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# Particuology

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## Composition of carbohydrates, surfactants, major elements and anions in PM<sub>2.5</sub> during the 2013 Southeast Asia high pollution episode in Malaysia

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### ARTICLE INFO

#### Article history:

Received 16 April 2016

Received in revised form 17 April 2017

Accepted 22 April 2017

Available online xxx

#### Keywords:

Aerosol

Biomass burning

Levoglucosan

Surfactant

Haze

Inorganic composition

### ABSTRACT

Haze episodes have become a major concern in Malaysia over the past few decades and have an increasingly important impact on the country each and every year. During haze episodes from biomass burning in Southeast Asia, particularly from Sumatra, Indonesia, particulate matter PM<sub>2.5</sub> is found to be one of the dangerous sources of airborne pollution and is known to seriously affect human health. This study determines the composition of carbohydrates (as levoglucosan), surfactants, major elements, and anions in PM<sub>2.5</sub> during a 2013 haze episode. PM<sub>2.5</sub> samples were collected from Universiti Kebangsaan Malaysia, Bangi, using a high volume sampler during a seven-day monitoring campaign during the peak of that year's haze episode. PM<sub>2.5</sub> concentrations ranged between 14.52 and 160.93 µg/m<sup>3</sup>, exceeding the 2005 WHO air quality guidelines for PM<sub>2.5</sub> (25 µg/m<sup>3</sup> for 24-h mean). The patterns for levoglucosan, surfactants, major elements, and anionic compositions were proportional to the PM<sub>2.5</sub> concentrations. Changes in PM<sub>2.5</sub> observed on days 3 and 4 were influenced by a combination of meteorological factors, which substantiate the theory that such factors play a pivotal role in haze episodes.

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### Introduction

Haze episodes caused by biomass burning have become a serious issue in Malaysia over the past three decades. Anthropogenic sources, such as biomass burning and agricultural land clearing, have been determined as the main sources of these episodes (Abas, Oros, & Simoneit, 2004a, 2004b; Engling, He, Betha, & Balasubramanian, 2014; Norela, Saidah, & Mahmud, 2013). The episodes mainly occur when there is a high aerosol content in the atmosphere together with the formation of secondary aerosols that are affected by meteorological conditions (Geng, Ryu, Maskey, Jung, & Ro, 2011; Husain, Ghauri, Yang, Khan, & Rattigan, 2004;

Sun, Zhuang, Tang, Wang, & An, 2006; Watson, 2002). Episodes of regional haze are problematic, because they extend across political borders. Thus, a forest fire and severe drought episode in Southeast Asia, as reported by Sun, Hong, and Wold (2010) and Mott et al. (2005), could cause problems with air pollution not only in Malaysia but also in Singapore, Brunei, the Philippines, and Thailand.

Malaysia is a tropical country which experiences uniform temperature and high humidity. However, wind flow patterns change according to various monsoons, i.e., the northeast and southwest monsoons (Malaysian Meteorological Department, 2008). Meteorological factors, such as temperature, relative humidity, rainfall, and wind direction have all been found to influence haze episodes. Haze events in Malaysia and other Southeast Asian countries usually occur during the southwest monsoon (June to September) because of the dry season (Amil, Latif, Khan, & Mohamad, 2016; Ee-Ling, Mustaffa, Amil, Khan, & Latif, 2015; Khan et al., 2016). According to Hyer and Chew (2010), during dry seasons, fires can

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**Fig. 1.** Sampling location for PM<sub>2.5</sub>.

be accidentally or intentionally started in forests and other vegetation areas, specifically in Sumatra and Kalimantan, which are two provinces in the neighboring country of Indonesia. In 1997, haze in Malaysia resulted from forest vegetation being cleared in Indonesia and consequent biomass burning products being transported over Malaysia by a southwesterly wind flow (Abas et al., 2004a, 2004b).

Biomass burning has been identified as a major source of fine suspended particulate matter (PM<sub>2.5</sub>) (Aouizerats, Van Der Werf, Balasubramanian, & Betha, 2015; Blake, Hinwood, & Horwitz, 2009; Goldammer, Statheropoulos, & Andreae, 2008; Xu, Tai, Betha, He, & Balasubramanian, 2014). PM<sub>2.5</sub> can be suspended in the atmosphere for a period of several days and spread several thousand kilometers away from its source (Akagi et al., 2012; Behera et al., 2015; Warneke et al., 2009). Dispersion of PM<sub>2.5</sub> from biomass emissions is the dominant cause of haze episodes, which may reduce visibility and absorb radiation (Abas et al., 2004a, 2004b; Heil, Langmann, & Aldrian, 2007; McMeeking et al., 2006). Furthermore, among the major effects of haze are public health issues involving the respiratory system, namely, infections, asthma, and conjunctivitis (Akagi et al., 2012; Awang et al., 2000; Du et al., 2011; Heil et al., 2007; Rappold et al., 2011; Sahani et al., 2014). It has been reported that during haze episodes, residents in communities exposed to haze have experienced a substantial increase in short-term cardiorespiratory hospitalizations (Mott et al., 2005).

