



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

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1 Abstract

2 The relationship between hygroscopic properties and chemical characteristics of Indonesian
3 biomass burning (BB) particles, which are dominantly generated from peatland fires, was
4 investigated using the humidified tandem differential mobility analyzer. In addition to peat,
5 acacia (a popular species at plantation) and fern (a pioneering species after disturbance by fire)
6 were used for experiments. Fresh Indonesian peat burning particles are almost non-hygroscopic
7 (mean hygroscopicity parameter, $\kappa < 0.06$) due to predominant contribution of water-insoluble
8 organics. The range of κ spans from $\kappa = 0.02$ – 0.04 (dry diameter = 100 nm, hereinafter) for Riau
9 peat burning particles, while that for Central Kalimantan ranges from $\kappa = 0.05$ – 0.06 . Fern
10 combustion particles are more hygroscopic ($\kappa = 0.08$), whereas the acacia burning particles have
11 a mediate κ value (0.04). These results suggest that κ is significantly dependent on biomass types.
12 This variance in κ is partially determined by fractions of water soluble organic carbon (WSOC),
13 as demonstrated by a correlation analysis ($R = 0.65$). κ of water soluble organic matter is also
14 quantified, incorporating the 1-octanol-water partitioning method. κ values for the water extracts
15 are high, especially for peat burning particles (A_0 (a whole part of water-soluble fraction): $\kappa =$
16 0.18 , A_I (highly water-soluble fraction): $\kappa = 0.30$). This result stresses the importance of both
17 WSOC fraction and κ of water soluble fraction in determining hygroscopicity of organic aerosol
18 particles. Values of κ correlate positively ($R = 0.89$) with fraction of m/z 44 ion signal quantified
19 using a mass spectrometric technique, demonstrating the importance of highly oxygenated
20 organic compounds in controlling hygroscopicity of Indonesian BB particles. These results can
21 be further utilized for investigating environmental and climatic impacts of Indonesian BB
22 particles in both regional and global scales.

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1 1. Introduction

2 Tropical peatland fires in Southeast Asia, which occur by combustion of both peat and
3 vegetation on it, have become frequent during the last few decades (van der Werf et al., 2010;
4 Reddington et al., 2014; Marlier et al., 2015; Spracklen et al., 2015; Stockwell et al., 2016). The
5 peatland fires keep smoldering for months, releasing huge amounts of greenhouse gases and fine
6 particles to the atmosphere, impacting the atmospheric radiation (Levine et al., 1999; Page et al.,
7 2002; van der Werf et al., 2010). In addition, the peatland burning particles cause transboundary
8 air pollution, influencing visibility and human health (Kunii et al., 2002; Wang et al., 2004;
9 Marlier et al., 2013; Crippa et al., 2016; Koplitz et al., 2016). These regional and global impacts
10 are closely related with water uptake properties of peatland burning particles, as water vapor
11 alters aerosol physical and chemical characteristics, such as particle diameter.

12 Water uptake properties of biomass burning particles, including that emitted from
13 peatlands, have been explored in laboratory by hygroscopic growth and cloud condensation
14 nuclei (CCN) measurements (Chand et al., 2005; Dusek et al., 2005; Day et al., 2006; Petters et
15 al., 2009; Carrico et al., 2010). In general, biomass burning particles are hygroscopic. For
16 instance, the reported range of hygroscopicity parameter, κ , which serves as a metric for water
17 uptake properties, varies from weakly ($\kappa = 0.02$) to highly hygroscopic ($\kappa = 0.80$) for freshly
18 emitted biomass burning particles (Day et al., 2006; Petters and Kreidenweis, 2008; Petters et al.,
19 2009; Carrico et al., 2010). A field observation of water uptake properties of Indonesian biomass
20 burning plumes also demonstrated that these particles are hygroscopic, with a median
21 hygroscopic growth in light scattering ($f(\text{RH})$) of 1.65 between 20% and 80% relative humidity
22 (RH) (Gras et al., 1999). On the other hand, freshly emitted Indonesian peat burning particles
23 generated in a laboratory were suggested to be non-hygroscopic with respect to a quite low $f(\text{RH})$
24 = 1.05 at 90% RH (Chand et al., 2005), and they were almost CCN inactive ($\kappa = 0.05$ for 100 nm
25 particles) (Dusek et al., 2005). The uniqueness of water uptake property of freshly emitted
26 Indonesian peatland burning particles as well as the discrepancy between the previously reported
27 laboratory and field data need to be consistently understood based on their chemical
28 compositions for accurate evaluation on the environmental impacts.



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

17 In this study, hygroscopic growth of Indonesian peatland burning particles was
18 investigated by a series of laboratory experiments to understand the relationships between water
19 uptake properties and chemical characteristics. Hygroscopic growth of fresh peat/biomass
20 burning particles was measured using the humidified tandem differential mobility analyzer
21 (HTDMA) (Massling et al., 2003; Gysel et al., 2004; Carrico et al., 2008, 2010; Dusek et al.,
22 2011). Chemical characterization was also conducted using the Aerodyne Time of Flight-Aerosol
23 Chemical Speciation Monitor (ToF-ACSM). In addition, ratios of water soluble organic carbon
24 (WSOC) to organic carbon (OC) were quantified. These measurements were also conducted for
25 WSOM fraction. Furthermore, WSOM was fractionated by the 1-octanol-water partitioning
26 method, providing data on hydrophilic fraction (Kuwata and Lee, 2017). These data were
27 synergistically combined to provide a detailed picture on water uptake properties of freshly
28 emitted Indonesian peatland burning particles.

29

30 **2. Experiment**



1 2.1. Combustion setup

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

13 The biomass samples were used without desiccation. Approximately 1.0 g of biomass
14 sample was combusted in a sealed 100 L stainless steel container using a crucible, which was
15 heated at 350 °C by a ribbon heater, thermocouple, and PID controller (Kuwata et al., 2017). The
16 target heating temperature was normally achieved within 2 – 3 min. Visual inspection confirmed
17 that the combustion condition was mostly smoldering, consistent with a previous report (Usup et
18 al., 2004). Particle-free air was continuously supplied to the container. Excess amount of
19 particle-free air was released to the laboratory, allowing conducting the experiments at room
20 pressure. Particles generated by the burning experiments were diluted by a two-stage dilution
21 system. Size distributions of biomass burning particles were measured using the Scanning
22 Mobility Particle Sizer (SMPS, TSI Inc.). The measurement range of the SMPS was set as 14.6 –
23 685.4 nm, and time resolution was 3-min. Chemical compositions of particles were quantified
24 using the Aerodyne ToF-ACSM (Fröhlich et al., 2013), while water uptake property was
25 measured using the HTDMA (Massling et al., 2003, 2007; Duplissy et al., 2009). Online
26 measurements with SMPS, ToF-ACSM, and HTDMA were all operated following the dilution.
27 Each combustion experiment lasted for ~ 1 h. Detailed descriptions about the ToF-ACSM and
28 HTDMA are provided in the following sections.

