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Determination of Trace Metals in Airborne Particulate Matter of Kuala Terengganu, Malaysia

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Abstract Results from the present study in Kuala Terengganu, Malaysia indicated a significant spatial variation but generally the total suspended particulate concentrations (mean = 17.2–148 μg/m^3) recorded were below the recommended Malaysia guideline for total suspended particulate (mean of 24-h measurement = 260 μg/m^3). Some of the elemental composition of particulate aerosol is clearly affected by non crustal sources, e.g. vehicular emission sources. Based on correlation and enrichment analyses, the elements could be grouped into two i.e. Pb, Cd and Zn group with sources from vehicular emission ($r > 0.6$; enrichment factor > 10) and Al, Fe, Mn and Cr group that appears to be of crustal origin ($r > 0.6$; enrichment factor < 10). It can also be concluded that the mean levels of Pb (1 ng/m^3), Cd (0.02 ng/m^3) and Zn (2 ng/m^3) in the study area are generally lower than other urban areas in Malaysia (Pb $<$ 181 ng/m^3; Cd $<$ 6 ng/m^3; Zn $<$ 192 ng/m^3).

Keywords Airborne particulate matter · Trace metals · Total suspended particulate · Kuala Terengganu · Malaysia

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Airborne particulate matters are typically range in size from a few nanometers in diameter to more than 100 micrometers (USEPA 1982). Relatively volatile organic compounds, heavy metal and those that become attached to airborne particles can be widely dispersed on very large scales. The impact of the fine particles on human health is of great concern worldwide. For example, in Malaysia during the 1997 smoke haze period, there were significant increase in asthma cases, acute respiratory diseases and conjunctivitis in areas worst hit by the haze (Afroz et al. 2003). This paper present the results of a study carried out to determine the levels of total suspended particulate (TSP) matter and their trace metal contents in Kuala Terengganu, the capital city of the state of Terengganu. The state is located in the east coast of Peninsular Malaysia with an estimated population of over 1 million. Air quality in the state is generally described as good. However, it has in recent times deteriorated to moderate resulting in reduced visibility during the peak period of the 1997 haze episode. The state, and its capital in particular, is also undergoing rapid development and urbanization, thus, this study is considered timely as it provides baseline data on air quality for future reference.

Materials and Methods

Sampling was carried out three times between October and December 2003 with the location of the six sampling sites shown in Fig. 1. These sites were chosen based on their difference in traffic density and were generally diffuse source oriented. TSP samples were collected using a mass flow controlled high volume air sampler (Environmental TISCH TE-5170, USA) fitted with a Whatman 41 filter paper. The sampler was placed ca. 1.5 m above ground

