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Characterization and Source Identification of Heavy Metals in Ambient PM_{10} and $PM_{2.5}$ in an Integrated Iron and Steel Industry Zone Compared with a Background Site

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ABSTRACT

The purpose of this study is to characterize heavy metals in ambient PM_{10} (particles with aerodynamic diameter below 10 μm) and $PM_{2.5}$ (particles with aerodynamic diameter below 2.5 μm) particles in a typical integrated iron and steel industry zone (HG) and a background site (ZWY) during February 2011 to January 2012 in the Yangtze River Delta (YRD) region, China. Twelve elements were measured to study their levels, size distribution and sources. At the two sampling sites, Fe was found as the dominated metal in the total detected metals in both particle sizes, followed by Zn and Pb. They were regarded as the marker elements of iron and steel production emission along with Cr and Mn. The concentrations of all measured heavy metals in HG were 1–3.53 times higher than those measured in ZWY. When compared with previous studies, the concentrations of steel related elements (Fe, Zn, Mn) in this work were significantly high. The highest correlation coefficient was observed in HG for Fe and Zn. Additionally, Cd was found as the most enriched heavy metal by the enrichment factor analysis, followed by Zn, Pb, and Cu. The main sources contributing to heavy metals at HG site were identified by principle component analysis: steel dust (including coal combustion of coal-fired power plant, coke making and steel making emission), vehicle emission and road re-suspension dust and soil dust. Besides, steel dust was also found as the possible source of heavy metals at ZWY site. The result suggested the steel dust has influence on the whole study area.

Keywords: Heavy metals; Steel production; Particulate matter; Source identification.

INTRODUCTION

Iron and steel have wide uses in construction and the manufacturing of machinery and equipment, which play an important role in the development of human civilization over several millennia. The iron and steel industry is highly intensive in both materials and energy, and the world crude steel production amount rose to a total of 1,607.2 million metric tons in 2013 (http://www.worldsteel.org/statistics/crude-steel-production/). Accompany with the production processes, a number of environmental issue occurred such as SO_2 and dust emissions to air from sinter plants, coke oven plants and blast furnace plants. The main outputs of process related emissions for the iron and steel production process are SO_2, NO_x, dust etc. Taiwo *et al.* (2014) found steelworks emissions account for 45% of measured PM_{10} mass in the vicinity of a major steelworks site in Port Talbot, South Wales (UK). Prati *et al.* (2000) reported 60% of the particulate matter in the Cornigliano area (Genoa, Italy) is emitted from the steel smelter. Results of many studies have confirmed that the dust emission from iron and steel production processes is an important source of ambient air particulate matter in some area (Prati *et al*., 2000; Kumar *et al*., 2001; Lv *et al*., 2006; Mazzei *et al*., 2006).

Heavy metal associated with atmospheric particles may accumulate in human being via inhalation and respiratory deposition, which may cause adverse effects on human health such as neuropathies symptoms, increased blood pressure and anaemia symptoms, kidney damage and increase the risk of lung and renal cancer (Vamvakas *et al*., 1993; Ewan and Pamphlett, 1996; Abernathy *et al*., 1999; Laden *et al*., 2000; Damek-Poprawa and Sawicka-Kapusta, 2003; Knaapen *et al*., 2004; Kampa and Castanas, 2008; Ning and Sioutas, 2010; Fang *et al*., 2013). As one of the specific heavy metal sources, the iron and steel production source can emit high

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concentrations of Fe and heavy metal Zn, Mn, Pb and Cd in atmospheric particles (Querol *et al*., 2007; Amodio *et al*., 2013). Machemer (2004) reported approximately 60% of blast furnace kish by volume consisted of spherical iron oxide particles in the respirable size range. In addition, concentrations of respirable Mn in atmospheric particles collected at local iron and steel facilities and in residential areas were about 53 and 1.6 times the inhalation reference concentration of 0.05 μg/m^3 for chronic inhalation exposure of Mn, respectively. Therefore, residents living in close proximity to the steel plants where there are no regulation protection arrangements are suffering from health risk. And the impact of atmospheric heavy metal pollution caused by iron and steel production emission on nearby residents should be draw attention.

The characterization of heavy metals in ambient air particulate matter emission from steel plants have been reported over countries around the world, including United Kingdom, Spain, Poland, Italy, Turkey, Australia, Korea etc. (Kim *et al*., 2002; Mazzei *et al*., 2006; Cetin *et al*., 2007; Querol *et al*., 2007; Tsai *et al*., 2007; Pastuszka *et al*., 2010; Amodio *et al*., 2013; Hleis *et al*., 2013; Mohiuddin *et al*., 2014; Taiwo *et al*., 2014). However, there is scarcely literature on the heavy metals in ambient particulate matter emission from steel plants of China, which is the biggest steel producing country and accounted for 48.5% of world steel production in 2013. Comprehensive understanding the status of atmospheric heavy metals pollution caused by steel production is the basic requirement for controlling the pollution and providing essential data to study the global biogeochemical cycling of heavy metals in the ecosystem.

For these purposes, an aerosol sampling campaign from February 2011 to January 2012 was conducted in a typical integrated iron and steel industry zone and a background site in the Yangtze River Delta (YRD) region, China. The concentrations of twelve heavy metals (including Fe) in PM_{10} and $PM_{2.5}$ collected at the two sampling sites were measured to study their levels, size distribution and sources. In order to find out the difference of the characterization of heavy metals emission from steel plants over different countries, a summarization and comparison were made in this work. As a complement to previous studies, investigating the specific marker element of steelmaking emission source and identifying the main sources with influence the concentration levels of measured heavy metals in the iron and steel production zone were also carried out. The enrichment factor and principle component analysis coupled with Pearson correlation analysis were used to discriminate the emission sources in the integrated iron and steel industry zone.

