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Variation in Day-of-Week and Seasonal Concentrations of Atmospheric $PM_{2.5}$-Bound Metals and Associated Health Risks in Bangkok, Thailand

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Abstract While effective analytical techniques to promote the long-term intensive monitoring campaign of particulate heavy metals have been well established, efforts to interpret these toxic chemical contents into policy are lagging behind. In order to ameliorate the interpretation of evidence into policies, environmental scientists and public health practitioners need innovative methods to emphasize messages concerning adverse health effects to state and local policymakers. In this study, three different types of health risk assessment models categorized by exposure pathways. Namely, ingestion, dermal contact, and inhalation were quantitatively evaluated using intensive monitoring data of 51 $PM_{2.5}$-bound metals that were collected on three consecutive days, from 17 November 2010 to 30 April 2011 in the heart of Bangkok. Although different exposure pathways possess different magnitudes of risk for each $PM_{2.5}$-bound metal, it can be concluded that ingestion of dust causes more extensive risk to residents compared with inhalation and dermal contact. The investigation of enrichment factors reveals the overwhelming influences of vehicular exhausts on 44 selected metal concentrations in Bangkok. These findings are in agreement with previous studies that highlight the role of public transportation and urban planning in air pollution control.

In the past few years, there have been increasing concerns about air pollutants and the risks they cause to the environment and people, particularly in urban and rural environments (Pongpiachan 2013; Pongpiachan and Paowa 2014; Pongpiachan et al. 2009, 2013a, b, 2014a, b, 2015a, b, 2016). Chemical analysis of fine particles, especially the compositions of selected metals, has been steadily conducted in Asian countries over the past few decades (Hussain et al. 2015; Keshavarzi et al. 2015; Norouzi et al. 2016; Pongpiachan and Iijima 2015; Wang et al. 2016). Vehicle exhaust, municipal waste incinerators, and coal-fired power plants appear to be major sources of airborne metals in most urban areas (Ćujić et al. 2016; Font et al. 2015; Gunawardena et al. 2012). Recently, regional smoke-induced haze as a result of agricultural waste burning and peat fires in Central Kalimantan, Indonesia, Malaysia, and southern Thailand have been widely acknowledged as the main contributors of airborne heavy metals in Southeast Asia (Ahmed et al. 2016; Betha et al. 2013). Substantial epidemiological evidence has persistently demonstrated that fine particulate matter is closely connected to enhanced risk of respiratory diseases and cardiovascular symptoms (Zeng et al. 2016; Zhang et al. 2016).

Therefore, numerous investigations have concentrated on annual and monthly averages and seasonal variations in atmospheric contents of selected metals (Izhar et al. 2016;

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Pandey et al. 2014), which are exceedingly useful to provide an extensive perspective on the source contributions of targeted pollutants. Although several interventions, such as improvements in fuel quality and vehicle technologies, shifting of the industrial fuel mix, and moving factories and businesses out of residential zones, may have been responsible for better urban air quality (Gupta et al. 2010), there is a lack of information associated with the fate of particulate heavy metals and their adverse health impacts. A previous study found that the concentrations of heavy metals in the total suspended particle (TSP) from urban-residential zones and an industrial area in Korea on misty days were significantly ($p < 0.05$) higher than on clear days, especially in the case of Pb and Mn (Lee and Park 2010). Results and recent analyses from numerous studies highlight the role of vehicle exhaust as the major source of airborne metals in the urban atmosphere (Gunawardena et al. 2012; Pant and Harrison 2013; Pongpiachan and Iijima 2015).

Regardless of the amount of information on the atmospheric concentrations and periodical variations of selected metals, knowledge of the impacts of day-of-week trends on the temporal variations is still lacking. While other studies have elucidated the impacts of human activity on both diurnal and weekly fluctuations, only a few studies have shown in-depth, quantitative evidence associated with the risk assessments of particulate metals in the urban atmosphere (Betha et al. 2013; Du et al. 2013; Ferreira-Baptista and De Miguel 2005; Izhar et al. 2016; Keshavarzi et al. 2015; Wang et al. 2016; Zhou et al. 2014). To the best of our knowledge, no data are available from long-term intensive sampling of $PM_{2.5}$-bound metals in Thailand. Thus, the major goals of this assessment are to investigate the day-of-week trends of particulate metals throughout the intensive sampling campaign of $PM_{2.5}$ and to conduct a human health-risk assessment of metal toxicity in the heart of metropolitan Bangkok, Thailand.

Experiment

Description of Sampling Sites, Climatic Conditions, and Sample Collection

In this study, the top roof of the Mahamakut building, Chulalongkorn University (CHAOS: 13°44′9.07″N 100°31′50.26″E) was chosen as a $PM_{2.5}$ monitoring station, because the site is located in the heart of Bangkok, encompassed by commercial offices, department stores, restaurants, and business buildings (Fig. 1). It has a roof height of 57 m. There were no obstacles in the vicinity of the sampling device, which was intentionally positioned to sample winds from all angles. To ensure that the amount of selected metals in the sample is much larger than the instrumental detection limit (IDL), MiniVol^{TM} portable air samplers (Airmetrics) were used to collect $PM_{2.5}$ for 72 h at CHAOS. The MiniVol's pump draws in air at 5 L min^{-1} through a particle size separator (impactor) and then through a 47-mm filter. The 2.5-micron particle ($PM_{2.5}$) separation is achieved by impaction. It is important to note that neither PM_{10} nor TSP samples were obtained for this study. All samples ($n = 44$) were collected on three consecutive days, from 17 November 2010 to 30 April 2011, at CHAOS. This monitoring interval covers a rainy period, including the great flood of 2011 in Thailand. As illustrated in Fig. 2, the 5-day back trajectory analysis of air mass that passed through CHAOS reflects the impacts of two major monsoon winds—the southwest monsoon (SWM) and

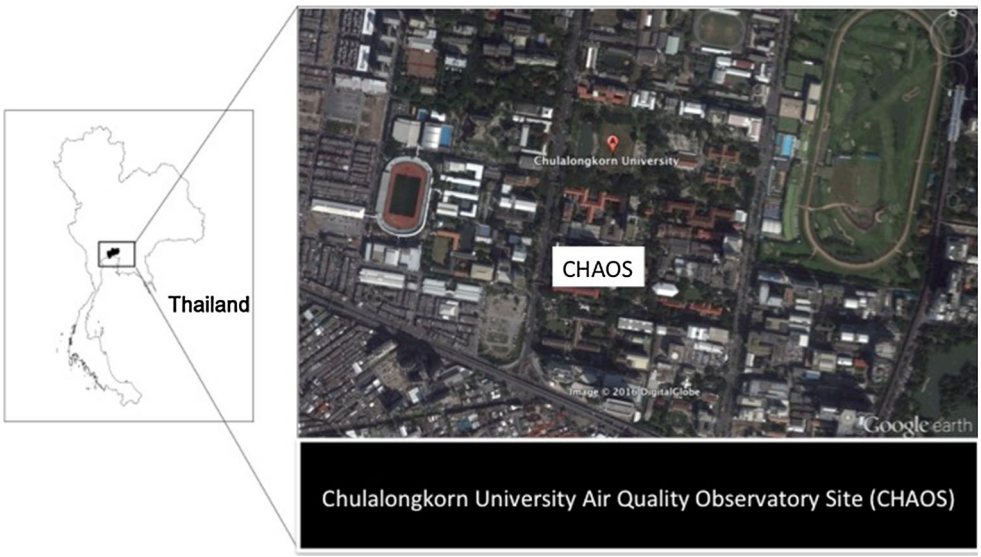

Fig. 1 Map of Chulalongkorn University Air Quality Observatory Site (CHAOS)

