A Key Indicator of Transboundary Particulate Matter Pollution Derived from Indonesian Peatland Fires in Malaysia

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ABSTRACT

We characterized ambient total suspended particulates (TSP) based on ground-based samplings in Malaysia during non-haze days and haze ones affected by Indonesian peatland fires. Furthermore, a key indicator of Indonesian peatland fire was determined based on chemical characterization of TSP in Malaysia. TSP samples were chemically analyzed to determine organic carbon (OC), elemental carbon (EC), inorganic ions, and biomarkers (solvent-extractable organic compounds derived from biomass burning). Regarding OC and EC, concentrations of OC1 and OP (pyrolyzed OC) defined by IMPROVE_A protocol increased remarkably during the haze episodes. On the contrary, there were no significant differences in concentrations of OC4, EC, and EC fractions between the haze and non-haze samples. Regarding inorganic ions, sulfate and ammonium concentrations increased in strong haze days, however, it is difficult to use these compounds as indicators for Indonesian peatland fires in light haze days due to the partial overlapping of the variation ranges of sulfate and ammonium concentrations in non-haze days. Concentrations of many biomarkers derived from cellulose, hemicellulose, and lignin pyrolysis products were significantly increased during strong haze days but not during light haze days except *p*-hydroxybenzoic acid. We proposed the OP to OC4 ratio as a potential indicator of transboundary haze pollution from Indonesian peatland fires at the receptor sites even in light haze.

Keywords: Carbonaceous aerosols; Air pollution; Biomass burning.

INTRODUCTION

During every dry season from June to October, many hotspots from peatland fires are observed in Sumatra and Kalimantan islands, Indonesia. Due to the southwest monsoon in Southeast Asia during this period, smoke particles and gases originating from peatland fires in Sumatra Island travel to the west coast of Peninsular Malaysia, resulting in frequent transboundary haze pollution (Mahmud, 2009). Transboundary smoke haze causes degradation of local air quality and health impacts in Malaysia (Othman *et al.*, 2014; Sahani *et al.*, 2014).

To prevent, monitor, and mitigate transboundary haze pollution, the ASEAN (Association of Southeast Asian Nations) Agreement on Transboundary Haze Pollution was established in 2002. After 12 years of waiting, Indonesia finally ratified the agreement very recently on September 16 in 2014 as the last ASEAN country. Then the action to mitigate transboudary haze pollution from the Indonesian peatland fires is expected to be encouraged in combination with science-based information. However, the current basic scientific knowledge of the transboundary haze pollution such as the key indicators of the haze is still insufficient to aid policy actions.

Few reports (See *et al.*, 2007; Betha *et al.*, 2013; Fujii *et al.*, 2014a, 2015) have been presented concerning chemical characterization of particulate matter (PM) at the peatland fire sources in Indonesia. Fujii *et al.* (2014a) reported that organic matter derived from the Indonesian peatland fires is extremely important since organic carbon (OC) constituted approximately 70% of the $PM_{2.5}$ mass at the source. Thus, organic components in PM during the haze periods are considered dominant in Malaysia. In fact, there are reports that concentrations of some particulate organic compounds such as levoglucosan and palmitic acid were drastically increased in strong haze days compared to those in non-

haze days in Malaysia (Fang *et al.*, 1999; Abas *et al.*, 2004a, b). These organic compounds can be detected in PM not only from Indonesian peatland fires (Fujii *et al.*, 2015) but also from domestic biomass burnings (Simoneit *et al.*, 1999). In the case of a strong haze episode, extremely high concentrations of the compounds can be utilized as key indicators to specify the impact of Indonesian peatland fires at receptor sites in Malaysia. However, comparable concentrations of the compounds from Indonesia and local sources lead to difficulty in distinguishing the impact of Indonesian peatland fires in case of light haze. Therefore, unique indicators of Indonesian peatland fires are strongly needed to distinguish from other biomass burning sources at receptor sites. However no studies of these indicators have been conducted at the receptor sites in Malaysia.

We characterized ambient total suspended particulates (TSP) based on ground-based samplings in Malaysia during non-haze days and haze ones affected by Indonesian peatland fires. Furthermore, a key indicator of Indonesian peatland fires was determined based on chemical characterization of TSP in Malaysia.

METHODS

Sampling Site and Period

The TSP samplings were performed from June 23 to July 8 in 2014 at the roof of a building in Universiti Kebangsaan Malaysia (UKM), Bangi, Selangor, Malaysia shown in Fig. 1. A detailed description about the sampling sites has been given in our former reports (Fujii *et al.*, 2014b, 2016). Bangi is 89 m above sea level and located approximately 25 km south from Kuala Lumpur and approximately 35 km from Malacca Strait. Two areas of low- and medium-technology industrial areas exist nearby the sampling site within Bangi. The other industrial areas are Petaling Jaya which is located approximately 30 km northwest of Bangi, Nilai (~35 km south) and Bukit Rambai (~100 km southeast). Because June is the southwest monsoon season in Malaysia, the PM concentrations in Bangi can be affected by the sources of nearby industrial areas and distant sources in Nilai, as well as from the biomass burning activities from Sumatra, Indonesia.