The composition of PM<sub>2.5</sub> during haze episode can indicate sources and impacts of that matter on both the environment and human health. Using compositions of PM<sub>2.5</sub>, the full range of its potential sources can be identified. The toxicity of each element exposed to populations can be also used to assess human health (Amil et al., 2016; Khan et al., 2016). Levoglucosan is a specific and general indicator of biomass emissions in fine particulate matter samples (Latif et al., 2012; Simoneit et al., 1999). A study by Hoffmann, Tilgner, Iinuma, and Herrmann (2010), showed that the degradation of levoglucosan, especially in humid environments and acidic conditions, make it an effective source marker for biomass burning activities, owing to its high abundance in smoke-impacted aerosol. Being stable in the atmosphere, with no decay over 8 h exposure to sunlight (Latif et al., 2012; Puxbaum et al., 2007), levoglucosan makes a suitable molecular marker of biomass burning. Furthermore, studies of surface active agents (surfactants), an organic pollutant, have found very high concentrations during haze episodes. This may influence the solubility of materials in the atmo-

sphere (Brimblecombe & Latif, 2004; Hanif et al., 2009; Wahid, Latif, & Suratman, 2013) and, at high concentrations, surfactants may also affect the human respiratory system (Zimmer, Baron, & Biswas, 2002). Surfactants in the atmosphere can generate more cloud water because of the reduction of surface tension in a droplet. They can behave like cloud condensation nuclei, which may influence the climate system (Ellison, Tuck, & Vaida, 1999; Latif, Anuwar, Srithawirat, Razak, & Ramli, 2011; Tabazadeh, 2005). Major elements and anions in ambient air are important indicators of various sources of particulate matter during haze episodes. According to Sunder Raman, Hopke, and Holsen (2008), particulate matter usually consists of several elements (Si, Al, Ca, Fe, Ti, V, Cr, Ni, Cu, Zn, Pb) and inorganic ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>), which may originate from a variety of sources related to anthropogenic activities.

Given the above issues, this paper presents the compositions of levoglucosan and surfactants in PM<sub>2.5</sub> during their peak in haze episodes in 2013. It was determined that PM<sub>2.5</sub> should be monitored because it is believed to pose one of the greatest health risks, because it lodges directly in into the lungs. Our study also addressed selected major elements (Ca, Mg, K, and Na), anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and PO<sub>4</sub><sup>3-</sup>), and the influence of meteorological factors on the composition of PM<sub>2.5</sub>. Because studies of PM<sub>2.5</sub> compositions during haze episodes in Southeast Asia are very limited, this research should be useful for the scientific record and may increase public awareness of haze, especially on its effect on human health and atmospheric visibility, particularly in tropical countries.

## Materials and methods

### Sampling location

Bangi is a suburban area about 23 km south of the city center of Malaysia's capital, Kuala Lumpur. Since the 1970s, it has grown to become a suburban area, including both residential and industrial areas. In the present study, the sampling station was atop the Biology Building at the Universiti Kebangsaan Malaysia, Bangi Campus (2°55.47'N, 101°46.39'E). This four-story building is about 20 m above ground level and was constructed in 1977. It is near to the campus's main road. Fig. 1 shows the exact sampling location.

### Sampling procedures

$\text{PM}_{2.5}$  samples were collected using a high volume sampler (HVS,  $\text{PM}_{2.5}$ , Thermo Fisher, USA) equipped with quartz filter paper (QMA, 0.2- $\mu\text{m}$  pore size, Whatman, USA). Before sampling, the filter paper was pre-heated in a muffle furnace (Carbolite, England, UK) at a temperature of 500 °C for 3 h to remove any organics. The sampling was conducted for 24 h at a flow rate of 1.13  $\text{m}^3/\text{min}$  over seven days (21–27 June 2013). These days were reported to have hazy conditions by the Malaysian Department of Environment (DOE, 2013) and Rahman (2013). Before and after sampling, the filter papers were stored for at least 24 h in a desiccator and weighed on a 5-digit electronic microbalance (Shimadzu AUX220, Japan).

