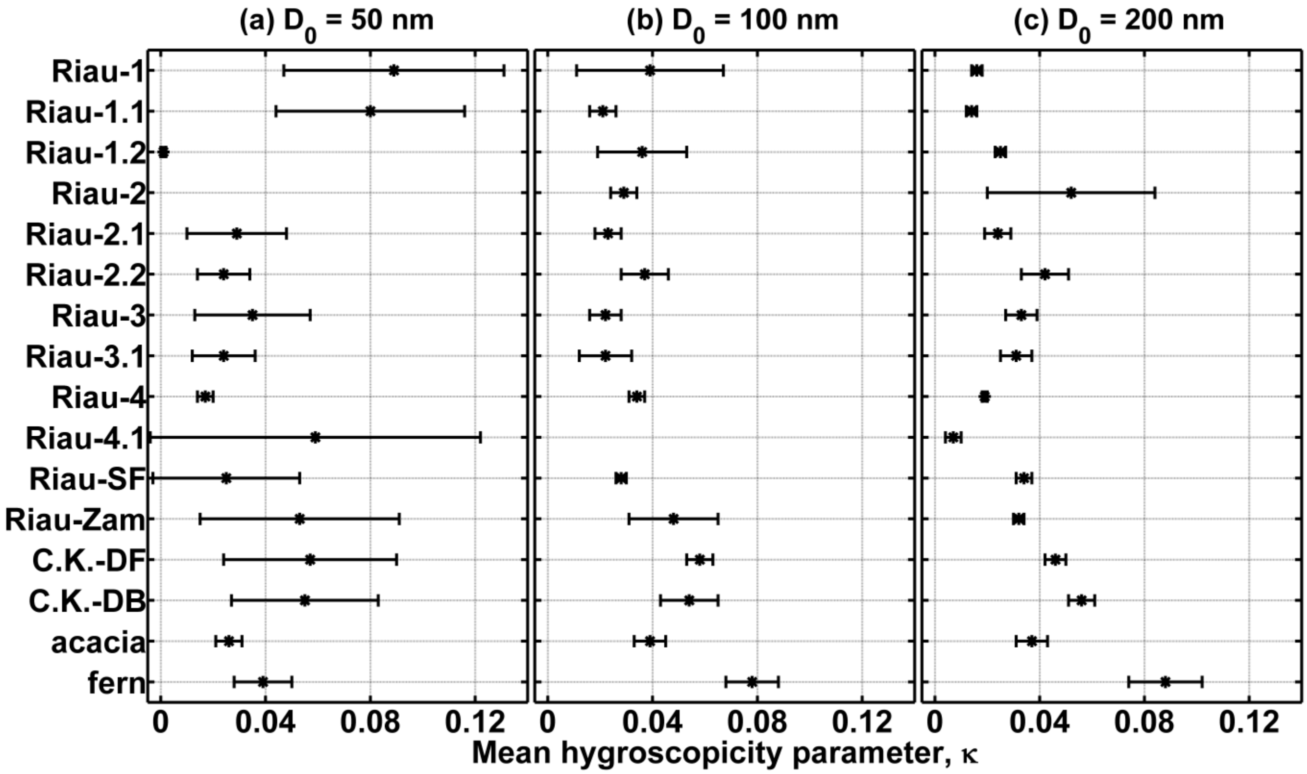

Fig.3 Mean κ values of fresh Indonesian biomass burning particles measured for (a) D_0 = 50 nm, (b) D_0 = 100 nm, and (c) D_0 = 200 nm particles. In all cases, κ values are lower than 0.1. The largest κ values were measured for fern burning particles (D_0 = 100 nm and D_0 = 200 nm). Particles emitted from combustion of peat at Central Kalimantan are generally more hygroscopic than those from Riau, Sumatra. Error bars denote the corresponding standard deviations.

