

RESEARCH ARTICLE

10.1002/2016JD025897

Key Points:

- Emissions of CH₄ and aerosol particles from tropical peatland burning are regulated by temperature
- CH₄ emission from combustion of charcoal is much lower than that from peat
- Temperature and burning history need to be considered in estimating emission

Supporting Information:

- Supporting Information S1

Correspondence to:

M. Kuwata,
kuwata@ntu.edu.sg

Citation:

Kuwata, M., F. M. Kai, L. D. Q. Yang, M. Itoh, H. Gunawan, and C. F. Harvey (2017), Temperature and burning history affect emissions of greenhouse gases and aerosol particles from tropical peatland fire, *J. Geophys. Res. Atmos.*, 122, 1281–1292, doi:10.1002/2016JD025897.




Received 4 SEP 2016

Accepted 27 DEC 2016

Accepted article online 30 DEC 2016

Published online 21 JAN 2017

Temperature and burning history affect emissions of greenhouse gases and aerosol particles from tropical peatland fire

Mikinori Kuwata^{1,2} , Fuu Ming Kai^{3,4}, Liudongqing Yang⁵ , Masayuki Itoh² , Haris Gunawan⁶, and Charles F. Harvey^{3,7}

¹Asian School of the Environment and Earth Observatory of Singapore, Nanyang Technological University, Singapore, Singapore, ²Center for Southeast Asian Studies, Kyoto University, Kyoto, Japan, ³Center for Environmental Sensing and Modeling, Singapore-MIT Alliance for Research and Technology, Singapore, ⁴Now at National Metrology Centre, Agency for Science, Technology and Research, Singapore, ⁵Division of Chemistry & Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore, ⁶Center for Disaster Studies, Riau University, Pekanbaru, Indonesia, ⁷Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA

Abstract Tropical peatland burning in Asia has been intensifying over the last decades, emitting huge amounts of gas species and aerosol particles. Both laboratory and field studies have been conducted to investigate emission from peat burning, yet a significant variability in data still exists. We conducted a series of experiments to characterize the gas and particulate matter emitted during burning of a peat sample from Sumatra in Indonesia. Heating temperature of peat was found to regulate the ratio of CH₄ to CO₂ in emissions ($\Delta\text{CH}_4/\Delta\text{CO}_2$) as well as the chemical composition of particulate matter. The $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio was larger for higher temperatures, meaning that CH₄ emission is more pronounced at these conditions. Mass spectrometric analysis of organic components indicated that aerosol particles emitted at higher temperatures had more unsaturated bonds and ring structures than that emitted from cooler fires. The result was consistently confirmed by nuclear magnetic resonance analysis. In addition, CH₄ emitted by burning charcoal, which is derived from previously burned peat, was lower by at least an order of magnitude than that from fresh peat. These results highlight the importance of both fire history and heating temperature for the composition of tropical peat-fire emissions. They suggest that remote sensing technologies that map fire histories and temperatures could provide improved estimates of emissions.

1. Introduction

Geological records indicate that biomass burning of wildfires started at least 419 Myr ago [Glasspool and Scott, 2010]. The occurrence of wildfire has sharply increased following the industrial revolution and concurrent conversion of land use [Pechony and Shindell, 2010; Heald and Spracklen, 2015]. Wildfires are projected to be more pronounced in the future as a result of changes in human activities and climate [Pechony and Shindell, 2010].

Wildfires in tropical peatland in Asia have increased rapidly in recent years. Most tropical peatland are in Sumatra and Borneo [Yu et al., 2010] and have their origin 3000–5000 years ago after sea level dropped from its last high stand. Analysis of charcoal in peat core samples from Kalimantan island demonstrated that wildfires have only become common in the last millennium [Hope et al., 2005]. During the last couple of decades, wildfire in tropical peatland have become very frequent, especially in dry years associated with El Niño [Field et al., 2009]. Rapid development and degradation of peatlands are now causing peatland fire even during nondrought years [Gaveau et al., 2014].

Peatlands become dry and flammable as the water table drops below the land surface, allowing the peat at the surface to dry [Field et al., 2016]. Hayasaka et al. [2014] found that fires began when the water table dropped to 30 cm below the peat surface and became more severe as the water table fell further. Wosten et al. [2008] recommend that the water table should be maintained at a depth less than 40 cm to maximize peatland resilience to fire. However, many tropical peatlands are now drained for agriculture, often for oil palm plantations, and are now prone to wildfires [Page et al., 2002]. As more and more peatlands are drained, the underlying soil has become flammable in greater expanses of land. The resulting increase in wildfires has impacted both the global climate and local environment. For instance, an intense tropical peatland fire event

Table 1. Emission Ratios CH₄ and CO₂ ($\Delta\text{CH}_4/\Delta\text{CO}_2$) for Indonesian Wildfire/Peatland Fire Reported in Literature

Location ^a	$\Delta\text{CH}_4/\Delta\text{CO}_2$ (ppmv/ppmv)	Reference
<i>Laboratory Experiment</i>		
Alaska/Minnesota	0.0135	[Stockwell et al., 2014]
Canada	0.0135	[Stockwell et al., 2014]
Kalimantan	0.0215	[Stockwell et al., 2014]
North Carolina	0.0281	[Stockwell et al., 2014]
Sumatra	0.0336	[Christian et al., 2003]
Sumatra	0.0017–0.0326 (CH ₄ /CO ₂) _{max} : 0.0149–0.0326 ^b (CH ₄ /CO ₂) _{ss} : 0.0079–0.012 ^b	This study
<i>Ground Observation</i>		
Central Kalimantan	0.0261	[Hamada et al., 2013]
Central Kalimantan	0.0167	[Stockwell et al., 2016]
Central Kalimantan	0.00753–0.0197	[Parker et al., 2016]
<i>Aircraft Observation</i>		
Japan Airlines flights landing/departing Singapore	0.00454 ^c	[Matsueda and Inoue, 1999]
<i>Satellite Observation</i>		
Kalimantan	0.0062–0.0136	[Parker et al., 2016]
Sumatra	0.0066–0.0088	[Parker et al., 2016]

^aOrigin of peat samples for laboratory experiments. Sampling sites for observations.

^bTemperature range: 280–450°C. See the text for details.

^cCalculated from reported values of $\Delta\text{CH}_4/\Delta\text{CO}$ and $\Delta\text{CO}/\Delta\text{CO}_2$.

occurred in 2015, emitting 380 Tg C to the atmosphere, which is comparable to the annual carbon emission from Japan [Field et al., 2016]. Mass concentration of aerosol particles emitted from the wildfire can be as high as 3.7 mg m⁻³, influencing both cloud formation and the radiative balance of the equatorial Asian region [Rosenfeld, 1999; Ge et al., 2014; Stockwell et al., 2016]. Furthermore, air pollution induced by haze has impacted human health in the region [Kunii et al., 2002; Marlier et al., 2013]. Studies on emissions of greenhouse gases as well as aerosol particles from tropical peat burning are necessary; however, only limited research has been reported and the results are variable [Christian et al., 2003; Stockwell et al., 2014; Parker et al., 2016]. For instance, emission ratios of CH₄ and CO₂ ($\Delta\text{CH}_4/\Delta\text{CO}_2$) are summarized in Table 1. The measured values of $\Delta\text{CH}_4/\Delta\text{CO}_2$ range from 0.0045 to 0.033, meaning that the magnitude of variability is a factor of 7. Even for in situ observations at the Central Kalimantan Province in Indonesia, the variability of the data is as large as a factor of 3 [Hamada et al., 2013; Parker et al., 2016; Stockwell et al., 2016]. For instance, Parker et al. [2016] quantified the range of $\Delta\text{CH}_4/\Delta\text{CO}_2$ as 0.00753 to 0.0197 by conducting ground observation. However, the cause of the variability has never been investigated.

