Characteristics of carbonaceous aerosols emitted from peatland fire in Riau, Sumatra, Indonesia

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Abstract

Biomass burning is a significant source of fine particulate matter (PM$_{2.5}$). Forest, bush, and peat fires in Kalimantan and Sumatra, Indonesia are major sources of transboundary haze pollution in Southeast Asia. However, limited data exist regarding the chemical characteristics of aerosols at sources. We conducted intensive field studies in Riau Province, Sumatra, Indonesia, during the peatland fire and non-burning seasons in 2012. We characterized PM$_{2.5}$ carbonaceous aerosols emitted from peatland fire based on ground-based source-dominated sampling. PM$_{2.5}$ aerosols were collected with two mini-volume samplers using Teflon and quartz fiber filters. Background aerosols were also sampled during the transition period between the non-burning and fire seasons. We analyzed the carbonaceous content (organic carbon (OC) and elemental carbon (EC)) by a thermal optical reflectance utilizing the IMPROVE_A protocol and the major organic components of the aerosols by gas chromatography/mass spectrometry. PM$_{2.5}$ aerosols emitted from peatland fire were observed in high concentrations of 7120 ± 3620 µg/m$^3$ and were primarily composed of OC (71.0 ± 5.11% of PM$_{2.5}$ mass). Levoglucosan exhibited the highest total ion current and was present at concentrations of 464 ± 183 µg/m$^3$. The OC/EC ratios (36.4 ± 9.08), abundances of eight thermally-derived carbon fractions, OC/Levoglucosan ratios (10.6 ± 1.96), and Levoglucosan/Mannosan ratios (10.6 ± 2.03) represent a signature profile that is inherent in peatland fire. These data will be useful in identifying contributions from single or multiple species in atmospheric aerosol samples collected from peatland fires.

Keywords: Carbonaceous aerosol; PM$_{2.5}$; Levoglucosan; Mannosan; Biomass Burning

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Highlights

- PM$_{2.5}$ aerosols emitted from peatland fire in Indonesia were characterized.
- PM$_{2.5}$ aerosols emitted from peatland fire were primarily composed of OC.
- We found some source indicators that were inherent in peatland fire.
1. Introduction

Peatland is organic soil that has formed for over thousands of years from decomposed vegetation and other life forms, and peat deposits can extend up to seven meters in thickness (Wulandari, 2002). In Southeast Asia, smoke originating from peatland fires in Kalimantan and Sumatra in Indonesia is a major cause of transboundary haze pollution.

In general, approximately 80–90% of the smoke particles produced by biomass burning is in the PM$_{2.5}$ size range, and these particles are primarily composed of organic carbon, which constitutes 50–60% of the total particle mass (Phuleria et al., 2005; Schollnberger et al., 2002; Reid et al., 2005). PM$_{2.5}$ aerosols present a high risk of deposition in the alveoli of lungs and are associated with a greater general health risk than coarse aerosols (Federal Register, 2006; Lippmann, 1998).

According to version 3 of the Global Fire Emissions Database (GFED), average PM$_{2.5}$ emissions from fire (including deforestation, savanna, forest, agricultural waste, and peat fires) from 1997 to 2010 in Indonesia are 2.9 Tg/year, accounting for 9.2% of global fire PM$_{2.5}$ emissions and 62% of Southeast Asian fire emissions. In Indonesia, peatland fire is a dominant source of PM$_{2.5}$ emissions, accounting for 55% of all fire sources. Thus, it is a significant emission source of PM$_{2.5}$ aerosols in Indonesia.

Many peatland fires occur on Sumatra and Kalimantan islands during the dry season, emitting
gases and smoke aerosols that cause atmospheric pollution (haze) and adversely affect the health of people living in surrounding areas. For example, an unprecedented Indonesian fire episode occurred in 1997–1998 due to the El Niño–Southern Oscillation (ENSO) event at that time. Extensive forest fires, including peatland fires, resulted in the development of a smog blanket that covered an immense area of 4 million km² in Southeast Asia. This smog affected the livelihoods and health of 75 million people in six countries and completely toppled their lives. Moreover, the smog resulted in the closure of airports; it was cited as the possible cause of an air crash near Medan, Sumatra, and a tanker collision in the Straits of Malacca (Stolle and Tomich, 1999). Air pollution attained previously unknown levels in East Kalimantan, Singapore, and Kuala Lumpur, with daily average particulate matter reaching extremely hazardous levels (4000 µg/m³; Heil et al., 1998). Although ENSO events considerably contribute to the occurrence of Indonesian fires, pollution from smoke haze is a recurrent problem in Indonesia and neighboring countries, even in non-ENSO years (Tacconi, 2003).

