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# Chemical speciation of water-soluble ionic components in PM<sub>2.5</sub> derived from peatland fires in Sumatra Island

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## ABSTRACT

We conducted a field study to characterize water-soluble ionic species in PM<sub>2.5</sub> from peatland fires using ground-based samplings at fire sources and receptor sites in the Riau Province, Sumatra, Indonesia. We determined the concentrations of PM<sub>2.5</sub> mass, water-soluble ions, and some chemical elements. Through PM<sub>2.5</sub> field samplings at three peatland fire sources, we have shown that the mass fractions of typical peatland fire water-soluble ionic components tend to differ between peatland fire sources. Thus, our results indicate that PM<sub>2.5</sub> source profiles of water-soluble ionic components for peatland fire must be selected with extreme caution if applied to a receptor model. From the viewpoint of ionic composition of each peatland fire sample, Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> were consistently dominant anions and cations, respectively, for all peatland fire samples, i.e., NH<sub>4</sub>Cl was a consistently dominant component. Through field samplings of the ambient PM<sub>2.5</sub> in Pekanbaru during peatland fire-induced haze and non-haze periods, we found differences in PM<sub>2.5</sub> mass and total water-soluble ionic component concentrations between haze and non-haze samples. Four components, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>, showed highly elevated levels during haze periods. Since these four ions are recognized as the major secondarily formed aerosol components, the increased total concentrations of water-soluble ionic components during haze periods can mainly be derived from the gas-to-aerosol conversion process. The ionic compositions of haze samples at receptor sites are obviously different from those at peatland fire source samples. In particular, NH<sub>4</sub>Cl, which is characteristic of peatland fire PM<sub>2.5</sub> sources, is low at sites during haze periods.

## 1. Introduction

Biomass burning (BB), which covers forest and peatland fires, burning of agricultural waste, and use of biofuels for cooking, is a major source of primary aerosol particles in Southeast Asia (Akagi et al., 2011; Stockwell et al., 2015). In Indonesia, haze caused by smoke from peatland fires is a frequent dry season occurrence each year. These fires are caused by a range of activities, such as land clearing by companies and small-scale farmers, unintentional escaped fires, and other activities (Tacconi, 2016). Fires are more pronounced during El Niño years owing to the severe drought conditions that lead to biomass dryness (Page et al., 2002; Huijnen et al., 2016). Generally, 80 %–90% of BB aerosols comprises particulate matter 2.5 μm or smaller in aerodynamic diameter (PM<sub>2.5</sub>; Reid et al., 2005). The dense haze in Indonesia worsens the domestic air quality, and transported haze affects air quality in

surrounding countries, such as Malaysia and Singapore (Betha et al., 2014; Behera and Balasubramanian, 2014; Engling et al., 2014; Fujii et al., 2015b, 2016; 2017; He et al., 2010; Pavagadhi et al., 2013; See et al., 2006). This haze has caused serious air pollution in the Southeast Asia, leading to a reduced visibility, adverse health impacts (Harrison et al., 2009; Koplitz et al., 2016), and economic losses (e.g., World Bank, 2016). Furthermore, the large volume of carbon dioxide associated with the strong and continuous haze is a global climate change threat (Page et al., 2002). Additionally, smoke aerosols affect regional climate by reducing the incoming solar radiation at the surface, absorbing radiation in the atmosphere, altering cloud properties, and possibly changing the precipitation patterns.

The transboundary haze phenomenon, associated with the Indonesian peatland fires, is an international issue to be solved. The Association of Southeast Asian Nations (ASEAN) agreement on

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transboundary haze pollution was signed in 2002 by 10 ASEAN member nation governments to mitigate Indonesian peatland fire aerosol impacts, and was finally ratified by the Indonesian parliament in 2014. This agreement can be supported and implemented through an effective strategy and international framework based on the latest scientific knowledge, such as physicochemical speciation of fire aerosols and their human health risks with accurate source apportionments at the source and receptor sites. Chemical speciation of aerosols from Indonesian peatland fires have been conducted at receptor sites in Malaysia (e.g., Fujii et al., 2015b, 2016; Sulong et al., 2017) and Singapore (e.g., Betha et al., 2014; Engling et al., 2014; See et al., 2006; Urbančok et al., 2017). On the contrary, data regarding the chemical characteristics of peatland fire smoke at sources in Kalimantan (Betha et al., 2013; Hayasaka et al., 2014; Jayarathne et al., 2018; Stockwell et al., 2016) and Sumatra (Fujii et al., 2014, 2015a; See et al., 2007) are limited, and little has been reported on the comprehensive chemical characterization of fire smoke for health risk analysis and source speciation among the various BB types.

