Characteristics of carbonaceous aerosols emitted from peatland fire in Riau, Sumatra, Indonesia (2) – Identification of organic compounds –

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Abstract

Smoke emitted from Indonesian peatland fires has caused dense haze and serious air pollution in Southeast Asia such as visibility impairment and adverse health impacts. To mitigate the Indonesian peatland fire aerosol impacts, an effective strategy and international framework based on the latest scientific knowledge needs to be established. Although several attempts have been made, limited data exist regarding the chemical characteristics of peatland fire smoke for the source apportionment. In order to identify the key organic compounds of peatland fire aerosols, we conducted intensive field studies based on ground-based and source-dominated sampling of $PM_{2.5}$ in Riau Province, Sumatra, Indonesia, during the peatland fire seasons in 2012. Levoglucosan was the most abundant compound among the quantified organic compounds at $8.98 \pm 2.28\%$ of the $PM_{2.5}$ mass, followed by palmitic acid at $0.782 \pm 0.163\%$ and mannosan at $0.607 \pm 0.0861\%$. Potassium ion was not appropriate for an indicator of Indonesian peatland fires due to extremely low concentrations associated with smoldering fire at low temperatures. The vanillic/syringic acids ratio was 1.06 ± 0.155 in this study and this may be a useful signature profile for peatland fire emissions. Particulate n-alkanes also have potential for markers to identify impact of Indonesian peatland fire source at a receptor site.

Keywords

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Highlights

➢ Organic compounds in $PM_{2.5}$ emitted from peatland fires were characterized.
➢ Potassium cannot be used as a source indicator for peatland fires.
We found some potential source indicators of peatland fire.

1. Introduction

Biomass burning (BB) can be defined as an open or quasi-open combustion of a nonfossilized vegetative or organic fuel [Akagi *et al.*, 2011]. BB is the largest source of primary fine carbonaceous aerosols and the second largest source of trace gases in the global atmosphere [Guenther *et al.*, 2006; Andreae and Merlet, 2001; Bond *et al.*, 2011]. Aerosols emitted from BB have direct as well as indirect effects on climate and are a predominant cause of transboundary haze pollution [Tacconi, 2003]. In general, 80% to 90% of smoke aerosols produced by BB are in the $PM_{2.5}$ size range [Reid *et al.*, 2005], indicating the importance of $PM_{2.5}$ as an indicator of BB.

In Indonesia, many hotspots of peatland fires have been detected in the Sumatra and Kalimantan Islands during the dry season. Peatland is a terrestrial wetland ecosystem where organic matter production exceeds its decomposition, resulting in net accumulation [Page *et al.*, 2006]. Smoke emitted from Indonesian peatland fires has caused dense haze and serious air pollution in Southeast Asia such as visibility impairment and adverse health impacts. [Harrison *et al.*, 2009]. Though El Niño–Southern Oscillation (ENSO) events considerably contribute to the occurrence of peatland fires due to biomass dryness under severe drought conditions, pollution from peatland fires is a repeated problem in Indonesia and neighboring countries, even in non-ENSO years [Tacconi, 2003].

To mitigate the Indonesian peatland fire aerosol impacts, an effective strategy and international framework such as ASEAN Agreement on Transboundary Haze Pollution [ASEAN Haze Action

60   Online] based on the latest scientific knowledge needs to be established. Although several

61   attempts have been made, limited data exist regarding the chemical characteristics of peatland fire

62   smoke [Betha *et al.*, 2013; Fujii *et al.*, 2014; See *et al.*, 2007] for source speciation. Recently, we

63   determined the main components of $PM_{2.5}$ in the vicinity of Indonesian peatland fires and showed

64   organic carbon constituted ~70% of the $PM_{2.5}$ mass, indicating organic matter is extremely

65   important [Fujii *et al.*, 2014]. In general, each individual plant species emits a chemical

66   fingerprint of natural and thermally altered organic constituents upon burning, which is source

67   specific and unique in composition [Oros *et al.*, 2006]. See et al. (2007) reported polycyclic

68   aromatic hydrocarbons and water soluble organic ions in $PM_{2.5}$ collected in the open field within

69   a 100 m circumference from the boundary of the peatland fires. However, these compounds

70   accounted for only ~1.45 weight% of $PM_{2.5}$. Therefore, it is necessary to explain the organic

71   compounds in Indonesian peatland fire aerosols in depth and find key source indicators.

72   In this study, we quantitatively characterized major organic compounds of the aerosols derived

73   from Indonesian peatland fires to determine potential source profile and indicators. These data

74   will provide useful information to evaluate the contribution of Indonesian peatland fire aerosols

75   to the air quality in Southeast Asia.

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2. Materials and methods

2.1. Sampling locations

The sampling was performed in Riau, Sumatra, Indonesia. A detailed description about the sampling sites has been given in our former report [Fujii *et al.*, 2014]. In brief, the sampling site was located at Sepahat Village in Bengkalis Regency, Riau Province, Sumatra, Indonesia. The sampling site was enclosed by peatland and forest, and the rainy season lasts from September to January, with an average rainfall of 809–4078 mm year^{-1}, and the dry season normally lasts from February to August.

