SHORT RESEARCH AND DISCUSSION ARTICLE



# Assessment of selected metals in the ambient air  $PM_{10}$  in urban sites of Bangkok (Thailand)

Siwatt Pongpiachan<sup>1</sup> · Akihiro Iijima<sup>2</sup>

Received: 19 July 2015 /Accepted: 24 November 2015  $\oslash$  Springer-Verlag Berlin Heidelberg 2015

Abstract Estimating the atmospheric concentrations of  $PM_{10}$ -bounded selected metals in urban air is crucial for evaluating adverse health impacts. In the current study, a combination of measurements and multivariate statistical tools was used to investigate the influence of anthropogenic activities on variations in the contents of 18 metals (i.e., Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Sb, Ba, La, Ce and Pb) in ambient air. The concentrations of  $PM_{10}$ -bounded metals were measured simultaneously at eight air quality observatory sites during a half-year period at heavily trafficked roads and in urban residential zones in Bangkok, Thailand. Although the daily average concentrations of Al, V, Cr, Mn and Fe were almost equivalent to those of other urban cities around the world, the contents of the majority of the selected metals were much lower than the existing ambient air quality guidelines and standard limit values. The sequence of average values of selected metals followed the order of Al>Fe>Zn>Cu>Pb> Mn>Ba>V>Sb>Ni>As>Cr>Cd>Se>Ce>La>Co>Sc. The probability distribution function (PDF) plots showed sharp symmetrical bell-shaped curves in V and Cr, indicating that crustal emissions are the predominant sources of these

Responsible editor: Philippe Garrigues

 $\boxtimes$  Siwatt Pongpiachan pongpiajun@gmail.com two elements in  $PM_{10}$ . The comparatively low coefficients of divergence (COD) that were found in the majority of samples highlight that site-specific effects are of minor importance. A principal component analysis (PCA) revealed that 37.74, 13.51 and 11.32 % of the total variances represent crustal emissions, vehicular exhausts and the wear and tear of brakes and tires, respectively.

**Keywords** Metals  $\cdot PM_{10} \cdot Multivariate$  statistics  $\cdot$ Enrichment factor . Bangkok

# Introduction

During the past few years, there have been significant concerns over various potential adverse health effects of enhanced  $PM_{10}$  levels in the urban atmosphere, which are mainly associated with anthropogenic activities. One of the many crucial aspects of the  $PM_{10}$  study in ambient air is predominantly related to its mutagenicity and carcinogenicity (Pongpiachan 2013a, b; Pongpiachan et al. 2013, 2015a, b). Another interesting issue is deeply connected to the chemical compositions of metals in  $PM_{10}$ . Previous studies have indicated that the majority of metals favourably existed in finer particles because they possess lower densities and a larger surface area per volume unit and organic matter content (Charlesworth et al. 2003; Madrid et al. 2008; Yatkin and Bayram 2008a, b). Several studies have highlighted the adverse health impacts of exposure to ambient metals, such as lead (Rosen 1995). mercury (Ratcliffe et al. 1996). cadmium (Yang et al. 2014). chromium (Berardi et al. 2015). arsenic (Wang et al. 2014a, b) and vanadium (Zwolak 2014).

There is no current comprehensive study focusing on the  $PM_{10}$ -bounded heavy metals or a calculation of the enrichment factors in the urban atmosphere of Bangkok.

<sup>&</sup>lt;sup>1</sup> NIDA Center for Research and Development of Disaster Prevention and Management, School of Social and Environmental Development, National Institute of Development Administration (NIDA), 118 Moo 3, Sereethai Road, Klong-Chan, Bangkapi, Bangkok 10240, Thailand

<sup>&</sup>lt;sup>2</sup> Department of Regional Activation, Faculty of Regional Policy, Takasaki City University of Economics, 1300 Kaminamie, Takasaki, Gunma 370-0801, Japan

Meanwhile, the majority of studies have highlighted the health risk assessment of total suspended particles (TSP) collected from a few air quality observatory sites in developed countries, but there is a lack of information on the metals in  $PM_{10}$ collected simultaneously from multiple locations, particularly in Southeast Asian countries, which poses a greater health risk to residents. Consequently, it would be valuable to observe a series of data sources on the representative urban emissions of metals; this information would be crucial for the Pollution Control Department (PCD) to develop relevant air quality standards and for the scientific community to accumulate adequate baseline data for worldwide cities.

The main purpose of this study was to assess both the temporal and spatial distribution characteristics of selected metals in  $PM_{10}$  collected from multiple PCD air quality observatory sites to evaluate their behaviour in Bangkok. In addition, the strength of crustal and noncrustal sources was carefully evaluated by applying the concept of enrichment factors coupled with statistical methods based on Pearson correlation coefficients, hierarchical cluster analysis (HCA) and principal component analysis (PCA) for determining and distinguishing the pollution sources and their contribution. Particulate metals have both natural sources and anthropogenic sources. Since the metal compositions of the two major sources (i.e. anthropogenic and natural sources) overlap, the impact of anthropogenic metals in the environment must be both quantitatively and qualitatively evaluated against a dynamic background of natural metals. This can be conducted by using numerous combinations of statistical techniques. For statistical treatment, multivariate statistical methods such as HCA and PCA are employed for the purpose of source apportionment. In this study, HCA was conducted for the qualitative classification of sources with the agglomerative hierarchical clustering method and the squared euclidean distance. In addition, the standardisation was not conducted for this study since standardisation is not always appropriate prior to the clustering (Milligan and Cooper 1987). PCA was performed with the Varimax rotation (only factors with eigenvalues >1) to quantitatively categorise a large number of emission sources into five principal components (PCs).