METHODS

Site Details

The Banshan base of Hangzhou iron and steel plants was selected as the study object, which belongs to Hangzhou iron and steel group company and located at the Yangtze River Delta (YRD) region, China. As an typical integrated steelworks, the company taking place in large industry complexes and are characterized by networks of product flows and energy flows between the various production units such as sinter plants, coke oven plants, blast furnaces, rolling mills and cast-house. The annual steel production capacity is about 4 million tons and the cast iron and steel production is 2.67×10^6 tons and 3.42×10^6 tons in 2013, respectively (http://en.hzsteel.com/web/index.asp). The dust emission from these units had reached 1896.14 tons in 2013. In this study, the dust emission from the iron and steel production activities in the integrated steelworks is defined as steel dust.

Sampling campaign was undertaken simultaneously at two sites: (1) The Hanggang monitor station (HG) is in the Gongshu district on the north of Hangzhou city (situated at N30°21′16″, E120°11′9″ and the altitude is ~15 m high), which is affected directly by the iron and steel production industry activities. (2) The Zhiwuyuan (ZWY) site is located at Hangzhou Botanical Garden in the Xihu district (situated at N30°15′9″, E120°07′28″, the altitude is ~5 m high). As an urban background site, ZWY is located near West Lake scenery spot with no direct industry source emission. The distance between two sampling sites is over 12 km. The location of sampling sites was shown in Fig. 1.

Sampling

At each site, PM_{10} and $PM_{2.5}$ samples were synchronized collected from February 2011 to January 2012. Each sampling began at 8:00 local time and continued for 18–22 h. All samples were collected using medium-volume samplers (Wuhan Tianhong Intelligence Instrumentation Facility, TH-150 Medium Volume Sampler) operating at a flow rate of 100 L/min with a 10 μm and 2.5 μm cut-point impactor in parallel, respectively. Ambient particulate matter was collected on acetate-fiber filters for elemental analysis. After the sampling campaign, a total of 72 available PM_{10} samples and 70 available $PM_{2.5}$ samples were obtained and 22 invalid samples were rejected due to the sampler's malfunction, filter's fracture, or other unexpected accidents during sampling time. The filters were transported to the sampling site and back in sealed plastic boxes.

Chemical Analysis

The determination of concentrations of Ti, V, Cr, Cd, Mn, Fe, Co, Ni, Cu, Zn, and Pb was carried out by inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo, X serial) (Hall, 1992; Bi *et al*., 2007). And the element As was determined by atomic fluorescence spectrometer (AFS-9230). For this, each filter was cut into pieces and placed in 50 mL microwave digestion vessel with 6 mL HNO_3 (GR) and 2 mL H_2O_2 (GR). Then the samples were digested under the setting progress. After above procedure the solution was diluted with deionized water to 50 mL. Filter and reagent blanks were processed following the sample treatment. QA/QC included reagent blanks, analytical duplicates, and analysis of the certified reference material (CRM). Duplicate samples and blanks (including filters) were approximately 10% of all the samples, with relative standard deviation less than 5%. CRM were used to ensure accuracy and precision (National Research Center of CRM, China) (Bi *et al*., 2007; Wang *et al*., 2013).

Fig. 1. Location of sampling sites: HG (industrial site) and ZWY (background site).

The recovery rates for the considered metals in the CRM were between 80 and 115%.

Statistical Analysis

Statistical treatment of data including Pearson correlation analysis and principal component analysis were carried out using the SPSS 10.0 statistical software.

Enrichment Factor Analysis

In previous studies, the enrichment factor (EF) is an effective tool to discriminate the natural sources from the anthropogenic sources of atmospheric heavy metals (Petaloti *et al*., 2006; Yongming *et al*., 2006; Ayrault *et al*., 2010). The enrichment factor is commonly defined by the following relation:

$$EF = ([E])/([R])_{sample}/([E]/[R])_{crustl} \quad (1)$$

where E represents considered element, and R is the reference element for crustal material. $([E])/([R])_{sample}$ is the concentration ratio of E to R in the aerosol sample, and $([E]/[R])_{crustl}$ is the mean concentration ratio of E to R in the crust.

Fe, Mn and Ti are frequently used as reference elements (Isakson *et al*., 1997; Yongming *et al*., 2006; Basha *et al*., 2010). Considered the sampling site at HG in the vicinity of iron and steel industry area, Mn and Fe were not selected as the reference elements. Due to the relatively stability of Ti and the lack of anthropogenic sources, the enrichment factors (EFs) were calculated using the background value of Ti in China soil (1990). If EF approaches unity, the crust soil is the predominant source. Operationally, given the local variation in soil composition, if EF > 10, the anthropogenic source has a significant contribution to the element (Yongming *et al*., 2006; Basha *et al*., 2010).

RESULTS AND DISCUSSION

Heavy Metals Levels and Comparison with Other Sites

The elemental concentrations of measured heavy metals in PM_{10} and $PM_{2.5}$ for the two sampling sites are depicted in Table 1 and Fig. 2., Fe (iron) was found to be the dominate metal in PM_{10} and $PM_{2.5}$ and contributed significantly to the total detected metal mass loading ranges from 50%–76% at the two sampling sites. Similar magnitude rank of heavy metals concentrations were found at the two sites for PM_{10} and $PM_{2.5}$. Fe presented the maximum concentration at the two sites for both particle sizes, followed by Zn, Pb, Mn, Cu, Ti, As, Cr, V, Ni, Cd, Co for PM_{10} and Zn, Pb, Cu, Mn, Ti, As, Cr, V, Ni, Cd, Co for $PM_{2.5}$ at HG site, and Zn, Pb, Mn, Cu, Ti, As, V, Cr, Ni, Cd, Co for PM_{10} and Zn, Pb, Cu, Mn, As, Ti, V, Cr, Ni, Cd, Co for $PM_{2.5}$ at ZWY site. This result is consistent with the conclusion of previous study conducted by Cao *et al.* (2009) who obtained the similar rank of elemental concentrations in Hangzhou during 2001–2002.

