Journal of Tropical Resources and Sustainable Science

journal homepage: jtrss.org

Identification of Polycyclic Aromatic Hydrocarbon and Heavy Metal in PM_{10} from Urban and Rural School Ambient

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Received 13 April 2017
Accepted 9 May 2017
Online 24 November 2017

Keywords:
PM_{10} fluctuation, automotive exhaust, roadside school, children risk

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Abstract

Particulate matter (PM_{10}) is a major pollutant of concern as it can be adsorbed with toxic substances like heavy metals and organic compounds like polycylic aromatic hydrocarbons (PAH). Automobile exhaust was among the most significant contributor towards the particulate matter problem in roadside areas of Malaysia. In addition, most of the school in Malaysia located close to the roadside to ease accessibility that consequently further increase health risk among children. In this study, aerosol samples from school ambient in urban area (Kota Bharu) and rural area (Jeli) were analysed for PAH and concentration of heavy metal (Pb, Zn and C) identification. Result found the concentration of PM_{10} was higher in urban site than rural site with mean concentration Kota Bharu and Jeli is 52.57μg/m^3 and 39.21 μg/m^3 respectively. The 1-methylnaphthalene was the only PAH detected in both urban and rural areas. Result suggested that the concentration of lead (Pb) is the most prominent heavy metal measured in Jeli, while concentration of zinc (Zn) is the most significant of heavy metal in Kota Bharu.

1. Introduction

Air pollution incidence was regarded as a serious problem which raised the concern for air quality in rapidly expanding cities like Chicago, Mexico City, Lagos, Cairo, Tokyo and Athens during the period of 1970s till 1980 (Valavanidis et al., 2008). Airborne particulate matter has high tendency to affect health and act as a foundation that damage the economy (Amarsaikhan et al., 2014). Particles in the atmosphere can be divided based on their size as coarse particulate matter and fine particulate matter. Particles with size less than 2.5 μm ($PM_{2.5}$) were referred as fine particles while those with size 2.5 μm to 10 μm (PM_{10}) were regarded as coarse particles (Chow et al., 1994; Motallebi et al., 2003). However, PM_{10} are the most important pollutant as they can carry numerous toxic elements from both anthropogenic and natural sources. The sources of PM may vary widely depending with human activities, including open burning (Afroz et al., 2003), dusts from roads (Karar et al., 2006; Wahid et al., 2014), construction sites (Karar et al., 2006; Dominick et al., 2012), combustion of fossil fuel (electric generation and internal combustion engines) (Afroz et al., 2003), motor vehicles (Lenschow et al., 2001; Afroz et al., 2003; Wahid et al., 2014), biomass burning (Chow el at., 1992; Abas et al., 2004) and industrial activities (Karar et al., 2006).

However, in Malaysia air pollutants from combustion of fuel in by automobile exhaust was regarded as the major cause of air pollution among developed areas in Malaysia (Rahman et al., 2015). This statement can be proved when data collected from the past 5 year study in year 2003 showed that approximately 70-75% of air pollutants in Malaysia were estimated to originate from mobile sources (Afroz et al., 2003). Particle emitted from automobile exhaust contains elemental carbon, organic compounds, including PAHs and trace amount of heavy metals from eng7ine abrasion and corrosion (Aryal et al., 2013). Polycyclic aromatic hydrocarbon (PAHs) belongs to a class of complex organic compounds, including carbon and hydrogen with at least two benzene rings fused to it (Azhari et al., 2011; Jamhari et al., 2014). However, the effect of air pollutants was severe to children due to their active behaviour, higher ingestion rate and inhalation rates with respect to their body size than adults.