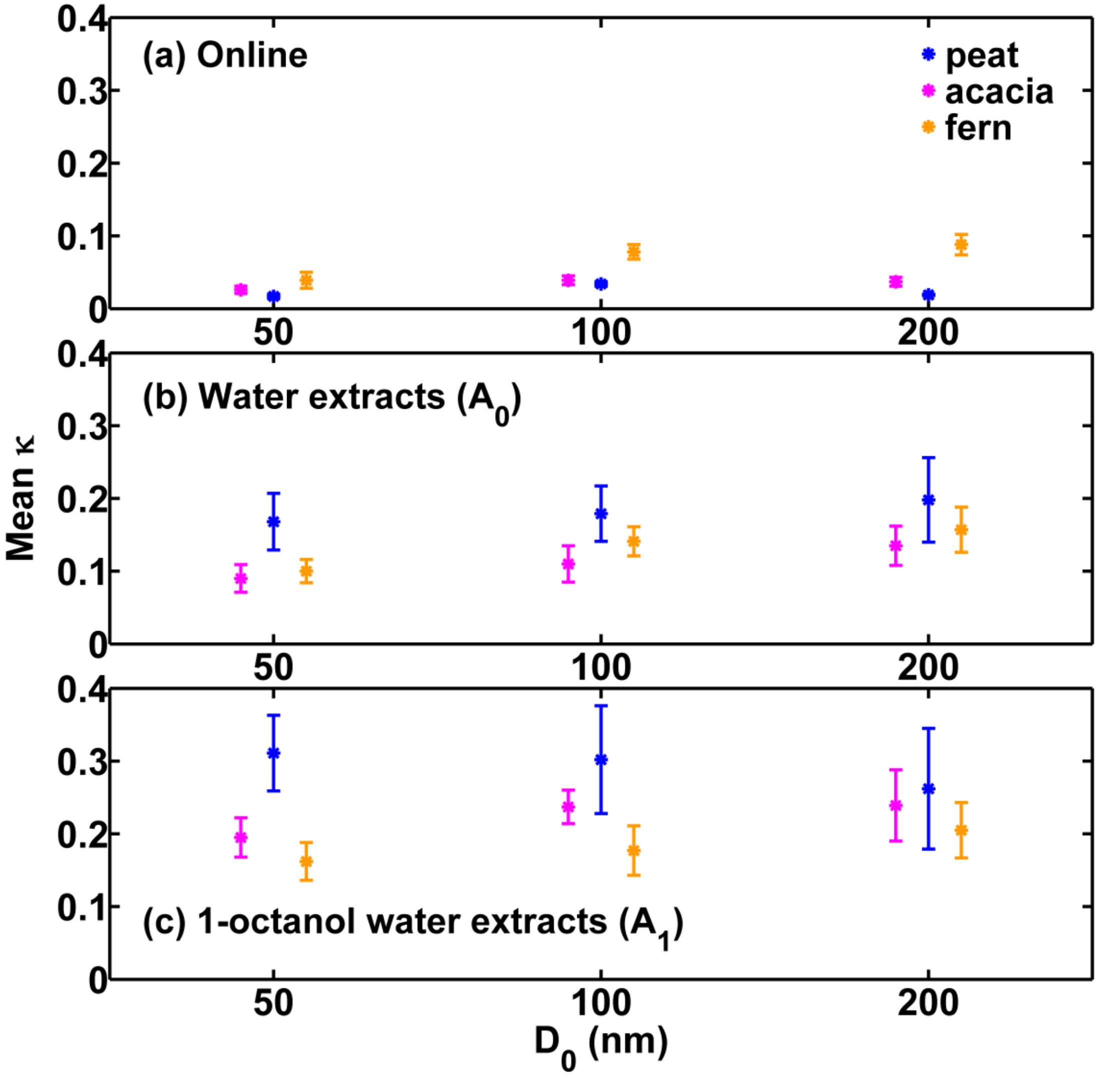

Fig.4 Comparison of κ values for (a) online, (b) water extracts (A_0), and (c) 1-octanol water extracts (A_1). The data for peat (Riau-4), acacia, and fern are shown. Indonesian peat burning particles are almost non-hygroscopic for online data, while their water soluble organic fractions are highly hygroscopic.

