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RESEARCH ARTICLE

Characterization of rainwater chemical composition after a Southeast Asia haze event: insight of transboundary pollutant transport during the northeast monsoon

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Abstract Open biomass burning in Peninsula Malaysia, Sumatra, and parts of the Indochinese region is a major source of transboundary haze pollution in the Southeast Asia. To study the influence of haze on rainwater chemistry, a short-term investigation was carried out during the occurrence of a severe haze episode from March to April 2014. Rainwater samples were collected after a prolonged drought and analyzed for heavy metals and major ion concentrations using inductively coupled plasma mass spectroscopy (ICP-MS) and ion chromatography (IC), respectively. The chemical composition and morphology of the solid particulates suspended in rainwater were examined using a scanning electron microscope coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). The dataset was further interpreted using enrichment factors (EF), statistical analysis, and a back trajectory (BT) model to find the possible sources of the particulates and pollutants. The results show a drop in rainwater pH from near neutral (pH 6.54) to acidic (<pH 4.00) during the haze to non-haze transitional period, suggesting that the deposition rate of sulfate and nitrate in the atmosphere via the precipitation process was relatively lower compared to the mineral components. Zinc, nitrate, and calcium, which were the predominant elements in the first rainwater samples. Besides, the results of the SEM-EDS indicated that the zinc was possibly originated from anthropogenic activities which are consistent with the results obtained from EF. The BT model showed that pollutants transported from the mainland of Indo-China and the marine region in the South China Sea

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were responsible for the high pollution event in the study area. These findings can be useful in identifying contributions of pollutants from single or multiple sources in rainwater samples during haze episodes.

Keywords Trace elements · Rainwater · Air pollution · Drought · Biomass burning · Malaysia

Introduction

Biomass burning is a common issue and received deep concern among countries in tropical Asia. Smoke haze related to biomass burning is a recurring environmental problem which affects air quality not only in the source regions but also in the surrounding areas. In fact, biomass burning may have an acidifying effect on rainwater which can cause problems to human health, buildings, and crops (Crutzen and Andreae 1990; Cachier and Ducret 1991). South East Asia (SEA) is a region that has been severely affected by haze from biomass burning in recent years (Norela et al. 2013; Othman et al. 2014; Radojevic 2003). Thus, air quality study in SEA is important to understand the sources and impacts on earth's ecosystem.

Tropical Asia has been recognized to be the highest biomass burning region in Asia and has experienced some of the most severe wild land fire events under extreme climatic conditions (Page et al. 2002). Chang and Song (2010) estimated the average annual burned area in tropical Asia to be 85,277 km^2 year^{-1}, releasing 122 Tg year^{-1} of CO_2, and 0.63 Tg year^{-1} of CH_4. In SEA, haze events normally occur during the southwest monsoon (June to August) (Mahmud 2009) and from January to February (springtime haze) every year. Fire hotspots in the Indo-China peninsula, including mainland territory of Thailand, Laos, Cambodia, Myanmar, Vietnam, and Malaysia, are known to contribute substantial haze to the region (Chang and Song 2010; Khan et al., 2015a,b Khan et al. 2016; Lin et al. 2009). The occurrence of these hotspots in the region is primarily attributed to slash and burn agricultural practices and land clearing activities, especially during dry weather conditions.

Wet precipitation after a haze event plays an important role in scavenging soluble components and suspended particulates from the atmosphere. Depending on the source and ambient atmospheric chemistry, rainwater after a haze event often displays an acidic character (Balasubramanian et al. 1999; Radojevic and Tan 2000). Previous published works have been focused on the August–September haze, but few studies have discussed the effects of the March–April haze on rainwater chemistry in the SEA (Budiwati et al. 2016). Therefore, it is the purpose of this study to investigate the effects of haze during the northeast monsoon on the rainwater chemistry in Malaysia.

Methodology

Sample collection

Wet-only deposition (rainwater) samples were collected from 16 March to 15 April 2014 on the rooftop (height ~10 m above ground) of the Faculty of Science and Technology, National University of Malaysia (UKM) (2°55′20.23″N, 101°46′48.80″E). Samples were collected after a prolonged drought and haze period. The details of the sampling station are described in a previous air study by Khan et al. (2015c). The sampling station is located in Bangi, approximately 25 km south of Kuala Lumpur city center and 35 km east of heavy industrial districts such as Shah Alam and Klang. The Titiwangsa mountain range and a large area of forest reserve are located to the eastern side of the sampling point. Rainwater samples were collected using a 20-cm diameter polyethylene funnel connected to a 2-L high-density polyethylene (HDPE) receiving bottle during each rain event. The rainwater samples were collected from the beginning of rain until the end for each event. After each precipitation event, the funnels and collection bottles were removed and replaced with others that had previously undergone the washing procedure (Al-Momani 2003) (Fig. 1).