northeast monsoon (NEM). Generally, SWM transports a stream of warm moist air from the Indian Ocean towards Thailand, which is responsible for heavy precipitation over the country, usually starting in mid-May and ending in mid-October. As shown clearly in Fig. 2, the NEM started in November 2010 and ended in February 2011, carrying cold and dry air from the anticyclone in mainland China over Bangkok. In addition, triplicate weight measurements of each Teflon filter were conducted before and after monitoring, following the 24-h equilibration period. The average net mass for each Teflon filter was achieved by subtracting the pre-deployment weight from the average of the post-sampling readings using a Mettler Toledo AB204-S electronic microbalance (Columbus, OH). The monitoring protocol was based on 'Quality Assurance Guidance Document 2.12; Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods' (US EPA 1998).

Analysis of Selected Metals

Energy dispersive X-ray fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PAN analytical B. V., the Netherlands) was used to determine the concentrations of elements collected on the $PM_{2.5}$ Teflon® membrane filters. All samples were analysed directly without any preparation procedures (Watson et al. 1999). Using a three-dimensional polarizing geometry with twelve secondary targets, a good signal to background ratio and low detection limits were achieved. The X-ray source was a side window X-ray tube with a gadolinium (Gd) anode operated at an accelerating voltage of 25–100 kV and a current of 0.5–24 mA (maximum power: 600 W). The characteristic X-ray radiation was detected by a germanium detector (PAN 32) cooled at liquid nitrogen temperature. The system was coupled with a PC-based multichannel analyser. Each sample was analysed for 40 min to obtain a spectrum of X-ray counts versus photon energy, with the individual peak energies matching specific elements, and peak areas corresponding to elemental concentrations (Brouwer 2003). Energy calibration was performed by placing a standard sample before the detector, the energies of which were known, and the compositions were similar to that of the samples of interest. The ED-XRF spectrometer was calibrated with thin-film standards obtained from Micro Matter Co. (Arlington, WA), and laboratory Teflon® membrane filter blanks were analysed to evaluate the analytical bias. In total, 51 elements were detected: Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pd, Ag, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, W, Ir, Au, Hg, Tl, Pb, and U.

As a part of the Quality Assurance/Quality Control (QA/QC) processes, the accuracies and precisions of the ED-XRF analyses for both Teflon® and quartz filters have been reported in previous publications (Cao et al. 2012; Xu et al. 2012). Field blanks, laboratory filter blanks, and National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2783 were used to monitor potential sources of contamination, instrument performance, analytical accuracy, and precision. Before analysis

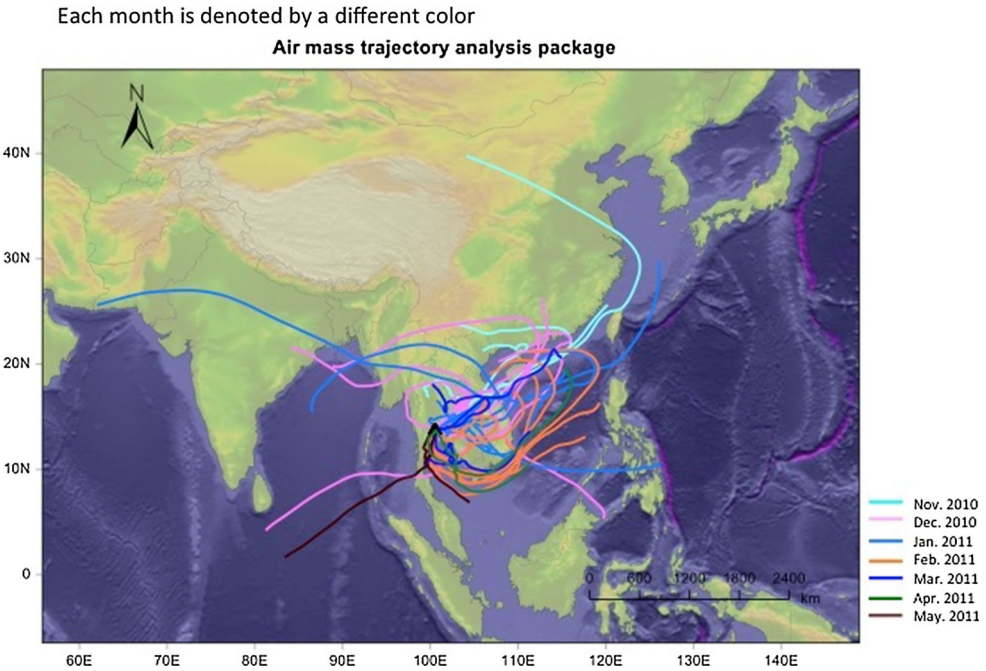

Fig. 2 Five-day back trajectory analysis of air mass that passed through CHAOS from November 2010 to May 2011

of the samples, SRM 2783 samples were first determined, and the relative error between the measured value and its real value was calculated. The accuracies of element concentrations analysed by ED-XRF were accepted only if the relative errors were less than 20%. To evaluate uncertainties associated with personal, indoor, and outdoor monitoring, duplicate samples were evaluated using the relative percent difference (RPD). Replicate analysis was conducted on every eighth sample, and the RPD should be less than 20%. In this study, to further assess the overall performance of the air-quality monitoring procedures and to evaluate which elements are reportable, for a given element, concentrations of samples in a given set should exceed the minimum detection limit (MDL), which is defined as three times the standard deviation (3σ) of the measured concentrations of the 8–12 procedural blanks, for ED-XRF measurements.

Health-Risk Assessment of Heavy Metals

Three different types of models were applied to calculate human exposure to particulate metals, which are the average daily dose (ADD: mg kg^{-1} day^{-1}) of selected metal via ingestion (ADD_{ing}), dermal contact (ADD_{derm}), and inhalation (ADD_{inh}) as exposure pathways can be considered employing Eqs. (1), (2), and (3):

$$ADD_{ing} = \frac{c \times R_{ing} \times CF \times EF \times ED}{BW \times AT} \quad (1)$$

$$ADD_{derm} = \frac{c \times SA \times CF \times SL \times ABS \times EF \times ED}{BW \times AT} \quad (2)$$

$$ADD_{inh} = \frac{c \times R_{int} \times EF \times ED}{PEF \times BW \times AT} \quad (3)$$

where ADD_{ing} is the daily exposure amount of selected metals via ingestion (mg kg^{-1} day^{-1}), ADD_{derm} is the daily exposure amount of selected metals via dermal contact (mg kg^{-1} day^{-1}), and ADD_{inh} is the daily exposure amount of selected metals via inhalation (mg kg^{-1} day^{-1}). These three models are based on the Exposure Factors Handbook proposed by the Environmental Protection Agency of the United States (US EPA 1997). In addition, exposure factors for dose models can be described as follows:

c: concentration of the selected metals in $PM_{2.5}$ (μg g^{-1}) (this study)
R_{ing}: ingestion rate of soil (mg day^{-1}) (100 for adults; US EPA 1989)
EF: exposure frequency (days $year^{-1}$) (350 for adults; Du et al. 2013)
ED: exposure duration (years) (24 for adults; US EPA 2001)
BW: average body weight (kg) (55.9 for adults; Du et al. 2013)
AT: average time (days) (365 × ED) (US EPA 1989)
CF: conversion factor (kg mg^{-1}) (1×10^{-6}) (Du et al. 2013)
R_{inh}: inhalation rate (m^3 day^{-1}) (20 for adults; Du et al. 2013)
PEF: particle emission factor (m^3 kg^{-1}) (1.32×10^9; Du et al. 2013)
SA: surface area of the skin that contacts the dust (cm^2) (5000 for adults; Du et al. 2013)
SL: skin adherence factor for dust (mg cm^{-2}) (1; Du et al. 2013)
ABS: dermal absorption factor (metal-specific) (0.001; Du et al. 2013)

The variance in toxicity potentials resulting from input parameter uncertainties (Huijbregts et al. 2000). As a consequence, it is important to note that numerous uncertainties can dramatically change the predicted values of ADD_{ing}, ADD_{derm}, and ADD_{inh}. For instance, the gravimetric analysis of $PM_{2.5}$ has both positive and negative artifacts and thus one should bear in mind that some biases are shown to have systematic seasonal characteristics (Malm et al. 2011). A previous study indicated that inhalation rates (m^3 kg^{-1} day^{-1}) for healthy normal-weight individuals were higher by 6–21% compared with their overweight/obese counterparts (Brochu et al. 2006). Interestingly, infants and children between the age of 3 weeks to less than 7 years inhale 1.6–4.3 times more air than adults aged 23–96 years (Brochu et al. 2006). In this study, a hazard quotient (HQ) and hazard index (HI) also were used to highlight the noncarcinogenic risks of a single metal and the total noncarcinogenic risks of different metals through the previously mentioned three possible exposure pathways (US EPA 1997). The equations for computing the HQ and HI are:

$$HQ = \frac{ADD}{RfD} \quad (4)$$

$$HI = \sum HQ_i \quad (5)$$

where RfD stands for the reference dose (mg kg^{-1} day^{-1}) cited from other studies (US EPA 1993; Ferreira-Baptista and De Miguel 2005). Previous investigations indicate that if the HQ is less than one, then the noncarcinogenic effects appears to be negligible. On the contrary, when HQ is greater than one, it is most likely that a negative health impact exists. Furthermore, if the HQ is greater than ten, a high chronic risk is almost inevitable (Leung et al. 2008; Zhou et al. 2014). Because there are no reliable sources of reference values of carcinogenic risk via ingestion and dermal exposure, it is extremely difficult to calculate the carcinogenic risk of selected metals through these two

exposure pathways. As a consequence, in this study, the carcinogenic risks of Ni, Cr, and Cd resulting from inhalation were estimated, and the lifetime average daily dose (LADD) was computed and multiplied by the slope factor (SF) to generate the cancer risk level, as written below:

$$\mathrm{LADD_{inh}} = \frac{\mathrm{ADD_{inh}}}{7} \tag{6}$$

$$\mathrm{Risk} = \mathrm{LADD} \times \mathrm{SF} \tag{7}$$

All the exposure parameter values used in this study were described in detail in previous studies (Du et al. 2013; Zhou et al. 2014).

Time Series Approach

An autocorrelation plot (Box–Jenkins method), also known as a correlogram, is an excellent means of evaluating randomness in a dataset. This statistical process is essentially crucial to assess the validity of any statistical conclusions. For instance, the autocorrelation plot can extract essential information hidden inside noise, such as replicating formats of an interval signal, or categorize the disregarded fundamental frequency in a signal implied by its harmonic frequencies. Over the past decades, autocorrelation plots have been extensively applied in numerous atmospheric environmental studies, including a simulation of the daily average PM_{10} concentrations at Ta-Liao (Liu 2009), an investigation of the relationship between solar–lunar cycles and the Earth climatic system (Alvarez-Ramirez et al. 2011), a study of aerosol optical depth over New Delhi (Taneja et al. 2016), and an examination of the influence of meteorological factors and trace gaseous species on daily hospital walk-ins and admission as a consequence of respiratory diseases in Chiang-Mai (Pongpiachan and Paowa 2014).

Because autocorrelation denotes the likeness between detections as a function of the time lag between them, it seems rational to assess the randomness of $PM_{2.5}$-bound metals with time by applying this statistical method. This unsystematic data distribution can be examined by calculating autocorrelations for individual variables at separate time lags. If the temporal variation of particulate metals is random, the autocorrelations should theoretically be close to zero for any and all time-lag intervals. On the contrary, in the case of non-randomness, one or more of the autocorrelations should be significantly nonzero. The computation of autocorrelation plots can be described as follows. First, the *y*-axis represents the autocorrelation coefficient, which can be calculated using Eq. (8),

$$R_h = \frac{C_h}{C_0} \tag{8}$$

where R_h is the autocorrelation coefficient of particulate metals, and ranges between -1 and $+1$. It is crucial to emphasize that C_h is an autocovariance function, which can be described by Eq. (9),

$$C_h = \frac{1}{N}\sum_{t=1}^{N-h}(Y_t - \bar{Y})(Y_{t+h} - \bar{Y}) \tag{9}$$

where N, t, h, Y_t, $\bar{Y}$, and Y_{t+h} stand for the total number of selected metals, time, time lag, concentration of selected metal at time t, average of selected metal concentrations, and concentration of selected metal at time $t + h$, respectively. It is also important to note that C_0 is the variance function, which can be written as

$$C_0 = \frac{\sum_{t=1}^{N}(Y_t - \bar{Y})^2}{N} \tag{10}$$

Second, the *x*-axis indicates the time lag, h ($h = 1, 2, 3, \ldots$). Finally, the confidence bands have a specified range that relies on sample size and can be calculated using Eq. (11):

$$\pm\frac{Z_{1-\alpha/2}}{\sqrt{N}} \tag{11}$$

where N is the sample size, Z is the cumulative distribution function of the standard normal distribution, and α is the significance level.

Enrichment Factors of Selected Metals

Over the past few years, the enrichment factor (EF) has been broadly used to assess the impact of traffic emissions, manufacturing emissions, and mining coupled with ore processing on particulate elemental concentrations and atmospheric elemental contents (Li et al. 2012; Wang et al. 2014; Zhang et al. 2015). Despite some ambiguities associated with the protocol for choosing the reference element, Al, Fe, and Si are continually used for the EF calculations (López et al. 2005). In this study, Fe was adopted as a reference presuming the minor impacts of pollutant Fe and the upper continental crustal composition given by Rudnick (2003). The EF of an element E in a $PM_{2.5}$ sample can be described as

$$\mathrm{EF} = \frac{(E/R)_{\mathrm{Air}}}{(E/R)_{\mathrm{Crust}}} \tag{12}$$

where R is a reference element. If EF approaches one, the crust can be regarded as the major source. In addition, Statistical Program for Social Sciences (SPSS) version 13

was used for Simple Linear Regression Analysis (SLRA), the t test, and analysis of variance (ANOVA).