Compared with the background site (ZWY), except Cd in $PM_{2.5}$, all identified heavy metals exhibited higher concentrations collected at the iron and steel production industries zone (HG) for PM_{10} and $PM_{2.5}$ particles, which signifies the presence of anthropogenic sources possibly from steel production zone. The concentration of Cd in $PM_{2.5}$ at HG site is slightly lower than ZYW that suggests the influence of anthropogenic activities for Cd in HG is not obvious. From Table 1, it can be found Fe, Mn, Cr in HG site is about 2–3 times higher than that in ZWY site in both particle sizes which suggests the iron and steel production processes have a significant influence on HG site. According to the BAT(Best Available Techniques) reference documents on the Production of Iron and Steel from joint research center of the European Commission (http://eippcb. jrc.ec.europa.eu/reference/), Fe, Pb, Zn and some other heavy metals will be emitted from several units such as sinter/pellet plant and blast furnace in iron and steel industries. Therefore, Fe, Zn, Cr, Mn and Pb were identified as the marker element of iron and steel production emission. Under the influence of steel manufacturing, the concentrations of measured metals are typically high, as described by Querol *et al.* (2007) who compared the concentration range of trace elements in Spanish urban

Table 1. Comparison of heavy metals concentrations in PM_{10} and $PM_{2.5}$ collected at HG and ZWY with steel-related sites (Units: ng/m^3).

			Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Pb	Reference
HG	PM_{10}	Mean	100.8	15.6	19.2	180.0	5542.7	2.4	10.7	154.0	1018.6	21.2	4.0	195.2	This study
		S.D.	8.2	1.8	2.1	18.3	1028.9	0.3	2.1	26.5	298.3	3.4	0.4	37.8	
ZWY	PM_{10}	Mean	31.5	9.6	7.5	68.9	1692.8	1.1	6.2	117.1	794.6	16.3	3.8	158.7	
		S.D.	7.6	2.1	1.8	33.8	556.5	0.3	1.6	17.5	367.0	5.0	1.0	51.6	
HG	$PM_{2.5}$	Mean	24.9	7.9	8.4	54.2	2321.0	0.8	5.2	69.9	729.2	16.8	3.3	161.6	
		S.D.	2.7	1.4	1.1	5.3	788.5	0.1	1.4	7.3	261.2	3.4	0.4	33.0	
ZWY	$PM_{2.5}$	Mean	9.8	7.2	4.4	16.8	850.0	0.5	3.9	69.8	592.6	13.2	3.6	134.7	
		S.D.	2.3	1.5	1.2	8.8	389.1	0.1	1.0	5.3	240.7	4.1	0.8	42.2	
WHO				1000	0.25*	150			25			6.6	5	500	
Ref 1	PM_{10}	Mean		17.9	85.7	198.8			29.0	117.0	424.5	51.0	12.9	261.0	(Duan and Tan, 2013)
		S.D.		16.5	110.9	363.4			39.4	163.3	336.6	67.0	19.6	275.7	
Ref 2	$PM_{2.5}$	Mean	50		10	110	2410		10	40	440	60		200	(Zhou *et al.*, 2014)
		S.D.	20		10	70	1190		10	30	270	70		100	
Ref 3	PM_{10}	Range		3–35	4–64	29–680		1–6	3–30	10–171	113–4390	7–298	2–46	182–2107	(Lv *et al.*, 2006)
Ref 4	$PM_{2.5}$	Mean	61	17	58	113	1187	1.1	20	54	681	32	4.6	149	(Chen *et al.*, 2008)
		S.D.	29	10	39	87	1193	0.5	14	29	297	27	3.2	122	
Ref 5	PM_{10}	Mean	32.6	13.1	25.1	50.3	1633	1.53	37.9	41.1	240	6.06	3.24	243	(Kim *et al.*, 2002)
	/TSP	S.D.	30.3	7.1	22.1	31.9	926	0.75	21.6	22.0	133	4.58	2.46	135	
Ref 6	$PM_{2.5}$	Range			12–54	21–119	1374–9607		5–142	39–204			4–38	80–2537	(Pastuszka *et al.*, 2010)
Ref 7	PM_{10}	Mean	25	8	25	87		0.5	33	33	420	1.8	1.2	103	(Querol *et al.*, 2007)
Ref 8	PM_{10}	Mean	7.6	1.9	2.7	20.6		5.5	3.5	2.0	8.4				(Mohiuddin *et al.*, 2014)
	$PM_{2.5}$	Mean	3.8	1.3	1.9	8.3		1.2	2.4	1.3	6.3				
Ref 9	PM_{10}	Mean		15	109	138	2674		12	61	3206		9	555	(Cetin *et al.*, 2007)
		S.D.		5	51	92	1270		2	33	2567		9	515	
Ref 10	$PM_{2.5}$	Mean		0.52	3.48	5.72	173		0.20	1.89	43.0		0.26	4.42	(Taiwo *et al.*, 2014)
		S.D.		0.23	1.52	7.6	237		0.33	1.21	85.55		0.55	3.88	

*: This value set for Cr (VI).

Ref 1: Average levels of atmospheric heavy metals and As in 44 major cities in China during the last 10 years.

Ref 2: The sampling site located in an industrial area surrounded by several iron and steel plants in Ji'nan city, eastern China.

Ref 3: An industrial site surrounded by several plants including a big steel production plant in Wuhan city, central China.

Ref 4: An industrial site (Baoshan) located in the northeast part of Shanghai, is a well-known steel manufacturing area in China.

Ref 5: One sampling site situated in the first and second industrial complex of Taejon city, Korea.

Ref 6: A traffic site located in Zabrze, a town has intensive industrial activities, lie in Poland.

Ref 7: Two urban sites (Llodio and Basauri) influenced by emissions from steel manufacturing in Spain.

Ref 8: Three sampling sites were located in the vicinity of integrated iron and steel processing industries in New South Wales and South Australia.