## Materials and methods

# Description of the air quality observatory sites and  $PM_{10}$ sample collection

In this study, eight air quality observatory sites, namely Klongchan National Housing Authority (KHA; 13° 49′ 11.761″ N 100° 34′ 33.190″ E), Nonsreewitayakom High School (NWS; 13° 42′ 28.937″ N 100° 32′ 50.443″ E), Singharaj Pitayakhom High School (SPS), Huakwang National Housing Authority (HHA; 13° 46′ 41.720″ N 100° 34′ 06.760″ E), Thonburi Power Substation (TPS; 13° 43′ 39.205″ N 100° 29′ 11.776″ E), Chokchai 4 Police Box (CPB; 13° 47′ 33.474″ N 100° 35′ 45.879″ E), Dindang National Housing Authority (DHA; 13° 46′ 59.544″ N 100° 32′ 25.618″ E) and Badindecha High School (BHS; 13° 46′ 10.745″ N 100° 36′ 52.433″ E), were carefully chosen for the investigation of selected metals in  $PM_{10}$  (see Fig. 1). It is notable and should be underlined that CPB, DHA and TPS were positioned near traffic routes, while KHA, NWS, HHA, SPS and BHS were located at the residential zones. Therefore, CPB, DHA, TPS and KHA, as well as NWS, HHA, SPS and BHS can be considered representatives of "vehicular exhausts" and "urban residential background", respectively. Air sampling was conducted in 24-h periods at all air quality sites simultaneously once every month from January to June 2008 constructing a database of 48 individual air samples (i.e.  $6 \times 8 = 48$ ). Graseby-Anderson high-volume air samplers TE-6001 were used to achieve unmanned 24-h samplings for  $PM_{10}$ . A total of 48 air samples were acquired using highvolume-yielding sample volumes of approximately  $1632 \text{ m}^3$ for each 24-h sample. PM<sub>10</sub> were collected on  $20 \times 25$ -cm Whatman glass fibre filters (GFFs) at a flow rate of approximately 1.133 m<sup>3</sup> min<sup>-1</sup> (i.e. 40 cfm). A more comprehensive explanation of the air sampling method was given in "Compendium Method IO-2.2. Sampling of ambient air for PM<sub>10</sub> using an Andersen Dichotomous Sampler". In addition, all of the information of 11 meteorological parameters was provided by PCD, and the abbreviations, namely Rain, CO, WS, SO<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub>, T, RH, Rad, WD and P, represent precipitation, carbon monoxide, wind speed, sulphur dioxide, ozone, nitrogen dioxide, ambient temperature, relative humidity, solar radiation, wind direction and atmospheric pressure, respectively.

### Analysis of selected metals

Sample preparation and analytical procedure were described in detail in the previous studies (Iijima et al. 2009, 2010). Briefly, sample-loaded filters were placed into PTFE vessels and digested in a mixture of 2 mL of hydrofluoric acid (50 % atomic absorption spectrometry grade; Kanto Chemical Co. Inc.), 3 mL of nitric acid (60 % electronic laboratory grade; Kanto Chemical Co. Inc.) and 1 mL of hydrogen peroxide (30 % atomic absorption spectrometry grade; Kanto Chemical Co. Inc.) in a microwave digestion system (Multiwave; Anton Parr GmbH). The microwave oven was operated under the condition of 700 W for 10 min and 1000 W for a further 10 min. Hydrofluoric acid was evaporated by heating the sample solutions at 200 °C on a hot plate. The digested solutions were further diluted with 0.1 mol  $L^{-1}$  nitric



Fig. 1 A map of eight air quality observatory sites in Bangkok

acid (prepared from 60 % nitric acid) and added to obtain a 50-mL sample. The concentrations of Al, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Cd, Sb, Ba, La, Ce and Pb were determined by inductively coupled plasma mass spectrometry (Agilent 7500cx, Agilent Technologies Inc.). All the analytical procedures were validated by using the standard reference material (SRM) 1648 (urban particulate matter) that was prepared by the US National Institute of Standard and Technology (NIST). The analytical results were in good agreement with the certified or reference values.

# Statistical analysis

In an attempt to evaluate the fate of trace metals as measured in  $PM_{10}$ , an analysis of variance (ANOVA), hierarchical cluster analysis (HCA) and principal component analysis (PCA) with Varimax rotation (v. 13.0 SPSS Inc., Chicago, IL, USA) were performed on the dataset. PCA has been used extensively in receptor modelling to classify the main potential source categories influencing a provided receptor site. This statistical analysis functions on sample-to-sample variations of the normalised atmospheric concentrations. PCA does not straightforwardly gain concentrations of selected metals from numerous potential sources but ascertains a minimum number of common factors whose variance often explains most of the variance in the species.

### Results and discussion

# Comparison of  $PM_{10}$ -bounded selected metal concentrations

The 24-h concentrations of particulate Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Sb, Ba, La, Ce and Pb are listed in Table 1. In general, all of the concentrations of selected metals were above the detection limit. Atmospheric Al had the highest daily average concentration of  $1047 \pm 785$  ng m<sup>-3</sup>, with concentrations ranging between 193 and 2946 ng  $m^{-3}$ . Fe was the second most abundant species in the atmosphere, with a daily average concentration of 951 $\pm$ 572 ng m<sup>-3</sup>. The atmospheric concentrations of Zn ranged between 39 and 930 ng m<sup>-3</sup>. Cu, Pb and Mn also had comparatively high concentrations in the atmosphere, with daily average levels of 98.6±57.8, 53.5±50.8 and 35.3±26.0 ng m<sup>-3</sup>, respectively. The maximum concentration that was recorded for Cu was 295 ng m<sup>-3</sup>, while Pb had a maximum level of 253 ng m<sup>-3</sup>. Sc presented the lowest atmospheric concentrations, reaching an average concentration that was 5817 times lower than that of Al and 5283 times lower than that of Fe. Co presented similarly low concentrations. To globally evaluate the  $PM_{10}$ bounded selected metal concentrations as measured in Bangkok, the statistical descriptions of the 18 selected metals of the present study were compared with a selection of previous studies in similar environments (see Table 1). Despite

# **Table 1** Statistical description of  $PM_{10}$ -bound heavy metals (ng m<sup>-3</sup>) Annual standard limit This study Spain<sup>a</sup> Korea<sup>b</sup> China<sup>c</sup> Brazil<sup>d</sup> Brazil<sup>d</sup> Italy<sup>e</sup> Denmark<sup>f</sup> Sweden<sup>g</sup> Zaragoza R1 R2 R3 Baoshan Putuo Bonsucesso Botafogo BD ID GG DB Odense Tange Stockholm Aver Stdev Aver Stdev Aver Aver Aver Aver Stdev Aver Stdev Aver Stdev Aver Stdev Aver Aver Aver Aver Aver Aver Aver StdevAl 1047 785 2690 3180 N.A. N.A. N.A. 3712 2.315 3115 3.232 N.A.



