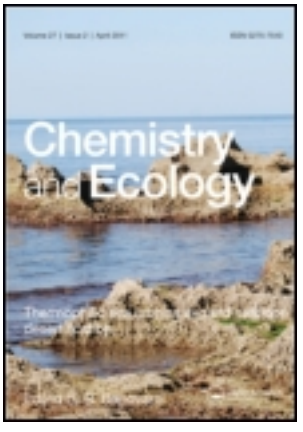

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gche20

Cluster analysis of inorganic elements in particulate matter in the air environment of an equatorial urban coastal location

Yusri Yusup [a] & Abbas F.M. Alkarkhi [a]
[a] School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

Available online: 19 Apr 2011

To cite this article: Yusri Yusup & Abbas F.M. Alkarkhi (2011): Cluster analysis of inorganic elements in particulate matter in the air environment of an equatorial urban coastal location, Chemistry and Ecology, 27:3, 273-286

To link to this article: http://dx.doi.org/10.1080/02757540.2010.547491

Chemistry and Ecology
Vol. 27, No. 3, June 2011, 273–286

Taylor & Francis
Taylor & Francis Group

Cluster analysis of inorganic elements in particulate matter in the air environment of an equatorial urban coastal location

Yusri Yusup* and Abbas F.M. Alkarkhi

School of Industrial Technology, Universiti Sains Malaysia, Penang, Malaysia

(*Received 25 July 2010; final version received 6 December 2010*)

Concentrations of nine inorganic elements (Na, Zn, Ca, Fe, Ni, Mn, Cu, Cd and Al) in particulate matter (PM_{10}) in the air of an equatorial urban coastal location during 2009 were studied during summer and winter monsoon seasons using high-volume sampling techniques. Atomic absorption spectrophotometry was used to analyse the samples. The concentrations of most inorganic elements were higher during summer than winter, except for Cu and Zn. The main inorganic elements in PM_{10} are Na, Zn and Ca. High concentrations of Na and Ca are due to marine aerosols. Analysis of enrichment factors showed that inorganic elements are from non-crustal sources. Cluster analysis identified five clusters in the summer and six in the winter: (1) PM_{10}–Ni, (2) Zn–Na, (3) Fe–Cu–Ca–Cd, (4) Mn and (5) Al for summer; and (1) PM_{10}, (2) Zn, (3) Fe–Ni, (4) Cu–Ca–Na–Cd, (5) Mn and (6) Al for winter. Combining both correlation and cluster analysis, it was found that Fe–Cu–Cd was from industry/vehicle emissions, Zn was from resuspended soil, Mn was from metallurgical processes, Ni was from a nearby power plant and Al was from crustal sources. Inorganic element concentrations could be a good indicator of local sources of PM_{10}.

Keywords: air pollution; PM_{10}; correlation coefficient analysis; AAS; monsoon

1. Introduction

The largest anthropogenic emissions of atmospheric inorganic elements occur in Asia, and according to Juneng et al. [1] many parts of Asia are plagued by airborne particulate matter. Primary air pollutants, such as particulate matter, are emitted by two types of sources: anthropogenic sources (e.g. industry, vehicles, combustion sources, bare lands and open burnings) and natural sources (e.g. volcanic eruptions, wildfires and marine aerosols). This particulate matter comprises small particles, water droplets, elemental carbon, organic carbon and various metal and ionic elements [2].

Airborne particulates affect human health and this depends on the particle size distribution and chemical composition [3]. Furthermore, exposure to higher concentrations of fine particulate matter which contains inorganic elements can have deleterious health impacts on living organisms [4]. Short- and long-term exposure to particulate matter are related to mortality, hospital admission, decreased lung function and related health symptoms [5]; a study by Vichit-Vadakan et al. [6] reported a statistical significance between daily mortality and concentrations of PM_{10}. PM_{10} or particulate matter $< 10\,\mu m$ can penetrate the trachea and lower aerodynamic diameter fractions

*Corresponding author. Email: yusriy@usm.my

ISSN 0275-7540 print/ISSN 1029-0370 online

DOI: 10.1080/02757540.2010.547491
http://www.informaworld.com

can even reach the alveoli [7]. The duration of particulate matter suspended in the air and its impact on living organisms and the environment are greatly dependent on particle size [8]. It was also stated by Santamaria et al. [7] that inorganic elements in urban areas are significantly higher than their natural concentrations due to human activities, leading to the realisation that air quality standards based on total suspended solids (PM_{10}, $PM_{2.5}$) alone are not sufficient. It has also been postulated that human health may deteriorate because of PM_{10} from biomass burning containing redox-active metals such as Fe due to the reactive nature of the radicals produced [9,10].

Many developing countries in Asia are involved in heavy industrialisation, urbanisation and the transportation industry, and therefore have a higher concentration of air pollutants than other, more developed countries. There are a number of studies on particulate matter and its composition in Asian countries, where a similarity of these countries is their atmospheric conditions (although intensity of traffic, and energy consumption and generation vary widely) [11]. Recent work in particulate matter and inorganic elements (in South East Asia) include Tippayawong et al. [5] in Thailand, Balasubramaniam et al. [12] in Singapore, See et al. [13] in Indonesia and Tahir et al. [14] in Malaysia.

Malaysia has seen a decrease in air quality since the 1990s because of rapid infrastructural development. The three main sources of air pollution in Malaysia are mobile, stationary and open burning sources. According to Afroz et al. [15], mobile sources contribute the most to air pollution in Malaysia. Motor vehicles make up 70% of total emissions and stationary sources, e.g. factories and industry, 20%. To further worsen the situation, southwesterly winds carry large quantities of particulate matter from neighbouring countries because of uncontrolled biomass burning which further deteriorates the air quality of Malaysia on a national scale. Prone to severe haze in the past, between 1983 and 1997, Malaysia experienced sporadic haze conditions over the years.

To assess the air quality of Penang, Malaysia in terms of PM_{10} and inorganic elements, the objectives of this study are to identify the main sources of PM_{10} and inorganic elements, whether crustal or non-crustal, in addition to finding the relationship between different inorganic elements and PM_{10} during the summer and winter monsoons through correlation analysis, as well as to determine the similarities between selected parameters through cluster analysis. Statistical analysis such as descriptive statistics, correlation analysis and cluster analysis were used to analyse the data and achieve the preceding objectives.