29 Two filter samples were also collected simultaneously for each of the experiments.
30 Particles were collected onto two 47 mm diameter filters housed in stainless steel filter holders



1 (BGI Inc.) for half an hour at flowrates of 5.0 lpm. Teflon filters (0.2 μm pore size, Fluoropore™,
2 Sigma Aldrich) were used for WSOM samples, while quartz filter samples were employed for
3 carbon analysis by the thermal-optical method. The collected samples were stored under
4 refrigeration at $-20\text{ }^{\circ}\text{C}$ until analysis.

5 **2.2. Extraction and nebulization of WSOM**

6 Filter samples were extracted using approximately 20 ml of ultrapure water (Type I) by
7 sonicating them for 30-min at room temperature. The resulting solutions were filtered through
8 0.2 μm PTFE syringe filters (514-0070, VWR), yielding water extracts (denoted as A_0 , i.e., a
9 whole part of or bulk water-soluble fraction). An aliquot of A_0 was mixed with the same volume
10 (5 ml) of 1-octanol (Wako first grade, Wako) using a separatory funnel for classification by 1-
11 octanol-water extraction (Valvani et al., 1981). The aqueous phase following the 1-octanol-water
12 extraction is denoted as A_I (slightly less than 5 ml), corresponding to the highly water-soluble
13 fraction. Details of the extraction method are provided in Kuwata and Lee (2017).

14 The aqueous solutions were nebulized using a glass nebulizer. A mass flow controller
15 (MC-20 SLPM-D, Alicat Scientific, Inc.) was used to regulate the flow rate (3.5 lpm) of particle-
16 free air supplied to the nebulizer. Following nebulization, the sample was desiccated by a
17 diffusion dryer (Model 42000, Brechtel Manufacturing, Inc.) filled with silica gel (Chameleon
18 83000.360, VWR International). The desiccated particles were measured using the HTDMA,
19 ToF-ACSM, and SMPS. The analysis of A_0 and A_I were conducted only for peat (sampled from a
20 burnt area, Riau-4), acacia, and fern samples.

21 **2.3. HTDMA**

22 Hygroscopic growth of particles was measured using the HTDMA (Massling et al., 2003,
23 2007; Duplissy et al., 2009; Gysel et al., 2009). The HTDMA system consists of three major
24 components: 1) the first DMA (TSI Inc. Model 3081) to select monodisperse particles of a
25 specific diameter, 2) the humidification unit for hydrating the classified particles at a target RH,
26 and 3) the second DMA (TSI Inc. Model 3081) and a condensation particle counter (CPC, TSI
27 Inc. Model 3775) to detect humidified size distributions (Figure S1).



1 Aerosol particles were dried using a diffusion dryer (Model 42000, Brechtel
2 Manufacturing, Inc.), and introduced to the first DMA at a flow rate of 0.3 lpm. The first DMA
3 selected 50, 100, and 200 nm particles. Both the first and second DMAs were operated at sheath-
4 to-sample flow ratios of 10:1. The resulting monodisperse particles were exposed to a predefined
5 RH environment using two Nafion membrane tubes (Permapure Inc. Model MD-110-12S-4) in
6 series. The target RH, which was set at 90%, was regulated by controlling the flow ratio of
7 humidified and dry air flows via a PID controlling software (National Instruments Inc. Labview).
8 The particle residence time between the humidifier and the second DMA was approximately
9 10 seconds. The RH-controlled humid air was used as the sheath flow for the second DMA. The
10 RH and temperature of the second DMA were continuously monitored at both the sample inlet
11 and sheath outlet using two capacitive RH and temperature probes (Rotronic Inc. Hygroclip
12 HC2-S). The RH differences between the sample and sheath flows were less than 2%. RH of
13 humidified sample air was slightly higher than that of the sheath outflow for the setup shown in
14 Figure S1.

15 The operating conditions of the DMAs were checked using 100 ± 3 nm polystyrene latex
16 particles (PSL, Thermo Scientific Inc., Cat. No.: 3100A). Hygroscopic growth of particles in the
17 HTDMA was calibrated by measuring growth factor (g), which is defined as a diameter ratio of
18 humidified ($D(RH)$) and dry particles (D_0) ($g = D(RH)/D_0$), of ammonium sulfate particles.
19 The measured value of g at RH = 85% was 1.71 ($D_0 = 150$ nm), which is comparable to a
20 literature data ($g = 1.69$) (Tang and Munkelwitz, 1994). The stability of detected RH of the
21 HTDMA system was within $\pm 1.0\%$ RH (peak-to-peak) for the target RH of 90% (Figure S2).
22 Volume mean growth factor (GF) was calculated using measured probability density function of
23 g ($c(g, D_0)$) as $GF = (\int_0^\infty g^3 c(g, D_0) dg)^{1/3}$.

24 **2.4. Chemical characterization**

25 The Aerodyne ToF-ACSM was utilized to measure chemical compositions of non-
26 refractory submicron particles (NR-PM₁) (Fröhlich et al., 2013). Five specific chemical
27 components, including organic matter (OM), sulfate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺),
28 and chloride (Cl⁻), were quantitatively detected (Allan et al., 2003), with a time resolution of 3-
29 min.



1 Bulk OC, elemental carbon (EC), and WSOC contents were also analyzed for 10 samples
2 (Table 3) using quartz-fiber filter samples (47 mm in diameter). All the quartz-fiber filters were
3 prebaked at 900 °C for 3 h before sampling. The filter samples were stored in a refrigerator (−20
4 °C) until analysis. For each sampling, a back-up quartz-fiber filter was used to account for
5 potential influence of adsorption of gas phase organic components (Turpin et al., 1994). OC
6 loading on the back-up filter was subtracted from that on the front filter to estimate particulate
7 OC (i.e., corrected OC).

