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VARIATION OF PM$_{10}$ AND HEAVY METALS CONCENTRATION OF SUB-URBAN AREA CAUSED BY HAZE EPISODE

(Variasi PM$_{10}$ dan Kepekatan Logam Berat di Kawasan Separa-Bandar disebabkan oleh Episod Jerebu)

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Abstract

A severe haze episode has swept across Malaysia in late June until October 2015 and has caused sharp rises of Air Pollution Index (API) across the country. This study was conducted to evaluate the effects of haze event on the API sub-indices during 10 days of the sampling period. The air particulate samples (PM$_{10}$) were collected at an open site in UiTM Jengka, Pahang by using high volume air sampler (HVAS). The standard acid digestion method was applied to dissolve the sample and the concentrations of heavy metals were analyzed by inductively coupled plasma – optical emission spectrometry (ICP–OES). The API sub-indices were calculated based on the standard method applied by Department of Environment (DOE) Malaysia. The results showed significant differences in PM$_{10}$ mass between haze and non-haze days, which were ranged between 28.4 µg/m^3 to 132.9 µg/m^3 and 17.3 µg/m^3 to 34.7 µg/m^3 for the respective two sampling intervals, haze and non-haze days. The mass concentrations of the studied metals did not show any significant different between the two intervals which indicates other constituent of particulate has contributed to the different weight of PM$_{10}$. The highest API sub-indices during haze days was recorded as 89 which is classified as moderate level of air pollution. The overall results clearly showed that haze event has increased the PM$_{10}$ mass of the surrounding air but not the concentration of heavy metals.

Keywords: API sub-indices, haze episode, high volume air sampler, particulate matter less than 10 µm

Abstrak

Episod jerebu yang teruk telah melanda Malaysia pada akhir bulan Jun hingga Oktober 2015 dan telah menyebabkan peningkatan mendadak Indeks Pencemaran Udara (API) di seluruh negara. Kajian ini dijalankan untuk menilai kesan daripada peristiwa jerebu kepada nilai sub-indeks API sepanjang 10 hari tempoh pensampelan. Sampel udara (PM$_{10}$) telah dikumpulkan di kawasan terbuka di UiTM Jengka, Pahang dengan menggunakan alat pensampel udara isipadu tinggi (HVAS). Kaedah pencernaan asid telah digunakan untuk melarutkan sampel dan kepekatan logam berat telah dianalisis menggunakan spektrometer pancaran optik plasma gandingan aruhan (ICP–OES). Sub-indeks API dikira berdasarkan kaedah piawai yang digunakan oleh Jabatan Alam Sekitar (JAS) Malaysia. Hasil kajian menunjukkan perbezaan yang signifikan bagi jisim PM$_{10}$ antara hari berjerebu dan bukan jerebu, yang direkodkan antara 28.4 µg/m^3 hingga 132.9 µg/m^3 dan 17.3 µg/m^3 kepada 34.7 µg/m^3 bagi masing-dua selang pensampelan, hari jerebu dan hari tidak jerebu. Kepekatan jisim logam yang dikaji tidak menunjukkan sebarang perbezaan yang signifikan antara kedua-dua selang yang menunjukkan konstituen lain zarah telah menyumbang kepada berat PM$_{10}$. Sub-indeks API paling tinggi semasa hari jerebu telah direkodkan sebagai 89 yang diklasifikasikan sebagai pencemaran udara tahap sederhana. Keputusan keseluruhan jelas menunjukkan bahawa peristiwa jerebu telah meningkatkan jisim PM$_{10}$ di udara sekitaran tetapi tidak bagi kepekatan logam berat.

Kata kunci: sub-indeks API, episod jerebu, alat pensampel udara isipadu tinggi, jirim partikel kurang daripada 10 µm

Introduction

Since a few decades ago until now, South East Asia has experienced severe air pollution phenomenon referred as haze [1]. Haze is caused by the emissions from biomass fires [2] and is formed when gaseous pollutants react in the atmosphere. Haze has been a continuing problem in the Southeast Asia's region, and Malaysia is one of the countries that have been badly affected by haze. A significant amount of particulate matters has been transported from a neighboring country, Indonesia due to the uncontrollable biomass fires [2]. The event increases fine particles concentration suspended in air and could give an adverse effect on human health. In September 2015, Malaysia had experienced deterioration of air quality due to massive land and forest fires in Sumatra and Kalimantan, Indonesia [3]. Thirty-four areas in the country recorded unhealthy air quality status for the first time in Malaysia's history since 1997. API reading has reached up to 200 which caused most of the schools to be closed.