Such a significant variability in chemical characteristics also exists for aerosol particles emitted from peatland burning. For instance, laboratory experiments demonstrated that emission ratios of organic carbon (OC) and elemental carbon (EC) from peatland burning can vary by more than an order of magnitude (OC/EC = 13–151) [Christian et al., 2003; Iinuma et al., 2007]. Although the range agrees with that from a recent field study (OC/EC = 27–129), causes of the variability have not been identified [Stockwell et al., 2016]. This comparison of OC/EC ratios demonstrates that emission characteristics of particulate species from peatland burning are still highly uncertain. Identification of controlling factors for emission characteristics from peatland burning is necessary for both gas and particulate species.

Peat fires typically occur at low temperature [Rein, 2009] because the shallow water table limits the temperature of the overlying fire. This low-temperature burning is described as smoldering and is classified in stages, including pyrolysis of organic matter, charcoal formation, and charcoal burning [Usup et al., 2004; Rein, 2009]. Thermogravimetric-differential thermal analysis (TG-DTA) of a Kalimantan peat sample demonstrated that the heating temperature is important in determining these stages. Namely, charcoal formation occurs when peat is heated in between 260°C and 360°C, and charcoal burning occurs vigorously at around 440°C [Usup et al., 2004]. These temperature ranges are comparable to that observed during a peatland fire event in Kalimantan, indicating that all of these processes are important [Usup et al., 2004]. However, impacts of different burning stages of peat on emissions of aerosol particles and greenhouse gases have not been investigated.

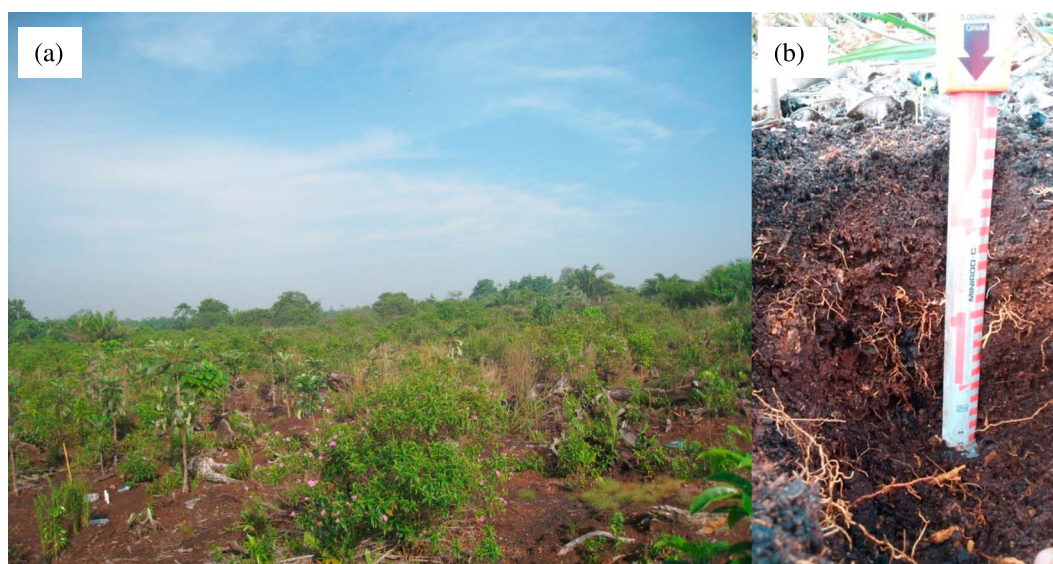


Figure 1. Photos of the peat sampling site at Benkalis district, Riau province in Sumatra. (a) Photograph of the sampling area, demonstrating that the site is a drained and cleared peatland. (b) Photograph of the cross section of peat at the sampling point.

In addition to heating temperature, the burning process is also affected by the history of previous burning. For instance, TG-DTA analysis of humic acid extracted from peat sampled at a burned area in Kalimantan does not have a significant peak corresponding to the temperature of charcoal formation, while it still has a strong signal in the temperature range of charcoal burning [Yustiawati *et al.*, 2015]. On the other hand, humic acid from unburned peat demonstrated peaks for both charcoal formation and burning upon TG-DTA analysis. Considering that most peatland fires occur in previously deforested areas, the impact of preceding fire events on the forthcoming peat burning needs to be considered in estimating emission of aerosol particles as well as greenhouse gases [Gaveau *et al.*, 2014; Konecny *et al.*, 2016].

We conducted a series of temperature-controlled peat burning experiments to investigate how heating temperature controls the composition of greenhouse gases and aerosol particles, helping to understand how environmental temperature of peat could affect emission of gas and particulate species. In addition, some charcoal burning experiments were also conducted, simulating recurring peatland fires.

2. Experiment

A peat core sample was sampled at Benkalis district, Riau province in Sumatra (1.38°N, 101.44°E; approximately 10 m above sea level) for the burning experiment (Figure 1). The sampling site was already disturbed by human activity and previously experienced fire at least 3 times (2002, 2004, and 2007). Peatland fire at the area of the sampling site is known to affect air quality of surrounding countries such as Singapore [Gaveau *et al.*, 2014]. To minimize the effects of previous peat fires on peat quality, we sampled peat at a depth of 30–40 cm from the surface with 100 mL stainless steel containers. The sample container was subsequently sealed for storage. The peat sample in the stainless steel container was directly used for the experiment, meaning that moisture content was not changed.

A schematic diagram of the experimental setup is shown in Figure 2. A 100 L stainless steel chamber, equipped with an air inlet and outlet, was employed. Particle-free compressed air was continuously supplied to the chamber from the inlet, and the chamber outlet was connected to instruments. The chamber was kept at the room pressure by venting excess amounts of air through a T-shaped fitting. The total flow rate of air passing through the chamber, which was regulated by flowrates of instruments connected to the chamber, was approximately 2 lpm. A melting pot was placed in the chamber. Approximately 1.4 g of peat sample was put in the melting pot. The melting pot was equipped with a heating tape (FGR-030, Omega Engineering, Stamford, CT) and a thermocouple. Both the heating tape and the thermocouple were connected to a proportional integral differential temperature controller (E5GN, Omron, Japan), regulating the heating

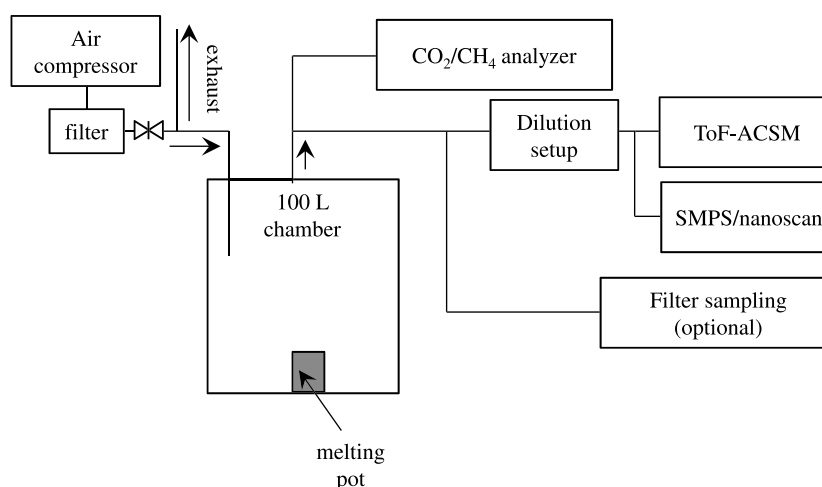


Figure 2. A schematic diagram of the experimental setup. Abbreviations, ToF-ACSM: time-of-flight aerosol chemical speciation monitor, SMPS: scanning mobility particle sizer.

temperature. Approximately 2 min was required to heat the sample to a desired temperature. Replicated experiments were conducted for 3 times at a heating temperature of 300°C, confirming the reproducibility of the experiment (Table S1 in the supporting information).