Results and Discussion

Statistical descriptions of 51 selected $PM_{2.5}$-bound metals collected during the monitoring campaign at CHAOS are compared with data for other cities (Table 1). Overall, all the selected particulate metal contents were higher than the IDL. $PM_{2.5}$-bound Na showed the highest 72 h average content of 19,375 ± 8830 ng m^{-3}, with concentrations ranging between 4792 and 37,610 ng m^{-3}. S was the second most abundant species in the atmosphere, with an average of 17,045 ± 7744 ng m^{-3}. The particulate contents of W ranged between 13,402 and 14,015 ng m^{-3} with an average of 13,653 ± 160 ng m^{-3}. K, Cs, and La also had comparatively high concentrations in the atmosphere, with daily average levels of 7676 ± 3137, 3023 ± 527, and 2476 ± 233 ng m^{-3}, respectively. Interestingly, the average content observed for Cd was 113 ng m^{-3}, which exceeded the EU standard (i.e., 5 ng m^{-3}) by 23 times (EEA 2015). As and Ni had average concentrations of 11 ± 26 and 32 ± 24 ng m^{-3}, surpassing the limits specified in the EEA standard by 1.8 times and 1.6 times, respectively. In contrast, the level of particulate Hg measured in Bangkok (i.e., 28 ng m^{-3}) was comparable to values observed in Croatia (i.e., 20 ng m^{-3}) and the UK (i.e., 24 ng m^{-3}) (EEA 2015). Only Pb exhibited comparatively low atmospheric concentrations of 297 ± 126 ng m^{-3}, 1.7 times lower than those of the EEA standard (i.e., 500 ng m^{-3}). This finding was in good agreement with Thailand's ambitious program to eliminate lead in gasoline, which resulted in the successful halt in the sale of regular octane 91 gasoline since 1 January 2013. The Energy Policy Management Committee of Thailand agreed at the meeting on 28 November 2012 to adjust the ethanol price formula in accordance with the portion of ethanol produced from cassava root. As a consequence of this action, the current ethanol consumption rate is approximately 3.0 million litres per day (DEDE 2016).

In consideration of global scale comparisons, the $PM_{2.5}$-bound selected metal contents obtained from this study were carefully compared with a selection of previous studies of urban atmospheres (Table 1). Despite some fundamental constraints present with the $PM_{2.5}$ sampling intervals and periodicities, it seems plausible to contextualise the selected metal contents detected at CHAOS. As illustrated in Table 1, the 72-h average concentrations of Cr, Mn, and Ni were almost equivalent to those of Baoshan (Wang et al. 2013). Similar levels of Fe, Cu, and Zn were observed in the urban atmosphere of Putuo (Wang et al. 2013), Rio de Janeiro (Da Silva et al. 2015), and Agra (Kulshrestha et al. 2009), respectively. It is important to note that the 72-h average concentrations of V, Cr, Mn, and Hg were considerably less than the existing international air quality guidelines and standard limit values for trace metal species proposed by the WHO air quality guidelines for Europe, the European Commission Air Quality Standards, the National Ambient Air Quality Standards of the US EPA, and the National Air Quality Act of the South African Department of Environmental Affairs.

Day-of-Week Trends of Particulate Metals

To evaluate the effect of day-of-week trends on variations of the 51 selected metal contents, the data were further categorized into two groups: weekday and weekend. "Weekday" was defined as the average metal concentrations collected from Monday to Friday, and "weekend" was the average of 3-day metal contents measured from Saturday to Sunday. Surprisingly, no statistical differences ($p < 0.05$) were observed between the 51 selected metal contents of these two groups. Further investigations were conducted using the diagnostic binary ratios of metal concentrations observed during weekdays ($Conc_{weekday}$) and weekends ($Conc_{weekend}$). When the $Conc_{weekday}$/$Conc_{weekend}$ value is greater than one, it appears rational to assume that vehicular exhaust during weekdays plays an important role in governing $PM_{2.5}$-bound metal concentrations in ambient air in Bangkok. On the other hand, if the $Conc_{weekday}/Conc_{weekend}$ value is equal to one, it seems reasonable to conclude that there is no major difference in emission source strengths between the two periods. In this study, the average $Conc_{weekday}/Conc_{weekend}$ value of 51 selected metals was 1.09 ± 0.22, indicating that the day-of-week trend was of minor importance.

This data interpretation is in good accordance with the mass percent compositions of $PM_{2.5}$-bound selected metals (Fig. 3). The average mass percentage compositions of selected trace elements followed the order: Na or S > W > K > Cs > La > Eu > Si > Tb > Fe > Mg > Al > Sm > Ca for both monitoring periods. The almost identical descending order of selected elements between the two sampling categories underlines the comparatively homogeneous distribution of 51 chemical compositions throughout the urban atmosphere of Bangkok. In other words, the road traffic emissions quickly overwhelmed other potential sources of selected metals during the monitoring campaign. Further assessment of day-of-week trends was conducted by introducing the concept of fingerprinting characteristics of selected metal profiles. Because a simple diagnostic binary ratio of two or three selected metals is sensitive to both chemical and biological degradation and may be insufficient to categorize air pollutants, the best strategy to study the behaviour of

Table 1 Statistical description of $PM_{2.5}$-bound metals (ng m^{-3}) obtained from this study compared with those of other major cities

Country	Thailand (this study)				(China)[a]	(China)[a]	(China)[b]	(China)[c]	(India)[d]	(Spain)[e]	(Finland)[f]	(USA)[g]	(Belgium)[h]	(Brazil)[i]	(USA)[j]
City	Bangkok				Baoshan	Putuo	Hangzhou	Hong Kong	Agra	Barcelona	Helsinki	Florida	Average of six cities	Rio de Janeiro	Tampa
	Aver	SD	Min	Max											
Na	19,375	8830	4792	37,610											
Mg	1481	502	800	2671											
Al	1316	315	453	2063									58		17
Si	2083	822	559	4686									128		
P	120	104	N.D.	328											
S	17,045	7744	5747	47,556											
Cl	307	144	87	723											
K	7676	3137	2170	14,820									149		
Ca	1030	283	501	1803									61		
Sc	17	12	N.D.	58											
Ti	85	29	10	174									4		
V	27	19	N.D.	77									7	16	
Cr	39	12	19	87	31	9	13	1	600	6			2	66	0.20
Mn	201	74	48	337	132	66	46	10	100	10	3	2	7	104	0.53
Fe	1441	362	791	2391	2381	1328	726	100	1900	0.3	100	80	129	6496	11
Co	10	8	N.D.	39										1.1	
Ni	32	24	10	164	27	9	7	4	300	6	2	1	6	9.8	0.41
Cu	136	31	92	241	29	15	76	5	200	50	3	2	6	158	0.33
Zn	796	311	299	1437	465	236	651	200	900	200	10	10	48	316	3.6
Ga	71	49	N.D.	174											
As	11	26	N.D.	106											0.50
Se	51	23	N.D.	106											0.48
Br	82	41	N.D.	154											
Rb	32	20	N.D.	67									1		
Sr	50	18	19	77											
Y	17	13	N.D.	48											
Zr	180	60	87	318											
Nb	71	21	19	125											
Mo	82	21	39	116											
Pd	161	54	87	309											
Ag	109	69	N.D.	260											
Cd	113	66	N.D.	260	3	1								1.5	0.26
In	156	49	96	289											

