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Identification of Cation Elements in PM_{10} Concentration in Industrial Area of Penang

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Abstract

This study aims to investigate the concentrations of particulate matter with aerodynamic diameter less than 10 micron (PM_{10}) and their associated cation elements in PM_{10}. The sample of PM_{10} were collected at Royal Malaysian Customs Department (N5° 22' 012"; E100° 23'589") located in Perai Industrial Area, Penang, from June to September 2015. The sampling was carried out during the southwest monsoon and a total of 12 samples were collected using low volume sampler (LVS). Result suggested that there are five elements that commonly identified from PM sampled which are ammonium, sodium, potassium, calcium and magnesium. The concentrations of the cation from all four months in the industrial area shows the order of $NH_4^+ > Ca^+ > K^+ > Mg^{2+} > Na^+$. The lowest and highest concentrations calculated both were ammonium (0.012 µg/m³) in July and (0.873 µg/m³) September, respectively.

1. Introduction

Particulate matter (PM) is one of the factors that cause the declining of the urban air quality both in developed and developing countries. The majority of Asian countries have undergone rapid economic development during the last decade thus contributed to higher emission of air pollutants. Increased of urbanisation, industrialization, and vehicular usage in these cities, coupled with trans-boundary haze pollution and Asian dust (AD) phenomenon. The concentrations and chemical composition of aerosol vary from day to day; hence, aerosol behaviour must be observed for a long period, in order to achieve a more precise source identification of the aerosols (Okuda *et al*, 2004). Regarding by this issue, a PM monitoring program have been conducted at six cities in Asia that have two distinct seasons; dry and wet which include Bandung, Bangkok, Beijing, Chennai, Manila, and Hanoi. In all six cities, the levels of PM_{10}, 54 - 262 µg/m^3, and $PM_{2.5}$,44 - 168 µg/m^3, were found high, especially during the dry season, and for the wet season, PM_{10} and $PM_{2.5}$ decrease to 33 - 180 µg/m^3 and 18 - 104 µg/m^3. The PM spatial and temporal distribution and the reconstructed mass give qualitative information on major contributors to PM levels in a city (Oanh *et al*, 2006). In the recent decades, particulate matter has been one of the major interesting research subjects in China. Most of the time, northern part of China is the main location of the research as several studies have revealed for a long term PM_{10} trend for key cities from year 2001 to 2011 by Cheng et al. (2013), the annual PM_{10} concentration decreased from 116.4 µg/m^3 in 2001 to 85.3 µg/m^3 in 2011, at a rate of~3 µg/m^3 per year. In year 2013, the annual mean of PM_{10} concentrations in urban, rural village and rural field sites were 180 ± 171 µg/m^3, 182 ± 154 µg/m^3, and 128 ± 89 µg/m^3, respectively (Li et al., 2014).

Particulate matter has linked to the significant health problems, including premature mortality, chronic respiratory disease, respiratory emergency room visits and hospital admissions, aggravated asthma, acute respiratory symptoms, and deceased lung function (Fierro, 2000). This is because, when the particulates enter the lungs, it will decrease the oxygen intake and cause the respiratory problem (Alias,2007).

Malaysia ambient air quality guideline was introduced to overcome the health problem cause by the particulate matter based on PM_{10}. However, the guideline not considered the effect of inorganic chemical composition such as toxic heavy metals and ions. Moreover, there is no baseline information regarding the cation elements which one of the main composition of particulate matter in Malaysia. At the best of our knowledge, very few research were conducted on associated ions in PM_{10} concentration, while none of the research conducted in Penang. Encouraged by the lack of the information, this study embarked focusing on cation elements such as potassium, calcium, magnesium,

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ammonium and sodium found in PM10 concentrations sampled from industrial area of Penang. The comprehensive study of cation elements was carried out in order to identify the most common cation found in PM10.

2. Materials and Methods

2.1. Sampling Location

Penang is an island-state that located between E 100° 8' and E 100°32' longitude and N 5° 8' and N 5° 35' latitude in northern region of Peninsular Malaysia that cover approximately 1,030 km^2. Penang made up by two separate area known as Penang Island and Seberang Perai on the mainland. The sampling location is located at Royal Malaysian Customs **Department, Perai** (N 5° 22' 012" E 100° 23' 589") near the fire station in the Perai industrial area (N 5° 23' 4704" E 100° 23' 1977") (NHERI, 2010) as shown in Figure 1.