Infant or child is extremely vulnerable to environmental interference because their organs are developing rapidly at an early stage of development, making them more susceptible to functional damage or disorders (Darus et al., 2012). It is speculated that children exposed to genotoxic environmental pollution have a high risk to develop cancer and other associated

eISSN Number: 2462-2389

health risk in the future (Tuntawiron et al., 2007; Jyethi et al., 2014). This was proven by Ruchirawat et al. (2007), as the DNA breaks for students in urban city, Bangkok was abruptly high with decreased DNA repair capacity compared to children's in rural areas based on the result by cytogenetic challenge assay which reflects higher chromosomal deletions per metaphase. Another study conducted in Sweden and United Kingdom also shows evidence that childhood cancer increases with exposure to motor vehicle exhaust (Tuntawiroon et al., 2007). As a conclusion, children living in capital cities might be exposed to with abruptly high amounts of cancer-causing air pollutants than children living in rural areas.

Therefore, this study aims to identify the PAH species and the concentration of heavy metals found in PM_{10} samples from urban and rural school ambient. From the identification and characterization of heavy metals found in the area, students and other school stakeholders will recognize environmental health threats that may be present in school areas and create awareness of this air pollution issues among the member of society.

2. Materials and Methods

2.1. Study Area

The study area chosen for sampling were Kota Bharu and Jeli in Kelantan as shown in Figure 1. The sampling site for Kota Bharu and Jeli were carried out at SMK Kubang Kerian 1 (N05º 7086, E 101º 7356) and SK Batu Melintang (N 06º 0925, E102º 2777), respectively. Kota Bharu was one of the rapidly growing towns in the state of Kelantan located in the east coast of Peninsular Malaysia. The total population in Kota Bharu is approximately 425,294 people and the city was the centre for business, industrial and government establishment (Fadzil et al., 2008). Meanwhile, Jeli was considered a new developed town of Kelantan that consisting of 9,690 populations in total and was regarded as a rural area (Jeli Land and Administration Office, 2014).

Figure1: Sampling location in rural area at SK Batu Melintang, Batu Melintang, Jeli

2.2. Sample Collection and Preparation

The aerosol samples were collected using a low volume air sampler (LVAS) (Model LV-20P, Shibata, Japan) fitted with PM_{10} selective inlet for 24 hours. The sampler was placed at a height of 1.5 m and the air flow rate of the sampler was set at 20 L/min. The glass fibre filters were baked in oven before sample collection to remove organic contaminants at 300°C for 5 h (Jamhari et al., 2014). All fresh and exposed filter papers were placed in a desiccator to absorb any moisture at 25°C for 24 h after baking (Lee et al., 2008).

The glass fibre filter paper was weighed before sampling and after sampling using microbalance and placed in a desiccator maintained at 25°C (Omar et al., 2002; Bahry et al., 2009). The mass of particulate matter on the filter paper was determined by the gravimetric method using microbalance to an accuracy ±0.000001 g. The gravimetric mass was measured at controlled humidity of 54.5% relative humidity (RH) and a temperature of 22.6°C. The initial mass of the filter paper was then subtracted with the final mass of the filter paper after sampling. All the exposed filter papers were folded and re-wrapped in aluminium foil and were stored in chiller at 4°C till the day of sample analysis.

2.3. PAH and Heavy Metals Identification

The detailed sample extraction methods were described by Salam et al. (2011). The aerosol samples ware extracted with 20 ml of dichloromethane (DCM) in an ultrasonic bath, centrifuged at 3000 RPM for 10 minutes and evaporated using rotary evaporator and nitrogen evaporator. The extracts were analyzed using GC-MS with 30 mm fused silica capillary column, 0.25 mm internal diameter and 0.25 μm film thicknesses. The GC temperature was held at 65°C for 2 minutes and raised to 280°C at 6°C/min. The sample was then held isothermally at 280°C for 20 minutes using helium as the carrier gas. The samples of 1 μL were injected under SCAN mode for qualitative analysis of PAHs. The PAHs was identified by comparing the spectrum found in the sample with the GCMS library. Quality control was conducted to ensure both sampling and measurement errors are minimized by conducting field blanks. The blank sample was run before the samples were analyzed to ensure there was no contamination. None of the target PAHs was detected in any sample when the procedural blank sample was run. All the glassware involved in this experiment were cleaned and rinsed with hexane and distilled water before baking in oven (5 hours at 200°C) to reduce sample error due to contamination.