2.2. Sample collection and analysis

PM$_{2.5}$ aerosol samples emitted from peatland fires were collected on June 14–16, 2012. Peat soil, fallen trees (hardwoods), oil palm, and bush were mainly burned during this period. Two mini-volume samplers (MiniVol^{TM} TAS, Airmetrics) were utilized to continuously collect PM$_{2.5}$ aerosols on Teflon and quartz fiber filters for 2.5–5.2 h at a flow rate of 5 L min^{-1}. PM$_{2.5}$ aerosols were collected at ~1.5 m above ground level from several peatland fire hotspots on 7 occasions. Wind speeds in the peatland fire samplings ranged from 0.610 to 6.21 m s^{-1} (average speed: 2.50 m s^{-1}), 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

95   organic material. After sampling, Teflon and quartz fiber filters were stored in a refrigerator under

96   4 and –20°C, respectively, until analysis. Each Teflon filter was weighed using a microbalance

97   (ME5-F, Sartorius) with a sensitivity of ±1 µg in a stable environment of 25.7 ± 0.4 °C (average ±

98   standard deviation) and 26.0 ± 0.6 RH% before and after sampling to determine $PM_{2.5}$ mass

99   concentrations. After gravimetric analysis, each Teflon filter was analyzed for water-soluble

100   inorganic ions by ion chromatography (HIC-10A, Shimadzu). In this study, only data of

101   potassium ions (K^+) is considered for discussion.

102   Solvent-extractable organic compounds obtained from the quartz fiber filters were quantified

103   by gas chromatography/mass spectrometry (GC/MS). Organic compound speciation was

104   accomplished as follows. Aliquots from the quartz fiber filter were spiked with internal standards

105   of methyl β-L-arabinopyranoside, 1,2,3-hexanetriol, (S)-(+)-ketopinic acid, and triacontane-d_{62}

106   before extraction. Each spiked filter was extracted by ultrasonic agitation for 3×20 min periods

107   using 4 mL of a dichloromethane/methanol mixture (3/1, v/v) (dichloromethane: Kanto Chemical,

108   purity >99.5%; methanol: Wako, purity >99.7%). The combined extracts were filtered through a

109   Teflon syringe filter (pore size 0.1 µm), dried completely under a nitrogen stream, and

110   redissolved to 2 mL in a dichloromethane/methanol mixture (3/1, v/v). Subsequently, 1 mL of the

111   concentrated extracts were dried completely under a nitrogen stream and used for derivatization

112   as follows. Before GC/MS analysis, trimethylsilyl derivatization was conducted for the extracts

113   with 10 µL of *N*,*O*-bis-(trimethylsilyl)-trifluoroacetamide with 1% trimethylchlorosilane and 45

114   µL of pyridine for 3 h at 70 °C, and then ~9 µg of tetracosane-d_{50} dissolved in 45 µL of

115   dichloromethane was added as a syringe spike (second internal standard).

116   The derivatized samples were analyzed on a Shimadzu GC/MS system (GCMS-QP2010-Plus,

117   Shimadzu) equipped with a 30 m HP-5MS column (0.25 µm film thickness, 0.25 mm ID). The

118   carrier gas was helium (purity 99.9995%) at a pressure of 59.4 kPa (36.6 cm s^{-1} at 65 °C). The

119   GC oven temperature program was as follows: isothermal at 65 °C for 5 min, 65 °C to 300 °C at

120   10 °C min^{-1}, and then 300 °C for 20 min. The injection port and transfer line were maintained at

121   300 °C. The data for quantitative analysis were acquired in the electron impact mode (70 eV).

122   The mass spectrometer was operated under selected ion monitoring mode, and the monitored ions

123   for quantification are shown in Table 1. Regarding internal standards, the monitored ions of

124   methyl *β*-L-arabinopyranoside, 1,2,3-hexanetriol, (*S*)-(+)-ketopinic acid, triacontane-d_{62}, and

125   tetracosane-d_{50} were 217, 145, 75, 66, and 66 m/z, respectively. The recovery ratios of known

126   amounts of the standards on quartz fiber filters are presented in Table 2. In addition,

127   solvent-extractable organic compounds as targets on field blank filters were analyzed, which

128   showed no contamination.

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3. Results and discussion

PM$_{2.5}$ mass concentrations and fractions of organic compounds in PM$_{2.5}$ emitted from peatland fires are shown in Table 3. The PM$_{2.5}$ mass concentration was 7130 ± 3630 μg m^{-3}, and quantified organic compounds accounted for $14.4 \pm 2.55\%$ of the PM$_{2.5}$ mass. Though particulate K$^+$ has been suggested as a tracer for BB [Chuang *et al.*, 2013], it was only $0.0423 \pm 0.0400\%$ of the PM$_{2.5}$ mass in this study. Levoglucosan was the most abundant compound among the quantified organic compounds at $8.98 \pm 2.28\%$ of the PM$_{2.5}$ mass, followed by palmitic acid at $0.782 \pm 0.163\%$ and mannosan at $0.607 \pm 0.0861\%$.

3.1. Cellulose pyrolysis products

Levoglucosan mainly derived from pyrolysis of cellulose is widely accepted as a major organic component in fine smoke aerosols from BB. Mannosan and galactosan are minor constituents compared to levoglucosan and are derived from the pyrolysis of hemicellulose. These compounds cannot be formed by hydrolysis or by the microbial alteration of carbohydrate and are specific to burning [Simoneit *et al.*, 1999].

The K$^+$/levoglucosan ratio can be used as an indicator to roughly estimate the combustion state such as flaming or smoldering combustion of BB [Gao *et al.*, 2003; Pio *et al.*, 2008; Chaung *et al.*, 2013]. This is because more K$^+$ remains in the aerosol phase compared with levoglucosan when the combustion temperature is higher [Chuang *et al.*, 2013]. For flaming and smoldering

150   savannah forest fires, the ratios were 33.3 and 0.2–0.6, respectively [Gao *et al.*, 2003]. In this

151   study, the K^+/levoglucosan ratio was 0.00537 ± 0.00562 and extremely lower than the ratios

152   reported anywhere else [e.g., Gao *et al.*, 2003; Sullivan *et al.*, 2008]. This indicates the

153   Indonesian peatland fires studied were predominantly smoldering at even lower temperature than

154   the smoldering combustions of other BBs in previous studies. An extremely low K^+ fraction

155   $(0.0423 \pm 0.0400\%$ of $PM_{2.5}$ mass) also supports that conclusion. Thus, unlike many other BB

156   sources, K^+ derived from the Indonesian peatland fires should not be used as a source indicator.