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

16

17 **3. Results and discussion**

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

24 **3.1. Hygroscopic growth factor**

25 Figure 2 shows normalized particle number size distributions of peat sampled from a
26 burnt area (Riau-4), acacia leaves, and fern burning particles following hygroscopic growth at
27 RH = 90% ($D_0 = 100$ nm). The data shown in Figure 2 includes both online (a) and offline ((b):
28 A_0 , and (c): A_I) measurements. In all cases, narrow monodisperse distributions were observed,



1 demonstrating that chemical compositions of particles were uniform (Gysel et al., 2007; Carrico
2 et al., 2010). For online measurements, diameter change induced by hygroscopic growth was
3 minimal for the peat and acacia burning particles ($g = 1.05 \sim 1.09$), while diameter of fern
4 burning particles significantly increased following exposure to high RH ($g = 1.17$). The variation
5 in hygroscopic properties is originated from differences in organic chemical composition, as
6 these biomass burning particles contain negligible fractions of inorganic ionic species
7 (Budisulistiorini et al., 2017).

8 Table 2 summarizes all the values of GF. Values of GF for most of peat samples from
9 burnt peatland in Riau were less than 1.1. Sampling depths of peat did not significantly affect GF.
10 There was no clear size-dependence of GF. For instance, GF values of particles from combustion
11 of peat at drained and burnt areas in Riau were 1.07 ± 0.04 ($D_0 = 50$ nm), 1.06 ± 0.02 ($D_0 =$
12 100 nm), and 1.07 ± 0.02 ($D_0 = 200$ nm). Particles emitted from the undisturbed forest area in
13 Riau (i.e., Riau-Zam) were more hygroscopic (GF = 1.11 for $D_0 = 100$ nm) than those generated
14 from other samples from Riau, while GF of particles emitted by combustion of a peat sample
15 from the secondary forest in Riau (i.e., Riau-SF) was very similar to those from Riau peat
16 samples from burnt areas (i.e., Riau-1~4). The similarity is probably due to the short distance
17 between the two sampling sites (less than 10 km). Particles emitted from peat samples collected
18 at Central Kalimantan (i.e., C.K.-DB and C.K.-DF) were relatively more hygroscopic (GF > 1.11)
19 than those from Riau.

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

29 3.2. Hygroscopicity parameter (κ)



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

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

4 where $\sigma_{s/a}$ is the surface tension of the solution/air interface (0.0718 N m⁻¹ at 25 °C), M_w is the
5 molecular weight of water (18 g mol⁻¹), R is the universal gas constant (8.31 J K⁻¹ mol⁻¹) and T is
6 temperature (298 K). The κ value is related with molar volume of water soluble compounds
7 (M_s/ρ_s), which is calculated from both the molecular weight (M_s) and density (ρ_s) by the
8 following equation (Rose et al., 2008).

$$9 \quad \kappa = i_s \frac{\rho_s M_w}{\rho_w M_s} \quad (2),$$

10 where i is van't Hoff factor, ρ_w is the density of water. The calculated values of κ are
11 summarized in Figure 3 and Table 2.

12 The range of κ for peat burning particles in Riau (sampled from burnt areas) is 0.02 to
13 0.04, while that for Central Kalimantan samples is 0.05 to 0.06 (100 nm). These values may be
14 compared with CCN activity of peat burning particles reported by Dusek et al. (2005). Based on
15 the experimental data by Dusek et al. (2005), the critical supersaturation for CCN activation of
16 Indonesian peat burning particles is derived as 0.53% for 100 nm particles. This value can be
17 converted to κ of 0.05, which is very similar to the values summarized in Figure 3 and Table 2.
18 The consistently low values of κ suggest that water uptake by freshly emitted peat burning
19 particles is minimal. The range of κ observed for acacia and fern burning particles ($\kappa = 0.04$ – 0.08)
20 is comparable to that observed for less hygroscopic mode by previous laboratory experiments on
21 biomass burning particles (Carrico et al., 2010).

22 The values of κ observed for water extracts (A_0) span from 0.11 (acacia, 100 nm) to 0.18
23 (peat sampled from a burnt area, Riau-4, 100 nm) (Figure 4 and Table 2). The κ value for peat
24 burning particles (A_0) is significantly higher than those emitted from the acacia and fern leaves,



1 highlighting the importance of understanding hygroscopicity of WSOM as well as water soluble
2 fraction in quantitatively understanding water uptake properties. The value of κ for acacia
3 burning particles is similar to that was measured for WSOM extracted from a prescribed forest
4 fire experiment in Georgia (USA) ($\kappa = 0.10$), which was estimated from a molar volume of $1.6 \times$
5 $10^{-4} \text{ m}^3 \text{ mol}^{-1}$ (Asa-Awuku et al., 2008).

6 The κ values for A_I are higher than those for A_0 . Namely, κ observed for A_I were 0.30
7 (peat sampled from a burnt area, Riau-4), 0.24 (acacia), and 0.18 (fern), respectively. Kuwata
8 and Lee (2017) demonstrated that classification of WSOM by XAD-8 column, which is one of
9 the most frequently used materials for solid phase extraction of WSOM, has a strong relationship
10 with 1-octanol-water partitioning coefficient (K_{OW}). Namely, XAD-8 column selectively traps
11 hydrophobic chemical species in WSOM, which tend to partition to 1-octanol phase ($K_{OW} > 1$).
12 Thus, hydrophilic fraction separated by XAD-8 is dominantly composed of chemical species,
13 which has $K_{OW} < 1$. The WSOM in A_I is also dominantly composed of organic compounds with
14 lower values of K_{OW} ($K_{OW} < 1$), suggesting that A_I and WSOM classified by XAD-8 are
15 comparable. The κ value of biomass burning WSOM separated by XAD-8 is estimated as 0.29,
16 using molar volume ($6.2 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) estimated from a CCN measurement by Asa-Awuku et
17 al. (2008). The comparison provides a typical range of κ for hydrophilic ($K_{OW} < 1$) fraction of
18 WSOM emitted from biomass burning as 0.2~0.3.

19 3.3. κ (online) and WSOC/OC

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



1 The WSOC fractions for acacia and fern burning particles were relatively higher (WSOC/OC =
2 3.42–6.56%) than those from peat combustion.