The concentration of chemical composition of particulate matter (PM$_{10}$) has also been widely investigated in haze studies because it is directly connected to the potential human health risk [4]. The increases in respiratory diseases, cancer risk, cardiovascular mortality, hospital admissions and morbidity of human beings was due to the long-term exposure to the high concentration of PM$_{10}$ in the ambient air [5, 6]. There was also a remarkable positive interaction between the concentrations of the total suspended particulate (TSP) and lung dysfunctional in children [7].

Studies relating the effects of air pollutants on human health are rarely conducted in rural or sub-urban areas because of many reasons which depend on the particular site. In general, it was related to cost, man-power and the benefit of the study outcome. This study was conducted specifically to measure the API based on the measured gravimetry sub-indices and to evaluate the metal concentration along the sampling intervals in sub-urban site during haze episode. It is hope that the outcome of this study could be used as a supporting data for the related local agencies to evaluate and observe the effect of haze event on the local sub-urban population.

Materials and Methods

Sampling site

PM$_{10}$ levels was monitored for a period of 24-hours for 10 days during haze condition (17/09/15 to 3/10/15) and non-haze condition (1/3/16 to 13/03/16) at an open site in Universiti Teknologi MARA Pahang Campus. The specific latitude was at 3° 46'6.50" N and 102° 32'43.41" E. In general, the chosen studied location experiences an ambient temperature of 38 °C to 40 °C during daytime and gradually decreases along the night. The position was almost 200 meters away from the main road and no major industrial activities operated around the area.

Sample collection

Air particulate samples (PM$_{10}$) were collected on the pre-weight glass fiber filter with diameter 203 x 254 mm^{2} (Advantec GA–55) using the high volume air sampler (Sibata HV – 1000F) instrument. The air particulate collector was operated with a constant flow rate at 1054 L/min. Samples were taken for 10 times (17 September to 3 October 2015). The loaded filters were conditioned in the desiccator for a week before the weight of the total gravimetrical mass was measured.

Sample treatment-wet digestion

The exposed filter (195 x 250 mm^{2}) was cut into 12 strips. For the purpose of acid extraction, the filter strips were cut into a smaller size. The selection and preparation of filters, extraction, and extraction of metals from filter strip were carried out based on the USEPA method (USEPA-Method IO-3.2, 1999).The exposed filter strip was dissolved in a mixture of 20 mL of 3% HNO$_3$ and 10 mL of 8% HCl solution. The mixture was heated using hot plate for 120 minutes at 150 °C until dryness and cooled at room temperature. The deionized water was added and filtered before bringing up to the final volume 100 ml. The metal concentrations in this study were analysed by using ICP – OES.

Assessment of soil contamination
Enrichment factor (EF) were evaluated to verify heavy metals in soil originate from geogenic or anthropogenic origins. It is frequently supposed that the contents of elements in a natural medium can be justified specially by crust or geogenic origin [8, 9]. The EF value was calculated based on the following formula in equation 1 below:

$$EF = (M/Fe) \text{ sample} / (M/Fe) \text{ reference} \tag{1}$$

where M is the metal in consideration and Fe is a reference metal. To develop the sensitivity of the EF to the iron mine influence, the soil at a reference site was utilized as a reference. According to Zhang and Liu [10], EF values between 0.05 and 1.5 reveal that the metal is exclusively from crustal origins or natural developments; however, EF values higher than 1.5 imply that the origins are more probable to be anthropogenic.

PM_{10} gravimetry mass distribution trend
The mass concentration of the suspended particulates with the size limited to 10 micron and below was calculated by using the following equation 2:

$$TSP = [(W_f - W_i) / Vt] \times 10^6 \tag{2}$$

where TSP is defined as concentration of particulate matter, $\mu g/m^3$, W_f is the final weight of the filter paper (grams), W_i is the initial weight of the filter paper (grams), V_t is the total volume of air sampling and 10^6 is conversion factor from grams to micrograms.

