

Original Research

Source Identification of Heavy Metals in Particulate Matter (PM₁₀) in a Malaysian Traffic Area Using Multivariate Techniques

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Abstract

This study was conducted to determine heavy metal concentrations in particulate matter (PM₁₀) and the source identification in the areas affected by traffic during the southwest monsoon from June to July 2014. Collection of the particulate samples was done at three sampling sites that have varying traffic densities (high, medium, and low). Samples were collected using a high-volume air sampler. Heavy metals in the particulate matter (PM₁₀) were assessed with inductively coupled plasma mass spectrometry. The results show that the mean concentrations of PM₁₀ for high-, medium-, and low-density traffic were found to be 207.63±7.82, 164.92±10.68, and 90.09±20.70 µg m⁻³, respectively. The concentrations in high- and medium-density areas were found to be significantly higher than 150 µg m⁻³ for 24 hrs as per Recommended Malaysian Air Quality Guidelines (RMAQG). The heavy metals found were dominated by Ba and Fe, followed by Cu > V > Zn > Pb > Mn > Cr > As > Ni > Cd > Co. A comparison of the concentrations of heavy metals with the United State Environmental Protection Agency (USEPA) and World Health Organization (WHO) guidelines revealed that As was higher than the standards in high- and medium-density areas. Cluster analysis (CA) and principal component analysis (PCA) were employed in the identification of the sources of metals for high-, medium-, and low-traffic densities. The CA identified three clusters for high-, medium-, and low-traffic densities, while PCA extracted four sources for high-, medium-, and low-traffic densities and the major pollution sources identified were vehicle exhaust emission, non-exhaust emission (brake and tire wear), and re-suspension dust.

Keywords: particulate matter, PM₁₀, heavy metals, multivariate techniques, source apportionment

Introduction

Particulate matter (PM) in the atmosphere is among the most important pollutants of the environment affecting the atmosphere at different concentrations. Moreover, it affects human health when it enters the respiratory system [1]. Recent studies on the health problems associated with exposure to particulate matter (PM) with an aerodynamic diameter of 10 μm or less (PM_{10}) have identified a variety of health-related problems that include deterioration in lung function, chronic pulmonary disease, heart disease, and premature death, along with a rise in mortality [2-4].

Airborne particulates are significant conveyors of metals, some of which are toxic and typically exist naturally and excessively in the environment. These particulates carrying levels of heavy metals in various forms pose a serious health risk when breathed in or swallowed [1]. Consequently, heavy metals in association with PM definitely affect the biological and physiological functioning of the human body.

Traffic emission and road dust have often been used for detecting heavy metal environmental pollution [5]. Hence, the degrees of heavy metal pollution in road dust reported worldwide have existed for decades [6]. Metals, including Cd, Co, Ni, Pb, and Zn, may be grouped as road-specific heavy metals. They are primarily a result of combustion residues, losses from fuels, engine, transmission oils, brake linings, exhaust catalysts, and abrasion from tires and road pavement [7-8]. A high number of motor vehicles, together with more industries and a huge quantity of road dust, are suspected to contribute to the level of PM_{10} in the atmosphere [9]. Some research has been conducted on the properties of heavy metal levels in road dust produced by vehicular activities [5, 10]. For instance, the concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt, Germany were the highest values on a main street with high traffic density. Non-exhaust sources contributed almost the same levels as engine exhaust on a high-traffic road in London. The non-exhaust particles are normally derived from abrasive sources such as tire wear, brake wear, and road surface abrasion. Brake and tire wear contribute significantly to the presence of heavy metals in urbanized areas, and especially in places with high traffic [8]. Furthermore, particle re-suspension from the road surface is very important, particularly in drier weather [8].

In Malaysia, automobile emissions alone contributed about 82% of pollutants, including particulate matter and organic and inorganic compounds in the atmosphere, while the remaining 18% were from various sources including industry, power stations, and domestic and commercial sources (DOE 1996) [11]. Previous studies have found that the deterioration of air quality in Peninsular Malaysia has become more pronounced in recent times, primarily due to the continuous dust fall-out and the increase in concentration of suspended particulate matters in the ambient air along congested roadsides. These problems are principally attributed to the emissions from motor vehicles and open burning [9, 12].

The concentration of Zn in PM_{10} was once reported as the highest compared to Cr and Mn in urban areas in Malaysia, which indicated an association between Zn and emissions from tire use, car brakes, and different types of petrol [12-13]. However, recent studies on heavy metals in PM_{10} have shown that Fe had the highest levels, indicating that vehicular emissions were the main source of PM_{10} around a very busy highway [14]. Generally, the most commonly reported heavy metals composition in PM_{10} were Pb, Zn, Co, Cd, Cu, Fe, As, and Ni, which are associated with vehicular emissions [12, 15-16]. Therefore, the aims of this present study were to examine the heavy metals such as Pb, Zn, Co, Cd, Cu, Fe, As, and Ni in particulate matter (PM_{10}), and to identify the source of heavy metals in PM_{10} using cluster analysis (CA) and principal component analysis (PCA). This research can serve as a guide for policy formulation in order to develop a framework for vehicular traffic in urban Malaysia. It would also contribute to the growing literature about heavy metals concentrations in atmospheric PM_{10} in these areas.

Material and Methods

Study Area

Cheras is a southeastern suburb of Kuala Lumpur, the Malaysian capital city. The township (3.0422°N, 101.7706°E) is adjacent to Ampang and Kajang, which are major towns within the metropolitan area. Cheras is one of the major towns in the Klang Valley region, which is highly populated with high transportation density. The town is warmest in the month of March, and experiences heavy rains during the month of November as the northeast monsoon moves in from October to March. The climate of the area during the study period (June to July 2014) is characterized as tropical, receiving daily average rainfall of about 2.3 mm, temperature fluctuating between 28 and 31°C, and wind speed of 3.69 m/s with a direction of about 206.83SW [17]. For this study, the sampling sites were located in different traffic densities as shown in Fig. 1 high (CH), medium (CM), and low (CL) traffic density. High traffic density refers to areas near the highway with average traffic volume (56,316 vehicle/day) [18], while the medium density are areas around the city center closer to major roads with average traffic volume of nearly 11,645 vehicle/day. However, the low-density areas refer to those locations around the neighborhood with minor roads, characterized by low traffic volume with an average of 2,800 vehicles/day (field survey).