2. Methodology

2.1. *Description of study area*

PM_{10} sampling was conducted daily for six months, in 2009, in the campus of Universiti Sains Malaysia, Penang, Malaysia during weekdays under a variety of weather conditions using a sampling time of 24 h. The sampling site was located on the rooftop of the School of Industrial Technology. This building is a four-storey structure with a height of $\sim$15 m. Universiti Sains Malaysia is located in Penang, at a latitude of 5°25′ N and a longitude of 100°19′ E. Penang has two major monsoon seasons, summer and winter, and to a lesser degree, spring and autumn transition seasons. Sampling was done for both seasons: June, July and August for the summer months and September, October and December for the winter months.

Briefly, Penang is a fast-developing state with housing projects continuously in construction because of its high property market value. Penang is also known as a tourism destination and is part of the UNESCO's World Heritage City Programme. It also has a large semiconductor-related industrialised area in the southeastern section of the island. Across the strait from Penang Island, is the Prai industrialised zone which consists of some major petrochemical, chemical, refineries and fertilisers industries with various other smaller industries.

2.2. *Sampling and analysis*

The high-volume sampler (HVS) Ecotech Model 0-HV2000-001 was used to collect PM_{10} samples with an average time of 24 h. High-volume air sampling employs a gravimetric method to determine the concentration of suspended particulate matter in the atmosphere. Ambient air was drawn into the size-selective inlet at a constant flow rate of 1.13 standard $m^3 \cdot min^{-1}$ ($67.8\,m^3 \cdot h^{-1}$) or $40\,ft^3 \cdot min^{-1}$.

Glass microfibre filter papers (Whatman, CAT No. 1820-866), 20.3×25.4 cm, were used. The filter paper was prepared by drying in an oven at 100 °C for 1 h and then placed in a desiccator to cool. The balance used to weigh the filter paper was the analytical balance Sartorius Model BP301s. A sealed plastic bag was used to store the filter paper before being placed in the HVS to sample air for 24 h. The initial and final volumetric flow rates of the HVS were recorded. The filter paper was then removed from the HVS and stored in a sealed plastic bag before being weighed (Manual Reference Method: RFPS-0706-162).

To digest the sample, the filter paper was cut into strips of 1.9×20.3 cm and folded before inserting into 250 mL beaker. Fifteen millilitres of 3 M nitric acid (analytical grade, QRëC™ CAS: 7697-37-2) were poured into a beaker, covered and heated on a hotplate for 30 min. The sample was left to cool at room temperature for 30 min. Deionised water was added and the mixture was poured into a 100 mL volumetric flask. The sample was then filtered into a polyethylene sample bottle using a 125-mm filter paper and refrigerated until it was ready to be analysed (USEPA Method IO-3.1) [16].

Aluminium was determined using a HACH Odyssey DR/2400P Spectrophotometer with HACH reagents according to the Eriochrome Cyanine R (ECR) method. The reagents used are ECR Reagent Powder Pillow, Hexamethylene Buffer Reagent Powder Pillow and ECR Masking Reagent Solution. The metals Fe, Zn, Cu, Mn, Ca, Cd, Na and Ni were analysed using a Perkin–Elmer AA-100 flame atomic absorption spectrophotometer (AAS) (following the USEPA Method IO-3.2) [16] as used by Chuersuwan et al. [17] and Shah and Shaheen [18]. The metals estimated in blanks were $<10\%$ of the sample-averaged metal concentrations. AAS was used to determine the concentration of the inorganic elements by comparing the absorbance of sample solutions with the corresponding standard solutions. The standard solutions for the inorganic elements under investigation were prepared from stock solutions just before utilisation. Various dilutions of standard solutions (Na 1.70238.0500, Zn 1.19806.0500, Ca 1.19778.0500, Fe 1.19781.0500, Ni 1.19781.0500, Mn 1.19789.0500, Cu 1.19786.0500, Cd 1.19777.0500, analytical grade, Merck, Denmark) according to the Standard Conditions and Characteristic Concentration Checks for Atomic Absorption were used to obtain calibration diagrams or calibration curves for each run. Care was taken if concentrations exceeded the calibration curve, whereupon the sample was re-analysed (this was often observed for Zn and Na because this sampling site was close to the coast).

2.3. *Statistical analysis*

Statistical analysis such as descriptive statistics, correlation analysis and cluster analysis were used to analyse the data for PM_{10} and inorganic element concentrations in air ($\mu g \cdot m^{-3}$).

2.3.1. *Cluster analysis*

Cluster analysis (CA) is a multivariate technique, whose primary purpose is to classify the objects of the system into categories or clusters based on their similarities, where the objective is to find an optimal grouping for which the observations or objects within each cluster are similar, but

the clusters are dissimilar to each other. Hierarchical clustering is the most common approach in which clusters are formed sequentially. The most similar objects are grouped first, and these initial groups are merged according to their similarities. Eventually, as the similarity decreases, all subgroups are fused into a single cluster. CA was applied to inorganic elements in PM_{10} from sampling of air using a single linkage method. In the single linkage method, the distance or similarity between two clusters A and B is defined as the minimum distance between a point in A and a point in B (Euclidean distance).

At each step, the distance was found for every pair of clusters and the two clusters with the smallest distance (largest similarity) were merged. After two clusters were merged, the procedure was repeated for the next step: the distances between all pairs of clusters were calculated again, and the pair with minimum distance was merged into a single cluster. The result of a hierarchical clustering procedure can be displayed graphically using a tree diagram, also known as a dendrogram, which shows all the steps in the hierarchical procedure [19,20].

3. Results and discussion

To describe qualitatively the emission profile of the area of study, it can be said that sources of air pollution near the sampling site include emissions from open land caused by real-estate development, vehicles, the chimneys of faculty buildings and an industrial area that mainly consists of the semiconductor industry ($\sim$3 km from the sampling station) and a heavily industrialised area situated across the strait $<$10 km from the sampling site. Thus, there was a large contribution of air pollutants from industries in addition to vehicular emissions. Because the sampling site has a coastal location, with a distance from the sea of 1.40 km, high concentrations of Na and Ca from sea spray can be expected.