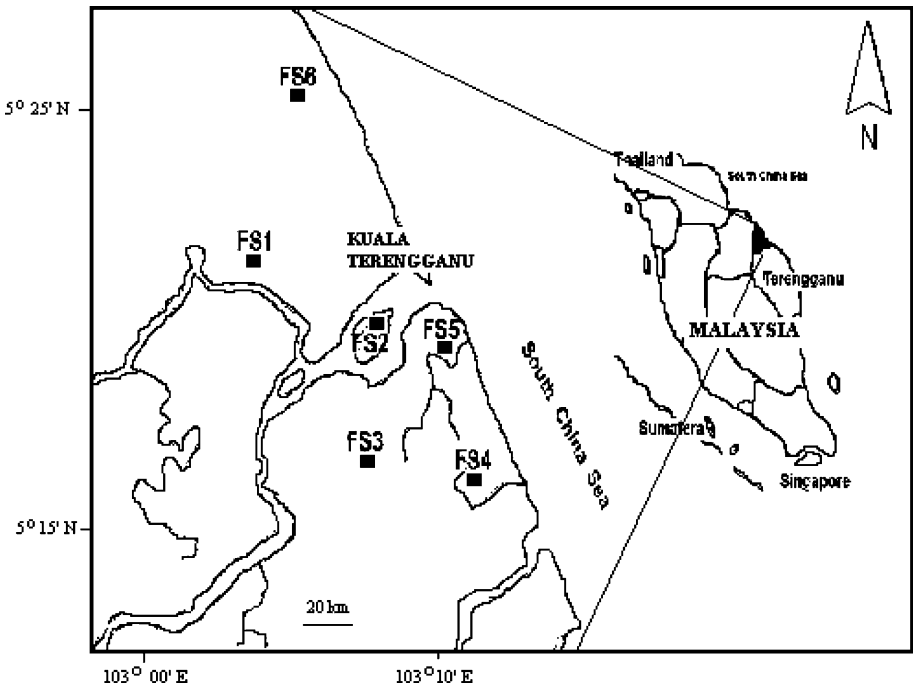

Fig. 1 Sampling station during the present study

level and away from any obstructions to the free flow of air around the sampler. The sampler was operated at a known flow rate (1.13 m^3/min) for 24 h. The filters were equilibrated in a desiccator for 24 h before weighing, prior to and after sample collection.

Exposed filter papers were subjected to acid digestion using a mixture of 7 mL nitric acid (65%, GR, Merck), 5 mL hydrogen peroxide (40%, AR, Hamburg) and 1 mL hydrofluoric acid (40%, GR, Merck) in a microwave oven for 25 min at 210°C followed by the addition of 1 g of boric acid. The resultant solutions were then diluted to 25 mL with 18.2 MΩ de-ionized water and stored in polyethylene bottles at 4°C until further analyses. Trace metals concentration was determined using the inductive coupled plasma with optical emission spectrophotometer (ICP-OES) (Varians, Visca Pro). Standard reference material, NIST SRM1648 (Urban Particulate Matter) and filter blanks were subjected to similar digestion protocol for quality assurance and quality control purposes. Results showed that the recoveries for all the metals measured were in the range of 80%–118%. The detection limits were 0.71 ng/m^3 for Al, 0.14 ng/m^3 for Mn, 1.59 ng/m^3 for Cr, 24.9 ng/m^3 for Fe, 20.9 ng/m^3 for Zn, 0.05 ng/m^3 for Cd and 1.52 ng/m^3 for Pb. All concentrations reported in this study have been corrected for the recoveries obtained.

Results and Discussion

Table 1 shows the TSP results obtained in this study. Highest mean concentration was observed at site FS5 with a value of 148 μg/m^3 followed by FS3 site with mean value of 123 μg/m^3. These two sites were in the city center with relatively tall building and high population and traffic density. Generally suburban sites i.e. FS1, FS4 and FS6 exhibited lower TSP loading. Interestingly site FS2, which is located in one of the highest traffic density area, recorded the lowest mean level of TSP i.e. 17.2 μg/m^3. The FS2 site is located on a highway bridge which is an open space facing the South China Sea. Thus the strong winds blowing across the bridge played an important role in dispersing and diluting the TSP generated in the area. Although there were significant variations in TSP concentrations with sites monitored ($p < 0.05$), the TSP values obtained were still well below the recommended Malaysia guideline for TSP (mean of 24-hour measurement = 260 μg/m^3; Department of Environment). The summary of the statistical values for selected metals is also shown in Table 1. In general, Al was the most abundant element (accounting for almost all of 69% ± 7.4% of the total mass balance) at all stations followed by Fe (29% ± 5.2%). Zn was the third most abundant (1.8% ± 1.2%) with concentration much lower than the above two metals. The rest of the trace metals (Pb, Mn, Cr and Cd) were present in lower concentrations and accounted only 0.92% ± 0.75% from the total mass balance. The ambient concentrations of metals at specific location are largely dependent on the point source emissions and atmospheric transport process. Significant spatial variations ($p < 0.05$) were observed for all metals studied. In FS1, FS3 and FS4, the concentrations of the metals follow the trend of Al > Fe > Zn > Mn > Pb > Cr > Cd, whereas in FS2 and FS5 sampling stations showed the

Table 1 Mean values, standard deviation and ranges of TSP (μg/m^3) and selected metals (ng/m^3) at each sampling stations