Sumatra's Riau Province is a primary peatland fire hotspot, and organic carbon from fires there accounted for ~70% of PM<sub>2.5</sub> mass (Fujii et al., 2014). Additionally, the organic compounds were identified quantitatively in PM<sub>2.5</sub> to specify potential source indicators of peatland fires (Fujii et al., 2015a). However, these analyses were performed only for seven samples and the chemical properties of water-soluble inorganic ions and metals for the remaining 30% of PM<sub>2.5</sub> mass have not been specified. Therefore, an integrated analysis with chemical speciation of inorganic components for additional samples is required to improve peatland fire source identification reliability.

Herein, PM<sub>2.5</sub> emitted from Indonesian peatland fires was characterized with a focus on water-soluble ionic components. This was based on ground samplings of PM<sub>2.5</sub> near fire sources in the Riau Province, Sumatra, Indonesia. We highlighted differences in PM<sub>2.5</sub> source profiles among some Indonesian peatland fire sites. Furthermore, we determined the characteristics of the water-soluble ionic components in ambient PM<sub>2.5</sub> away from the fire source during periods of peatland fire-induced haze.

## 2. Materials and methods

Table S1 shows details on samplings on peatland fire sources, which were conducted in the Siak, Kampar, and Payung Sekaki districts of Riau Province as shown in Fig. S1. We also conducted background samplings in Siak district for comparison, and conducted peatland fire-induced haze and non-haze samplings in the city of Pekanbaru (Fig. S1). In this study, background samplings are defined as samplings in the non-peatland fire days around Siak. During our ambient PM<sub>2.5</sub> sampling periods from September 11 to 16 in 2015 in Pekanbaru, haze occurred as shown in Fig. S2, and we regarded these samples as haze samples.

We used a PM<sub>2.5</sub> sampler (ChemComb model 3500 speciation sampling cartridge, Thermo) equipped with two volatile organic compound denuders to reduce the organic gas artifacts to continuously collect PM<sub>2.5</sub> on 47 mmφ polytetrafluoroethylene (PTFE) filters for 3–4 h (peatland fire source) or 12 h (background, haze, and non-haze) at a flow rate of 10 L min<sup>-1</sup>. A 47 mmφ quartz fiber (backup) filter was placed after the PTFE (main) filter for each sampling to confirm gas absorption and/or desorption effects from the PTFE filter. We collected PM<sub>2.5</sub> at several peatland fire sites (~5 m away from peatland fire hotspots) on 13 occasions and at a background site (Siak) on two occasions. Additionally, we collected ambient PM<sub>2.5</sub> samples for haze and non-haze in Pekanbaru on six and three occasions, respectively. After sampling, we determined the concentrations of PM<sub>2.5</sub> mass, water-soluble ions, and some chemical elements in the main (PTFE) filter samples. Some water-soluble ion concentrations related to gas absorption and/or desorption were determined for the backup (quartz fiber) filters. Based on the water-soluble ion results, as shown in Fig. S3, we found that gas absorption and/or desorption effects were low in this

study. The average mass ratios of backup to main filter values for each ionic component at peatland fire source were C<sub>2</sub>O<sub>4</sub><sup>2-</sup> = ~0, Cl<sup>-</sup> = 0.049, NO<sub>3</sub><sup>-</sup> = 0.10, SO<sub>4</sub><sup>2-</sup> = 0.062, and NH<sub>4</sub><sup>+</sup> = 0.045. Thus, we did not perform corrections of water-soluble ions for the main filter samples using backup filter values.

To determine PM<sub>2.5</sub> mass concentrations, we weighed the PTFE filter using a microbalance (ME-5-F, Sartorius) with a sensitivity of ± 1 μg in a stable environment of 20°C–23°C and 30%–40% RH both before and after sampling. We used the PTFE filters to quantify water-soluble ions using ion chromatography (IC) (HIC-10A, Shimadzu and ICS-2000, Dionex). Each filter was extracted by ultrasonic agitation in 4 mL of deionized water for 20 min, and the extract was filtered through a PTFE syringe filter (pore size: 0.45 μm) and analyzed using IC. In this study, we analyzed four anions (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) and five cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>). We analyzed three elements (Cl, S, and K) on the PTFE filters using an energy-dispersive X-ray fluorescence (EDXRF) spectrometer (EDXL300, Rigaku). A detailed description of the quantification procedure, method detection limit, precision, and accuracy can be found in Okuda et al. (2013, 2014).