3.1. *Particulate matter* (PM_{10})

Descriptive statistics of PM_{10} concentrations are given in Table 1 for summer and winter seasons with inorganic element concentrations. PM_{10} concentration ranges from a minimum of 7 to 273 $\mu g \cdot m^{-3}$ during the summer season and from 14 to 155 $\mu g \cdot m^{-3}$ during the winter season. The difference between the summer and winter seasons was statistically insignificant, as exhibited by using ANOVA. This may be due to different meteorological conditions and emission rates which caused the relatively large standard deviations and ranges [21] between the seasons. The mean levels were 70.7 $\mu g \cdot m^{-3}$ during the summer season and 58.7 $\mu g \cdot m^{-3}$ during the winter season (Figure 1), which were below the World Health Organization (WHO) primary standard of 80 $\mu g\, m^3$ for both seasons and higher than the WHO secondary standard of 60 $\mu g \cdot m^{-3}$ for the summer season (as cited in Shah and Shaheen [18]) [22]. However, there were three instances (3% of collected data), 3 August (175 $\mu g \cdot m^{-3}$), 12 August (273 $\mu g \cdot m^{-3}$) and 10 September (155 $\mu g \cdot m^{-3}$), when the 24 h PM_{10} concentration exceeded the air quality standard for Malaysia of 150 $\mu g \cdot m^{-3}$. Determined PM_{10} concentrations also exceeded the 24 h Thailand standard of 120 $\mu g \cdot m^{-3}$ on 10 occasions (13% of collected data).

Monthly averages for weekday concentrations during the observation period were in the range 60–80 $\mu g \cdot m^{-3}$ with a decrease in the concentration during December to 40 $\mu g \cdot m^{-3}$. The month of August, during the summer season, has the largest standard deviation ($73.1 \pm 72.0\ \mu g \cdot m^{-3}$ with a median of 57.1 $\mu g \cdot m^{-3}$) compared with other months, with extreme high and low concentrations of PM_{10}. The lowest concentration of PM_{10} determined was 7.40 $\mu g \cdot m^{-3}$ on 25 August, whereas the highest PM_{10} concentrations was 273 $\mu g \cdot m^{-3}$.

Hazy atmospheric conditions suspected to be from transboundary sources were the reason for the very high PM_{10} concentrations observed in July and August, but due to unexpected rain, the

Table 1. Descriptive statistics of inorganic element concentration in air for selected parameters (summer and winter seasons), $n = 75$.

Parameter	Min.	Max.	Mean	Median	Std.
		Summer season			
PM_{10}	7.00	273	70.7	58.5	49.4
Al	>LOD	0.0300	0.0100	0.0100	0.00
Zn	0.340	4.24	1.91	1.87	0.670
Fe	>LOD	0.970	0.330	0.430	0.290
Cu	>LOD	0.180	0.0200	0.005	0.0300
Ca	0.0100	2.29	1.46	1.53	0.450
Na	1.36	12.9	7.46	7.67	2.18
Mn	>LOD	0.230	0.0300	0.0300	0.0300
Ni	>LOD	0.180	0.0500	0.0500	0.0400
Cd	>LOD	0.0700	0.0200	0.0200	0.0200
		Winter season			
PM_{10}	14.0	155	58.7	49.9	34.3
Al	>LOD	0.0100	0.0100	0.0100	0.00
Zn	1.21	4.91	2.84	2.85	0.810
Fe	>LOD	0.520	0.260	0.250	0.150
Cu	0.0100	0.0800	0.0300	0.005	0.0200
Ca	0.0300	1.66	0.940	0.930	0.480
Na	1.96	12.2	7.07	7.69	3.44
Mn	0.0100	0.0400	0.0200	0.0200	0.0100
Ni	>LOD	0.110	0.0300	0.0100	0.0400
Cd	>LOD	0.0500	0.0100	0.005	0.0200

Notes: Concentration is given in $\mu g \cdot m^{-3}$; >LOD denotes lower than the limit of detection and the value 0.005 reflects half of the limit of quantification (LOQ).

Figure 1. Season averaged concentration for PM_{10} ($\mu g \cdot m^{-3}$).

concentration of PM_{10} was suppressed, which led to the high standard deviation and average of the data for these months. This was consistent with the findings of Juneng et al. [1] that PM_{10} peaks in July and August. This was strongly associated with the bimodal annual cycle of rainfall in their area. Juneng et al. also state that during this period, the number of forest fires in central Sumatra increased and particles were carried to their site by southerly and southwesterly winds. Meanwhile, low PM_{10} values were observed in December at this site due to decreased anthropogenic activities during the holidays.

Table 2. Particulate matter concentration at four stations, from work done by Tahir et al. [14] and Pengchai et al. [24]

Station	Highest concentration of PM_{10} ($\mu g \cdot m^{-3}$)
Yuparaj, Thailand	149
Municipality Hospital, Thailand	150
Saraphee, Thailand	182
Lamphun, Thailand	182
Din Daeng, Thailand	144
Kuala Terengganu, Malaysia	148
Penang, Malaysia (present study)	273

It has been determined from much related research that climate conditions such as the winter and summer seasons influence PM_{10} concentrations. For example, the relationship between PM_{10} and meteorology was confirmed when the coarse mass fraction showed a characteristic increase with wind speed during summer months, whereas fine aerosol mass and its elemental composition exhibited a conspicuous temporal pattern associated with northeasterly winds during winter at Kumar and Sarin's [23] site of study. From the data obtained, it was observed that the concentration of PM_{10} was higher in the summer season than in the winter because of a lack of precipitation. The reduced amount of precipitation during the summer season left a larger background concentration of air pollutants. Furthermore, ambient temperatures are typically higher in summer than winter. Ambient temperature was found to have the strongest correlation with total suspended particulate matter because atmospheric convection and dispersion were suppressed, such as during severe haze episodes, when the atmosphere tended to be very stable, leading to suspension of the pollutants [14,18]. It was also discovered by Bin Yusup et al. [24] that vertical movement of the atmosphere in the convective/daytime condition in this area (because of it being in an urban area) was lower than for other regions and thus hampers dispersion of air pollutants.

Pengchai et al. [25] found that the PM_{10} concentration was higher during the summer season and added that it often exceeded the 24 h Thailand air-quality standard for all of their sites (refer to Table 2 for a comparison between the highest concentration of PM_{10} determined in a nearby urban area and present study). During hazy conditions, the average PM_{10} concentrations in Kuala Lumpur, the capital of Malaysia, and Selangor, a fast-developing industrialised Malaysian state, are 171 and 131 $\mu g \cdot m^{-3}$, respectively [15]. This shows that this site is vulnerable to very high PM_{10} concentrations because its highest PM_{10} concentration was 273 $\mu g \cdot m^{-3}$, even though Kuala Lumpur has the third highest PM_{10} concentration in South East Asian, next to Beijing, China and Bangkok, Thailand [26].