Heavy metals from samples were extracted using the acid digestion method by NIOSH 7300 Method (SERAS). The filter samples were digested with concentrated nitric acid (HNO_3) and heated. The solution was then rinsed with deionised water and heated again

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before filtering and diluted in a volumetric flask. The sample was analysed for lead (Pb), zinc (Zn) and cadmium (Cd) using Flame Atomic Absorption Spectrometry model Analyst 800 (Perkin Elmer). Each of 10 ml of lead (Pb), cadmium (Cd) and zinc (Zn) stock solution were pipetted into each 1000 ml volumetric flask. About 20 ml of diluted nitric acid (25% concentrated nitric acid) and were filled to the mark of each volumetric flask with deionised water and mixed well. The extract was then brought for heavy metal analysis. The calibration curve was used to determine the unknown concentration of heavy metal. The standard was run for every five samples to check the spectrometry calibration.

3. Results and Discussion

3.1. Descriptive Statistics of PM_{10} Concentrations

The average concentration of PM_{10} recorded at Kota Bharu (urban) was higher than Jeli (rural) with 52.57 $\mu g/m^3$ (ranging from 24.86 - 99.55 $\mu g/m^3$) and 39.21 $\mu g/m^3$ (ranging from 18.01 - 86.05 $\mu g/m^3$), respectively, as shown using a box and whisker plot in Figure 2. The result also illustrated that variations in PM_{10} concentration measured in Kota Bharu were significantly higher than the concentration measured in Jeli as indicated by differences between upper and lower quartile and the box part. The average concentration of PM_{10} for both rural and urban areas does not exceed the limit set by Recommended Malaysia Ambient Air Quality Guidelines (RMAAQG). However, the average concentration of PM_{10} for urban area exceeded limit set by the EU Commission.

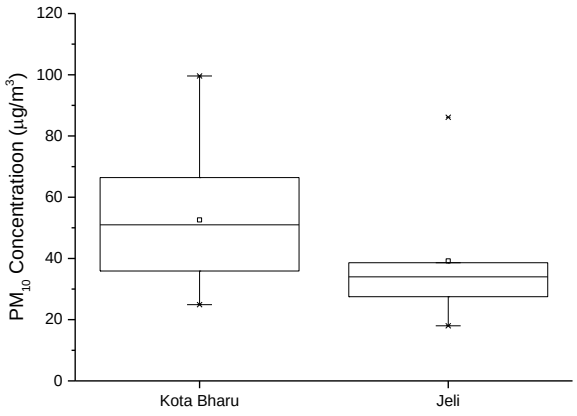

Figure 2: Box and whisker plot of PM_{10} concentration in Kota Bharu and Jeli

3.2. Daily and Monthly Variation of PM_{10} Concentration

The daily average PM_{10} concentration was used to analyse the monthly variations of PM_{10} for both urban and rural area as illustrated in Figure 3 and 4, respectively. In April, the highest concentration of PM_{10} was on the 24th of April with 99.55 $\mu g/m^3$ and the lowest was on the 23rd of April with 51.01 $\mu g/m^3$. For May, the concentration of PM_{10} was the highest on 7th of May which was 56.08 $\mu g/m^3$ and the lowest was recorded on 14th of May with 37.52 $\mu g/m^3$. The highest concentration of PM_{10} in June was recorded on 23rd of June with 37.94 $\mu g/m^3$ while the lowest was measured on 4th of June with 24.86 $\mu g/m^3$. Meanwhile, for rural which in Jeli site the highest concentration of PM_{10} in April was measured on 26th of April which was 38.39 $\mu g/m^3$ and the lowest was on the 27th of April with 32.78 $\mu g/m^3$ as shown in Figure 3. In May, high concentration of PM_{10} was recorded on 9th of May 76.63 $\mu g/m^3$ and lowest concentration was on 17th of May with 33.21 $\mu g/m^3$. In June PM_{10} concentration was the highest for 6th of June with 86.05 $\mu g/m^3$ had exceeded the European Union limit but still below RMAQG limit. While the PM_{10} concentration on 7th of June with 19.42 $\mu g/m^3$ was the lowest.