Sampling Collection

Particulate matter (PM_{10}) samples were collected daily during the southwest monsoon for 24 hours excluding the weekend, from midday on 24 June to 4 July 2014. Altogether, 24 PM_{10} samples were taken with high-volume samplers (USA, model B/MV2000HX), which were

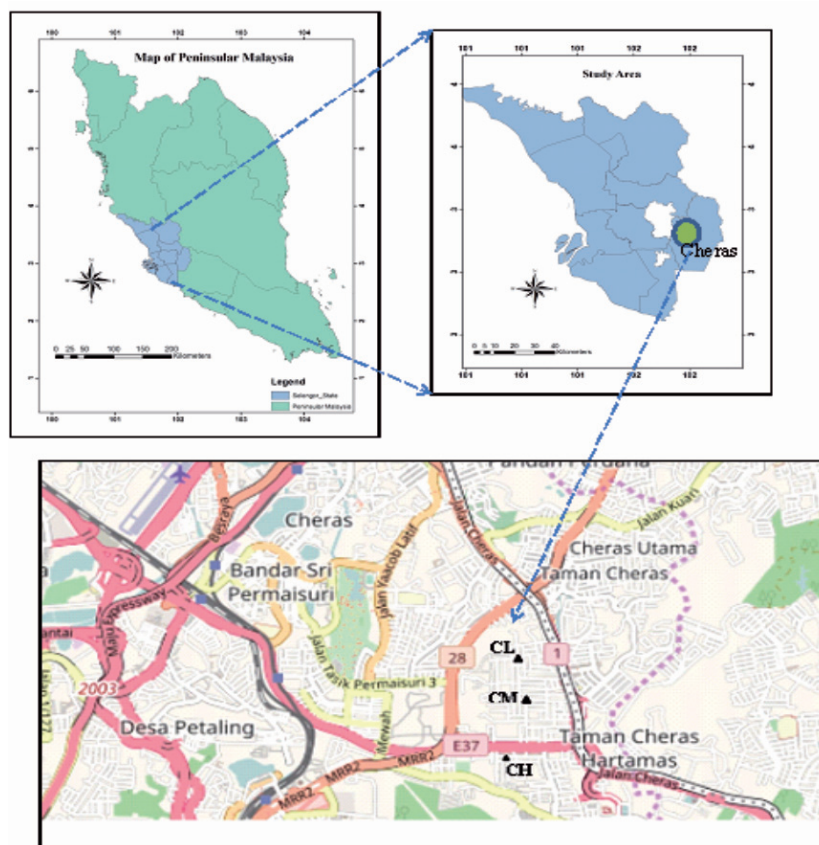


Fig. 1. Sampling sites (CH, CM, and CL) in Cheras traffic area.

designed especially for PM_{10} at a specified flow rate of $1.13 \text{ m}^3/\text{min}$ with an inlet height of 1 m. Samples were collected from three sampling sites with different traffic densities (highway, medium, and low densities) using glass fiber filters (Whitman EPM 2000, $20.3 \times 25.4 \text{ cm}$). The sampling points are about 1 km from each other and around 16, 10, and 7 m from the roads for high-, medium-, and low-traffic densities, respectively. The filters were periodically checked as per manufacturer's instructions to ensure the reliability of PM_{10} data [19].

Gravimetric Analysis

The levels of particulate matter (PM_{10}) were determined gravimetrically by weighing the filters before and after sample collection. The filters were kept for 24 h in a desiccator, which was maintained at 50% relative humidity at 20°C [20]. An analytical balance with a precision of 0.1 mg was employed for weighing the filters. The PM_{10} concentration levels were obtained on the basis of the sample quantities obtained and the volume of pumped air [20].

Chemical Analysis

For heavy metal analysis, half of the PM_{10} filter paper was cut into smaller pieces and placed into a 150 ml conical flask. The filters were extracted with

100 ml mixture of hydrochloric and nitric acid (3:1) using a hot plate acid [20]. Digestion was conducted in the fume chamber for one and a half hours [21]. It was then cooled and filtered using $0.45 \mu\text{m}$ filters and refrigerated in a pre-cleaned robust polyethylene bottle until analysis [22-23]. The determination of the heavy metals was undertaken using an inductively coupled plasma mass spectrometer (ICP-MS Perkin Elmer Elan 9000). The calibration of the ICP-MS was performed with standard multi-element solutions. The concentrations of PM_{10} composition were corrected from the reagent and filter blank samples. These reagent and filter blanks were exposed to similar digestion procedure for quality assurance (QA) and quality control (QC) purposes. The recovery (%) of the heavy metals using standard reference material (NIST SRM1648a for urban particulate matter) was obtained from the U.S. National Institute of Standards and Technology (NIST). Results exhibited that the recoveries for all the metals measured were in the range 79-95%. The detection limits were 0.12 ng m^{-3} for Pb, 0.10 ng m^{-3} for Zn, 0.05 ng m^{-3} for Co, 0.02 ng m^{-3} for Cd, 0.3 ng m^{-3} for Cu, 0.4 ng m^{-3} for Fe, 0.3 for As, and 0.13 ng m^{-3} for Ni.