The overall (or averaged during the sampling period) air quality at this site, in terms of PM_{10}, was below the Malaysian air-quality standard. Nevertheless, the instances of high PM_{10} concentrations that causes the large spread around the mean indicate that there are short-term sources of PM_{10} [5], e.g. an increase in vehicular emissions and/or increased activity from the two industrial areas nearby and open surfaces of land, which were 0.5 km from sampling station, as well as the nearby coal-fired power plant.

3.2. *Inorganic elements in PM_{10}*

Descriptive statistics for inorganic element concentrations in PM_{10}, including the mean, standard deviation, maximum and minimum values for selected inorganic elements in PM_{10} are given in Table 1. Na exhibited the highest average concentration during the summer season of 7.46 $\mu g \cdot m^{-3}$. The concentration of the other main inorganic elements in descending order was Zn (1.91 $\mu g \cdot m^{-3}$) and Ca (1.46 $\mu g \cdot m^{-3}$). The highest mean concentration of inorganic elements in the winter season was of the same order as the summer season. Thus, the dominant inorganic elements in PM_{10} are Na, Zn and Ca for this site.

The concentration of most inorganic elements was higher in the summer season than in the winter, except for Zn and Cu. The concentrations of the inorganic elements were arranged in the following order: for the summer season, Na > Zn > Ca > Fe > Ni > Mn > Cu > Cd > Al; and for the winter season, Na > Zn > Ca > Fe > Cu, Ni > Mn > Al, Cd. The two seasons were statistically different based on inorganic element concentrations as determined by MANOVA. The percentage of mass concentrations of crustal elements (defined as Al) from total PM_{10} mass concentrations was on average 26% and this was higher than reported by Limbeck et al. [21].

The inorganic elements Mn, Ni and Cd observed can be compared with annual WHO and US-EPA standards for atmospheric metal concentrations. The WHO standard is $0.150\,\mu g \cdot m^{-3}$ for Mn, $0.00038\,\mu g \cdot m^{-3}$ for Ni and $0.005\,\mu g \cdot m^{-3}$ for Cd, whereas the US-EPA standard is $0.500\,\mu g \cdot m^{-3}$ for Mn, $0.00024\,\mu g \cdot m^{-3}$ for Ni and $0.006\,\mu g \cdot m^{-3}$ for Cd (as cited in Shah and Shaheen [18]) [22]. The median concentration of Mn was 3.00×10^{-2} and $2.00 \times 10^{-2}\,\mu g \cdot m^{-3}$ for the summer and winter seasons, respectively, which was below WHO and US-EPA standards, whereas the concentration of Ni was 5.00×10^{-2} and $1 \times 10^{-2}\,\mu g \cdot m^{-3}$ for the summer and winter seasons, respectively (although the standard deviation was large) making it up to 200 times higher than the US-EPA and WHO standards; the median concentration of Cd during the summer and winter seasons was 2.00×10^{-2} and $5 \times 10^{-3}\,\mu g \cdot m^{-3}$, respectively (with equally large standard deviation), which was four times higher than either of the worldwide standards. The high values of Ni and Cd may be due to the chosen sampling duration of six months as opposed to an averaging time of one year that was adopted for the WHO and US-EPA standards [18,22].

The higher range and standard deviation for both seasons and for some inorganic element concentrations, as seen in Table 1, indicate that there exists a random source or sink of inorganic elements that is normally from anthropogenic sources such as Fe, Cu, Mn, Ni and Cd, whereas Al, Zn, Ca and Na exhibit a smaller range that can be traced to natural sources such as crustal sources or sea sprays [18].

The concentrations of Na, Zn and Ca account for 25% of the concentration of PM_{10}. Na and Ca are from sea salt, which is a natural source if the site is close to the sea, as is the case for the present study [26]. The concentration of most inorganic elements was higher in summer than in winter because of the prevalence of hazy atmospheric conditions, and thus higher PM_{10} concentrations, and the decreased frequency of rain during the summer season. Climate changes can also affect the sources of air pollutants, as suggested by Glantz et al. [27] who state that primary marine aerosol production changes with surface temperature and wind speed. The concentration of various elements, such as Al, Zn, Pb, C (elemental carbon), attached to particulate matter was also found to be related to meteorological parameters [28]. Except for Cu and Zn, it can be seen that Al, Ca, Na, Mn, Ni, Fe and Cd concentrations were higher during the summer season than the winter season, which is consistent with the results obtained by Pengchai et al. [25]. It was found that Zn has a positive correlation with relative humidity [18] and this can be seen in the present study where Zn concentrations are higher during the winter season when relative humidity was high, whereas Cu does not show a specific pattern with season or meteorological conditions.

The results obtained in present study were compared with similar studies in Thailand and Malaysia, as shown in Table 3. It can be seen that Zn, Na, Ni and Cd exhibited higher concentrations during the winter and summer seasons in the present study than in similar studies. This was due to the coastal and industrial nature of the area in the present study. The concentration of Al was lower. This was because compared with the areas listed in Table 3, the study area does not have large ground surfaces exposed to wind that would suspend PM_{10} originating from crustal sources, from which Al is mainly known to originate. Other inorganic elements studied did not show a clear trend because the concentrations are sometimes higher or lower than the concentration in the present study. Slightly higher values of Cd and Ni are noted and other concentrations are of the same magnitude as seen by other researchers.

Table 3. Concentrations ($\mu g \cdot m^{-3}$) of all inorganic elements analysed in present study [14,17,24].