Sample Collection and Analysis

A high volume air sampler (Thermo) was utilized to continuously collect TSP on quartz fiber filters for 18 hours (19:30–13:30 (+1 day) in local time) at a flow rate of 1.13 $m^3 min^{-1}$. During the sampling periods, ambient temperature and relative humidity were continuously monitored by a thermohygrometer (EL-USB-2, Lascar). Before sampling, quartz fiber filters were heat-treated at 900°C for 4 hours. After sampling, TSP samples were chemically analyzed to determine OC, elemental carbon (EC), inorganic ions, and biomarkers (solvent-extractable organic compounds derived from biomass burning).

The carbonaceous contents of the aerosols were quantified using a DRI Model 2001 OC/EC Carbon Analyzer, which employs thermal optical reflectance method following the IMPROVE_A protocol. A detailed description of quantification

Fig. 1. Map of Bangi showing the sampling sites.

has been given elsewhere (Fujii *et al.*, 2014a).

Aliquots from the quartz fiber filters were used for analysis of inorganic ions. Each filter was extracted by ultrasonic agitation for 20 min periods using 5 mL ultrapure water. The extract was filtered through a PTFE syringe filter (pore size 0.45 μm) and analyzed by ion chromatography (HIC-10A, Shimadzu). In this study, three anions (chloride, nitrate, and sulfate) and five cations (sodium, ammonium, potassium, calcium, and magnesium) were quantified.

Solvent-extractable organic compounds obtained from the quartz fiber filters were quantified by gas chromatography/mass spectrometry (GC/MS). Organic compound speciation was basically accomplished following the procedures of our former reports (Fujii *et al.*, 2014a, 2015). Aliquots from the quartz fiber filters were spiked with internal standards of methyl *β*-L-arabinopyranoside, 1,2,3-hexanetriol, (*S*)-(+)-ketopinic acid, palmitic acid-d_{31}, and cholesterol-d_7 before extraction. Each spiked filter was extracted by ultrasonic agitation for 2 × 20 min periods using 10 mL of a dichloromethane/methanol mixture (3/1, v/v) (dichloromethane: Kanto Chemical, purity > 99.5%; methanol: Kanto Chemical, purity > 99.8%). The combined extracts were filtered through a PTFE syringe filter (pore size 0.2 μm), dried completely under a gentle stream of nitrogen gas, and redissolved to 0.5 mL in a dichloromethane/methanol mixture (3/1, v/v). Subsequently, an aliquot of the redissolved extract was dried completely under a gentle stream of nitrogen gas and used for

derivatization as follows. Before GC/MS analysis, trimethylsilyl derivatization was conducted for the extracts with 10 µL of *N,O*-bis-(trimethylsilyl)-trifluoroacetamide with 1% trimethylchlorosilane and 45 µL of pyridine for 3 h at 70°C, and then ca. ~0.189 µg of tetracosane-d_{50} dissolved in 45 µL of dichloromethane was added as a syringe spike (second internal standard).

The derivatized samples were analyzed on a Shimadzu GC/MS system (GCMS-QP2010-Plus, Shimadzu) equipped with a 30 m HP-5MS column (0.25 µm film thickness, 0.25 mm ID). The carrier gas was helium (purity 99.9995%) at a pressure of 73.0 kPa (37.2 cm s^{-1} at 100°C). The GC oven temperature program was as follows: isothermal at 100°C for 5 min, 100–220°C at 10 °C min^{-1}, 220–300°C at 20 °C min^{-1}, and then 300°C for 20 min. The injection port and transfer line were maintained at 300°C. The data for quantitative analysis were acquired in the electron impact mode (70 eV).

The mass spectrometer was operated under selected ion monitoring mode, and the monitored ions for quantification are shown in Table S1. Regarding internal standards, the monitored ions of methyl *β*-L-arabinopyranoside, palmitic acid-d_{31}, 1,2,3-hexanetriol, (*S*)-(+)-ketopinic acid, cholesterol-d_7, and tetracosane-d_{50} were 217, 344, 145, 239, 336, and 66 m/z, respectively. The recovery ratios of known amounts of the standards on quartz fiber filters are presented in Table S2.

RESULTS AND DISCUSSION

Meteorological Conditions and Air Quality

The ambient temperature and relative humidity during the sampling periods ranged from 25 to 35°C and 55 to 91%, respectively. There were not great differences in variation

patterns of ambient temperature and relative humidity for each sampling as shown in Fig. S1. Fig. 2 shows the hourly variations of Malaysian Air Pollutant Index (MAPI) from June 23 to July 9, 2014 at Putrajaya which is located approximately 10 km to the west from the sampling site. The data were obtained from the web site of official air pollutant index of the Department of Environment Ministry of Natural Resources and Environment. We also represent the each sampling period with sample IDs from M0624 to M0708 in Fig. 2. In Malaysia, the air quality status is reported in terms of MAPI. The MAPI is calculated based on the concentrations of five major pollutants which are ground level ozone, carbon monoxide, nitrogen dioxide, sulphur dioxide, and particulate matter of less than 10 µm in size (PM$_{10}$). MAPI values of 0–50, 51–100, 101–200, 201–300, and > 300 represent good, moderate, unhealthy, very unhealthy, and hazardous air quality status, respectively (Department of Environment, 2014). The MAPI data shown in Fig. 2 roughly consisted of three groups: unhealthy levels (101 ≤ MAPI ≤ 200) were observed over about 12 hours on June 24 and 25 (Period I); moderate levels (51 ≤ MAPI ≤ 100) were dominated from June 26 to 29 (Period II); good levels (MAPI ≤ 50) were dominated from June 30 to July 8 (Period III). Based on the MAPI data, we categorized three haze periods (strong haze, light haze, and non-haze) during the sampling periods as follows. At the sampling site, strong haze occurred during the sampling periods of M0624 and M0625 (Period I). Light haze occurred during the sampling periods of M0626, M0627, and M0629 (Period II). Other samples (M0630–M0708) were collected during the non-haze periods (Period III).