Table 1 continued

Country	Thailand (this study)				(China)[a]	(China)[a]	(China)[b]	(China)[c]	(India)[d]	(Spain)[e]	(Finland)[f]	(USA)[g]	(Belgium)[h]	(Brazil)[i]	(USA)[j]
City	Bangkok				Baoshan	Putuo	Hangzhou	Hong Kong	Agra	Barcelona	Helsinki	Florida	Average of six cities	Rio de Janeiro	Tampa
	Aver	SD	Min	Max											
Sn	245	64	135	395											
Sb	146	61	58	328											
Cs	3023	527	1745	4310											
Ba	550	187	318	1215											
La	2476	233	2025	2970											
Ce	628	208	299	1215											
Sm	1227	359	675	2208											
Eu	2164	446	1205	3491											
Tb	1680	467	839	2729											
Hf	221	84	10	424											
Ta	28	42	N.D.	174											
W	13,653	160	13,402	14,015											
Ir	39	30	N.D.	116											
Au	105	59	10	251											
Hg	28	42	N.D.	154											
Tl	33	19	N.D.	67											
Pb	297	126	106	646	133	59	128		1100	100	6	5	21	52	0.78
U	115	35	48	212											

[a] Wang et al. (2013)

[b] Bao et al. (2010)

[c] Hagler et al. (2007)

[d] Kulshrestha et al. (2009)

[e] Querol et al. (2001)

[f] Pakkanen et al. (2001)

[g] Olson et al. (2008)

[h] Bencs et al. (2010)

[i] Da Silva et al. (2015)

[j] Pancras et al. (2006)

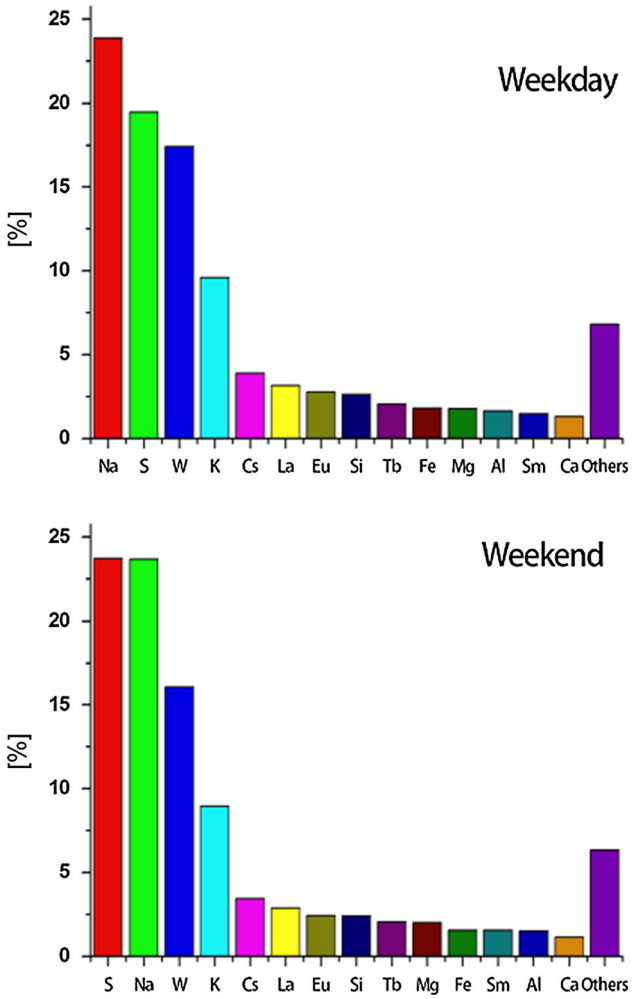

Fig. 3 Mass percent compositions of $PM_{2.5}$-bound selected metals from November 2010 to April 2011 at CHAOS

particulate metals is to employ all 51 metal profiles. In this study, the assumption was that air masses collected at CHAOS are well homogenised and site-specific factors that affect the inconsistency of the individual metal contents and fingerprint patterns are of minor importance.

As clearly illustrated in Fig. 4, the average logarithmic concentration profiles of 51 selected metals in $PM_{2.5}$ collected at CHAOS from Monday to Sunday are, to some extent, similar to one another. The logarithm concentration profile presented in Fig. 4 allows a rapid visual categorization of group 1: Monday, Tuesday, Saturday, Sunday; group 2: Wednesday, Thursday; group 3: Friday. Figure 4 displays the distribution characteristics of group 1, corresponding to the three major features. First, the most abundant quantified metals in decreasing order are: Na > S > Si > Mg > Al > P in the period-3 element group; second, Y, Co, and Sc are the three most abundant elements in the transition metal group; third, W is the most abundant metal in the period-6 element group. Some remarkable differences were detected in group 2 and group 3. For instance, the lowest average level of Ta was detected in the period-6 element group on Fridays (i.e., group 3), whereas Hg exhibited a minimum value on Wednesdays and Thursdays (i.e., group 2). Some dissimilarity in the logarithm profiles observed each day likely reflects some heterogeneity in the degree of vehicle flow. Despite the fact that CHAOS might be subject to specific-site impacts (e.g., resuspension of fine particles, heavy metal particles embedded in tyre dust, automobile repair shops, incinerators, and iron/steel works), it can be seen that the metal profiles for each day are astonishingly homogeneous. The insufficiency of differences between sampling days indicates that the source signatures of several metals become less prominent, conceivably because of consistent emission intensities and/or comparatively well-mixed air masses.

Autocorrelation of Selected Metals

Randomness is one of the most crucial assumptions that conventionally highlights all statistical processes. To avoid any suspect standard statistical conclusions, the concept of autocorrelation was applied to assess the randomness in the dataset, which can be achieved by computing autocorrelations for metal concentrations at altering time lags as written in Eq. (8)–(11). If the dataset is random, such autocorrelation should theoretically approach zero by dropping immediately from one at zero lag to near zero at lags equal to one or larger for any and all time-lag intervals. In the case of nonrandomness, one or more of the autocorrelations will subsequently be significantly nonzero. Despite some dissimilarity in the alterations of concentrations observed in some metals, the autocorrelation approach displayed a considerably strong sinusoidal wave in Ba, Cd, Ce, Rb, Ca, Ga, and Tb (Figs. S3A–S3B). Interestingly, some moderate sinusoidal waves were detected in Hf, Hg, In, Ir, K, La, Mg, Mn, Mo, Nb, Ni, S, Sb, Sc, Si, Sm, Ti, V, Y, Zn, and Zr (Figs. S3A–S3B). In addition, some characteristic features of autocorrelation plots are illustrated in Fig. 5.