3 Figure 5 compares κ and WSOC/OC ratios. κ and WSOC/OC correlate to some extent (R
4 = 0.65), although the variation ranges for both variables are small. Fern burning particles contain
5 significantly higher fraction of WSOM than other samples, providing an explanation for higher κ
6 value for fern burning particles. Nevertheless, the correlation between these two parameters is
7 not tight. This result suggests that other factors, such as chemical composition and hygroscopic
8 property of water soluble fraction, should also be considered to quantitatively understand water
9 uptake property.

10 **3.4. κ and OM mass spectra**

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

25 The mass spectra of A_0 are significantly different from those of online measurements. The
26 most abundant ion in the mass spectra of A_0 is m/z 44. Hydrocarbon peaks, such as m/z 41, 43, 55,
27 and 57, are still significant, yet less abundant than those of the online measurements. In addition,
28 contributions of m/z 60 and 73 are also enhanced. These results consistently support the idea that



1 A_0 fraction is highly oxygenated. Especially, A_0 fraction for peat burning particles is much more
2 oxidized than those of fern and acacia samples.

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

12 Figure 7 displays f_{44} , f_{60} , and mean κ for different types of Indonesian biomass burning
13 particles. The data points in Figure 7 distribute to two different regions. Low f_{44} and f_{60} values are
14 observed for particles emitted from Sumatran peat burning (i.e., Riau-1, -2, -3, -4). The f_{44} of
15 acacia burning particles is slightly higher but f_{60} is low. By contrast, distinctly higher f_{44} and f_{60}
16 are observed for fern, undisturbed peat (Riau), and peat (Central Kalimantan) burning particles.
17 This is also in accordance with ^1H NMR analysis, which suggests that functional group
18 distributions of peat and acacia burning particles are significantly different from that emitted
19 from fern burning particles (Figure S3). The higher WSOC fraction and κ of fern burning
20 particles could be related with the higher f_{44} and f_{60} .

21 Figure 8 correlates κ with f_{44} for both online and offline measurements of peat sampled at
22 a burnt area (Riau-4), acacia and fern burning particles. Similar correlations for all the biomass
23 burning samples are displayed in Figure S4 of the supplementary material. The correlation of
24 these two variables is represented as $\kappa = 2.31 \times f_{44} + 0.02$ ($R = 0.89$). The slope is very close to
25 that reported for the relationship between the hygroscopicity of organics (κ_{org}) and f_{44} ($\kappa_{org} =$
26 $2.2 \times f_{44} - 0.13$, Duplissy et al., 2011). The correlation demonstrates that the degree of
27 oxidation, which is represented by f_{44} , is the key controlling parameter in determining
28 hygroscopicity of Indonesian biomass burning particles. As discussed above, f_{44} of peat burning
29 particles (Riau-4) is extremely small (Table 3). Minimal water uptake by peat burning particles



1 (Riau-4) could be associated with low water soluble fraction (Table 3), considering that both κ
2 and f_{44} for the corresponding A_0 or A_I sample are high.

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

16

17 **4. Conclusions**

18 Hygroscopic growth of freshly emitted Indonesian biomass burning particles was
19 investigated in laboratory using the humidified tandem differential mobility analyzer (RH =
20 90%). The biomass samples included peat, fern, and acacia leaves collected at Riau and Central
21 Kalimantan in Indonesia. Hygroscopicity was measured for the freshly emitted particles (online),
22 bulk water-soluble fraction (A_0), and highly water-soluble fraction (i.e., fraction with lower K_{OW}
23 values) classified by the 1-octanol-water partitioning method (A_I). Hygroscopicity parameter κ
24 was derived from the growth factor data. Chemical compositions of these particles were also
25 quantified using both online and offline techniques.

26 Hygroscopicity of fresh Indonesian peat burning particles is highly dependent on the
27 origin and condition (e.g., pristine and disturbed) of peat. Particles emitted from combustion of
28 disturbed peat in Riau were nearly non-hygroscopic (mean $\kappa = 0.02$ – 0.04), while those from



1 undisturbed areas were more hygroscopic ($\kappa = 0.03$ – 0.05). Particles emitted from Central
2 Kalimantan peat samples were generally more hygroscopic ($\kappa = 0.05$ – 0.06) than those from Riau.
3 For biomass samples, acacia burning particles were slightly hygroscopic ($\kappa = 0.03$ – 0.04), and
4 fern burning particles were the most hygroscopic ($\kappa = 0.04$ – 0.09) among all samples. These
5 values loosely correlated with ratio of WSOC to OC ($R = 0.65$). This result suggests that WSOC
6 fraction could play an important role in determining κ , yet other factors, such as difference in
7 hygroscopicity of slightly and highly water-soluble fractions, should also be considered.

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

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

19 Our experimental results are consistent with previous laboratory studies, which reported
20 insignificant water uptake by fresh Indonesian peat burning particle (Chand et al., 2005; Dusek et
21 al., 2005). On the contrary, Gras et al. (1999) showed that particles observed in wildfire plume
22 from Kalimantan were hygroscopic. The differences between field observation and laboratory
23 experiments could be caused by atmospheric processes (e.g., secondary formation and chemical
24 aging of particles), and likely resulted from the differences of burnt materials, their origins and
25 combustion conditions in practical situations as well. In the future, observations of both chemical
26 composition and hygroscopic growth of particles emitted from peatland fires need to be
27 conducted both at vicinity and downstream regions to address the question. The last but not the
28 least, results obtained from this work can be further developed and applied for modeling studies,



1 improving estimation of aerosol radiative forcing introduced by Indonesian peat burning
2 particles in both regional and global scales.

3

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18



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

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

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

5 # D&UB represents the drained but unburnt case.

