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## Geochemical and statistical analysis of trace metals in atmospheric particulates in Wuhan, central China

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**Abstract** The geochemical characteristics of trace metals (As, Cr, Co, Cd, Cu, Mn, Ni, Pb, V and Zn) in PM<sub>10</sub> in Wuhan, the biggest metropolitan in central China, as well as their sources and contributions were analyzed. As PM<sub>10</sub> has been the principal contaminant of air in Wuhan for years, concentrations of trace metals were measured in PM<sub>10</sub> using high-volume samplers at one urban (Hankou) and one industrial (Changqian) site in Wuhan between September 2003 and September 2004. Based on the results, PM<sub>10</sub> in Wuhan is characterized by relatively high levels of As, Cd, Mn, Pb and Zn compared

with other Asian cities. The time-series of these elements indicated that As, Cu and Zn at both sites have similar trends, whereas Pb levels showed different patterns due to different emission sources. Factor analysis was applied to the datasets focusing on the apportionment of the mass of selected trace metals. Results indicate that Pb, Cd and As have a common source (smelting) at both sites, whereas the sources of Ni vary from coal combustion and steel in Changqian to mineral and traffic in Hankou.

**Keywords** PM<sub>10</sub> · Geochemistry · Statistic analysis · Time series

### Introduction

Epidemiological studies in recent years have been concerned with sources and behaviors of atmospheric aerosols due to associations with health hazards such as respiratory and cardiovascular diseases leading to higher mortality and morbidity (Schwartz 1993; Lee et al. 2000; Hoek et al. 2002).

In epidemiological and controlled exposure studies, one of the most important characteristics found to be contributing to toxicity of aerosol is metal content (WHO 2003). High atmospheric levels of heavy metal-bearing particulate matter could have a considerable impact on the environment and human health (Schwartz 1994; Berico et al. 1997); especially if these are in the grain size range of thoracic and alveolar particles (PM<sub>10</sub> and PM<sub>2.5</sub>). Studies from Canada suggested that iron,

zinc and nickel may be especially important (Burnett et al. 2000). Studies from Utah Valley have suggested that close to steel mills, transition metals could be important (Soukup et al. 2000; Beckett 2001; Dye et al. 2001; Ghio and Devlin 2001).

Specific trace metals are of major concern for their potential carcinogenic effect, and also play an important role in our understanding of the chemical reactions in the atmosphere. For instance, sources of SO<sub>2</sub> found in clouds can be distinguished using Se, As and Sb as tracers, so as to study the chemical transformation of SO<sub>2</sub> in the atmosphere (Husain 1989).

Trace metals are released into the atmosphere by means of the combustion of fossil fuels and wood, high-temperature industrial activities and waste incinerations. Natural emissions are mainly from volcanism, wind erosion, as well as from forests fires and the

oceans (Allen et al. 2001). Specifically, the combustion of fossil fuels constitutes the principal anthropogenic source for Be, Co, Hg, Mo, Sb, Se and Sn from coal and Ni and V from heavy oils. Fossil fuel combustion also contributes to anthropogenic release of As, Cr, Cu, Mn and Zn. The larger percentage of As, Cd, Cu, Ni and Zn is emitted from industrial metallurgical processes. Exhaust emissions from gasoline may contain variable quantities of Pb, Cu, Zn, Ni and Cd. Zn emission is also associated with tyre rubber abrasion (Pacyna 1998).

Some countries have already paid attention to these toxic elements in airborne particulates and taken measures to deal with them. For example, lead has been extensively studied as a result of its high toxicity (Harrison 1986; Pacyna et al. 1991) with emissions from vehicles dominating atmospheric inputs. As part of strategies to reduce emissions from road traffic and improve air quality, leaded fuel was banned from domestic sale in America in the mid 1970s. Its use in Europe has also decreased substantially from 1978 and it was banned from domestic sale on 1 January 2000. The European Union has set air quality limits for Pb in PM10 particles and has encouraged the member states to provide data concerning PM2.5 (EU Directive 1999/30/EC 1999), and it has also implemented a directive dealing with air quality standards concerning trace metals (Cd, Ni, As, Hg) in PM10 particles.

Wuhan is the biggest metropolitan city in central China, with a total population of more than 8 million, where PM10 has long been recognized as the principal atmospheric pollutant. However, no systematic work has been done on trace elements in PM10 (particulate matter with aerodynamic mean diameter smaller than 10  $\mu\text{m}$ ) at Wuhan up till now. Waldman et al. (1991) reported the levels of PM10, PM2.5 and major and trace components for a period of 2 weeks in winter 1988. The unique geographic location of Wuhan, connecting eastern and western China, makes it an ideal study area for source identification of toxic elements with an environmental significance like As, Cd and Pb.

In this paper, concentrations of a number of trace metals, including As, Cr, Co, Cd, Cu, Mn, Ni, Pb, V and Zn in PM10 were measured at two sites in the Wuhan (one urban background site and the other industrial site) during the period from September 2003 to September 2004. Temporal and spatial variations and meteorological factors affecting the accumulation of potentially toxic elements in PM10 were discussed. Principal component analysis was used to identify the main particulate matter (abbreviated as PM) sources with influence on the levels of these elements in the study areas, and multilinear regression was used to apportion the mass emitted by the different sources.

## Materials and methods

### Sampling

PM10 sampling was performed simultaneously at two air quality monitoring stations (Fig. 1) belonging to the Environment Protection Bureau of Wuhan, one urban site (Hankou) and the other industrial site (Changqian). The Hankou station is located in downtown Wuhan, and the Changqian station in a heavy industry region in the eastern side of the city.

The Hankou station (114°17'1"E, 30°37'11"N, 23 m asl) is located in a residential area in the northern area of Wuhan city, on the roof of a five-floor building of a school. There are no industrial pollution sources, but domestic sources such as house heating and cooking are intensive. In a distance of about 1,500 m, there are 24 small boilers and 280 ton boilers for heating and cooking. The distance of the site to the major busy roads is about 100 m. Consequently, major urban emissions close to the sampling site are road traffic, heating and cooking emissions and PM10 is the long-term principal contaminant.