Concentrations of CH₄ and CO₂ were measured by using a cavity-enhanced absorption instrument (Ultraportable Greenhouse Gas Analyzer, Los Gatos Research Inc., Mountain View, CA). A part of the experiments were conducted immediately after factory calibration by the manufacturer. The repeatability and precision of the instrument are less than 0.25 ppb, as confirmed by actual long-term field observations [Sweeney *et al.*, 2016]. Teflon tubing was used to sample gas from the chamber. A particle filter connected to the tubing removed particles in the sampled gas.

Chemical composition and size distribution of aerosol particles were measured by using online instruments following dilution. A two-step dilution system was employed to control particle concentration entering the instruments. In the first step, sample air from the burning chamber containing aerosol particles was mixed with particle-free dry air generated by a diffusion dryer (Model 42000, Brechtel Manufacturing, Inc. Hayward, CA), a particle filter, and an air compressor (DVH130, Nitto Kohki, Tokyo, Japan). The flow rate of dry air was controlled at 1 lpm, using a needle valve and a mass flowmeter (Model 4140, TSI, Inc. Shoreview, MN). The mixed airflow was introduced to an Erlenmeyer flask (250 ml), facilitating homogeneous mixing. A portion of the outflow from the flask was introduced to the second dilution, and excess amount of air was pumped out from the setup. The excess flow rate was regulated by a needle valve as 1 lpm. In the second dilution step, the flow rate of dry compressed air was regulated by using a mass flow controller (MC-Standard Series, Alicat, Tuscon, AZ). The flow rate was adjusted to keep particle mass concentrations at less than 10 mg m⁻³. Typically, the flow rate was set as around 0.3 lpm.

Following dilution, the chemical compositions of aerosol particles were measured by using the Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM; Aerodyne, Inc. Billerica, MA) [Froehlich *et al.*, 2013]. The ionization efficiency of the ToF-ACSM was calibrated by using ammonium nitrate (VWR, Radnor, PA) particles produce using a nebulizer. Number size distribution of aerosol particles was measured by using a scanning mobility particle sizer (SMPS; Model 3936, TSI, Inc, MN) or via nanoscan (Model 3910; TSI, Inc, MN). These instruments were calibrated by using polystyrene latex spheres (Nanosphere; Thermo Fisher Scientific, Waltham, MA).

Aerosol particle were also collected on Teflon filters for proton nuclear magnetic resonance (¹HNMR) analysis. The heating temperatures for the filter samples were set as 300, 350, and 450°C. Aerosol particles were sampled by using 47 mm Teflon filters (P0450, Sigma-Aldrich, St. Louis, MO), which were installed in filter holders (BGI, Inc., MA). The sampling flow rate was of 5 L min⁻¹. The collected filter samples were stored in a freezer (−27°C) until analysis. Filter samples were extracted by using an ultrasonic bath by 1.5 mL of CDCl₃ (DLM-7-100S, Cambridge Isotope Laboratories, Inc., Tewksbury, MA) for 15 min. Solid debris in the resulting solutions were removed by a polytetrafluoroethylene syringe filter. The filtered solutions were transferred to 5 mm NMR tubes.

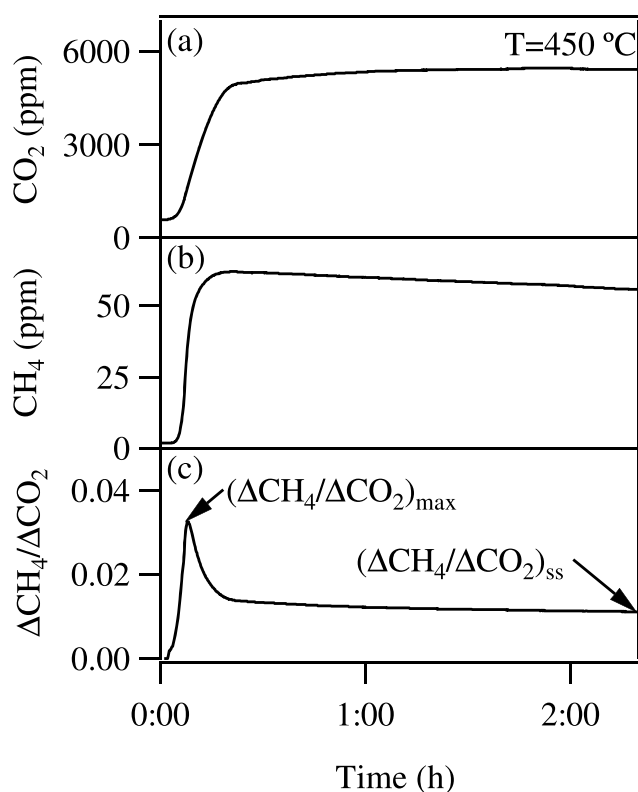


Figure 3. Time series of data for a peat burning experiment at a heating temperature of 450°C. (a) CO₂ and (b) CH₄ concentrations. The emission ratios of CO₂ and CH₄ ($\Delta\text{CH}_4/\Delta\text{CO}_2$ (ppmv/ppmv)) is also shown. See the text for details.

variation of emission processes creates a maximum value for CH₄ and CO₂ ($\Delta\text{CH}_4/\Delta\text{CO}_2$ (ppmv/ppmv)) at around 8 min (Figure 3c). The ratio subsequently decreases to a quasi-steady state value, due to decrease of CH₄ and gradual increase in CO₂ concentrations. The maximum value is defined as $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$, while the quasi-steady state ratio is called as $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$. These values are analyzed in detail in section 4.1.

3.2. Chemical Characteristics of Organic Aerosol Materials

Figure 4 shows mass spectra of organic aerosol materials emitted from peat burning. In general, fractions of $m/z44$ (f_{44}), which serves as a marker for degree of oxidation, are small. On the other hand, fractions of $m/z43$ (f_{43} ; C_3H_7^+ , $\text{C}_2\text{H}_3\text{O}^+$), which is typically pronounced for hydrocarbon-like organic materials, are prominent [Ng *et al.*, 2011]. Consistently, a series of fragment ions for aliphatic hydrocarbons, which are represented as $\text{C}_n\text{H}_{2n \pm 1}$ (e.g., $m/z41$, 55, 57, 69...), are also significant. These characteristics consistently demonstrate that aerosol particles emitted from peat smoldering have aliphatic hydrocarbon structure, and they are only slightly oxygenated. A marker ion of biomass burning, which is $m/z60$ (mainly $\text{C}_2\text{H}_4\text{O}_2^+$), is commonly observed for the whole temperature range [Cubison *et al.*, 2011]. This ion is known to be produced during electron impact ionization of levoglucosane-like species; these are emitted from pyrolysis of cellulose [Cubison *et al.*, 2011]. Examples of levoglucosane-like species include mannosan and galactosan. Emission of these species from peat burning was confirmed by chemical analysis of peat burning particles at molecular levels, consistent with the present experiment [Iinuma *et al.*, 2007]. The fractions of high molecular weight fragment ions ($m/z > 100$) were 0.23 ± 0.04 (1σ).