Statistical Analysis

The data obtained was analyzed using univariate and multivariate methods using SPSS software version

20.0 (student version of the statistical package for social sciences) and XLSTAT 2015 software. Basic statistical parameters such as mean, standard deviation, and maximum and minimum values were used for the analysis of the data for atmospheric PM₁₀ and heavy metals concentrations. One-way analysis of variance (ANOVA) was used to detect the significant difference between metals from different sampling sites ($P < 0.05$). Multivariate statistical analysis, including CA and PCA, was used to identify the source apportionment of the heavy metals in PM₁₀ in the study area as previously conducted by other researchers [23, 24].

Cluster Analysis

CA is a multivariate technique used for the classification of a system of objects into groups or clusters on the basis of their similarities. The primary aim is to determine an optimal grouping for clusters with similar observations and those that were dissimilar to other clusters. The aim of CA is to determine a systematic organization of the variables based on shared common characteristics of groups/clusters. In this way it cognitively facilitates the prediction of common properties on the basis of overall group membership [13]. Cluster analysis was applied to heavy metals in PM₁₀ from an air sampling standardized matrix of samples by means of the complete linkage method, and the outcomes were recorded as a dendrogram.

Principal Component Analysis

PCA is the most commonly applied method of multivariate statistical analysis among various options [25, 26]. It is a procedure that determines data patterns and then expresses them on the basis of their similarities and differences. PCA explains how the variables are quantitatively related in the form of groups within the data, which minimizes the number of variables and dimensionality in a data-set utilizing a reduced number of linearly independent new variables, which are major components (PCs). This means that the variables are maximally correlated with one component, but have little or no correlation with the others. Thus the components are arranged in descending order (from the largest to the smallest contributor) as precisely as possible with few major components [26-27]. The post-rotation factor loadings are classified as strong (> 0.70), moderate ($0.50-0.70$), and weak (< 0.50) [27]. PCA groups the variables as major components (PCs), with their eigenvalues, variability (%), and cumulative values (%) of individual and collective PCs. These are applied in the plotting of a graph that identifies the PCs with eigenvalues exceeding 1 that are to be retained [28]. The measurement of sampling adequacy applied was the Kaiser-Meyer-Olkin (KMO) followed by the execution of the PCA. This was done in others to obtain the evaluation of the appropriateness of PCA as well as to check the adequacy of samples. Proceeding to the next level is done only if the KMO value is 0.5 and above [29].

Results and Discussion

Table 1 presents a statistical summary of PM₁₀ and associated heavy metals for three sampling sites during the period of study (southwest monsoon). The mean concentration of PM₁₀ for high-, medium-, and low-density traffic was found to be 207.63 ± 7.82 , 164.92 ± 10.68 , and $90.09 \pm 20.70 \mu\text{g m}^{-3}$, respectively. The maximum and minimum values of high-, medium-, and low-density traffic were 217.24, 196.35, and 181.54 (max.), and 152.29, 126.47, and 69.32 (min.) $\mu\text{g m}^{-3}$, respectively. These levels of PM₁₀ were higher than the $150 \mu\text{g m}^{-3}$ for 24 hrs recommended by the U.S. EPA and Recommended Malaysian Air Quality Guidelines (RMAQG). On the contrary, the low density was found well below these limits, because low density characterized by low traffic volume ranged between 3,000-1,200 vehicle/day. The results also exposed significant differences among sites ($P < 0.05$) for PM₁₀. The results were consistent with the findings of [9, 13], where PM₁₀ concentrations were higher during the southwest monsoon. This is because high density has a higher traffic load and is characterized by movement of heavy-duty vehicles where great number of particulates are produced and pollute the atmosphere. Also, studies by [14] have reported that the concentration of PM₁₀ over the Klang Valley is generally high during the southwest monsoon due to the contribution of biomass burning from regional sources.

The mean concentrations for different heavy metals at various sites (high, medium, and low densities) are shown in Table 1. The significant variations ($P < 0.05$) were seen between the heavy metals in three sites, where the highest mean concentration was found for Ba at (729.29 ± 44.42 , 649.21 ± 62.48 , and $312.35 \pm 155.52 \text{ ng m}^{-3}$) for the three densities, respectively, while Fe was recorded as the second values at for all the sites followed by $\text{Cu} > \text{V} > \text{Zn} > \text{Pb} > \text{Mn} > \text{Cr} > \text{As} > \text{Ni} > \text{Cd} > \text{Co}$. However, medium and low traffic densities followed this order: $\text{Zn} > \text{V} > \text{Cu} > \text{Pb} > \text{Mn} > \text{Cr} > \text{As} > \text{Ni} > \text{Cd} > \text{Co}$ and $\text{Zn} > \text{V} > \text{Cu} > \text{Cr} > \text{Pb} > \text{Mn} > \text{As} > \text{Ni} > \text{Cd} > \text{Co}$, respectively. These metals are frequently linked with traffic sources, either vehicular exhaust emissions or non-engine combustion sources, such as fuel combustion, tires, and clutch wear along with road dust [29-30]. Among the heavy metals, the levels of As were found to exceed the U.S. EPA standards and WHO guidelines, whereas Pb and Cd were below the standards (Table 1). These results are in line with previous studies [12, 15] where high concentrations were reported for Fe, although this study revealed higher concentrations as conducted during the southwest monsoon, whereas the concentrations were lower compared with the findings of [31]. The results revealed that the high traffic density recorded high concentrations of heavy metals compared with medium and low, which may be characterized by high traffic volume vehicles [5]. Moreover, the lower amount of rainfall during the southwest monsoon season increased the density of air pollutants. Also, other meteorological parameters such as low wind speed, wind direction, high temperature, and relative humidity ambient temperatures

Table 1. Statistical summary of PM₁₀ (µg m⁻³) and heavy metals (ng m⁻³) in study area.

