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Source Identification of Particulate Matter in a Semi-urban Area of Malaysia Using Multivariate Techniques

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Abstract This study aims to determine the composition and sources of particulate matter with an aerodynamic diameter of 10 μm or less (PM_{10}) in a semi-urban area. PM_{10} samples were collected using a high volume sampler. Heavy metals (Fe, Zn, Pb, Mn, Cu, Cd and Ni) and cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were detected using inductively coupled plasma mass spectrometry, while anions (SO_4^{2-}, NO_3^-, Cl^- and F^-) were analysed using Ion Chromatography. Principle component analysis and multiple linear regressions were used to identify the source apportionment of PM_{10}. Results showed the average concentration of PM_{10} was 29.5 ± 5.1 μg/m^3. The heavy metals found were dominated by Fe, followed by Zn, Pb, Cu, Mn, Cd and Ni. Na^+ was the dominant cation, followed by Ca^{2+}, K^+ and Mg^{2+}, whereas SO_4^{2-} was the dominant anion, followed by NO_3^-, Cl^- and F^-. The main sources of PM_{10} were the Earth's crust/road dust, followed by vehicle emissions, industrial emissions/road activity, and construction/biomass burning.

Keywords Particulate matter · Elemental composition · Soluble ions · Multivariate analysis · Source apportionment

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The issue of air pollution is widespread throughout the world and has adverse consequences on both human health and the environment. Particulate matter (PM) is one of the most common air pollutants and as such is used to monitor the level of environmental pollution (Viana et al. 2008). Recent findings on the health problems experienced following exposure to PM with an aerodynamic diameter of 10 μm or less (PM_{10}) include a decline in lung function and an increase in respiratory symptoms, chronic pulmonary disease, heart disease and premature death along with a rise in mortality (Mukae et al. 2001; Miller et al. 2007). The concentration of PM_{10} itself is dependent on several factors which include climate, season, land use and geographical location. A higher traffic density and the use of fossil fuel for combustion (heating purposes) might explain why the concentration of PM_{10} was found to be higher during the cold season (Harrison et al. 1997; Tsitouridou et al. 2003). Urban background, as a result of a high number of motor vehicles, more industries and a large quantity of road dust are also suspected to contribute to the level of PM_{10} in the atmosphere (Juneng et al. 2011).

In order to predict the sources of PM_{10}, it is necessary to determine its composition. PM_{10} usually consists of several

elements (Si, Al, Ca, Fe, Ti, V, Cr, Ni, Cu, Zn, Pb), inorganic ions (SO_4^{2-}, NO_3^-, Na^+, NH_4^+, K^+) and volatile organic compounds (Sunder-Raman et al. 2008). Previous studies on the composition of PM_{10} in Malaysia have shown that Fe recorded the highest reading of heavy metals, which indicated that heavy-duty vehicle emissions were the main source of PM_{10} around an incredibly busy highway (Ismail et al. 2011). However, according to Sulaiman et al. (2005), the concentration of Zn was the highest compared to Fe, Cr and Mn which showed an association between Zn and emissions from the use of car brakes, tyres and also different types of petrol fuel in vehicles (Sternbeck et al. 2002). According to Mohd Tahir et al. (2008), the majority of the trace elements recorded in the city centre were recorded at higher levels than at inner and outer city stations.

This paper presents the composition of PM_{10} in Bangi, which is a semi-urban area in Malaysia. The analyses focused on selected heavy metals (Fe, Zn, Pb, Cu, Mn, Cd and Ni) and ions (Na^+, Ca^{2+}, K^+, Mg^{2+}, SO_4^{2-}, NO_3^-, Cl^- and F^-). The source identification of PM_{10}, based on the elements detected from the samples in this area, was evaluated using a combination of principle component analysis (PCA) and multiple linear regression (MLR) techniques. This research may be useful for scientific records and raising public awareness since very few studies on the source tracking of these chemical contaminants have been conducted, particularly in tropical countries.