Figure 1: Sampling location at Penang First Bridge (Source: Google Map, 2016)

2.2. Aerosol Sampling

PM_{10} sample collected from June until September 2015 at Royal Malaysian Customs Department in Perai Industrial Area, Penang. The sampling was done between June and September 2014 which undertake during the southwest monsoon. Sample collected using 25mm in diameter quartz filter paper (Sibata Co.Japan) by Low Volume Air Sampler (LV-20P). The filter paper weighed before the sampling procedure with five-digit electronic microbalance (DC12V 0.3A, Japan) and denoted as initial weight. PM_{10} sample collected using filter holder NW-3510 for the coarse particle at flow rate of 20 L/min over a 24 h period for each sample. The filter paper was enfolded with aluminium foil and placed into furnace for 5 h at 500°C to evacuate all the impurities from the filter paper prior to sampling activity. During the sampling procedures, a blank filter paper was placed inside the LVS without operating the flow meter to obtain the field blank which will be essential during chemical analysis. Right after the sampling, the filter papers were weight once again to obtain the final weight. The gravimetric mass for the particulate matter determine by the difference between initial and final weight. The sampled filter paper then enfolded back with aluminium foil after measuring the final weight and stored in a refrigerator at -20° C prior to chemical analysis.

2.3. Chemical Analysis

The chemical analysis for the soluble ionic species of cation (potassium, ammonium, calcium, magnesium and sodium) after the sample collection then further with the ion extraction and then assayed for cation determination using the Ion Chromatography.

The portions of filter paper for analysis were placed into centrifuge tube. Both the filter paper and centrifuge tube were weight. The centrifuge tube then added with 50 ml of deionized water for the ion extraction. The centrifuge tube with the samples were placed in the ultrasonic bath (< 27°C) with medium frequency for 25 min and then shaken by the laboratory shaker for one hour. The samples then filtered and kept in the 4° C for chemical analysis process. The extracted sample was then injected into ion chromatography for the detection of cation using eluent 1.7 mM HNO_3 and 1.7 mM dipicolinic acid.

2.4. Quality Assurance and Quality Control

The particulate matter mass measurement should be carried out in a controlled environment of temperature and relative humidity to obtain the accurate gravimetric measurement. In addition, the field blank filter paper was ensured to be sampled at same spot as the sampling location for similar sampling duration because the field and procedure blanks were used to determine the cross contamination for every samples. Both blank filter papers also undergo similar digestion and analysis procedures.

3. Results and Discussion

3.1. PM_{10} Concentration

The average concentration of PM_{10} showed a variation between months of sampling by comparing simple descriptive statistic. Table 1 present the range (min and maximum), median, mean and standard deviation (std) of the PM_{10} concentrations. From this table, it can be view that the highest mean concentration of the PM_{10} at the industrial is in July by 50.58 µg/m³ followed by June, 44.21 µg/m³. The single most striking observation to emerge from the data comparison was the maximum value of July that striking to the 91.67 µg/m³ that increase the standard deviation to 35.71µg/m³ that show the data in July vary greatly compared to the September that only have 4.34 µg/m³. The lowest average concentrations can be seen from the table by 25.63 µg/m³ in September that ranged from 22.38 to 30.56 µg/m³. The concentrations of PM_{10} collected during the sampling period were below the Malaysian Ambient Air Quality Guidelines (RMAAQG) that is 150 µg/m³ for 24 h average.

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Table 1 Concentrations of PM_{10} fraction measured in Perai Industrial Area

Month	Min (μg/m³)	Max (μg/m³)	Median (μg/m³)	Mean (μg/m³)	Std (μg/m³)
June	29.51	61.46	41.67	44.21	16.13
July	27.08	91.67	32.99	50.58	35.71
August	29.51	43.06	31.60	34.72	7.26
Sept	22.38	30.56	23.96	25.63	4.34

Figure 2 presents the monthly concentrations during the sampling period in industrial area. The result suggested that the pattern of the PM_{10} concentration fluctuate from June until September 2015 but on 9th July 2015, the value dramatically increase compared to the day before. But, the plot shows declining and in August and slightly change in until September. The concentrations of PM_{10} during sampling period display small range of changes except for the 9th July 2015 because throughout the period is in the same southwest monsoon. The average of meteorological parameter of humidity is 75.6%, the wind direction is 220°, and wind speed is 7.5 m/s, temperature is 29.4°C and rainfall is 1.5 mm. The larger particles of aerosols were highly correlated with the meteorological parameter such as wind speed, indicative of soil dust and /or sea salt origin (Schwartz, 1996).