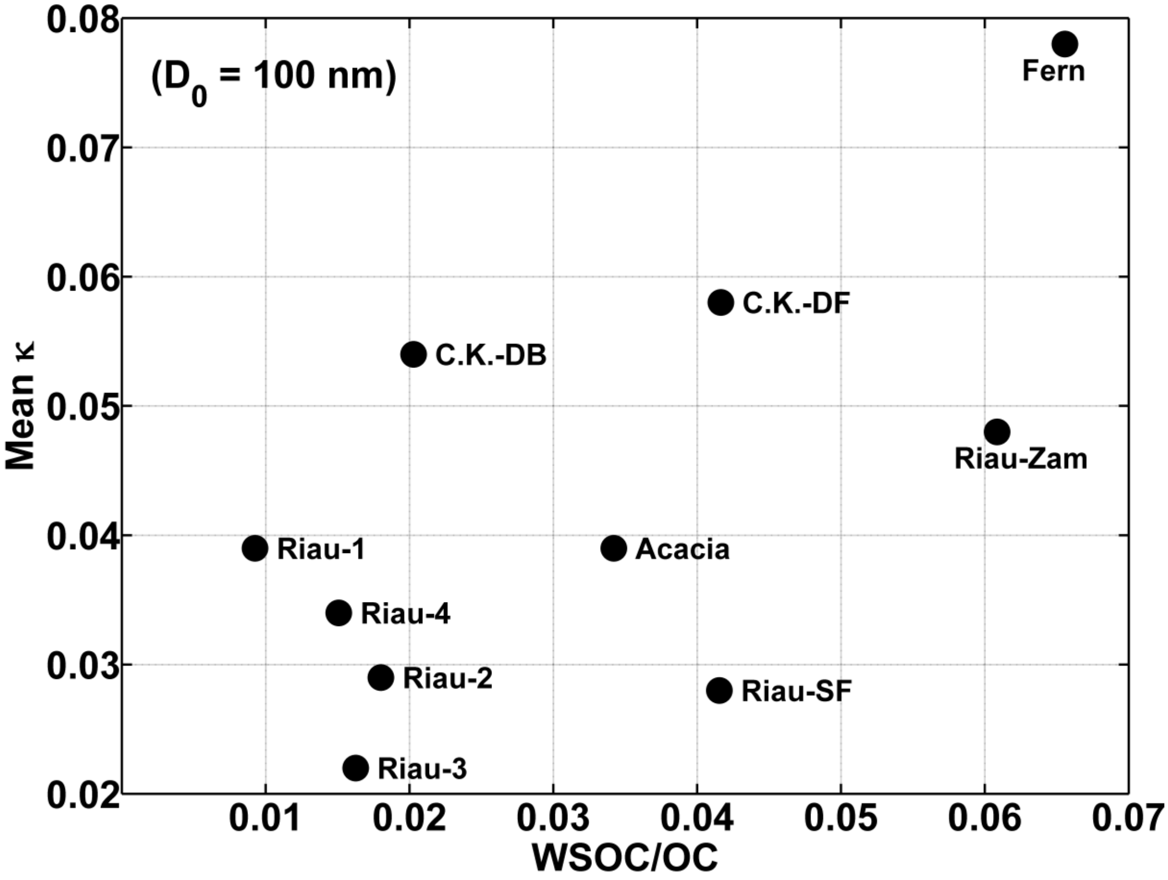

Fig.5 Correlation of κ and WSOC/OC ratio for different types of Indonesian peat and biomasses.

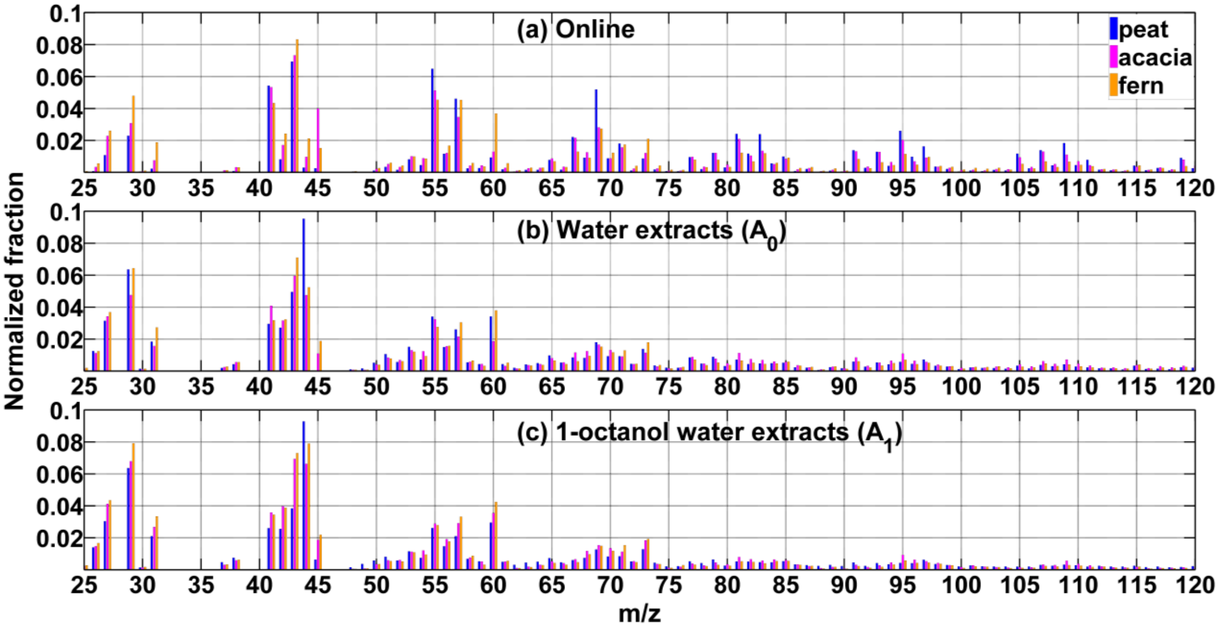

Fig.6 Mass spectra of organics in Indonesian biomass burning particles measured for peat, acacia, and fern samples. (a) online, (b) A_0, and (c) A_1 data are shown. Ion signals (*m/z*) from hydrocarbon-like organic compounds (e.g., *m/z* 41, 43, 55, 57) are prominent for online data, while intensities of ions for oxygenated organics (e.g., *m/z* 44) and biomass burning tracers (e.g., *m/z* 60, 73) are relatively less intense. On the other hand, both *m/z* 44 and *m/z* 60 signals are significant for mass spectra of A_0 and A_1. See the text for details.