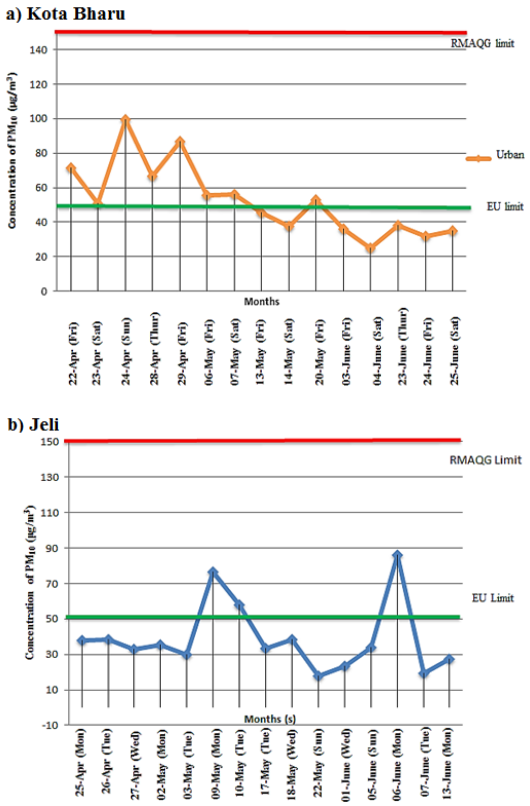

Figure 3: Daily variation of PM_{10} concentration in (a) Kota Bharu and (b) Jeli

The sources of PM_{10} in Malaysia mostly arise from natural sources (forest fires or biomass burning), industrial activity, power station operation, fossil fuel burning and transportations. Therefore, traffic and meteorological factors are the most related variables to explain the fluctuations of PM_{10} concentration in the study area. The average concentration of PM_{10} in urban areas was higher than Jeli as in Figure 2. A daily and monthly variation in PM_{10} concentrations is highly depends on changes in meteorological conditions. Annually, Malaysia experienced an intermission period, which associated with high intensity of rainfall from April

eISSN Number: 2462-2389

to May. The less amounts of rainfall contribute to higher concentrations of particulate matter in ambient air (Alias et al., 2007). The rain reduces the concentration of particulate matter collected through washout or wet deposition process (Alias et al., 2007). The concentration of particulate matter in ambient air also affected by the variations in source strengths and meteorological conditions such as mixing heights, precipitation, relative humidity, wind speed and direction as supported by air mass trajectories (Mkoma & Mjemah, 2011).

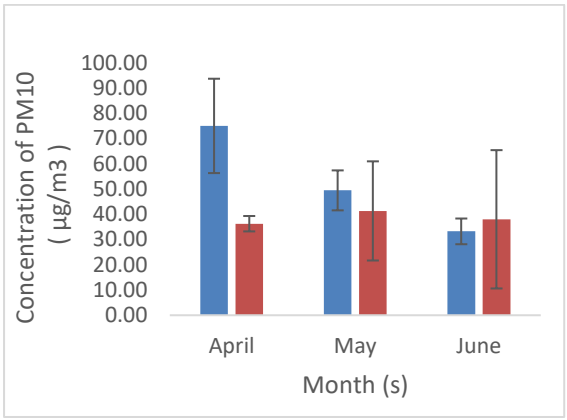

Figure 4: Monthly variation of PM_{10} concentration in Kota Bharu and Jeli

3.3. PAH in Urban and Rural Area

PAH detected was 1-methylnaphthalene from both urban and rural site sample as represented by Table 4 and 5. The frequency of detection was higher in the urban site which was in April and May while for rural site it was detected only in June. 1-methylnaphthalene was detected in the sample from urban and rural area as it was a common pollutant released from combustion of fossil fuels, wood, exhaust smokes and industrial discharge. PAHs was not detected in June might be due to the rainfall observed during the sampling days that reduce the amount of PAHs in atmosphere.