## 3. Results and discussion

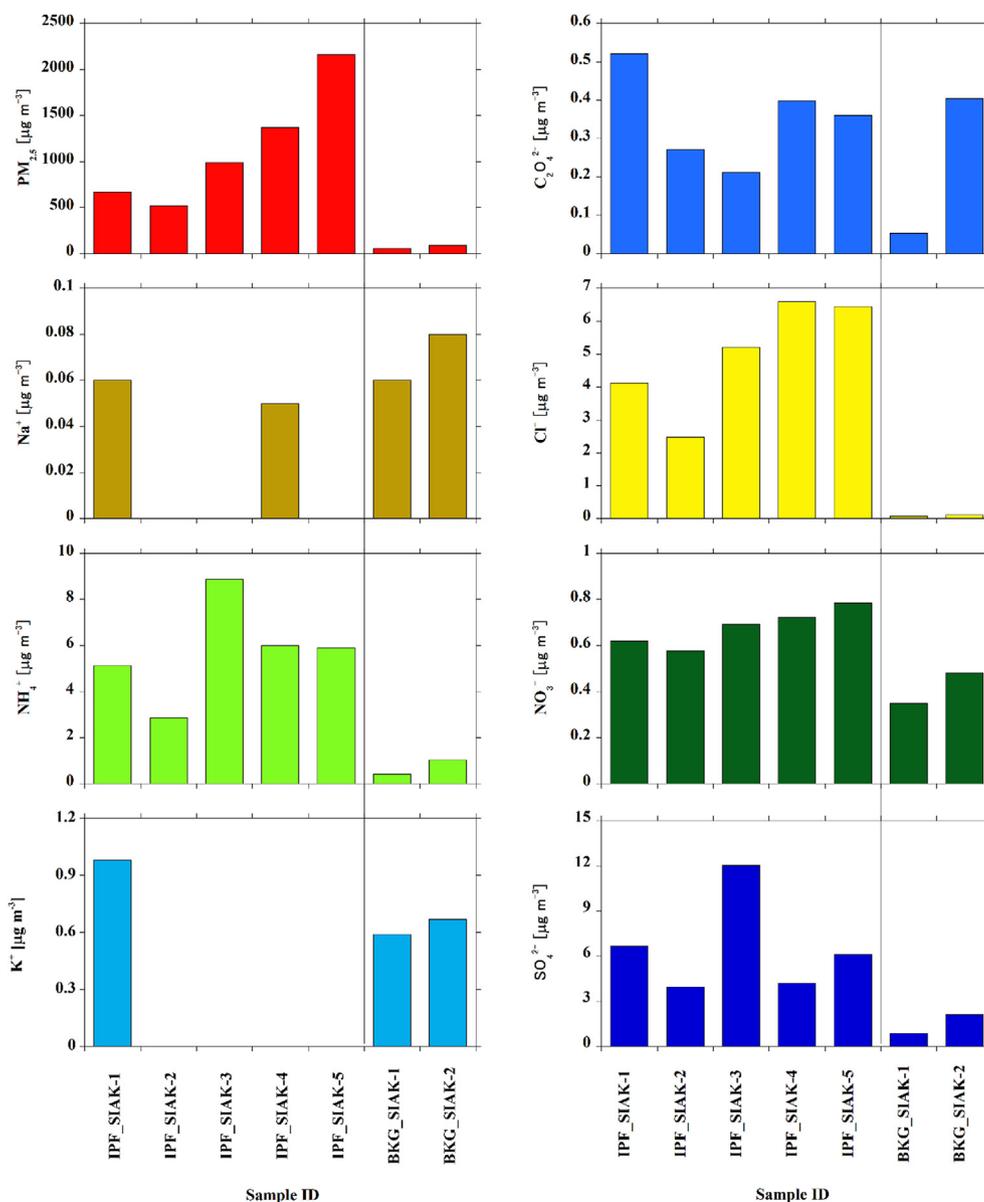
### 3.1. Comparison of the species concentrations quantified by both IC and EDXRF

We compared the concentrations of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and K<sup>+</sup> quantified by IC with those of Cl, S, and K quantified by EDXRF for internal quality assurance of the data (Fig. S4). The Cl<sup>-</sup>/Cl and K<sup>+</sup>/K ratios for all quantified samples were 0.91 ± 0.21 (average ± standard deviation) and 1.07 ± 0.23, respectively, which shows good agreement between the Cl and K concentrations quantified by IC and EDXRF. However, mass concentrations of S determined using IC (SO<sub>4</sub><sup>2-</sup>/3) were clearly lower than those determined by EDXRF. The S concentration ratios between IC and EDXRF for peatland fire source, non-haze, and haze samples were 0.53 ± 0.13, 0.68 ± 0.14, and 0.62 ± 0.084 (unit: μg μg<sup>-1</sup>), respectively. It should be noted that EDXRF determined PM<sub>2.5</sub> total elemental concentration whereas IC determined the water-soluble fraction. The discrepancy between S concentrations determined using IC and EDXRF may be due to the presence of water-insoluble S compounds other than sulfate in PM<sub>2.5</sub> (Yamasoe et al., 2000). In this study, Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations of all samples were below the method detection limit.