### Sample extraction

One-eighth of the filter paper of a  $\text{PM}_{2.5}$  sample was cut into squares (1 cm × 1 cm) and placed in a 400-mL glass vial with 30 mL of deionized water. Next, the samples were ultra-sonicated (S70H, Elmasonic, Germany) for 45 min at an average temperature of 40 °C and then filtered using cellulose acetate filter paper (Whatman, Germany, 47-mm diameter, 0.2- $\mu\text{m}$  pore size) with the filtration apparatus linked to a vacuum pump (Millipore, USA). The filtered solution was brought to a volume of 250 mL with deionized water in a volumetric flask and transferred to a polyethylene bottle. Prior to analysis, the samples were kept at 4 °C in a refrigerator.

### Determination of levoglucosan

The anthrone method used by Laurentin and Edwards (2003), Morris (1948), Scaramboni et al. (2015), and Srithawirat and Brimblecombe (2015) was used for determination of sugar-based carbohydrates. This method determined the total concentration of carbohydrates in the samples by assuming that levoglucosan was the dominant carbohydrate species in atmospheric aerosol, particularly in relation to biomass burning emissions (Fartas, Othman, Rajeb, & Latif, 2009; Othman & Latif, 2013). The reaction from carbohydrate mixing with anthrone reagents in acidic conditions produced different color intensities, depending on the quantity of the glucose-based carbohydrate in the sample. Samples were combined with sulfuric acid and anthrone reagent and then boiled until the reaction occurred.

The anthrone reagent for levoglucosan analysis was prepared by dissolving 0.2 g of powdered anthrone (9,10-dihydro-9-oxoanthracene) in 100 mL of 97% sulfuric acid. This solution was left to stand for 45 min until all the powder fully dissolved. The solution was prepared in advance of levoglucosan analysis and used within 12 h (Laurentin & Edwards, 2003). 10 mL of the anthrone reagent was pipetted into a Pyrex tube (150 × 25 mm, 55 mL), which contained 5 mL of the levoglucosan standard solution (0.1–1 mM) prepared from levoglucosan standard powder (Sigma-Aldrich, USA). Mixing was done in cold water. Afterward, the solution was transferred into a water bath at temperature 100 °C for 10 min, to produce a green dye infusion. Then, the solution was put into bowl of ice for 5 min to reduce the temperature immediately to 4 °C. After that, the solution was soaked for 5 min at a temperature of 20 °C to prevent condensation of the apparatus. Samples were then analyzed similar to standard solutions, using a UV spectrophotometer (Labomed Inc., USA) with wavelength 620 nm against deionized water, with a detection limit of 0.079  $\mu\text{g}/\text{m}^3$ .

### Determination of surfactants

Surfactants were determined by the colorimetric method based on the formation of a chloroform-extractable ion-association com-

plex, as done by Chitikela, Dentel, and Allen (1995), Hanif et al. (2009), Jaafar et al. (2014), Latif and Brimblecombe (2004), Razak, Latif, Jaafar, Khan, and Mushrifah (2014), and Wahid et al. (2013). Anionic surfactants as methylene blue active substances (MBAS) comprised two stages of extraction. A 20-mL sample was put into a 40-mL vial equipped with a Teflon liner and screw cap. 2 mL of alkaline buffer and 1 mL of methylene blue, followed by 5 mL of chloroform, were added to the vial contents. The vial was then tightly closed before being shaken for 2 min using a vortex mixer. Afterward, it was left for several minutes to allow the separation phase to occur. The chloroform layer produced was then transferred using a Pasteur pipette to a new vial that contained 22 mL of deionized water and 1 mL of acid methylene blue. This vial was shaken for ~2 min using a vortex mixer. Then, the chloroform layer was transferred and put into a quartz cell using a Pasteur pipette. Absorbance of the chloroform phase was measured using an UV–Vis spectrophotometer (Labomed Inc., USA) at a wavelength of 650 nm. Sodium dodecyl sulphate (SDS) (0.5–2  $\mu\text{M}$ ) was used as a standard solution for anionic surfactants analysis. The limit of detection in this analysis was estimated as 0.001  $\mu\text{g}/\text{m}^3$  and the average recovery for MBAS analysis was 88%.