Although some discrepancies existed in the autocorrelation plots among the selected metals, the correlograms had several common features. First, the majority of correlograms have both positive and negative correlations. Second, almost all of the correlograms fall within the confidence band (i.e., upper critical value of +0.305 and lower critical value of −0.305), as calculated using Eq. (11). Third, there is no evident pattern, such as the first 20 lags having positive correlations and the second 20 lags having negative correlations. Fourth, unlike other types of correlograms, which normally start with a moderately high autocorrelation at lag 1 then gently decline, the autocorrelation plots obtained in this study exhibit an alternating

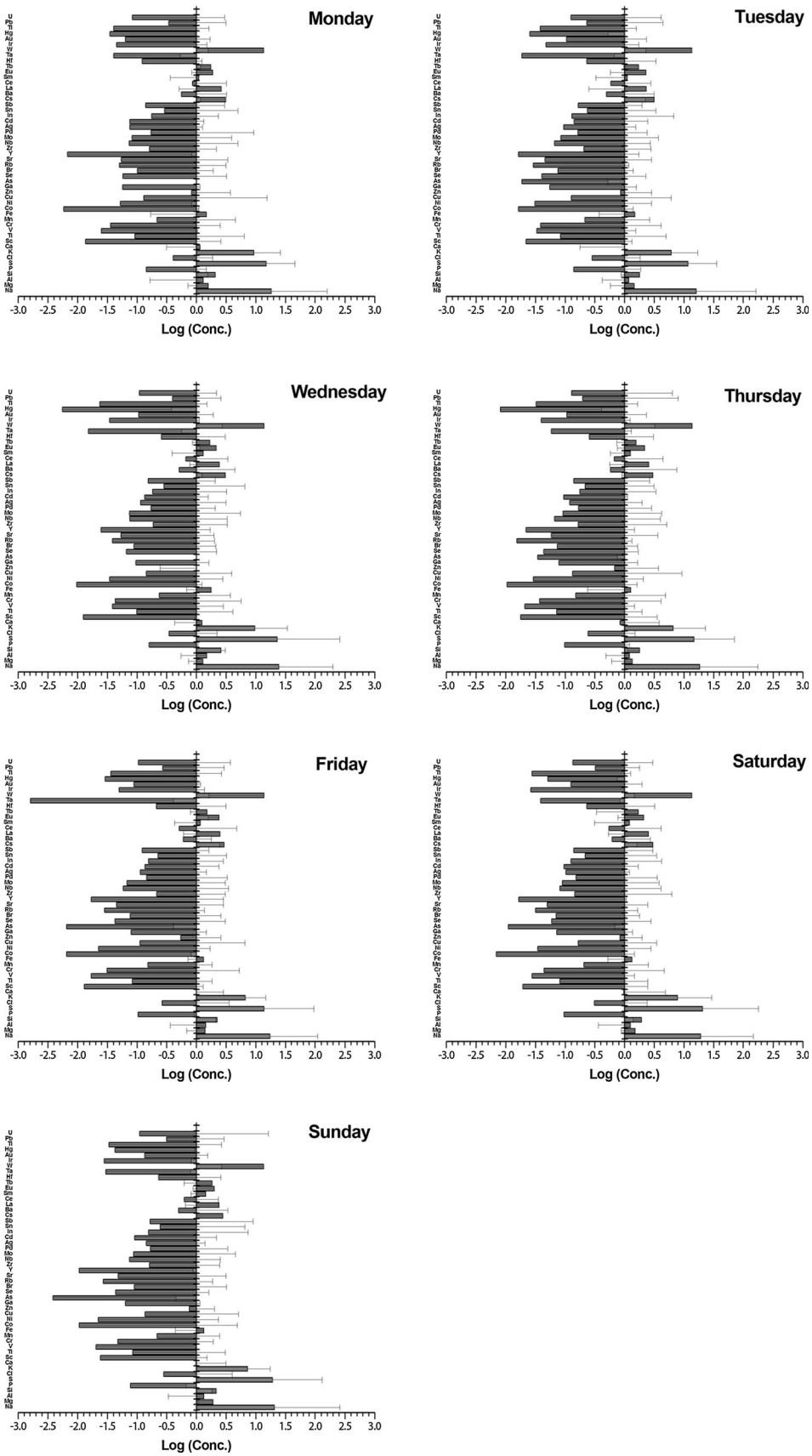

Fig. 4 Logarithmic concentration profiles of 51 selected metals in $PM_{2.5}$ collected at CHAOS from November 2010 to April 2011

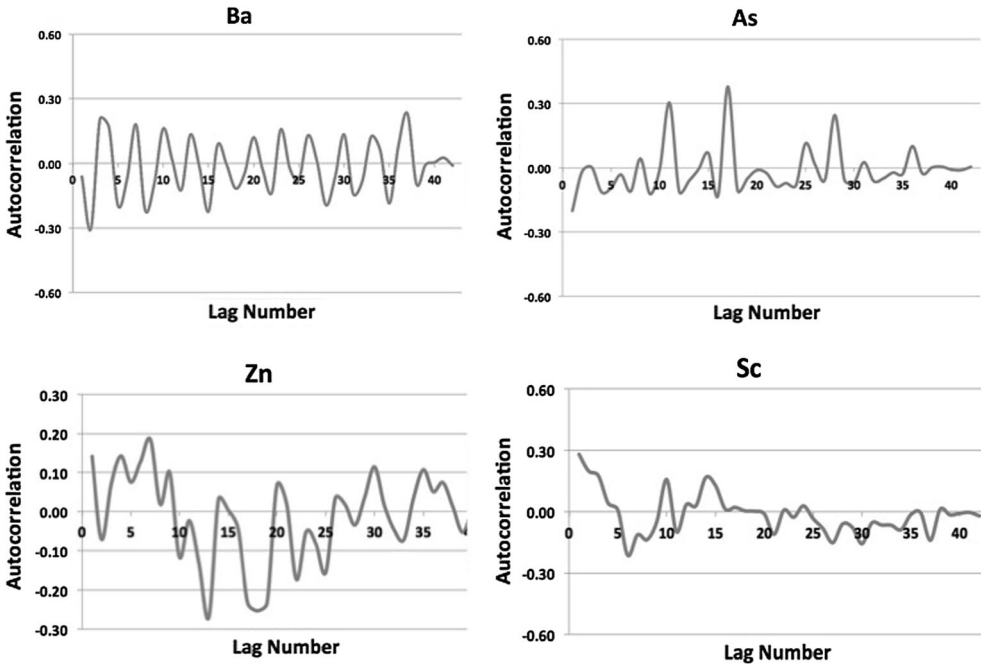

Fig. 5 Plots of autocorrelations using contents of As, Ba, Sc, and Zn in $PM_{2.5}$ collected at CHAOS from November 2010 to April 2011

sequence of both positive and negative spikes that do not decay to zero. These characteristic features underline the fact that $PM_{2.5}$-bound metals collected at CHAOS are indeed random and the underlying autocorrelation plot has the signature of a sinusoid.