157   Other specific indicators are badly needed.

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159   *3.2. Lignin pyrolysis products*

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161   Lignin is one of the major components of biomass (20–35 wt% of dry matter), and is known to

162   be an aromatic polymer consisting of phenylpropane units linked through various ether and C–C

163   types of linkages. Its aromatic structures vary depending on the species; softwood lignins contain

164   guaiacyl (G) types exclusively, whereas hardwood lignins include both G and syringyl (S) types,

165   and herbaceous plants include G, S, and *p*-hydroxyphenyl types. Thus, the compositions of these

166   aromatic nuclei in the lignin pyrolysis products from BB would be useful for identifying the

167   biomass type. In fact, Simoneit et al. (1993) reported that lignin pyrolysis products in BB aerosols

168   have the potential to provide a unique source signature or profile.

169   In this study, various lignin G- and S-unit-originated compounds had higher yields. Vanillin

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170 (V), coniferyl aldehyde, vanillic acid (VA), and homovanillic acid are derived from the G units,

171 whereas syringaldehyde (S), syringic acid (SA), and homosyringic acid are derived from the S

172 units. The detection of both G- and S-derived compounds is explicable that the vegetation in the

173 Indonesian peatland mainly consists of hardwood and herbaceous species. There was no detection

174 of dehydroabietic acid as a resin pyrolysis product, as frequently reported for SWB (Softwoods

175 burning) [Simoneit, 1977; Lin *et al.*, 2010], which is also consistent with the vegetation.

176   VA and SA derived from lignin pyrolysis were abundant organic compounds in our samples

177 (VA: 5.63 ± 1.45, SA: 5.37 ± 1.33 mg g^{-1} PM$_{2.5}$) comparable to palmitic acid (7.82 ± 1.63 mg g^{-1}

178 PM$_{2.5}$) and mannosan (6.07 ± 0.861 mg g^{-1} PM$_{2.5}$) as shown in Table 3. These two compounds

179 have been detected during the haze episodes in Malaysia [Abas *et al.*, 2004] and Singapore [He *et*

180 *al.*, 2010], suggesting that the haze arose from Indonesian peatland fires. Therefore, these two

181 compounds may travel long distances (~300 km) as smoke from Indonesian peatlands to

182 Malaysia. Since the relative content of G and S units in lignin are different depending on the

183 biomass type, as discussed above, the VA/SA mass ratios from BB would also vary. Consequently,

184 the mass ratio of VA/SA is expected to be used as an indicator for BB source discrimination. The

185 VA/SA mass ratio in the peatland fire was 1.06 ± 0.155. For comparison with other BB samples,

186 VA/SA ratios reported for various source samples are presented in Fig. 1, which shows

187 differences in VA/SA ratios between peatland fire and other emission sources in tropical zone.

188   Thus, this ratio has the potential for the source discrimination of peatland fire in tropical zone.

189   Comparison of the VA/SA ratio with those of the sources in Southern United States and

190   California (Fig. 1) may also indicate VA/SA ratio can be a potential indicator for source

191   discrimination. However, there are few reports regarding SA and VA at sources [Fine *et al.*, 2002;

192   Nolte *et al.*, 2001; Oros *et al.*, 2006; Simoneit *et al.*, 1993; 1999]. Further accumulation of these

193   data at several sources is required to enhance the usefulness of SA/VA ratio as a source indicator.

194   The relationships between the aldehydes (V or S) and carboxylic acid (VA or SA) contents in

195   PM$_{2.5}$ collected at peatland fire sources are shown in Fig. 2. Linear regressions through the origin

196   in Fig. 2 were assumed because V/VA and S/SA ratios must be zero when V and S are equal to

197   zero, respectively. Interestingly, the results show fairly good linear relationships, with slopes of

198   0.122 ± 0.0224 (V/VA, coefficient of determination: $R^2 = 0.887$) and 0.446 ± 0.0905 (S/SA, $R^2 =$

199   0.955). Note that the V/VA and S/SA ratios were fairly constant independent of the sampling sites

200   of the peatland fires. Due to the nature of aldehydes, V and S are expected to be more susceptible

201   to photochemical and/or chemical oxidation than VA or SA during their movement away from the

202   peatland fire. Net et al. (2011) reported the heterogeneous reactions of ozone with V, S, VA and

203   SA, in presence and absence of simulated solar light. They showed that VA and SA were the main

204   oxidation products of V and S, respectively, and no reaction product from VA and SA was

205   detected during the ozonolysis of VA and SA under 6 ppm ozone concentration. Since conversion

206 rates of V to VA and S to SA are not necessarily identical, the VA/SA ratios may be changed

207 during transportation of peatland fire aerosols. Therefore, we estimated possible variations of this

208 ratio derived from peatland fires under several conditions by oxidation in the atmosphere as

209 follows: (1) all V is completely converted to VA, (2) all S is completely converted to SA, (3) all V

210 and S are completely converted to VA and SA, respectively, (4) present condition (this study). It

211 is shown that at most, variation of VA/SA ratios ranged from –32.5 to 14.2% (Table 4). These

212 possible variations will not largely affect source discrimination for peatland fires.