Ref 9: The industrial site nearby steel plants with electric arc furnaces located in Izmir, Turkey.

Ref 10: The sampling site (Fire station) located in the vicinity of the integrated steelworks complex located at Port Talbot, in South Wales, UK. The integrated iron and steel facility is the largest steel producer in the UK and one of the biggest steel producers in Europe.

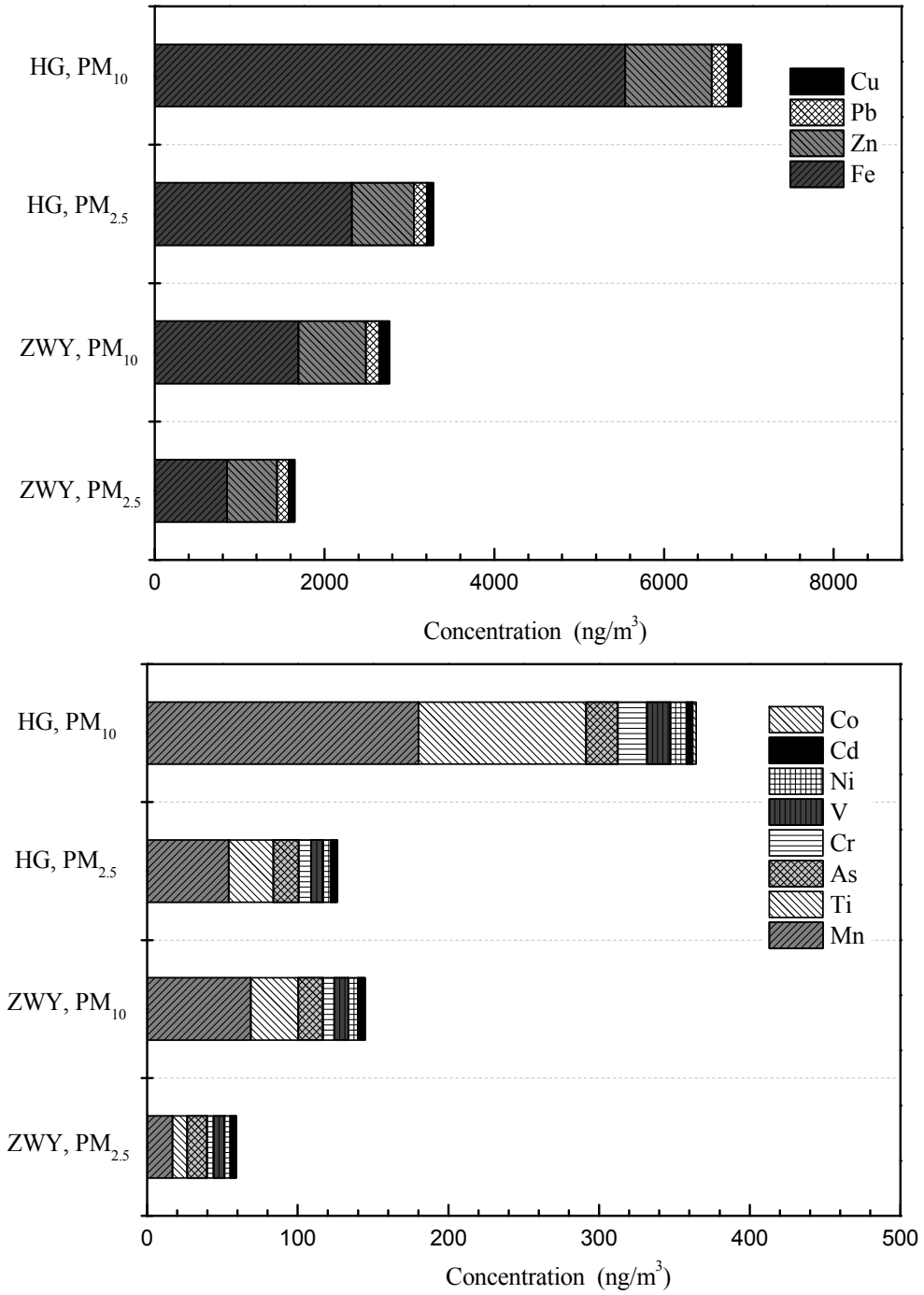

Fig. 2. Concentrations of heavy metals in PM_{10} and $PM_{2.5}$ collected at the two sampling sites.

background stations and the sampling sites under the influence of emissions deriving from metallurgy.

Compared to some industry sites which were also influenced by the iron and steel manufacturing processes over the world, (Table 1), all measured heavy metals in PM_{10} collected at HG site are in the ranges of the heavy metals levels in an industry area including a big steel production plant in Wuhan (China). For $PM_{2.5}$, they are also in the ranges of measured metal concentrations in Zabrze (Poland) except Cr and Cd. The concentrations of Cu and Zn in $PM_{2.5}$ at HG are higher than the industry site in Ji'nan, exceeding about 70% and 65%, respectively. As for the sampling site near the famous Baosteel Group Corporation (one of the biggest steelmaking corporation in China) in Shanghai, the concentrations of Fe, Cu, Zn and Pb in $PM_{2.5}$ are lower than that at HG site, especially for Fe(less than half). Moreover, the concentration of Fe in PM_{10} in HG is 3.4 times higher than that in the industry site of Taejon (Korea) and about 2 times higher than Izmir (Turkey) and New South Wales (Australia). Besides, the concentrations of Mn and Cu in HG were significant higher than these industry sites. Moreover, the annual mean

concentrations of Ti, V, Cr, Mn, Fe, Ni, Cu and Zn at HG were all higher than New South Wales (Australia) and the largest integrated iron and steel facility of UK located at South Wales. On the whole, the ambient levels of heavy metals in HG are high, whereas the concentrations of heavy metals in South Wales (UK) appeared to be the lowest. Though for most elements, the relative low concentrations measured at ZWY site reflects the clean nature of the ambient air there, the concentration levels in ZWY even higher than some industries sampling site in New South Wales (Australia) and Spain.