Materials and Methods

Bangi is situated in the south of Hulu Langat district, in the state of Selangor, Malaysia. It is about 25 km south of Kuala Lumpur city centre. Bangi was previously surrounded by palm oil estates but in the last few decades has grown to become a semi-urban area with many residential and industrial areas. For this study, the sampling station used is located at the main entrance of Universiti Kebangsaan Malaysia, Bangi Campus (N02°55.47′ E101°46.39′). During peak hours, this station experiences a high flow of traffic, particularly on weekdays, due to a high level of traffic from Universiti Kebangsaan Malaysia. Figure 1 shows the sampling location for this study.

The PM_{10} sampling took place between November 2011 and January 2012 for 21 days. The sampling was undertaken using a high volume sampler (HVS) equipped with fibreglass filter paper (Whatman EPM 2000, size 20.3 cm × 25.4 cm). Before sampling, the filter paper was pre-heated in a furnace oven at a temperature of 500°C for 5 h. The filter paper was stored in a desiccator for 24 h before being weighed using a 5-digit analytical balance (Shimadzu). The sampling was conducted for 24 h at a flow rate of 1.13 m^3/min. After sampling, the filter paper was returned to the desiccator for 24 h then reweighed before being stored in the refrigerator at a temperature of ≤4°C until further analysis.

For the metal analysis, a quarter of the PM_{10} filter paper was cut into smaller pieces (1 cm × 1 cm) and placed into a 100 mL conical flask. Then, 40 mL of nitric acid and 10 mL of perchloric acid (4:1 ratio) were put into the flask and the mixture was heated on a heating plate to digest the filter paper. Digestion was conducted in the fume chamber for about 1 h and 30 min as performed by Latif et al. (2011). After that, the sample solution was left to cool in the fume chamber before being filtered using a vacuum pump equipped with a fibreglass filter paper (Whatman 47 mm diameter, 0.2 μm pore size). The sample was