Laboratory analysis

After collection, the rainwater samples were immediately measured for pH. pH values of the rainwater samples were measured using a Thermo Fisher Scientific ORION (USA) pH probe (9157BNMD). Rainwater samples were acidified using analytical-grade concentrated nitric acid as a preservation measure, and then the heavy metals (Al, Cu, Fe, Mn, Ni, Pb and Zn) and major elements (Ca, Mg, Na, and K) were analyzed using ICP-MS (Perkin Elmer ELAN 9000, USA). Un-acidified samples were used to determine the major ions using ion chromatography (ICP) (Metrohm Pro 850, Switzerland). Metrosep C4 100 and Metrosep A Supp 5 columns were used to detect the anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$). To better understand the contribution of suspended particles in the atmosphere on rainwater chemistry, we collected solid phase particles associated in the first and final rain events and analyzed for its morphology and chemical composition. For the examination of suspended particles in rainwater, 100 ml of the sample was filtered (using a vacuum pump) through a 0.22-μm Whatman cellulose membrane. The solid phase materials with particle size >0.22 μm that were retained on the surface of filter paper were then air-dried and precoated with a thin layer of Au before examination by scanning electron microscopy (SEM) (LEO 1450VP, Germany)
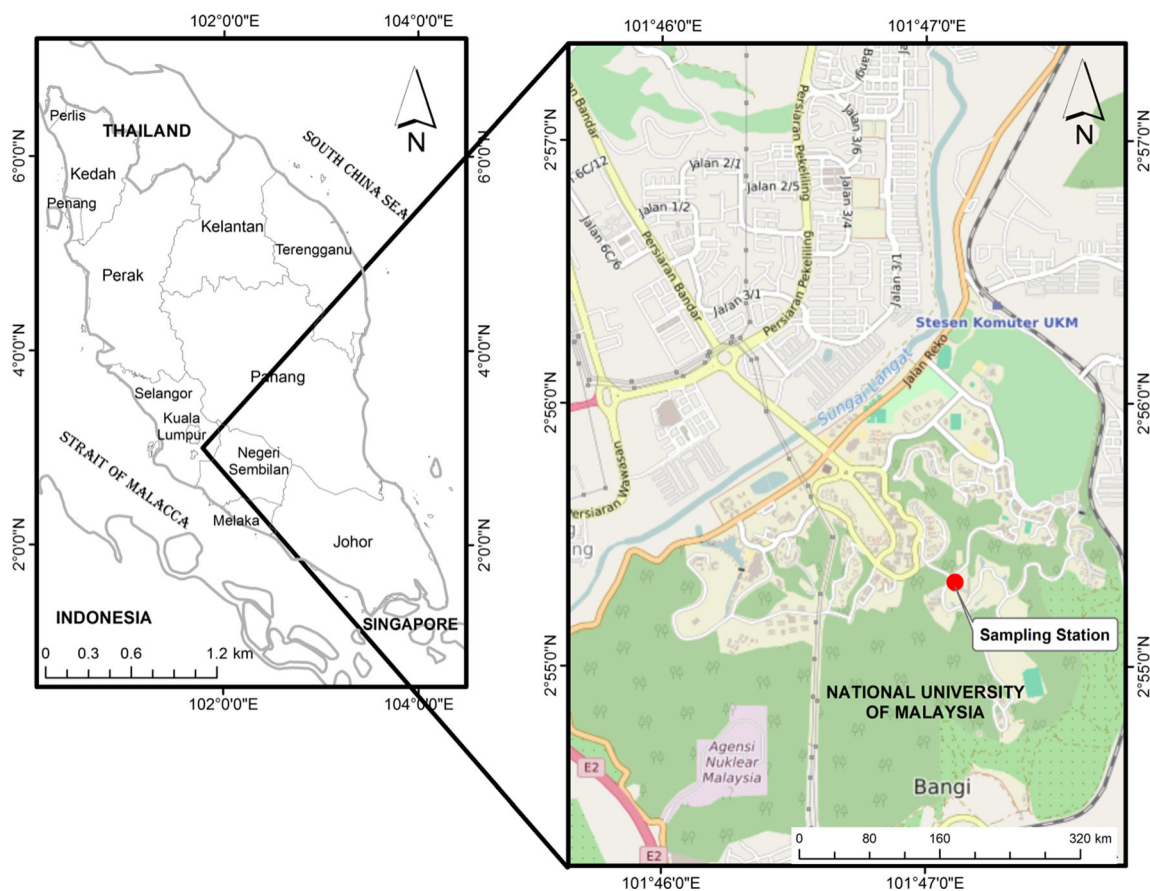
Fig. 1 Sampling location at UKM campus, Bangi (Khan et al. 2015c)

fitted with energy-dispersive X-ray spectroscopy (EDS) (Oxford, UK) for visual and chemical validation.

Quality control and quality assurance (QA/QC)

As part of the QA/QC procedures, the chemical analysis of all samples was carried out in duplicates. The pH meter was calibrated with standard solutions of pH 4.0 and 7.0 prior to sample measurement. All collection bottles and glassware involved in the rainwater sampling were acid-soaked (0.1 M HNO_3) and rinsed with deionized water prior to oven-drying. Subsequently, the bottles were sealed and stored in a dry and clean environment to avoid potential contamination. A sample blank was also measured during the elemental analysis. Perkin Elmer Quality control standard 3 was used as a multi-element standard solution. Instrumental calibration was carried out prior to each analysis. Other precautionary measures for water analysis were adopted based on standard methods described in APHA (1995). The method detection limits (MDL) for ICP-MS were 1.51 (Al), 0.21 (Cu), 0.31 (Mn), 0.09 (Ni), 0.12 (Pb), 0.12 (Zn), 0.17 (Fe), 60 (Ca), 10 (Mg), 40 (Na), and 10 $\mu g \ L^{-1}$ (K). For ion chromatography, the MDL were 30 (NO_3^-), 20 (Cl^-), and

110 $\mu g \ L^{-1}$ (SO_4^{2-}). The MDL was calculated by dividing the standard deviation (SD) of the response by the calibration slope (S) and multiplied by 3.3 as shown in Eq. (1):

$$MDL = \frac{SD}{S} \times T \qquad (1)$$

where MDL = method detection limit

SD = standard deviation of the result values

T = student's t value appropriate for 99% confidence interval which has the value of 3.3

Statistical analysis

Two types of statistical analyses, one-way analysis of variance (ANOVA) and hierarchical agglomerative clustering analysis (HACA), were used in this study. ANOVA was used to determine the significant difference among the heavy metals and major ions. HACA was used to classify and determine the possible sources of pollutants deposited in the rainwater. These methods have been widely used in classifying and determining the sources for major ions and heavy metals in the atmosphere (Alahmr et al. 2012; Báez et al. 2007; Han et al. 2014; Kazi et al. 2009).

Enrichment factors

Enrichment factors (EFs) were used to determine whether the pollutants in the rainwater originated from natural or anthropogenic sources. This indicator has been widely used for similar purposes by Al-Momani (2003), Hu et al. (2003), Latif et al. (2015), and Razak et al. (2015). EFs were calculated using Eq. (2):

$$EF = \frac{\left(\frac{C_x}{Al}\right)_{\text{rainwater}}}{\left(\frac{C_{ref}}{Al}\right)_{\text{earth's crust}}} \qquad (2)$$

where C_x is the concentration of the pollutant of interest, and C_{ref} is the concentration of the reference pollutant (Taylor 1964). Aluminum (Al) was used as the reference pollutant in this study, as the primary source of Al is from soil (i.e., it is crustal in nature). The reason behind this is because it has low spatial variability and stable chemical properties as mentioned in Hu et al. 2014. However, Fe also has been reference pollutant used in previous studies (Baptista et al. 2000; Taylor and McLennan 1995). Parallel to Fe, Al is also widely cited as the reference pollutant used in calculation of EFs (Huang and Lin 2003; Hong et al. 2011). EF values can be classified into several categories: (i) an EF approaching 1 shows the element is of crustal origin, (ii) an EF <2 shows a low enrichment, (iii) an EF = 2–5 shows a moderate enrichment, (iv) an EF = 5–20 shows a significant enrichment, and (v) an EF = 20–40 shows an extremely high enrichment (Khan et al. 2010; Lu et al. 2009; Yongming et al. 2006).