### 3.2. Chemical composition of peatland fire and background PM<sub>2.5</sub> in Siak

In this section, we discuss the PM<sub>2.5</sub> chemical characterization of peatland fire sources in Siak compared with that of background PM<sub>2.5</sub> in the same district. The average PM<sub>2.5</sub> concentration near the peatland fire sources was 1100 μg m<sup>-3</sup>, which is much higher than that of the background (70 μg m<sup>-3</sup>), as shown in Table S2. The significant differences in the total concentrations of water-soluble ionic components between peatland fire and background samples are also shown in Table S2. Fig. 1 shows that Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> concentrations at the peatland fire sources are consistently higher than the background, with remarkable differences in Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup>. K<sup>+</sup> has been extensively used as BB indicator (Chuang et al., 2013); however, K<sup>+</sup> concentrations in PM<sub>2.5</sub> between peatland fire and background samples in Siak were comparable. K<sup>+</sup> has a reported boiling temperature of approximately 760 °C (Chuang et al., 2013). Thus, this result is because Indonesian peatland fires are in a smoldering phase with a slow and low-temperature form of burning, as shown in our previous research (Fujii et al., 2015a).

Table 1 and Fig. S5 show the mass fraction of water-soluble ionic components in PM<sub>2.5</sub>. The mass fractions of total water-soluble ions (the sum of quantified water-soluble ions) in PM<sub>2.5</sub> for peatland fire are lower than for the background. The mass fractions for each water-



**Fig. 1.** Concentrations of  $PM_{2.5}$  and water-soluble ionic components at Indonesian peatland fire aerosol (IPF) source and background aerosol (BKG) sources in Siak (SIAK).

**Table 1**

Results of speciation of water-soluble ionic components in  $PM_{2.5}$  for Indonesian peatland fire aerosols (IPF) in the Siak (SIAK), Kampar (KMP), and Payung Sekaki (PS) districts, and background aerosols (BKG) in Siak.

compound	IPF_SIAK		IPF_KMP		IPF_PS		IPF_ALL		BKG_SIAK-1	BKG_SIAK-2
	range	av $\pm$ sd	range	av $\pm$ sd	range	av $\pm$ sd	range	av $\pm$ sd		
$PM_{2.5}$ [ $\mu g m^{-3}$ ]	520–2200	1100 $\pm$ 660	450–1200	820 $\pm$ 310	280–670	380 $\pm$ 190	280–2200	810 $\pm$ 530	54	87
Ions [ $mg g^{-1} PM_{2.5}$ ]										
$C_2O_4^{2-}$	0.17–0.78	0.40 $\pm$ 0.26	0.28–1.2	0.73 $\pm$ 0.38	0.62–1.8	0.93 $\pm$ 0.59	0.17–1.8	0.66 $\pm$ 0.45	0.99	4.6
$Cl^-$	3.0–6.2	4.8 $\pm$ 1.2	5.2–60	29 $\pm$ 23	9.0–12	10 $\pm$ 1.5	3.0–60	14 $\pm$ 16	1.3	1.3
$NO_3^-$	0.36–1.1	0.73 $\pm$ 0.30	0.73–2.3	1.5 $\pm$ 0.72	1.6–3.1	2.1 $\pm$ 0.68	0.36–3.1	1.4 $\pm$ 0.80	6.5	5.5
$SO_4^{2-}$	2.8–12	7.1 $\pm$ 4.2	3.0–6.2	4.5 $\pm$ 1.4	3.8–5.9	4.9 $\pm$ 1.1	2.8–12	5.6 $\pm$ 2.9	16	24
$Na^+$	BL–0.087	–	BL (all)	–	BL (all)	–	BL–0.087	–	1.1	0.90
$NH_4^+$	2.7–9.0	5.9 $\pm$ 2.5	4.5–41	21 $\pm$ 16	9.0–12	10 $\pm$ 1.3	2.7–41	12 $\pm$ 10	7.7	12
$K^+$	BL–1.5	–	BL–2.8	–	BL (all)	–	BL–2.8	–	11	7.70
Total ions	9.1–27	19 $\pm$ 8.2	14–110	58 $\pm$ 38	24–31	28 $\pm$ 3.2	9.1–110	34 $\pm$ 26	45	56