Through the comparison analysis with some steel-related sites in previous studies, it can be concluded that the pollution of iron and steel production activities in HG site is heavier. However, the simple comparison is insufficient. The factors which affect the concentration levels of heavy metals were not taken into consideration, such as the influence of some other sources. The sources with influence the concentration levels of heavy metals in the sampling sites were identified and discussed at last.

Distribution of Heavy Metals in the Fine and Coarse Particulate Matter

The ratios of $PM_{2.5}$ to PM_{10} of heavy metals concentrations were calculated and the highest value is Cd, followed by Pb, As and Zn, which are all near 0.80 in both sampling sites and indicated that these heavy metals were major existed in fine particulate matter and may come from anthropogenic sources. Considering the smaller diameter particles are easier to be inhaled into human body and could results in severe health issue, the heavy metals in fine fraction should be paid more attentions. The values of Mn, Co and Ti were lower than 0.50 or less. This result suggested that these metals almost combined with coarse particles, which main derived from crust or road fugitive dust. As for Fe, Cu, Cr, V and Ni, that the values close to 0.5shows a wide size distributions in particulate matter of these elements and an appearance of mixed sources. A similar result on the ratio of heavy metals concentrations in $PM_{2.5}$ to TSP was reported by Deng *et al.* (2006) and it was found that Cd, Cr, Ni, Pb and Zn exhibited a predominant occurrence in the fine particle fraction (78–108%), except Cu (25%).

Sources of Heavy Metals in Ambient Air

Enrichment Factor Analysis

Enrichment factors (EFs) of heavy metals were calculated to discriminate the crustal source from the anthropogenic sources of atmospheric heavy metals. Fig. 3 shows that the most enriched heavy metals were Cd, Zn, Pb, Cu, As (almost all > 100) as well as Ni and Cr in both particle sizes collected at the two sampling sites, which suggested that these heavy metals are from anthropogenic origin, due to a variety of pollution emissions may contribute to the heavy metals loading in the ambient atmospheric particulate matter. The slight enrichment of V, Mn, Fe and Co with EF values nearly 10 reveals mixed anthropogenic and soil/road fugitive dust origins.

From Fig. 3., compared with HG site, it seems all elements in both particle sizes collected at ZWY have higher EF values, especially for Cu, Zn, As, Cd and Pb. The stronger enrichment of these heavy metals in ZWY revealed their main origins were anthropogenic sources and the contribution of crustal source was slight. There is no direct industry emission around this site (ZWY), so the atmospheric transportation was considered as an important source for these heavy metals.

In this study, the EF values of all selected heavy metal are higher in $PM_{2.5}$ than that in PM_{10} especially for Pb, Zn, Cu, Cd and As, which is consistent with the results of previous studies (Chan *et al*., 1997; Dietl *et al*., 1997; Petaloti *et al*., 2006; Wang *et al*., 2006). Since these elements are major distributed in fine particles which mainly come from anthropogenic sources, they show higher EF values.

Inter-Elemental Correlation

Pearson's correlation coefficients of heavy metals in PM_{10} and $PM_{2.5}$ collected at both sampling sites are summarized in Table 2 and Table 3. The possible sources around the sampling sites can be qualitatively identified from the correlation matrix by analyzing the value which represents the linear coefficient of correlation between elements. The strong correlations of Fe-Mn (0.935), Fe-Zn (0.933), Mn-Zn (0.851) in PM_{10} particles in HG suggested they may have a common origin and can be attributed to the metal emissions from iron and steelmaking industry activities near HG site. This result has good agreement with previous study conducted by Mohiuddin *et al* (2014) during analyzing the correlation of Fe-Mn-Zn from iron and steel industry sites. However, there are no apparent correlations among Fe, Mn and Zn in ZWY site which revealed these elements may come from different sources. The strong correlations between As, Cr, Cd and Pb in PM_{10} at HG revealed these heavy metals possibly originated from the same source from the iron and steelmaking processes. Besides, Cr, Ni and V also have significant correlations among them which suggests the possibly contribution of the fuel coal and oil combustion (Tian *et al*., 2012).

The correlations of heavy metals in $PM_{2.5}$ and PM_{10} are similar but there are some differences between them. Compared to PM_{10}, the correlation coefficient of Fe-Mn-Zn in $PM_{2.5}$ are considerably weak. As for HG site, contrary to PM_{10}, the elemental Mn with Cr, Pb, As and elemental Co with Ni, Cr, Ti, V have significantly strong correlations (> 0.5) in $PM_{2.5}$. This result can be explained by the size distribution patterns of heavy metals. For example, Cd, Pb, Zn and As were mainly exist in fine particles and Mn, Co, Ti almost combine with coarse particles, the details are described in the above section.

Principle Component Analysis

Previous studies had confirmed heavy metals in particulate matter have a variety of contributing sources (Thurston and Spengler, 1985; Hope, 1997; Yang *et al*., 2003; Querol *et al*., 2006; Hjortenkrans *et al*., 2007; Tian *et al*., 2010). The primary anthropogenic sources of most enriched elements were summarized from literatures and listed in Table 4. Combined with enrichment factor analysis, the markers of various sources can be identified as: (1) Ti, Co