3.4. Heavy Metal in Urban and Rural

Figure 5 and 6 showed the variations weight distributions of heavy metals measure at urban and rural school ambient, respectively. Heavy metal characterized in this study was Pb, Cd and Zn. The result indicates that all the determined heavy metals were within the permissible limited set by the World Health Organization (WHO, 2011). Lead, Pb was present only in the rural sample with concentration ranging from 0.076 µg/m^3 to 0.669 µg/m^3. Zinc was present in urban and rural site with concentration ranging between 0.016 µg/m^3 to 0.094 µg/m^3 and 0.001 µg/m^3 to 0.155 µg/m^3. Meanwhile, cadmium ranged between 0.022 µg/m^3 to 0.041 µg/m^3 from urban site and 0.061 µg/m^3 to 0.108 µg/m^3 in rural sites.

Table 4: PAH found in urban area PM_{10} samples

No	Sample date	Concentration of PM_{10} (µg/m^3)	Weather	PAHs detected	Ring number
1	22nd April 2016 (Friday)	51.01	Sunny	1-methyl naphthalene	2
2	24th April 2016 (Sunday)	99.55	Sunny	Not detected	-
3	14th May2016 (Saturday)	37.52	Sunny	Not detected	-
4	7th May 2016 (Saturday)	56.08	Sunny	1-methyl naphthalene	2
5	4th June 2016 (Saturday)	24.86	Sunny	Not detected	-
6	23rd June 2016 (Thursday)	37.94	Rainy	Not detected	-

Table 5 PAH found in rural area PM_{10} samples

No	Sample date	Concentration of PM_{10} (µg/m^3)	Weather	PAHs detected	Ring number
1	27th April 2016 (Wednesday)	32.78	Sunny	1-methyl naphthalene	2
2	26th April 2016 (Tuesday)	38.39	Sunny	Not detected	-
3	22nd May 2016 (Sunday)	18.01	Sunny	Not detected	-
4	09th May 2016 (Monday)	76.63	Sunny	Not detected	-
5	07th June 2016 (Tuesday)	19.42	Rainy	Not detected	-
6	06th June 2016 (Monday)	86.05	Rainy	Not detected	-

The presence of Pb in Jeli samples majorly due to automobile emission as well as the deposition process that occurred in the vicinity of the roadside (Darus et al., 2012). High concentrations of Pb found in this study may be as the consequences of the high number of vehicles passing through close to sampling area. Vehicles that use leaded gasoline might contribute to higher emission of Pb in the atmosphere, but Pb in ambient air has decreased considerably with the phase down of lead in gasoline (Geiger and Cooper, 2010).

Sources of other heavy metals such as Zn also related to automobile emission (Darus et al., 2012). Both urban and rural areas had detected Zn elements. The sources of Zn in dust may originate from automotive sources such as from wear and tear of vulcanized rubber tyres, lubricating oils and corrosion of galvanized vehicular parts (Darus et al., 2012). It may also come from human activities such as mining, steel production, coal and waste burning (Geiger and Cooper, 2010). Meanwhile, Cd element only presents in rural and urban

eISSN Number: 2462-2389

samples from burning of fossil fuels, incineration of municipal waste, or from zinc, lead and copper smelters. According to Geiger and Cooper (2010), smoke from cigarette smoking is also another source of airborne Cd.