The hotspot counts in Sumatra Island, Indonesia are shown in Fig. 3. The hotspots were detected by the National Oceanic and Atmospheric Administration satellite 18 (1.1
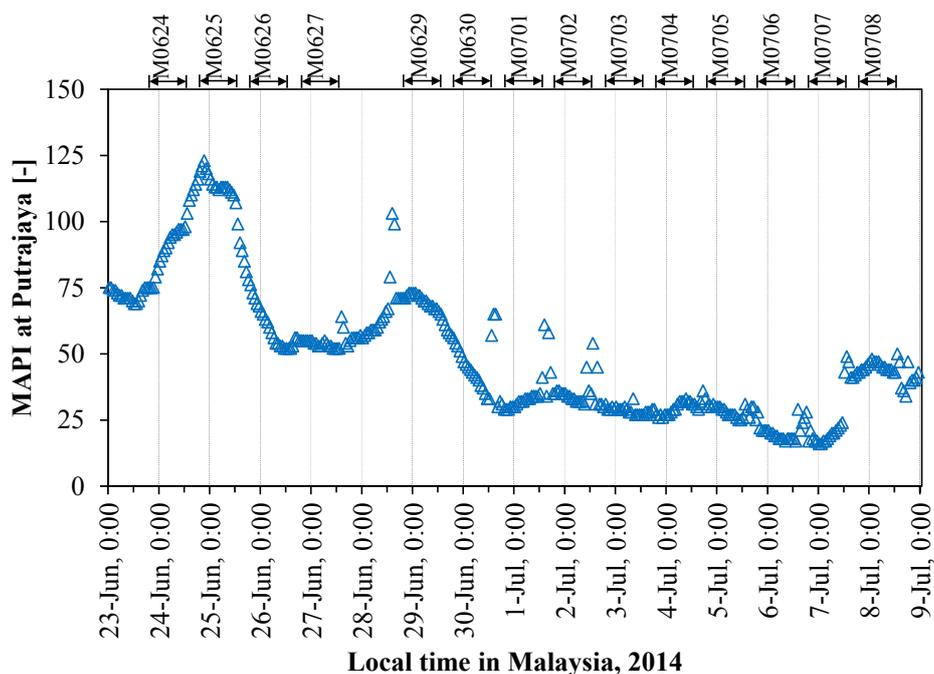

Fig. 2. Hourly variations of Malaysian Air Pollutant Index (MAPI) from June 23 to July 9 in 2014 at Putrajaya.
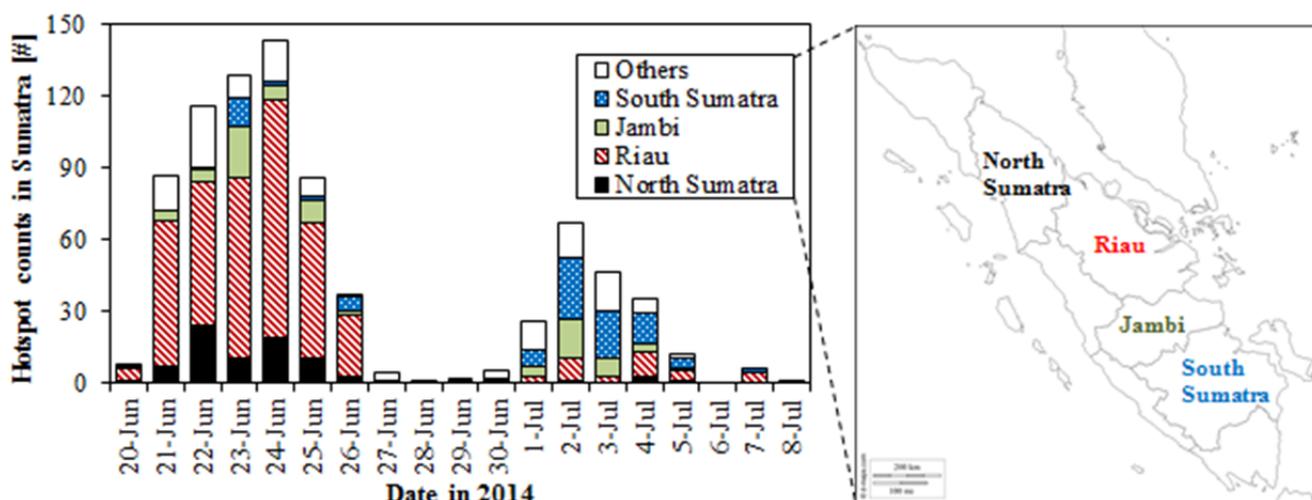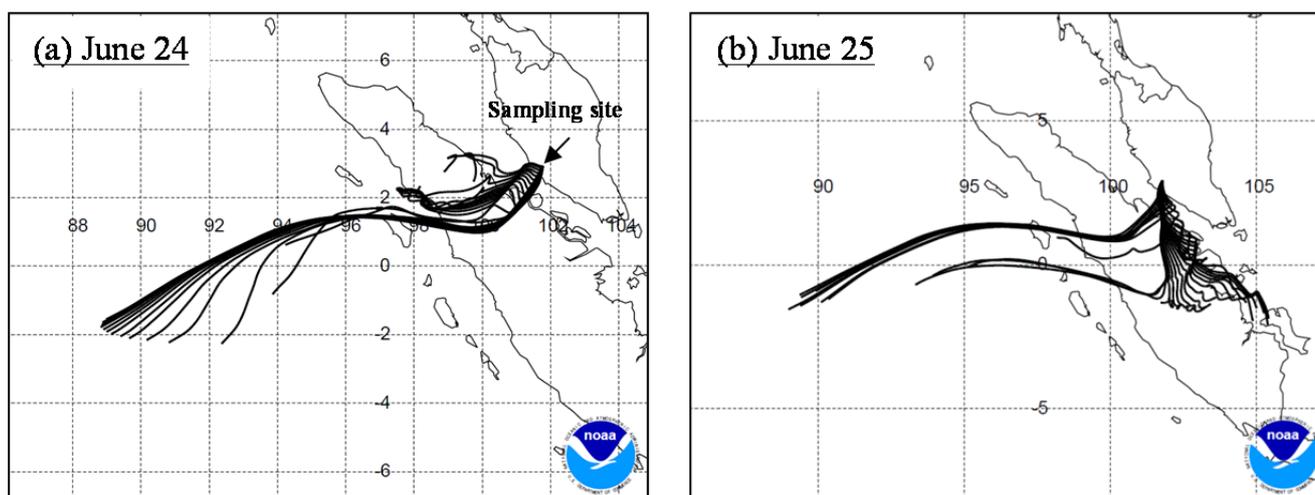
Fig. 3. Monthly hotspot counts in Sumatra Island during the sampling periods.