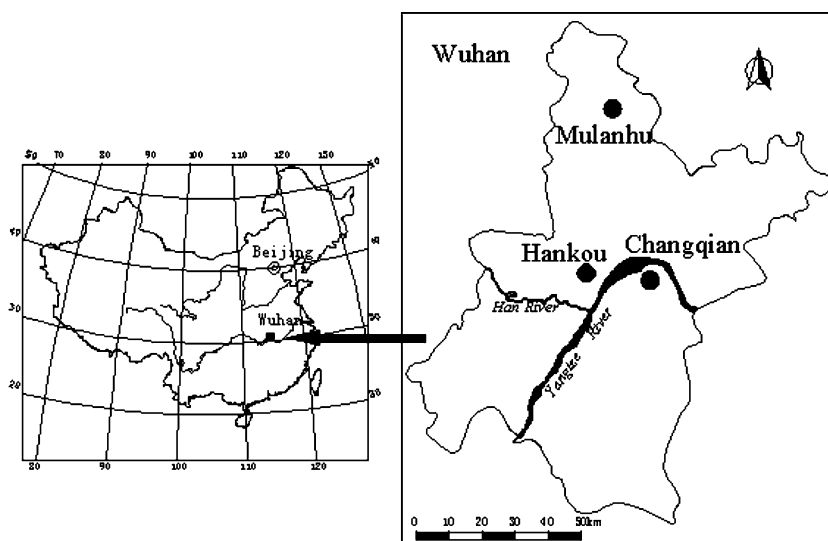
The Changqian station (114°25'38"E, 30°36'37"N, 38.5 m asl) is located in north-eastern Wuhan, on the roof of a three-floor building of a factory-affiliated hospital. Industrial activities are intensive in the vicinity of this station, including steel production (Wuhan Steel Company, one of the largest steel companies in China), coke and iron alloy manufacturing, coal power generation, petroleum chemical engineering and smelting. It has been estimated by the Environment Protection Bureau of Wuhan that the emissions from these industrial activities account for 34% of secondary particulate matter, 57% of primary dust and 45% of the SO<sub>2</sub> emissions in Wuhan city. Coal combustion in Changqian accounts for up to 54% of total coal combustion emissions in Wuhan. The monitored values of PM10 and SO<sub>2</sub> in Changqian are well above those in other monitoring stations administered by the Bureau.

The 24-h PM10 sampling was performed twice every other week by means of Wuhan Tianhong high-volume samplers (Th-1000CII, 63 m<sup>3</sup>/h) equipped with a PM10 impactor inlet and particles collected on 20.3 × 25.4 cm quartz microfiber filters (QF20 Schleicher and Schuell). The sampling was performed from September 2003 to September 2004 at the two sites simultaneously, with a total of 119 PM10 samples collected at the two stations.

PM10, SO<sub>2</sub>, NO<sub>2</sub> and ozone concentrations were continuously monitored automatically on site by DA-SIBY instruments, provided by the Environment Protection Bureau of Wuhan.

In addition to the samples from the two sites, six samples of PM10 were obtained at the Mulanhu site in northern Wuhan city, which is located in the Mulanhu

**Fig. 1** Location of the sampling sites (Changqian and Hankou) in Wuhan city



Lake area, 40 km away from downtown Wuhan. This site has been used by the Wuhan Environmental Protection Bureau as a regional background site in the same air quality monitoring network as the Hankou and Changqian sites.

#### Sample analysis

Collected samples (filters) were conditioned after sampling in a dissector at 20–25°C during 48 h prior to gravimetric determination of the PM<sub>10</sub> mass. Subsequently, 25% of each filter together with a blank filter was acid digested (2.5 ml HNO<sub>3</sub>; 5 ml HF; 2.5 ml HClO<sub>4</sub>) following the methodology devised by Querol et al. (1998). The solutions obtained were used for the determination of concentrations of major and trace elements in PM<sub>10</sub> by means of ICP-AES and ICP-MS. A quarter of each filter and blank filter was also extracted with distilled water at 60°C in order to obtain the water-soluble fraction. The solutions obtained by filtering were used for determination of the concentrations of water-soluble anions (sulphate, nitrate and chloride) by capillary electrophoresis and the levels of NH<sub>4</sub><sup>+</sup> by means of Colorimetry FIA. Contents of major soluble cations (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>) were determined in the water leachates by ICP-AES. A fraction of each filter was used to determine directly the total C content by using an elemental C analyzer.

The digestions of blank filters loaded with 4–6 mg of NBS1633b reference material were used to ensure analysis quality for the same levels of the sample digestion concentrations. Relative analytical errors ranged between 3 and 10% for the different elements were studied.

#### Data processing

Factor analysis (FA), according to the methodology described by Thurston and Spengler (1985), was applied to the Hankou and Changqian datasets. This analysis was performed based on a varimax rotated FA with the aim to identify the main sources affecting the aerosol composition, followed by a multilinear regression analysis (MLRA) to quantitatively estimate the daily source contributions. According to these authors, at least 50 samples are necessary for this analysis, a condition which was fulfilled by both datasets. The analytical results were processed using STATISTICA 4.2 (StatSoft Inc. 1999).

In this statistical method, a set of multiple intercorrelated variables (i.e., the chemical elements analyzed) is replaced by a smaller number of independent variables (factors) by orthogonal transformations/rotations (Salvador et al. 2003). This is achieved by diagonalizing the correlation matrix of the variables, i.e. by computing their eigenvalues and eigenvectors (Henry and Hidy 1979). Each factor is a linear combination of the original variables that explain a maximum of the total variability of the dataset, and is uncorrelated with the rest. The coefficients of the linear combinations (loadings) represent the degree of correlation between the variables and the factor. Thus, the chemical elements with higher loadings in each factor are interpreted as principal components or fingerprints of the emission source that it represents. The analysis is considered only valid if the sum of the variability of the dataset explained by the different factors is > 75%.