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214 *3.3. n-alkanes*
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216   Particulate *n*-alkanes originate from both biogenic and anthropogenic sources. Anthropogenic

217 sources of *n*-alkanes include incomplete fossil fuel combustion, lubricant oils, and biomass

218 burning, while wind erosion of leaf epicuticular waxes, direct suspension of pollen, vegetation

219 debris, and microbial degradation are major natural sources of particulate *n*-alkanes [Ladji *et al.*,

220 2014; Simoneit, 1989; Rogge *et al.*, 1993a, b; Kavouras *et al.*, 2002]. In this study, we mainly

221 focus on *n*-alkanes more than C_{19} (nonadecane) since *n*-alkanes less than C_{20} (icosane) may

222 result in some volatilization from the filter in tropical zone [Abas *et al.*, 2004].

223   Total particulate *n*-alkanes (C_{20}–C_{33}) mass were abundant at 2.15 ± 0.490 weight% of $PM_{2.5}$

224 mass in this study. Table 3 shows the mass fraction of individual particulate *n*-alkanes in $PM_{2.5}$.

225 The carbon number maximum concentration in *n*-alkanes was C_{27}, indicating that peatland fire

226   source was categorized as biogenic sources (higher plant wax) [Abas *et al.*, 2004].

227   For comparison of our peatland fire samples with other emission sources, mass fraction of

228   particulate total *n*-alkanes (C_{20-33}) in PM for various source samples are presented in Fig. 3.

229   Particulate total *n*-alkanes from noncatalyst-equipped automobiles, catalyst-equipped automobiles,

230   heavy-duty diesel trucks, tire wear, road dust, and brake lining sources were in the $PM_{2.0}$ size

231   range [Rogge *et al.*, 1993a, b]. Particulate total *n*-alkanes from pine wood with green needles

232   burning and savanna grass burning sources were in the $PM_{3.5-0.05}$ range [Iinuma *et al.*, 2007].

233   Particulate total *n*-alkanes from meat cooking source were in the $PM_{1.8}$ range [Schauer *et al.*,

234   1999]. Figure 3 shows significant differences in the fraction of total *n*-alkanes (C_{20-33}) in PM

235   between the peatland fire and other emission sources. In particular, the fraction of peatland fire

236   source was much higher than those from tire wear, road dust, brake lining, pine wood with green

237   needles burning, savanna grass burning, and meat cooking.

238   Figure 4 illustrates the comparison of molecular distributions of particulate *n*-alkanes obtained

239   from our peatland fire samples and vehicle-related emission sources which show high abundance

240   of particulate *n*-alkanes in PM (see Fig. 3). The distribution of particulate *n*-alkanes in PM

241   emitted from peatland fires obviously differs from those of other emissions. Particularly, C_{27}, C_{28},

242   and C_{29} mass fractions in particulate total *n*-alkanes (C_{20-33}) in this study were 4.57–26.6 times

243   higher than those from other emissions as shown in Fig. 4. Thus, if a receptor site is affected by

244   Indonesian peatland fire source, C_{27}, C_{28}, and C_{29} mass concentrations and fractions in

245   particulate total n-alkanes (C_{20-33}) would be increased.

246   Abas et al. (2004) reported particulate n-alkanes (C_{15-36}) concentrations in PM during the haze

247   episodes in Kuala Lumpur, Malaysia. At that time, particulate total n-alkanes (C_{15-36})

248   concentrations ranging from 410 to 1009 ng m^{-3} during the haze episodes were much higher than

249   that (C_{16-41}) at the non-haze day of 26 ng m^{-3}, as well as levoglucosan [Abas et $al.$, 1996, 2004].

250   The four molecular distributions of particulate n-alkanes (C_{20-33}) during the haze episodes in

251   Malaysia were reconstructed in Fig. 5 according to their paper [Abas et $al.$, 2004], and compared

252   with that of our peatland fire samples. DUMG and DSP samples were collected during the day

253   time, and NUMG and NSP samples were collected during the night time. Roughly, the molecular

254   distributions of particulate n-alkanes during the haze episodes in Malaysia were comparable to

255   that of our peatland fire samples. Increase in total concentrations and molecular distributions of

256   particulate n-alkanes during the haze episodes are considered to be caused by Indonesian peatland

257   fires. Therefore, particulate n-alkanes can serve as potential markers to identify impact of

258   Indonesian peatland fire source at a receptor site like Malaysia.

259

4. Conclusion

In order to identify the key organic compounds of peatland fire aerosols, we conducted intensive field studies based on ground-based and source-dominated sampling of $PM_{2.5}$ in Riau Province, Sumatra, Indonesia, during the peatland fire seasons in 2012. Levoglucosan was the most abundant compound among the quantified organic compounds at $8.98 \pm 2.28\%$ of the $PM_{2.5}$ mass, followed by palmitic acid at $0.782 \pm 0.163\%$ and mannosan at $0.607 \pm 0.0861\%$. K^+ was not appropriate for an indicator of Indonesian peatland fires due to extremely low concentrations associated with smoldering fire at low temperatures. In terms of lignin pyrolysis products, V/VA and S/SA ratios were fairly constant independent of the sampling sites of the peatland fires. The VA/SA ratio was 1.06 ± 0.155 in this study and this may be a useful signature profile for peatland fire emissions after allowing for the uncertainty of the conversion rates of aldehydes (V, S) to acids (VA, SA). Particulate n-alkanes also have potential for markers to identify the impact of Indonesian peatland fire source at a receptor site.

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Table Captions

394   Table 1. Analytes, internal standards employed for GC/MS.

395   Table 2. Recovery ratios of target and internal standards.

396   Table 3. Bulk chemical compositions of $PM_{2.5}$ emitted from peatland fires (average $\pm$ standard

397   deviation).