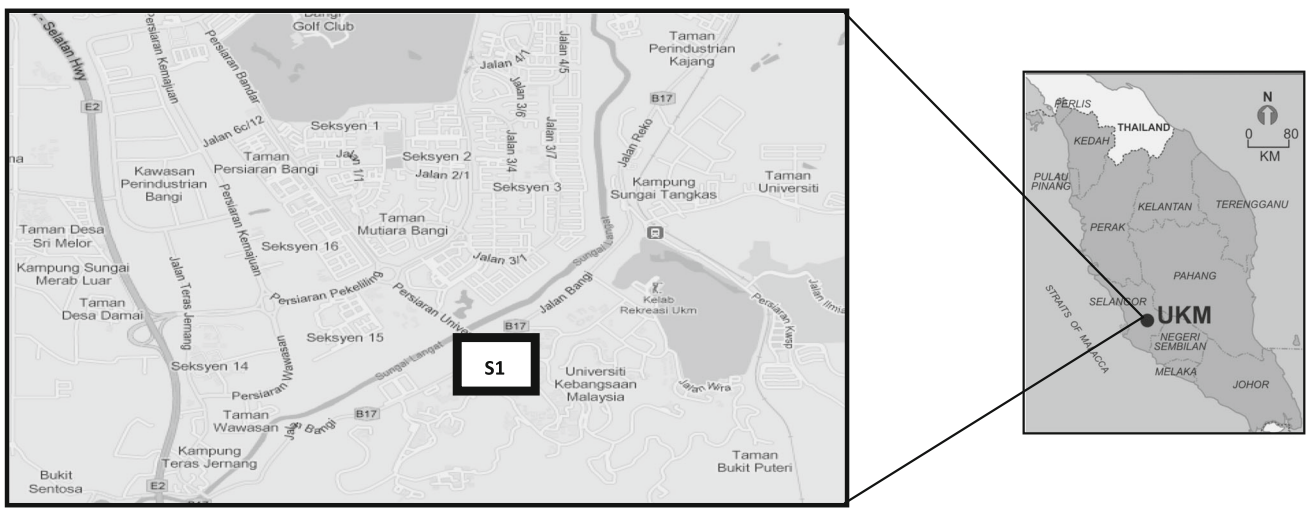

Fig. 1 Sampling location (*S1*) at Universiti Kebangsaan Malaysia, Bangi

transferred to a volumetric flask and diluted to 250 mL using deionised water. The determination of the heavy metals was undertaken using inductively coupled plasma mass spectrometry (ICP-MS PerkinElmer Elan 9000). Calibration of the ICP-MS instrument was performed with standard multi-element solutions. The detection limits for the analysis of heavy metals using this methodology were 0.07 ng/m^3 for Cu, 0.17 ng/m^3 for Pb, 0.10 ng/m^3 for Zn, 0.10 ng/m^3 for Fe, 0.03 ng/m^3 for Cd and 0.13 ng/m^3 for Ni.

For the ionic composition, a quarter of the PM_{10} filter paper was cut into smaller pieces (1 cm × 1 cm) and then placed in a 250 mL conical flask. 100 mL of deionised water was added and ultrasonic shakers were used for extraction at 60°C for 1 h. Next, the samples were filtered using a vacuum pump equipped with a 47 mm fibreglass filter paper (0.2 μm pore size). The samples were then transferred to a 250 mL volumetric flask and diluted using deionised water. The determination of the cations (Na^+, Ca^{2+}, K^+ and Mg^{2+}) was achieved through the use of an Inductively Coupled Plasma Mass Spectrometer (ICP-MS PerkinElmer Elan 9000), with a detection limit of 0.1 ng/m^3 for Na^+, 0.07 ng/m^3 for Ca^{2+}, 0.07 ng/m^3 for K^+ and 0.1 ng/m^3 for Mg^{2+}. Meanwhile the determination of the anions (SO_4^{2-}, NO_3^-, Cl^- and F^-) was undertaken using Ion Chromatography (IC-Metrohm 850 IC plus) with a detection limit of 0.77 ng/m^3 for SO_4^{2-}, 0.27 ng/m^3 for NO_3^-, 0.40 ng/m^3 for Cl^- and 0.23 ng/m^3 for F^-. In order to maintain the quality of the results, all instruments involved in the study were calibrated before use. The field blank sample was also analysed for the control analysis. The results were corrected based on the average blank concentration. A recovery test, which was in the range of 85 %–117 %, was also conducted for each analysis.

The data obtained was analysed using SPSS version 17.0 (Student Version of the Statistical Package for Social Sciences). Several analyses were undertaken, such as: the normality test, one-way ANOVA and Pearson correlation. In addition, the multivariate analyses were used to identify the sources of pollution that contributed to the PM_{10} concentrations recorded at the study area. PCA was utilised together with MLR using the XLSTAT 2012 software. After the data was found to be normally distributed, PCA was performed using the varimax rotation method. This ensured the variable was maximally correlated with one component but had little correlation with the others (Mohd Tahir et al. 2013; Wahid et al. 2013). The factor loadings after rotation were classified as strong (>0.70), moderate (0.50–0.70) and weak (<0.50). However, in this study, only strong factor loadings were chosen to clarify the sources of PM_{10} in the study area. MLR was used to calculate the contribution of each parameter to the level of PM_{10} by predicting the variability between independent and dependant variables (Shi et al. 2011). The results of the factor scores were used as the variables in MLR models. They were compared, based on the modelling performance, by referring to the coefficient of determination (R^2). In this study, each variable was independently introduced to a linear regression model with PM_{10} concentrations as the dependent variable. Once the possible sources of PM_{10} were clarified, the contribution of each source was defined using the backward stepwise technique based on the R^2 value. Using this method, the largest R^2 value indicated the best linear model.

Results and Discussion

The average concentration of PM_{10} recorded in Bangi was 29.5 ± 1.5 μg/m^3, with the minimum and maximum values of 24.7 and 34.8 μg/m^3, respectively. This level of PM_{10} was well below the 150 μg/m^3 recommended by the Malaysian Government in the Recommended Malaysian Air Quality Guidelines (RMAQG). In this study, the sampling stations only experienced a high volume of traffic during peak hours: in the morning, during the lunch hour and after working hours when the majority of university staff were using the main entrance. This situation may have resulted in the concentration of PM_{10} recorded here, which is moderate when compared to other studies in Malaysia which focused on urban areas (Mohd Tahir et al. 2008; Mohd Tahir et al. 2013).