Riau Province in Sumatra is one of the primary hotspots for peatland fire during the dry season, and the smoke aerosols generated there cause haze in Riau and in neighboring countries such as Malaysia and Singapore (Harahap, 2012; Hong, 2012). However, limited data exist regarding the chemical characteristics of these smoke aerosols (Othman and Latif, 2013; See et al, 2007) and the effects of aerosols from peatland fires on the atmospheric environment and human health. To
investigate these effects, the chemical characterization of fresh smoke aerosols from peatland fire
is necessary. In this study, the carbonaceous species of PM$_{2.5}$ aerosols emitted from peatland fire
were characterized by directly sampling PM$_{2.5}$ aerosols at fire hotspots in Riau Province.
Moreover, we determined source indicators of carbonaceous species of smoke from peatland fires
for source apportionment. These data can help in identifying single or multiple species in
atmospheric aerosol samples that contribute to peatland fires.

2. Materials and methods

2.1. Sampling locations

The sampling locations in this study are illustrated in Fig. 1. The burning site and background
site were located at Sepahat Village and Sukajadi Village, respectively, in Bengkalis Regency,
Riau Province. The burning site was surrounded by peatland and forest, and the background site
was located ~50 km away from the burning site and housing estates. Bengkalis Regency lies on
the east coast of Sumatra Island and consists of several islands. This district covers an area of
1,204,423 km$^2$, in which nearly 85% of the land exhibits low topography and is covered with
tropical forests, with an average elevation of only 2.0–6.1 m above sea level. Most of the soils are
organosols or peat soils; that is, they contain abundant organic substances. The temperature in a
Bengkalis is strongly influenced by the tropical marine climate and is typically 26–32°C. The
rainy season generally lasts from September to January, with an average rainfall of 809–4078 mm/year, and the dry season usually spans February to August. Fig. 2 illustrates monthly hotspot counts in Riau in 2011 and 2012 based on Indofire datasets, confirming that many hotspots are detected in the area during the dry season.

2.2. Sample collection and analysis

In 2012, background and peatland fire PM$_{2.5}$ aerosol samples were collected on May 16–17 and June 13–17, respectively. Two mini-volume samplers (MiniVol™ TAS, Airmetrics) were utilized to continuously collect PM$_{2.5}$ aerosols on Teflon and quartz fiber filters for 24 h (background) and 2.5–5.2 h (peatland fire), respectively, at a flow rate of 5 L/min. PM$_{2.5}$ aerosols were collected at several burning sites, about 1.5 m away from peatland fire hotspots and a background site on 7 and 4 occasions, respectively. Wind speeds in the peatland fire samplings ranged from 0.610 to 6.21 m/s (average: 2.50 m/s) and aerosols were collected in smoke plumes. Quartz fiber filters were heat-treated at 900°C for 4 h before sampling to remove any absorbed organic materials.

Filter samples were analyzed to determine PM$_{2.5}$ mass concentrations, carbonaceous content (organic carbon (OC) and elemental carbon (EC)), and the quantity of key biomarkers. The Teflon filter was weighed using a microbalance (ME5-F, Sartorius) with a sensitivity of ±1 µg in a stable environment of 25.7 ± 0.432°C (average ± standard deviation) and 26.0 ± 0.607
RH% before and after sampling, respectively, to determine PM$_{2.5}$ mass concentrations.

The carbonaceous contents of the aerosols collected in the quartz fiber filters were quantified using a DRI Model 2001 OC/EC Carbon Analyzer, which employs thermal optical reflectance following the IMPROVE_A protocol. The IMPROVE_A temperature defines temperature plateaus for thermally-derived carbon fractions as follows: 140°C for OC$_1$, 280°C for OC$_2$, 480°C for OC$_3$, and 580°C for OC$_4$ in helium (He) carrier gas; 580°C for EC$_1$, 740°C for EC$_2$, and 840°C for EC$_3$ in a mixture of 98% He and 2% oxygen (O$_2$) carrier gas (Chow et al., 2007).