Effect of biomass fire hotspots and HYSPLIT back trajectories

Figure 3 shows the locations of biomass fire hotspots coupled with the synoptic scale wind vector on the 15, 16, and 17 March 2014. The concentrations of the pollutants in rainwater were relatively high or maximum on those dates. Similarly, the highest value of the air pollutants index (API) measured during the sampling period was recorded on 16 March 2014. API is an indicator air pollution level in Malaysia based on the highest sub-indexes of main criteria air pollutants (PM_{10}, CO, SO_2, NO_2, and O_3). During haze event, high API, which is usually represented by PM_{10} sub-index (Amil et al. 2016), indicates high concentration of particulate matter in the atmosphere, which may contribute to the high level of heavy metals in the rain water. The wind speed was relatively higher over the South China Sea and transported the air mass towards the inland of Peninsular Malaysia. The locations of the fire hotspots were observed more in the Indo-China region compared to the Sumatra and Kalimantan regions of Indonesia. Thus, the wind sector and number of hotspots affect the concentration of pollutants in ambient air. Other studies also reported higher numbers of biomass fire hotspots in the Indo-China region during the northeast monsoon in Malaysia (Chang and Song 2010; Khan et al., 2015a, b, c; Mustaffa et al. 2014). Air mass back trajectories (BTs) were calculated using the online version of the hybrid single particle Lagrangian trajectory model (HYSPLIT) (http://ready.arl. noaa.gov/HYSPLIT.php) (Stein et al. 2015). During the estimation of back trajectories, the main input parameters were 120 h total transport of air mass, 500 m as releasing height, and 6 h as trajectory intervals. The results of the BT showed that the air mass was mainly originated from the South China Sea and inland of Indo-China region (Fig. 4).

Results and discussion

Variation of pH

The pH of rainwater collected in Klang Valley from 16 March 2014 to 15 April 2014 varied from 3.67 to 6.54 as shown in Table 1. The pH of rainwater on the first raining event was less acidic with a value of 6.54. The neutralization effect largely explains the relatively higher rainwater pH during the first rain, which mainly arises from biomass burning and soil mineral particles suspended in the atmosphere. Biomass burning and soil mineral particles are commonly known to contribute a substantial amount of Ca and Mg that may act to neutralize the rainwater acidity (Balasubramanian et al. 1999; Radojevic 2003; Sanhueza et al. 1989). This explanation is consistent with the high Ca and Mg concentrations observed in the first rain. However, it should be mentioned that besides alkaline mineral dusts ($CaCO_3$), ammonia (NH_3) might also play a considerable role in the neutralizing of rainwater (Balasubramanian et al. 1999; Das et al. 2005). To distinguish the relative neutralization of rainwater by crustal components and ammonia, the neutralization factors (NFs) were calculated. NFs were calculated as explained by Saxena et al. (1996) and Possanzini et al. (1988):

$$NF_{NH_4^+} = \frac{[NH_4^+]}{2[SO_4^{2-}] + [NO_3^-]} \qquad (3)$$

$$NF_{Ca^{2+}} = \frac{[Ca^{2+}]}{[SO_4^{2-}] + 2[NO_3^-]} \qquad (4)$$

$$NF_{Mg^{2+}} = \frac{[Mg^{2+}]}{[SO_4^{2-}] + 2[NO_3^-]} \qquad (5)$$

From the calculation, the NF_{NH4}^+ was less than both NF_{Ca}^{2+} and NF_{Mg}^{2+}, where the factors were calculated as 0.10 for NH_4^+, 3.56 for Ca^{2+}, and 0.31 for Mg^{2+}. This suggests that the crustal components (soil mineral particles) can

Table 1 Variations of measured pH and air pollutant index in rainwater during haze 2014 in Klang Valley

Date of sampling	Air pollutant index (API)	pH
16 March 2014	135	6.54
19 March 2014	51	4.38
20 March 2014	57	4.26
31 March 2014	63	3.81
3 April 2014	65	3.73
7 April 2014	54	4.17
8 April 2014	49	4.06
9 April 2014	51	4.14
10 April 2014	50	4.00
12 April 2014	54	4.20
14 April 2014	53	3.67
15 April 2014	54	3.82

neutralize a larger fraction of the available acid in the first rain. The presence of soil mineral dusts and its geochemical composition in the first rainwater samples were further visualized under a scanning electron microscope which will be further explained later in the text.

To assess the balance between acidity and alkalinity, the ratio of acidifying potential (AP) to neutralizing potential (NP) was calculated using Eq. (6):

$$\frac{AP}{NP} = \frac{\left[SO_4^{2-}\right] + \left[NO_3^-\right]}{\left[Ca^{2+}\right] + \left[NH_4^+\right]} \qquad (6)$$

A ratio of less than one and ranging from 0.04 to 0.60 indicates that the NP dominates the AP, in which the dominance of alkaline constituents prevents the acidification of rainwater as explained by Tay et al. (2014). The mean concentrations of these ionic components generally increase with increasing pH value. Such increase is especially notable for Ca^{2+}. This trend is usually expected for the alkaline cations but not for the anions. Based on the assumption that the acidity of the precipitation arises from the presence of H_2SO_4 and HNO_3, one would expect the concentrations of sulfate and nitrate ions to be highest, leading to the lowest pH. This could partially be explained by the extremely high concentrations of calcium which appear to have a neutralizing effect on acidity. This neutralizing effect had also been observed earlier (Gorham 1976; Saxena et al. 1996; Xu and Han 2009). Acidic precursors such as sulfate and nitrate ions can be partially neutralized by alkaline substances.

In the majority of the rain events at our sampling site, most of the sulfate and nitrate were not associated with hydrogen ions. Instead, they occurred as salts associated with other elements (e.g., $MgSO_4$, $CaSO_4$). While some of the measured free hydrogen ions were no doubt donated by strong acids of sulfate and nitrate, weak and organic acids could have accounted for the

major portion. Possible explanations are that (i) the sampling site may be receiving alkaline dust such as from limestone quarries in the region and, thus, neutralization could have taken place and (ii) as the sampling site is not in the vicinity of severe pollution sources, air masses appear to have a long atmospheric residence time in which to undergo chemical reactions before deposition in a rain event (Lee and Low 1984).

The Malaysian API ranges from good (0–50) to moderate (51–100), unhealthy (101–200), very unhealthy (201–300), and hazardous (greater than 300) (Othman et al. 2014).