| Element | High (CH) | | | Medium (CM) | | | Low (CL) | | | USEPA ngm ⁻³ | WHO ngm ⁻³ |
|------------------|---------------|---------|--------|---------------|--------|--------|---------------|--------|--------|----------------------------|--------------------------|
| | Mean±SD | Max | Min | Mean±SD | Max | Min | Mean±SD | Max | Min | | |
| PM ₁₀ | 207.63±7.82 | 217.24 | 196.35 | 164.92±10.68 | 181.54 | 152.29 | 90.09±20.70 | 126.47 | 69.32 | 150 | 50 |
| As | 6.84±1.57 | 10.16 | 5.6 | 6.86±1.51 | 9.15 | 5.14 | 4.23±1.18 | 6.11 | 2.65 | 6 | 6 |
| Pb | 24.26±5.65 | 36.63 | 18.43 | 13.5±3.97 | 21.47 | 9.19 | 7±1.59 | 8.87 | 5.21 | 1,500 | 500 |
| Cu | 103.78±16.16 | 125.28 | 79.18 | 20.76±5.83 | 26.9 | 13.94 | 10.18±3.51 | 15.67 | 4 | - | - |
| Ni | 3.18±1.15 | 5.67 | 2.02 | 2.12±0.72 | 3.59 | 1.42 | 1.40±.29 | 1.93 | 0.91 | 20 | 20 |
| Cd | 1.75±0.72 | 2.83 | 0.83 | 0.77±0.55 | 1.91 | 0.24 | 0.19±0.14 | 0.44 | 0.04 | 6 | 5 |
| Co | 0.22±0.07 | 0.35 | 0.14 | 0.18±0.10 | 0.41 | 0.09 | 0.09±0.03 | 0.15 | 0.06 | - | - |
| Mn | 19.84±4.39 | 25.83 | 14.23 | 12.72±3.18 | 17.44 | 7.68 | 5.15±1.18 | 6.88 | 3.74 | - | - |
| Zn | 54.69±7.02 | 70.84 | 48.9 | 42.83±5.26 | 47.39 | 32.36 | 31.66±3.59 | 36.29 | 24.98 | - | - |
| Fe | 629.11±280.74 | 1087.63 | 331.21 | 390.05±136.26 | 621.83 | 228.24 | 143.43±56.35 | 280.23 | 109.52 | - | - |
| Cr | 13.05±2.52 | 17.06 | 9.81 | 10.05±1.61 | 12.56 | 7.54 | 7.68±1.39 | 9.84 | 5.78 | - | - |
| V | 54.40±13.77 | 68.82 | 34.1 | 37.29±7.07 | 45.21 | 24.59 | 19.08±1.88 | 21.79 | 16.63 | - | 1,000 |
| Ba | 729.29±44.41 | 767.3 | 662.83 | 649.21±62.48 | 741.62 | 520.76 | 321.35±155.52 | 542.54 | 117.59 | 0 | 0 |

Table 2. Principal component loadings of PM₁₀ and heavy metals in high, medium, and low densities.

| Parameters | High (CH) | | | | Medium (CM) | | | | Low (CL) | | | |
|-----------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | F1 | F2 | F3 | F4 | F1 | F2 | F3 | F4 | F1 | F2 | F3 | F4 |
| PM10 | 0.18 | 0.685 | 0.194 | -0.576 | 0.562 | -0.104 | 0.111 | -0.65 | -0.436 | -0.162 | -0.811 | -0.348 |
| As | 0.955 | 0.184 | 0.04 | 0.129 | 0.731 | -0.221 | -0.256 | 0.137 | -0.419 | 0.567 | 0.405 | -0.165 |
| Pb | 0.971 | -0.014 | 0.06 | -0.039 | 0.98 | -0.008 | -0.074 | 0.167 | -0.301 | -0.272 | 0.536 | -0.582 |
| Cu | 0.751 | -0.15 | -0.443 | 0.078 | -0.121 | 0.027 | 0.789 | -0.329 | 0.296 | -0.138 | 0.919 | -0.082 |
| Ni | 0.948 | 0.167 | -0.156 | 0.14 | 0.886 | -0.086 | -0.334 | -0.117 | -0.547 | 0.761 | 0.123 | 0.173 |
| Cd | 0.948 | 0.167 | -0.156 | 0.14 | 0.235 | 0.915 | -0.034 | 0.234 | -0.891 | -0.194 | -0.045 | -0.119 |
| Co | 0.361 | -0.603 | 0.638 | 0.105 | 0.936 | -0.258 | 0.103 | 0.008 | 0.161 | -0.77 | 0.146 | 0.243 |
| Mn | 0.653 | 0.008 | 0.467 | -0.357 | 0.549 | -0.426 | 0.512 | 0.553 | -0.633 | 0.071 | 0.397 | 0.597 |
| Zn | 0.916 | -0.143 | 0.17 | -0.175 | 0.663 | 0.601 | -0.05 | -0.357 | -0.73 | -0.139 | 0.606 | -0.03 |
| Fe | 0.826 | -0.24 | 0.195 | 0.439 | 0.838 | -0.101 | 0.399 | 0.203 | -0.645 | -0.622 | 0.083 | 0.226 |
| Cr | -0.476 | 0.235 | 0.805 | 0.205 | 0.382 | 0.853 | -0.188 | 0.131 | 0.596 | -0.406 | 0.634 | -0.162 |
| V | 0.329 | 0.818 | 0.129 | 0.434 | 0.796 | 0.374 | 0.291 | -0.068 | -0.007 | 0.904 | 0.286 | -0.145 |
| Ba | -0.69 | 0.151 | 0.02 | 0.519 | -0.545 | 0.678 | 0.445 | 0.137 | 0.911 | 0.31 | 0.09 | 0.192 |
| Eigenvalue | 7.138 | 1.771 | 1.645 | 1.256 | 5.05 | 2.135 | 1.865 | 1.06 | 4.198 | 3.14 | 3.015 | 1.089 |
| Variability (%) | 54.91 | 13.62 | 12.65 | 9.67 | 41.17 | 17.4 | 15.2 | 8.156 | 32.29 | 24.15 | 23.19 | 8.37 |
| Cumulative % | 54.91 | 68.53 | 81.19 | 90.85 | 41.17 | 58.56 | 73.77 | 88.8 | 32.29 | 56.44 | 79.64 | 88.01 |