Elements	Season	Yuparaj, Thailand	Municipality Hospital, Thailand	Saraphee, Thailand	Lamphun, Thailand	Kuala Terengganu, Malaysia	Din Daeng, Thailand	Present study
Fe	Winter	0.14 ± 0.16	0.13 ± 0.19	0.11 ± 0.15	0.11 ± 0.15	0.05 ± 0.03	2.13 ± 0.92	0.260 ± 0.150
	Summer	0.44 ± 0.34	0.31 ± 0.33	0.46 ± 0.44	0.59 ± 0.49	–	–	0.330 ± 0.290
Ca	Winter	1.62 ± 1.49	1.48 ± 1.01	0.83 ± 0.47	0.64 ± 0.33	–	4.79 ± 2.38	0.940 ± 0.480
	Summer	2.22 ± 1.05	1.75 ± 1.46	2.10 ± 1.73	2.11 ± 1.66	–	–	1.46 ± 0.450
Cd	Winter	–	–	–	–	–	–	0.0100 ± 0.0200
	Summer	–	–	–	–	–	–	0.0200 ± 0.0200
Mn	Winter	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	–	0.09 ± 0.09	0.0200 ± 0.0100
	Summer	0.03 ± 0.02	0.02 ± 0.02	0.03 ± 0.02	0.03 ± 0.02	–	–	0.0300 ± 0.0300
Cu	Winter	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.03	0.01 ± 0.01	–	0.09 ± 0.04	0.0300 ± 0.0200
	Summer	0.01 ± 0.01	0.02 ± 0.01	0.04 ± 0.03	0.02 ± 0.02	–	–	0.0200 ± 0.0300
Ni	Winter	0.0 ± 0.01	0.00 ± 0.01	–	0.01 ± 0.02	–	0.03 ± 0.20	0.0300 ± 0.0400
	Summer	0.0 ± 0.01	0.00 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	–	–	0.0500 ± 0.0400
Al	Winter	0.27 ± 0.17	0.24 ± 0.23	0.19 ± 0.12	0.15 ± 0.11	0.14 ± 0.10	3.02 ± 2.73	0.0100 ± 0.00
	Summer	0.52 ± 0.24	0.33 ± 0.18	0.47 ± 0.27	0.62 ± 0.64	–	–	0.0100 ± 0.00
Na	Winter	–	–	–	–	–	1.88 ± 1.19	7.07 ± 3.44
	Summer	–	–	–	–	–	–	7.46 ± 2.18
Zn	Winter	0.29 ± 1.56	0.31 ± 1.56	0.04 ± 0.07	0.3 ± 1.38	–	0.84 ± 0.47	2.84 ± 0.81
	Summer	0.08 ± 0.05	0.1 ± 0.21	0.09 ± 0.08	0.08 ± 0.09	–	–	1.91 ± 0.670

Note: – denotes lower than the limit of detection (LOD).

As a comparison, Pengchai et al. [25] found that Fe was more concentrated in the summer and commented that Fe was most concentrated in PM_{10} when compared with other inorganic elements, such as Al, Ca and Zn. The authors also expressed that this should be taken into consideration during a PM_{10} pollution episode. Chuersuwan et al. [17] and Tippayawong et al. [5] also reported Fe as most concentrated in PM_{10} compared with other inorganic elements. Fe was also one of the major elements and accounted for the high percentage of total trace elements concentration in a study by Balasubramaniam et al. [12]. A possible source, other than crustal sources, of Fe was discovered to be from a peat fire or vegetative burning episode that occurred in Sumatra, Indonesia [13]. Vegetative burning does not often occur at this site, thus explaining the lower concentration of Fe compared with other metals in PM_{10}. Tahir et al. [14] state that Al was the highest inorganic element concentration for all of their stations followed by Fe and Zn, whereas the other elements (Pb, Mn, Cr and Cd) have a lower concentration than other metals in their observations. The authors obtained a higher concentration of Al in their observation because the main source of PM_{10} was from crustal sources, whereas most of the inorganic elements observed here are from non-crustal sources, as discussed below.

3.2.1. *Enrichment factors*

The inorganic element characteristic of PM_{10} can be determined by normalising concentrations of the inorganic element to their corresponding crustal concentrations to obtain enrichment factors (EF) which can be used to establish the contribution of crustal source to inorganic elements in PM_{10}. The ratio of metals to Al was normally used to indicate crustal origins using the following equation:

$$\mathrm{EF_x} = \frac{C_{\mathrm{x,PM}}/C_{\mathrm{Al,PM}}}{C_{\mathrm{x,crustal}}/C_{\mathrm{Al,crustal}}},$$

where $C_{\mathrm{x,PM}}$, $C_{\mathrm{Al,PM}}$, $C_{\mathrm{x,crustal}}$ and $C_{\mathrm{Al,crustal}}$ are the concentration of metal X in PM_{10}, concentration of Al in PM_{10}, concentration of metal X in crustal and concentration of Al in crustal, respectively. Crustal concentrations ratios used for Zn/Al, Fe/Al, Cu/Al, Mn/Al, Ni/Al and Cd/Al are 0.000861, 0615, 0.00068, 0.012, 0.0009 and 0.0000024 [12], respectively. Although crustal metal concentration ratios vary for different areas, it can be assumed that EF values >10 are of non-crustal origin [12]. The geometric median was used to calculate a representative value for each EF.

Assuming that the anthropogenic source of Al near the sampling site was small, it was determined that Zn, Cu, Mn, Ni, Cd and Fe are not solely crustal in origin, furthermore, Cd, Ni and Zn had significantly high EF values (refer to Figure 2). The lowest EF value was 40 for Fe, which was enriched by nearby industries. The highest EF value was for Cd, which normally originates from vehicular emissions, whereas Zn was from constant emissions from excavation or resuspended soil and industries nearby [29]. Based on EF analysis, Tahir et al. [14] showed that Cd and Zn can be related to vehicular emissions sources, whereas Al and Fe can be of crustal origin. From the obtained results, the above-mentioned metals are indicators of significant man-made sources for this observational site. Because EF values for Fe, Cu, Mn, Ni and Cd vary, the emission sources for these metals are continuously changing. Relatively low concentrations of Al also suggest a low impact of crustal origins on PM_{10} inorganic element concentrations.

The presence of a severe haze on 12 August did not increase the inorganic element concentrations in PM_{10}, suggesting that PM_{10} mass consists of other major constituents beside inorganic elements, for example organic carbon [17]. This was further supported by the discovery that the main source of organic compounds in PM_{10} was from biomass burning during a Malaysian haze phenomenon [30]. Thus, inorganic element concentrations can be a good indicator of local sources of PM_{10}.

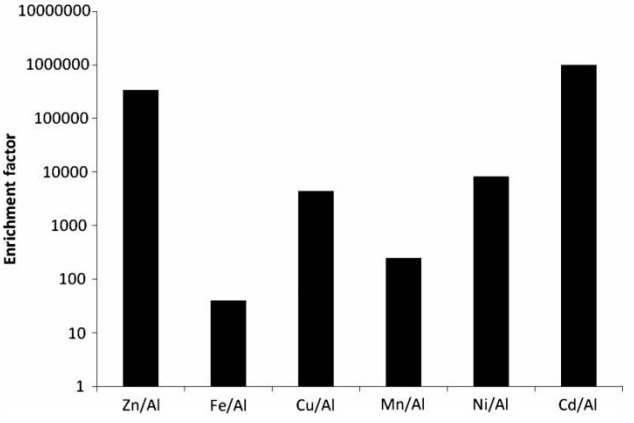

Figure 2. Enrichment factors of different inorganic element combinations.