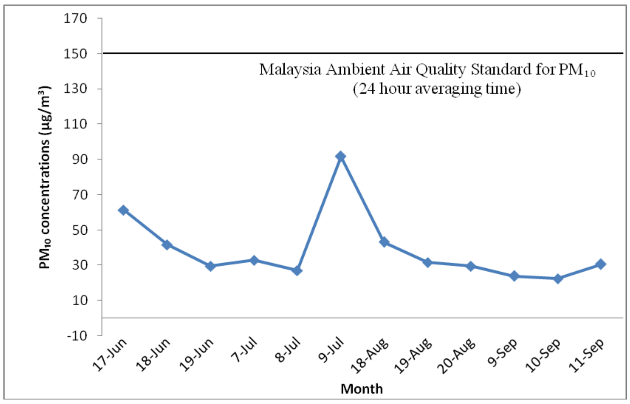

Figure 2: Monthly concentrations (μg/m³) of PM_{10}

Table 2 shows some related meteorological parameters that effected the concentrations of PM_{10} in the industrial area in Penang during the sampling period. September display high precipitation by 16.3 mm and the lowest by July, 0.7 mm. Temperature on June is the highest by 29.4° and descending until 26.9° on September.

The highest concentrations recorded on July have the lowest precipitation value 0.7 mm and highest wind direction value 305°. This allowed the occurrence of dust as the particulate matter relatively correlated with rainfall and relative humidity (Owoade *et al.*, 2012). On June, even though the temperature showed higher value than in July by 29.4 °C but the precipitation also higher than July that effect the lower mean concentrations of PM_{10} for the reason that the rainfall rinse out the particulate matter and decline resuspension of dust (Giri *et al., 2007)*. The precipitation was highest during sampling period on September that recorded value 16.3 mm which produce lowest concentrations of PM_{10}.

3.2. Cation Concentration in Particulate Matter

Table 3 displays the overview of means, standard deviations (std), range and medians of cation concentrations in Perai Industrial Area. As can be seen from Table 3, the cation concentration range of sodium, ammonium, potassium, calcium and magnesium obtained varied from 0.037 - 0.147 mg/kg, 0.020 -0.873 mg/kg, 0.031- 0.177 mg/kg, 0.097- 0.376 mg/kg, and 0.009 - 0.107 mg/kg, respectively. The concentrations of the cations from all four months in the industrial area shows the descending order of $NH_4^+ > Ca^+ > K^+ > Mg^{2+} > Na^+$. Based on Table 3, the ammonium shows the highest average (mean ± std) concentrations by 0.333 ± 0.38 mg/kg and the sodium as the lowest average with 0.086 ± 0.05 mg/kg.

Table 2 Mean concentrations of PM_{10} and related meteorological variables

	PM_{10} (μg/m³)	Relative humidity (%)	Precipitation (mm)	Temperature (°C)	Wind direction (°)
17-19/6/2015	44.21	75.6	1.5	29.4	220
7-9/7/2015	50.58	83.5	0.7	28.6	305
18-20/8/2015	34.72	78.0	2.8	28.5	283.33
9-11/9/2015	25.63	87.0	16.3	26.9	300

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Table 3: Elemental average concentration of cation in PM_{10}

Components	Concentrations of cation in PM_{10} (mg/kg)		
	Mean ± Std	Range	Median
Sodium	0.086 ± 0.05	0.037 - 0.147	0.076
Ammonium	0.333 ± 0.38	0.020 - 0.873	0.199
Potassium	0.087 ± 0.07	0.031 - 0.177	0.069
Calcium	0.227 ± 0.11	0.097 - 0.376	0.217
Magnesium	0.097 ± 0.01	0.009 - 0.107	0.097

Figure 3 shows sodium has the lowest concentrations in July but fluttered pattern in August and September. Then, the ammonium present dramatically changes on September after showed fluctuation for July and August. Potassium declined from July to August but gently arose in September. Differ with other elements, calcium sharply changes every month. The magnesium display slightly changes for all months.