Cationic surfactants as disulphine blue active substances (DBAS) were also determined, using the colorimetric method. 20 mL of the sample was put into a 40-mL vial equipped with a Teflon liner and screw cap. 2 mL of the acetate buffer and 1 mL of the disulphine blue solution were put into the vial. 5 mL of chloroform was added and the solution was shaken using a vortex mixer. After 2 min, the vial was left to allow separation. A Pasteur pipette was then used to transfer the chloroform layer from the vial to a quartz cell. Absorbance was measured at a wavelength of 628 nm. Zephiramine (benzyl dimethyl tetradecyl ammonium chloride dehydrate) (0.5–1.5  $\mu\text{M}$ ) was used as the standard solution for cationic surfactants analysis. The limit of detection for this analysis was estimated as 0.001  $\mu\text{g}/\text{m}^3$  and the average recovery for MBAS analysis was 85%.

### Determination of water soluble major element and ionic composition

The major elements (Ca, Mg, K, and Na) were determined using inductively coupled plasma-mass spectrometry (Perkin Elmer ELAN 9000, USA). The limits of detection for Ca, Mg, K, and Na were 0.07, 0.1, 0.07, and 0.1 ng/ $\text{m}^3$ , respectively. Anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ ) were determined using ion chromatography (850 model 881 Compact IC Pro, Metrohm, USA). The type of eluent used was 3.2 mmol/L  $\text{Na}_2\text{CO}_3$  with flow rate 0.7 mL/min. The limits of detection for  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  were 0.005, 0.005, 0.006, 0.001, and 0.004  $\mu\text{g}/\text{m}^3$ , respectively. The individual standard solution (Merck, Germany) was used in the calibration procedure. Average recoveries for all water-soluble ionic elements were determined to be within 87–96%.

### Meteorological data and statistical analyses

The meteorological data used were recorded by the Malaysian Meteorological Department. These data (temperature, relative humidity, rainfall, wind speed, and wind direction) were from a station near the  $\text{PM}_{2.5}$  sampling station, i.e., the Serdang Agricultural Centre (3°0'N, 101°42'E). Several analyses were carried out to statistically interpret the data. Analysis of variance (ANOVA) was conducted on all the data collected and Pearson correlation was used to determine their relationships. The data were also analyzed using SPSS version 18.0 (student version of the Statistical Package for Social Sciences) and XLSTAT 2013 software. To simulate pollutant transport in the atmosphere, analysis of a 120-h backward trajectory (BT) for wind direction was developed using

**Table 1**

Concentrations of PM<sub>2.5</sub>, levoglucosan, anionic surfactants (MBAS) and cationic surfactants (DBAS) during haze episode.

	Haze episode	PM <sub>2.5</sub> ( $\mu\text{g}/\text{m}^3$ )	<sup>a</sup> Levoglucosan ( $\mu\text{g}/\text{m}^3$ )	<sup>b</sup> MBAS (ng/m <sup>3</sup> )	<sup>c</sup> DBAS (ng/m <sup>3</sup> )
Day 1	21 June 13	47.8	0.75	74.9	27.6
Day 2	22 June 13	67.5	0.92	178.3	33.1
Day 3	23 June 13	146.2	1.05	237.8	66.2
Day 4	24 June 13	160.9	1.09	273.0	56.6
Day 5	25 June 13	80.7	0.89	160.7	41.4
Day 6	26 June 13	37.9	0.49	96.9	38.6
Day 7	27 June 13	14.5	0.65	66.0	26.2

<sup>a</sup> Concentration of levoglucosan is based on total carbohydrate measurement.

<sup>b</sup> MBAS is anionic surfactants as methylene blue active substances.

<sup>c</sup> DBAS is cationic surfactants as disulphine blue active substances.

the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4.9) model. Biomass fire hotspot data were coupled with BT to represent: (i) pre-haze, (ii) haze, and (iii) post-haze events. Periods associated with those three events were 12–19 June, 20–28 June, and 29 June–6 July 2013, respectively.

#### Quality control

All instruments involved in the study were calibrated before use, and powderless gloves were used to handle filter papers during all the experiments. To avoid contamination, every item of glassware used was washed with deionized water and soaked in 20% nitric acid overnight. The glassware was then rinsed with deionized water and allowed to dry before further use. Field blanks (filter papers placed on the HVS for 24 h without the instrument being turned on) were analyzed in the same manner as the samples. All data presented were corrected based on the blank concentration and the recoveries.