After running the FA, a number of factors corresponding to the number of sources are obtained. The variables with higher loadings for each factor constitute

tracers for each source, allowing for the identification of the emission sources. However, several runs are usually performed on the FA before the final result is obtained. In these previous runs different combinations of variables are introduced in the analysis to test the robustness of the result. Variables such as PM10 and gaseous species ( $\text{NO}_2$ ,  $\text{SO}_2$ ) are then included in the analysis, as they frequently serve as source tracers and thus help to identify the chemical profile of some of the sources. Once the final number of factors (sources) is established, the FA is repeated including only independent variables of PM10 composition.

After the main PM10 sources are identified, the respective quantitative contributions are derived by means of MLRA. In this analysis, PM10 (or the levels of a given PM10 component) is considered the dependent variable and the absolute factor scores obtained in the FA are the independent variables. As a result of this process, an interception constant is obtained. If this constant is  $>0$ , it represents the PM10 mass not explained by the sources identified (i.e., unaccounted mass by the model). However, if this constant is  $<0$ , then the result has no physical meaning and the interception constant must be set to zero. Finally, estimations of the daily source contributions of the different sources to the daily PM levels are obtained as the product of the daily absolute factor scores and the multilinear regression coefficients.

## Results and discussion

### Trace elements concentration levels

The concentrations of the measured elements in PM10 at both sites during the sampling period are shown in Table 1. Annual averages for Changqian and Hankou monitoring stations and comparisons between the concentrations at the two sites are given in terms of minimum, maximum and median of the values.

In Table 2, concentrations of these trace elements obtained at the urban (Hankou) station and the industrial (Changqian) station for the study period are compared with data reported for other sites in Asian cities (Zheng et al. 2004; Sun et al. 2004; Ho et al. 2003).

The levels of As registered at Wuhan (66 and 70  $\text{ng}/\text{m}^3$  at the urban and industrial stations, respectively) are similar to those described for the Beijing industrial site (65  $\text{ng}/\text{m}^3$ ), slightly higher when compared with the Beijing urban site, Shanghai and Taiwan (40, 42 and 50  $\text{ng}/\text{m}^3$ , respectively), and clearly higher than those recorded at Hong Kong and Tokyo (6 and 2  $\text{ng}/\text{m}^3$ ). These differences could be related to the intensive coal combustion or industrial activities, such as steel manufacture, around Wuhan. The European target value for the annual As concentration is 6  $\text{ng}/\text{m}^3$  according to

2004/107/CE. The levels of As measured for most EU cities fall in the range 0.2–2.0  $\text{ng}/\text{m}^3$ , with only some Cu smelting, Zn production or ceramic hot spots reaching the levels of 5–15  $\text{ng}/\text{m}^3$ .

The levels of Cd are very similar at all the sites (9 to 12  $\text{ng}/\text{m}^3$ ) with the exception of Tokyo (2  $\text{ng}/\text{m}^3$ ). The higher Chinese values may be due to coal combustion or smelting emissions. The European target value for the annual Cd concentration is 5  $\text{ng}/\text{m}^3$  according to 2004/107/CE. The levels of Cd measured for most EU cities fall in the range 0.2–1.0  $\text{ng}/\text{m}^3$ , and only some steel production hot spots reach the levels of 2–3  $\text{ng}/\text{m}^3$ .

The levels of Ni (4 and 12  $\text{ng}/\text{m}^3$  at the urban and industrial stations, respectively) are relatively low at Wuhan when compared with Beijing (70–75  $\text{ng}/\text{m}^3$ ) and Taiwan (50  $\text{ng}/\text{m}^3$ ), but similar to the other Asian cities considered (5–14  $\text{ng}/\text{m}^3$ ). The slightly higher levels measured at Changqian with respect to Hankou point towards a major industrial origin for Ni at Wuhan. The European target value for the annual Ni concentration is 20  $\text{ng}/\text{m}^3$  according to 2004/107/CE. The levels of Ni measured for most EU cities fall in the range 2–10  $\text{ng}/\text{m}^3$ , with only some steel production hot spots reaching the levels of around 30  $\text{ng}/\text{m}^3$ .

The levels of Pb measured at Wuhan (409 and 615  $\text{ng}/\text{m}^3$  for the urban and industrial sites) were similar to those reported for Shanghai (515  $\text{ng}/\text{m}^3$ ), but markedly higher than those reported for the other cities (64, 82, 90 and 240–340  $\text{ng}/\text{m}^3$  for Tokyo, Hong Kong, Taiwan and Beijing). The European limit value for Pb is 500  $\text{ng}/\text{m}^3$ , although at most of urban monitoring sites levels  $<30$ –50  $\text{ng}/\text{m}^3$  are reported in EU. The relatively higher levels of Wuhan could be related to the high contribution of the smelting industry, but also from coal combustion and leaded gasoline. Since the levels of Pb in Beijing are lower by 1/2 than those measured at Wuhan, and the traffic input in Beijing is much higher than in Wuhan, the Pb traffic contribution is estimated to be low at Wuhan. During the past few years due to the limitation of leaded additives in gasoline and application of unleaded gasoline at Wuhan, a decrease of Pb levels has been observed so that the ratio of traffic Pb to total Pb decreased. Consequently, the high levels of Pb registered in Wuhan may be related to industrial emissions from the steel manufacture or other metallic based industry or from coal combustion.