<sup>a</sup> López et al. (2005)

<sup>b</sup> Lee et al. (2006) (RI Seoul, Incheon, Suwon, R2 Deajon, Jeonju, Kwangju, R3 Deagu, Ulsan, Pusan)

 $\rm^c$  Wang et al. (2013)

 $^d$  Silva et al. (2015)

e Dongarrà et al. (2007) (BD Boccadifalco, ID Indipendenza, GC Giulio Cesare, DB Di Blasi)

f Kemp (2002)

<sup>g</sup> Johansson et al. (2009)

h European Commission Air Quality Standards

<sup>i</sup> WHO air quality guidelines for Europe

<sup>j</sup> National Ambient Air Quality Standards of the US Environmental Protection Agency

<sup>k</sup> National Air Quality Act of the South African Department of Environmental Affairs

Aver Aver Stdev

some discrepancies with the  $PM_{10}$  monitoring periods and frequencies, it appears reasonable to contextualise the selected metal concentrations as measured at PCD air quality observatory sites in Bangkok. As indicated in Table 1, the daily average concentrations of Al, V, Cr, Mn and Fe were comparable with those of Boccadifalco (Dongarrà et al. 2007). Zaragoza (López et al. 2005). Odense (Kemp 2002). Deajon, Jeonju and Kwangju (Lee et al. 2006). and Di Blasi (Dongarrà et al. 2007). respectively. In addition, the daily average concentrations of V, Cr, Mn, Ni and Pb were much lower than the existing ambient air quality guidelines and standard limit values for trace metal species (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) European Commission Air Quality Standards (2012).

#### Pearson correlation analysis

The average values of the selected trace elements analysed followed the order Al>Fe>Zn>Cu>Pb>Mn>Ba>V>Sb> Ni>As>Cr>Cd>Se>Ce>La>Co>Sc. The three maximum concentrations that were obtained from this study (i.e. Al, Fe and Zn) were similar to those of Zaragoza (López et al. 2005). Boccadifalco, Indipendenza, Giulio Cesare and Di Blasi (Dongarrà et al. 2007) but different from those of Baoshan (Wang et al. 2013). Several trace elements that were obtained from this study were primarily associated with the unique geographic location of Bangkok specifically and to the Chao Phraya Delta in general. While Al, Sc, V, Mn, Fe, As and Ba are plausibly from the impact of the closeness of the Asian continent and the crustal elements, Cr, Co, Ni, Cu, Zn and Cd are believed to be from anthropogenic inputs, mainly vehicular exhausts. This data interpretation is based on a detailed investigation of airborne trace metals and their potential major sources at Lhasa, the largest city in the Tibetan Plateau (Cong et al. 2011). Selected elements in the studied area followed a decreasing order of Fe>Zn>Cu>Cd, which was also consistent with a previous study of surface dust samples that were collected from the walls of residential buildings in Phitsanulok, Thailand (Srithawirat and Latif 2015). highlighting the fact that these four elements were predominantly associated with elemental crust.

In general, a high correlation coefficient between Fe and Zn indicates pollution emissions associated with human activities, incineration, imperfect combustion of hydrocarbon fuels or merely from natural sources (Gao et al. 2002). Because the correlation coefficient of these two elements was comparatively low  $(R=0.20)$ , it appears reasonable to consider geographical input as a major source of Fe and Zn (Table 2). This interpretation agrees well with the relatively high positive correlation coefficients of Fe–Al ( $R=0.95$ ), Fe–Sc ( $R=0.95$ ), Fe– Cr ( $R=0.81$ ), Fe–As ( $R=0.91$ ), Fe–Ba ( $R=0.71$ ) and Fe–Mn

 $(R=0.97)$ , indicating the predominance of crustal emissions on these elements over other sources (Table 2). In addition, the weak correlation coefficients of Ni–Pb (R=−0.08), Ni–Cr  $(R=-0.03)$  and Ni–Fe  $(R=-0.23)$  indicate that industrial activities are of minor importance because these metals are chemical markers of industrial emissions (Begum et al. 2004; Song et al. 2006; Yatkin and Bayram 2008a, b).

### Spatial and temporal distribution of selected metals

To evaluate the spatial and temporal distribution of selected metals, the probability distribution function (PDF) was applied to all samples collected from the eight air quality observatory sites from January to June 2008, as previously mentioned in "Description of the air quality observatory sites and  $PM_{10}$  sample collection". The PDF is a function that describes the relative probability of this random variable taking on a provided value. The probability of a random variable falling within a particular region is given by the Gaussian distribution, which can be described as follows:

$$
y = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(\frac{-(x-\mu)^2}{2\sigma^2}\right) \tag{1}
$$

where y,  $\sigma$ ,  $\sigma^2$ ,  $\mu$  and x represent the PDF, standard deviation, variance, average and atmospheric concentration of each selected metal, respectively. As a part of the analysis of random phenomena, skewness was used to measure the asymmetry of the probability distribution of selected metals in  $PM_{10}$ . In the case of unimodal distribution, negative skew suggests that the tail on the left site of the PDF is longer than the right side indicating that the mass of the distribution is concentrated on the right of the figure. If the mean of the selected metal concentrations is greater than the middle, the graph will be negative skew. This can be explained by several reasons such as unusually high level of selected metals from long-range transportation or accidental explosions (i.e. only few samples with unexpectedly high concentrations). On the contrary, positive skew underlines that the tail on the right side is longer than the left side. In other words, the mass of the distribution is concentrated on the left of the figure. This will happen when the mean of the selected metal concentrations is less than its own middle. A temporary low level of selected metals may responsible for this phenomena. If the mean is in the middle, it appears more likely to have a figure of symmetrical Gaussian distribution. This represents a conventional normal distribution without any interruptions from other extreme events (e.g. accidental explosions or long-range transportation).