#### Results and discussion

##### PM<sub>2.5</sub> and levoglucosan during haze episode

Results for PM<sub>2.5</sub> in ambient air during haze episodes are shown in Table 1. The concentrations of PM<sub>2.5</sub>, 14.5–160.9  $\mu\text{g}/\text{m}^3$ , were considered extremely high, particularly on days 3 (146.2  $\mu\text{g}/\text{m}^3$ ) and 4 (160.9  $\mu\text{g}/\text{m}^3$ ) of the sampling period. These levels far exceed the US Environmental Protection Agency (USEPA) air quality standard guidelines for PM<sub>2.5</sub> (35  $\mu\text{g}/\text{m}^3$  for 24-h mean) and the WHO air quality guideline (PM<sub>2.5</sub> 25  $\mu\text{g}/\text{m}^3$  for 24-h mean). According to USEPA (2010), exposure to fine particle pollution can have harmful cardiovascular effects such as heart attacks and strokes, and lead to premature death. It is also linked to other serious health problems.

To determine the occurrence of biomass burning (Schkolnik & Rudich, 2006), we performed levoglucosan analysis, because levoglucosan is present in all wood smoke in the atmosphere and is therefore useful as a parameter for tracing both forest (Simoneit et al., 1999) and peat soil (Othman & Latif, 2013) burning. Table 1 presents levoglucosan concentrations in the PM<sub>2.5</sub> samples. The highest concentration was on day 4 (1.09  $\mu\text{g}/\text{m}^3$ ) and the lowest on day 6 (0.49  $\mu\text{g}/\text{m}^3$ ). This high level of levoglucosan was most likely attributable to the presence of highly cellulose materials in peat soil, which is related to pyrolysis reaction during biomass combustion (Othman & Latif, 2013). The presence of levoglucosan in our samples strongly suggests that PM<sub>2.5</sub> is affected by the smoke generated by biomass burning (Simoneit et al., 1999). The distribution and ratio of levoglucosan in the smoke were influenced by aeration, heat intensity and the duration of smoldering and flaming conditions (Abas et al., 2004a, 2004b). Moreover, according to Hoffmann et al. (2010) and Latif et al. (2011), the initial concentration of levoglucosan can decrease as it tends to spread and be diluted upon exposure to hydroxide ions. Given high concentra-

**Table 2**  
Major element and anionic compositions in PM<sub>2.5</sub> during haze episode ( $\mu\text{g}/\text{m}^3$ ).

	Ca	Mg	K	Na	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>
Day 1	0.13	0.63	0.78	0.41	0.002	0.14	0.83	1.80	0.08
Day 2	0.15	0.65	0.73	0.33	0.01	0.31	0.85	1.61	1.23
Day 3	0.13	0.55	0.74	0.26	0.03	0.15	1.26	3.84	0.22
Day 4	0.11	0.57	0.89	0.34	0.03	0.16	1.63	5.79	0.29
Day 5	0.10	0.41	0.42	0.19	ND	0.16	1.63	4.86	0.19
Day 6	ND	0.31	0.32	0.23	ND	0.04	0.68	2.60	0.30
Day 7	ND	0.26	0.37	0.14	0.01	0.01	0.02	1.24	0.24

ND: not detected.

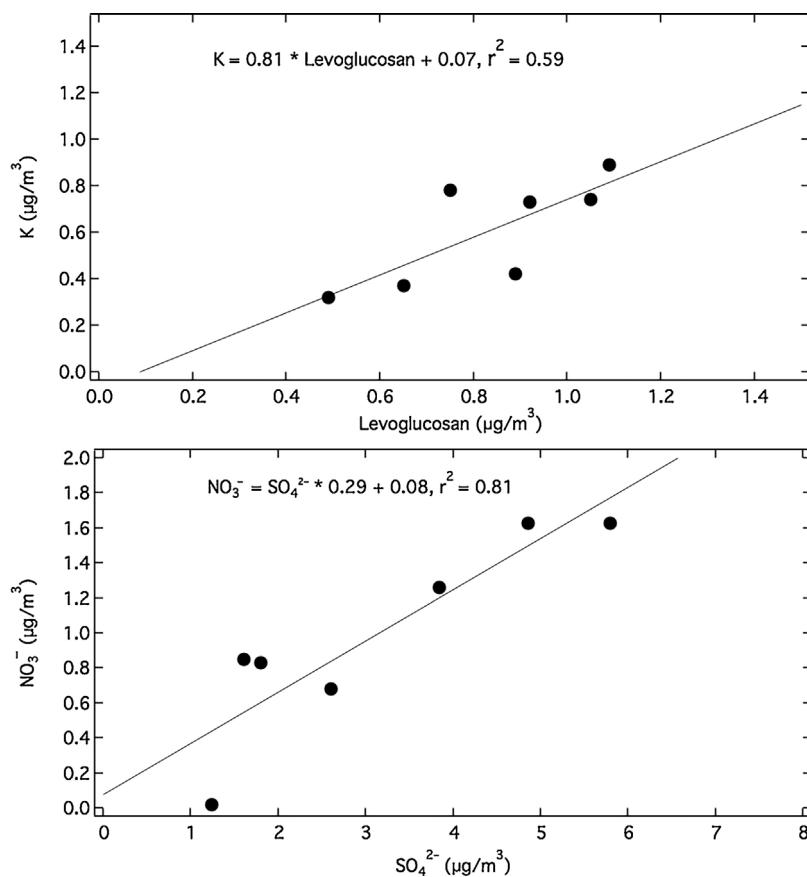
tions of levoglucosan, Abas et al. (2004a, 2004b) showed that the 1991 haze episode was contributed by biomass burning, supported by Abas and Simoneit (1996).