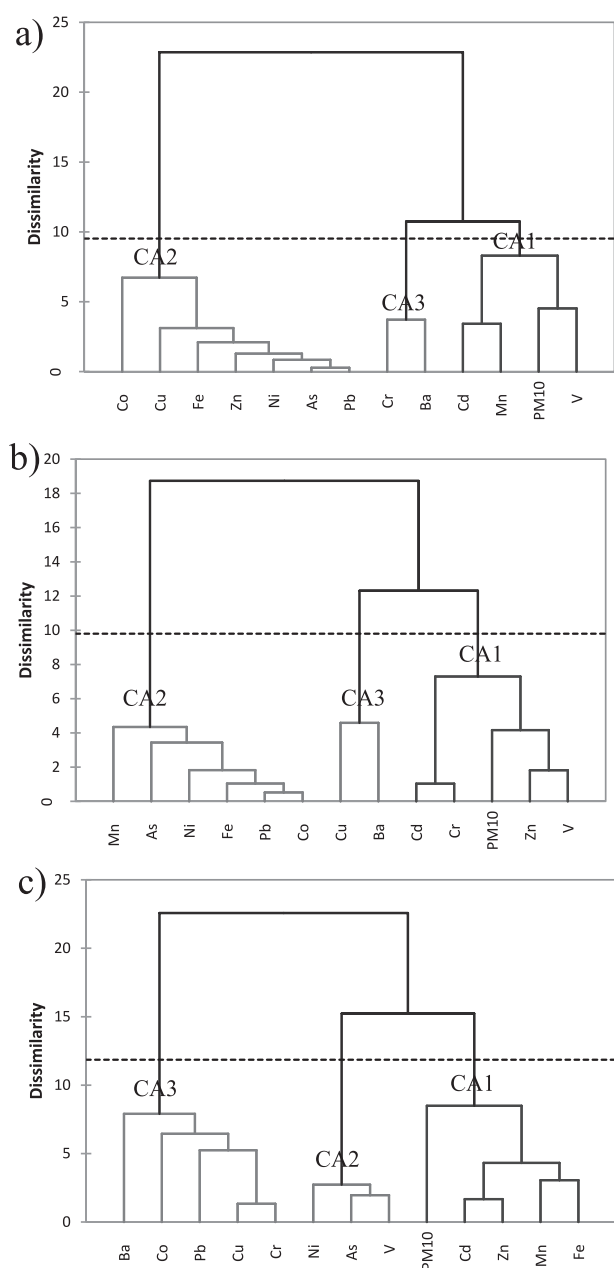


Fig. 2. Cluster analysis of PM_{10} and heavy metals: a) high, b) medium, and c) low traffic densities.

commonly increased the concentrations of heavy metals during the southwest monsoon [13].

Multivariate statistical analysis was applied for eight heavy metals for different traffic densities (high, medium, and low) utilizing PCA and CA to evaluate potential contributing sources of heavy metals in the study area which are considered of the most prevalent and useful statistical methods for uncovering the potential structure of a set of variables [12].

CA was also employed in order to determine the sources of heavy metals in PM_{10} based on the similarity of the elements in the group for the three sampling sites (high, medium, and low density). CA for (high density) is presented in a dendrogram, where the variables are grouped into three statistically dissimilar clusters depending on the

similarities between the variables and dissimilarities with other groups. Fig. 2a) shows cluster analysis using the total linkage procedure for the high traffic density that was classified into three clusters. The first cluster consisted of V, PM_{10} , Mn, and Cd, which could be associated with vehicle exhaust and non-exhaust (brake and tire wear) [7, 29]. The second cluster was comprised of Pb, As, Ni, Zn, Fe, Cu, and Co, possibly originating from vehicle exhaust and brake wear [7, 32], and the third cluster consisted of two metals, Ba and Cd, which most likely came from non-exhaust emission sources [33-34]. The dendrogram of cluster analysis for medium traffic density was also classified into three clusters Fig. 2b). The first cluster was comprised of V, Zn, PM_{10} , Cr, and Cd, whereas the second cluster consisted of metals such as Co, Pb, Fe, Ni, As, and Mn, which could have emanated into the local atmosphere from vehicle exhaust and non-exhaust [7, 35]. The third cluster contained Ba and Cu, which reveal that the brake wear was the main sources [36]. Fig. 2c) shows cluster analysis for low-density traffic, which exhibited three clusters categorized as CA1, comprising of Fe, Mn, Zn, Cd, and PM_{10} , probably coming from vehicle exhaust and non-exhaust emissions. CA2 consisted of V, As and Ni these were believed to be from exhaust emissions and brake wear [16], while the third cluster included Cr, Cu, Pb, Co, and Ba, which indicates that exhaust and nonexhaust are the main source for these metals [33]. These clusters provided evidence that the variables have different behaviors in each site. Moreover, since the study was conducted during the southwest monsoon where the atmosphere was characterized by haze, it can be concluded that apart from vehicular emissions, other likely sources of PM_{10} can be from the haze, which makes it exhibit the same character in the three traffic densities (high, medium, and low) as shown in Fig. 2.

PCA was also used to infer possible common sources of heavy metals in PM_{10} . Even though the result obtained from CA shows classification of the elements based on sources, the PCA (unlike CA) gives detailed information with regards to classification. In this study PCA was used for the eight parameters and it produced seven PCs for high, medium, and low densities, respectively. However, only PCs with eigenvalue greater than 1 are considered to be the most important [23], thus three PCs for high density and four for medium and low density seem to be significant (Figs 3a-c, Table 2), and the higher the eigenvalue of a PC, the higher the contribution of that PC to the source of PM_{10} and heavy metals [27]. Moreover, in this study the Kaiser-Mayer-Olkin (KMO) test of heavy metals data illustrates 0.62, 0.74, and 0.51 for the high, medium, and low traffic densities, respectively. This considers that all variables are adequate and can apply for further analysis. The Bartlett's test of sphericity exposed the heavy metals data to the sphericity assumption since it had noticed a chi-square value of 41.337 ($p < 0.05$, $df = 28$), then confirming that the data variables were associated and not orthogonal. This suggests that PCA will allow for interpretation of the variability in the data with less than the number of variables.