As clearly illustrated in Fig. 3, some characteristic features can be extracted directly from the original images. First, a sharp symmetrical bell-shaped curve was detected for V and Cr. Because the observed values of the parameter are more





Fig. 2 Statistical descriptions of 18 selected metals collected from eight air quality observatory sites in Bangkok from January to June 2008



Fig. 3 Probability distribution function of 18 selected metals collected from eight air quality observatory sites in Bangkok from January to June 2008

Table 3 COD values between individual pairs of sampling sites computed individually for each element employing the entire data set for monthly concentrations

	Al	Sc	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	C <sub>d</sub>	Sb	Ba	La	Ce <sup>1</sup>	Pb
<b>BHS-KHA</b>	0.16	0.20	0.19	0.34	0.06	0.09	0.64	0.59	0.49	0.08	0.12	0.18	0.28	0.33	0.22	0.29	0.27	0.12
<b>BHS-HHA</b>	0.21	0.27	0.21	0.27	0.14	0.16	0.66	0.46	0.13	0.23	0.14	0.18	0.25	0.16	0.21	0.23	0.23	0.08
<b>BHS-NWS</b>	0.31	0.36	0.30	0.33	0.22	0.26	0.67	0.49	0.33	0.31	0.24	0.22	0.41	0.30	0.28	0.30	0.31	0.15
<b>BHS-SPS</b>	0.15	0.29	0.39	0.40	0.36	0.21	0.54	0.55	0.49	0.45	0.41	0.31	0.52	0.56	0.27	0.11	0.15	0.39
<b>BHS-TPS</b>	0.44	0.49	0.37	0.45	0.38	0.42	0.73	0.54	0.20	0.41	0.31	0.45	0.39	0.34	0.50	0.38	0.38	0.57
<b>BHS-DHA</b>	0.39	0.45	0.21	0.41	0.34	0.41	0.63	0.52	0.37	0.26	0.28	0.44	0.36	0.31	0.60	0.33	0.34	0.25
<b>BHS-CPB</b>	0.27	0.28	0.28	0.25	0.20	0.28	0.51	0.46	0.24	0.26	0.13	0.31	0.48	0.16	0.39	0.28	0.28	0.13
KHA-HHA	0.13	0.18	0.21	0.40	0.11	0.11	0.70	0.61	0.46	0.18	0.16	0.26	0.30	0.34	0.19	0.30	0.28	0.10
<b>KHA-NWS</b>	0.24	0.35	0.35	0.42	0.22	0.23	0.75	0.59	0.32	0.28	0.26	0.29	0.41	0.25	0.29	0.39	0.38	0.15
<b>KHA-SPS</b>	0.17	0.33	0.36	0.48	0.38	0.21	0.76	0.62	0.42	0.45	0.41	0.36	0.53	0.61	0.27	0.26	0.18	0.37
<b>KHA-TPS</b>	0.42	0.50	0.40	0.55	0.38	0.42	0.81	0.67	0.41	0.39	0.35	0.49	0.43	0.33	0.51	0.48	0.47	0.54
<b>KHA-DHA</b>	0.34	0.46	0.25	0.48	0.33	0.39	0.70	0.62	0.32	0.27	0.33	0.49	0.38	0.22	0.58	0.42	0.42	0.24
<b>KHA-CPB</b>	0.22	0.27	0.29	0.37	0.19	0.26	0.74	0.71	0.35	0.23	0.15	0.24	0.42	0.24	0.37	0.32	0.36	0.16
<b>HHA-NWS</b>	0.21	0.29	0.23	0.18	0.19	0.22	0.52	0.20	0.30	0.17	0.21	0.22	0.32	0.27	0.17	0.24	0.25	0.13
<b>HHA-SPS</b>	0.13	0.28	0.29	0.21	0.35	0.16	0.53	0.22	0.46	0.43	0.41	0.38	0.56	0.55	0.29	0.16	0.17	0.37
<b>HHA-TPS</b>	0.41	0.50	0.26	0.39	0.36	0.38	0.48	0.24	0.22	0.27	0.24	0.43	0.29	0.40	0.44	0.37	0.39	0.56
<b>HHA-DHA</b>	0.34	0.45	0.16	0.41	0.31	0.37	0.55	0.47	0.32	0.21	0.27	0.38	0.27	0.31	0.56	0.28	0.31	0.22
<b>HHA-CPB</b>	0.21	0.23	0.26	0.27	0.15	0.24	0.47	0.47	0.22	0.10	0.10	0.30	0.46	0.22	0.31	0.24	0.24	0.12
NWS-SPS	0.24	0.42	0.31	0.24	0.35	0.18	0.61	0.23	0.30	0.45	0.36	0.39	0.56	0.59	0.41	0.27	0.32	0.44
NWS-TPS	0.36	0.45	0.22	0.37	0.29	0.28	0.64	0.25	0.31	0.20	0.22	0.35	0.36	0.46	0.36	0.44	0.45	0.53
<b>NWS-DHA</b>	0.25	0.35	0.21	0.31	0.26	0.21	0.56	0.46	0.16	0.26	0.20	0.31	0.40	0.32	0.47	0.31	0.33	0.22
NWS-CPB	0.13	0.16	0.30	0.28	0.18	0.11	0.53	0.53	0.28	0.11	0.25	0.29	0.55	0.27	0.23	0.16	0.12	0.21
<b>SPS-TPS</b>	0.42	0.59	0.35	0.44	0.44	0.35	0.64	0.28	0.40	0.43	0.44	0.55	0.60	0.59	0.62	0.40	0.42	0.61
<b>SPS-DHA</b>	0.38	0.52	0.24	0.47	0.37	0.34	0.64	0.49	0.31	0.32	0.35	0.49	0.55	0.61	0.69	0.33	0.38	0.47
<b>SPS-CPB</b>	0.24	0.36	0.45	0.32	0.29	0.17	0.44	0.52	0.45	0.42	0.43	0.37	0.63	0.54	0.52	0.22	0.29	0.37
<b>TPS-DHA</b>	0.24	0.33	0.24	0.33	0.19	0.20	0.54	0.47	0.31	0.28	0.19	0.35	0.17	0.27	0.33	0.24	0.25	0.49
<b>TPS-CPB</b>	0.42	0.49	0.27	0.40	0.34	0.31	0.54	0.45	0.21	0.21	0.26	0.48	0.56	0.27	0.24	0.49	0.48	0.60
DHA-CPB	0.32	0.38	0.28	0.34	0.23	0.24	0.42	0.56	0.29	0.19	0.30	0.43	0.51	0.22	0.37	0.39	0.36	0.29

concentrated in the middle than in the tails, it seems rationale to assume a considerably strong homogeneous distribution of V and Cr in  $PM_{10}$ , which were much less affected by the human activities. This result can also be inferred as a consequence of the fairly convincing crustal emissions of these two metals.