398   Table 4. Possible variations of VA/SA mass ratios derived from peatland fires under several

399   conditions by oxidation in the atmosphere.

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Analyte	m/z used for quantification	Internal Standard
levoglucosan	204	methyl β-L-arabinopyranoside
mannosan	204	methyl β-L-arabinopyranoside
galactosan	204	methyl β-L-arabinopyranoside
vanillin	194	1,2,3-hexanetriol
syringaldehyde	239	1,2,3-hexanetriol
coniferylaldehyde	220	methyl β-L-arabinopyranoside
p-hydroxybenzoic acid	267	methyl β-L-arabinopyranoside
vanillic acid	297	(S)-(+)-ketopinic acid
syringic acid	253	(S)-(+)-ketopinic acid
homovanillic acid	326	methyl β-L-arabinopyranoside
homosyringic acid	239	methyl β-L-arabinopyranoside
palmitic acid	117	methyl β-L-arabinopyranoside
n-alkanes (C_{20-33})	57	triacontane-d_{62}

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411   Table 1.

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Compounds	Addition [μg]	Recovery ratio [%]	Recoveries of Target/IS [-]
levoglucosan	82.0	94.0±7.58	1.04±0.0461
mannosan	25.5	92.9±9.01	1.03±0.0410
galactosan	9.95	89.0±8.45	0.984±0.0239
vanillin	2.25	86.2±12.2	0.978±0.0832
syringaldehyde	8.70	97.9±13.9	1.11±0.0939
coniferylaldehyde	1.70	101±24.7	1.12±0.205
p-hydroxybenzoic acid	11.8	85.1±6.58	0.943±0.0556
vanillic acid	15.7	84.5±7.14	1.01±0.0757
syringic acid	18.3	92.6±9.93	1.10±0.0964
homovanillic acid	1.00	92.0±13.1	1.02±0.0647
homosyringic acid	1.01	105±14.8	1.17±0.0921
palmitic acid	18.2	98.9±11.3	1.10±0.152
icosane	5.00	85.3±8.13	1.26±0.231
heneicosane	5.00	85.9±8.42	1.27±0.238
docosane	5.00	86.3±9.48	1.27±0.235
tricosane	5.00	85.6±10.9	1.26±0.226
tetracosane	5.00	84.0±12.3	1.23±0.220
pantacosane	5.00	81.9±14.0	1.20±0.215
hexacosane	5.00	80.9±15.4	1.18±0.215
heptacosane	5.00	79.4±16.7	1.16±0.209
octacosane	5.00	77.7±17.8	1.13±0.201
nonacosane	5.00	75.4±18.8	1.09±0.193
triacontane	5.00	72.3±18.9	1.04±0.182
hentriacontane	5.00	69.2±20.4	0.990±0.180
dotriacontane	5.00	66.1±21.4	0.939±0.181
tritriacontane	5.00	62.7±22.6	0.884±0.194
methyl *β*-L-arabinopyranoside	8.32	90.6±10.1	-
1,2,3-hexanetriol	4.34	88.2±10.1	-
(*S*)-(+)-ketopinic acid	4.92	84.1±8.30	-
triacontane-d_{62}	8.40	70.3±16.6	-

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413 Table 2.

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Organic compounds	[mg g^{-1} PM$_{2.5}$]
levoglucosan	89.8±22.8
mannosan	6.07±0.861
galactosan	2.01±0.256
vanillin	0.665±0.124
syringaldehyde	2.30±0.452
coniferylaldehyde	0.329±0.0916
p-hydroxybenzoic acid	1.72±0.346
vanillic acid	5.63±1.45
syringic acid	5.37±1.53
homovanillic acid	0.435±0.0974
homosyringic acid	0.259±0.0702
palmitic acid	7.82±1.63
icosane	0.527±0.339
heneicosane	0.913±0.440
docosane	1.53±0.545
tricosane	1.70±0.473
tetracosane	1.70±0.444
pantacosane	2.62±0.572
hexacosane	1.42±0.399
heptacosane	2.89±0.562
octacosane	2.10±0.297
nonacosane	1.78±0.352
triacontane	0.968±0.180
hentriacontane	1.84±0.368
dotriacontane	0.631±0.112
tritriacontane	0.874±0.152

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Table 3.

Condition by oxidation	VA/SA mass ratio
(1) All V conversion to VA	1.21±0.173
(2) All S conversion to SA	0.715±0.0856
(3) All V and S conversion to VA and SA, respectively	0.811±0.0921
(4) No S and V conversion to VA and SA, respectively	1.06±0.155

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432   Table 4.

433   **Figure Captions**

434   Fig. 1. Comparison of VA/SA mass ratios of $PM_{2.5}$ obtained from peatland fire and other burning

435   sources. Error bar in this study indicates standard deviations.

436   Fig. 2. Concentrations of G vs. S units derived from lignin pyrolysis in $PM_{2.5}$ emitted from

437   Indonesian peatland fires (R^2: coefficient of determination).

438   Fig. 3. Comparison of mass fraction of particulate total n-alkanes (C_{20-33}) in PM obtained from

439   peatland fire and other burning sources.