Main compositions in the collected rainwater

Ions and heavy metals in rainwater

The first sample of rainwater was collected on the first day of rain during the haze episode in Klang Valley. Table 2 shows the descriptive statistics of the ions, heavy metals, and major element compositions in 12 samples of rainwater collected during the 2014 haze episode in Klang Valley. The ionic average concentrations in rainwater were in the order of NO_3^- ($1500 \pm 1090\ \mu g\ L^{-1}$) > SO_4^{2-} ($1940 \pm 1150\ \mu g\ L^{-1}$) > Cl^- ($380 \pm 190\ \mu g\ L^{-1}$). The concentrations of SO_4^{2-} ranged from 510 to 4230 $\mu g\ L^{-1}$. For Cl^- and NO_3^-, the concentrations ranged from 50 to 620 $\mu g\ L^{-1}$ and from 630 to 3890 $\mu g\ L^{-1}$, respectively (Table 2). High concentrations of heavy metals were measured in rainfall events after period of dryness in March 2014 and experienced a gradual drop in the subsequent rainfall events (Fig. 2). Previous studies conducted in Malaysia by Norela et al. (2013), Latif et al. (2015), and Razak et al. (2015) showed that SO_4^{2-} was the dominant anion in rainfall. These findings are similar to those of Fujii et al. (2016). They reported SO_4^{2-} was at 23.0 to 55.9 wt% of total ions in PM_{10} over UKM campus which is similar location to this study. SO_4^{2-} can originate from various possible sources including agricultural activities (Tay et al. 2014; Fujii et al. 2016, Das et al. 2005). Previous studies reported that SO_4^{2-} found in sugar marker such as levoglucosan was largely originated from peat fires (Kehrwald et al. 2012; Zhang et al. 2010; Fujii et al. 2016).

Long-range transport of aerosols from industrial activities, motor vehicles, and biomass burning can also contribute to the amount of SO_4^{2-} in this study area. Cl^- is expected to be present in the rainwater mainly due to the transport of sea spray from the marine region towards the land (Budhavant et al. 2012), especially at the time of sampling due to the movement of wind from the northeast (South China Sea) direction. The low concentration of NO_3^- may be attributed to the lower contribution of vehicle emissions to the study area, and/or the uptake of nitrate aerosol was lower in this rain event.

The average concentrations of heavy metals in the rainwater followed the decreasing order of Zn > Fe > Al > Mn > Cu > Pb > Ni (Table 2). The highest average concentration observed was Zn with an average value of 28.12 $\mu g\ L^{-1}$ ($\pm 22.87\ \mu g\ L^{-1}$). The lowest heavy metal in the rainwater was Ni with an average value

Table 2 Summary of descriptive statistics of major ions and heavy metals in rainwater samples

Elements	Min	Max	Median	Average	Std dev
Heavy metals ($\mu g\,L^{-1}$)					
Al	5.91	43.10	16.12	18.31	11.23
Cu	0.58	5.65	2.30	2.39	1.56
Mn	0.52	4.24	2.43	2.43	1.21
Ni	0.18	4.19	1.02	1.56	1.17
Pb	0.37	4.69	2.11	2.19	1.45
Zn	3.42	86.78	15.20	28.12	22.87
Fe	4.03	44.89	15.21	19.70	11.41
Major ions ($\mu g\,L^{-1}$)					
Cl^-	50	620	470	380	190
NO_3^-	630	3890	1490	1940	1150
SO_4^{2-}	510	4230	1210	1500	1090
Major elements ($\mu g\,L^{-1}$)					
Ca	120	1180	320	390	280
Mg	40	120	40	90	30
Na	70	310	150	150	60
K	30	470	210	230	120

of $1.56\,\mu g\,L^{-1}$ ($\pm 1.17\,\mu g\,L^{-1}$). Such a trend is similar to the order of heavy metal concentrations reported in Razak et al. (2015). In this study area, Zn, Pb, and Ni could be potentially originated from biomass burning emissions and anthropogenic sources such as heavy industrial emissions and traffic emissions nearby UKM campus. These metals can also be derived from traffic emission source (Bove et al. 2014). The anthropogenic source could include fuel combustion from motor vehicles on the UKM campus, Bangi, or pollutants originated from cities in the east coast such as

Terengganu (based on the HYSPLIT output). In addition, Amodio et al. (2014) summarized previous studies on heavy metals deposited in the rainwater at different regions of the world.

The elements Mn, Ni, Cu, and Pb were moderately enriched compared to the mean crustal elements indicating the presence of other sources contributing to these elements. The potential sources could be particles from automobile emissions, vehicle wear, and road dust as these sources can contribute to significant Cu, Pb, and Zn in rainwater (Wetang'ula and Wamalwa 2015). Behera et al. (2015) observed that the concentration of Zn was enriched when there is a contribution from biomass burning or wood combustion. Previous studies conducted by Gautam et al. (2013), Khan et al. (2015a), Khan et al. (2015b), and Khan et al. (2016) concluded that during March to April 2014, the Indo-China peninsular regions in SEA experienced wild land forest fires and agricultural crop burning and that forest conversion fires may be responsible for the intense haze episodes in Malaysia.

The major element average concentrations followed the decreasing order of Ca > K > Na > Mg. Previous studies conducted in Malaysia by Norela et al. (2013) and Norela et al. (2009) showed that the major elements that dominated the rainfall composition were K and Ca, respectively. The highest average concentrations of the major elements observed was Ca with a range of 120 to 1180 $\mu g\,L^{-1}$ (± 0.28) and the lowest observed was K with a range of 30 to 470 $\mu g\,L^{-1}$ (± 0.12). Huang et al. (2013), Khan et al. (2016), Mustaffa et al. (2014), and Tsai et al. (2013) also suggested that water-soluble K is a good indicator of biomass burning emission. The biomass burning emissions can be accounted for both local and regional sources as indicated by the number of hot spots and the trajectory analyses within the selected
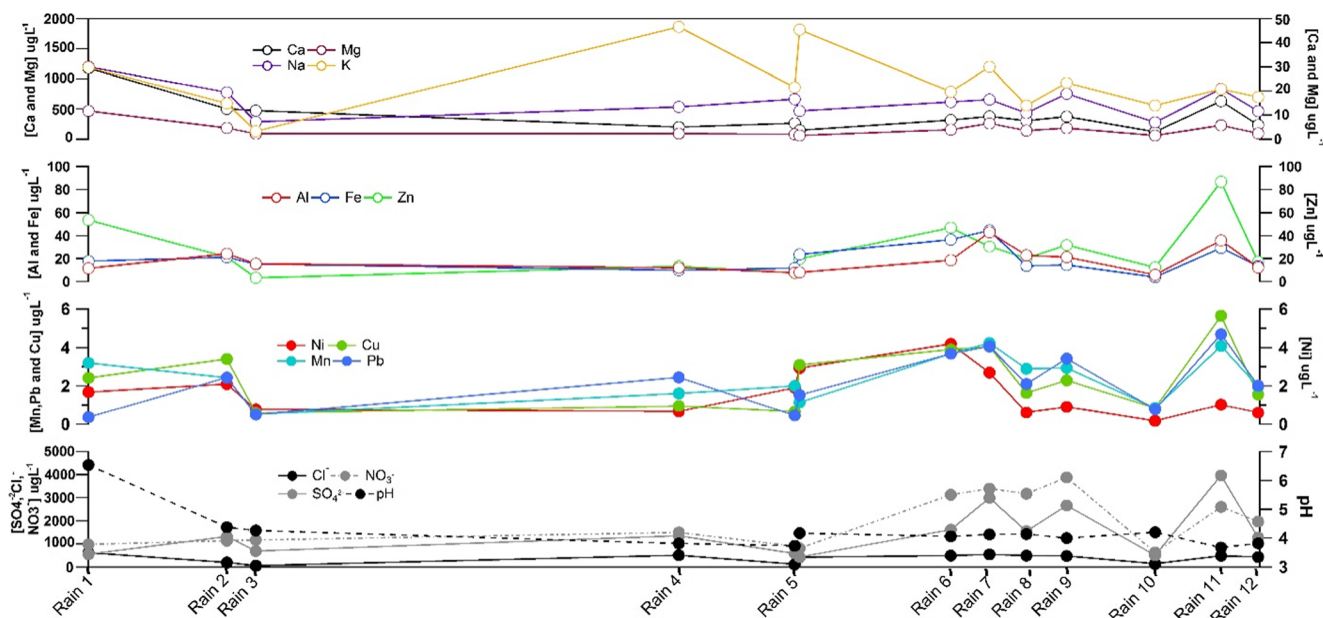