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



- 1 **Table 2.** Volume weighted mean GF and κ values (average \pm 1 standard deviation, S.D.) of
 2 different types of Indonesian peat and biomasses. The results of their aqueous extracts (A_0 and
 3 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 \pm	1.09 \pm	1.04 \pm	0.089 \pm	0.039 \pm	0.016 \pm
			0.07	0.06	0.01	0.042	0.028	0.002
		Riau-1.1	1.15 \pm	1.05 \pm	1.04 \pm	0.080 \pm	0.021 \pm	0.014 \pm
			0.06	0.01	0.01	0.036	0.005	0.002
		Riau-1.2	1.00 \pm	1.08 \pm	1.06 \pm	0.001 \pm	0.036 \pm	0.025 \pm
			0.002	0.04	0.01	0.001	0.017	0.002
		Riau-2	–	1.07 \pm	1.12 \pm	–	0.029 \pm	0.052 \pm
				0.01	0.06		0.005	0.032
		Riau-2.1	1.06 \pm	1.06 \pm	1.06 \pm	0.029 \pm	0.023 \pm	0.024 \pm
			0.04	0.01	0.01	0.019	0.005	0.005
	Riau-2.2	1.05 \pm	1.09 \pm	1.10 \pm	0.024 \pm	0.037 \pm	0.042 \pm	
		0.02	0.02	0.02	0.010	0.009	0.009	
	Riau-3	1.07 \pm	1.05 \pm	1.08 \pm	0.035 \pm	0.022 \pm	0.033 \pm	
		0.04	0.01	0.01	0.022	0.006	0.006	
	Riau-3.1	1.05 \pm	1.05 \pm	1.08 \pm	0.024 \pm	0.022 \pm	0.031 \pm	
0.02		0.02	0.01	0.012	0.010	0.006		
Riau-4	1.04 \pm	1.08 \pm	1.05 \pm	0.017 \pm	0.034 \pm	0.019 \pm		
	0.01	0.01	0.002	0.003	0.003	0.001		
Riau-4.1	1.07 \pm	0.99 \pm	1.02 \pm	0.059 \pm	N/A	0.007 \pm		
	0.10	0.01	0.01	0.063		0.003		
(Burnt peatland)	Riau D&B[#]	1.07 \pm	1.06 \pm	1.07 \pm	0.040 \pm	0.029 \pm	0.026 \pm	
		0.04	0.02	0.02	0.023	0.010	0.007	
(Secondary forest)	Riau-SF	1.04 \pm	1.07 \pm	1.09 \pm	0.025 \pm	0.028 \pm	0.034 \pm	
		0.05	0.004	0.01	0.028	0.002	0.003	
(Undisturbed area)	Riau-Zam	1.10 \pm	1.11 \pm	1.08 \pm	0.053 \pm	0.048 \pm	0.032 \pm	
		0.07	0.04	0.004	0.038	0.017	0.002	
Kalimantan	C.K.-DF	1.11 \pm	1.13 \pm	1.11 \pm	0.057 \pm	0.058 \pm	0.046 \pm	
		0.06	0.01	0.01	0.033	0.005	0.004	
	C.K.-DB	1.11 \pm	1.12 \pm	1.13 \pm	0.055 \pm	0.054 \pm	0.056 \pm	
0.05		0.02	0.01	0.028	0.011	0.005		
	acacia	1.05 \pm	1.09 \pm	1.09 \pm	0.026 \pm	0.039 \pm	0.037 \pm	
	fern	1.08 \pm	1.17 \pm	1.20 \pm	0.039 \pm	0.078 \pm	0.088 \pm	
		0.02	0.02	0.03	0.011	0.010	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
		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
		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

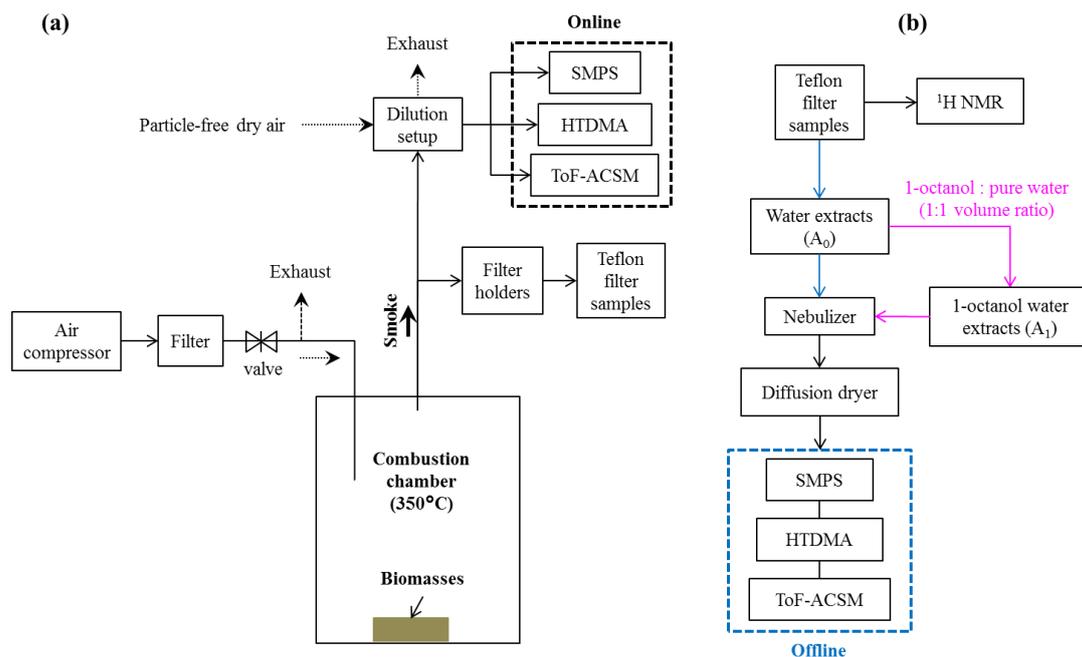
- 1 – Data is unavailable due to low particle number concentration.
- 2 # **Riau D&B** represents the averages of all the D&B peat samples collected from different
- 3 depths of the Sumatran peatlands (i.e., samples used for **Exp. 1-10** in Table 1).
- 4 * **Peat** in Table 2 refers to the Riau-4 sample collected from burnt peatlands in Sumatra (see
- 5 Sect.2 for details).