	FS1	FS2	FS3	FS4	FS5	FS6
TSP	42.2 ± 9.82 (30.9–48.5)	17.2 ± 9.93 (9.33–28.3)	123 ± 17.9 (105–141)	53.6 ± 31.0 (30.4–88.9)	148 ± 15.9 (131–162)	22.4 ± 6.91 (17.5–27.3)
Al	161 ± 97.4 (50–231)	100 ± 18 (79–111)	43.2 ± 27.0 (12.3–62.7)	78.4 ± 7.02 (70.8–84.6)	143 ± 103 (48–254)	26.3 ± 4.42 (23.2–29.5)
Mn	0.76 ± 0.34 (0.38–0.99)	0.91 ± 0.32 (0.59–1.22)	0.32 ± 0.16 (0.16–0.49)	0.96 ± 0.93 (0.39–2.04)	0.94 ± 0.45 (0.54–1.44)	0.50 ± 0.32 (0.26–0.73)
Cr	0.12 ± 0.03 (0.08–0.15)	0.18 ± 0.05 (0.12–0.23)	0.04 ± 0.02 (0.01–0.07)	0.04 ± 0.01 (0.02–0.04)	0.14 ± 0.11 (0.01–0.25)	bdl
Fe	53.6 ± 25.9 (24.2–72.7)	52.1 ± 3.28 (48.6–55.1)	26.5 ± 6.63 (20.4–33.6)	33.7 ± 6.72 (28.5–41.3)	61.3 ± 32.5 (32.6–96.6)	8.89 ± 2.45 (7.16–10.6)
Zn	1.67 ± 1.06 (0.50–1.92)	4.29 ± 1.96 (2.03–5.66)	2.34 ± 1.60 (0.53–3.57)	2.88 ± 3.04 (0.90–6.39)	2.77 ± 1.18 (1.53–3.90)	0.06 ± 0.007 (0.05–0.69)
Cd	0.024 ± 0.005 (0.02–0.03)	0.04 ± 0.01 (0.01–0.05)	0.011 ± 0.001 (0.010–0.012)	0.02 ± 0.01 (0.01–0.03)	0.03 ± 0.01 (0.006–0.03)	0.002 ± 0.1$^{10-5}$ (0.002–0.003)
Pb	0.17 ± 0.06 (0.13–0.25)	3.01 ± 0.42 (2.52–3.33)	0.25 ± 0.21 (0.04–0.46)	0.45 ± 0.11 (0.32–0.54)	1.12 ± 0.75 (0.26–1.63)	bdl

bdl below detection limit

trend of Al > Fe > Zn > Pb > Mn > Cr > Cd. For FS6 sampling station, the trend of trace metal concentrations is Al > Fe > Mn > Zn > Cd with the exception of Pb and Cr as both metal concentrations was found below the detection limit.

Table 2 compares heavy metals in TSP samples measured in this study for Kuala Terengganu with other literature values. Mean concentrations of metals found in this study were much lower to those reported for major industrial areas (e.g. Air Keroh in Malacca and Teluk Kalung in Terengganu) and cities (e.g. Kuala Lumpur) in Peninsular Malaysia (Latif and Othman 1999; Rashid et al. 1999). The main difference was due to Kuala Terengganu town being less urbanized and lower industrial activities compared to these areas. Furthermore, the values obtained from this study were lower compared to various urban locations worldwide (Hien et al. 2001; Fang et al. 2003; Okuda et al. 2004; Munir et al. 2006).

Trace metals in aerosols were derived from various sources. The degree to which trace elements in the aerosols are enriched, or depleted, relative to a specific source can be assessed using enrichment factors (EF). For crustal sources, Al is normally used as the source indicator element and the Earth's crust as the source material (Chester et al. 1997). Chester et al. (1997) calculated EF using the following equation:

$$\mathrm{EF} = (C_{\mathrm{xp}}/C_{\mathrm{p}})/(C_{\mathrm{xc}}/C_{\mathrm{c}})$$

Where, C_{xp} and C_{p} is the concentration of a trace metal x and Al in the particulate, respectively and C_{xc} and C_{c} are their concentrations in average crustal material. By convention, an EF value of <10 is taken as an indication that a trace metal in an aerosol has a significant crustal source, and these are termed the non-enriched elements (NEE). In contrast, an EF value of >10 is considered to indicate that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEE) (Chester et al. 1997; Herut et al. 2001).