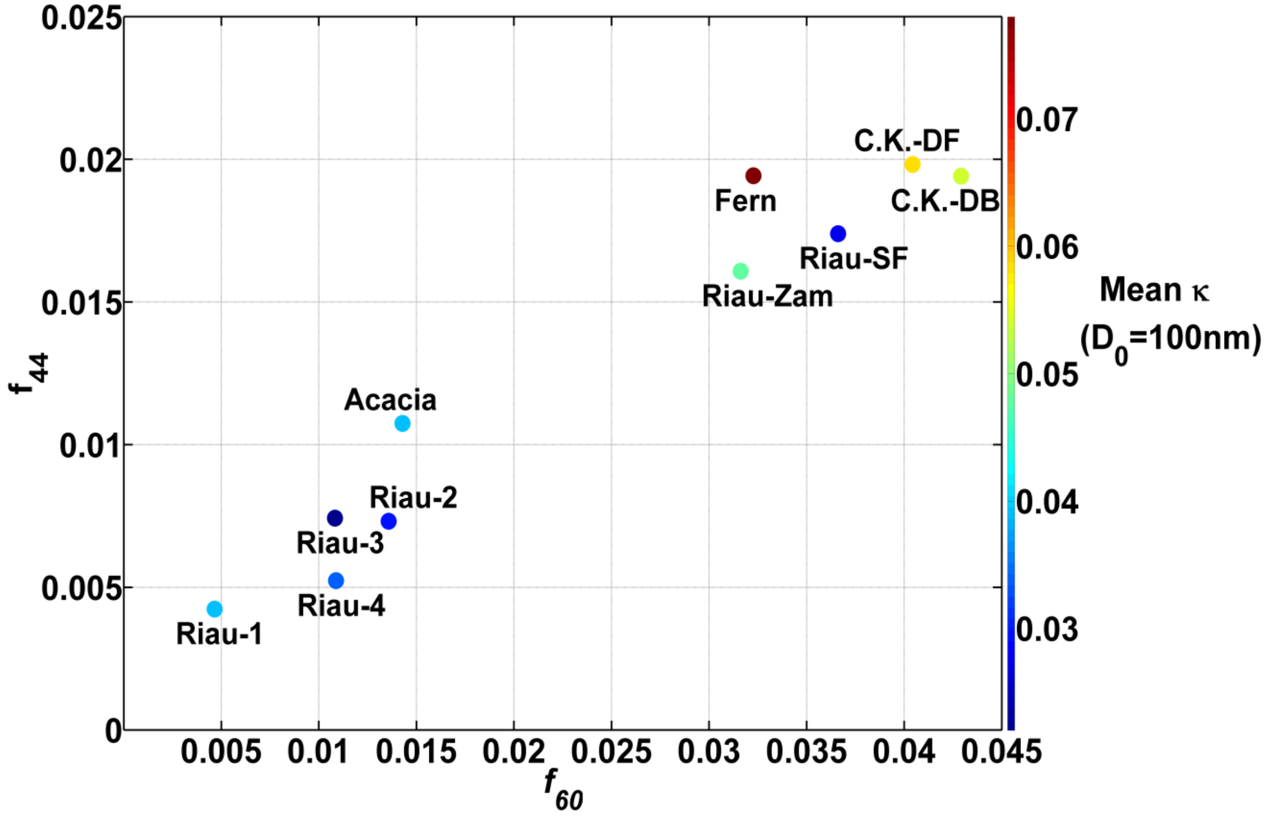

Fig.7 Correlation of f_{44} and f_{60} for different types of Indonesian peat and biomasses.