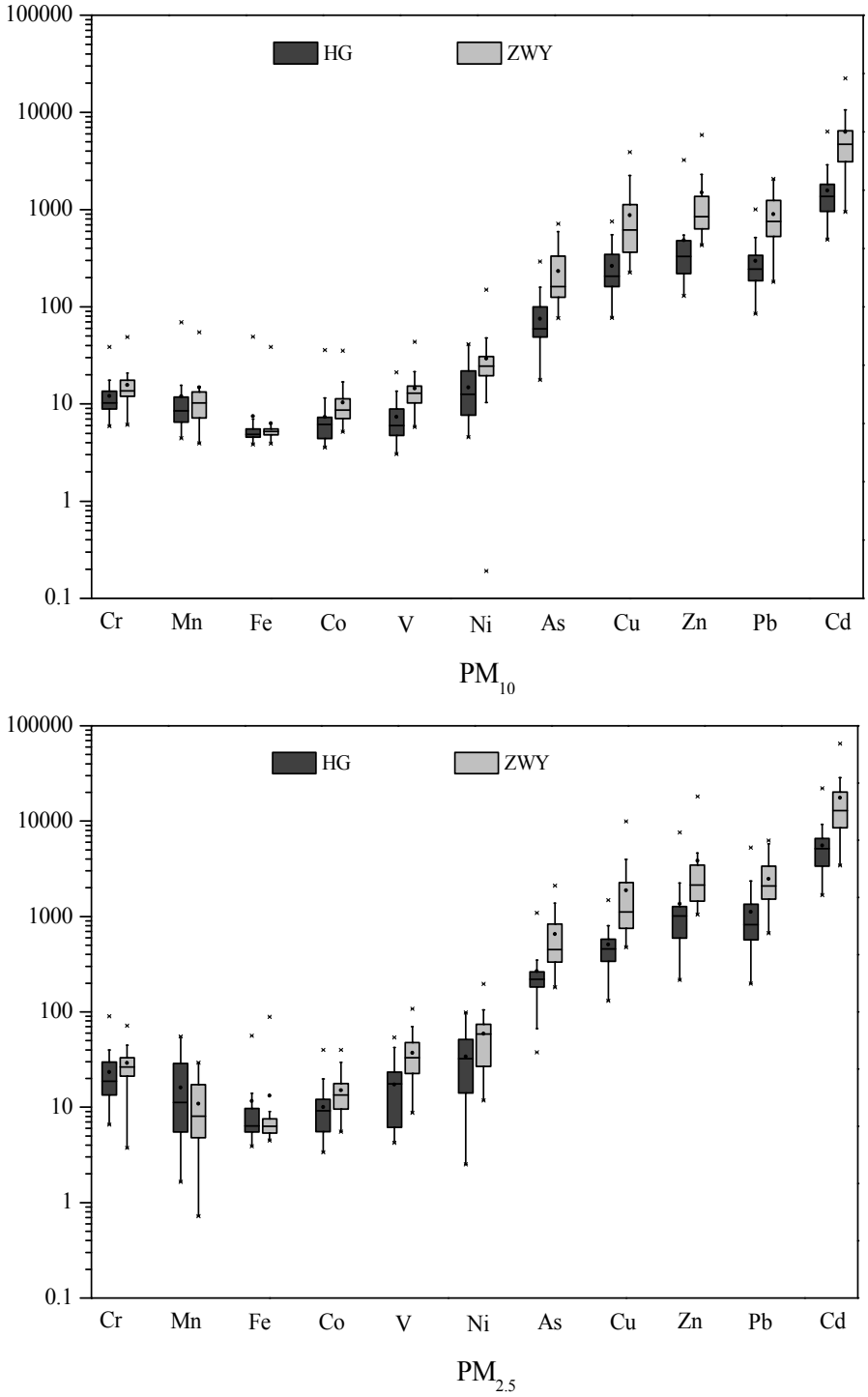

Fig. 3. Boxplot of enrichment factors for heavy metals at the two sampling sites.

and Mn for soil and road re-suspended dust; (2) Fe, Cd, Cu, Mn, Pb and Zn for iron and steel production processes; (3) Cd, Cr, Cu, Pb and Zn for vehicle emission; (4) As, Cr, Cu, Mn, Ni, Pb and Zn for coal combustion; (5) Ni and V for oil combustion.

In order to identify the possible sources contributing to heavy metals in ambient air particles qualitatively, principal component analysis (PCA) with varimax rotation and retention of principal components having eigenvalues greater than 1.0 was used to identify major elements associated with different sources. The percent of variance explained by each significant factor was calculated by using the software (SPSS 10.0) with measured heavy metals as variables for both particle sizes. The factor loadings from PCA analysis at the sampling sites for PM_{10} and $PM_{2.5}$ particles were shown in Table 5 and Table 6. Factor loading above 0.1 have been shown in the tables and values great than 0.5 are in bold.

Table 2. Correlation matrix for heavy metals in PM_{10} samples collected at HG and ZWY site. Bold entries indicate "strong" correlations.

Elements	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Ti	V	Zn
HG												
As	1	**0.578****	0.210	**0.650****	0.176	0.135	**0.722****	0.317	**0.788****	0.376*	0.165	0.272
Cd		1	0.206	0.487**	0.269	0.108	0.385	0.429*	**0.560****	0.336	0.399*	0.302
Co			1	**0.620****	0.203	–0.055	0.377	**0.520****	0.284	**0.651****	**0.786****	–0.026
Cr				1	0.314	–0.035	**0.870****	**0.658****	**0.781****	**0.680****	**0.594****	0.091
Cu					1	–0.040	0.081	0.378	0.061	0.134	0.260	0.065
Fe						1	**0.828****	–0.230	–0.006	0.149	–0.089	**0.952****
Mn							1	0.464	**0.808****	**0.660****	0.360	**0.796****
Ni								1	**0.557****	0.290	**0.793****	–0.139
Pb									1	0.353*	0.314	0.174
Ti										1	0.493**	0.145
V											1	0.009
ZWY												
As	1	**0.634****	0.252	**0.558****	0.459*	–0.019	0.037	0.428*	**0.865****	**0.584****	0.296	–0.156
Cd		1	0.214	0.483**	0.419*	0.042	0.218	0.335	**0.689****	0.418*	0.248	–0.028
Co			1	**0.718****	0.194	0.160	0.372	**0.727****	0.435*	**0.721****	**0.700****	0.294
Cr				1	**0.534****	0.173	0.160	**0.910****	**0.700****	**0.914****	**0.696****	0.013
Cu					1	–0.032	–0.076	0.459**	0.454**	0.435*	0.377*	–0.208
Fe						1	0.006	0.151	0.107	0.285	0.119	0.419*
Mn							1	0.184	0.191	0.310	0.298	0.417*
Ni								1	**0.593****	**0.867****	**0.850****	–0.041
Pb									1	**0.708****	0.480**	0.001
Ti										1	**0.717****	0.118
V											1	–0.018