1 **Table 3.** Summary of chemical characteristics of different types of Indonesian peat and biomass
 2 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
	peat*	0.179	9.5	15.8	N/A	N/A	N/A
A0	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
	peat*	0.302	9.3	16.0	N/A	N/A	N/A
A1	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

3



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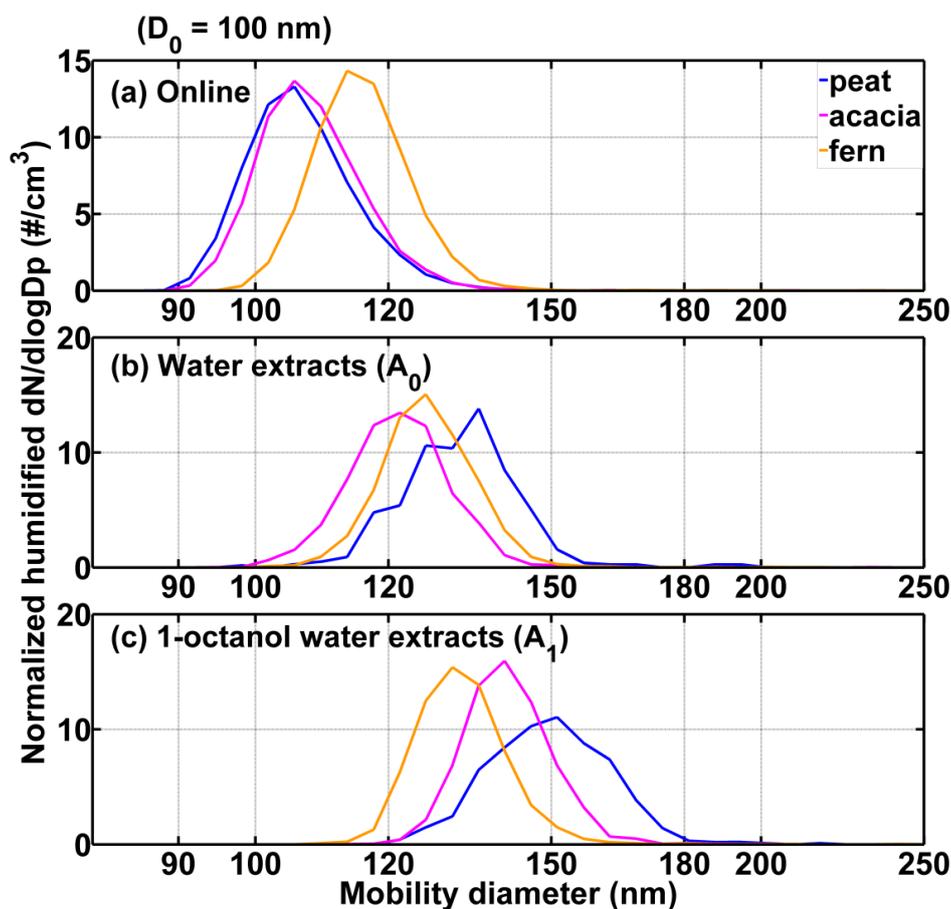
2 **Fig. 1** Schematic diagrams of the laboratory experimental setups.

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

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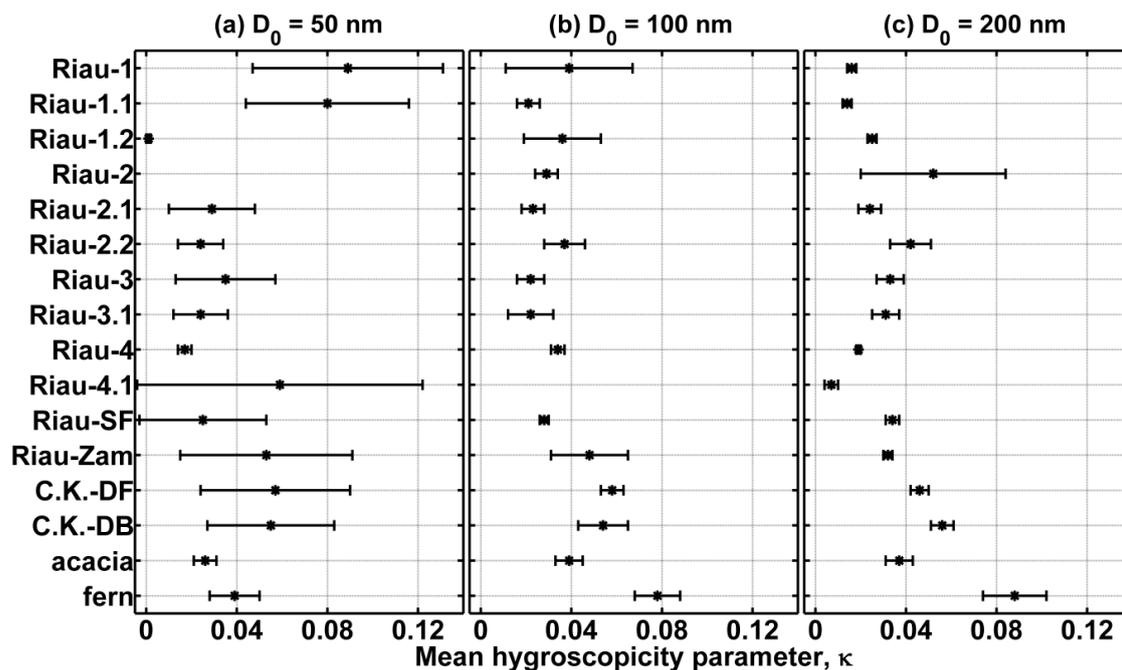
3 **Fig.2** Normalized number size distributions measured by the HTDMA ($D_0 = 100$ nm; RH =
4 90%) of peat, fern and acacia burning particles. (a) online data, (b) A_0 , and (c) A_1 . For online data,
5 peat burning particles are nearly non-hygroscopic, while fern burning particles are more
6 hygroscopic. Aqueous extracts of peat burning particles are the most hygroscopic among the
7 three types of biomasses. The x-axis is on a logarithmic scale.