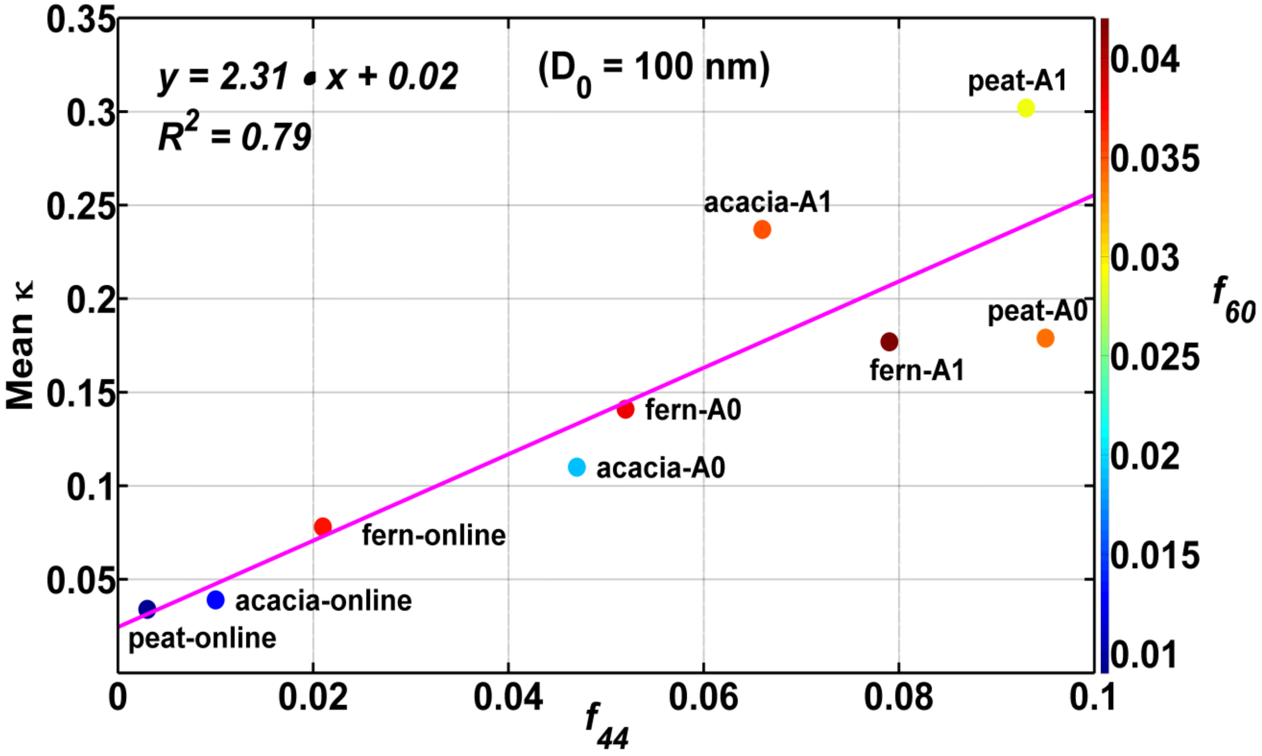

Fig.8 Correlation of κ and f_{44}. The magenta line shows the result of fitting by the least-squares method.

Supplementary Information

Water Uptake by Fresh Indonesian Peat Burning Particles is Limited by Water Soluble Organic Matter

Jing Chen[1, *], Sri Hapsari Budisulistiorini[1], Masayuki Itoh[2], Wen-Chien Lee[1, 3], Takuma Miyakawa[4], Yuichi Komazaki[4], LiuDongQing Yang[1], and Mikinori Kuwata[1, 2, *]

[1] {Earth Observatory of Singapore, Nanyang Technological University, Singapore}

[2] {Center for Southeast Asian Studies, Kyoto University, Japan}

[3] {Division of Chemistry and Biological Chemistry, Nanyang Technological University, Singapore}

[4] {Research and Development Center for Global Change, Japan Agency for Marine-Earth Science and Technology, Japan}