Second, Al, Sc, Mn and Fe showed noticeably broad peaks with flat tops of right skewedness distributions, emphasising the higher degree of means than modes. These positive skewedness curves are consistent with the temporal distribution patterns of these four metals, as illustrated in Fig. 2, indicating the common sources of natural emissions, which are mainly associated with the geographic location of Bangkok. Third, Ba, Sb and Se demonstrated sharp positive skewedness curves, indicating that the bulk of metal concentrations were to the left of the mean. The similarities of the asymmetrical distribution curves of Ba, Sb and Se agree well with its own temporal distribution patterns and thus underline the importance of anthropogenic activities on these three metals (see Figs. 2 and 3). It is also important to mention that the concentrations of these three metals are high in January and March. Several reasons are responsible for this trend. Since January and March are generally defined as cold period, a low-level atmospheric temperature inversion can be easily occurred and thus can lead to pollution such as smog and other metals being trapped close to the ground, with possible adverse effects on health. On the contrary, a comparatively high temperature in April is due to thermal expansion and subsequently dilutes the metal concentrations in Summer. Precipitations in May and June are also responsible for the reduction of selected metals during the rainy season. Previous studies also highlight the tyre and brake wear as a major source of Fe, Ba, Cu, Sn and Zn in  $PM_{10}$ , while plastic incineration and brake pad wears of automobiles were suspected as main contributors of Sb (Alves et al. 2015; Furuta et al. 2005). In addition, an unexpectedly high levels

Fig. 4 A dendrogram derived from hierarchical cluster analysis of selected metals and other meteorological parameters



of Ba, Sb and Se can be ascribed as a consequence of traffic congestion in the middle of new year celebration activities in the first week of January.

## Intersite comparison-coefficient of divergence

One of the most difficult tasks in the data evaluation was merely the large number of selected metals coupled with its comparatively high deviations of  $PM_{10}$ -bounded chemical component concentrations. Furthermore, it appears problematic to evaluate the local and regional impacts on emission source strengths of selected metals. To assess the similarities or differences in the temporal distribution patterns of selected metals of the eight air quality observatory sites, the computation of coefficients of divergence  $(COD_{ik})$  is suggested (Limbeck et al. 2009; Wilson et al. 2005). which can be described as follows:

$$
COD_{jk} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( \frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2}
$$
 (2)

where  $x_{ij}$  denotes the atmospheric concentration of the selected metal on sampling event  $i$  at air quality observatory site  $j$ ,  $x_{ik}$  is the atmospheric concentration of this element for the identical event i at air quality observatory site  $k$ , and  $n$  is the number of total sampling events. It is important to mention that both short- and long-term measurements can be applied to the concept of using COD due to its self-normalising process (Wongphatarakul et al. 1998). When the COD value approaches zero, this trend can be interpreted as a strong similarity of emission sources between the two sites. In contrast, a COD value close to one indicates the dissimilarity of the two assessed air quality observatory sites.

As illustrated in Table 3, the majority of selected metals demonstrated comparatively low COD values (<0.30), indicating that the  $PM_{10}$ -bounded Al, Sc, V, Cr, Mn, Fe, Zn, As, Se, La and Ce levels of all eight sites were predominantly affected by comparable sources (e.g. regional crustal emissions or long-range transport) during the monitoring period and only to a minor magnitude by site-specific local emissions, which were expected to be accountable for the discrepancies between the individual air quality observatory sites. Relatively low COD average values  $(n=28)$  were observed for Fe (0.26 $\pm$ 0.10), Mn (0.27 $\pm$ 0.10), As (0.27 $\pm$ 0.10), Zn  $(0.28\pm0.11)$ , V  $(0.28\pm0.07)$  and Al  $(0.28\pm0.10)$ , suggesting that emission sources are either spatially homogeneously dispersed or that there are no crucial specific emission sources and that the  $PM_{10}$ -bounded concentration of these metals might be occupied by regional crustal emissions and/or long-range transport. Because a previous study conducted in Vienna highlighted the re-suspension of road dust, the weathering of facades and construction activities as three main sources of Al, Mn and Sb (Limbeck et al. 2009). it is logical to interpret the comparatively low COD values of these three elements as a consequence of a homogeneous mixture of air mass from road dust re-suspension coupled with construction activities in Bangkok. In addition, the comparatively low COD values that were observed for Ba  $(0.38\pm0.15)$ , Fe  $(0.26\pm0.10)$  and Cu  $(0.33\pm0.10)$  reflect the uniformity of emissions inside the city, such as brake abrasion of motor vehicles, which implies ubiquitous sources for these elements releasing uninterruptedly independent from seasonal or meteorological fluctuations (Lough et al. 2005; Handler et al. 2008).

### Potential source contributions of selected metals

HCA was performed to identify the homogeneous group of individual selected metals in  $PM_{10}$  samples that were collected from eight PCD air quality observatory sites. The results in the dendrogram (Fig. 4) distinguish the 18 individual metals coupled with 11 meteorological parameters into two major clusters. The first major cluster  $(n=26)$  consists of Sc, Rain, Co, La, CO, WS, Cd, Ce, Se,  $SO_2$ , As, Sb, Cr, V, Ni,  $O_3$ , NO<sub>2</sub>, T, Mn, Ba, Pb, RH, Cu, Rad, Zn and WD, as illustrated in Fig. 4. The first cluster shows fairy strong affinities of Co, La, Cd, Ce, Se, As, Sb, Cr, V and Ni with CO,  $SO_2$ ,  $O_3$  and  $NO_2$ , which are mainly produced by traffic emissions, underlining the importance of vehicular exhausts on these ten metals. Because Cu and Zn are highly associated with RH, Rad and WD in the first cluster, it appears reasonable to interpret this fact as a consequence of predominant geographical sources over these two metals. These findings are also consistent with those of the Pearson correlation analysis and PDF patterns as previously mentioned in "Pearson correlation analysis" and "Spatial and temporal distribution of selected metals", respectively. The second sub-cluster contains Al, Fe and P. This result can be ascribed to the overwhelming influence of crustal emissions on these two metals, which agrees well with previous discussions comparing the  $PM_{10}$ -bounded selected metal concentrations in "Comparison of  $PM_{10}$ -bounded selected metal concentrations".