3.2.2. *Correlation analysis*

The correlation matrixes of selected parameters concentrations in air were examined to determine the relationship between different parameters. The correlation data for the selected parameters are presented in Table 4. For the summer season, a strong negative relationship was seen between Fe and Al, whereas a strong positive relationship exists between Fe and Cu, Ca, Na and Cd. Zn exhibited a strong positive relationship with Na only. Other positive relationships were seen between Cu and Ca and between Ca and Na. For the winter season, different behaviour was exhibited by selected parameters, Fe exhibited a strong positive relationship with Ni only, whereas Cu was positively correlated with Ca, Na and Cd. Ca was also positively correlated with Na

Table 4. Linear correlation coefficient between concentrations of PM_{10} and inorganic elements in air, $n = 75$.

	PM_{10}	Al	Zn	Fe	Cu	Ca	Na	Mn	Ni	Cd
					Summer					
PM_{10}	1	−0.12	−0.10	−0.14	−0.09	0.07	0.02	−0.10	0.28	−0.14
Al		1	−0.20	−0.32*	−0.09	−0.12	−0.02	−0.14	−0.02	−0.02
Zn			1	0.21	−0.22	0.10	0.58**	0.24	−0.18	0.28
Fe				1	0.40**	0.37**	0.31*	0.17	0.05	0.37*
Cu					1	0.35*	−0.02	−0.10	0.15	0.09
Ca						1	0.31*	0.17	−0.08	0.22
Na							1	−0.03	0.03	0.28
Mn								1	0.10	0.12
Ni									1	0.02
Cd										1
					Winter					
PM_{10}	1	0.13	0.20	−0.01	−0.18	−0.07	−0.21	−0.13	−0.09	−0.09
Al		1	0.12	−0.31	0.016	−0.14	−0.35	−0.06	−0.34	0.13
Zn			1	0.10	0.06	0.17	0.25	−0.19	0.06	0.08
Fe				1	0.03	−0.01	0.22	−0.03	0.51**	0.003
Cu					1	0.71**	0.58**	0.28	0.15	0.48**
Ca						1	0.73**	0.07	0.29	0.39*
Na							1	−.077	0.437(*)	0.31
Mn								1	−0.001	0.19
Ni									1	−0.28
Cd										1

Notes: **Correlation is significant at the 0.01 level (two-tailed); *correlation is significant at the 0.05 level (two-tailed).

and Cd, whereas Na exhibited a strong relationship with Ni. Other parameters did not show a significant relationship with any parameter under study such as between PM_{10} and the inorganic elements determined. Elements with the same concentration trend or high correlations tend to have common emission sources, and when no distinct profile was observed, the elements are emitted continuously without being influenced by seasonal or meteorological variations [21].

It can be said that correlation analysis helps in giving insights into the sources of inorganic elements. The negative correlation between Fe and Al indicates that both could be from the same source, although inversely related, which explains the high EF value mentioned previously and points to the sources of Fe being mainly anthropogenic (e.g. industrial and/or vehicular emissions). Because Fe was positively correlated with Cd, a long-range contribution from vehicles is also possible. The source of Ca and Na was from marine aerosols. The positive correlation between Cu, Ca, Na and Zn shows that most of their sources originate from the direction of the sea where most industrial areas are located and where reclamation of land was being conducted. This was supported by the fact that the highest contribution of anthropogenic sources, such as coal combustion, vehicular exhaust and residue oil combustion, was associated with wind direction [31]. During the winter season, Ni and Fe were positively correlated suggesting that Fe might also originate from the nearby coal-burning power plant or long-range vehicular emissions situated next to the sea, and this was further supported by the correlation between Na and Ni. Different behaviour for selected parameters in the summer and winter seasons was due to the scavenging effect of rain, which does not effectively wash out fine particles, and usually contains Ni from heavy-oil combustion sources or fuel-burning power plants [32].

In summary, six groups can be classified according to source. Fe–Cu–Cd was from industrial, vehicular and fugitive emissions, Na–Ca was from sea spray, Zn was from excavation or resuspended soil dust, Ni was from the heavy oil-fired power plants, Al was from crustal sources and Mn was from metallurgical-processing industries.

3.2.3. *Cluster analysis*

The data were further analysed using CA to identify the sources of inorganic elements and PM_{10} according to the similarity of the elements in the group during the two seasons (summer and winter). CA gives information regarding whether two variables are correlated, as well as the direction of the relationship, be it positive or negative, but CA does not provide information on similarities with other variables in terms of behaviour. Similarities can only be studied by CA in presence of other variables (not just two variables) regardless of the relationship between them, for example, if two variables are correlated it does not necessarily mean they will be in the same cluster. CA for the summer season rendered a dendrogram as shown in Figure 3, grouping the parameters into five statistically different clusters: (cluster 1) PM_{10} and Ni; (cluster 2) Zn and Na; (cluster 3) Fe, Cu, Ca Cd; (cluster 4) Mn alone; and (cluster 5) Al alone. CA for the winter season exhibited a different grouping, as shown in Figure 4; six clusters can be recognised: (cluster 1), PM_{10} alone; (cluster 2) Zn alone; (cluster 3) Fe and Ni; (cluster 4) Cu, Ca, Na and Cd; (cluster 5) Mn alone and (cluster 6) Al alone.

This grouping gives evidence that some parameters have different behaviour in each season. However, Mn and Al have the same behaviour in both seasons. Because Al and Mn exhibit the same clusters for both season, it can be concluded that their sources are different from the other inorganic elements. Al is a well-known crustal element [12], whereas sources of Mn are due to metallurgical emissions from nearby industries [33].