To analyze organic aerosol mass spectra of peat burning particles in more detail, square of Pearson correlation coefficients (r^2) of individual ion signals were mapped (Figure 5). The values of r^2 for highly correlating ions ($r^2 \geq 0.6$) are plotted in Figure 5 (positive correlation (Figure 5b) and negative correlation (Figure 5c)), and tabulated in Table S2. The selection of r^2 of 0.6 is somewhat arbitrary. Figure 5 only shows highly correlating ions, and the correlation coefficients of all the combinations of ions are provided in Figure S1 in the

The samples were analyzed by Bruker AMX 300 spectrometer at 300 MHz frequency for ¹H NMR analysis. NMR spectra of each of the samples were measured for eight scans. The spectra were phase-corrected by using Mestre-C software package (Mestrelab Research, Spain). Further data analysis, including estimation of baseline and calculation of integrated peak areas, was carried out by using Igor Pro (WaveMetrics, Inc. Portland, OR). The signal from isotopic impurity in the solvent (CHCl₃, 7.25 ppm) was employed to calibrate the spectra.

3. Results

3.1. CH₄ and CO₂

Figure 3 shows an example of time series data for CH₄ and CO₂. Heating of the peat sample was initiated at 0:00, and both CO₂ and CH₄ concentrations started increasing after around 3 min. The increase rate of CH₄ concentration starts declining after 10 min, while a similar transition happens at 18 min for CO₂. The difference in temporal

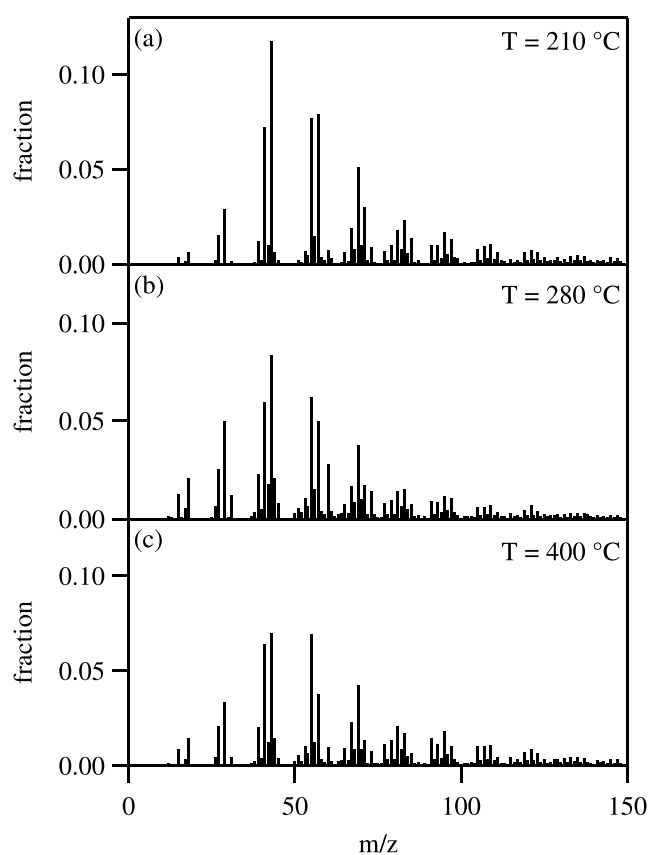


Figure 4. ACSM mass spectra of organic aerosol particles emitted from peat smoldering at different temperature. (a) 210°C, (b) 280°C, and (c) 400°C.

ing ionization and fragmentation processes. The values of r^2 are higher for smaller values of n (e.g., $n = 1$ and 2). Correlations of ions worsen for higher values of n , indicating that original chemical structures of oligomers are preserved to some extent, although thermal decomposition and electron impact ionization processes in the instrument fragments molecules.

Figure 6 shows an example of ^1H NMR spectrum for peat burning particles ($T = 350^\circ\text{C}$) extracted by CDCl_3 . Major functional groups were identified, following the method proposed by *Decesari et al.* [2000]. Saturated aliphatic hydrogens (C-H), which are found at 0.6–1.8 ppm, are the dominant contributor to the ^1H NMR spectrum. Especially, an intense peak for methylene chains ($-\text{CH}_2-$) is found at around 1.2–1.6 ppm [*Decesari et al.*, 2000]. The significant methylene signal indicates that peat burning particles are dominantly composed of aliphatic hydrocarbons, consistent with the ToF-ACSM mass spectra (Figure 4). These results are qualitatively consistent with the data reported by *Iinuma et al.* [2007], who found that n-alkanes and alkenes are one of the dominant compounds in peat burning particles. A clear and distinct peak for levoglucosan is found at 5.3 ppm, supporting the conclusion from the ToF-ACSM analysis that peat burning particles contain levoglucosan-like species [*Chalbot et al.*, 2014; *Paglione et al.*, 2014]. In addition, both H-C-C (1.8–3.2 ppm) and H-C-O (3.2–4.4 ppm) were clearly identified. Signals for aromatic hydrogen (6.5–8.2 ppm) were also detected, although these peaks overlap with the strong signal of CHCl_3 , which is originated from isotopic impurity of the solvent (Figure S2). As the region is located at the tail of CHCl_3 peak, the data between 7.0 and 7.95 ppm were excluded from quantitative analysis.

4. Discussion

4.1. Temperature Dependence

Figure 7 shows both $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$ and $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$ as a function of heating temperature of peat samples. The lowest values of $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$ and $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$ were observed for $T < 260^\circ\text{C}$. The values

supporting information. Figure 5 is symmetric with respect to the line of $(m/z)_y = (m/z)_x$ because of the nature of cross correlation map.

The correlation coefficient map for positive correlations has two regions. One is denoted as region A ($10 < (m/z)_x < 102$ and $10 < (m/z)_y < 102$), and another is defined as region B ($77 < (m/z)_x < 215$ and $77 < (m/z)_y < 215$). These two regions have an overlapping region at ($77 < (m/z)_x < 102$ and $77 < (m/z)_y < 102$). Most of the important ions for chemical characteristics of the organic mass spectra, including m/z 43, 44, and 60, are included in region A, meaning that the region contains rich information about chemical characteristics. On the other hand, region B is useful in characterizing structures of oligomers. In the case of region B, highly correlating ions are mostly located on the lines, which correspond to $(m/z)_y = (m/z)_x - 14n$ (where n is an integer) (Figure 5). The molecular weight of $-\text{CH}_2-$ group is 14, indicating that these good correlations are caused by losses of $-\text{CH}_2-$ group dur-