Table 4 displays the principal component patterns for the Varimax-rotated components of the selected metal dataset coupled with meteorological parameters. To enable the further interpretation of potential selected metal sources, a PCA model with five significant PCs, each representing 37.74, 13.51, 11.32, 8.67 and 6.68 % of the variance, thus accounting for 77.92 % of the total variation in the data, was calculated. The first component (PC1) shows the high loading on crustal metals (i.e. Al, Fe and Mn), with no observed significant correlations in any trace gaseous species. Furthermore, the negative correlation of  $SO<sub>2</sub> (-0.51)$  in PC1 indicates that imperfect combustion of fossil fuels (e.g. coal) plays a minor role in this Table 4 Principal component analysis of 18 selected metals with trace gaseous coupled with meteorological parameters



component. It is therefore logical to note that the crustal emissions contribute 34.7 %. The second component (PC2) has higher loadings for V, Co, Cu, Pb, Se and Zn. Previous studies have highlighted the importance of Se and Zn as elemental markers of coal combustion (Almeida et al. 2006; Hien et al. 2001; Lee et al. 2008). It is also important to note that Pb as well as V, Co and Zn are the most commonly used tracer element for identifying vehicular emissions. Despite the introduction of unleaded petrol in Thailand in 1992, lead is still used as an elementary marker because of its comparatively high persistence in road dust particles (Banerjee 2003). Therefore, PC2 can be considered representative of traffic emissions, explaining 13.5 % of the total  $PM_{10}$ .

PC3 indicates considerably strong positive correlations of Ba, CO and  $NO<sub>2</sub>$  coupled with a negative correlation of  $O<sub>3</sub>$ .

Unlike those of trace gaseous CO and  $NO<sub>2</sub>$ , the correlation coefficient of  $O_3$  was negatively correlated with the others, highlighting the mechanism of  $O_3$  formation from  $NO_x$ . Because Ba has been widely employed as an elementary marker for brake and tyre wear emissions (Lough et al. 2005; Gietl et al. 2010). it seems plausible to consider particle emissions from idling in traffic and frequent acceleration and braking as the main contributors of this PC, which is responsible for 11.3 % of the total variance. One of the main concerns when performing any source apportionment study employing multivariate methods is to confirm a high ratio between the number of samples collected and the number of variables being analysed, and if that ratio is extremely low, the data interpretations can be misleading (Pant and Harrison 2012). For instance, in this study, data from 48 samples were analysed for 29 variables. Additionally, the results from the HCA and PCA in many cases did not agree well with each other. For instance, while the HCA results indicated the strong affinity of Co, La, Cd, Ce, Se, As, Sb, Cr, V and Ni with trace gaseous species, reflecting vehicular emission as a major source of these elements, the results from the PCA showed only Ba to have good positive correlations with CO and  $NO<sub>2</sub>$ 

#### Enrichment factors of the selected metals

(Table 4).

The concept of the enrichment factor (EF) has been widely used to evaluate the contribution of vehicular exhaust (Zhang et al. 2015). industrial emissions (Li et al. 2012) and mining coupled with ore processing (Wang et al. 2014a, b) to atmospheric elemental contents. Although there is no specific rule for selecting the reference element, Si, Al and Fe are frequently used for the computations of EF (López et al. 2005). For individual selected metals, Fe was used as a reference assuming minor contributions of the pollutant Fe and the upper continental crustal composition given by Rudnick (2003). The EF of an element  $E$  in a  $PM_{10}$  sample can be described as

$$
EF = \frac{\left(E/R\right)_{Air}}{\left(E/R\right)_{Crust}}\tag{3}
$$

where  $R$  is a reference element. If EF approaches one, the crustal can be considered the predominant emission source. The analytical results are displayed in Fig. 5, and the sequence of EF in Bangkok was Cd>Sb>Ba>Se>La>Ce>Cu>Zn> Pb>As>Ni>V>Cr>Mn>Co>Fe>Sc>Al. Additionally, the results can be categorised as follows (arbitrary scale) (Karageorgis et al. 2009). (i) Ni, V, Cr, Mn, Co, Fe, Sc and Al are not enriched (less than  $Log (EF)=1$ ); (ii) Cu, Zn, Pb and As are slightly enriched (Log (EF) ranges from 1 to 3); (iii) Ba, Se, La and Ce are moderately enriched (Log (EF) ranges from 3 to 4); and (4) Cd and Sb are extremely strongly enriched



Fig. 5 Logarithms of EF of 18 selected metals collected at eight air quality observatory sites in Bangkok from January to June 2008

(Log (EF) is greater than 4). These results indicate that geographical sources, such as crustal emissions, the re-suspension of urban soils/road dusts, and maritime aerosols, are conceivably the prevailing sources for these selected metals. Comparable interpretations were also proposed by Wu et al. (1994). who reported that the majority of the atmospheric Al over Chesapeake Bay was derived from soil. The extremely low Log (EF) value of Al (−0.44) that was obtained in the current study is consistent with that of Wu et al. (1994). In contrast, the extremely high Log (EF) values (>4) that were obtained for Cd and Sb underline the strong influences of anthropogenic emissions on these two elements, plausibly vehicular emissions, which agrees well with previous studies (Lough et al. 2005; Almeida et al. 2006; Crawford et al. 2007; Begum et al. 2011). In addition, the comparatively high Log (EF) values of Ba and Se are consistent with those results of the PCA as previously discussed in "Potential source contributions of selected metals^, suggesting that traffic emissions are the main contributors of these two metals.