The levels of Mn (116 and 227  $\text{ng}/\text{m}^3$  at the urban and industrial stations, respectively) are similar to those reported for Beijing and Shanghai (110–195  $\text{ng}/\text{m}^3$ ), but higher than those reported for Hong Kong, Tokyo and Taiwan (23–70  $\text{ng}/\text{m}^3$ ). The slightly higher levels measured at Changqian with respect to Hankou point toward a major industrial origin for Mn at Wuhan. The WHO guidelines for Mn recommend not exceeding an annual mean of 150  $\text{ng}/\text{m}^3$ . The levels of Mn for most EU cities are in the range of 10–30  $\text{ng}/\text{m}^3$ , although

**Table 1** Minimum, maximum and medium of the toxic elements in PM10 at all sites (in ng/m<sup>3</sup>)

	As	Cd	Pb	Cr	Zn	Ni	Co	Mn	V	Cu
Hankou (urban site) ( <i>n</i> = 60)										
Minimum	4	1	66	2	122	1	0.2	18	0.4	6
Maximum	341	40	1,288	35	2,029	15	3	287	23	173
Median	38	8	307	9	534	3	1	106	6	27
Changqian (industrial site) ( <i>n</i> = 59)										
Minimum	7	2	182	4	113	3	1	29	3	10
Maximum	298	46	2,107	64	4,390	30	6	680	35	171
Median	56	10	526	19	676	10	2	206	17	47
Mulanhu (background site) ( <i>n</i> = 6)										
Minimum	4	1	94	3	157	1	0.4	34	3	7
Maximum	45	6	205	8	285	8	2	100	11	16
Median	14	3	166	7	251	3	1	51	4	12

higher levels (80–150 ng/m<sup>3</sup>) are measured around steel production areas.

The levels of Cu (40 and 54 ng/m<sup>3</sup> at the urban and industrial stations, respectively) are similar to those reported for Tokyo and Hong Kong (27–40 ng/m<sup>3</sup>), but lower than those reported for Beijing, Shanghai and Taiwan (70–250 ng/m<sup>3</sup>). The levels of Cu measured at Wuhan fall into the usual concentration range found for most EU cities (20–50 ng/m<sup>3</sup>).

The levels of Co (1 and 2 ng/m<sup>3</sup> at the urban and industrial stations, respectively) are similar to those reported for Tokyo (1 ng/m<sup>3</sup>), but lower than those reported for Beijing and Shanghai (3–5 ng/m<sup>3</sup>). The levels of Co for most EU cities are fall in the range 0.2–1.0 ng/m<sup>3</sup>.

The levels of Zn (676 and 863 ng/m<sup>3</sup> at the urban and industrial stations, respectively) are similar to those reported for Beijing (505–780 ng/m<sup>3</sup>), but higher than those reported for Tokyo, Hong Kong and Taiwan (233–380 ng/m<sup>3</sup>), and lower than those reported for Shanghai (1,409 ng/m<sup>3</sup>). The levels of Zn measured for most EU cities fall in the range 20–100 ng/m<sup>3</sup>, and only some steel or ceramic hot spots reach the levels of 200–500 ng/m<sup>3</sup>.

The levels of Cr (11 and 23 ng/m<sup>3</sup> at the urban and industrial stations, respectively) are similar to those reported for Beijing, Shanghai and Taiwan (20–40 ng/m<sup>3</sup>),

but higher than those reported for Tokyo and Hong Kong (6 ng/m<sup>3</sup>). The slightly higher levels measured at Changqian with respect to Hankou point toward a major industrial origin for Cr at Wuhan. The levels of Cr measured for most EU cities fall in the range 1–10 ng/m<sup>3</sup>, and only some steel hot spots reach the levels of 20–30 ng/m<sup>3</sup>, similar to the levels measured at Changqian.

The levels of V (7 and 17 ng/m<sup>3</sup> at the urban and industrial stations, respectively) are similar to those reported for the Beijing urban site, Shanghai and Taiwan (10–18 ng/m<sup>3</sup>), but higher than those reported for Tokyo and Hong Kong (5–6 ng/m<sup>3</sup>), and lower than those reported for Beijing industrial (64 ng/m<sup>3</sup>). The slightly higher levels measured at Changqian with respect to Hankou point toward a major industrial origin for V at Wuhan. The levels of V measured for most EU cities fall in the range 5–15 ng/m<sup>3</sup>, a concentration range very close to the Wuhan value. The WHO guidelines for V recommend not exceeding a daily value of 1,000 ng/m<sup>3</sup>.

Based on the above considerations, Wuhan is characterized by relatively high levels of As, Cd, Mn, Pb and Zn compared with other Asian cities, and by high As, Cd, Mn, Ni, Pb, Zn and Cr levels compared with EU cities. The levels of Cu, Co and V are similar to those reported for most EU cities.

**Table 2** Comparison of mean concentrations of As, Pb and Cd (ng/m<sup>3</sup>) in PM10 at Changqian and Hankou for the study period with data reported for selected Asian cities

	Limit value	Beijing <sup>a</sup>		Wuhan		Shanghai <sup>b</sup>	Hong Kong <sup>c</sup>	Taiwan <sup>b</sup>	Tokyo <sup>b</sup>
		Industrial Annual	Urban Annual	Industrial Annual	Urban Annual	13 months	3 months	6 years	5 years
As	6	65	40	70	66	42	6	50	2
Cd	5	9	9	12	10	11	ND	10	2
Pb	500	340	240	615	409	515	82	90	64
Cr	ND	24	40	23	11	32	6	20	6
Zn	ND	780	505	863	676	1,409	295	380	233
Ni	20	70	75	12	4	14	9	50	5
Co	ND	4	5	2	1	3	ND	ND	1
Mn	150	195	110	227	116	186	23	70	30
V	1,000	64	13	17	7	18	5	10	6
Cu	ND	70	80	54	40	170	40	250	27

ND no data

<sup>a</sup>Sun et al. (2004)

<sup>b</sup>Zheng et al. (2004)

<sup>c</sup>Ho et al. (2003)



## Time-series of trace metals levels

Figure 2 shows the comparison between Changqian (industrial hot spot) and Hankou (urban site) of mean monthly concentrations of the trace metals studied in PM10 from September 2003 to September 2004. Monthly levels of Co, Cr, Mn, Ni and V are markedly higher at the industrial site throughout the year, showing also a similar seasonal trend and thus indicating a possible common industrial source. The levels of Cu and Pb are only slightly higher at this site, whereas those of As, Cd and Zn are similar at both sites. The monthly variation of the levels of Cu, As and Zn is simultaneous, pointing also to a possible common origin. The levels of As, Cd, Cu and Pb are some months higher at the urban than that of at the industrial site.