The group Zn–Na in the summer season originates from resuspended soil and excavation processes, whereas Ca–Cu–Cd is from industrial or vehicular emissions during both summer and winter season. The groups Fe–Ni during the winter season and Fe–Cu–Ca–Cd during the summer

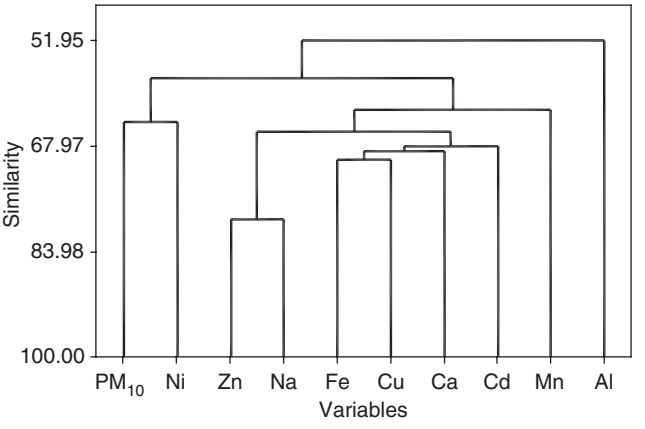

Figure 3. Dendrogram showing the clustering of selected air parameters in the summer season.

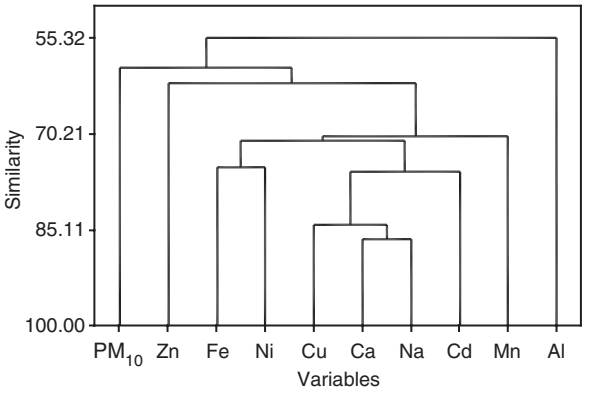

Figure 4. Dendrogram showing the clustering of selected air parameters in the winter season.

season suggest that Fe originates from power plant, vehicular and industrial emissions during both seasons. For the summer season, PM_{10} and Ni was statistically similar where lack of precipitation increased the amount of Ni in PM_{10}, whereas during the winter season Ni was statistically similar to Fe where it was not greatly affected by precipitation that comes with the season. During the winter season, Na was grouped with Ca, Cu and Cd, in contrast to Zn during the summer season, also because of the decrease in precipitation during the summer months. The strong similarity between Ca and Na with Cd and Cu indicates that the latter inorganic elements are carried by wind from nearby industrial areas and roads situated beside the sea in the winter months.

4. Conclusions

The average PM_{10} concentration recorded was below the Malaysian air-quality standard. Even so, there were high concentrations of PM_{10} in July and August because of transboundary air pollution. The concentration of all the inorganic elements determined, except Cu (no seasonal pattern) and Zn (positive correlation with relative humidity), was higher in summer than in winter, and this might be due to the presence of haze and wet deposition. Based on analysis of enrichment factors, it can be said that the inorganic element composition of the local PM_{10} was due to anthropogenic sources rather than crustal/natural sources; high concentrations of Ca and Na

were due to sea salts. The concentration of different parameters was arranged in the following order: for summer, Na > Zn > Ca > Fe > Ni > Mn > Cu > Cd > Al; and for winter, Na > Zn > Ca > Fe > Cu, Ni > Mn > Al, Cd. The orders of the inorganic element concentrations are generally the same for both seasons, with negligible differences. From correlation analysis, the inorganic element Fe was found to be from the same source as Al, albeit inversely related, namely crustal sources. Fe was determined to be from industrial or vehicular emissions and the nearby coal-fired power plant because it was strongly correlated with Ni usually originating from heavy-oil combustion processes. Zn and Mn were determined to originate from resuspended soil from excavation sites and nearby metallurgical industries, respectively. Correlation analysis and cluster analysis produced six main inorganic element groups from different sources: Fe–Cu–Cd from industrial/vehicular emissions; Na–Ca from sea salts; Zn from resuspended soil from excavation sites; Ni from coal-fired power plants; Mn from metallurgical industries; and Al from crustal sources. Thus, inorganic element concentration might be a good indicator of local sources of PM_{10}.

Acknowledgements

We would like to thank Universiti Sains Malaysia (USM) for their contribution in terms of infrastructure and financial contribution by awarding us their Short Term Grant 304/PTEKIND/639014. We also thank Nurul Jannah and Khairul Azhar for their expert analysis of the samples. We would also like to extend our gratitude to the anonymous reviewers for their constructive criticisms and comments.

References

[1] L. Juneng, M.T. Latif, F.T. Tangang, and H. Mansor, *Spatio-temporal characteristics of PM_{10} concentration across Malaysia*, Atmos. Environ. 43 (2009), pp. 4584–4594.
[2] H.L. Chiang and Y.S. Huang, *Particulate matter emissions from on-road vehicles in a freeway tunnel study*, Atmos. Environ. 43 (2009), pp. 4014–4022.
[3] J. Hlavay, K. Polyak, and G. Wesemann, *Particle-size distribution of mineral phases and metals in dusts collected at different workplaces*, Fresenius J. Anal. Chem. 344 (1992), pp. 319–321.
[4] D.C. Snyder, J.J. Schauer, D.S. Gross, and J.R. Turner, *Estimating the contribution of point sources to atmospheric metals using single-particle mass spectrometry*, Atmos. Environ. 43 (2009), pp. 4033–4042.
[5] N. Tippayawong, P. Pengchai, and A. Lee, *Characterization of ambient aerosols in Northern Thailand and their probable sources*, Int. J. Environ. Sci. Technol. 3 (2006), pp. 359–369.
[6] N. Vichit-Vadakan, N. Vajanapoom, and B. Ostro, *The Public Health and Air Pollution in Asia (PAPA) project: estimating the mortality effects of particulate matter in Bangkok, Thailand*, Environ. Health Perspect. 116 (2008), pp. 1179–1182.
[7] J. Santamaria, M. Fernandez, J. Mendez, and M.T. Bomboi, *Particle-size distribution of metals in the atmosphere of Madrid (Spain)*, Fresenius J. Anal. Chem. 337 (1990), pp. 362–365.
[8] V.A. Dutkiewicz, S. Alvi, B.M. Ghauri, M.I. Choudhary, and L. Husain, *Black carbon aerosols in urban air in South Asia*, Atmos. Environ. 43 (2009), pp. 1737–1744.
[9] S. Karthikeyan, R. Balasubramanian, and K. Iouri, *Particulate air pollution from bushfires: human exposure and possible health effects*, J. Toxicol. Environ. Health A 69 (2006), pp. 1895–1908.
[10] A. Valavanidis, K. Fiotakis, E. Bakeas, and T. Vlahogianni, *Electron paramagnetic resonance study of the generation of reactive oxygen species catalysed by transition metals and quinoid redox cycling by inhalable ambient particulate matter*, Redox Report 10 (2005), pp. 37–51.
[11] K.F. Chang, G.C. Fang, J.C. Chen, and Y.S. Wu, *Atmospheric polycyclic aromatic hydrocarbons (PAHs) in Asia: a review from 1999 to 2004*, Environ. Pollut. 142 (2006), pp. 388–396.
[12] R. Balasubramanian and W.B. Qian, *Characterization and source identification of airborne trace metals in Singapore*, J. Environ. Monit. 6 (2004), pp. 813–818.
[13] S.W. See, R. Balasubramanian, E. Rianawati, S. Karthikeyan, and D.G. Streets, *Characterization and source apportionment of particulate matter $<= 2.5\,\mu m$ in Sumatra, Indonesia, during a recent peat fire episode*, Environ. Sci. Technol. 41 (2007), pp. 3488–3494.
[14] N.M. Tahir, S.C. Poh, S. Suratman, M.M. Ariffin, N.A.M. Shazali, and K. Yunus, *Determination of trace metals in airborne particulate matter of Kuala Terengganu, Malaysia*, Bull. Environ. Contamin. Toxicol. 83 (2009), pp. 199–203.
[15] R. Afroz, M.N. Hassan, and N.A. Ibrahim, *Review of air pollution and health impacts in Malaysia*, Environ. Res. 92 (2003), pp. 71–77.