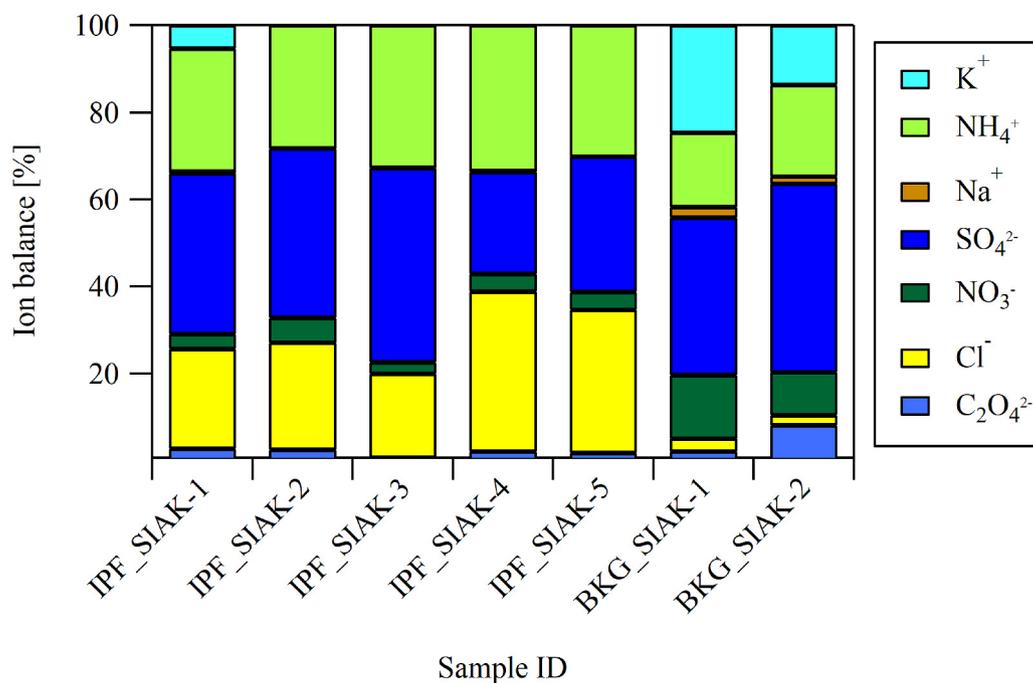


Fig. 2. Percentage of anion and cation contribution to total PM<sub>2.5</sub> ions based on equivalent concentrations at Indonesian peatland fire (IPF) and background (BKG) sources in Siak (SIK).

soluble ionic component (C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, and K<sup>+</sup>) at peatland fire sources are also lower than for the background. On the contrary, only the Cl<sup>-</sup> mass fraction is remarkably higher for peatland fire than for the background.

Fig. 2 shows the anion and cation contribution percentage in the total ions in PM<sub>2.5</sub> (equivalent concentration base) for peatland fire and background aerosols. The average equivalent ratios of total anions to cations for peatland fire and background aerosols are 1.1 (standard deviation = 0.10) and 1.4, respectively. Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are the dominant peatland fire species, accounting for 47% and 46% of total anions on average, respectively. NH<sub>4</sub><sup>+</sup> is the dominant cation, accounting for an average of 98% of total cations. SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> are the dominant background aerosol anion species (SO<sub>4</sub><sup>2-</sup>: 68% and NO<sub>3</sub><sup>-</sup>: 17%) and NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> are the dominant cations (NH<sub>4</sub><sup>+</sup>: 65% and K<sup>+</sup>: 30%). These results suggest that the dominant ionic compounds in PM<sub>2.5</sub> for peatland fire aerosols are NH<sub>4</sub>Cl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (the equivalent ratio of NH<sub>4</sub><sup>+</sup> to the sum of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> = 1.1 ± 0.090). For the background aerosols, it is considered that one of dominant ionic compounds in PM<sub>2.5</sub> is (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

### 3.3. Differences in ionic compositions of PM<sub>2.5</sub> at several peatland fire sources

To determine the differences in PM<sub>2.5</sub> source profiles of Indonesian peatland fire focusing on water-soluble ionic components among fire sites, we conducted PM<sub>2.5</sub> samplings at three peatland fire locations (Siak, Kampar, and Payung Sekaki). The total mass fractions of the quantified water-soluble ionic components in PM<sub>2.5</sub> in Siak, Kampar, and Payung Sekaki were 1.9 ± 0.82%, 5.8 ± 3.8%, and 2.8 ± 0.32%, respectively (Table 1), which showed higher fractions in Kampar than in other sites (Fig. S6). Interestingly, the mass fraction of SO<sub>4</sub><sup>2-</sup> in total ions appears to decrease as the mass fraction of total ions in PM<sub>2.5</sub> for peatland fire increases (Pearson correlation coefficient  $r = -0.67$ ,  $p$  value < 0.05), whereas the Cl<sup>-</sup> mass fraction increases ( $r = 0.72$ ,  $p < 0.05$ ) as shown in Fig. 3. Differences in biomass or combustion temperature in those fires may contribute to the opposite trends for SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>.

See et al. (2007) reported that the average total mass fraction of

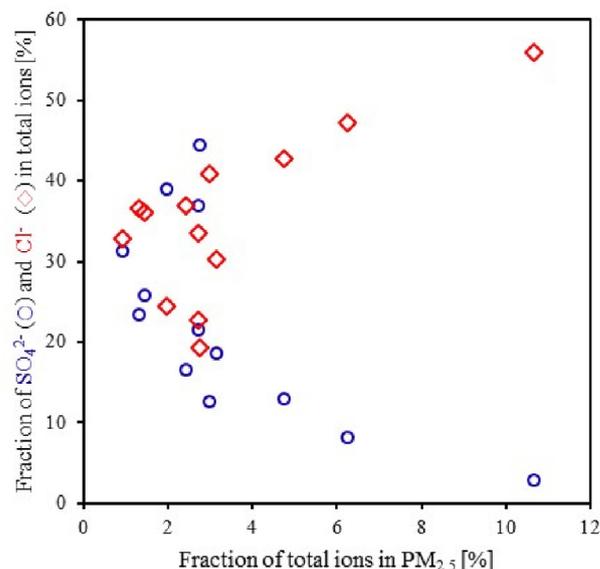


Fig. 3. Plot of total PM<sub>2.5</sub> ion fraction vs. SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> fraction in total ions for peatland fire samples.