* Correspondence to: chen.jing@ntu.edu.sg; kuwata@ntu.edu.sg

S1. A brief introduction to the HTDMA setup

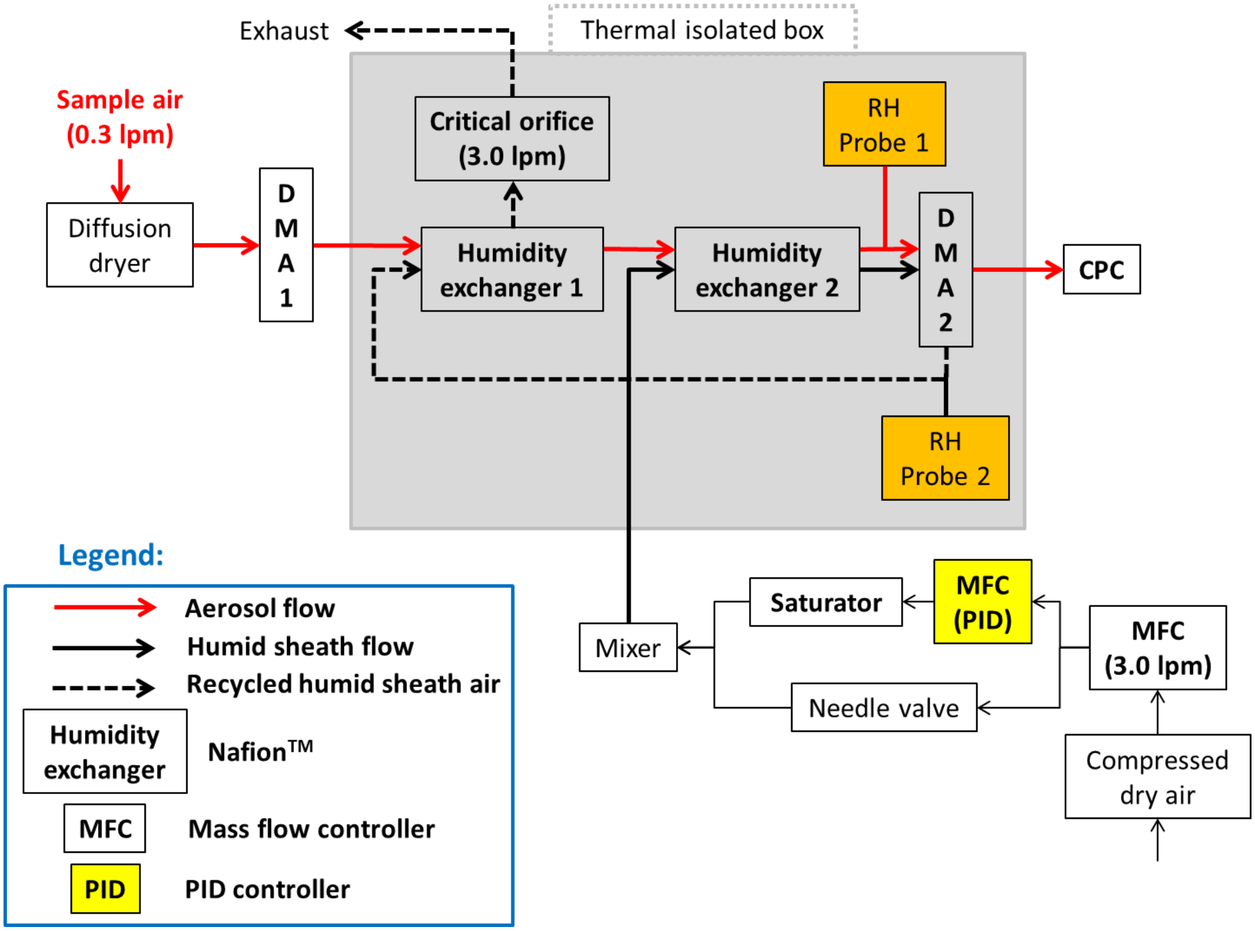

Fig.S1 Schematic diagram of the HTDMA system.

S2. RH stability in the humidified DMA (DMA2)

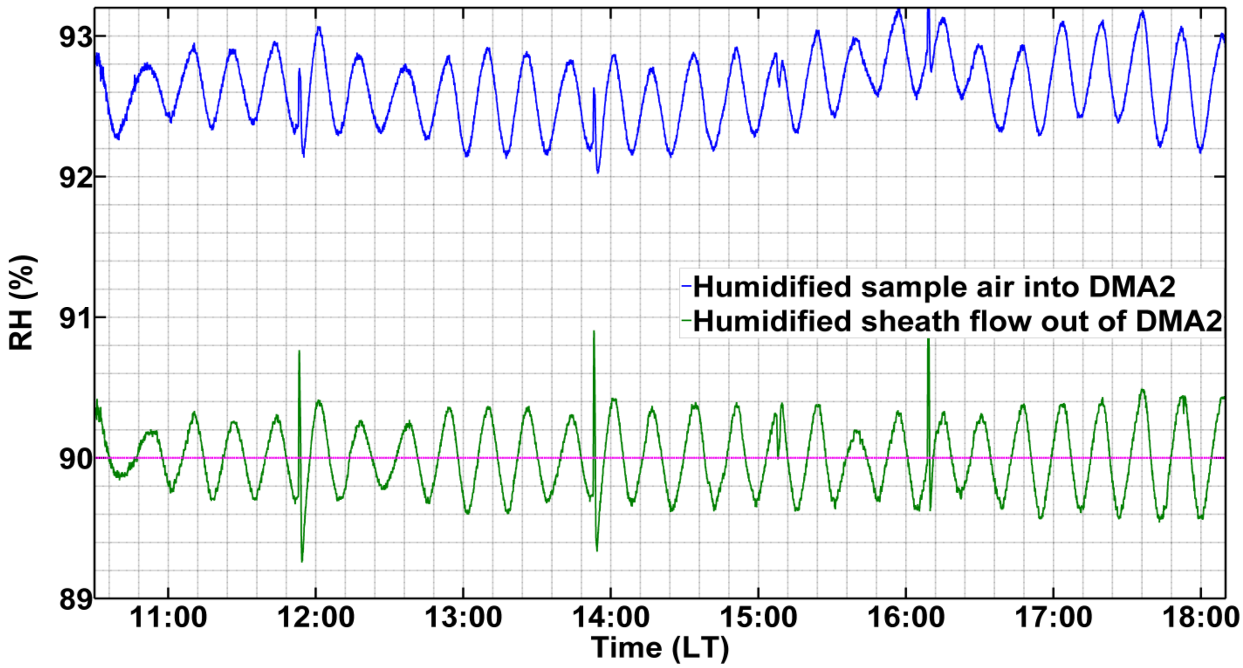

Fig.S2 RH recordings of both humidified sample air and humidified sheath flow are both fluctuating within ± 1% RH (peak-to-peak). RH of the sample flow is always higher than that of the sheath flow. The magenta line denotes the RH set point of 90%.