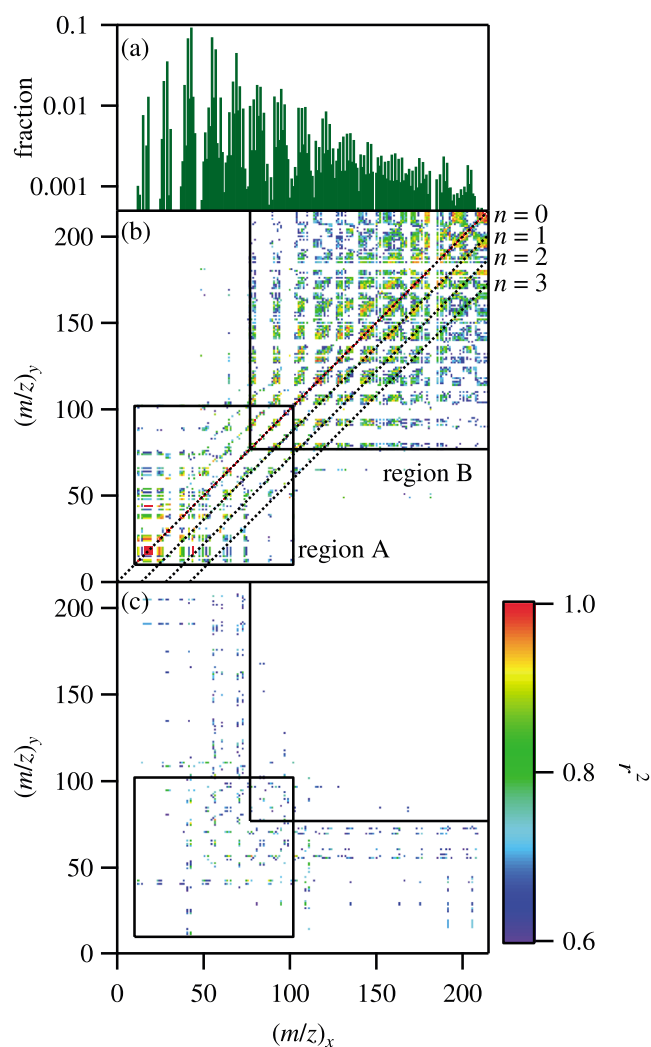


Figure 5. (a) A mass spectra of peat smoldering organic aerosol particles, (b) correlation coefficients (r^2) of positively correlating ions, and (c) negatively correlating ions. Only ion sets with $0.60 \geq r^2$ are shown in Figures 5b and 5c. Maps of whole ions are available in Figure S1. Regions A and B correspond to the areas for chemical characteristics and oligomers, respectively. The dashed lines in Figure 5b correspond to $(m/z)_y = (m/z)_x - 14n$ [$n = 0, 1, 2, 3$]. See the text for detail.

gases. The temperature-dependent emission could be induced by alternations in cracking and decomposition processes to form gaseous species at elevated temperature ranges, as previously demonstrated for other types of biofuel burning such as wood [Horne and Williams, 1996]. A caveat in interpreting this result is inhomogeneity in temperature during the burning process. Although heating temperature of the melting pot containing peat samples was precisely controlled, thermal inhomogeneity could exist for peat samples due to exothermic oxidation processes.

The range of emission ratios $\Delta\text{CH}_4/\Delta\text{CO}_2$ observed in our experiments encompasses ratios that are reported in previous laboratory experiments as well as a field observation (Table 1). The observed range of $\Delta\text{CH}_4/\Delta\text{CO}_2$ in the present study almost completely covers the range of emission ratios reported in previous laboratory as well as field studies. For instance, the maximum value of $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$ (0.0326) is comparable to the value of $\Delta\text{CH}_4/\Delta\text{CO}_2$ observed for a Sumatran peat burning experiment (0.0336) [Christian et al., 2003]. In addition, the range of $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$ (0.0017–0.012) is similar to the values quantified by recent satellite observation ($\Delta\text{CH}_4/\Delta\text{CO}_2 = 0.0062\text{--}0.0136$) [Parker et al., 2016]. Influence of emissions from combustion of nonpeat

of $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$ and $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$ increased abruptly for temperatures above about 280°C, and then increased almost linearly to the maximum temperature of 450°C. Linear regression analysis indicates that the ratios at 280°C (3.3×10^{-2} for $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$ and 1.1×10^{-2} for $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$) increase at rates of 8.1×10^{-5} (ppmv/ppmv/T) and 1.4×10^{-5} (ppmv/ppmv/T) as the temperature is increased up to 450°C (Figure 7).

This temperature dependence in gas emission from peat burning could be related with different stages of burning. Exothermic combustion process of charcoal formation starts at temperatures between 260 and 280°C [Usup et al., 2004]. Only negligible amount of CH_4 is emitted from peat at temperatures lower than the threshold, suggesting that CH_4 emission is not significant for the endothermic pyrolysis process in the temperature range. Following the initiation of exothermic combustion processes, emission of CH_4 increased with temperature. These temperature ranges correspond to charcoal ($280^\circ\text{C} < T < 370^\circ\text{C}$) and ash ($370^\circ\text{C} < T < 450^\circ\text{C}$) formation stages, as confirmed by visual inspection of the samples following burning experiments. These results demonstrate that heating temperature, which eventually regulates burning stages, plays a critical role in determining the emissions of greenhouse

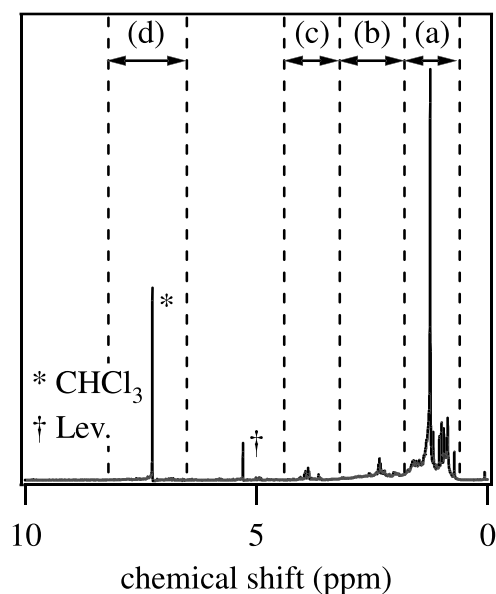


Figure 6. A ^1H NMR spectrum of peat burning particles ($T = 350^\circ\text{C}$) extracted by CDCl_3 . Different regions in the spectrum are classified as (a) C-H, (b) H-C=C, (c) H-C-O, and (d) aromatic hydrogen.

hand, f_{44} is more pronounced at higher temperature. In addition, intensities of ions for nonaliphatic species, such as $m/z51$ (C_4H_3^+), are more pronounced for higher temperature. In the following temperature dependences these features are discussed in detail.

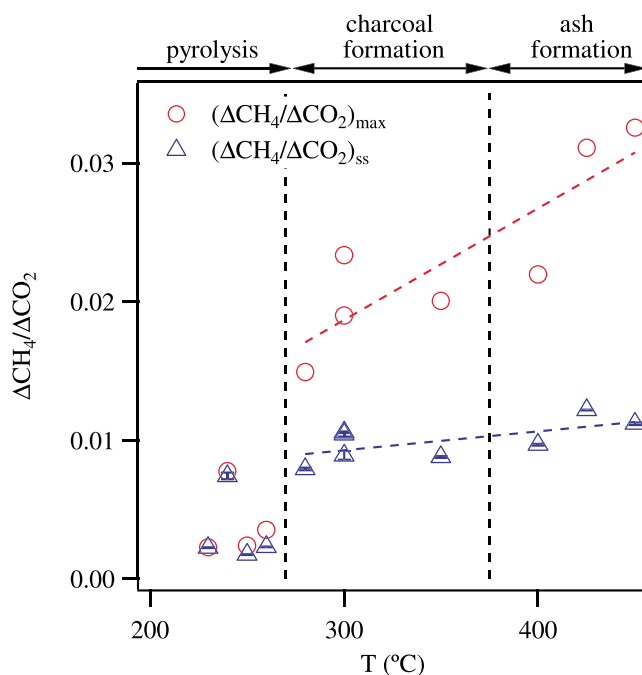


Figure 7. Emission ratio of CH_4 and CO_2 ($\Delta\text{CH}_4/\Delta\text{CO}_2$ (ppmv/ppmv)) plotted as a function of temperature. The dashed lines were obtained by linear regression of the data. $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$ corresponds to the maximum value of $\Delta\text{CH}_4/\Delta\text{CO}_2$ during each set of experiments (red open circle), while $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$ denotes the values observed at the final stages of experiments (blue open triangle).

materials would be negligible at least for the recent field observations, considering that only a limited amount of vegetation is currently available over peatland in Central Kalimantan [Konecny et al., 2016]. Thus, the variability in observed values of $\Delta\text{CH}_4/\Delta\text{CO}_2$ needs to be related with either smoldering condition or composition of peat. The present result summarized in Table 1 and Figure 7 suggests that temperature of peat could be an important parameter in explaining the variability of $\Delta\text{CH}_4/\Delta\text{CO}_2$ ratio from peatland burning.