##### Surfactants in PM<sub>2.5</sub>

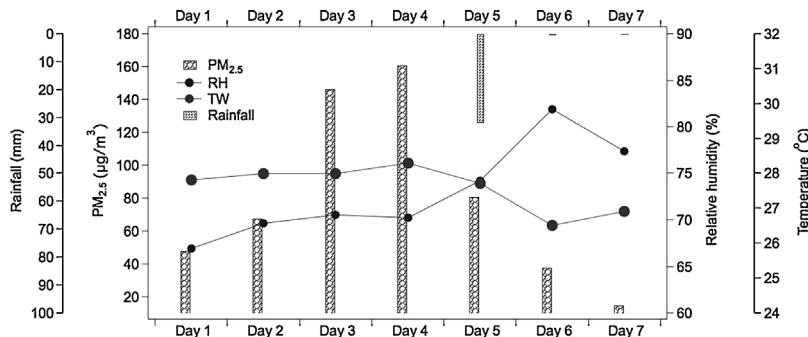
Anionic surfactants as MBAS and cationic surfactants as DBAS in PM<sub>2.5</sub> samples during the 2013 haze episode are shown in Table 1. The concentrations of surfactants in the PM<sub>2.5</sub> samples were dominated by MBAS as compared to DBAS, over the entire 7-day sampling period. The highest MBAS concentration was recorded on day 4 (273.0 ng/m<sup>3</sup>) and the lowest on day 7 (66.0 ng/m<sup>3</sup>), whereas DBAS showed the highest concentration on day 3 (66.2 ng/m<sup>3</sup>) and lowest on day 7 (26.2 ng/m<sup>3</sup>). These higher MBAS concentrations indicate that combustion products from biomass burning may well contain a large quantity of organic substances. The results of the present study correlate with those from Wahid et al. (2013), who found that biomass burning was one of the major sources of MBAS in PM<sub>2.5</sub>. Furthermore, Latif et al. (2005) indicated that biomass burning in Southeast Asia contributed to the amount of anionic surfactants in the atmosphere. In our study, we observed significant correlations between PM<sub>2.5</sub> and MBAS concentrations ( $R^2 = 0.922$ ) and between levoglucosan and MBAS concentrations ( $R^2 = 0.780$ ).

##### Major element and anionic composition in PM<sub>2.5</sub>

Table 2 shows concentrations of water-soluble ionic elements in the PM<sub>2.5</sub> samples during haze episodes. One-way ANOVA revealed no significant variations ( $p > 0.05$ ) between the elements studied. Average concentrations of the major elements followed the order K > Mg > Na > Ca, whereas that of anions was SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup> > PO<sub>4</sub><sup>3-</sup> > F<sup>-</sup>. From the table, it is seen that most of the ionic elements had their highest level on day 4 of the sampling period (SO<sub>4</sub><sup>2-</sup> = 5.79  $\mu\text{g}/\text{m}^3$ , NO<sub>3</sub><sup>-</sup> = 1.63  $\mu\text{g}/\text{m}^3$ , and K = 0.89  $\mu\text{g}/\text{m}^3$ ) and that overall, the concentrations of anions and major elements such as SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and K were higher than those during non-haze days in Amil et al. (2016) and Ee-Ling et al. (2015). The very high levels of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and K indicate that they may have resulted from combustion processes (Othman & Latif, 2013). According to See, Balasubramanian, and



**Fig. 2.** Correlation between K and levoglucosan and between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  during haze episode.