The average concentration of heavy metals and ions recorded are shown in Table 1. Significant variations ($p < 0.05$) were observed between the elements studied,

Table 1 Heavy metals (ng/m^3) and ionic compositions (μg/m^3) in PM_{10} samples

Elements	Unit	Average concentration	Range
Fe	ng/m^3	172 ± 35	(132–192)
Zn	ng/m^3	84.5 ± 21.2	(64.9–107)
Pb	ng/m^3	23.1 ± 7.09	(18.3–31.3)
Cu	ng/m^3	6.08 ± 0.11	(5.06–6.72)
Mn	ng/m^3	4.43 ± 0.86	(3.47–5.15)
Cd	ng/m^3	0.39 ± 0.11	(0.28–0.50)
Ni	ng/m^3	0.05 ± 0.05	(0.04–0.10)
Na^+	μg/m^3	10.8 ± 9.76	(0.0–19.0)
Ca^{2+}	μg/m^3	0.20 ± 0.11	(0.08–0.27)
K^+	μg/m^3	0.16 ± 0.06	(0.12–0.23)
Mg^{2+}	μg/m^3	0.01 ± 0.001	(0.007–0.01)
SO_4^{2-}	μg/m^3	2.52 ± 0.72	(2.04–3.35)
NO_3^-	μg/m^3	0.36 ± 0.001	(0.00–1.08)
Cl^-	μg/m^3	0.35 ± 0.08	(0.27–0.43)
F^-	μg/m^3	0.04 ± 0.03	(0.02–0.07)

where Fe recorded the highest average concentration (172 ± 35 ng/m^3) relative to the other heavy metals. Generally, vehicle exhaust emissions and brake friction from motor vehicles along with road dust were considered to be the most likely contributors to the higher Fe levels in the PM_{10} samples (Mohd Tahir et al. 2009; Mansha et al. 2012). As the study area experienced a high volume of traffic on the roads, notably during peak hours, the concentration of Fe might also increase. In addition, the occurrence of construction activity around the study area may have led to a higher concentration of Fe (Mazzei et al. 2008). The second highest heavy metal concentration was Zn (84.5 ± 21.2 ng/m^3) followed by Pb > Cu > Mn > Cd > Ni. These elements are often associated with traffic emissions, either vehicular exhaust emissions or non-engine combustion sources, such as tyres and clutch wear (Sternbeck et al. 2002; Mohd Tahir et al. 2013).

For the ionic composition, significant variations ($p < 0.05$) were observed between the elements studied. For cations in PM_{10}, the concentrations of the elements followed the trend of $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$, whereas for anions the trend was $SO_4^{2-} > NO_3^- > Cl^- > F^-$ respectively. For cations, the average concentration of Na^+ had the highest level (10.8 ± 9.76 μg/m^3) compared with the other cations studied. According to previous studies, the majority of Na^+ originates from the Earth's crust and marine aerosol (Orlic et al. 1999). The Earth's crust source, also proven as the source of Ca^{2+} (Viana et al. 2008), gave the second highest cation concentration in PM_{10} samples (0.204 ± 0.106 μg/m^3). For anions, overall, SO_4^{2-} showed the highest concentration (2.52 ± 0.724 μg/m^3) followed by $NO_3^- > Cl^- > F^-$. This most likely occurred as a result of the photochemical process which converts SO_2 to SO_4^{2-} (Terzi et al. 2010). The second highest anion concentration was NO_3^- (0.358 ± 0.001 μg/m^3) which indicates that PM_{10} might also originate from motor vehicle emissions, particularly those from diesel fuel (Shukla and Sharma 2008).