Table 2 shows the PCA results for high, medium, and low densities. The four PCs with eigenvalues greater than 1 obtained for high traffic density seem to be significant sources of PM₁₀ and heavy metals, making up more than 92% of the total variance. The first component with 51.24% total variance and an eigenvalue of 4.611 exhibits the highest loadings of As, Pb, Cu, Ni, Cd, Zn, and Fe, where Mn showed moderate loadings. These heavy metals could have originated from a mixture of vehicle exhaust and non-exhaust sources (brake and tire wear) [29, 35]. The second component accounted for 13.62% of total variance, consisting of a high loading of V with a moderate loading of PM₁₀. The possibility originated from the combustion of engine oil, and brake and tire wear

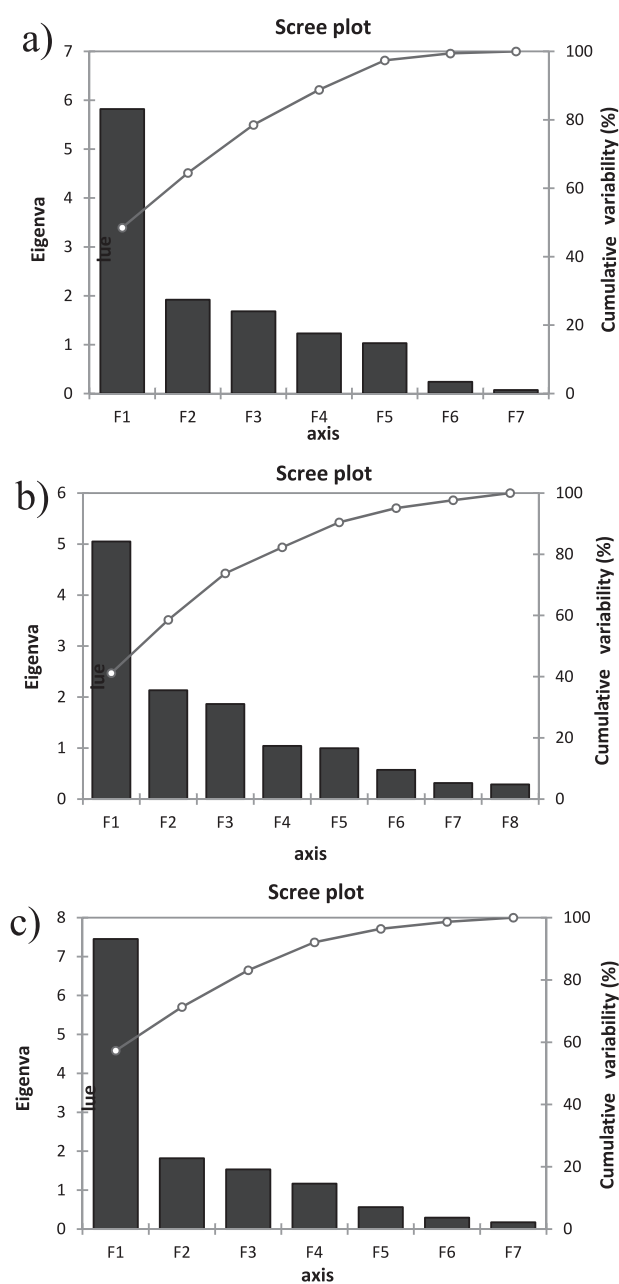


Fig. 3. Scree plot of principal components: a) high, b) medium, and c) low traffic densities.

[28, 33, 37]. The third component, which accounted for 12.65% of the total variance, had the highest loading of Cr and moderate loadings of Co, which mainly originated from exhaust and non-engine combustion sources (brake wear) [31]. The fourth component explains 9.67% of the total variability and consists of moderate loading of Ba. This suggests a brake wear source [8].

Similarly, four components for medium density show 88.8% of cumulative variance. The first component accounts for 41.17% of total variance, and consists of the highest loading of As, Pb, Ni, Co, Fe, and V, and moderate contributions from PM₁₀, Mn, and Zn, with a weak contribution of Cr, which mostly originates from vehicle exhaust emissions and non-exhaust (brake and tire wear) [1, 38-39]. The second component, which accounts for 17.4% of the total variance, has the highest loading of Cd and Cr, and moderate loading of Zn and Ba with a weak loading of V, which is mainly produced from exhaust, combustion of engine oil, brake wear, and tire wear [37, 39, 40]. The third component explains 15.2% of the total variability and exhibits a high contribution of Cu and moderate loading of Mn, while Fe shows weak loading, which mainly resulted from exhaust and brake wear [5, 8, 12]. However, the fourth component accounts for 8.16% of the total variability, which has a moderate loading of Mn only. This could be emitted from exhaust emission and brake wear [40].

Likewise, four PCs exhibit 88.01% of cumulative variance. The first component has a high factor loading for Ba only and moderate loading of Cr, which are associated with automobile exhaust and brake wear emissions [8, 31]. The second component, which accounts for 24.15% of total variance, has the highest loading of Ni and V with a moderate loading of As, which indicates that diesel engine exhaust sources, combustion of engine oil, and brake wear are the main sources of these metals [35, 41]. The third component contains the highest loading of Cu with significant contributions from Pb, Zn, and Cr, and a weak contribution of Mn, which originated from vehicle exhaust and brake and tire wear [6, 33, 40]. However, the fourth component accounts for 8.37 of the total variability and was associated with Mn, which originated from exhaust and brake wear [40].