S3. Comparison of normalized particle number size distributions measured with the HTDMA system

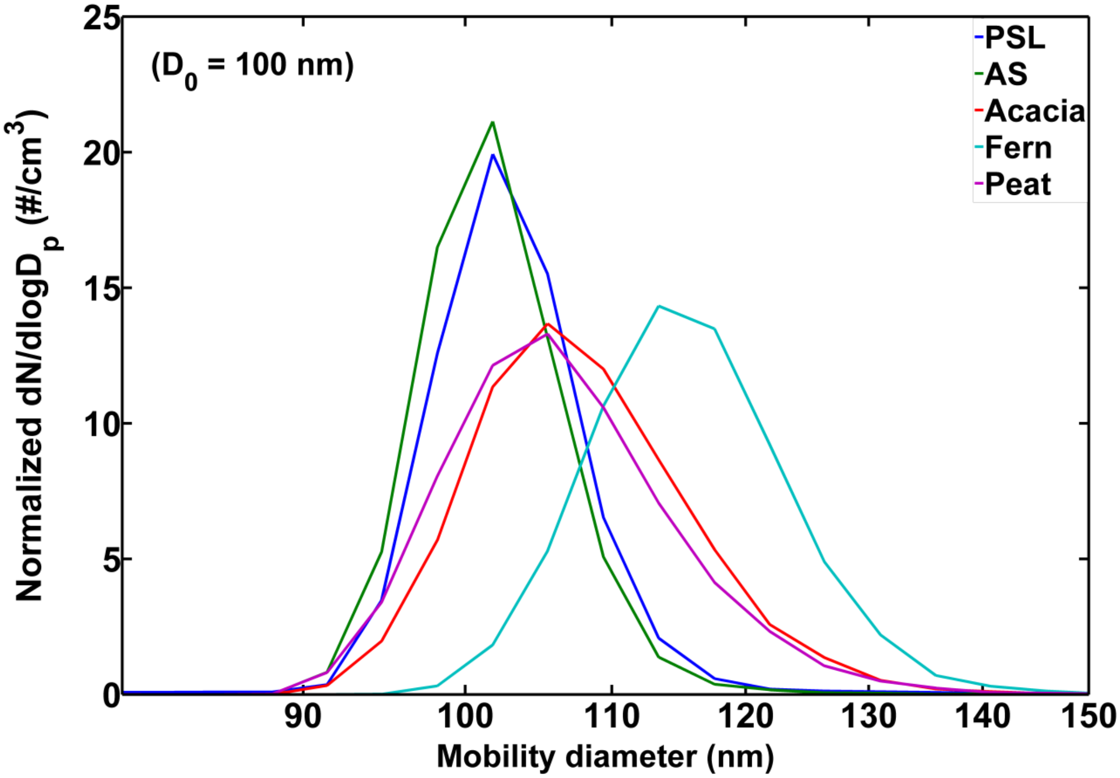

Fig.S3 Normalized particle number size distributions of 100 nm PSL and ammonium sulfate (AS) particles under dry scans (RH < 10%), and of 100 nm peat, acacia, and fern burning particles following humidification (RH = 90%) measured with the HTDMA system.

~~S3~~S4. ^{1}H NMR measurements

NMR samples were prepared by dissolving particles collected on a filter in either $CDCl_3$ or D_2O. $CDCl_3$ dissolves most of organic compounds, including both water soluble and insoluble species. On the other hand, only water-soluble organic species will dissolve in D_2O (Decesari et al., 2000; Graham, et al., 2002). The NMR spectra were measured using Bruker AMX-300 spectrometer at 300 MHz frequency.