The results from the factor loading after varimax using PCA are shown in Table 2. Four main factors with eigenvalues >1 were identified with a total variance of 78.03 % in the PM_{10} samples. The first factor (F1) gave a high factor loading for Ni, Na^+, Ca^{2+} and K^+ which is thought to be derived primarily from the construction activities occurring in the areas surrounding the campus as well as biomass burning (Tsitouridou et al. 2003). The second factor (F2) showed the dominancy of Zn, followed by Cd and Pb, which are markers for industrial emissions and originate from road activities such wear from rubber tyres, friction from braking and fuel combustion (Mazzei et al. 2008). The third factor (F3) was dominated by Fe, Mn and SO_4^{2-} which demonstrated the Earth's crust as a source along with the existence of road dust (Viana et al. 2008). The fourth factor (F4) correlated with F^- which may well have been derived from vehicle emissions (Mansha et al. 2012). Figure 2 shows the PCA ordination score plots which visualise the distribution of samples on the respective factor axes.

Table 2 Factor loading after varimax rotation using PCA

Elements	F1	F2	F3	F4
Fe	0.039	−0.028	**0.885**	0.179
Zn	−0.149	**0.941**	0.005	−0.070
Pb	−0.159	**0.866**	0.115	0.020
Cu	0.454	0.069	0.243	0.523
Mn	0.034	0.127	**0.914**	0.017
Cd	0.070	**0.927**	0.202	−0.118
Ni	**0.796**	−0.019	0.031	−0.051
Na^+	**0.777**	−0.073	0.077	0.349
Ca^{2+}	**0.769**	−0.038	0.108	0.497
K^+	**0.760**	−0.180	0.118	−0.192
Mg^{2+}	0.461	0.423	0.621	−0.191
SO_4^{2-}	0.166	0.075	**0.718**	0.274
NO_3^-	−0.272	0.440	0.437	−0.667
Cl^-	0.437	0.631	−0.300	0.205
F^-	0.010	−0.007	0.259	**0.925**
Eigenvalue	4.177	3.762	2.206	1.560
Variability (%)	27.845	25.077	14.707	10.399
Cumulative	27.845	52.923	67.630	78.029

Factors in bold indicated as strong factors (>0.70)

The R^2 values and standardised coefficient resulting from the MLR analysis are shown in Table 3, while the equation for the model is presented in Eq. (1).

$$PM_{10} = 2.96 \times 10^{-5} - (3.27 \times 10^{-7})F1 + (5.85 \times 10^{-7})F2 + (3.73 \times 10^{-6})F3 - (1.20 \times 10^{-6})F4 \quad (1)$$

where F1 = construction/biomass burning, F2 = industrial emissions/road activity, F3 = Earth's crust/road dust, F4 = vehicle emissions.

Based on the backward stepwise technique, the R^2 for each individual variable were determined to predict the major sources of PM_{10} in this study area. Based on the result, the largest R^2 (0.298) was detected from F3 (Earth's crust/road dust), followed by F4 (vehicle emissions, $R^2 = 0.085$), F2 (industrial emissions/road activity, $R^2 = 0.007$) and F1 (construction/biomass burning, $R^2 = 0.002$). It appears that the Earth's crust/road dust has contributed significantly to the PM_{10} concentrations recorded in this semi-urban area probably due to the effects of wind velocity and wind direction. This result concurs with those from several previous studies (Tsitouridou et al. 2003; Viana et al. 2008; Mohd Tahir et al. 2013).

By way of a conclusion, the average concentration of PM_{10} was found to be well below the Recommended