## **Conclusions**

Apart from several limitations of the current study, including an inadequate number of samples (i.e.  $n<100$ ), the use of unweighted models such as PCA, difficulties in most cases to distinguish vehicle exhaust from non-exhaust vehicle emissions, a comparatively low number of sampling sites and insufficient use of other organic markers, the Bangkok air quality can be categorised as relatively polluted with  $PM_{10}$ -bounded metals under the current international air quality guidelines. The application of multivariate statistical tools was also useful for characterising the crustal emissions as well as the influence of vehicular exhaust and industrial release. The extremely high Log (EF) values of Cd and Sb coupled with the moderately high Log (EF) values of Ba, Se, La and Ce indicate that these metals are not crustal derived and thus encourage policymakers to consider the full range of regulations including trace elements.

Acknowledgments This work was performed with the approval of the National Institute of Development Administration (NIDA), Thailand, and financial support from the Department of Regional Activation, Faculty of Regional Policy, Takasaki City University of Economics, Japan. The author acknowledges the research staff from the Pollution Control Department (PCD), Ministry of Natural Resources and Environment (MNRE), Thailand, for their contribution in the sampling and some laboratory work. The authors also acknowledge Ms. Mattanawadee Hattayanone and Ms. Thanpahtt Chaichombhoo for their contribution on graphic designs.

## References

- Almeida SM, Pio CA, Freitas MC, Reis MA, Trancoso MA (2006) Source apportionment of atmospheric urban aerosol based on weekdays/weekend variability: evaluation of road re-suspended dust contribution. Atmos Environ 40:2058–2067
- Alves CA, Gomes J, Nunes T, Duarte M, Calvo A, Custódio D, Pio C, Karanasiou A, Querol X (2015) Size-segregated particulate matter and gaseous emissions from motor vehicles in a road tunnel. Atmos Res 153:134–144
- Banerjee ADK (2003) Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environ Pollut 123:95–105
- Begum BA, Kim E, Biswas SK, Hopke PK (2004) Investigation of sources of atmospheric aerosol at urban and semi-urban areas in Bangladesh. Atmos Environ 38:3025–3038
- Begum BA, Biswas SK, Hopke PK (2011) Key issues in controlling air pollutants in Dhaka, Bangladesh. Atmos Environ 45(40):7705– 7713
- Berardi R, Pellei C, Valeri G, Pistelli M, Onofri A, Morgese F, Caramanti M, Mirza RM, Santoni M, De Lisa M, Savini A, Ballatore Z, Giuseppetti GM, Cascinu S (2015) Chromium exposure and germinal embryonal carcinoma: first two cases and review of the literature. J Toxicol Environ Health A 78(1):1–6
- Charlesworth S, Everett M, McCarthy R, Ordóñez A, de Miguel E (2003) A comparative study of heavy metal concentration and distribution in deposited street dusts in a large and a small urban area: Birmingham and Coventry, West Midlands, UK. Environ Int 29: 563–573
- Cong Z, Kang S, Luo C, Li Q, Huang J, Gao S, Li X (2011) Trace elements and lead isotopic composition of  $PM_{10}$  in Lhasa, Tibet. Atmos Environ 45(34):6210–6215
- Crawford J, Chambers S, Cohen DD, Dyer L, Wang T, Zahorowski R (2007) Receptor modelling using positive matrix factorization, back trajectories and Radon-222. Atmos Environ 41:6823–6837
- Dongarrà G, Mannoa E, Varricaa D, Vultaggiob M (2007) Mass levels, crustal component and trace elements in  $PM_{10}$  in Palermo, Italy. Atmos Environ 41:7977–7986
- European Commission. Air quality standards [homepage on the Internet]. No date [updated 2012 Nov 30; cited 2013 Jan 24]. Available from: http://ec.europa.eu/environment/air/quality/standards.htm
- Furuta N, Iijima A, Kambe A, Sakai K, Sato K (2005) Concentrations, enrichment and predominant sources of Sb and other trace elements in size classified airborne particulate matter collected in Tokyo from 1995 to 2004. J Environ Monit 7(12):1155–1561
- Gao Y, Nelson ED, Field MP, Ding Q, Li H, Sherrell RM, Gigliotti CL, Van Ry DA, Glenn TR, Eisenreich SJ (2002) Characterization of atmospheric trace elements on  $PM_{2.5}$  particulate matter over the

New York–New Jersey harbour estuary. Atmos Environ 36:1077– 1086

- Gietl JK, Lawrence R, Thorpe AJ, Harrison RM (2010) Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. Atmos Environ 44:141–146
- Handler M, Puls C, Zbiral J, Marr I, Puxbaum H, Limbeck A (2008) Size and composition of particulate emissions from motor vehicles in the Kaisermühlen-Tunnel, Vienna. Atmos Environ 42:2173–2186
- Hien PD, Binh NT, Truong Y, Ngo NT, Sieu LN (2001) Comparative receptor modelling study of TSP,  $PM_2$  and  $PM_{2-10}$  in Ho Chi Minh city. Atmos Environ 35:2669–2678
- Iijima A, Sato K, Fujitani Y, Fujimori E, Saitoh Y, Tanabe K, Ohara T, Kozawa K, Furuta N (2009) Clarification of the predominant emission sources of antimony in airborne particulate matter and estimation of their effects on the atmosphere in Japan. Environ Chem 6: 122–135
- Iijima A, Sato K, Ikeda T, Sato H, Kozawa K, Furuta N (2010) Concentration distributions of dissolved Sb(III) and Sb(V) species in size-classified inhalable airborne particulate matter. J Anal At Spectrom 25:356–363
- Johansson C, Norman M, Burman L (2009) Road traffic emission factors for heavy metals. Atmos Environ 43:4681–4688
- Karageorgis AP, Katsanevakis S, Kaberi H (2009) Use of enrichment factors for the assessment of heavy metal contamination in the sediments of Koumoundourou Lake, Greece. Water Air Soil Pollut 204: 243–258
- Kemp K (2002) Trends and sources for heavy metals in urban atmosphere. Nucl Inst Methods Phys Res B 189:227–232
- Lee BK, Lee HK, Jun NY (2006) Analysis of regional and temporal characteristics of  $PM_{10}$  during an Asian dust episode in Korea. Chemosphere 63:1106–1115
- Lee S, Liu W, Wang Y, Russell AG, Edgerton ES (2008) Source apportionment of  $PM<sub>2.5</sub>$ : comparing PMF and CMB results for four ambient monitoring sites in the southeastern United States. Atmos Environ 42:4126–4137
- Li YM, Pan YP, Wang YS, Wang YF, Li XR (2012) Chemical characteristics and sources of trace metals in precipitation collected from a typical industrial city in Northern China. Huan Jing Ke Xue 33(11): 3712–3717
- Limbeck A, Handler M, Puls C, Zbiral J, Bauer H, Puxbaum H (2009) Impact of mineral components and selected trace metals on ambient PM<sub>10</sub> concentrations. Atmos Environ 43:530–538
- López JM, Callén MS, Murillo R, García T, Navarro MV, de la Cruz MT, Mastral AM (2005) Levels of selected metals in ambient air  $PM_{10}$  in an urban site of Zaragoza (Spain). Environ Res 99:58–67
- Lough GC, Schauer JJ, Park JS, Shafer MM, Deminter JT, Weinstein JP (2005) Emissions of metals associated with motor vehicle roadways. Environ Sci Technol 39:826–836
- Madrid F, Barrientos ED, Madrid L (2008) Availability and bioaccessibility of metals in the clay fraction of urban soils of Sevilla. Environ Pollut 605–610
- Milligan GW, Cooper MC (1987) A study of variable standardization. College of Administrative Science Working paper series, 87–63. The Ohio State University, Columbus, OH
- Pant P, Harrison R (2012) Critical review of receptor modelling for particulate matter: a case study of India. Atmos Environ 49:1–12
- Pongpiachan S (2013a) Diurnal variation, vertical distribution and source apportionment of carcinogenic polycyclic aromatic hydrocarbons (PAHs) in Chiang-Mai, Thailand. Asian Pac J Cancer Prev 14(3): 1851–1863
- Pongpiachan S (2013b) Vertical distribution and potential risk of particulate polycyclic aromatic hydrocarbons in high buildings of Bangkok, Thailand. Asian Pac J Cancer Prev 14(3):1865–77
- Pongpiachan S, Choochuay C, Hattayanone M, Kositanont C (2013) Temporal and spatial distribution of particulate carcinogens and