Conclusions

Concentration levels of PM₁₀ and related heavy metals were studied at three sampling sites with different traffic densities (high, medium, and low) during the southwest monsoon. The mean concentrations of PM₁₀ for high-, medium-, and low-density traffic was found to be 207.63±7.82, 164.92±10.68, and 90.09±20.70 μg m⁻³, respectively. These concentrations of PM₁₀ levels were seen to be significantly higher in highway and medium-density sites compared to low-density sites, and both were higher than for the U.S. EPA and RMAQG. Overall, the trend of heavy metals recorded in the study area was in the order Ba > Fe > Cu > V > Zn > Pb > Mn > Cr > As

> Ni > Cd > Co, while medium and low traffic densities followed the orders, respectively, Ba > Fe > Zn > V > Cu > Pb > Mn > Cr > As > Ni > Cd > Co and Ba > Fe > Zn > V > Cu > Cr > Pb > Mn > As > Ni > Cd > Co. Between the heavy metals As was found to exceed the U.S. EPA and WHO guidelines.

The results also revealed significant differences among sites ($P < 0.05$) for PM_{10} and heavy metals. Source identification study through CA and PCA helped identify different sources of heavy metals in PM_{10} in the local atmosphere, such as vehicle exhaust (fuel composition), non-exhaust (brake and tire wear), and re-suspension particles from different road dusts. Owing to the effects of PM_{10} , which is associated with health risks, the level of PM_{10} and its content of heavy metals, especially As, should be monitored frequently in order to achieve a healthy environment, especially within this study area. Also, this study indicated that for the future and effective management of Malaysian air quality, an effort should be made toward identification of point and non-point pollution sources as a priority in controlling air pollution.

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References

- DAS R., KHEZRI B., SRIVASTAVA B., DATTA S., SIKDAR P.K., WEBSTER R.D., Trace element composition of PM 2.5 and PM_{10} from Kolkata-a heavily polluted Indian metropolis. *Atmos Pollut Res.* **6** (5),742, **2015**.
- XIE Y., ZHAO B., ZHANG L., LUO R. Spatiotemporal variations of PM2. 5 and PM10 concentrations between 31 Chinese cities and their relationships with SO_2 , NO_2 , CO and O_3 . *Particuology.* **20**, 141, **2015**.
- ZUÑIGA J., TARAJIA M., HERRERA V., URRIOA W., GÓMEZ B., MOTTA J. Assessment of the Possible Association of Air Pollutants PM_{10} , O_3 , NO_2 With an Increase in Cardiovascular, Respiratory, and Diabetes Mortality in Panama City: A 2003 to 2013 Data Analysis. *Medicine.* **95** (2), e2464, **2016**.
- CAPASSO L., LONGHIN E., CALONI F., CAMATINI M., GUALTIERI M. Synergistic inflammatory effect of PM10 with mycotoxin deoxynivalenol on human lung epithelial cells. *Toxicol.* **104**, 65, **2015**.
- DUONG T.T., LEE B.-K. Determining contamination level of heavy metals in road dust from busy traffic areas with different characteristics. *J. Environ. Manage.* **92** (3), 554, **2011**.
- ONDŘÁČEK J., SCHWARZ J., ŽDÍMAL V., ANDĚLOVÁ L., VODIČKA P., BÍZEK V. Contribution of the road traffic to air pollution in the Prague city (busy speedway and suburban crossroads). *Atmos. Environ.* **45** (29), 5090, **2011**.
- AMATO F., PANDOLFI M., MORENO T., FURGER M., PEY J., ALASTUEY A. Sources and variability of inhalable road dust particles in three European cities. *Atmos. Environ.* **45** (37),6777, **2011**.
- HARRISON R.M., JONES A.M., GIETL J., YIN J., GREEN D.C. Estimation of the contributions of brake dust, tire wear, and resuspension to nonexhaust traffic particles derived from atmospheric measurements. *Environ. Sci. Technol.* **46** (12), 6523, **2012**.
- JUNENG L., LATIF M.T., TANGANG F. Factors influencing the variations of PM10 aerosol dust in Klang Valley, Malaysia during the summer. *Atmos. Environ.* **45** (26), 4370, **2011**.
- LAWRENCE S., SOKHI R., RAVINDRA K., MAO H., PRAIN H.D., BULL I.D. Source apportionment of traffic emissions of particulate matter using tunnel measurements. *Atmos. Environ.* **77**, 548, **2013**.
- AZMI S.Z., LATIF M.T., ISMAIL A.S., JUNENG L., JEMAIN A.A. Trend and status of air quality at three different monitoring stations in the Klang Valley, Malaysia. *Air Qual Atmos Health.* **3** (1), 53, **2010**.
- WAHID N., LATIF M., SUAN L., DOMINICK D., SAHANI M., JAAFAR S. Source Identification of Particulate Matter in a Semi-urban Area of Malaysia Using Multivariate Techniques. *Bull. Environ. Contam. Toxicol.* **92** (3), 317, **2014**.
- YUSUP Y., ALKARKHI A.F. Cluster analysis of inorganic elements in particulate matter in the air environment of an equatorial urban coastal location. *Chem. Ecol.* **27** (3), 273, **2011**.
- ISMAIL I., LAIMAN R., AHMAD H. Study of particulate matter (PM_{10}) concentration and elemental composition at damansara-puchong highway. In 2011 International Conference on Biology, Environment and Chemistry. Singapore. **2011**.
- TAHIR N.M., SURATMAN S., FONG F.T., HAMZAH M.S., LATIF M.T. Temporal distribution and chemical characterization of atmospheric particulate matter in the eastern coast of Peninsular Malaysia. *Aerosol Air Qual Res.* **13** (2), 584, **2013**.
- APEAGYEI E., BANK M.S., SPENGLER J.D. Distribution of heavy metals in road dust along an urban-rural gradient in Massachusetts. *Atmos. Environ.* **45** (13), 2310, **2011**.
- DOE, Malaysia. Environmental Quality Report. Putrajaya, Malaysia. **2014**.
- RTVM, Road Traffic Volume Malaysia, Ministry of Work Malaysia. **2014**.
- IO-2.1, M., Sampling of ambient air for total suspended particulate matter (SPM) and PM10 using high volume sampler. EPA/625/R-96/010a. Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. US-Environmental Protection Agency, Cincinnati, OH. **1999**.
- IO-3.1, M., Selection, preparation and extraction of filter material. EPA/625/R-96/010a Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. US-Environmental Protection Agency, Cincinnati, OH. **1999**.
- LATIF M.T., AZMI S.Z., NOOR A.D.M., ISMAIL A.S., JOHNY Z., IDRUS S. The impact of urban growth on regional air quality surrounding the Langat River Basin, Malaysia. *The Environmentalist.* **31** (3), 315, **2011**.
- SHAH M.H., SHAHEEN N. Seasonal behaviours in elemental composition of atmospheric aerosols collected in Islamabad, Pakistan. *Atmos. Res.* **95** (2) 210, **2010**.
- SHAH M.H., SHAHEEN N., NAZIR R. Assessment of the trace elements level in urban atmospheric particulate matter and source apportionment in Islamabad, Pakistan. *Atmos Pollut Res.* **3** (1), 39, **2012**.