**Fig. 3.** Variations of  $\text{PM}_{2.5}$  in relation to meteorological factors.

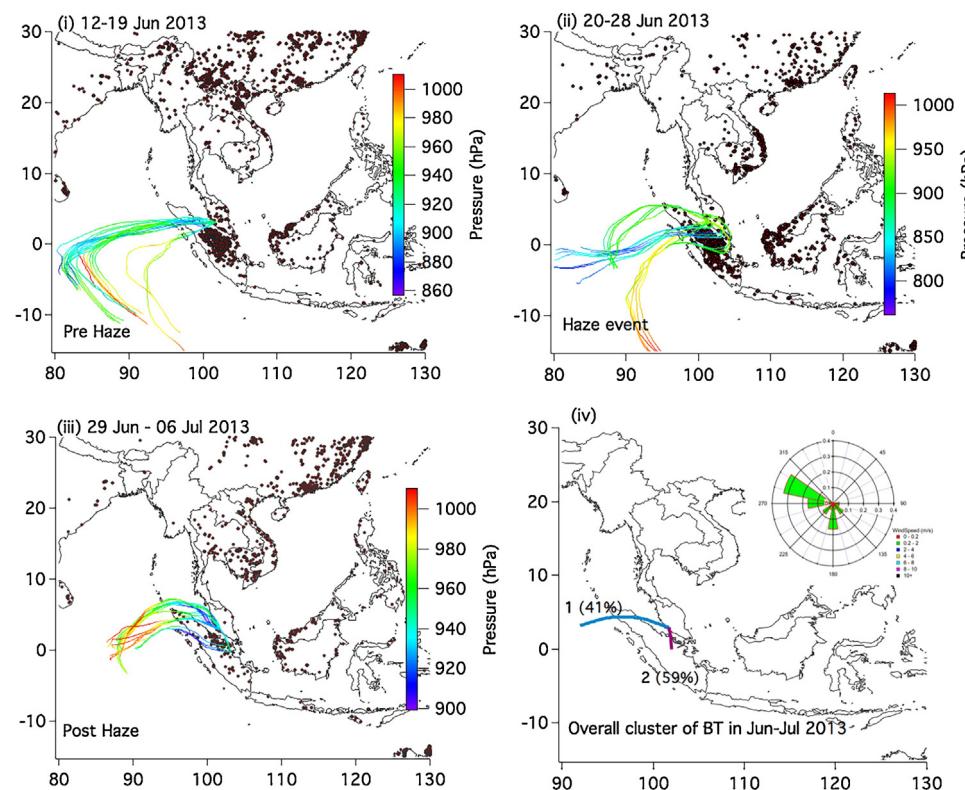
Wang (2006),  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are the most abundant ions in peat soil combustion, which originate from sulfurous and nitrogenous materials. K is deemed an effective indicator of biomass burning, particularly in relation to the combustion of straw from vegetables (Quiterio, Sousa, Arbilla, & Escalera, 2005; Xu et al., 2012).

Fig. 2 shows correlation between levoglucosan and K, as well as that between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  during the 7-day haze episode. There was strong association between levoglucosan and K (Pearson's  $r=0.77$ ), indicating that they may have the same sources, which are connected to the burning of biomass and peat soil (Norela et al., 2013; Othman & Latif, 2013). This theory is also supported by strong correlation between  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (Pearson's  $r=0.90$ ), which indicates the effects of combustion as mentioned in several studies (Coelho et al., 2011; Wahid et al., 2013).

#### Meteorological effects on $\text{PM}_{2.5}$ during haze episodes

Relationships between  $\text{PM}_{2.5}$  concentrations and meteorological parameters, including temperature, humidity, and rainfall during the 7-day sampling, are shown in Fig. 3. At the beginning of that sampling period, the  $\text{PM}_{2.5}$  concentration was low (days 1 and 2), but it rose dramatically on days 3 and 4. The concentration then declined as a result of rainfall (precipitation rate 31.8 mm) on day 5, and slowly decreased through day 7 along with the temperature, which decreased from 27.7 to 26.5 °C. Atmospheric relative humidity contrasted with temperature and was higher on day 6, a result of the heavy rainfall on the previous day.