**.Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

As for HG site, no matter PM_{10} or $PM_{2.5}$, factor 1 and factor 2 can be attributed to the steel dust. Factor 1 is dominated by As, Cd, Cr, Ni and Pb indicated the coal combustion of coal-fired power plant and coke making processes, which were observed in steel plants (http://eippcb.jrc.ec.europa.eu/reference/). Besides, Fe, Mn and Zn for factor 2 were also regarded as the marker elements of steel making emission and the correlations among these metals have been proved to be significantly strong. The mixed sources of vehicle emission (petrol-fired) and road re-suspension dust were responsible for Co, Ni, Ti and V on the third factor in both particle sizes. Ni and V which were emitted from oil combustion had been confirmed in several published literatures (Espinosa *et al*., 2001; Chao and Wong, 2002; Lin *et al*., 2005). The fourth factor with high loading of Cu for PM_{10} may be explained by the contribution of traffic (Xia and Gao, 2011). But for $PM_{2.5}$, soil dust was possible the major source of the last factor, which was loaded primarily by Co and Ti.

At the ZWY site, the first factor revealed the possible mixed sources of vehicle emission (petrol-fired) and road re-suspension dust in PM_{10} and $PM_{2.5}$. According to Table 4, Cr, Cu, Pb, Ni and V can be attributed to vehicle emission such as petrol/diesel combustion and rubber tire wear or brake lining wear. This result confirms the positive correlations among them in previous discussion. For the second factor in both particle sizes, high loading of As, Cd, Cr, Mn, Ni, Pb and V pointing to the fossil fuel combustion of coal and oil. The third factor of PM_{10} is correlated with Co, Ti, Mn and Zn, which may be contributed by soil dust. As the last factor of PM_{10} and $PM_{2.5}$ were mainly loading by steel-related metals, they were highlighting the contribution of steel dust, which comes from the iron and steel plant (HG) through atmospheric transportation.

According to the Kaiser criterion, the principal components with eigenvalues larger than 1.0 have dominant influences (Kaiser, 1960; Huang *et al*., 2009). The first two principal components of PM_{10} and $PM_{2.5}$ in HG site cumulatively account, respectively, for 54.067% and 48.651% of the total variance in the samples. The two factors were identified as steel dust and they reflected the majority information of the data. While in ZWY site, the last factors of PM_{10} and $PM_{2.5}$ were found as steel dust, which explained 9.548% and 23.369% of the total variance, respectively. From above discussion, not only the steel dust emission from the iron and steel production activities makes impact on HG site but it was also identified as one source of atmospheric heavy metals in the background site (ZWY), which means the steel dust has influence on the whole study area.

CONCLUSIONS

Heavy metals in PM_{10} and $PM_{2.5}$ collected in the iron and steel industry zone (HG) and an urban background site (ZWY) were analyzed. The results suggested the maximum element concentration was 5.54 $\mu g/m^3$ of Fe in PM_{10} at HG

Table 3. Correlation matrix for heavy metals in $PM_{2.5}$ samples collected at HG and ZWY site. Bold entries indicate "strong" correlations.

Elements	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Ti	V	Zn
HG												
As	1	**0.563****	0.291	**0.609****	**0.570****	0.097	**0.519**	0.059	**0.776****	0.439*	–0.160	0.189
Cd		1	0.229	0.319	0.435*	0.054	0.262	0.280	**0.526****	0.270	0.166	0.228
Co			1	**0.571****	0.407*	–0.229	0.090	0.362	0.377	**0.526****	**0.549****	–0.123
Cr				1	0.386	–0.234	**0.665***	0.340	**0.660****	0.470*	0.120	–0.156
Cu					1	0.159	0.269	0.119	0.377	**0.510****	0.059	0.272
Fe						1	**0.768****	**–0.523***	–0.106	0.109	–0.393*	**0.949****
Mn							1	0.141	**0.920****	0.307	0.010	**0.748****
Ni								1	0.173	–0.116	**0.790****	–0.348
Pb									1	0.366	–0.048	0.059
Ti										1	–0.065	0.091
V											1	–0.204
ZWY												
As	1	**0.670****	0.336	**0.598****	0.373*	–0.033	0.525*	0.267	**0.860****	**0.597****	0.200	–0.065
Cd		1	0.304	**0.533****	**0.603****	0.000	**0.607****	0.314	**0.719****	**0.517****	0.177	0.036
Co			1	**0.727****	0.056	0.015	0.414	**0.721****	0.497**	**0.740****	**0.804****	0.114
Cr				1	0.461**	–0.024	**0.892****	**0.810****	**0.778****	**0.834****	**0.598****	–0.024
Cu					1	–0.201	0.378	0.288	0.494**	0.297	0.017	–0.172
Fe						1	**0.829****	–0.158	0.087	0.139	–0.039	**0.881****
Mn							1	**0.632****	**0.769****	**0.686****	0.284	**0.620****
Ni								1	0.423*	**0.620****	**0.762****	–0.138
Pb									1	**0.768****	0.354*	0.072
Ti										1	**0.583****	0.134
V											1	–0.054

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 4. Anthropogenic sources of heavy metals in atmospheric particulate matter.