The 3-days backward air trajectories every 1 hours with 500 m above ground level arriving at the sampling site in local time were calculated during the sampling periods by the Hybrid Single Particle Lagrangian Integrated Trajectory model.

Fig. 4. Backward air trajectories on (a) June 24 and (b) 25 during the strong haze periods.

× 1.1 km resolution). The data during the sampling periods (Indofire) were provided by the ASEAN Specialised Meteorological Centre (ASMC). Hotspots are defined as image pixels whose brightness temperature exceed a pre-defined threshold value. A threshold digital count of 40 (corresponding to a brightness temperature of 321.3 K) is adopted by the ASMC for hotspot detection (ASEAN Haze Action Online). Many hotspots in Riau and North Sumatra were mainly detected on June 21–26; hotspots in South Sumatra were mainly detected on July 1–4. This suggests that the increase in MAPI on June 24 and 25 as shown in Fig. 2 is caused by the Indonesian peatland fires in Riau and North Sumatra. This conclusion can also be supported by the 72-hour backward air trajectories every 1 hour with 500 m above ground level arriving at the sampling site in local time on June 24 and 25 (Period I) as shown in Fig. 4. The trajectories were calculated by the Hybrid Single Particle Lagrangian Integrated Trajectory model (Draxler and Hess, 2004) based on meteorological data obtained from the

Global Data Assimilation. On June 24, the air parcels arriving at Bangi partly originated from the provinces of north Sumatra and Riau, while on June 25, they originated from the one of Riau and Jambi. The relatively high MAPI values on June 26–29 (Period II) within 3 days after the burning activities can be attributed to the transport of smoke from Sumatra as shown in Figs. S2 and S3.

OC and EC

The OC and EC concentrations over an entire period ranged from 9.71 to 74.6 μg m^{-3} and 3.28 to 9.45 μg m^{-3}, respectively. In Period III, the OC and EC concentrations were 13.5 ± 2.67 (average ± standard deviation) and 5.90 ± 2.26 μg m^{-3}, respectively, which show slight variations among the samples during the non-haze periods.

OC concentrations in Period I were over 4.87 times higher than the average of those in Period III, which show significant differences. OC concentrations in Period II were 2.02–2.60 times higher than the average of those in

Period III. In contrast, EC concentrations in Period I and II were 0.934–1.55 times higher than the average of those in Period III, which show no significant differences.

The concentration variations of OC and EC fractions (OC: OC1, OC2, OC3, OC4, and OP, EC: EC1–OP, EC2, EC3) are shown in Fig. 5. EC1–OP is the dominant fraction of EC, accounting for 94.1 ± 2.29 weight% of EC. Distinct differences in OC fractions except for OC4 were observed among the samples in three periods as shown in Fig. 5(a). In particular, the OC1 and OP concentrations in Period I were much (33.4 times at least) higher than the average of those in Period III. The OC2 and OC3 concentrations in Period I were over 3.24 higher than the average of those in Period III, respectively. Thus, the OC1, OC2, OC3, and OP were susceptible to Indonesian peatland fires. In contrast, the OC4 concentrations in Period I were 0.530–0.544 higher than the average of those in Period III, which show no significant effects of Indonesian peatland fires. Regarding EC fractions, similar variations like OC4 were observed (Fig. 5(b)): EC1–OP1, EC2, and EC3 concentrations in the Period I were 1.13–1.21, 1.98–2.21, and 1.66–2.04 times higher than the average of those in Period III. Thus, the OC4 and EC fractions were less susceptible to Indonesian peatlnad fires. Regarding the samples in Period II, only the OC1 and OP concentrations were over 12.2 times higher than the average of those in Period III, which show significant differences.