24. CALLÉN M., DE LA CRUZ M., LÓPEZ J., NAVARRO M., MASTRAL A. Comparison of receptor models for source apportionment of the PM₁₀ in Zaragoza (Spain). *Chemosphere*. **76** (8), 1120, **2009**.
25. SAHU B.K., BEGUM M., KHADANGA M., JHA D.K., VINITHKUMAR N., KIRUBAGARAN R. Evaluation of significant sources influencing the variation of physico-chemical parameters in Port Blair Bay, South Andaman, India by using multivariate statistics. *Marine pollution bulletin*. **66** (1), 246, **2013**.
26. RANJAN R.K., RAMANATHAN A., PARTHASARATHY P., KUMAR A. Hydrochemical characteristics of groundwater in the plains of Phalgu River in Gaya, Bihar, India. *ARAB J Geosci*. **6** (9), 3257, **2013**.
27. WAHID N.B.A., LATIF M.T., SURATMAN S. Composition and source apportionment of surfactants in atmospheric aerosols of urban and semi-urban areas in Malaysia. *Chemosphere*. **91** (11), 1508, **2013**.
28. AZID A., JUAHIR H., TORIMAN M.E., ENDUT A., KAMARUDIN M.K.A., RAHMAN M.N.A. Source Apportionment of Air Pollution: A Case Study In Malaysia. *Jurnal Teknologi*. **72** (1), **2014**.
29. MANSHA M., GHAURI B., RAHMAN S., AMMAN A. Characterization and source apportionment of ambient air particulate matter (PM_{2.5}) in Karachi. *Sci. Total Environ*. **425**, 176, **2012**.
30. TOH Y.Y., LIM S.F., VON GLASOW R. The influence of meteorological factors and biomass burning on surface ozone concentrations at Tanah Rata, Malaysia. *Atmos. Environ*. **70**, 435, **2013**.
31. DUBEY B., PAL A.K., SINGH G. Trace metal composition of airborne particulate matter in the coal mining and non-mining areas of Dhanbad Region, Jharkhand, India. *Atmos Pollut Res*. **3** (2), 238, **2012**.
32. WANG J., HU Z., CHEN Y., CHEN Z., XU S. Contamination characteristics and possible sources of PM₁₀ and PM_{2.5} in different functional areas of Shanghai, China. *Atmos. Environ*. **68**, 221, **2013**.
33. SONG F., GAO Y. Size distributions of trace elements associated with ambient particular matter in the affinity of a major highway in the New Jersey-New York metropolitan area. *Atmos. Environ*. **45** (37), 6714, **2011**.
34. MOOIBROEK D., SCHAAP M., WEIJERS E., HOOGERBRUGGE R. Source apportionment and spatial variability of PM_{2.5} using measurements at five sites in the Netherlands. *Atmos. Environ*. **45** (25), 4180, **2011**.
35. KHAN M., LATIF M., SAW W., AMIL N., NADZIR M., SAHANI M. Fine particulate matter associated with monsoonal effect and the responses of biomass fire hotspots in the tropical environment. *Atmos. Chem. Phys. Discuss*. **15**, 22215, **2015**.
36. PANT P., HARRISON R.M. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: a review. *Atmos. Environ*. **77**, **78**, **2013**.
37. HUANG X.H., BIAN Q., NG W.M., LOUIE P.K., YU J.Z. Characterization of PM_{2.5} major components and source investigation in suburban Hong Kong: A one year monitoring study. *Aerosol Air Qual Res*. **14** (1), 237, **2014**.
38. WANG Y., HOPKE P.K. A ten-year source apportionment study of ambient fine particulate matter in San Jose, California. *Atmos Pollut Res*. **4** (4), 398, **2013**.
39. DALL'OSTO M., QUEROL X., AMATO F., KARANASIOU A., LUCARELLI F., NAVA S. Hourly elemental concentrations in PM_{2.5} aerosols sampled simultaneously at urban background and road site during SAPUSS-diurnal variations and PMF receptor modelling. *Atmos. Chem. Phys*. **13** (8), 4375, **2013**.
40. YU L., WANG G., ZHANG R., ZHANG L., SONG Y., WU B. Characterization and source apportionment of PM_{2.5} in an urban environment in Beijing. *Aerosol Air Qual Res*. **13** (2), 574, **2013**.
41. GUGAMSETTY B., WEI H., LIU C.-N., AWASTHI A., HSU S.-C., TSAI C.-J. Source characterization and apportionment of PM₁₀, PM_{2.5} and PM_{0.1} by using positive matrix factorization. *Aerosol Air Qual. Res*. **12**, 476, **2012**.