Figure 2 shows the distribution of the EF of each element with sampling sites. The results indicated that Zn, Cd and Pb exhibited high enrichment suggesting non-crustal sources. Al and Mn appeared to be of crustal origin, as their EF was close to unity (Chester et al. 1997; Herut et al. 2001). Cr did not show significant enrichment and the atmospheric levels were lower than the median soil levels, thus Cr could also be grouped as NEE together with Al and Mn. It is worth noting that for element Pb, EF values calculated using the local data were relatively lower than those calculated using the world average from Ure and Berrow (1982). On the contrary, a reverse order was observed for the remaining elements. Factors responsible for these high EF and probable reasons for these enrichments are discussed below.

Table 2 Comparison of metal concentrations (ng/m^3) with other study areas

Location	Activities	Pb	Cd	Cu	Cr	Zn	References
Kuala Terengganu, Malaysia	Urban	1	0.02	13	0.1	2	Present study
Air Keroh, Malaysia	Industrial	2	6	–	18	192	(Latif and Othman 1999)
Kuala Lumpur, Malaysia	Urban	181	–	–	–	87	(Rashid et al. 1999)
Teluk Kalong, Malaysia	Industrial	2	6	–	42	21	(Latif and Othman 1999)
Beijing, China	Urban	430	7	110	19	770	(Okuda et al. 2004)
Ho Chi Minh City, Vietnam	Urban	125	–	30	6	299	(Hien et al. 2001)
Taichung, Taiwan	Urban	574	9	199	29	395	(Fang et al. 2003)
Islamabad, Pakistan	Urban	163	3	–	36	567	(Munir et al. 2006)