Fig. 2 Concentration of chemical compounds measured in rainwater

days (Fig. 3a–c). The trajectory analysis clearly showed the air mass passing through a hotspot area at Terengganu (east of the peninsular) before arriving at the Bangi area on 16 March 2014 (Fig. 4a–c).

The composition of suspended particles in rainwater determined by SEM-EDS analysis

All samples collected during the haze event were analyzed using SEM-EDS. The images of suspended particles in different rainwater events are shown in Fig. 5a, b. These particles were insoluble fraction composed of geogenic particles:

mineral fragments; agglomerates of various compositions formed by resuspended dust derived from soils and rocks; and anthropogenic particles that include particles of varied forms and compositions, originating mainly from combustion such as Zn and Mg. The chemical composition of the suspended particles collected on the first rain was in the order of Ca > Zn > Al > Na > K (Fig. 5a). We believe that the dust particles obtained from the first rain have been suspended in the atmosphere for an extended time period during the drought. The dusts were composed of soil particles, with high calcium content which are able to neutralize rain acidity. Such neutralization effect is well observed in the pH on the first day
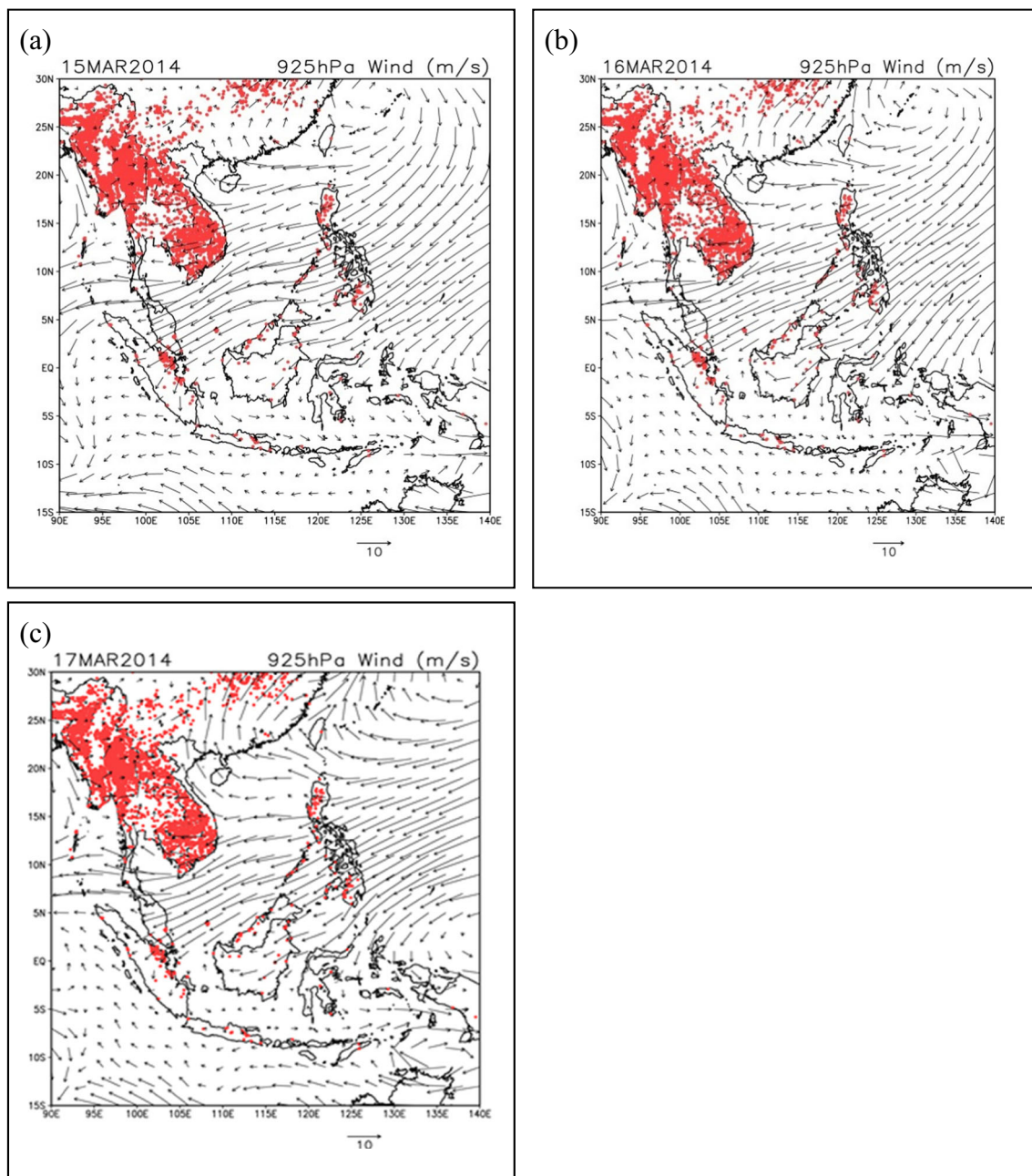