According to Shukla et al. (2009), nature clears the air by providing a removal mechanism for pollutants in the form of rain. In this process, atmospheric gases are absorbed and particulate matter is trapped in raindrops with which they fall to the ground. Further-



**Fig. 4.** HYSPLIT backward trajectories coupled with biomass fire data and wind rose at sampling station during 2013 haze episode.

more, wind direction and speed strongly affected haze episodes by transporting PM<sub>2.5</sub> to the sampling location. From the backward trajectories and wind rose analysis (Fig. 4), wind directions (as shown on the map in percentages) indicate the effect of wind at the sampling site. BTs in Fig. 4 were calculated during three periods in the year 2013, i.e., 12–19 June, 20–28 June, and 29 June–6 July. These were reported as being pre-haze, haze, and post-haze, respectively. The BT results demonstrate that the origin and transport of the pre-haze air mass was from marine and inland areas with a small number of fire hotspots. However, during the haze event, the air mass was transported over biomass fire-prone inland areas. Post-haze transport was over inland areas with very few biomass fire hotspots. Thus, the air mass transport could drive the trans-boundary pollution reaching the sampling area. As shown in Fig. 4, the three events show clear evidence of dense biomass fire hotspots during the haze episode and just before strong haze over Malaysia. However, a small number of fire locations were observed after the haze event. There were several possible sources of PM<sub>2.5</sub> during the forest-fire haze period. The obvious source was particles from distant areas of biomass burning, or their photochemical and oxidation products. Local sources of pollutants may be readily enhanced by moderate winds and a dry-season inversion, which traps the smoke plume (Afroz, Hassan, & Ibrahim, 2003). Based on Awang (1998), it could be determined that the PM<sub>2.5</sub> in atmospheric aerosol collected during haze episodes arose from the combined effects of biomass burning and anthropogenic local sources. In the sampling period during the southwest monsoon, the wind flow generally came from Sumatra in Indonesia (Mahmud, 2010), bringing with it particles from forest fires in several provinces. This, increased PM<sub>2.5</sub> concentrations in the atmosphere.

Meteorological factors are also important in the spread and elimination of PM<sub>2.5</sub> pollutants, as demonstrated by Sham, Cheang, Chow, and Lim (1991) in their study focused on the pattern of haze occurrence during August 1990 in the Klang Valley, Malaysia.

According to Perez et al. (2010) and Yadav, Sahu, Jaaffrey, and Beig (2014), the distributions of PM<sub>2.5</sub> concentrations result from various atmospheric processes such as dilution, emission, and accumulation, which are all affected by meteorological parameters.

## Conclusions

The concentration of PM<sub>2.5</sub> in the present study far exceeded USEPA air quality standard guidelines for PM<sub>2.5</sub> (35 µg/m<sup>3</sup> for 24-h mean) and the 2005 WHO air quality guidelines (25 µg/m<sup>3</sup> for 24-h mean). The concentration of levoglucosan strongly indicated that the haze was contributed to by biomass burning, as this parameter is widely used by other researchers. High concentrations of K (0.89 µg/m<sup>3</sup>), NO<sub>3</sub><sup>-</sup> (1.63 µg/m<sup>3</sup>), and SO<sub>4</sub><sup>2-</sup> (5.79 µg/m<sup>3</sup>) support the theory that the haze originated from biomass burning, as proposed in other studies. Moreover, wind trajectories prove that the haze in Malaysia originated from several locations in Indonesia, which are known to have forest burning. Concentrations of surfactants were greater on high PM<sub>2.5</sub> concentration days. Meteorological parameters such as rainfall, temperature, and relative humidity affected the haze upon interacting, altering the PM<sub>2.5</sub> concentration. Because of the adverse effects of PM<sub>2.5</sub>, which is smaller in size than other particulate matter, it deserves greater attention, particularly during haze episodes. Further detailed study using a greater number of samples and source apportionment should be conducted to differentiate between local and regional sources of particulate matter. Stringent and continuous monitoring must be undertaken to mitigate the effects of PM<sub>2.5</sub>. Additionally, countries in the study region should unite to better regulate activities that contribute to PM<sub>2.5</sub> increases. Finally, continuous forecasting is required to ensure that PM<sub>2.5</sub> emissions do not exceed proposed standards, and the assertion of laws should be continually practiced.

## Acknowledgments

We are very thankful to Universiti Kebangsaan Malaysia for University Research Grant DIP-2016-015 and the Royal Thai Embassy (UKM-Thai Window) (ST-2016-008). Special thanks to K. Alexander for assistance with proofreading of the manuscript.

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