–, data not available

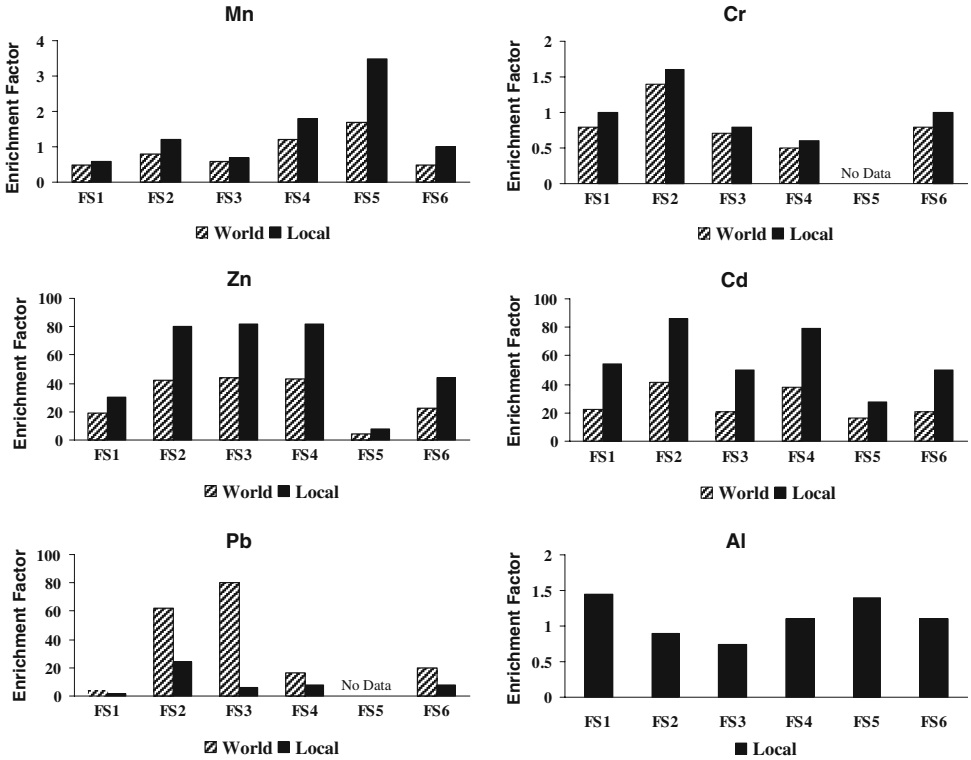

Fig. 2 Distribution of EFs for individual metals with sampling stations

Correlation calculations are a convenient and tested tool for source delineation of the particulate aerosol (Pandey et al. 1998). Table 3 present the Pearson linear correlation matrix of the elements for aerosol samples. The results showed a very strong positive correlation between Fe and Al ($r = 0.93$), suggesting they were from similar source. Similarly, a fairly strong correlation was observed between Pb and Cd ($r = 0.77$), again suggesting that these two elements could be derived from similar source but probably different from that of Fe and Al as the former elements showed weak correlations with the latter two elements. On the other hand, Cr showed fairly strong correlation with Pb ($r = 0.75$), Cd ($r = 0.83$) and interestingly, also with Fe ($r = 0.80$) and Al ($r = 0.67$). Zn showed moderate correlation with Pb, Cd and Fe but slightly weaker correlation with Al. Based on the correlation data, it was possible to suggest that Cr and Zn might be contributed by mixed sources. However, by combining the correlation and

Table 3 Correlation matrix of metals in suspended particulate composition

	Al	Mn	Cr	Fe	Zn	Cd	Pb
Al	1.00						
Mn	0.52	1.00					
Cr	0.67	0.49	1.00				
Fe	0.93	0.62	0.80	1.00			
Zn	0.30	0.73	0.58	0.55	1.00		
Cd	0.48	0.29	0.83	0.53	0.49	1.00	
Pb	0.24	0.31	0.75	0.46	0.59	0.77	1.00

enrichment analyses and in the absence of other industrial sources in the study area, it was possible to group the trace elements into two categories according to their possible origin; viz. Fe–Al–Mn–Cr group and Zn–Pb–Cd group. The Fe–Al–Mn–Cr group showed low enrichment factors (<10) and strong correlations between elements ($r = 0.62$–0.93), that suggest possible contribution from the crustal sources. The second group, Zn–Pb–Cd, showed high enrichment factors (>10) and high correlation between elements ($r = 0.59$–0.77) probably related to vehicular emission sources (e.g. engine exhaust, body part corrosion and tyre ware (Pandey et al. 1998; Li et al. 2001)). This was also evident by calculating the Pb/Cd ratio (Thomaidis et al. 2003). The average Pb/Cd ratios were calculated to be 73.4 for station FS2, 41.2 for FS9, 22.5 for FS4, 20.2 for FS5 and 7.28 for FS1 with the trend in order of FS2 > FS9 > FS4 > FS5 > FS1. The trend of Pb/Cd ratio was generally similar to the car density on the road at the sampling stations resulting in a higher Pb/Cd ratio corresponding to the higher car density on the road. Among the three elements, Zn acts as a new potential indicator of road vehicle pollutions (Al-Momani 2003), showed the highest average concentrations (0.06–4.29 μg/m^3) followed by lead (0.17–3.01 μg/m^3) and cadmium (0.002–0.040 μg/m^3). Another significant feature was that, station FS2 showed relatively low TSP concentration, yet elemental analysis results revealed the presence of high levels of most elements associated with vehicular emissions. This was probably related to the high traffic density on the adjacent high volume four-lane highway and measured the amount of metals trapped by the TSP.

In conclusion, although there was a significant spatial variation, generally the TSP concentrations in this study were still below the recommended Malaysia guidelines for TSP. Some of the elemental composition of particulate aerosol was clearly affected by non crustal sources, i.e. vehicular emission sources. Based on the correlation and enrichment analyses, the elements could be grouped into two: Pb, Cd and Zn group could be related to the vehicular emission sources whist the Al, Fe, Mn and Cr group appeared to be of crustal origin. It can also be concluded that the levels of Pb, Cd and Zn in the study area were generally lower than other cities in Malaysia, consistent with relatively less urbanized nature of the city of Kuala Terengganu.

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