The abundance of eight carbon fractions shows the characteristics of emission source (Watson *et al.*, 1994; Chow *et al.*, 2004) and the eight fractions have been used for source apportionment (e.g., Kim *et al.*, 2003; Kim and Hopke, 2004; Gu *et al.*, 2010). Fig. 6 shows the abundances of five OC fractions (OC1, OC2, OC3, OC4, and OP) of our samples. The OC1 in Periods I, II, and III accounted for 12.5, 10.2, and 1.34 weight% of OC, respectively, on average. The OC2 in Periods I, II, and III accounted for 27.5, 22.3, and 28.0 weight% of OC, respectively, on average. The OC3 in Periods I, II, and III accounted for 27.6, 32.0, and 43.6 weight% of OC, respectively, on average. The OC4 in Periods I, II, and III accounted for 2.36, 5.77, and 23.0 weight% of OC, respectively, on average. OP in Periods I, II, and III accounted for 30.0, 29.7, and 3.99 weight% of OC, respectively, on average. There is no big differences between the abundances of five OC fractions of the samples in Periods I and II, however, remarkable differences in OC1, OC4, and OP between the samples in Periods I and III were observed. The abundance of carbon fractions shows the characteristics of emission source as we mentioned above. Then, it is considered that OC concentrations in Period II were affected by Indonesian peatland fires as well as those in Period I.

Inorganic Ions

Table 1 shows the concentration variations of inorganic ions in Periods I, II, and III as well as the reference data (PM_{10}) in UKM by Wahid *et al.* (2014). In this study, the
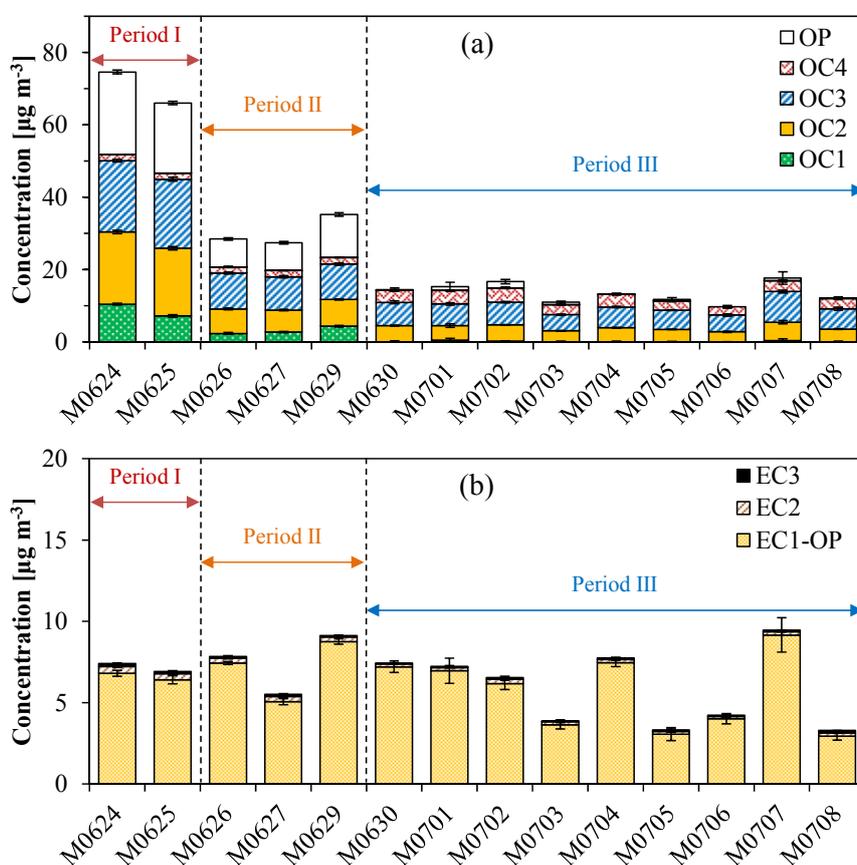

Fig. 5. Variations of carbon fractions ((a) OC, (b) EC) concentrations. Error bars indicate standard deviations.
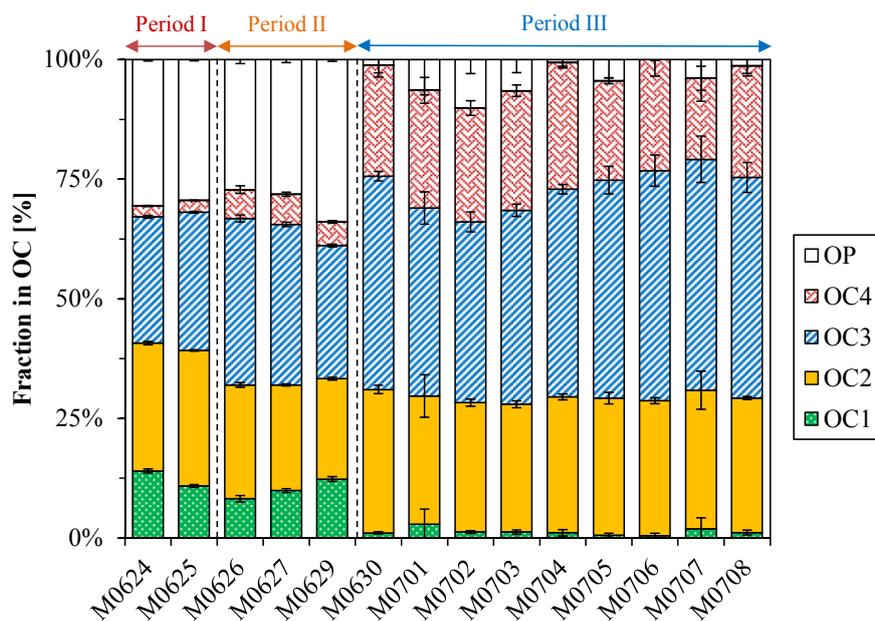
Fig. 6. Abundances (mass percentage of OC) of five thermally-derived organic carbon fractions during the haze and non-haze periods. Error bars indicate standard deviations.