Fig. 3 Wind directions and hot spot events during **a** 15 March 2014 and **b** 16 March, and **c** 17 March 2014
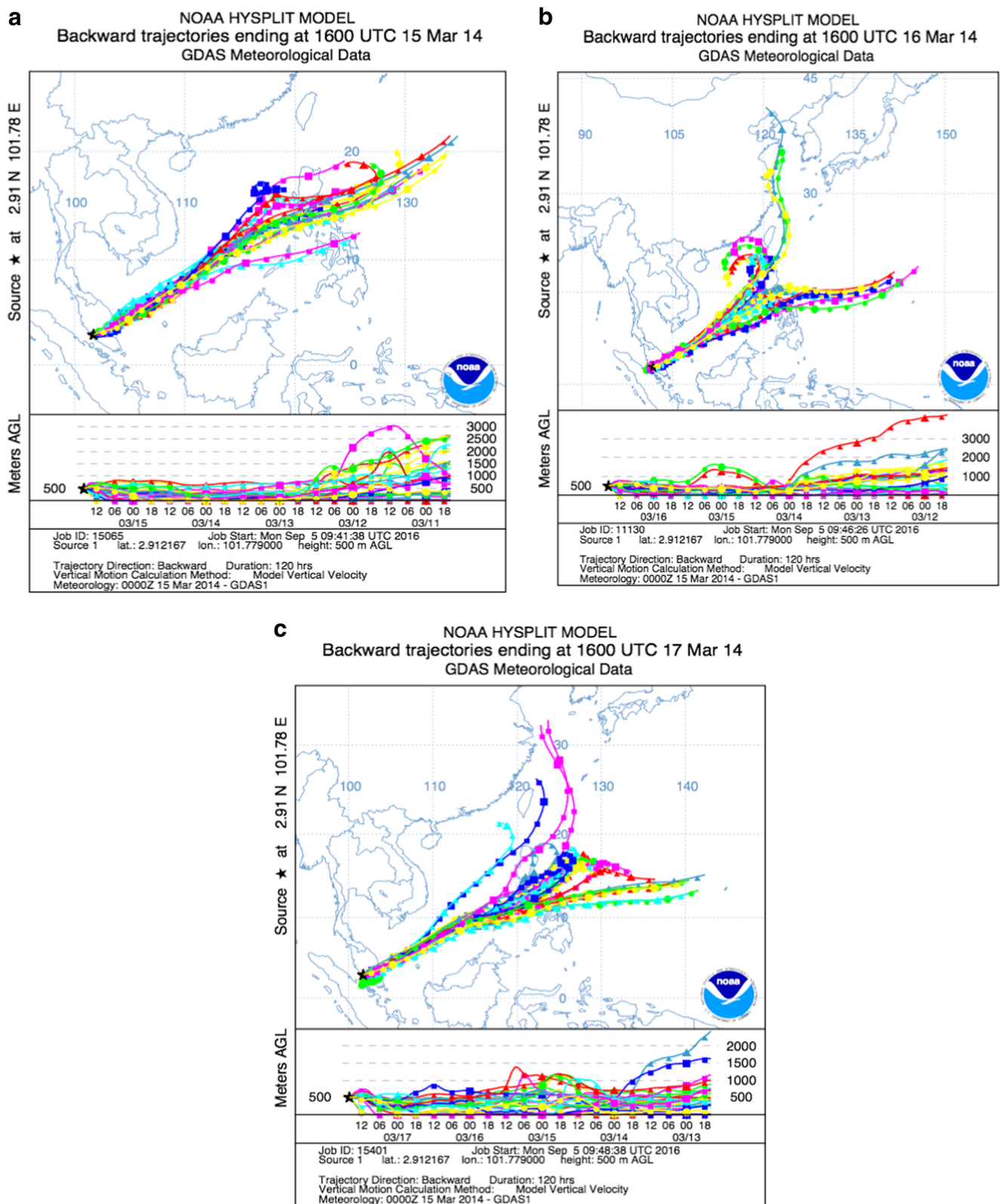
Fig. 4 HYSPLIT back trajectories for 120 h and 500 m releasing height at 16:00 UTC **a** 15 March 2014, **b** 16 March 2014, and **c** 17 March 2014 at around UKM sampling site

of rain event with a value of pH as 6.54 (Table 1). Figure 5b shows the 12th rainwater sample, where the chemical

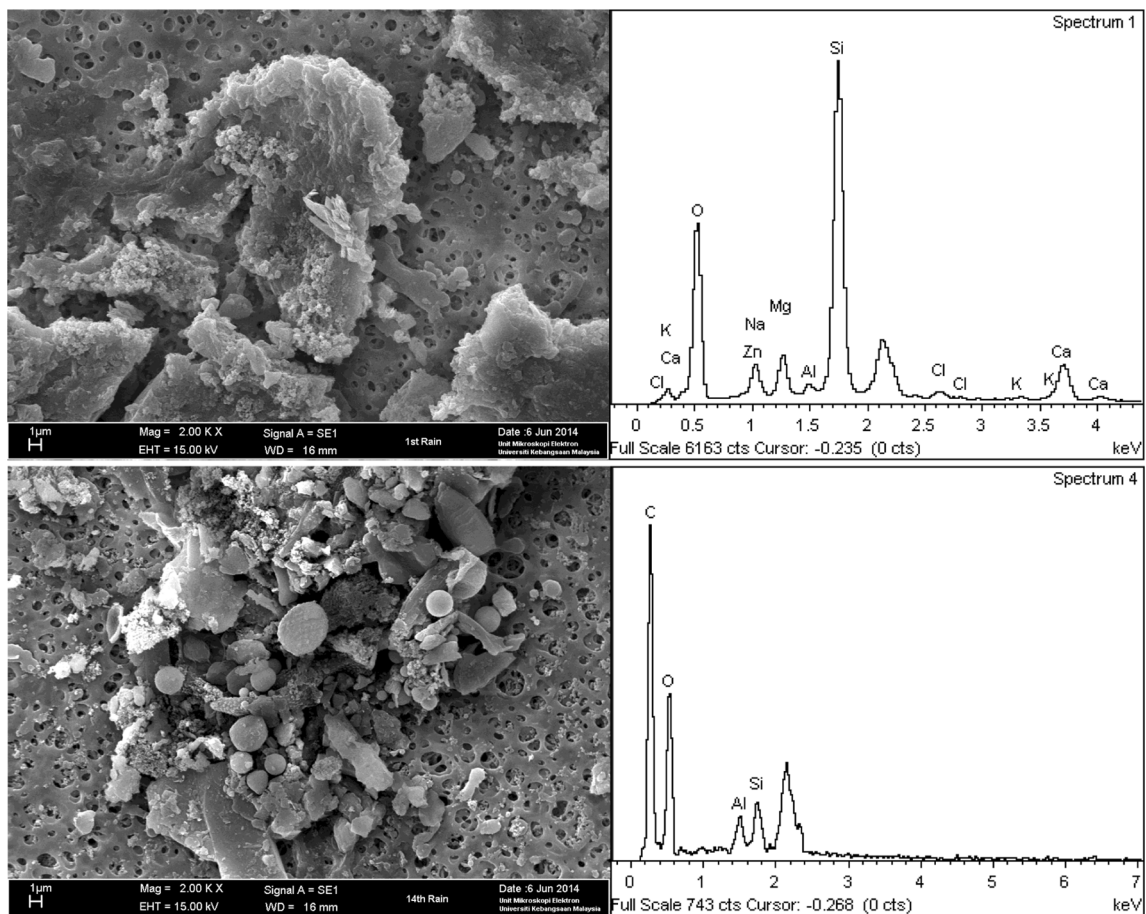composition of particles collected was mainly carbon and quartz. Other elements such as Mg and Zn are expected to