Health-Risk Assessment of Selected Metals

The concept of HI is widely used to evaluate human health risk of metal exposure to $PM_{2.5}$-bound metals. In the case of $HI < 1$, it appears reasonable to conclude that there is no significant risk of noncarcinogenic effects. In contrast, if $HI > 1$, there is a higher risk of carcinogenic effects, and the possibility is enhanced with increasing values of HI (Du et al. 2013; US EPA 2001). It is important to mention that $HQ < 1$ and $HQ > 1$ indicate "no adverse health effects" and "adverse health effects," respectively. In this study, the HQ and HI of Cr, Cu, Zn, Cd, Pb, and Ni were calculated and are listed in Table 2. It also is interesting to note that the average values of HQ of six metals for three pathways of exposures (i.e., ingestion, inhalation, and dermal contact) decrease in the sequence of ingestion > dermal contact > inhalation with the contribution of HQ_{ing} to HI of more than 60%. This indicates that ingestion is the main pathway of exposure to heavy metals that endanger human health. Although this finding is in good agreement with previous studies (Du et al. 2013; Zhou et al. 2014), dermal contact is evidently the dominant exposure route for some metals. For instance, Cr and Cd showed the highest contribution of HQ_{derm} to HI, with values of 71 and 83%, respectively. Despite the fact that the general population is exposed most frequently to ingestion through metal contaminated soil, food, and water, occupational exposure to Cr and Cd can occur through dermal contact.

Overall, HI value was reduced with the sequence Cd > Pb > Cr > Cu > Zn > Ni. Cd and Pb showed relatively high HI values of 4.92×10^{-2} and 8.15×10^{-3}, respectively, close to the safe level compared to other heavy metals (Table 2). Cd and Pb originating from agriculture in agro-ecosystems have been shown to exhibit severe toxic effects (Tutic et al. 2015). Early studies also found associations between Cd exposure and preterm low birth weights (Huang et al. 2016), adverse health impacts on vertebrae (Zaki et al. 2016), and Itai–Itai disease. Long-term exposure to low levels of Pb may result in conditions that include idiopathic intellectual disability (McDermott et al. 2011), cardiovascular disease (Navas-Acien et al. 2007), and stroke (Pocock et al. 1988). These results indicate that Cd and Pb can lead to many long-term adverse health problems in Bangkok. Thus, risk mitigation strategies and specific action plans should be incorporated in future policies for Bangkok. In this study, the $LADD_{inh}$ and adverse health risks triggered by inhalation of $PM_{2.5}$-bound Cr, Ni, and Cd are quantitatively identified. As shown in Table 3, the $LADD_{inh}$ values for all three heavy metals were all below 10^{-6} and ranged from N.D. to 1.32×10^{-9}. Additionally, the carcinogenic risks for all three heavy metals were virtually less than 10^{-6}. Because the cancer risk values obtained from this study were much lower than

Table 2 Hazard quotients and hazard index for non-carcinogenic metals in outdoor atmosphere of Bangkok

	Cr	Cu	Zn	Cd	Pb	Ni
HQ_{ing}						
Aver	9.55×10^{-4}	2.50×10^{-4}	1.96×10^{-4}	8.20×10^{-3}	6.11×10^{-3}	1.07×10^{-4}
SD	6.58×10^{-4}	1.93×10^{-4}	1.49×10^{-4}	1.02×10^{-2}	4.42×10^{-3}	9.01×10^{-5}
Min	2.44×10^{-4}	7.32×10^{-5}	4.79×10^{-5}	N.D.	2.38×10^{-3}	2.26×10^{-5}
Max	3.05×10^{-3}	1.07×10^{-3}	7.07×10^{-4}	6.11×10^{-2}	2.36×10^{-2}	5.81×10^{-4}
HQ_{inh}						
Aver	1.52×10^{-5}	3.76×10^{-8}	2.97×10^{-8}	1.24×10^{-6}	9.21×10^{-7}	1.35×10^{-6}
SD	1.05×10^{-5}	2.91×10^{-8}	2.25×10^{-8}	1.54×10^{-6}	6.67×10^{-7}	1.14×10^{-6}
Min	3.87×10^{-6}	1.10×10^{-8}	7.26×10^{-9}	N.D.	3.59×10^{-7}	2.85×10^{-7}
Max	4.85×10^{-5}	1.61×10^{-7}	1.07×10^{-7}	9.25×10^{-6}	3.55×10^{-6}	7.33×10^{-6}
HQ_{derm}						
Aver	2.39×10^{-3}	4.16×10^{-5}	4.90×10^{-5}	4.10×10^{-2}	2.04×10^{-3}	1.97×10^{-5}
SD	1.65×10^{-3}	3.22×10^{-5}	3.71×10^{-5}	5.08×10^{-2}	1.47×10^{-3}	1.67×10^{-5}
Min	6.09×10^{-4}	1.22×10^{-5}	1.20×10^{-5}	N.D.	7.94×10^{-4}	4.18×10^{-6}
Max	7.63×10^{-3}	1.78×10^{-4}	1.77×10^{-4}	3.05×10^{-1}	7.85×10^{-3}	1.08×10^{-4}
HI						
Aver	3.36×10^{-3}	2.91×10^{-4}	2.45×10^{-4}	4.92×10^{-2}	8.15×10^{-3}	1.28×10^{-4}
SD	2.31×10^{-3}	2.25×10^{-4}	1.86×10^{-4}	6.10×10^{-2}	5.90×10^{-3}	1.08×10^{-4}
Min	8.56×10^{-4}	8.55×10^{-5}	5.99×10^{-5}	N.D.	3.18×10^{-3}	2.70×10^{-5}
Max	1.07×10^{-2}	1.25×10^{-3}	8.84×10^{-4}	3.66×10^{-1}	3.14×10^{-2}	6.96×10^{-4}

Table 3 Lifetime average daily doses and risk for each carcinogenic metal via inhalation in outdoor atmosphere of Bangkok

	Cr	Cd	Ni
$LADD_{inh}$			
Aver	6.20×10^{-11}	1.78×10^{-10}	4.61×10^{-11}
SD	4.27×10^{-11}	2.20×10^{-10}	3.90×10^{-11}
Min	1.58×10^{-11}	N.D.	9.76×10^{-12}
Max	1.98×10^{-10}	1.32×10^{-9}	2.51×10^{-10}
Risk			
Aver	2.61×10^{-9}	1.12×10^{-9}	3.88×10^{-11}
SD	1.79×10^{-9}	1.39×10^{-9}	3.28×10^{-11}
Min	6.64×10^{-10}	N.D.	8.20×10^{-12}
Max	8.33×10^{-9}	8.33×10^{-9}	2.11×10^{-10}

the threshold value of 10^{-6}, which is as insignificant by the US EPA, it appears reasonable to conclude that the lifetime cancer risks from Cr, Ni, and Cd are negligible.