The levels of PM10 and trace metals are lower (by 30%) during the weekends (especially on Sunday) at the industrial site (Fig. 3). This is also the case for the urban site except for As and Cd, with relatively high levels even on Sundays (Fig. 4).

## Factor analysis

Factor analysis was applied to the Hankou and Changqian datasets and as a result a number of factors equal to the number of sources were obtained. The chemical elements with higher loadings in each factor are interpreted as fingerprints of the emission source, allowing for the identification of specific emission sources.

Before the final result is obtained, different combinations of variables are introduced in the analysis to test the robustness of the result. As specific sources emit some certain pollutants, which can be used as tracers of sources to determine sources, for instance, variables such as PM10 and gaseous species ( $\text{NO}_2$ ,  $\text{SO}_2$ ) are included in the analysis as they frequently serve as source tracers and thus help to identify the chemical profile of some of the sources.  $\text{NO}_2$  can be an indicator of traffic emissions, and  $\text{SO}_2$  of industrial emissions. In addition,  $\text{NO}_2$  also contributes to the generation of other oxidant pollutants and is a precursor of the formation of nitric acid and subsequently the nitrate component of PM (WHO 2003). Therefore, sector-specific profile for pollutants by source categories should be considered for identification of sources of PM. According to Siegel (2002), some toxic metals are introduced directly or indirectly into environment by some industrial processes, as summarized in Table 3. Besides, some sector-specific lists of pollutants as an indication to check pollutants from a specific source category were given by European Commission (2000), which is very useful to source apportionment. Once the final number of factors (sources) is established, the FA is repeated including

only independent variables in order to proceed to the quantification of these sources.

Table 4 shows the results of the FA performed on the Hankou dataset, which resulted in the identification of four factors representing 87% of the total variance of the dataset. According to their chemical tracers, these factors have been identified as follows.

The first factor accounts for 60% of the variance, with principal components being Al, Na, Mg, Ca, Fe, V, Co, Mn, Ni and PM10 (factor loadings 0.6–0.9); and secondarily K, Cr and  $\text{Cl}^-$  (0.4–0.5). These elements show typically with a mineral/crustal origin. Coal fly ash emissions are also characterized by high levels of Al, Mg, Ca, Fe and Na, which present high loadings in this factor, but the absence of  $\text{SO}_2$  suggests that other possible mineral matter emission sources, such as soil resuspension, construction and demolition works, are the major contributors to this factor.

The second factor represents 12% of the total variance of the samples in the dataset. It is made up by As, Pb, Cd, Cu, Cr, K, Mn and  $\text{SO}_2$  (0.6–0.9), and secondarily by Ca, Fe,  $\text{SO}_4^{2-}$  and Zn (0.4). High levels of As are typically found not only in industrial emissions related to smelting or metal-based industries but also from coal emissions.  $\text{SO}_2$  levels were found to present the highest factor loading in this factor. It should be also noted that K, usually related to biomass combustion, presents a high loading in this factor. It can be seen from the chemical profile that this factor represents a combination of industrial emissions from the Changqian industrial area. These may include steel manufacturing, smelting and coal combustion, among others.

The third factor accounts for 8% of the variance of the dataset and it is made up by  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  (0.8–0.9), and secondarily by PM10,  $\text{C}_{\text{nm}}$ , K and  $\text{NO}_3^-$  (0.4–0.5). The major components of this factor typically represent the regional pollution, being major secondary components of PM10. The other components represent also secondary components (nitrate), biomass combustion (K and  $\text{C}_{\text{nm}}$ ) or fossil fuel combustion ( $\text{C}_{\text{nm}}$ ). Therefore, this factor does not correspond to a specific local emission source, but rather to the regional pollution background with a component of long-range transport. It is interesting to note the low factor loadings of most metals, such as Co, Ni, As, Zn and Cr, which have been interpreted as tracers of “fresh” local emissions.

The fourth factor accounts for 7% of the variance of the samples, and its main tracers are  $\text{NO}_2$ ,  $\text{Cl}^-$ ,  $\text{C}_{\text{nm}}$ ,  $\text{NO}_3^-$ , Zn and Ni (0.6–0.8), and secondarily PM10,  $\text{SO}_2$ , V, Co, Cu, Ca and Fe (0.4–0.5). The first five components have been identified (Sternbeck et al. 2002; Adachi and Tainosho 2004) as tracers of road traffic emissions (both from exhaust emissions, and brake and tyre tread). Other components of this factor may also arise from diesel emissions ( $\text{SO}_2$ , V and Ni) or road pavement abrasion (Ca and Fe).