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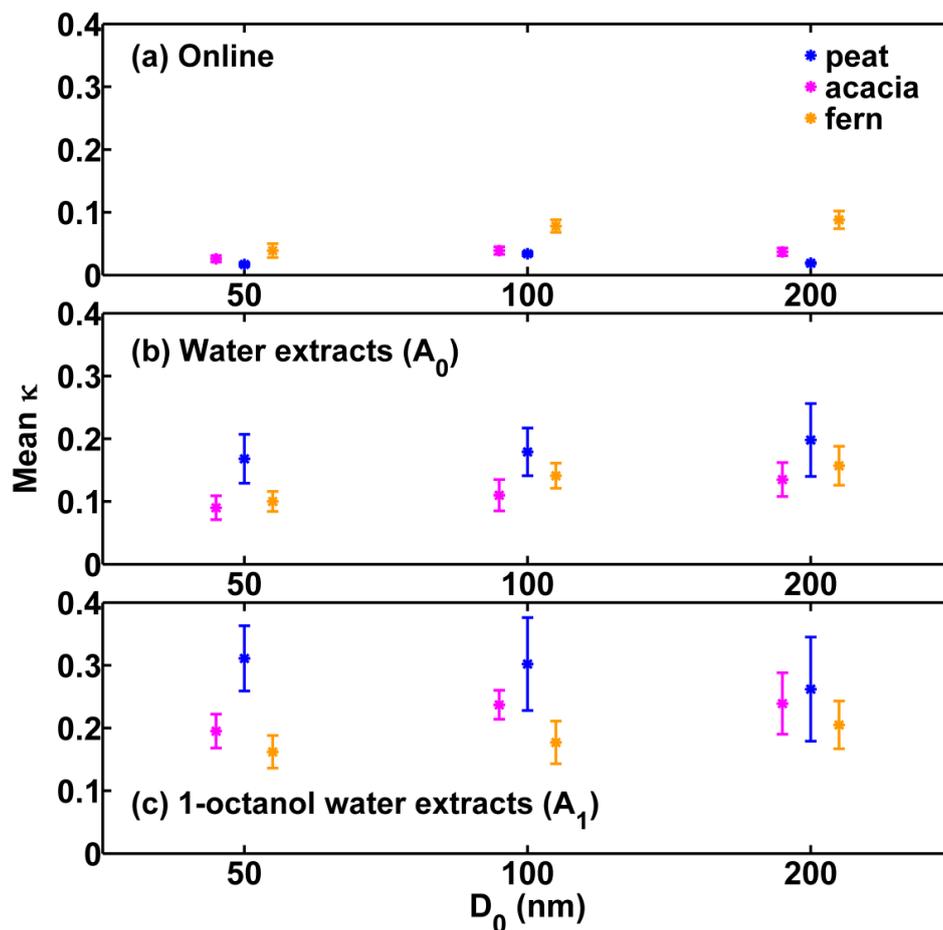
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3 **Fig.3** Mean κ values of fresh Indonesian biomass burning particles measured for (a) $D_0 = 50$ nm,
4 (b) $D_0 = 100$ nm, and (c) $D_0 = 200$ nm particles. In all cases, κ values are lower than 0.1. The
5 largest κ values were measured for fern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

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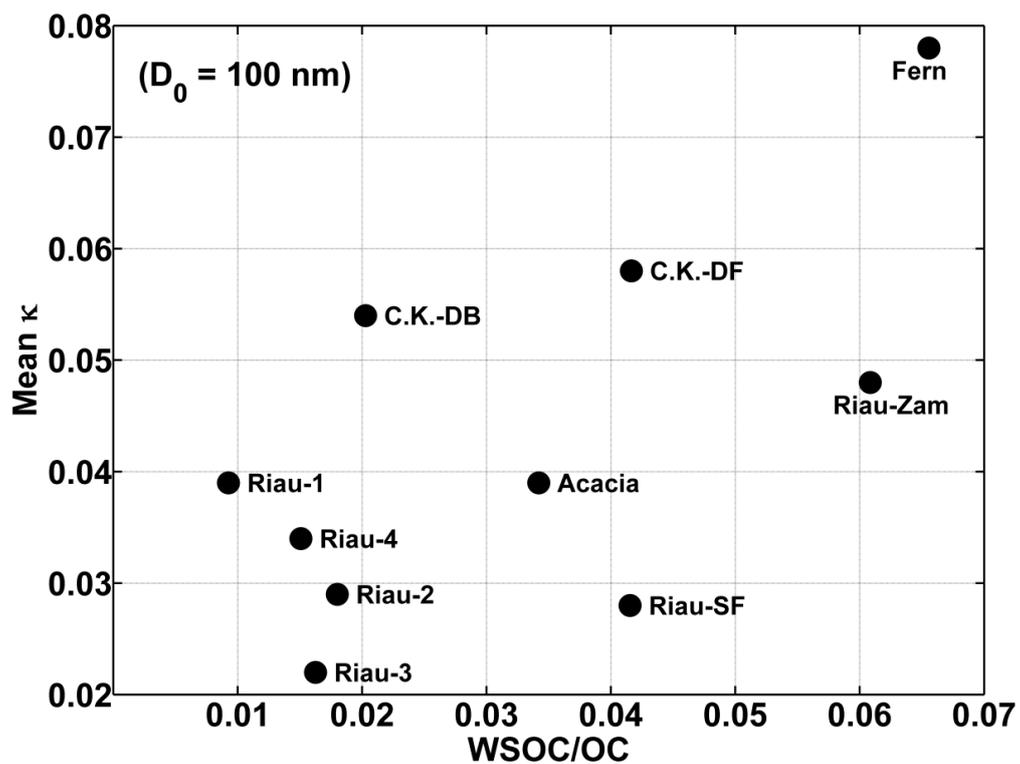
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3 **Fig.4** Comparison of κ values for (a) online, (b) water extracts (A_0), and (c) 1-octanol water
4 extracts (A_1). The data for peat (Riau-4), acacia, and fern are shown. Indonesian peat burning
5 particles are almost non-hygroscopic for online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

7

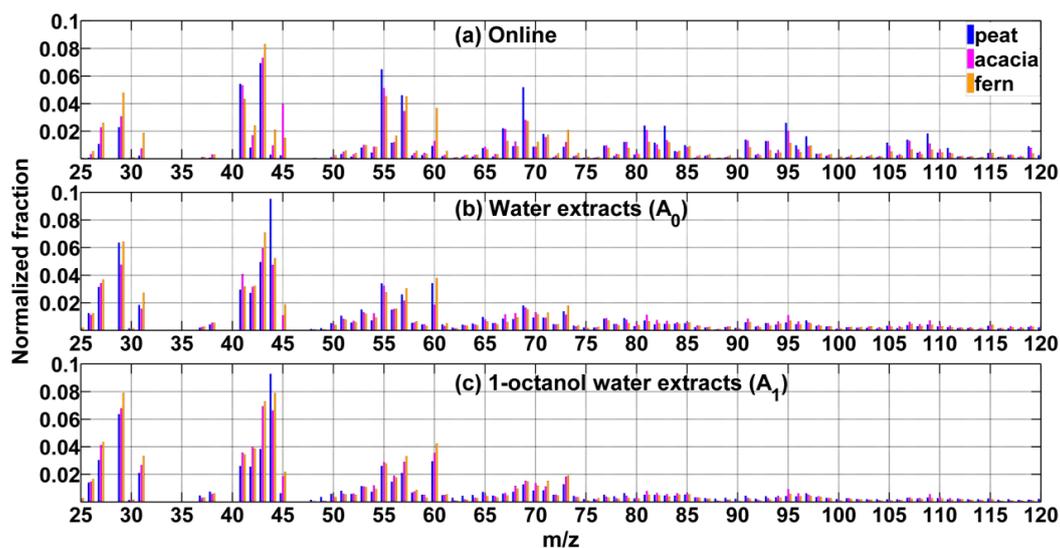


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3 **Fig.5** Correlation of κ and WSOC/OC ratio for different types of Indonesian peat and biomasses.