Table 1. Concentrations of inorganic ions [µg m^{-3}] in TSP (this study) and PM$_{10}$ (reference) during the haze and non-haze periods.

Compounds	TSP			PM$_{10}$
	Period I	Period II	Period III	Nov 2011–Jan 2012[a]
chloride	0.262–0.534	0.0654–0.117	0.0504–0.960	0.27–0.43
nitrate	1.24–6.08	1.03–2.83	0.673–1.77	0.00–1.08
sulfate	9.65–16.2	4.61–14.2	0.953–7.16	2.04–3.35
sodium	0.929–0.935	0.481–0.666	0.511–1.97	0.0–19.0
ammonium	2.67–6.99	0.879–4.40	0.123–1.88	N.A.[b]
potassium	1.81–1.91	0.752–2.18	0.662–1.83	0.12–0.23
magnesium	0.279–0.316	0.119–0.243	0.0906–0.228	0.007–0.01
calcium	1.24–2.03	0.933–1.28	0.451–0.950	0.08–0.27

a) data from Wahid et al., 2014., b) N.A.: Not Analyzed.

concentrations of total inorganic ions ranged from 4.14 to 35.0 µg m^{-3} and the most abundant inorganic ion was sulfate at 23.0–55.9 weight% of total ions. The concentrations of individual anions in our all samples decreased in the order of sulfate > nitrate > chloride. The average concentrations of individual cations in both of Periods I and II decreased in the order of ammonium > potassium > calcium > sodium > magnesium. On the other hand, those in Period III decreased in the order of potassium > ammonium > sodium > calcium > magnesium. Particularly, significant differences in sulfate and ammonium concentrations between the samples in Periods I and III were found in inorganic ion species. Engling *et al.* (2014) reported that the concentrations of sulfate and ammonium in the haze periods affected by Indonesian peatland fires were much higher (sulfate: ~6.53, ammonium: ~42.9 times) than those in the non-haze days, which is consistent with our results. Due to the partial overlapping of variation ranges of sulfate (0.953–7.16 µg m^{-3}) and ammonium (0.123–1.88 µg m^{-3}) concentrations between the samples in Periods II and III, it is difficult to use these

compounds as indicators for Indonesian peatland fires in light haze days. Potassium is a tracer for biomass burning in general (Chuang *et al.*, 2013), however, there were no significant differences in potassium concentrations between haze and non-haze samples. Fujii *et al.* (2015) reported that potassium derived from Indonesian peatland fires should not be used as a source indicator unlike many other biomass burning sources due to the extremely low potassium fraction (0.0423 ± 0.0400 weight% of PM$_{2.5}$) at the source, which is consistent with our results.

Comparison of inorganic ions concentrations in TSP (our data in Period III) and PM$_{10}$ (Wahid *et al.*, 2014) collected in UKM showed no significant differences except potassium, magnesium, calcium, and sodium. The former three ions may be derived from soil.

Biomarkers

Table 2 shows the concentrations of biomarkers in Periods I, II, and III. Total quantified biomarkers ranged from 177 to 1650 ng m^{-3} and the most abundant biomarker was

Table 2. Concentrations of biomarkers [ng m^{-3}] in TSP during the haze and non-haze periods.

Compounds	TSP		
	Period I	Period II	Period III
levoglucosan	968–1190	330–375	132–254
mannosan	94.5–167	37.7–42.6	16.8–29.2
galactosan	37.2–94.7	16.7–25.4	11.1–15.6
p-hydroxybenzoic acid	35.8–77.4	16.3–18.4	3.57–7.86
vanillic acid	14.6–59.5	4.39–9.28	0.895–8.78
syringic acid	14.8–31.7	4.17–6.40	1.34–5.03
vanillin	8.47–10.3	5.72–7.47	2.23–5.34
syringaldehyde	0.765–1.33	0.543–0.711	0.412–0.612
acetovanillone	1.10–3.65	0.657–1.01	0.338–0.665
acetosyringone	1.59–3.86	0.413–0.785	0.494–1.70
homovanillic acid	0.730–1.42	0.492–0.716	0.360–0.613
homosyiringic acid	0.797–1.29	0.705–1.03	0.473–0.902
dehydroabietic acid	4.88–6.43	4.91–8.71	2.61–8.03
cholesterol	3.90–5.68	3.11–4.20	1.54–4.77