440   Fig. 4. Comparison of molecular distributions of particulate n-alkanes obtained from peatland fire

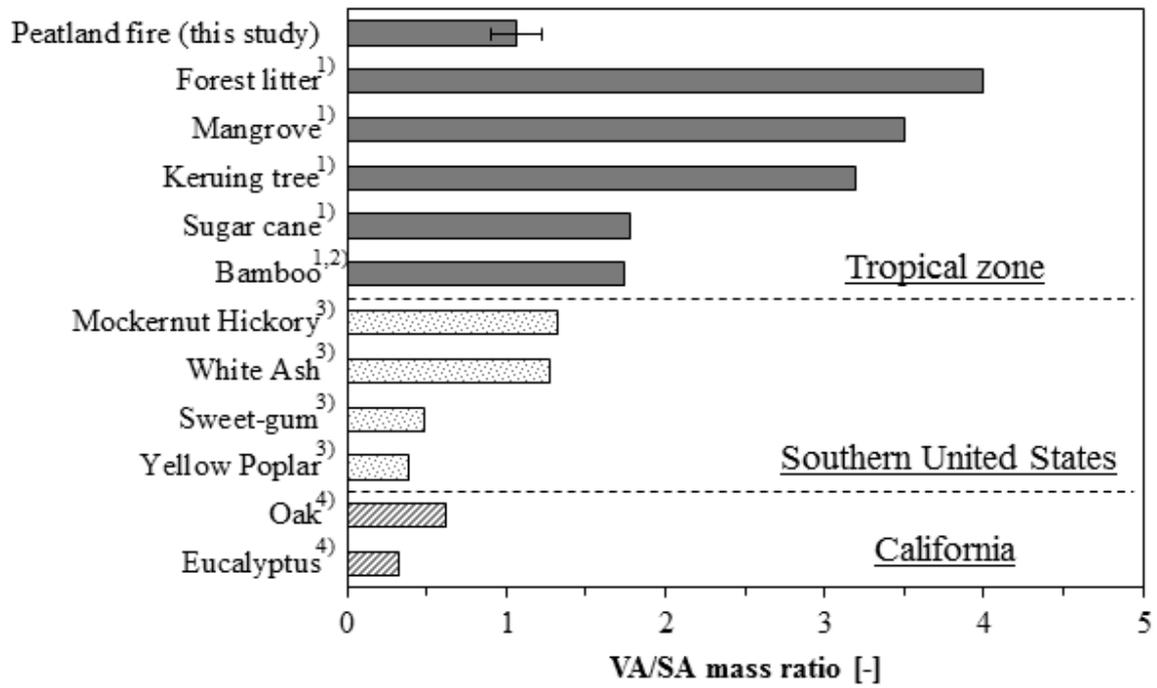441   and vehicle-related emission sources.

442   Fig. 5. Comparison of molecular distributions of particulate n-alkanes obtained from our peatland

443   fire samples and four samples during haze episodes in Malaysia.

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1) data from Simoneit *et al.*, 1999, 2) data from Oros *et al.*, 2006, 3) data from Fine *et al.*, 2002,

4) data from Nolte *et al.*, 2001.