quantified water-soluble ionic components in PM<sub>2.5</sub> collected in Riau, Sumatra Island in 2005 was 10%. Jayarathne et al. (2018) reported that it was 1.1% in Kalimantan Island in 2015. Our data fall within the range determined by these studies.

Fig. 4 shows PM<sub>2.5</sub> source profiles for typical water-soluble ionic components (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>) in different peatland fire sites. Table 1 shows the detailed information on the other water-soluble ionic components in this study. The average mass fractions of three typical PM<sub>2.5</sub> ionic components for peatland fire aerosols in Siak and Kampar from this study decrease in the order of SO<sub>4</sub><sup>2-</sup> > NH<sub>4</sub><sup>+</sup> > Cl<sup>-</sup> and Cl<sup>-</sup> > NH<sub>4</sub><sup>+</sup> > SO<sub>4</sub><sup>2-</sup>, respectively. The average mass fractions in both Payung Sekaki (this study) and Kalimantan (Jayarathne et al., 2018) decrease in the order of NH<sub>4</sub><sup>+</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup>, which shows the

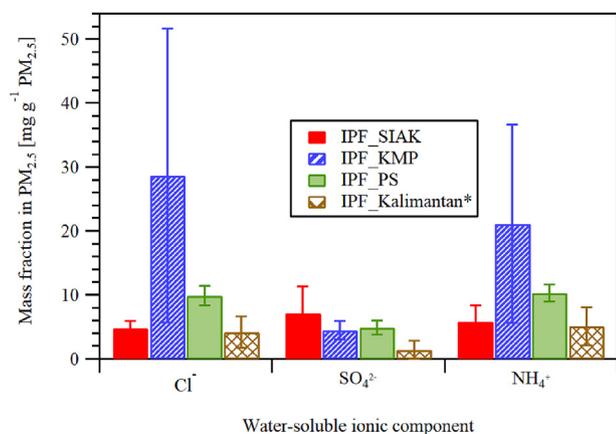


Fig. 4. Comparison of PM<sub>2.5</sub> source profiles for typical water-soluble ionic components at different Indonesian peatland fire (IPF) locations (SIAK = Siak, KMP = Kampar, and PS = Payung Sekaki). \*Data for Kalimantan was obtained from Jayarathne et al. (2018).

differences among peatland fire spots. This may be due to the type of biomass burned or combustion temperature as previously mentioned. Thus, our results show that PM<sub>2.5</sub> source profile of water-soluble ionic components for peatland fire must be selected with extreme caution if applied to a receptor model, such as chemical mass balance or source-oriented chemical transport model as an emission inventory.

Regarding the ion composition results for each peatland fire sample (Fig. 5), Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> are consistently dominant anions (Cl<sup>-</sup>: 62% on average) and cations (NH<sub>4</sub><sup>+</sup>: 98% on average), respectively, for all peatland fire samples. For some data especially in Siak, SO<sub>4</sub><sup>2-</sup> is also a dominant anion; however, these trends are not consistent with other results, especially those from Kampar. Our results show that Indonesian peatland fire aerosols are characterized by a consistently dominant composition of NH<sub>4</sub>Cl in PM<sub>2.5</sub> at the source in terms of water-soluble ionic components; however, in some cases, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> appears to be dominant.

### 3.4. Effects of peatland fires on ambient PM<sub>2.5</sub>

To clarify the effects of peatland fires on ambient PM<sub>2.5</sub> water-soluble ionic components, we conducted ambient PM<sub>2.5</sub> samplings in Pekanbaru during peatland fire-induced haze periods. For comparison, we conducted three PM<sub>2.5</sub> samplings during non-haze periods in Pekanbaru.