levoglucosan at 72.1–81.3 weight% of the total quantified biomarkers, followed by mannosan at 7.32–10.1% and galactosan at 3.12–6.58%. Levoglucosan is a specific indicator for cellulose burning emissions and generally formed during cellulose pyrolysis at temperatures more than 300°C (Shafizadeh, 1984; Simoneit *et al.*, 1999; Lin *et al.*, 2010). Some carbohydrate polymers (e.g., starch) also produce levoglucosan upon thermal alteration (Lakshmanan *et al.*, 1970; Lakshmanan and Hoelscher, 1970). However, it is not probable that cooking, baking, or toasting is a significant source of levoglucosan because the temperature attained during the process is not sufficient to pyrolyze carbohydrates to levoglucosan (Lin *et al.*, 2010). Mannosan and galactosan are minor constituents compared to levoglucosan and are derived from the pyrolysis of hemicellulose. The isomers of levoglucosan, mannosan and galactosan are derived from hemicellulose pyrolysis products and also used as tracers for biomass burning as well as levoglucosan (e.g., Engling *et al.*, 2014; Fujii *et al.*, 2014a; Zhu *et al.*, 2015). In this study, the concentrations of levoglucosan, mannosan, and galactosan in Period I were over 4.69, 4.29, and 2.95 times higher than the average of those in Period III, respectively, which show significant differences between them. However, the concentrations of these three compounds in Period II were up to 2.01 times (galactosan) higher than the average of those in Period III.

Various lignin unit originated compounds were quantified in the TSP samples. Lignin is known to be an aromatic polymer consisting of phenylpropane units linked through various ether and C–C types of linkages. Its aromatic structures vary depending on the species; softwood lignins contain guaiacyl (G) types exclusively, whereas hardwood lignins include both G and syringyl (S) types, and herbaceous plants include G, S, and *p*-hydroxyphenyl (H) types (Fujii *et al.*, 2015). In Table 2, vanillic acid, vanillin, acetovanillone, and homovanillic acid are derived from the G units, whereas syringic acid, syringaldehyde, acetosyringone, and homosyringic acid are derived from the S units. *P*-hydroxybenzoic acid may be derived from H units or secondary decomposition of G and S units compounds. In this

study, the concentrations of *p*-hydroxybenzoic acid, vanillic acid, and syringic acid in Period I were over 7.03, 4.75, and 4.49 times higher than the average of those in Period III, respectively, which show significant differences in the quantified lignin pyrolysis products. The concentrations of *p*-hydroxybenzoic acid in Period II were 3.21–3.60 times higher than the average of those in Period III, which also show significant differences. In contrast, no significant differences in the concentrations of other quantified lignin pyrolysis products are observed between our samples in Periods II and III as well as those of levoglucosan, mannosan, and galactosan.

Dehydroabietic acid and cholesterol were quantified as indicators for softwoods burning and meat cooking emission, respectively (Simoneit, 1977; Nolte *et al.*, 1999; Schauer *et al.*, 1999; Lin *et al.*, 2010). The concentration variations of these two biomarkers were slight even in a strong haze days, which show that the biomarkers from softwoods burning and meat cooking emissions were not influenced by the haze in this study.

In summary, some compounds such as levoglucosan and mannosan are expected to identify impacts of Indonesian peatland fires during "strong" haze days in Malaysia. However, there were no significant differences in biomarkers except *p*-hydroxybenzoic acid between the samples in "light" haze and non-haze days.