OC, EC, and total carbon (TC) were calculated from the eight carbon fractions as follows:

\[
OC = OC_1 + OC_2 + OC_3 + OC_4 + OP
\]  
(1)

\[
EC = EC_1 + EC_2 + EC_3 - OP
\]  
(2)

\[
TC = OC + EC
\]  
(3)

where OP (the amount of pyrolyzed OC) is defined as the carbon content measured after the introduction of O$_2$ until reflectance returns to its initial value at the start of analysis.

Two key biomarkers, levoglucosan and mannosan, 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 Fabbri et al., 2009 and Pashynska et al., 2002. Aliquots from the quartz fiber filter were spiked with the internal standard of methyl $\beta$-L-arabinopyranoside before extraction. Each spiked filter was extracted by ultrasonic agitation.
for 3 × 20 min periods using 3 mL of a dichloromethane/methanol mixture (3/1, v/v) (dichloromethane: Wako, purity >99.5%; methanol: Wako, purity >99.7%). The combined extracts were reduced to approximately 100 µL using a rotary evaporator (250 hPa, 40°C). Subsequently, the concentrated extract was filtered through a Teflon syringe filter (pore size 0.1 µm) and dried completely under a nitrogen stream. Prior to analysis, the total extracts were converted to trimethylsilyl derivatives by reaction with 150 µL of N,O-bis-(trimethylsilyl)-trifluoroacetamide with 1% trimethylchlorosilane and 90 µL of pyridine for 3 h at 70°C.

The derivatized samples were analyzed on a Shimadzu GC/MS system (GCMS-QP2010-Plus, Shimadzu) equipped with an Rtx-5Sil MS column (with selectivity similar to that of a mixture of 5% diphenyl and 95% dimethyl polysiloxane, 30 m × 0.25 mm I.D., 0.25 µm, RESTEK). Helium (purity 99.9995%) with an average velocity of 35.3 cm/s was used as the carrier gas. The GC oven temperature program was as follows: isothermal at 80°C for 5 min, 80–180°C at 3°C/min, then 180–300°C at 20°C/min, and maintained at 300°C for 5 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).

3. Results and discussion
3.1. PM$_{2.5}$ mass concentration

Background and peatland fire PM$_{2.5}$ concentrations determined by gravimetric analysis were 23.9 ± 2.53 µg/m$^3$ and 7120 ± 3620 µg/m$^3$, respectively; that is, peatland fire PM$_{2.5}$ concentrations were ~300 times higher than background concentrations. These extremely high PM$_{2.5}$ concentrations present a great risk to human health, particularly in the case of fire fighters. Since the high concentration is due to the sampling at 1.5 m away from the fire, a different value would be obtained in the different sampling distance.

3.2. OC and EC

The average OC concentrations from peatland fire and background were 4970 ± 3620 µg/m$^3$ and 9.42 ± 1.97 µg/m$^3$, respectively, and average EC concentrations were 133 ± 46.6 µg/m$^3$ and 3.23 ± 0.795 µg/m$^3$, respectively. In terms of the carbonaceous fractions in PM$_{2.5}$ aerosols, PM$_{2.5}$ aerosols emitted from peatland fire were composed of 71.0 ± 5.11% OC and 2.05 ± 0.509% EC. Conversely, background PM$_{2.5}$ aerosols were composed of 39.1 ± 5.08% OC and 13.5 ± 3.04% EC. The remaining undetermined mass can be attributed to the various functional groups in organic aerosols, inorganic ions, metals, soil and particle bound water.

OC to EC mass ratios (OC/EC) provide some indication of the origins of carbonaceous PM$_{2.5}$ (Cao et al., 2005; Chow et al., 1996; Gray et al., 1986; Turpin and Huntzicker, 1991). In this study, the average peatland fire and background OC/EC ratios were 36.4 ± 9.08 and 2.99 ± 0.738,
respectively. Few differences in the OC/EC ratio were observed, regardless of PM$_{2.5}$ mass concentrations, and the coefficient of variance for samples from peatland fire was 24.9%. See *et al.*, 2007 reported that the average OC/EC ratio was 2.42 for PM$_{2.5}$ aerosols collected in the open field within a 100 m circumference from the boundary of the Indonesian peatland fires in 2005. This value is much smaller than our result of 36.4. The discrepancy is due to the different measurement techniques for the OC-EC split. See *et al.*, 2007 adopted thermal method whose temperature of OC-EC split was 350°C. The method would cause significant overestimation of EC concentration in aerosol (Gelencsér, 2004). On the other hand, we utilized thermal-optical reflectance method with pyrolysis correction. OC/EC ratios from our peatland fire and other vegetative burning sources are illustrated in Fig. 3. OC/EC ratios ranged from 4.34 to 79.7; this discrepancy can be partly attributed to variations in the type and moisture content of the burning material.