Enrichment Factors of Selected Metals

As illustrated in Fig. 6, the sequence of *EF* logarithms for 44 selected metals in $PM_{2.5}$ observed at CHAOS from November 2010 to April 2011 was: W > In > Tb > Eu > Ir > Cd > Cs > Se > Hg > Sb > Pd > Sm > Sn > La > Mo > Au > Br > U > Hf > Tl > S > Ta > Pb > Zn > Ce > Nb > Cu > Ga > As > Ag > Sc > Zr > Ba > Cl > Y > Ni > Co > Cr > Rb > V > Mn > Sr > Fe > Al. These analytical results can be classified into four groups as an arbitrary scale according to previous studies (Karageorgis et al. 2009; Pongpiachan and Iijima 2015). First, V, Mn, Sr, Fe, and Al are not enriched (i.e., Log(EF) < 1). Second, S, Ta, Pb, Zn, Ce, Nb, Cu, Ga, As, Ag, Sc, Zr, Ba, Cl, Y, Ni, Co, Cr, and Rb are considerably enriched (i.e., 1 < Log(EF) < 3). Third, Sm, Sn, La, Mo, Au, Br, U, Hf, and Tl are highly enriched (i.e., 3 < Log(EF) < 4). Fourth, W, In, Tb, Eu, Ir, Cd, Cs, Se, Hg, Sb, and Pd are exceedingly highly enriched (i.e., Log(EF) > 4). Several factors, such as resuspension of road dust, sea salt aerosols from the Gulf of Thailand, crustal sources, and construction dust may dramatically affect the Log(EF) values.

It also is interesting to note that the exceptionally low Log(EF) (−0.52) of Al detected in this study is in good agreement with values reported by Pongpiachan and Iijima (2015) and Wu et al. (1994). Crustal emissions are plausible predominant sources of particulate Al over Bangkok, as equivalent studies have reported that the majority of Al over Chesapeake Bay was mainly derived from terrestrial soils (Wu et al. 1994). Conversely, the exceedingly great values of Log(EF) (>4) observed in W, In, Tb, Eu, Ir, Cd, Cs, Se, Hg, Sb, and Pd highlight the strong impact of traffic exhaust, consistent with early findings (Lough et al. 2005; Almeida et al. 2006; Crawford et al. 2007; Pongpiachan and Iijima 2015). It also is worth mentioning that almost 50% of Log(EF) was greater than three. Only 11% of

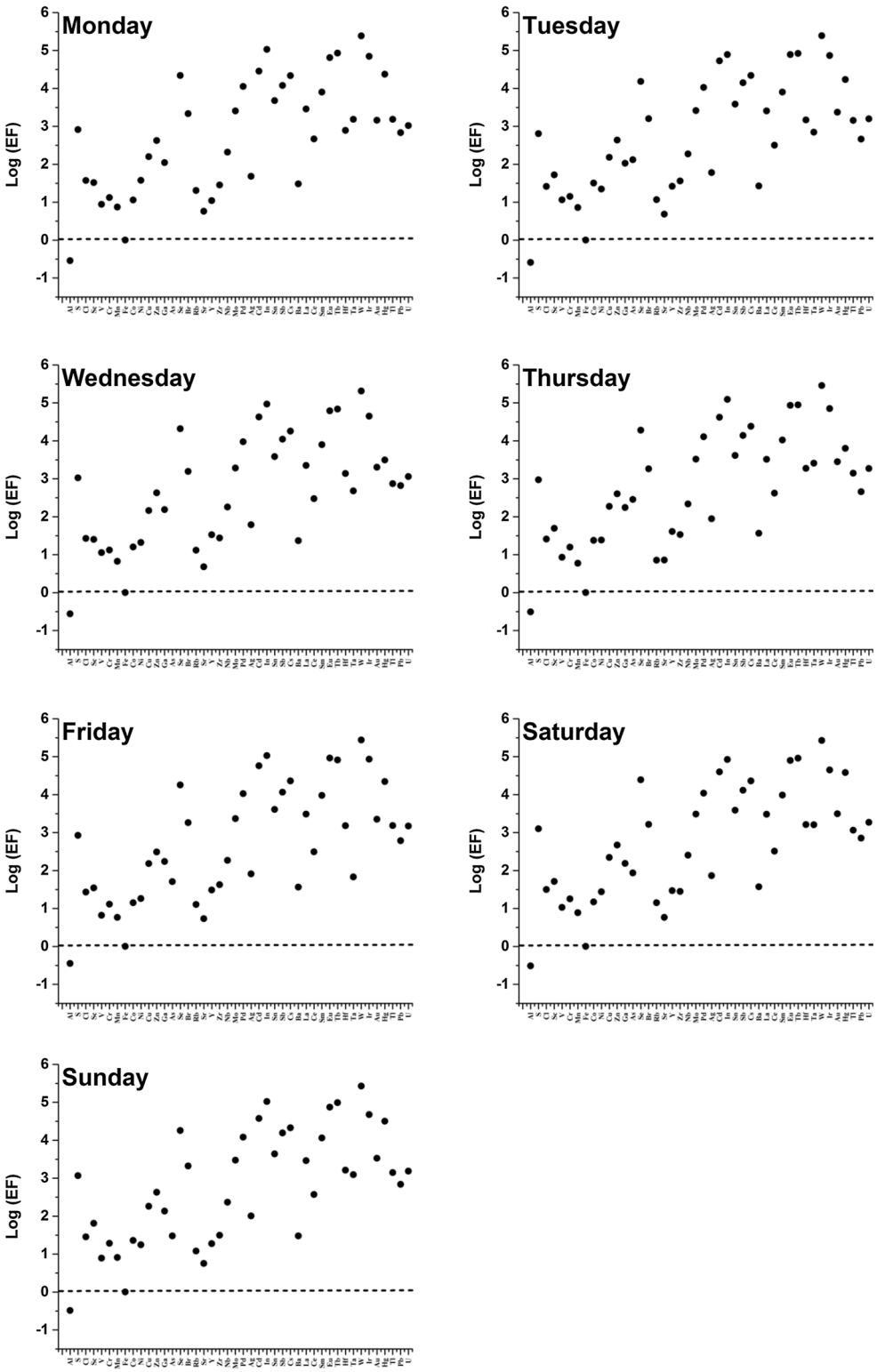

Fig. 6 Logarithms of EF of 44 selected metals in $PM_{2.5}$ collected at CHAOS from November 2010 to April 2011

Log(EF) was lower than one. This indicates the comparatively strong influence of anthropogenic activity, surpassing other factors, such as natural emissions. Further assessments of day-of-week trends in Log(EF) were conducted similarly to those of the logarithm concentration profiles, as previously discussed in Section "Day-of-week trends of particulate metals". Overall, the Log(EF) profiles show no obvious differences between the weekday and weekend groups. In general, these finding are in line with previous studies, emphasizing that undeviating emission

source strengths of vehicular exhaust play a major role in governing atmospheric metal contents over Bangkok, for both working and nonworking days.

Conclusions

Irrespective of the differences in emission source strengths of individual metal concentration levels determined each day, the overall fingerprints are almost equivalent to one another, suggesting comparatively homogeneous and consistent emissions of 51 selected metals in the urban atmosphere of Bangkok. Both logarithm concentration profiles and Log(EF) profiles suggest that anthropogenic emissions, mainly vehicular exhaust, might play a major role in controlling $PM_{2.5}$-bound metals over Bangkok. Despite some subtle differences in the autocorrelation plots, majority of the correlograms exhibit a sinusoidal pattern, indicating that the data are completely random. Although the HI values of Cr, Cu, Zn, Cd, Pb, and Ni are much lower than the safe level, the potential health risk is quite high for Cd and Pb. As a consequence, it is crucial to implement effective long-term action plans to reduce Cd and Pb in urban dust, such as promoting electric vehicles (EVs), building cycling infrastructure, and encouraging people to use public transportation.

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