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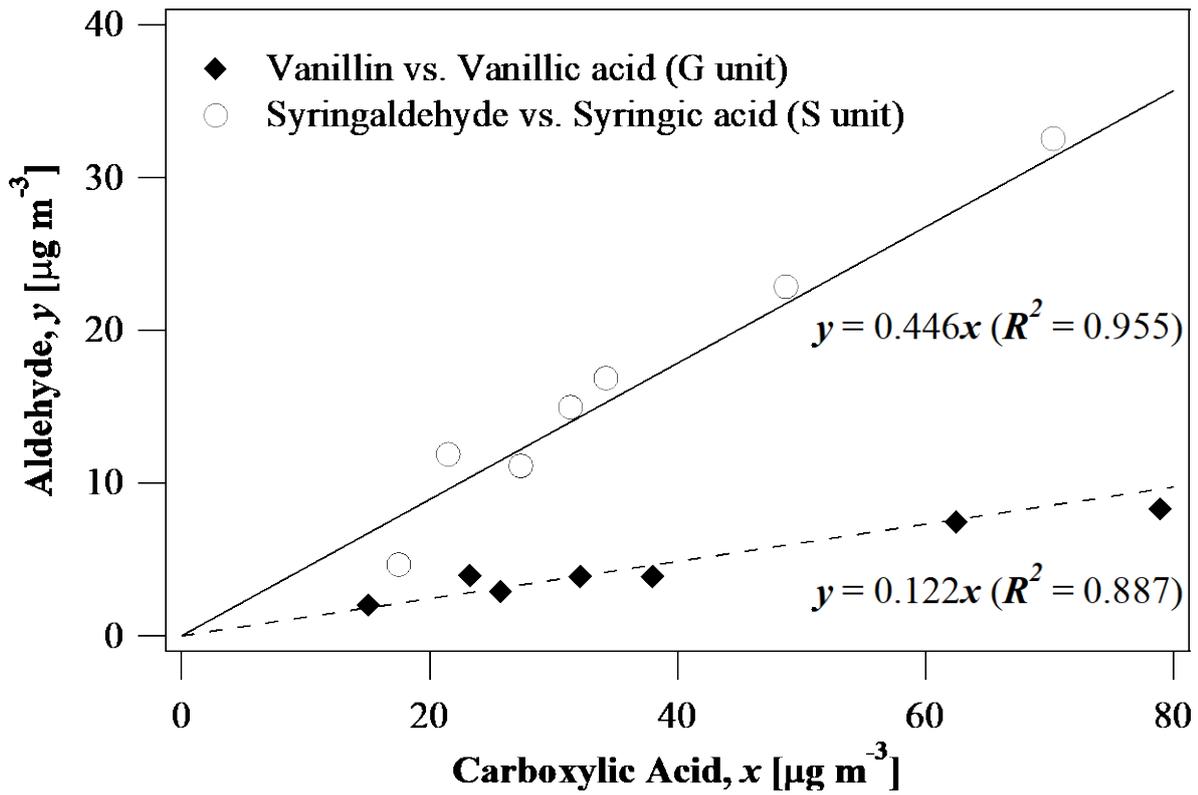453   Fig. 1.
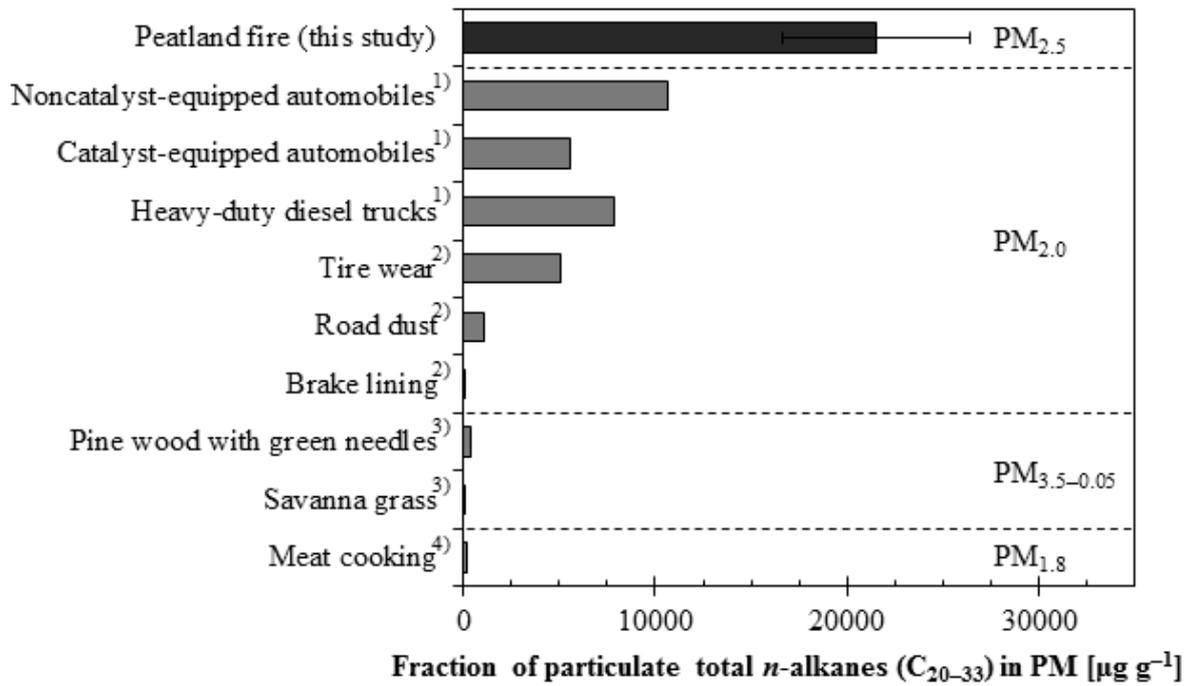
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$y = 0.446x \ (R^2 = 0.955)$

$y = 0.122x \ (R^2 = 0.887)$

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464   Fig. 2.

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Fraction of particulate total n-alkanes (C$_{20-33}$) in PM [µg g^{-1}]

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471　1) data from Rogge *et al.*, 1993a, 2) data from Rogge *et al.*, 1993b, 3) data from Iinuma *et al.*,

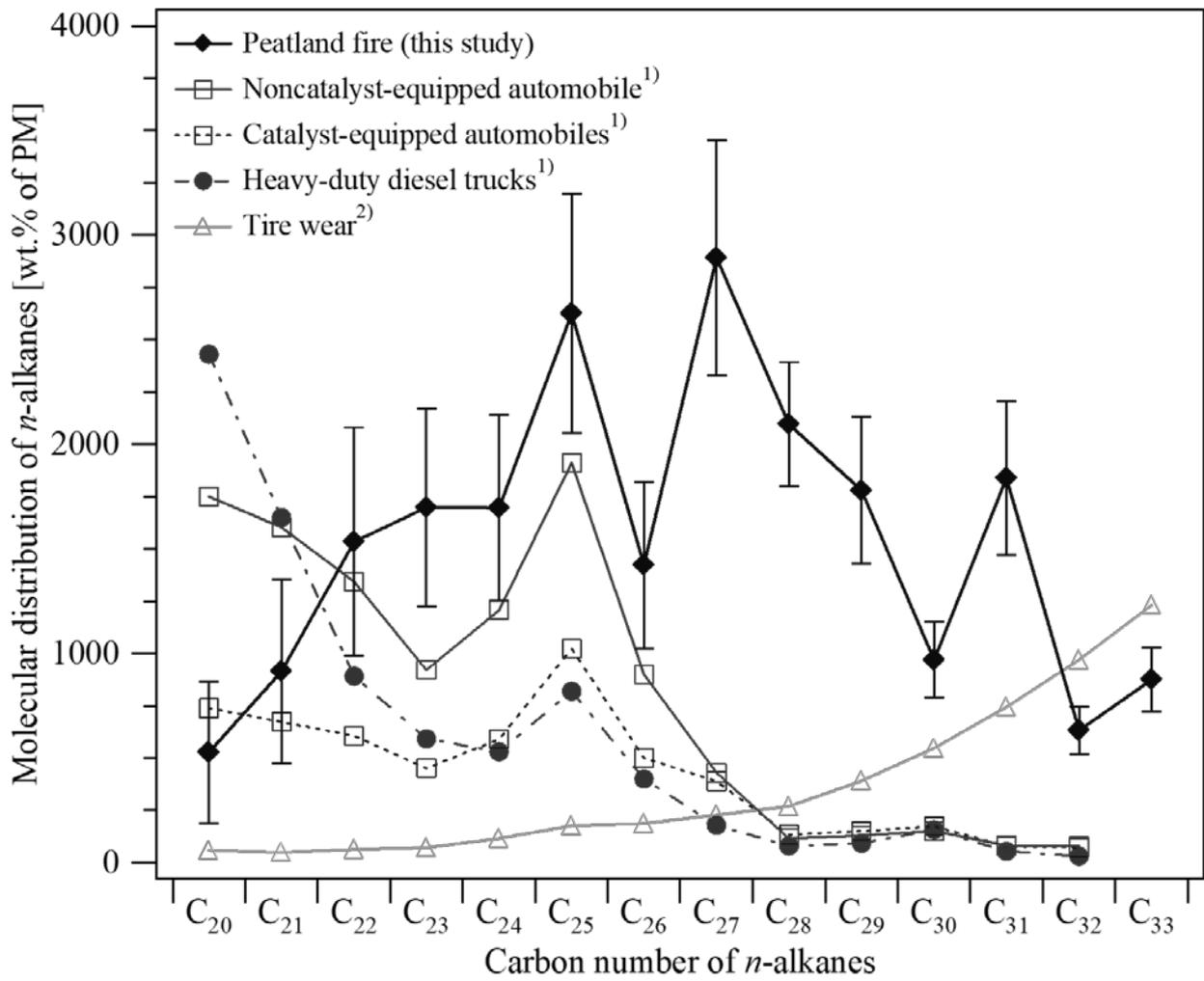472　2007, 4) data from Schauer *et al.*, 1999.