mutagens in Bangkok, Thailand. Asian Pac J Cancer Prev 14(3): 1879–1887

- Pongpiachan S, Tipmanee D, Khumsup C, Kittikoon I, Hirunyatrakul P (2015a) Assessing risks to adults and preschool children posed by PM2.5-bound polycyclic aromatic hydrocarbons (PAHs) during a biomass burning episode in Northern Thailand. Sci Total Environ 508:435–444
- Pongpiachan S, Hattayanone M, Choochuay C, Mekmok R, Wuttijak N, Ketratanakul A (2015b) Enhanced  $PM_{10}$  bounded PAHs from shipping emissions. Atmos Environ 108:13–19
- Ratcliffe HE, Swanson GM, Fischer LJ (1996) Human exposure to mercury: a critical assessment of the evidence of adverse health effects. J Toxicol Environ Health 49(3):221–270
- Rosen JF (1995) Adverse health effects of lead at low exposure levels: trends in the management of childhood lead poisoning. Toxicology 97(1-3):11–17
- Rudnick RL (2003) "The Crust", Volume 3 of the Treatise on Geochemistry, Elsevier
- Silva LID, Yokoyama L, Maia LB, Monteiro MIC, Pontes FVM, Carneiro MC, Neto AA (2015) Evaluation of bioaccessible heavy metal fractions in  $PM_{10}$  from the metropolitan region of Rio de Janeiro city, Brazil, using a simulated lung fluid. Microchem J 118:266–271
- Song Y, Zhang Y, Xie S, Zeng L, Zheng M, Salmon LG, Shao M, Slanina S (2006) Source apportionment of  $PM_{2.5}$  in Beijing by positive matrix factorization. Atmos Environ 40:1526–1537
- Srithawirat T, Latif MT (2015) Concentration of selected heavy metals in the surface dust of residential buildings in Phitsanulok. Thailand Environ Earth Sci. doi:10.1007/s12665-015-4291-0
- Wang J, Hu Z, Chen Y, Chen Z, Xu S (2013) Contamination characteristics and possible sources of  $PM_{10}$  and  $PM_{2.5}$  in different functional areas of Shanghai, China. Atmos Environ 68:221–229
- Wang W, Cheng S, Zhang D (2014a) Association of inorganic arsenic exposure with liver cancer mortality: a meta-analysis. Environ Res 135:120–125
- Wang L, Liang T, Zhang Q, Li K (2014b) Rare earth element components in atmospheric particulates in the Bayan Obo mine region. Environ Res 131:64–70
- Wilson JG, Kingham S, Pearce J, Sturman AP (2005) A review of intraurban variations in particulate air pollution: implications for epidemiological research. Atmos Environ 39:6444–6462
- Wongphatarakul V, Friedlander SK, Pinto JP (1998) A comparative study of PM2.5 ambient aerosol chemical databases. Environ Sci Technol 32:3926–3934
- Wu ZY, Han M, Lin ZC, Ondov JM (1994) Chesapeake Bay atmospheric deposition study, year 1: sources and dry deposition of selected elements in aerosol particles. Atmos Environ 28(8):1471–1486
- Yang J, Kim EC, Shin DC, Jo SJ, Lim YW (2014) Human exposure and risk assessment of cadmium for residents of abandoned metal mine areas in Korea. Environ Geochem Health. doi:10.1007/s10653-014- 9650-3
- Yatkin S, Bayram A (2008a) Determination of major natural and anthropogenic source profiles for particulate matter and trace elements in Izmir, Turkey. Chemosphere 71:685–696
- Yatkin S, Bayram A (2008b) Source apportionment of  $PM_{10}$  and  $PM_{2.5}$ using positive matrix factorization and chemical mass balance in Izmir, Turkey. Sci Total Environ 390:109–123
- Zhang H, Wang Z, Zhang Y, Ding M, Li L (2015) Identification of trafficrelated metals and the effects of different environments on their enrichment in roadside soils along the Qinghai-Tibet highway. Sci Total Environ 521-522C:160–172
- Zwolak I (2014) Vanadium carcinogenic, immunotoxic and neurotoxic effects: a review of in vitro studies. Toxicol Mech Methods 24(1):1– 12