Variation of sub-air pollution indexes
The sub-indexes API reading in this study was calculated solely based on the mass concentrations of PM_{10} with the following equation 3:

$$Ii = (Ci / Si) \times 100 \tag{3}$$

where Ii is type of pollutant, Ci is concentration of pollutant and Si is reference value (attention state).

Heavy metal mass concentration in PM_{10} samples
The mass concentration of heavy metals contained in the PM_{10} samples was calculated using the following equation 4:

$$C = [(C_i \times V_f \times UFA)] / Vstd \tag{4}$$

where C is Concentration ($\mu g/m^3$), C_i is metal concentration determined ($\mu g/L$) – data obtained from ICP, V_f is total sample extraction volume from extraction procedure (L), UFA is usable filter area (8" x 9")] divide exposed area of one strip, and Vstd is standard air volume pulled through the filter (m^3).

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Results and Discussion
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The gravimetry mass of the PM_{10} measured during and after haze event was summarized in Table 1.

The average concentration of particulate samples (10 micron and below) observed during 10 days of haze event was 81.20 $\mu g/m^3$. The highest value of PM_{10} concentration was recorded on 30 September 2015 with 132.96 $\mu g/m^3$, while the lowest value was recorded as 28.40 $\mu g/m^3$, on 21st September 2015. The average daily PM_{10} level recommended in the Malaysian Ambient Air Quality Guidelines for PM_{10} is 150 $\mu g/m^3$ [11]. Concentration of PM_{10} above 150$\mu g/m^3$ in 24 hours is considered unhealthy to humans. The overall PM_{10} mass concentration measured during non-haze condition was lower compared to samples collected during haze days. The average mass concentration of PM_{10} during non-haze day was measured as 26.88 $\mu g/m^3$, which was 66.89% lower compared to the value during the haze event. The highest value of PM_{10} mass concentration recorded during non-haze days (34.72 $\mu g/m^3$) was recorded on the 10th of March 2015 while the lowest value of PM_{10} mass concentration

(17.26 µg/m^3) was recorded on the 7th of March 2015. The results of this study clearly showed that all the particulate mass during the haze days were higher compared to the non-haze days at least by 30%.

Table 1. Mass of Particulate Matter (PM$_{10}$) during and after the haze episode

Sampling Date (Haze day)	PM$_{10}$ (µg/m^3)	Sampling Date (Non-Haze day)	PM$_{10}$ (µg/m^3)	% Mass Difference
17/9/15	46.72	1/3/2016	25.57	45.26
18/9/15	117.28	2/3/2016	25.76	77.79
19/9/15	102.85	3/3/2016	26.09	74.51
21/9/15	28.40	7/3/2016	17.26	39.22
28/9/15	83.48	8/3/2016	21.81	74.63
29/9/15	95.61	9/3/2016	31.63	62.52
30/9/15	132.96	10/3/2016	34.72	73.48
1/10/15	66.42	11/3/2016	29.12	56.16
2/10/15	88.23	12/3/2016	22.20	74.84
3/10/15	50.08	13/3/2016	34.66	30.60
Average	81.20	Average	26.88	60.90
Minimum	28.40	Minimum	17.26	30.60
Maximum	132.96	Maximum	34.72	77.79

The strong and medium winds during September to November 2015 probably was created turbulent conditions which causes frequent dust storm and hazy condition in the study area [12]. The hazy condition has built up high particulate matter levels in the low altitude ambient air. The result obtained in this study clearly shows that the haze event has increased the PM$_{10}$ gravimetry mass compared to the normal ambient condition. However, the average PM$_{10}$ concentration measured in this study for haze and non-haze events not exceed the concentration limit as recommended by the Malaysian Ambient Air Quality Guidelines by DOE [13].