Fig. 5 Scanning electron microscope (SEM) images of suspended particles in **a** 1st rain event with EDS spectra and **b** 12th rain event with EDS spectra

have washed away (scavenged) during the previous rain events. Therefore, the results obtained in this analysis suggest

that Zn is likely to be derived from anthropogenic sources rather than from soil dust. Besides, it is worth mentioning that

Table 3 Average enrichment factors (EFs) for elements in this study compared with previous studies

Enrichment factor (EF)				
Elements	This study	Wetang'ula and Wamalwa (2015)	Tay et al. (2014)	Das et al. (2005)	Mimura et al. (2016)
	(relative to Earth's crust)	(relative to Earth's crust)	(relative to seawater)	(relative to Earth's crust)	(relative to Earth's crust)
Cu	213	28.08	n.d	n.d	n.d
Mn	221	43.58	n.d	n.d	n.d
Ni	120	13.54	n.d	n.d	n.d
Pb	805	48.93	n.d	n.d	n.d
Zn	1974	274,153	n.d	n.d	n.d
Fe	1.75	n.d	n.d	n.d	n.d
Ca	0.05	n.d	64.9	33.0	25.1
Mg	0.01	n.d	5.80	16.5	2.07
Na	0.04	n.d	n.d	n.d	n.d
K	0.07	n.d	0.91	0.5	25.2
Cl^-	n.d	n.d	0.06	1.0	0.54
SO_4^{2-}	n.d	n.d	0.72	10.4	0.80

n.d no data

both solid particles collected from the 1st and 12th rainwater events comprised distinct morphology, confirming that these solid particles are of different origins.

Identification of sources of the rainwater composition

The source identification of the rainwater composition was conducted using enrichment factor (EF), correlation analysis, and hierarchical agglomerative clustering analysis (HACA). Detailed description is given in the following sections:

Enrichment factors

The results of the EF for each element contained in rainwater are shown in Table 3. This study revealed that the heavy metals in the rainwater samples were derived both from anthropogenic and natural sources (the Earth's crust). Fe, Ca, Mg, Na, and K originated from the Earth's crust and Cu, Mn, Ni, Pb, and Zn originated from anthropogenic sources. The EF values for elements originating from the Earth's crust were within the range 0.01 to 1.75. Zn recorded the highest average EF value of 1974, and Mg recorded the lowest value of 0.01. The decreasing pattern of average EF values recorded in this study is Zn > Pb > Mn > Cu > Ni > Fe > K > Ca > Na and Mg.

The EF values for Zn recorded in the study by Latif et al. (2015) were more than 16,000. Studies done by Kim et al. (2012) and Kyllönen et al. (2009) identified that Pb and Zn were originated from anthropogenic sources. A few studies showed different outcomes compared with this study. For example, the results obtained by Başak and Alagha (2004) and Mimura et al. (2016) illustrated that EF values for all the variables measured in the study were approaching 1 which implies that the variables originated from natural Earth's crust

sources. Uygur et al. (2010) also reported that variables such as Mg, K, Ca, Na, and Fe showed low EF values (<1.0). A study by Cheng and You (2010) revealed that the EF values for Pb, Zn, Na, Ni, and K are extremely high: Pb = 10,202,566; Zn = 27,921; Na = 4548; Ni = 3047; and K = 1008. Therefore, the results obtained in this study suggests that there is an extremely high probability of the Zn, Ni, Pb, Mn, and Cu originating from anthropogenic activities rather than desorption from soil dusts.

Correlation between major ions and heavy metals

Correlation analysis was carried out on the major elements and heavy metals to determine the relationship between elements in the collected rainwater (Table 4). The highest correlation was found between Ca and Mg ($r^2 = 0.91$; $p < 0.01$), suggesting both elements were derived from a common source. Mn exhibits the strongest positive correlation with SO_4^{2-} ($r^2 = 0.87$, $p < 0.01$) while Zn showed the weakest positive correlation ($r^2 = 0.10$, $p < 0.05$). Mg and Na showed the strongest correlation with an r^2 value of 0.87 ($p < 0.01$). This is similar to the results found by Latif et al. (2015) in dust fall ($r^2 = 0.96$, $p < 0.01$). For the relationship between heavy metals, it can be clearly seen in Table 3 that Fe and Ni showed the moderate significant correlation ($r^2 = 0.75$, $p < 0.01$). Satsangi et al. (1998) found a positive correlation between SO_4^{2-} and NO_3^- and suggested these may be derived from soil associated with Ca, Mg, and Na during the monsoon in Gopalpura, India. Such finding contradicts with the results in the present study where the SO_4^{2-} and NO_3^- associated with Ca, Mg, and Na were found to be weakly correlated (~$r^2 < 0.5$, $p > 0.01$), suggesting that both SO_4^{2-} and NO_3^- (anions) and Ca, Mg, and Na (elements) were derived from distinct sources.

Table 4 Pearson's correlations among the heavy metals and major ions in the rainwater samples

Elements	Al	Cu	Mn	Ni	Pb	Ca	Mg	Na	K	Zn	Fe	Cl⁻	NO₃⁻	SO₄²⁻
Al	1.00													
Cu	0.72	1.00												
Mn	0.76	0.76	1.00											
Ni	0.18	0.52	0.40	1.00										
Pb	0.80	0.78	0.74	0.27	1.00									
Ca	0.21	0.30	0.42	0.04	−0.07	1.00								
Mg	0.39	0.45	0.66	0.17	0.15	0.91	1.00							
Na	0.27	0.48	0.65	0.26	0.19	0.82	0.87	1.00						
K	−0.10	0.16	0.07	0.28	0.14	−0.08	0.09	0.25	1.00					
Zn	0.52	0.82	0.76	0.23	0.60	0.58	0.64	0.66	0.09	1.00				
Fe	0.74	0.81	0.71	0.75	0.67	0.18	0.38	0.30	0.15	0.52	1.00			
Cl⁻	0.36	0.49	0.68	0.22	0.52	0.33	0.57	0.51	0.55	0.59	0.44	1.00		
NO₃⁻	0.69	0.44	0.72	0.14	0.78	−0.04	0.19	0.12	−0.08	0.39	0.50	0.56	1.00	
SO₄²⁻	0.87	−0.40	0.87	0.70	0.80	−0.32	0.41	0.33	−0.04	0.10	0.71	−0.21	−0.34	1.00