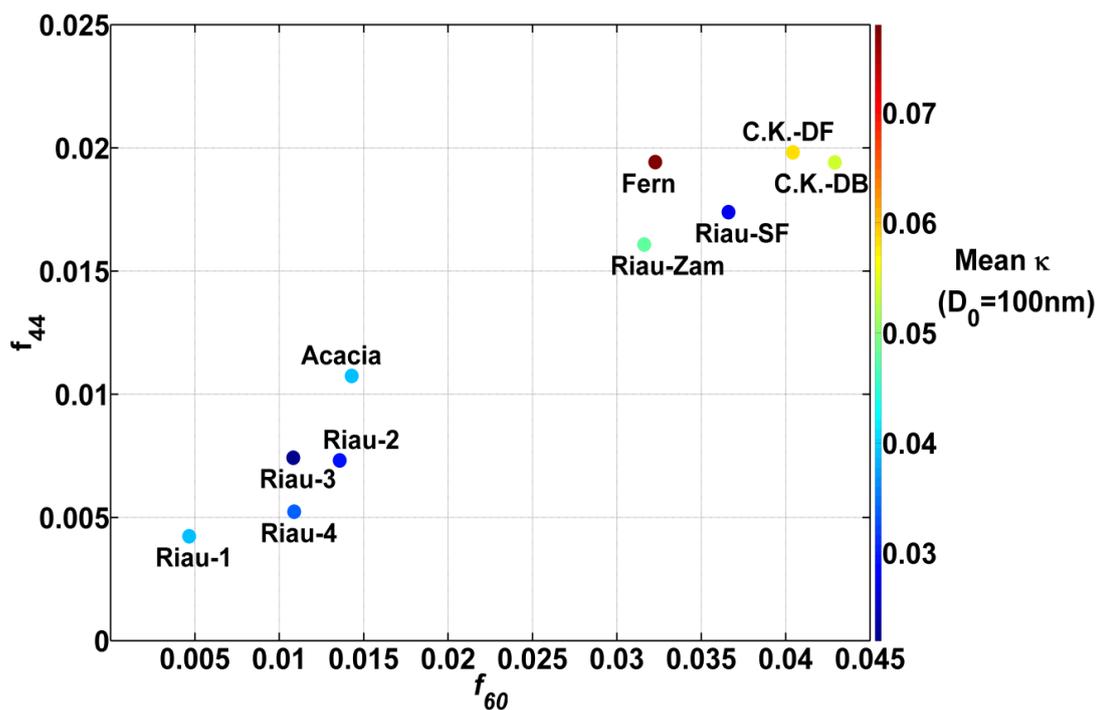
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2 **Fig.6** Mass spectra of organics in Indonesian biomass burning particles measured for peat, acacia,
3 and fern samples. (a) online, (b) A_0 , and (c) A_1 data are shown. Ion signals (m/z) from
4 hydrocarbon-like organic compounds (e.g., m/z 41,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

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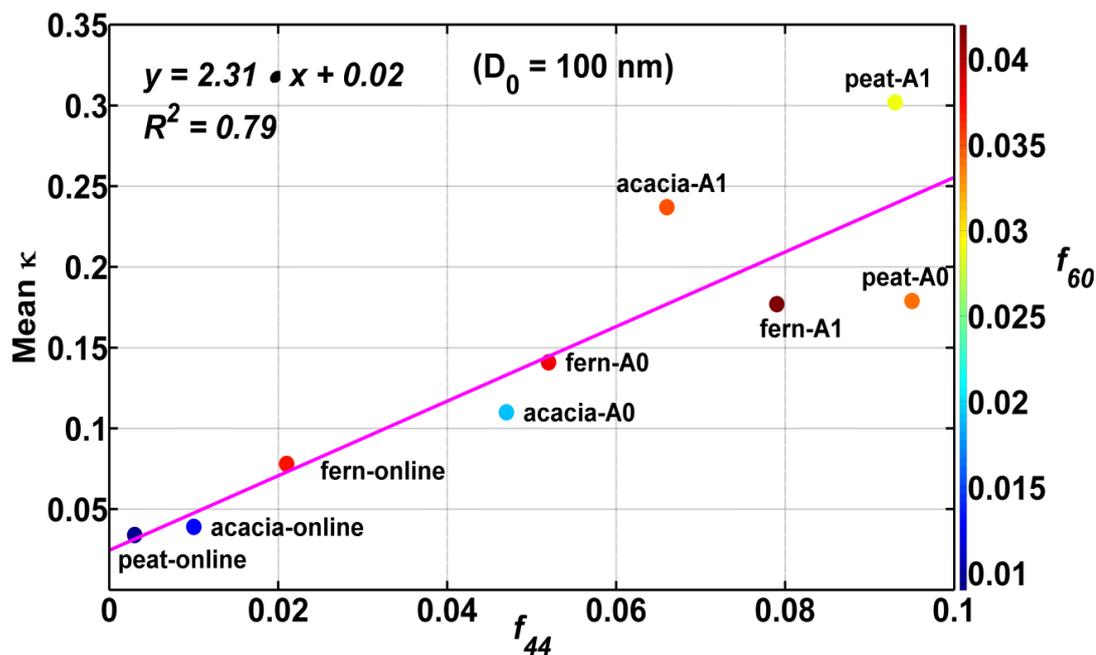
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3 **Fig.7** Correlation of f_{44} and f_{60} for different types of Indonesian peat and biomasses.

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1



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