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1) data from Rogge *et al.*, 1993a, 2) data from Rogge *et al.*, 1993b.

Fig. 4.

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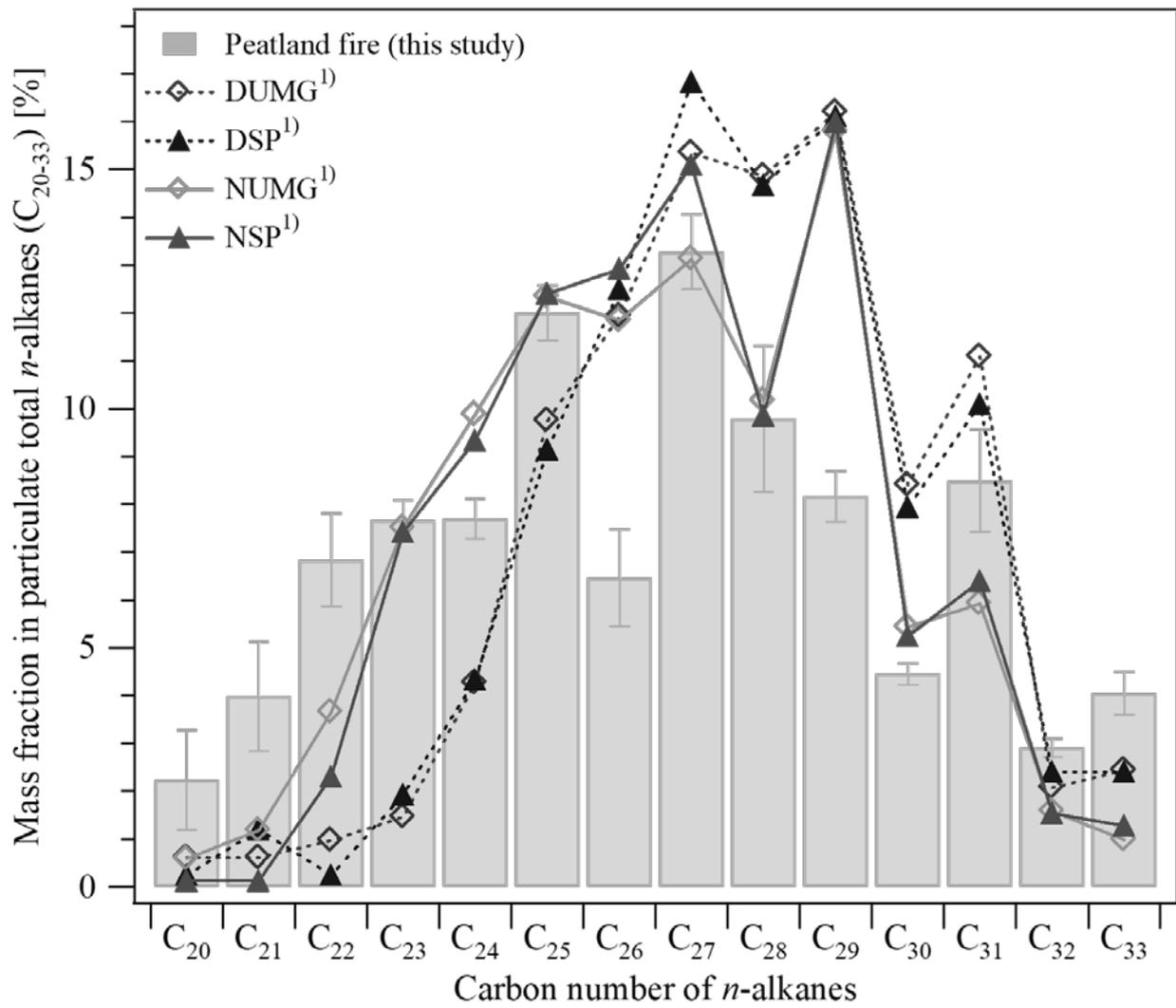
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491 1) data from Abas *et al.*, 2004.

492   Fig. 5.

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