Chemical composition of organic aerosol particles observed at different heating temperatures also has some different features. For instance, f_{43} tends to be higher at lower temperatures (Figure 4). On the other

hand, f_{44} is more pronounced at higher temperature. Dependences of f_{43} and f_{44} on heating temperature are shown in Figure 8, as examples. f_{43} gradually decreases at elevated temperatures, while f_{44} jumps almost twice at around 270°C . As discussed in a previous section for CH_4 emission, this temperature corresponds to the transition point from pyrolysis of organic species to exothermic oxidation of them. An implication of the temperature-dependent mass spectra is that organic aerosol particles emitted from exothermic combustion processes are more oxidized than that from pyrolysis of fuel. The gradual decrease in f_{43} demonstrates that chemical composition of aerosol particles continuously changes with temperature.

Cross-correlation analysis was employed to interpret the temperature dependence of f_{43} in more detail (Figure 5 and Table S2). Ions positively correlating with $m/z43$ include $m/z41$, 57, and 71. Including $m/z43$ itself, chemical formulas of these ions conform to $\text{C}_n\text{H}_{2n\pm 1}^+$, indicating that

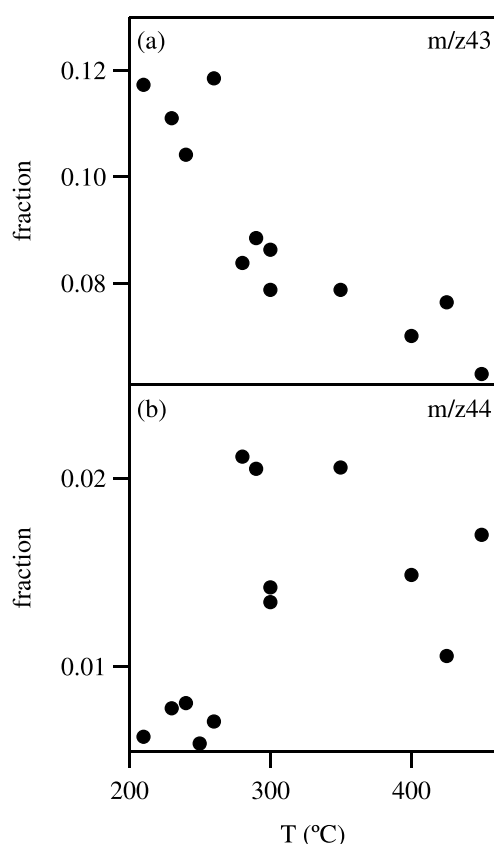


Figure 8. Fractions of some characteristic ions plotted as a function of temperature. (a) $m/z43$ and (b) $m/z44$.

peaks, which does not exist for the spectrum at 300°C, was also observed. These results support the analysis of the ToF-ACSM data that fractions of aromatic species increased at elevated temperatures. Previous laboratory experiments of biofuel and tobacco burning have identified higher fractions of polycyclic aromatic hydrocarbons (PAHs) in tar at higher temperatures, qualitatively consistent with the idea that the formation of aromatic species is more pronounced at elevated heating temperature [Horne and Williams, 1996; McGrath et al., 2007].

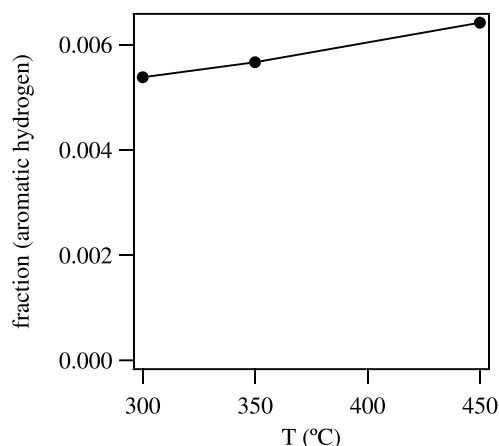


Figure 9. Fractions of aromatic hydrogen detected by $^1\text{H NMR}$ plotted against heating temperature.

these ions originated from aliphatic carbon chains. Interestingly, all of these ions negatively correlate with $m/z51$, which is more pronounced at higher temperatures (Figure S3). Ions positively correlate with $m/z51$ include 12, 13, 39, 50, 52, 53, 63, 66, 75, 76, 88, 89, 100, 101, and 102. Chemical formulas of these ions can be consistently explained as $\text{C}_n\text{H}_{0\sim(n+1)}^+$, indicating that ions in this family have double bonds and ring structures such as aromatic rings. The increased intensity of signals from these ions at higher temperature could be explained by enhanced fractions of aromatic and cyclic structures.

The $^1\text{H NMR}$ data provide a support for the interpretation of the data. The $^1\text{H NMR}$ data demonstrated enhancement of aromatic hydrogen at higher temperatures by up to 19% (Figure 9). At 300°C, intensities of peaks in between 6.5 and 6.82 ppm are minimal, and there is no obvious signal for the region of 7.65 and 7.9 ppm (Figure S2). Peaks in these regions enhanced at 350 and 450°C. In addition, appearance of new

4.2. CH_4 and CO_2 Emission From Charcoal

$\Delta\text{CH}_4/\Delta\text{CO}_2$ was also measured for charcoal forming from peat burning (Figure 10). Peat samples were heated to 300 and 350°C prior to these experiments, forming charcoal. Charcoals formed from peat were burned at 450°C. $\Delta\text{CH}_4/\Delta\text{CO}_2$ measured for charcoal smoldering was lower than that observed for peat smoldering at least by an order of magnitude. Namely, $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}$ ranged from 7.6×10^{-4} to 1.4×10^{-3} , and $(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}$ was measured as 1.3×10^{-4} to 1.4×10^{-4} . These values are lower than those for peat

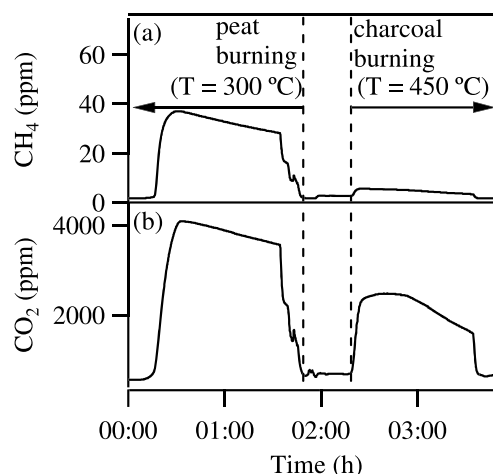


Figure 10. A comparison of (top) CH₄ and (bottom) CO₂ emissions from peat smoldering (left side of the figure) and smoldering of charcoal forming peat (right side of the figure). The corresponding values of $\Delta\text{CH}_4/\Delta\text{CO}_2$ are $\{(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}, (\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}\} = \{2.0 \times 10^{-2}, 8.8 \times 10^{-3}\}$ for peat burning, and $\{(\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{max}}, (\Delta\text{CH}_4/\Delta\text{CO}_2)_{\text{ss}}\} = \{7.6 \times 10^{-4}, 1.4 \times 10^{-4}\}$ for charcoal burning, respectively.

were shown to vary from 7.9×10^{-3} to 3.3×10^{-2} on a molar basis. A similar extent of variability in CH₄ emission from peat smoldering has been observed in previous laboratory experiments as well as in field observations, although the cause of the variation has been unclear [Christian *et al.*, 2003; Stockwell *et al.*, 2014; Parker *et al.*, 2016; Stockwell *et al.*, 2016]. Our result suggests that heating temperature, which could be as high as 400°C, may be one of the key controlling factors in determining emission ratios of gas and particulate matters from peatland burning. Furthermore, emission of CH₄ from peat charcoal burning was demonstrated to be lower than that from peat burning by more than an order of magnitude.