Heavy metal	Sources	References
As	Coal combustion	(Tian *et al*., 2010)
	Smelting furnace	(Yang *et al*., 2003)
Cd	Steel, plastics and pigments production	(Tian *et al*., 2010)
	Tire wearing	(Hjortenkrans *et al*., 2007)
Cr	Coal and oil combustion	(Tian *et al*., 2010)
	Rubber tire wear and vehicle emission(as an active agent in catalytic converters)	(Galvagno *et al*., 2002; Pastuszka *et al*., 2010)
Cu	Smelting furnace burning	(Yang *et al*., 2003)
	Vehicle emission(diesel combustion and brake lining wear)	(Weckwerth, 2001; Manoli *et al*., 2002; Xia and Gao, 2011)
	Coal combustion	(Thurston and Spengler, 1985)
Mn	Steel smelting	(Querol *et al*., 2006)
	Coal combustion	(Deng *et al*., 2014)
Ni	Petroleum and coal combustion	(Cercasov *et al*., 1998; Tian *et al*., 2012)
	Production and recycling of nickel–cadmium batteries	(Morselli *et al*., 2003)
Pb	Steel, plastics and pigments production	(Li *et al*., 2012)
	Coal combustion	(Zhang *et al*., 2009)
	Lead gasoline	(Yang *et al*., 2003)
	Waste incineration	(Zhang *et al*., 2002)
V	Mining and smelting of vanadium	(Hope, 1997)
	Oil combustion	(Cercasov *et al*., 1998)
Zn	Steel smelting	(Querol *et al*., 2006)
	Burning of incinerators, coal-fired boiler	(Thurston and Spengler, 1985; Yang *et al*., 2003)
	Waste incineration	(Deng *et al*., 2006)
	Vehicle emission (gasoline engine emissions and tire wearing)	(Salvador *et al*., 2004; Fang *et al*., 2006)

Table 5. Principle component analysis result of heavy metals concentrations in PM_{10} and $PM_{2.5}$ particles at HG site.

	Variables							
	PM_{10}				$PM_{2.5}$			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
As	**0.918**	0.103			**0.885**	0.105		
Cd	**0.695**	0.177	0.317		**0.569**	0.184	0.242	0.313
Co			**0.788**	0.205			0.402	**0.729**
Cr	**0.773**		0.497		**0.765**			0.388
Cu				**0.978**	**0.641**			0.104
Fe		**0.990**				**0.960**		
Mn	0.171	**0.951**			**0.551**	**0.729**		
Ni	**0.580**		**0.559**	0.299	0.135		**0.852**	0.204
Pb	**0.943**				**0.902**			
Ti	0.297	0.175	**0.798**		0.124	0.112		**0.954**
V	0.432		**0.672**				**0.930**	
Zn		**0.940**				**0.971**		
Eigenvalues	3.470	3.018	2.405	1.115	3.280	2.558	1.969	1.792
Proportion of variance (%)	28.920	25.148	20.042	9.293	27.335	21.315	16.410	14.936
Cumulative (%)	28.920	54.067	74.109	83.402	27.335	48.651	65.061	79.997

Table 6. Principle component analysis result of heavy metals concentrations in PM_{10} and $PM_{2.5}$ particles at ZWY site.

	Variables						
	PM_{10}				$PM_{2.5}$		
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3
As		**0.880**				**0.946**	
Cd	0.118	**0.838**				**0.601**	**0.638**
Co	**0.722**		0.385				
Cr	**0.805**	**0.526**			**0.867**	0.271	0.445
Cu	0.137	**0.593**			**0.680**	0.463	**0.940**
Fe				**0.978**		0.155	0.374
Mn	0.125	0.159	**0.920**		**0.533**	**0.705**	**0.500**
Ni	**0.898**	0.222			**0.595**	**0.523**	0.326
Pb	0.329	**0.872**			**0.852**		0.356
Ti	**0.774**	0.457	0.106	0.177	0.215	**0.858**	0.328
V	**0.825**				**0.559**	**0.600**	
Zn			**0.867**	0.267	**0.846**		**0.737**
Eigenvalues	3.493	3.210	2.007	1.146	3.793	3.613	2.804
Proportion of variance (%)	29.105	26.753	16.722	9.548	31.611	30.110	23.369
Cumulative (%)	29.105	55.858	72.580	82.128	31.611	61.721	85.090

site. Fe was found to be the dominated metal in PM_{10} and $PM_{2.5}$ and contributed significantly to the total detected metal mass loading ranges from 50%–76% at the two sampling sites. The concentrations of all measured heavy metals in HG were 1–3.6 times higher than those measured in ZWY. Fe-Mn-Zn had the strong Pearson's correlations in HG site but the correlations in ZWY (especially in PM_{10}) were weak. Fe, Zn and Mn were regarded as the marker elements of iron and steel production emission along with Cr and Pb. Compared with some industry sites in previous studies, the concentrations of steel-related elements (Fe, Zn, Mn) in this work were extremely higher than those areas where the sampling sites were also influenced by steel production activities, such as Spain and Australia. Considering the heavy pollution in industry zone, the health risk of the atmospheric heavy metals in the neighboring residential area should be paid attention. The ratios of $PM_{2.5}$ to PM_{10} of heavy metals concentrations for Mn, Co and Ti were lower than 0.5 or less. It was suggested that these elements almost combined with coarse particles, which mainly contributed by crust or road fugitive dust. And the element As, Pb and Zn mainly exist in fine particulate matter.

The EFs results showed the most enrichment heavy metals were Cd, Zn, Pb, Cu, As (almost all > 100) and Ni, Cr in both particle sizes. The results suggested that these heavy metals are from anthropogenic origins. Besides, Co, Fe and Mn with EF values below 10 reveals the mixed anthropogenic and soil/road fugitive dust origins. PCA results suggested soil dust, the mixed sources of vehicle emission and road re-suspension dust had been identified as the possible sources in HG site along with the steel dust (including coal combustion of coal-fired power plant, coke making process and steel making emission). Moreover, steel

dust from atmospheric transportation, vehicle emission and road re-suspension dust, coal combustion and soil dust were found as the potential sources for ZWY. In addition to the HG site, the steel dust was also identified as one source of atmospheric heavy metals in the background site (ZWY), which means the steel dust has influence on the whole study area.

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