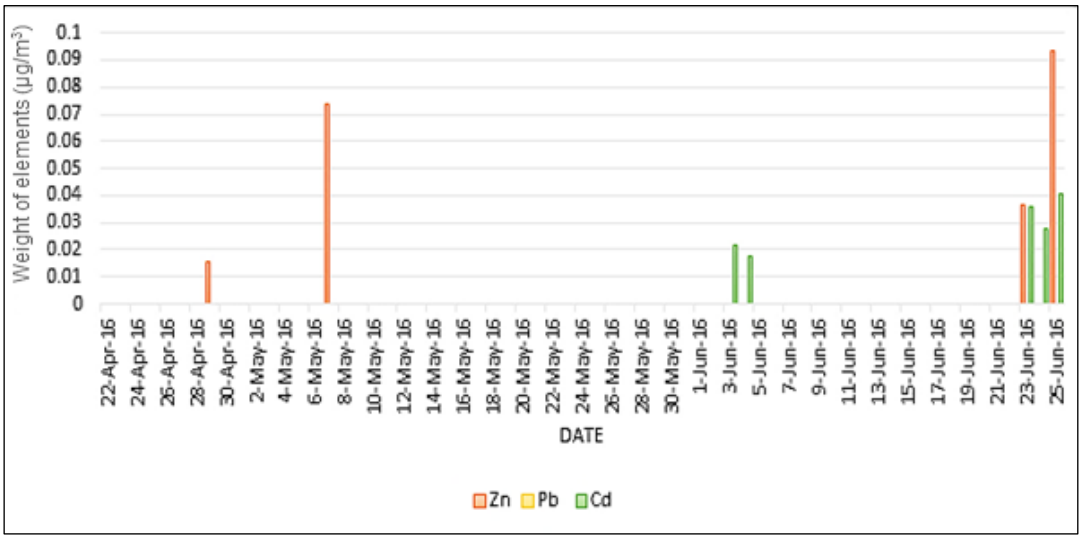

Figure 5: Heavy metal concentration in PM_{10} for urban site

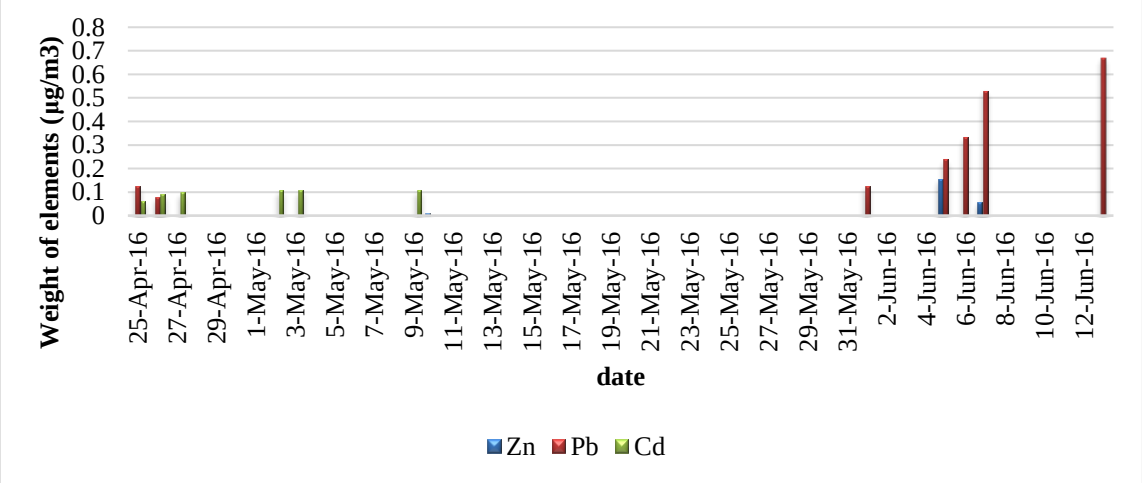

Figure 6: Heavy metal concentration in PM_{10} for rural site

4. Conclusion

The average concentration of PM_{10} recorded at Kota Bharu (urban) was higher than Jeli (rural) with 52.57 µg/m^3 and 39.21 µg/m^3, respectively. The concentration of PM_{10} for all samples is within the limit set by RMAQG. PAH detected in the study was 1-methylnaphthalene, a two ring PAH which shows there is a high influence of automobile exhaust in urban and rural site of Kelantan. Besides that, heavy metal characterized in the study, which are Pb, Cd and Zn were found in higher in rural sites compared to urban site. However, none of the characterized heavy metal exceeded the daily limit by WHO.

Acknowledgement

This study funded under grant R/FRGS/ A08.00/ 01228A/001/2016/000373 and authors would like to acknowledge Faculty of Agro Based Industries, Universiti Malaysia Kelantan, Universiti Sains Malaysia for their instruments in research. We would thank the principal of SK Batu Melintang and SMK Kubang Kerian for sample collection.

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eISSN Number: 2462-2389