Chemical compositions of aerosol particles emitted from peat smoldering were also shown to be temperature-dependent. Especially, detailed analysis of mass spectra demonstrated that significantly dehydrogenated ions ($\text{C}_n\text{H}_{0-(n+1)}^+$) are pronounced for elevated heating temperatures, indicating enhanced fractions of double bonds and cyclic structures. The finding was also supported by ¹HNMR analysis. PAHs, which are carcinogenic, are typical examples of this class of compounds.

These results suggest that both charcoal contents and temperature are playing important roles in determining emissions of gaseous and aerosol species, demonstrating that these parameters need to be quantified for the future field studies on tropical peatland burning. Mapping fire temperatures is now possible using infrared sensors on satellites and unmanned aerial vehicles (drones) [Brown *et al.*, 2015; Elvidge *et al.*, 2015]. A combination of these mapping techniques with temperature-dependent emission data may enable better estimation of the climatic and environmental impacts of peatland burning in equatorial Asian countries.

Following a burning event, surface of peatland is covered by charcoal formed from peat [Hudspith *et al.*, 2014]. In addition, some layers in peatland contain high fractions of charcoal, which formed during previous fire events [Yulianto *et al.*, 2004]. These charcoals in peatland would also serve as one of the fuels in future fire events, potentially affecting emission of gaseous species from peatland burning. Considering that most peatland fire in equatorial Asia occurs in disturbed and developed areas, burning history as well as charcoal contents of peat should be mapped to accurately estimate emissions of gaseous species [Gaveau *et al.*, 2014; Marlier *et al.*, 2015].

References

- Brown, B., W. Wei, R. Ozburn, M. Kumar, and K. Cohen (2015), Surveillance for Intelligent Emergency Response Robotic Aircraft (SIERRA)- VTOL Aircraft for Emergency Response, in *AIAA Infotech @ Aerospace*, American Institute of Aeronautics and Astronautics, Reston, Va.
- Chalbot, M. C. G., J. Brown, P. Chitranshi, G. G. da Costa, E. D. Pollock, and I. G. Kavouras (2014), Functional characterization of the water-soluble organic carbon of size-fractionated aerosol in the southern Mississippi Valley, *Atmos. Chem. Phys.*, *14*(12), 6075–6088, doi:10.5194/acp-14-6075-2014.

combustion processes by more than an order of magnitude (Table 1), implying minimal CH₄ emission from charcoal forming from previous peatland burning. The minimal emission of CH₄ from charcoal could be important in identifying controlling factors of CH₄ emission, as the tropical peatland fires typically occur at previously burned areas [Gaveau *et al.*, 2014; Konecny *et al.*, 2016].

5. Conclusions and Atmospheric Implications

We have demonstrated that emissions of gases and particulate matters from peat burning depend on heating temperature of smoldering. Emission ratios of CH₄ and CO₂ ($\Delta\text{CH}_4/\Delta\text{CO}_2$) due to peat smoldering

Acknowledgments

The authors acknowledge Osamu Kozan, Motonori Okumura, Jing Chen, and Wen-Chien Lee for their assistance with the experiments and useful discussion. M.K. was supported by the National Research Foundation Singapore under its Singapore NRF Fellowship scheme (National Research Fellow Award, NRF2012NRF-NRFF001-031), the Earth Observatory of Singapore, and Nanyang Technological University. M.I. was supported by the Ministry of Education, Culture, Sports, Science, and Technology for Science Research (15H05625), the Ministry of Environment for Global Environment Research (4-1504), and the Research Institute for Humanity and Nature, Japan. The data in the paper are available from Mikinori Kuwata (kuwata@ntu.edu.sg).