Key Indicators for Transboundary Air Pollution

The relative amounts of the individual anhydrosaccharides in biomass smoke PM can be used for further source assignment of specific biofuels (Fabbri *et al.*, 2009; Alves *et al.*, 2010). Levoglucosan/mannosan ratio is suggested as an indicator for source discrimination for Indonesia peatlnad fires through comparison of various biomass burning sources (Fujii *et al.*, 2014a). The variations of levoglucosan/mannosan ratios in this study are shown in Fig. 7(a). The levoglucosan/mannosan ratios ranged from 7.11 to 10.9 throughout the entire sampling period and there were no significant differences between the haze and non-haze samples. Fujii *et al.* (2014a) reported that the levoglucosan/mannosan ratio
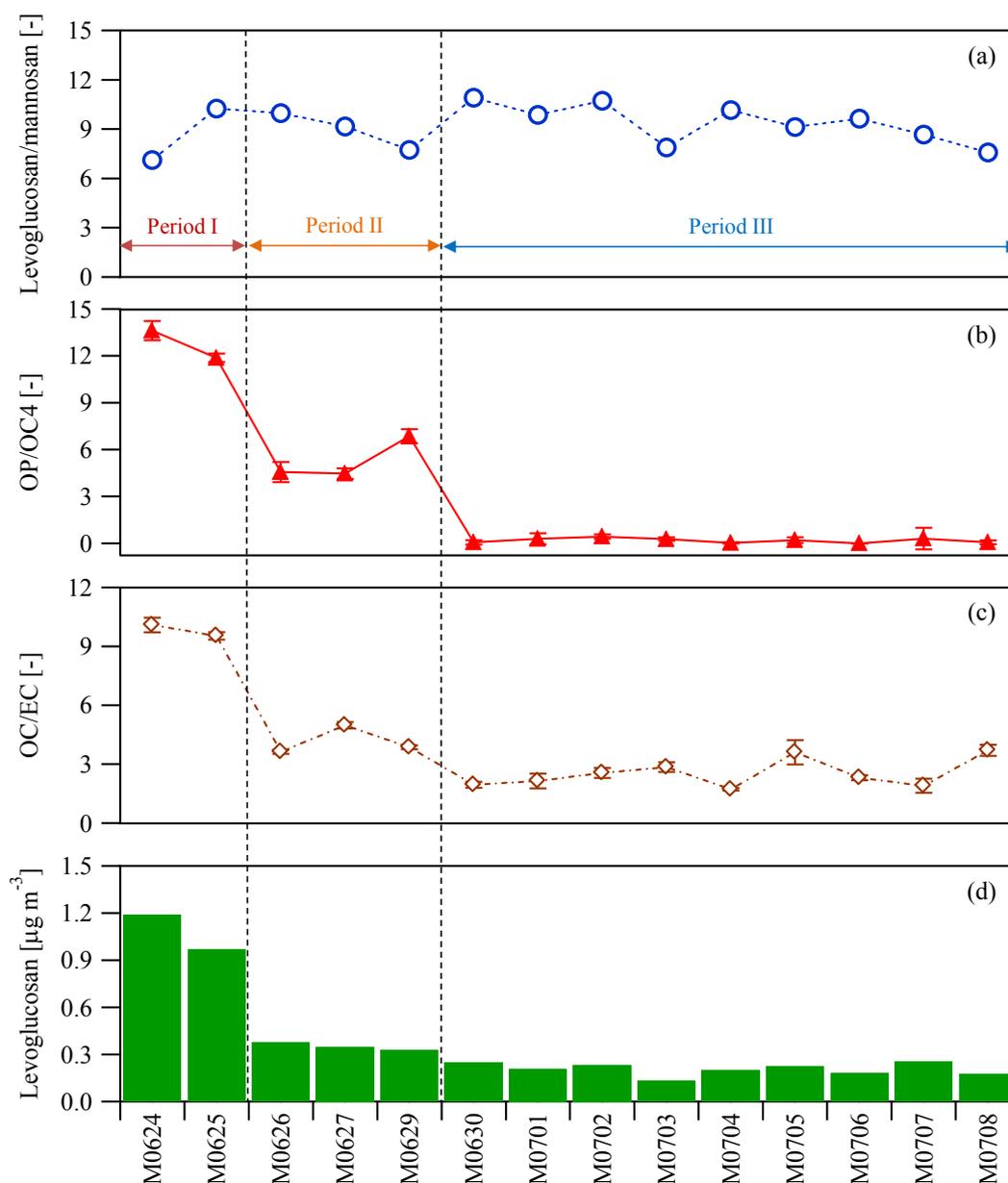
Fig. 7. Variations of levoglucosan/mannosan ratio, OP/OC4 ratio, OC/EC ratio, and levoglucosan concentrations. Error bars indicate standard deviations.

of the Indonesian peatland fire ranged from 7.09 to 14.0, which shows that our ratios are completely included within the range of peatland fire. This may be because almost all levoglucosan and mannosan in TSP were derived from Indonesian petland fires during the sampling periods, or the ratios derived from other domestic biomass burning sources were almost the same as that of Indonesian peatland fire.

As noted earlier, abundances of three thermally-derived carbon fractions (OC1, OC4, and OP) differ significantly in Periods I/II and Period III. In order to highlight the differences in the three Periods, variations of OP/OC4 ratio during the sampling periods are plotted in Fig. 7(b). The OP/OC4 ratios in Periods I, II, and III ranged from 11.9 to 13.6, 4.46 to 6.84, and 0 to 0.433, respectively. The OP/OC4 ratios in Periods I and II were over 67.0 and 25.2 times

higher than the average of those in Period III, respectively. The differences in the ratios between the haze and non-haze samples are much more significant than those in the concentrations of *p*-hydroxybenzoic acid. Therefore, the ratio can be a potential indicator of transboundary haze pollution derived from Indonesian peatland fires. Although the OC/EC ratio (Fig. 7(c)) and some biomarkers such as levoglucosan (Fig. 7(d)) and mannosan can separate strong haze samples (Period I) from non-haze samples (Period III), it is not possible to separate light haze samples (Period II) from non-haze ones. Thus, we suggest the OP/OC4 ratio as a useful indicator of transboundary haze pollution from Indonesian peatland fires at the receptor sites even in "light" haze.

CONCLUSIONS

Intensive field studies in Bangi, Selangor, Malaysia were conducted to determine the chemical characteristics of TSP during the haze days affected by Indonesian peatland fires and non-haze days. Regarding OC and EC, concentrations of OC1 and OP defined by IMPROVE_A protocol increased remarkably during the haze episodes. Furthermore, distinct differences in the distributions of OC fractions were found between haze and non-haze samples. On the contrary, there were no significant differences in concentrations of OC4, EC, and EC fractions between the haze and non-haze samples. Regarding inorganic ions, sulfate and ammonium concentrations increased in strong haze days, however, it is difficult to use these compounds as indicators for Indonesian peatland fires in light haze days due to the partial overlapping of the variation ranges of sulfate and ammonium concentrations in non-haze days. Regarding biomarkers, no significant differences in concentrations of dehydroabietic acid and cholesterol as indicators for softwoods burning and meat cooking emissions, respectively, were observed throughout the entire period. Concentrations of many biomarkers derived from cellulose, hemicellulose, and lignin pyrolysis products were significantly increased during strong haze days but not during light haze days except *p*-hydroxybenzoic acid. We proposed the OP/OC4 ratio as a potential indicator of transboundary haze pollution from Indonesian peatland fires at the receptor sites even in light haze.

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SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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