Abundances of eight thermally-derived carbon fractions differ by carbon sources (Cao *et al*., 2005; Chow *et al*., 2004; Watson *et al*., 1994). Fig. 4 illustrates the abundances of eight thermally-derived carbon fractions at both the peatland fire and background sites by mass percentage of total carbon. Distinct differences in carbon fractions were observed between the two sites. OC$_1$ accounted for 31.7 ± 2.21% of TC in peatland fire samples but only 0.710 ± 0.721% of TC in background samples. OC$_2$ accounted for 47.5 ± 0.948% of TC in peatland fire
samples and 13.9 ± 1.64% of TC in background samples. OC₃ accounted for 7.44 ± 1.57% of TC in peatland fire samples and 40.7 ± 2.62% of TC in background samples. OC₄ accounted for 1.22 ± 0.412% of TC in peatland fire samples and 15.7 ± 1.27% of TC in background samples. OP accounted for 9.28 ± 1.39% of TC in peatland fire samples and 3.95 ± 4.13% of TC in background samples. Lower EC fractions were observed in the peatland fire than the background samples. Thus, it was found that TC in PM₂.₅ aerosols derived from peatland fires was primarily composed of OC₁ and OC₂.

Fig. 5 illustrates the average percentages of eight fractions in PM₂.₅ for the peatland fire samples and those from other sources. The vegetation burning profiles used as reference were obtained by ground-based source-dominated sampling of the plumes of small controlled burns of wood debris at the Big Bend National Park in the US (see Chow et al., 2004). The carbon fraction abundances differ by emission source: OC₁ is enriched (23.9 ± 12.4%) in the vegetative burning profile; OC₂ is enriched (34.7 ± 2.16%) in the peatland fire profile; OC₃ is enriched (37.6 ± 15.9%) in the cooking profile; EC₂ is enriched (23.3 ± 10.4%) in the motor vehicle profile. In terms of the coefficient of variance, the carbon fraction obtained from peatland fire is more consistent than any source presented in Fig. 5. Thus, the peatland profile will be useful for source discrimination.

3.3. Key biomarkers
The organic compounds produced by peatland fires were analyzed by GC/MS, and an example of typical GC/MS total ion current (TIC) tracers for the total extract of peatland fire samples is presented in Fig. 6. Levoglucosan clearly exhibits the highest TIC peak in peatland fire samples, although mannosan and palmitic acid were also detected. Palmitic acid is one of the most basic units of plant fats, oils, and phospholipids (Simoneit, 2002). The major tracers in smoke emitted from biomass burning are the thermal degradation (pyrolysis) products of the biopolymers of cellulose and lignin in woody tissue. The thermal degradation of cellulose (also hemicelluloses) yields dehydromonosaccharide derivatives, which are predominant compounds in the smoke (Simoneit et al., 1999). The major compound is levoglucosan, with minor and variable amounts of galactosan and mannosan. These compounds cannot be formed by hydrolysis or by the microbial alteration of carbohydrates; thus, they are specific to burning (Simoneit et al., 1999). In addition, levoglucosan is considerably resistant to atmospheric degradation (Fraser and Lakshmanan, 2000). Therefore, levoglucosan and mannosan are regarded as key biomarkers in peatland fire aerosols like other biomass burnings.

The average levoglucosan concentrations from peatland fire and background samples were 464 ± 183 µg/m³ and 0.278 ± 0.155 µg/m³, respectively and the average mannosan concentration were 47.5 ± 25.6 µg/m³ and 0.0190 ± 0.0108 µg/m³, respectively. Levoglucosan and mannosan in background samples may have originated from wood burning for cooking, agricultural use,
among others. However, concentrations of levoglucosan and mannosan emitted in association with peatland fire events were much higher than their corresponding background concentrations. OC/Levoglucosan ratios vary to some extent for different burning conditions and wood types (Pio, et al., 2008). In this study, the average OC/Levoglucosan ratio in peatland fire was 10.6 ± 1.96 μgC/μg. For comparison of our peatland fire samples with biomass burning samples, the average OC/Levoglucosan ratios for various source samples are presented in Fig. 7, which shows significant differences in OC/Levoglucosan ratios between the peatland fire and other emission sources. Thus, this ratio may be useful for source discrimination for peatland fire. However, because levoglucosan is emitted from other biomass burning sources and there are other types of biomass burning in Riau, Sumatra, Indonesia, selection of only OC/Levoglucosan ratio for source apportionment of peatland fire can lead to overestimation of the contribution of peatland fire. Hence, other indicators for peatland fire are needed.