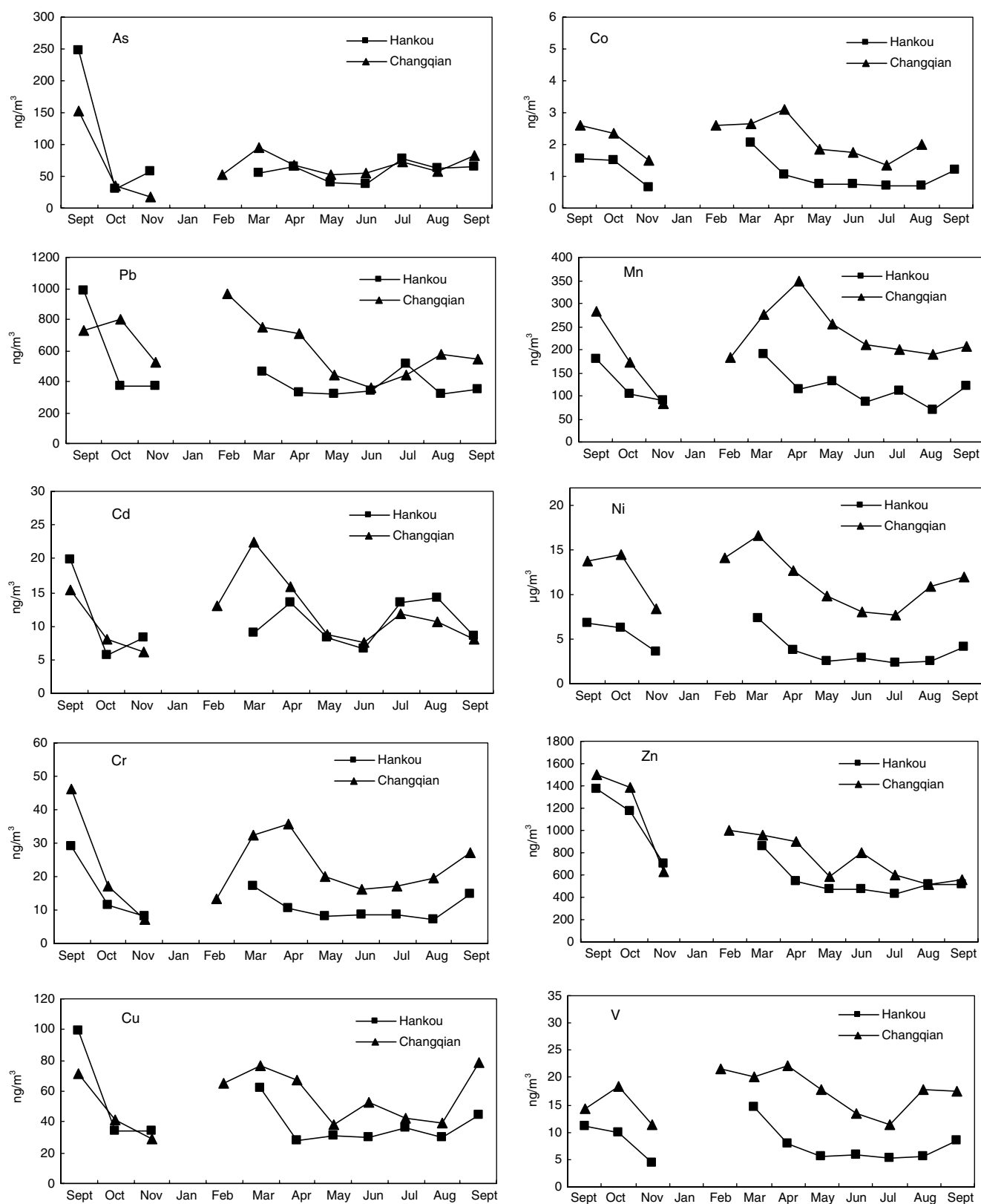
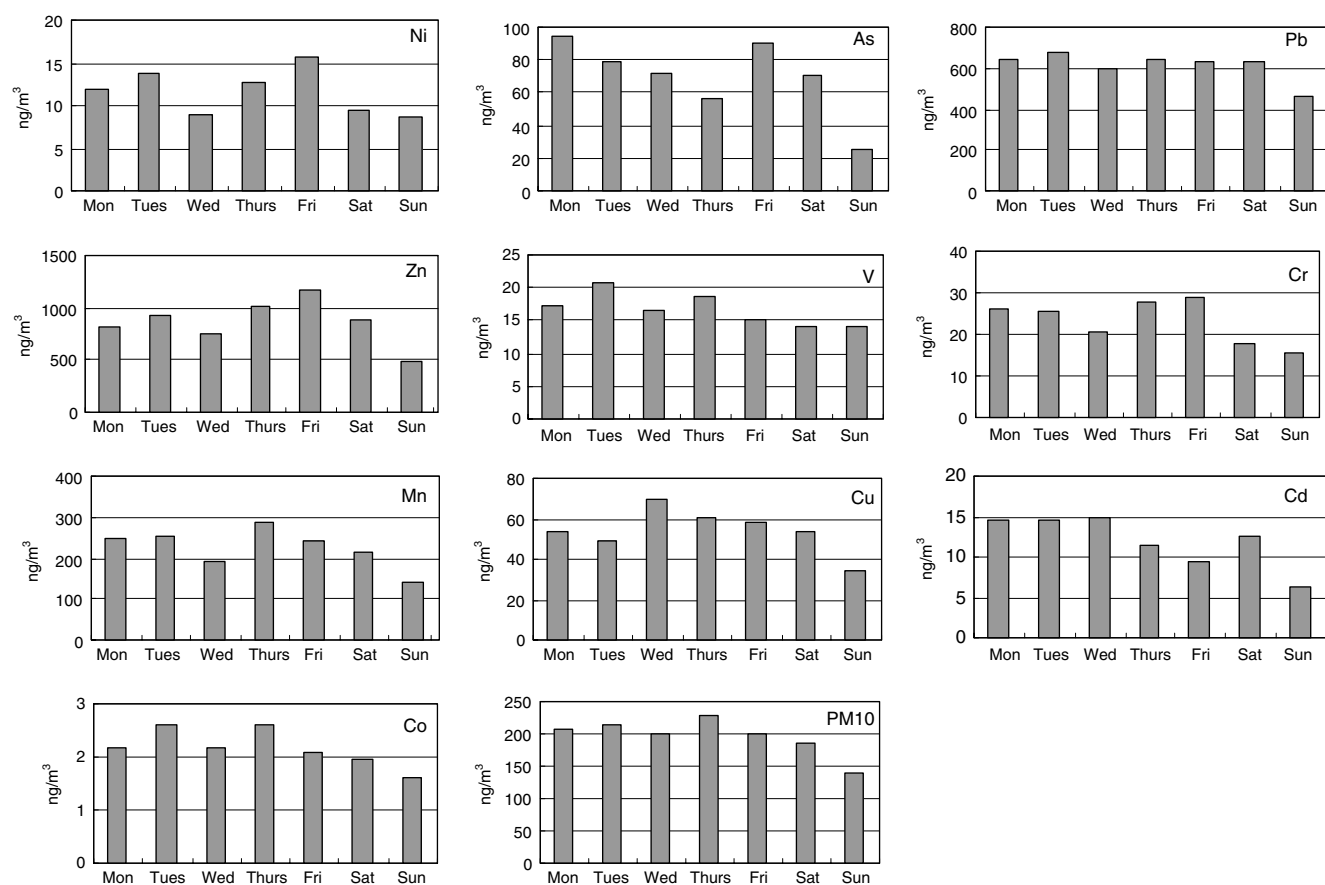


Fig. 2 Monthly levels of trace metals in PM10 in Changqian (industrial site) and Hankou (urban site)



**Fig. 3** Weekly variation of mean levels of PM10 and trace metals for Changqian (industrial site)

Table 5 shows the results of the FA performed on the Changqian dataset, which resulted in the identification of six factors representing 87% of the total variance of the dataset. According to their chemical tracers, these factors have been identified as follows.