Fig. 6 shows variations in the concentrations of PM<sub>2.5</sub> mass and water-soluble ionic components. PM<sub>2.5</sub> concentrations during haze

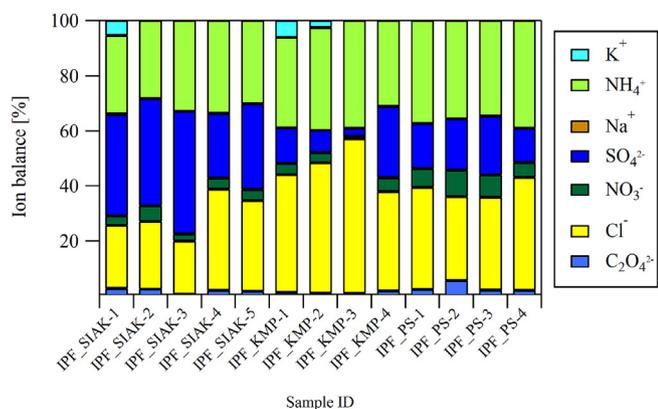


Fig. 5. PM<sub>2.5</sub> anion and cation weight percentage distributions based on equivalent concentrations at Indonesian peatland fire (IPF) sources in Siak (SIAK), Kampar (KMP), and PS (Payung Sekaki).

periods ( $270 \pm 61 \mu\text{g m}^{-3}$ ) were significantly higher than that during non-haze periods ( $43 \pm 36 \mu\text{g m}^{-3}$ ). Significant differences in the total concentrations of water-soluble ionic components are also observed between haze ( $33 \pm 6.5 \mu\text{g m}^{-3}$ ) and non-haze ( $5.5 \pm 2.6 \mu\text{g m}^{-3}$ ) samples. In particular, average concentrations of C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup> during the haze periods were 4.2, 4.5, 7.3, and 7.8 times higher than those during the non-haze periods. C<sub>2</sub>O<sub>4</sub><sup>2-</sup> is widely recognized as a tracer of secondary aerosols (Golly et al., 2019) as well as NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Additionally, C<sub>2</sub>O<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> concentrations for peatland fire aerosols in Siak are comparable to those for the background, as shown in Fig. 1. Thus, the increased total concentrations of water-soluble ionic components during haze periods may have been induced by peatland fires with secondary aerosol formation processes.

In the previous section, we demonstrated that peatland fire sources emit high concentrations of Cl<sup>-</sup> (Table S2). However, differences in Cl<sup>-</sup> concentrations between haze and non-haze samples in Pekanbaru are smaller than those of C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>. Therefore, haze samples have obviously different water-soluble ionic compositions than those of peatland fire samples, and patterns of ion balance of haze samples are similar to those of background aerosols, as shown in Fig. 7, i.e., abundant NH<sub>4</sub>Cl, which is characteristic of PM<sub>2.5</sub> at peatland fire sources, is obviously low during haze periods. This could be because NH<sub>4</sub>Cl is thermodynamically unstable as well as NH<sub>4</sub>NO<sub>3</sub> and formed through reversible phase equilibrium with precursor gases, such as NH<sub>3</sub> and HCl under normal ambient conditions (Behera et al., 2013; Pio and Harrison, 1987; Tang et al., 2016). Thus, our results show that peatland fires trigger haze conditions under high gaseous concentrations of NH<sub>3</sub>, as described in Whitburn et al. (2016), and HCl in ambient air around a peatland fire source.

## 4. Conclusion

We conducted a field study to characterize water-soluble ionic species in PM<sub>2.5</sub> emitted from peatland fires using ground-based samplings at fire sources and receptor sites in the Riau Province, Sumatra, Indonesia. We determined the concentrations of PM<sub>2.5</sub> mass, water-soluble ions, and some chemical elements. The main conclusions are as follows:

- PM<sub>2.5</sub> at peatland fire sources are characterized by a consistently dominant NH<sub>4</sub>Cl composition in terms of water-soluble ionic components. However, the mass fractions of typical water-soluble ionic components, as well as those of total quantified water-soluble ionic components, for peatland fires (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>) in PM<sub>2.5</sub> tend to differ between peatland fire sources. Thus, our results indicate that PM<sub>2.5</sub> source profiles of water-soluble ionic components for peatland fire must be selected with extreme caution if applied to a receptor model, such as chemical mass balance or source-oriented chemical transport model as an emission inventory.
- During the peatland fire-induced haze periods, four water-soluble ionic components, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>, were highly elevated. Since these four ions are widely recognized as the major secondarily formed aerosol components, the increased total concentrations of water-soluble ionic components during haze periods can mainly be derived from the gas-to-aerosol conversion process. On the contrary, an abundance of NH<sub>4</sub>Cl, which is characteristic of peatland fire PM<sub>2.5</sub> sources, is obviously low at receptor sites during haze periods. This could be because NH<sub>4</sub>Cl is thermodynamically unstable.
- Further studies based on the chemical characterization of fresh and aged peatland fire aerosols are needed to fully understand the transformation process via long-range transportation. Controlling factors to determine peatland fire PM<sub>2.5</sub> chemical compositions should be clarified (e.g., using controlled-laboratory burning experiments) to obtain a reliable source profile and accurate emission