[16] Center for Environmental Research Information (U.S.), *Compendium of methods for the determination of inorganic compounds in ambient air*, U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Research Information, National Risk Management Research Laboratory, Cincinnati, OH, 1999.
[17] N. Chuersuwan, S. Nimrat, S. Lekphet, and T. Kerdkumrai, *Levels and major sources of $PM_{2.5}$ and PM_{10} in Bangkok metropolitan region*, Environ. Int. 34 (2008), pp. 671–677.
[18] M.H. Shah and N. Shaheen, *Annual and seasonal variations of trace metals in atmospheric suspended particulate matter in Islamabad, Pakistan*, Water Air Soil Pollut. 190 (2008), pp. 13–25.
[19] R.A. Johnson and D.W. Wichern, *Applied Multivariate Statistical Analysis*, Prentice Hall, Upper Saddle River, NJ, 2002.
[20] A.C. Rencher, *Methods of Multivariate Analysis*, Wiley, New York, 2002.
[21] A. Limbeck, M. Handler, C. Puls, J. Zbiral, H. Bauer, and H. Puxbaum, *Impact of mineral components and selected trace metals on ambient PM_{10} concentrations*, Atmos. Environ. 43 (2009), pp. 530–538.
[22] World Health Organization, *Guidelines for Air Quality 2010*, World Health Organization, Geneva, 2000.
[23] A. Kumar and M.M. Sarin, *Mineral aerosols from western India: temporal variability of coarse and fine atmospheric dust and elemental characteristics*, Atmos. Environ. 43 (2009), pp. 4005–4013.
[24] Y. Bin Yusup, W.R.W. Daud, A. Zaharim, and M.Z.M. Talib, *Structure of the atmospheric surface layer over an industrialized equatorial area*, Atmos. Res. 90 (2008), pp. 70–77.
[25] P. Pengchai, S. Chantara, K. Sopajaree, S. Wangkarn, U. Tengcharoenkul, and M. Rayanakorn, *Seasonal variation, risk assessment and source estimation of PM_{10} and PM_{10}-bound PAHs in the ambient air of Chiang Mai and Lamphun, Thailand*, Environ. Monit. Assess. 154 (2009), pp. 197–218.
[26] M. Ebihara, Y.S. Chung, W. Chueinta, B.F. Ni, T. Otoshi, Y. Oura, F.L. Santos, F. Sasajima, Sutisna, and A.K.B.H. Wood, *Collaborative monitoring study of airborne particulate matters among seven Asian countries*, J. Radioanal. Nucl. Chem. 269 (2006), pp. 259–266.
[27] P. Glantz, E.D. Nilsson, and W. von Hoyningen-Huene, *Estimating a relationship between aerosol optical thickness and surface wind speed over the ocean*, Atmos. Res. 92 (2009), pp. 58–68.
[28] D. Guzman-Torres, A. Eiguren-Fernandez, P. Cicero-Fernandez, M. Maubert-Franco, A. Retama-Hernandez, R.R. Villegas, and A.H. Miguel, *Effects of meteorology on diurnal and nocturnal levels of priority polycyclic aromatic hydrocarbons and elemental and organic carbon in PM_{10} at a source and a receptor area in Mexico City*, Atmos. Environ. 43 (2009), pp. 2693–2699.
[29] Y.M. Han, J.J. Cao, Z.D. Jin, and Z.S. An, *Elemental composition of aerosols in Daihai, a rural area in the front boundary of the summer Asian monsoon*, Atmos. Res. 92 (2009), pp. 229–235.
[30] M.R. bin Abas, D.R. Oros, and B.R.T. Simoneit, *Biomass burning as the main source of organic aerosol particulate matter in Malaysia during haze episodes*, Chemosphere 55 (2004), pp. 1089–1095.
[31] X.F. Huang, J.Z. Yu, Z.B. Yuan, A.K.H. Lau, and P.K.K. Louie, *Source analysis of high particulate matter days in Hong Kong*, Atmos. Environ. 43 (2009), pp. 1196–1203.
[32] T. Okuda, S. Nakao, M. Katsuno, and S. Tanaka, *Source identification of nickel in TSP and $PM_{2.5}$ in Tokyo, Japan*, Atmos. Environ. 41 (2007), pp. 7642–7648.
[33] W.S. Yue, X.L. Li, J.F. Liu, Y.L. Li, G.L. Zhang, and Y. Li, *Source tracing of chromium-, manganese-, nickel- and zinc-containing particles (PM_{10}) by micro-PIXE spectrum*, J. Radioanal. Nucl. Chem. 274 (2007), pp. 115–121.