The first factor accounts for 48% of the variance, with principal components being Cd, As, Cu and Pb (factor loadings 0.7–0.8), and secondarily K, Cr, Mn, Fe,  $\text{Cl}^-$  and Co (0.4–0.5).  $\text{SO}_2$  and  $\text{NO}_2$  are excluded from this factor. Smelting is the most probable emission source for this chemical profile.

The second factor represents 13% of the total variance of the samples in the dataset, and it is made up by  $\text{SO}_2$ , Al, V and  $\text{NO}_2$  (0.6–0.9), and secondarily by Fe, Ni, Co and Na (0.4–0.5). Coal combustion is the most probable origin of this source.

The third factor accounts for 10% of the variance of the dataset and it is made up by Ca, Mg, PM10, Na, K, Mn, Al, (0.6–0.9), and secondarily by  $\text{C}_{\text{nm}}$ ,  $\text{SO}_4^{2-}$ , V and Co (0.4–0.6). The major components of this factor probably represent a mineral source such as cement manufacture (clinker fugitive emissions and fuel combustion from the furnace).

The fourth factor accounts for 7% of the variance of the samples, and its main tracers are  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{C}_{\text{nm}}$  and Zn (0.6–0.8), and secondarily by Pb,  $\text{NO}_2$ , PM10 and Co (factor loadings 0.4–0.5). As mentioned above, this profile corresponds probably to traffic emissions.

The fifth factor accounts for 5% of the variance of the samples, and its main tracers are  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  (0.8), and secondarily by K and  $\text{NO}_3^-$  (factor loadings 0.4). This factor is also similar to the one observed for Hankou, and it typically represents regional-scale pollution.

The sixth factor accounts for 4% of the variance of the samples, and its main tracers are Cr and Ni (0.7), and secondarily Mn, Zn, Fe and Co (factor loadings 0.4–0.5). The composition of this profile points to a steel production source.

#### Source apportionment of selected elements

Multilinear regression analysis was applied to the Hankou and Changqian datasets with the aim to apportion the mass of a series of selected elements (V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb and Fe) emitted by the PM sources identified in the previous section. The results obtained are summarized in Table 6 (Changqian) and 7 (Hankou).





**Table 4** Main factors/sources identified from results of FA obtained for Hankou

Hankou	Factor 1	Factor 2	Factor 3	Factor 4
PM10	<b>0.6</b>	0.3	0.5	0.5
SO <sub>2</sub>	0.2	<b>0.6</b>	0.2	0.5
NO <sub>2</sub>	0.3	0.2	0.3	<b>0.8</b>
C <sub>nm</sub>	0.3	0.2	0.4	<b>0.7</b>
Al	<b>0.9</b>	0.1	0.2	0.3
Ca	<b>0.8</b>	0.4	0.1	0.4
Fe	<b>0.8</b>	0.4	0.2	0.4
K	0.5	<b>0.7</b>	0.4	0.2
Mg	<b>0.9</b>	0.2	0.1	0.2
Na	<b>0.9</b>	0.1	0.1	0.2
SO <sub>4</sub> <sup>2-</sup>	0.3	0.4	<b>0.8</b>	0.0
NO <sub>3</sub> <sup>-</sup>	0.3	0.1	0.5	<b>0.7</b>
Cl <sup>-</sup>	0.4	-0.1	0.0	<b>0.8</b>
NH <sub>4</sub> <sup>+</sup>	0.0	0.0	<b>0.9</b>	0.2
V	<b>0.8</b>	0.3	0.0	0.5
Cr	0.5	<b>0.7</b>	-0.1	0.3
Mn	<b>0.7</b>	<b>0.6</b>	0.2	0.2
Co	<b>0.8</b>	0.3	0.0	0.5
Ni	<b>0.6</b>	0.3	-0.1	<b>0.6</b>
Cu	0.2	<b>0.8</b>	0.0	0.4
Zn	0.2	0.4	-0.2	<b>0.7</b>
As	0.1	<b>0.9</b>	0.0	0.0
Cd	0.1	<b>0.8</b>	0.2	-0.1
Pb	0.2	<b>0.9</b>	0.1	0.3