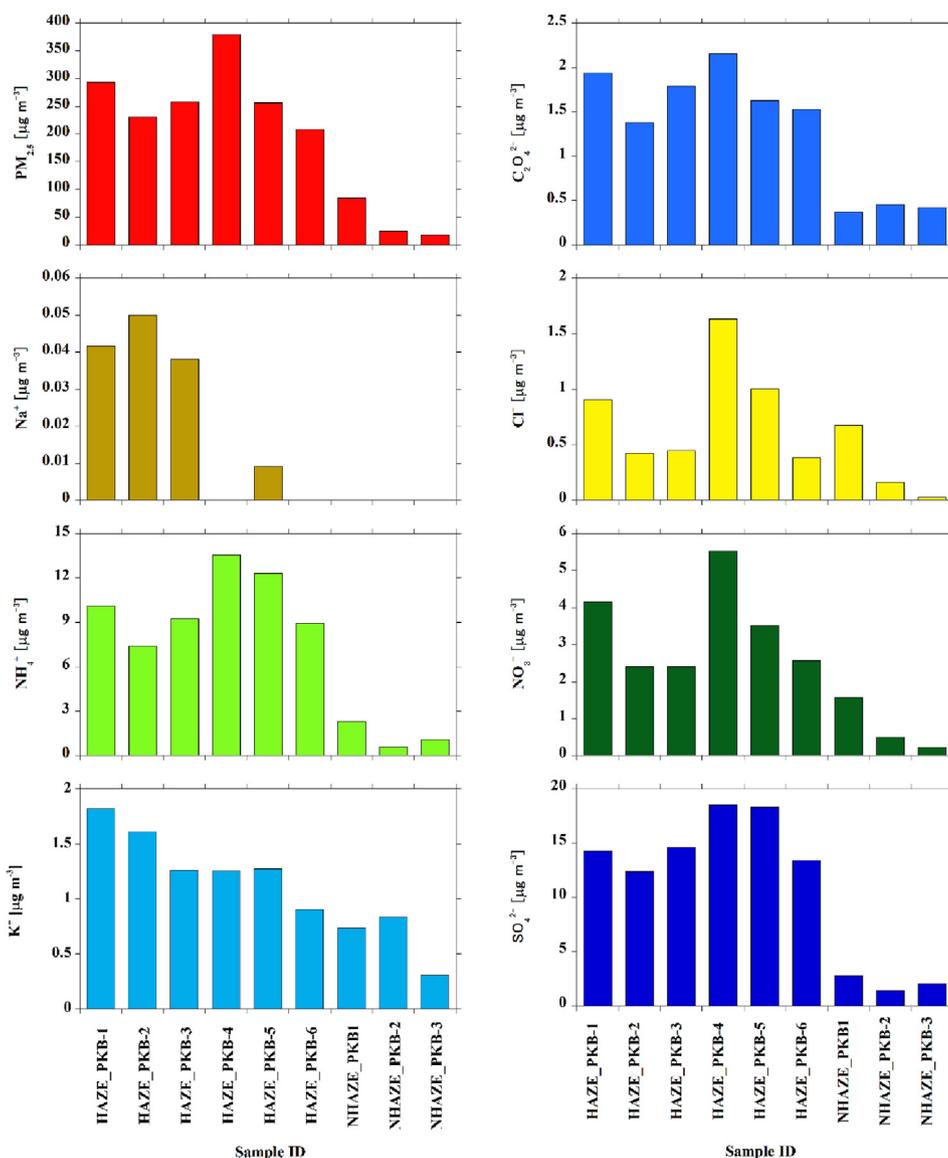


Fig. 6. Variabilities of  $PM_{2.5}$  and water-soluble ion concentrations during Indonesian peatland fire (IPF)-induced haze (HAZE) and non-haze (NHAZE) periods.

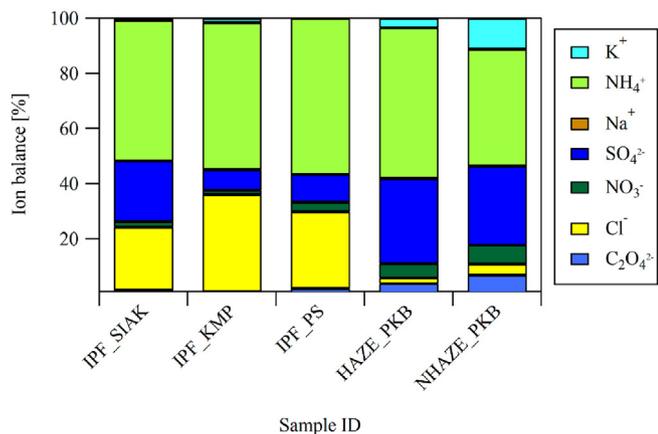


Fig. 7.  $PM_{2.5}$  anion and cation weight percentage distributions based on average equivalent concentrations for Indonesian peatland fire (IPF) source, haze (HAZE), and non-haze (NHAZE) samples. IPF source samples were collected in Siak (SIAK), Kampar (KMP), and Payung Sekaki (PS). Haze and non-haze samples were collected in Pekanbaru (PKB).

inventory.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apr.2019.02.009>.

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