- Christian, T. J., B. Kleiss, R. J. Yokelson, R. Holzinger, P. J. Crutzen, W. M. Hao, B. H. Saharjo, and D. E. Ward (2003), Comprehensive laboratory measurements of biomass-burning emissions: 1. Emissions from Indonesian, African, and other fuels, *J. Geophys. Res.*, *108*(D23), 4719, doi:10.1029/2003JD003704.
- Cubison, M. J., et al. (2011), Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies, *Atmos. Chem. Phys.*, *11*(23), 12,049–12,064, doi:10.5194/acp-11-12049-2011.
- Decesari, S., M. C. Facchini, S. Fuzzi, and E. Tagliavini (2000), Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach, *J. Geophys. Res.*, *105*(D1), 1481–1489, doi:10.1029/1999JD900950.
- Elvidge, C. D., M. Zhizhin, F.-C. Hsu, K. Baugh, M. R. Khomarudin, Y. Vetrira, P. Sofan, Suwarsono, and D. Hilman (2015), Long-wave infrared identification of smoldering peat fires in Indonesia with nighttime Landsat data, *Environ. Res. Lett.*, *10*(6), 065002, doi:10.1088/1748-9326/10/6/065002.
- Field, R. D., G. R. van der Werf, and S. S. P. Shen (2009), Human amplification of drought-induced biomass burning in Indonesia since 1960, *Nat. Geosci.*, *2*(3), 185–188, doi:10.1038/ngeo443.
- Field, R. D., et al. (2016), Indonesian fire activity and smoke pollution in 2015 show persistent nonlinear sensitivity to El Niño-induced drought, *Proc. Natl. Acad. Sci.*, *113*(33), 9204–9209, doi:10.1073/pnas.1524888113.
- Froehlich, R., et al. (2013), The ToF-ACSM: A portable aerosol chemical speciation monitor with TOFMS detection, *Atmos. Meas. Tech.*, *6*(11), 3225–3241, doi:10.5194/amt-6-3225-2013.
- Gaveau, D. L. A., et al. (2014), Major atmospheric emissions from peat fires in Southeast Asia during non-drought years: Evidence from the 2013 Sumatran fires, *Sci. Rep.*, *4*, 6112, doi:10.1038/srep06112.
- Ge, C., J. Wang, and J. S. Reid (2014), Mesoscale modeling of smoke transport over the Southeast Asian Maritime Continent: Coupling of smoke direct radiative effect below and above the low-level clouds, *Atmos. Chem. Phys.*, *14*(1), 159–174, doi:10.5194/acp-14-159-2014.
- Glasspool, I. J., and A. C. Scott (2010), Phanerozoic concentrations of atmospheric oxygen reconstructed from sedimentary charcoal, *Nat. Geosci.*, *3*(9), 627–630, doi:10.1038/ngeo923.
- Hamada, Y., U. Darung, S. H. Limin, and R. Hatano (2013), Characteristics of fire-generated gas emission observed during a large peatland fire in 2009 at Kalimantan, Indonesia, *Atmos. Environ.*, *74*, 177–181, doi:10.1016/j.atmosenv.2013.03.058.
- Hayasaka, H., I. Noguchi, E. I. Putra, N. Yulianti, and K. Vadrevu (2014), Peat-fire-related air pollution in Central Kalimantan, Indonesia, *Environ. Pollut.*, *195*, 257–266, doi:10.1016/j.envpol.2014.06.031.
- Heald, C. L., and D. V. Spracklen (2015), Land use change impacts on air quality and climate, *Chem. Rev.*, *115*, 4476–4496, doi:10.1021/cr500446g.
- Hope, G., U. Chokkalingam, and S. Anwar (2005), The stratigraphy and fire history of the Kutai Peatlands, Kalimantan, Indonesia, *Quat. Res.*, *64*(3), 407–417, doi:10.1016/j.yqres.2005.08.009.
- Horne, P. A., and P. T. Williams (1996), Influence of temperature on the products from the flash pyrolysis of biomass, *Fuel*, *75*(9), 1051–1059, doi:10.1016/0016-2361(96)00081-6.
- Hudspith, V. A., C. M. Belcher, and J. M. Yearsley (2014), Charring temperatures are driven by the fuel types burned in a peatland wildfire, *Front. Plant Sci.*, *5*, 714, doi:10.3389/fpls.2014.00714.
- Iinuma, Y., E. Brüeggemann, T. Gnauk, K. Mueller, M. O. Andreae, G. Helas, R. Parmar, and H. Herrmann (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, doi:10.1029/2006JD007120.
- Konecny, K., U. Ballhorn, P. Navratil, J. Jubanski, S. E. Page, K. Tansey, A. Hooijer, R. Vernimmen, and F. Siegert (2016), Variable carbon losses from recurrent fires in drained tropical peatlands, *Global Change Biology*, *22*(4), 1469–1480, doi:10.1111/gcb.13186.
- Kunii, O., S. Kanagawa, I. Yajima, Y. Hisamatsu, S. Yamamura, T. Amagai, and I. T. S. Ismail (2002), The 1997 haze disaster in Indonesia: Its air quality and health effects, *Arch. Environ. Health*, *57*(1), 16–22.
- Marlier, M. E., R. S. DeFries, P. S. Kim, D. Lagaveau, S. N. Koplitz, D. J. Jacob, L. J. Mickley, B. A. Margono, and S. S. Myers (2015), Regional air quality impacts of future fire emissions in Sumatra and Kalimantan, *Environ. Res. Lett.*, *10*(5), 054010, doi:10.1088/1748-9326/10/5/054010.
- Marlier, M. E., R. S. DeFries, A. Voulgarakis, P. L. Kinney, J. T. Randerson, D. T. Shindell, Y. Chen, and G. Faluvegi (2013), El Niño and health risks from landscape fire emissions in southeast Asia, *Nat. Clim. Change*, *3*(2), 131–136, doi:10.1038/nclimate1658.
- Matsueda, H., and H. Y. Inoue (1999), Aircraft measurements of trace gases between Japan and Singapore in October of 1993, 1996, and 1997, *Geophys. Res. Lett.*, *26*(16), 2413–2416, doi:10.1029/1999GL900089.
- McGrath, T. E., J. B. Wooten, W. G. Chan, and M. R. Hajaligol (2007), Formation of polycyclic aromatic hydrocarbons from tobacco: The link between low temperature residual solid (char) and PAH formation, *Food Chem. Toxicol.*, *45*(6), 1039–1050, doi:10.1016/j.fct.2006.12.010.
- Ng, N. L., M. R. Canagaratna, J. L. Jimenez, P. S. Chhabra, J. H. Seinfeld, and D. R. Worsnop (2011), Changes in organic aerosol composition with aging inferred from aerosol mass spectra, *Atmos. Chem. Phys.*, *11*(13), 6465–6474, doi:10.5194/acp-11-6465-2011.
- Page, S. E., F. Siegert, J. O. Rieley, H. D. V. Boehm, A. Jaya, and S. Limin (2002), The amount of carbon released from peat and forest fires in Indonesia during 1997, *Nature*, *420*(6911), 61–65, doi:10.1038/nature01131.
- Paglione, M., et al. (2014), Primary and secondary biomass burning aerosols determined by proton nuclear magnetic resonance (H-1-NMR) spectroscopy during the 2008 EUCAARI campaign in the Po Valley (Italy), *Atmos. Chem. Phys.*, *14*(10), 5089–5110, doi:10.5194/acp-14-5089-2014.
- Parker, R. J., H. Boesch, M. J. Wooster, D. P. Moore, A. J. Webb, D. Gaveau, and D. Murdiyarso (2016), Atmospheric CH₄ and CO₂ enhancements and biomass burning emission ratios derived from satellite observations of the 2015 Indonesian fire plumes, *Atmos. Chem. Phys.*, *16*, 10,111–10,131.
- Pechony, O., and D. T. Shindell (2010), Driving forces of global wildfires over the past millennium and the forthcoming century, *Proc. Natl. Acad. Sci. U.S.A.*, *107*(45), 19,167–19,170, doi:10.1073/pnas.1003669107.
- Rein, G. (2009), Smoldering combustion phenomena in science and technology, *Int. Rev. Chem. Eng.*, *1*, 3–18.
- Rosenfeld, D. (1999), TRMM observed first direct evidence of smoke from forest fires inhibiting rainfall, *Geophys. Res. Lett.*, *26*(20), 3105–3108, doi:10.1029/1999GL006066.
- Stockwell, C. E., et al. (2016), Field measurements of trace gases and aerosols emitted by peat fires in Central Kalimantan, Indonesia during the 2015 El Niño, *Atmos. Chem. Phys. Discuss.*, *16*, 11,711–11,732, doi:10.5194/acp-16-11711-2016.
- Stockwell, C. E., R. J. Yokelson, S. M. Kreidenweis, A. L. Robinson, P. J. DeMott, R. C. Sullivan, J. Reardon, K. C. Ryan, D. W. T. Griffith, and L. Stevens (2014), Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: Configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4), *Atmos. Chem. Phys.*, *14*(18), 9727–9754, doi:10.5194/acp-14-9727-2014.
- Sweeney, C., et al. (2016), No significant increase in long-term CH₄ emissions on North Slope of Alaska despite significant increase in air temperature, *Geophys. Res. Lett.*, *43*, 6604–6611, doi:10.1002/2016gl069292.

- Usup, A., Y. Hashimoto, H. Takahashi, and H. Hayasaka (2004), Combustion and thermal characteristics of peat fire in tropical peatland in Central Kalimantan, Indonesia, *Tropics*, *14*, 1–18, doi:10.3759/tropics.14.1.
- Wosten, J. H. M., E. Clymans, S. E. Page, J. O. Rieley, and S. H. Limin (2008), Peat-water interrelationships in a tropical peatland ecosystem in Southeast Asia, *Catena*, *73*(2), 212–224, doi:10.1016/j.catena.2007.07.010.
- Yu, Z., J. Loisel, D. P. Brosseau, D. W. Beilman, and S. J. Hunt (2010), Global peatland dynamics since the last glacial maximum, *Geophys. Res. Lett.*, *37*, L13402, doi:10.1029/2010GL043584.
- Yulianto, E., K. Hirakawa, and H. Tsuji (2004), Charcoal and organic geochemical properties as an evidence of Holocene fires in tropical peatland, Central Kalimantan, Indonesia, *Tropics*, *14*(1), 55–36.
- Yustiawati, et al. (2015), Effects of peat fires on the characteristics of humic acid extracted from peat soil in Central Kalimantan, Indonesia, *Environ. Sci. Pollut. Res.*, *22*(4), 2384–2395, doi:10.1007/s11356-014-2929-1.