C<sub>nm</sub> non-mineral carbon

**Table 5** Main factors/sources identified from results of FA obtained for Changqian

Changqian	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
PM10	0.2	0.3	<b>0.7</b>	0.4	0.3	0.2
SO <sub>2</sub>	0.0	<b>0.9</b>	-0.1	-0.1	0.1	0.0
NO <sub>2</sub>	0.0	<b>0.6</b>	0.2	0.5	0.3	0.2
C <sub>nm</sub>	0.2	0.1	0.5	<b>0.6</b>	0.3	0.3
Al	0.1	<b>0.8</b>	<b>0.6</b>	0.0	0.0	0.1
Ca	0.0	0.0	<b>0.9</b>	0.2	0.0	0.1
Fe	0.4	0.5	0.2	-0.1	0.2	0.5
K	0.5	0.0	<b>0.6</b>	0.2	0.4	0.0
Mg	0.2	0.3	<b>0.9</b>	0.0	0.0	0.1
Na	0.3	0.4	<b>0.7</b>	0.3	0.0	0.1
SO <sub>4</sub> <sup>2-</sup>	0.3	0.1	0.5	0.1	<b>0.8</b>	0.0
NO <sub>3</sub>	0.1	-0.1	0.3	<b>0.8</b>	0.4	0.2
Cl <sup>-</sup>	0.4	0.2	0.1	<b>0.8</b>	0.0	-0.1
NH <sub>4</sub> <sup>+</sup>	0.1	0.2	-0.2	0.3	<b>0.8</b>	0.1
V	0.0	<b>0.8</b>	0.5	0.2	0.0	0.2
Cr	0.5	0.1	0.2	0.0	0.1	<b>0.8</b>
Mn	0.5	-0.1	<b>0.6</b>	0.1	0.2	0.5
Co	0.4	0.6	0.4	0.4	0.0	0.4
Ni	0.0	0.4	0.0	0.3	0.0	<b>0.7</b>
Cu	<b>0.7</b>	0.2	0.2	0.4	0.0	0.2
Zn	0.3	-0.2	0.2	<b>0.6</b>	0.3	0.5
As	<b>0.8</b>	-0.2	0.1	0.0	0.3	0.2
Cd	<b>0.9</b>	0.1	0.2	0.2	0.0	0.1
Pb	<b>0.7</b>	0.2	0.1	0.5	0.3	0.2

C<sub>nm</sub> non-mineral carbon

emissions from Changqian. Once again, Zn was mainly emitted by traffic (52%), although 26% of the Zn mass in Hankou was also linked to Changqian emissions. As re-

**Table 6** Source contribution of six PM sources identified to the levels of V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sn, Sb, Pb and Fe in Changqian

	Smelting	Coal combustion	Mineral	Traffic	Secondary	Steel	Total (%)
V		61	24	10		8	103
Cr	29		14	13		48	104
Mn	21		50	12		28	111
Co	17	46	15	15		12	105
Ni		42		18		31	91
Cu	39	9	15	14		17	94
Zn	28		4	60		11	103
As	57		15			20	92
Cd	65		14	11		19	109
Sn	31		30	12	14	11	99
Sb	46		35	9		21	111
Pb	44	21		30		6	101
Fe	8	38			16	41	103

All values in percentage of mass

gards the mineral source, its chemical profile (Mg, Al<sub>2</sub>O<sub>3</sub>, Ca and Fe among others) clearly indicated the mineral origin of the particles, but the presence of other elements (V, Ni, Th and Se) could also indicate a certain degree of mixture with coal combustion emissions. However, the absence of SO<sub>2</sub> prevents this interpretation from being conclusive. Results show that 52% of the Mn mass is apportioned to the mineral source in Hankou (coinciding with the results from Changqian, 50%), while this source also contributes to a number of elements (60% of Fe, 59% of V, 56% of Co, 43% of Ni) which in Changqian resulted from coal combustion.

## Conclusions

The levels of PM10 were sampled at one urban and one industrial site (Hankou and Changqian, respectively) in

**Table 7** Source contribution of four PM sources identified to the levels of V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sn, Sb, Pb and Fe in Hankou

	Mineral	Changqian	Secondary	Traffic	Total (%)
V	59	17		26	102
Cr	29	46		19	93
Mn	52	45		5	102
Co	56	17		27	100
Ni	43	14		39	96
Cu	13	60		28	101
Zn	18	26		52	97
As		95			95
Cd	8	73	15		96
Sn	11	62	21	8	102
Sb	24	76			100
Pb	9	76		18	103
Fe	60	31		13	104

All values in percentage of mass

Changqian regional transport of pollutants from the Changqian area

Wuhan (central China) between September 2003 and September 2004, by means of high-volume samplers and using quartz fiber filters as collection substrates. Samples were analyzed by ICP-MS and ICP-AES with the aim to determine the levels of trace metals in the aerosol. To the best of our knowledge, the present study is the first systematic work on trace elements in PM<sub>10</sub> in central China to this date.

Based on our results, PM<sub>10</sub> in Wuhan is characterized by relatively high levels of As, Cd, Mn, Pb and Zn compared with other Asian cities, and by high As, Cd, Mn, Ni, Pb, Zn and Cr levels compared with EU cities. Levels of Cu, Co and V are similar to those reported for most EU cities. The European target value for the annual As concentration (6 ng/m<sup>3</sup>) would be exceeded by an order of magnitude in Wuhan and other Asian cities (Beijing, Shanghai and Taiwan). The levels of Cd in Wuhan and most of the Asian cities analyzed are higher than the European target value (5 ng/m<sup>3</sup>) by a factor of 2. The levels of Ni in Wuhan and in other Asian cities would be below the European target value (20 ng/m<sup>3</sup>). Finally, the European limit value for Pb (500 ng/m<sup>3</sup>) would be exceeded in Changqian and only slightly higher than the concentration registered in Hankou, whereas in most of the Asian cities considered (Tokyo, Hong Kong, Taiwan and Beijing) Pb levels are markedly lower than the European limit value.

The time-series of trace metals were analyzed, showing that similar trends were observed at both sites for

As, Cu and Zn, whereas Pb levels showed different patterns due to different emission sources.

Factor analysis identified the contribution of six sources to PM<sub>10</sub> in Changqian (smelting, coal combustion, mineral, traffic, secondary aerosols and steel manufacture) and four in Hankou (mineral, pollution from Changqian, secondary aerosols and traffic). Multilinear regression was then applied to apportion the mass of selected trace metals emitted by the different sources. Results indicate that Pb, Cd and As have a common source (smelting) at both sites, which in Changqian is responsible for 44–65% of the mass of these elements. Pollutants transported from nearby Changqian accounts for 95% of the As mass, 76% of the Pb mass and 73% of the Cd mass in Hankou. In Changqian traffic is a secondary source of Pb (30%), and steel of As (20%) and Cd (19%). Ni shows a wider range of sources at both sites, with coal combustion (42%) and steel (31%) in Changqian and mineral (43%) and traffic (39%) in Hankou.

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