Fig. 6 Dendrogram of cluster analysis on the 12 variables in rainwater samples
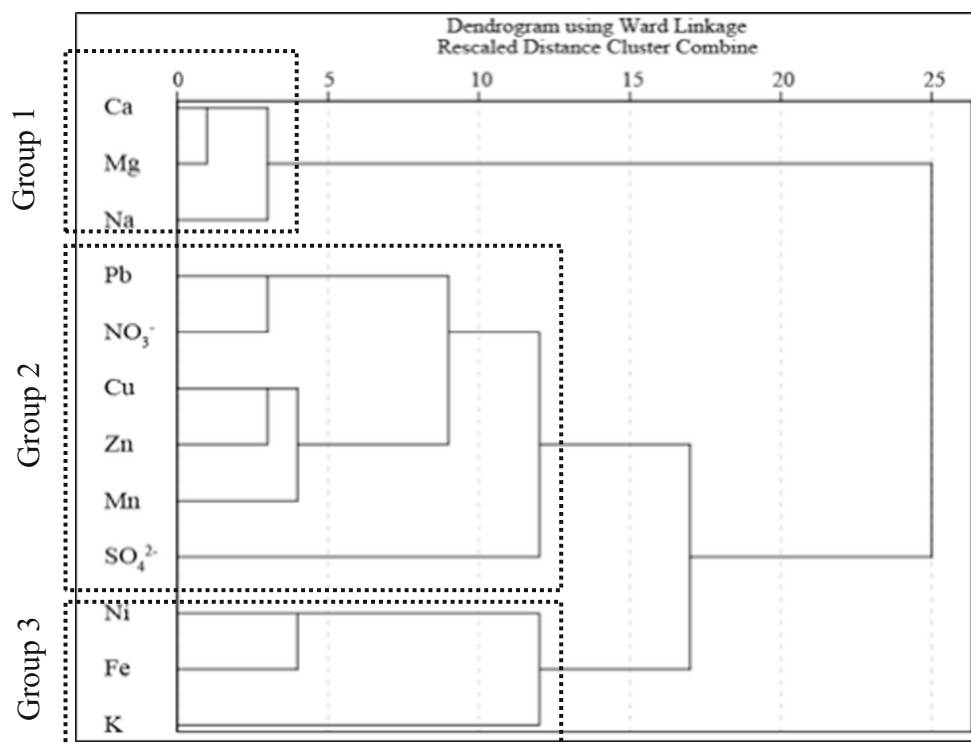
Norela et al. (2013) suggested that the main sources of Mg, Mn, and Zn in rainwater could be of natural origin. Strong correlations between Mg, Mn, and Zn were found by Norela et al. (2013) during the July to September haze in Peninsular Malaysia (mostly $r^2 > 0.8$, $p < 0.01$). The correlation values between metals in this study with $p < 0.01$ were Mn and Mg ($r^2 = 0.66$), Pb and Mg ($r^2 = 0.15$), Zn and Mg ($r^2 = 0.64$), Pb and Mn ($r^2 = 0.74$), Zn and Mn ($r^2 = 0.76$), and Zn and Pb ($r^2 = 0.60$), suggesting that haze during the northeast monsoon could be from both natural and anthropogenic sources. Based on Table 4, it can be seen that the heavy metals and major ions in the rainwater was influenced by anthropogenic sources such as vehicle emissions and biomass burning.

HACA clustering patterns

The dendrogram produced by HACA showing the distribution of the variables is depicted in Fig. 6. From the result, group 1 consists of Ca, Mg, and Na, whereas group 2 consists of Pb, NO_3^-, Cu, Zn, Mn, and SO_4^{2-} and group 3 includes Ni, Fe, and K. The classification of each of the variables into the same group is most likely because of the similar characteristics in terms of their sources. Variables in group 1 are correlated strongly to each other ($r > 0.82$) (Table 3). The EF values for these variables range from 0.01 to 0.05 which indicates that the sources of Ca, Mg, and Na are likely to be natural Earth's crust sources. Variables in group 2 also show a similar pattern as they have strong correlations with each other (Table 3). In terms of EF values, these variables recorded

values that were more than 200, suggesting these variables shared a common anthropogenic source. Group 3 is a mixed group where, based on the EF values, the sources of these variables are from both natural Earth's crust and anthropogenic sources. Only Ni and Fe show strong correlations in this group. Ni and Fe can be originated from industrial emissions. While, K can be originated from both anthropogenic such as fertilizers (Reimann and de Caritat 1998) and natural sources such as clay minerals.

Thus, the results of correlation and HACA reasonably explained the co-existence of Ni and Fe in group 3. However, it should be noted that the outcome of EF differs with the results from correlation analysis and HACA. Further works including analysis of dry precipitation is needed to examine the effects and relationships of dust fall on the chemical composition of rainwater. Long-term data collection and monitoring are needed to arrive at meaningful valuations and correlations between differences in composition over time and the type of meteorological events.

Conclusions

The monitoring results of pH demonstrated that the rainwater was acidic in nature, except the first rain after a long period of dry spell. The anthropogenic input of trace gases such as SO_x and NO_x might be the main reason to explain the acidic rain as the location of the sampling site was in close proximity to urbanized areas. Further, the results of pH and NF in the

rainwater samples showed that the pH value switch considerably from near neutral (pH 6.54) to acidic (<pH 4.00) during the haze to non-haze transitional period, suggesting that the removal of sulfate and nitrate via the precipitation process was relatively higher than the removal of the mineral components. The NF suggests that the crustal components (soil mineral particles) can neutralize a larger fraction of the available acid in the first rain. The results of the rainwater compositions showed that the most dominant anion recorded was NO_3^- followed by SO_4^{2-} and Cl^-. The trend in the average concentrations of heavy metals in the rainwater was Zn > Fe > Al > Mn > Cu > Pb > Ni. The highest average concentration reported for Zn was 28.12 $\mu g\ L^{-1}$ ($\pm$22.87 $\mu g\ L^{-1}$) while the major elements followed an order of Ca > K > Na > Mg. The results of the scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis indicated that Zn, Al, and Mg were possibly emitted from a similar anthropogenic origin. The source identification by EF, correlation, and HACA demonstrated nearly similar characteristics of Ca, Mg, and Na. The BT model and number of biomass fire locations showed that pollutants were transported from the mainland of Indo-China and marine region in the South China Sea. This study recommends a need for long-term monitoring of rainwater chemistry in the region especially during haze event.

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