The sub-API data measured during the haze and non-haze days was summarized in Figure 1. The average sub-indices API during the haze days were observed at the level of 54. The highest sub-indices API during the ten days of haze was 87 which were recorded on 30 September 2015, and the lowest sub-indices API was at the level 19, on 21 September 2015. Based on the measured Air Pollution Indices level, the sub-indices API measured during haze episode were categorized at moderate level (index level below than 100). If the API readings exceed 100, it will cause long-term health problems to humans such as cancer risk, cardiovascular mortality, and respiratory diseases [6] which is not the case in our study.
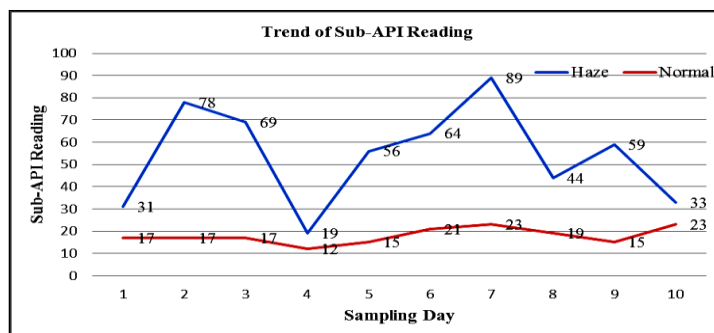

Figure 1. Sub-indices API during haze and non-haze days

In general, the sub-indices API observed along ten non-haze days were recorded at a lower index level compared to the haze days. The highest API level (at level 23) was observed on 13th of March 2016 and the lowest API reading (at level 12) was recorded on 7th of March 2016. All the API reading observed during non-haze days was not exceeded 50 in API reading which classified as good ambient air condition.

The average mass concentration of several atmospheric metal pollutants (Cu, Ni, Pb, Fe, Mn and Zn) during both haze and non-haze periods are presented in Table 2. The mean concentrations for the seven elements in PM_{10} samples follow the order of Zn, Fe, Cu, Pb, Mn, Cr and Ni during both haze and non-haze days. The average mass concentration of all studied elements contained in PM_{10} samples collected during haze period was only slightly different compared to the non-haze days (small ratio value). The low ratio of the mass concentration of Cu, Ni, Pb, Fe, Mn and Zn which were all below 1.5 ratio between haze and non-haze days clearly indicate that the haze particles has not affected the concentration levels of the studied elements in the PM_{10} samples.

Table 2.   Average concentration of heavy metals during haze and normal ambient condition

Elements	Haze Days (µg/m³)	EF Value	Non- Haze Days (µg/m³)	Haze/Non-Haze Ratio	Correlation Coefficient, r						
					Cu	Ni	Pb	Fe	Mn	Zn	Cr
Cu	0.092	0.89	0.083	1.1	1	0.25	0.42	0.21	0.61	0.76	0.75
Ni	0.012	0.23	0.009	1.3		1	0.07	0.09	0.27	0.09	0.16
Pb	0.042	0.33	0.039	1.1			1	0.32	0.52	0.63	0.53
Fe	0.969		0.815	1.2				1	0.11	0.30	0.27
Mn	0.030	0.66	0.028	1.5					1	0.67	0.61
Zn	39.691	1.23	32.230	1.2						1	0.98
Cr	0.020	0.11	0.018	1.1							1

High correlations (0.76 – 0.98) were observed for the pair of Cu, Cr and Zn which indirectly indicates that the metals probably were contributed by the same sources. Furthermore, the moderate correlations were observed for Cu-Mn. Pb-Mn, Pb-Zn, PB-Cr, Zn-Mn and Mn-Cr which correlated with the r values within 0.52 to 0.67. The moderate correlation between the metals suggested there would be various emitters released the metals around the study area. The other pairs which recorded low correlation coefficients indicate that the metals were not originated from the same emitters. Based on the correlation analysis of the element pairs and the EF values measured, it would be suggested that all the studied metals were originated from lithogenic or geogenic sources. With the overall observation, this finding suggests a reasonable uniformity in the contribution of the different metal sources to PM_{10}. The high mass concentration of PM_{10} samples measured during haze days would probably be influenced by the other constituents such as hydrocarbon, biological matter, organic and inorganic compounds and acid aerosols [14].

Conclusion
Studies about the air quality in the sub-urban areas are rarely done because there are less economic activities carried out in these areas compared to the urban sites. The results obtained from the study clearly showed that the Air Pollution Index (API) readings are generally at a scale below the guidelines set by the Department of Environment Malaysia. Moreover, the concentrations of heavy metals contained in the PM_{10} samples were still in the safe zone. The concentration of PM_{10} also below the guidelines set by the Department of Environment. It could be concluded that the metal concentration in PM_{10} was not directly influenced by the increasing PM_{10} mass during haze episode.

Acknowledgements

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