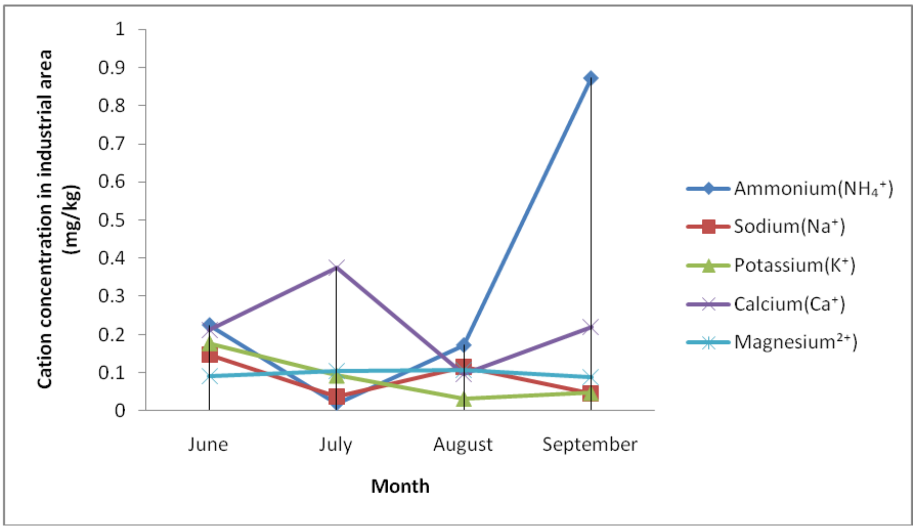

Figure 3: Monthly concentrations of cation

Pearson correlation coefficient was used to identify the relationship between PM_{10} concentration and cation as tabuled in Table 4. Correlation analysis method was used to analyse the relationship between the PM_{10} and the cation concentrations (Na^+, NH_4^+, K^+, Ca^+ and Mg^{2+}), the result of the correlational analysis are presented in the Table 4 that shows the relationship varied with correlation coefficients. Ammonium show the stronger negative relationship with r = -0.868 followed with moderate relationship of potassium, calcium and magnesium with r = 0.610, r = 0.609 and r = -0.38719. Sodium shows weak relationship with r = 0.102. Except the reverse result from sodium, all the elements correlate with the concentration of PM_{10} but was not significant even at 0.10. The potassium, calcium and sodium show the positive correlation with PM_{10} as it correlates with soil or crustal sources (John *et al*.,2007). Potassium and calcium show positive moderate relationship with particulate matter as the sampling site in the industrial area has heavy traffic during working days that become source of the K^+ and Ca^+ from the transportation that spread dust in the atmosphere of sampling area. The biomass burning also can be the major distribution of the Ca^+ (Alahmr *et al*., 2012).

Table 4: Correlation between PM_{10} and cation

	PM_{10}	Na^+	NH_4^+	K^+	Ca^+	Mg^{2+}
PM_{10}	1					
Na^+	0.101792	1				
NH_4^+	-0.86774	-0.29587	1			
K^+	0.610468	0.508234	-0.32875	1		
Ca^+	0.609854	-0.62844	-0.21185	0.310733	1	
Mg^{2+}	-0.38719	0.078049	0.723851	0.413576	0.031635	1

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4. Conclusion

The monthly concentrations of PM_{10} were measures at Perai Industrial Area, Penang from June to September 2015. The average concentrations of PM_{10} during sampling period were 39.79 ± 19.74 µg/m³ which is not exceeded the MAAQG of 150 µg/m³ Interim 1 by Department of Environment and the highest concentrations was on July by 50.58 µg/m³. Overall cation identification of PM_{10} in Perai was carried out using ion chromatography. The major cations of the particulate matter were considered to be ammonium by average concentrations, 0.33 ± 0.38 mg/kg, and lowest by sodium, 0.086 ± 0.05 mg/kg.

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