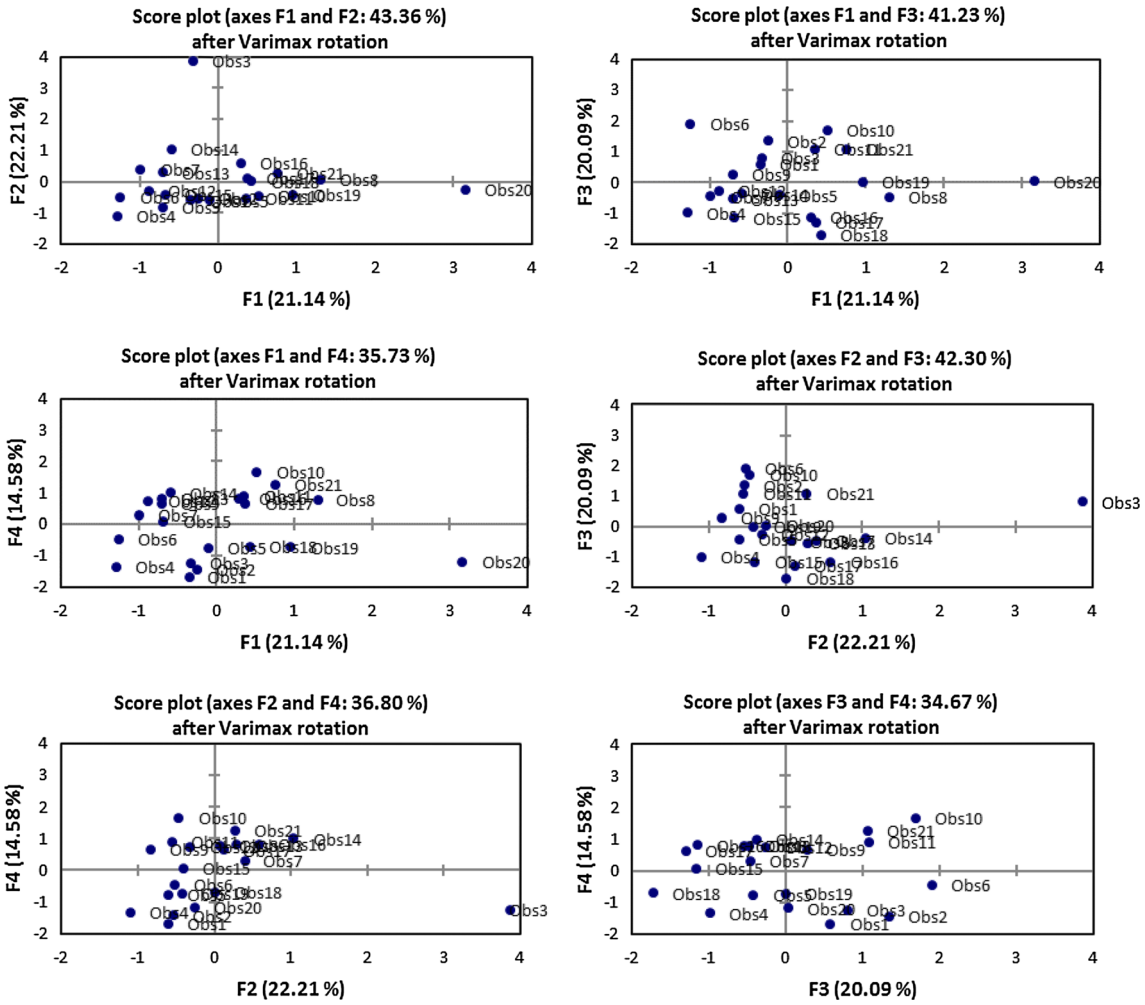

Fig. 2 PCA ordination score plots which visualise the distribution of samples on the respective factor axes

Table 3 Individual MLR output for each variable for source identification of PM_{10}

Variables	R^2	Standardised coefficients
PM_{10}—Construction/biomass burning	0.002	0.048
PM_{10}—Industrial emissions/road activity	0.007	0.086
PM_{10}—Earth's crust/road dust	0.298	0.546
PM_{10}—Vehicle emissions	0.085	0.293

Malaysian Air Quality Guidelines (RMAQG) of 150 μg/m^3 in 24 h. Overall, the trend of heavy metals recorded in the study area was Fe > Zn > Pb > Cu > Mn > Cd > Ni. A decreasing trend of cations in PM_{10} samples was shown to be $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$, while for anions it was $SO_4^{2-} > NO_3^- > Cl^- > F^-$, respectively. The PCA–MLR analysis clearly showed that the possible sources of PM_{10} in Bangi were dominated by the Earth's crust and road dust, followed by vehicle emissions. This study suggests that both natural and anthropogenic sources have contributed to the amount of PM_{10} in the ambient air. Due to the effects of PM_{10}, which may incur health risks, the level and the composition of PM_{10} should be monitored regularly in order to maintain a healthy environment, particularly within the university campus in question.

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