The relative amounts of the individual anhydrosaccharides in biomass smoke aerosols can be used for further source assignment of specific biofuels (Fabbri et al., 2009; Alves et al., 2010). Here, we investigated the Levoglucosan/Mannosan ratios and compared those ratios from peatland fire and other biomass burning sources. In this study, the average Levoglucosan/Mannosan ratios in peatland fire and background were 10.6 ± 2.03 and 14.5 ± 3.39, respectively. For comparison of our peatland fire samples with other biomass burning samples,
the average Levoglucosan/Mannosan ratios for various source samples are presented in Table 1, which shows the significant differences in Levoglucosan/Mannosan ratios between the peatland fire and other emission sources. Thus, this ratio should be more useful for source discrimination for peatland fire than OC/Levoglucosan ratio.

4. Conclusions

PM$_{2.5}$ carbonaceous aerosols were collected at a peatland fire hotspots and a background site on 7 and 4 occasions, respectively. PM$_{2.5}$ aerosols emitted from peatland fire were observed in very high concentrations (7120 ± 3620 µg/m$^3$) and were primarily composed of OC (71.0 ± 5.11% of PM$_{2.5}$ mass).

The OC/EC ratios (36.4 ± 9.08 for peatland fire), abundances of eight thermally-derived carbon fractions, OC/Levoglucosan ratios (10.6 ± 1.96 for peatland fire), and Levoglucosan/Mannosan ratios (10.6 ± 2.03 for peatland fire) observed here represent a signature profile that seems to be inherent in peatland fire emissions. Therefore, it is suggested that such profiles are useful for peatland fire source discrimination.

In future studies, additional chemical speciation for fresh and aged smoke from peatland fires will be required to estimate atmospheric environmental impacts and/or adverse health effects (e.g., humic-like substances, polycyclic aromatic hydrocarbons).
Acknowledgement

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References


Table Captions

Table 1. Range of Levoglucosan/Mannosan ratios in PM$_{2.5}$ emitted from several sources and background.
<table>
<thead>
<tr>
<th></th>
<th>Levoglucosan/Mannosan</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peatland fire</td>
<td>7.09–14.0</td>
<td>this study</td>
</tr>
<tr>
<td>Background</td>
<td>10.7–18.9</td>
<td>this study</td>
</tr>
<tr>
<td>Hardwoods burning</td>
<td>13.8–52.3</td>
<td>Engling et al., 2006</td>
</tr>
<tr>
<td>Softwoods burning</td>
<td>2.6–5.0</td>
<td>Engling et al., 2006</td>
</tr>
<tr>
<td>Grasses burning</td>
<td>108–203</td>
<td>Engling et al., 2006</td>
</tr>
</tbody>
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Table 1.
Figure Captions

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

Fig. 2. Monthly hotspot counts in Riau in 2011 and 2012.

Fig. 3. Comparison of OC/EC ratios in PM$_{2.5}$ emitted from peatland fire and other burning sources. Error bar in this study indicates standard deviation.

Fig. 4. Abundances (as mass percentage of total carbon) of eight thermally-derived carbon fractions of aerosols sampled at the peatland fire and background sites. Error bars indicate standard deviations.

Fig. 5. Carbon fraction composition of PM$_{2.5}$ combustion source profiles. Error bars indicate standard deviations.

Fig. 6. GC/MS total ion current (TIC) chromatograph of total extract showing major compounds of peatland fire aerosols.

Fig. 7. Comparison of OC/Levoglucosan ratios of PM$_{2.5}$ obtained from peatland fire and other burning sources. Error bar in this study indicates standard deviation.
Fig. 2.
Fig. 3.

\[ \text{OC/EC ratio [\%]} \]

- Peatland fire
- Coconut leaves
- Rice Straw
- Cow dung
- Biomass Briquettes
- Jackfruit Branches
- Fine forest

\[ ^a \text{data from Sheesley and Schauer, 2003, \ } ^b \text{data from Lee et al., 2005.} \]
Fig. 4.
a data from Chow et al., 2004.

Fig. 5.
Fig. 6.
a data from Sheesley and Schauer, 2003, b data from Lee et al., 2005.

Fig. 7.