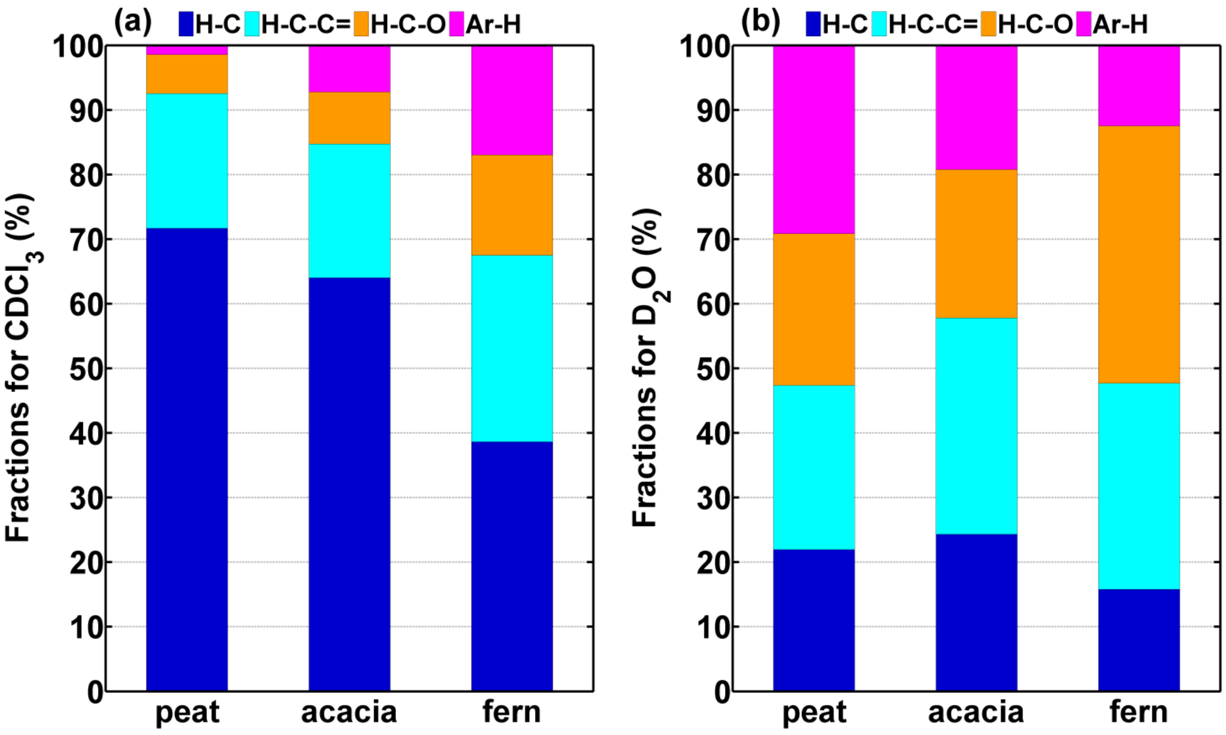

Fig.~~S3~~ S4 Functional group analyses for peat sampled from a burnt area (Riau-1), acacia and fern burning particles with (a) $CDCl_3$ and (b) D_2O, respectively. Four major functional groups identified from ^{1}H NMR analysis indicate that aliphatic compounds containing the H-C structure are the most abundant in fresh Indonesian peat, fern and acacia burning particles, while oxygenated compounds containing the H-C-C= and H-C-O groups are more likely to dominate in water soluble organic materials ~~(Lee et al., in preparation)~~. An example of the corresponding ^{1}H NMR spectra for peat burning particles dissolved in $CDCl_3$ can be found in Kuwata et al. (2017). Note that the NMR result of the peat sample in the D_2O case is only qualitative due to very weak signals were detected.

~~S4~~S5. Correlations between κ and OM mass spectra (mainly focusing on f_{44} and f_{60})

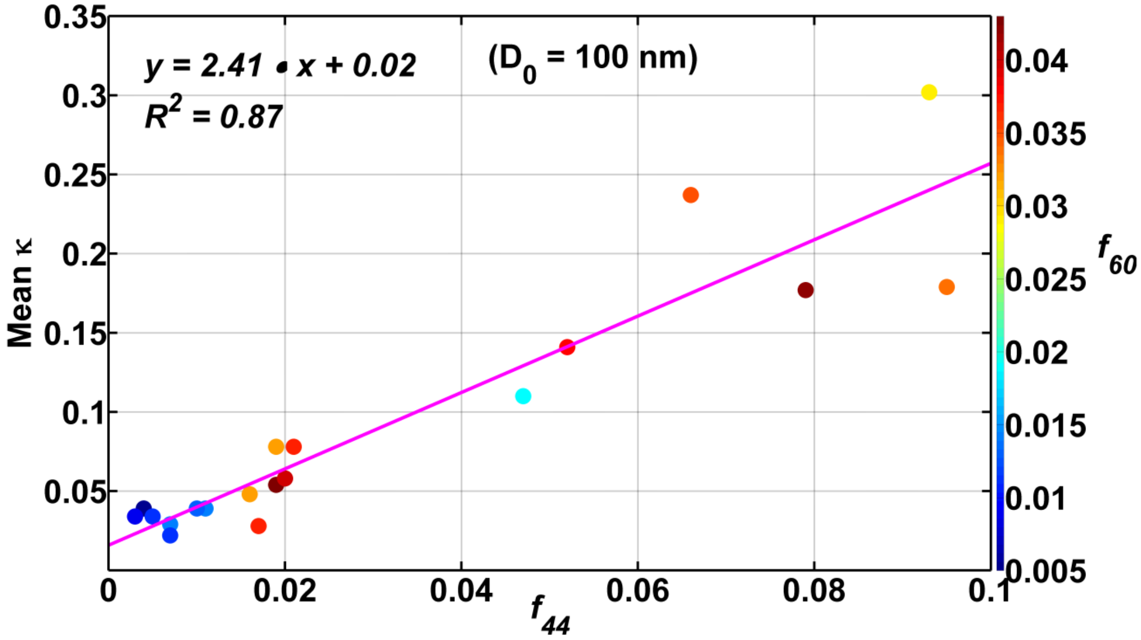

Fig.~~S4~~ S5 Correlation of κ and f_{44} for all the online and offline measurements.

References:

Decesari, S., Facchini, M. C., Fuzzi, S., Tagliavini, E. (2000). Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach. J. Geophys. Res. Atmos., 105: 1481-1489.

Graham, B., Mayol-Bracero, Olga L., Guyon, Pascal, Roberts, Gregory C., Decesari, Stefano, Facchini, M. Cristina, Artaxo, Paulo, Maenhaut, Willy, Köll, Peter, Andreae, Meinrat O. (2002). Water-soluble organic compounds in biomass burning aerosols over Amazonia 1. Characterization by NMR and GC-MS. J. Geophys. Res. Atmos., 107: 8047.

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