Science of the Total Environment 517 (2015) 215–221

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Mass concentration and health risk assessment of heavy metals in size-segregated airborne particulate matter in Changsha

Xiaoting Liu [a,b], Yunbo Zhai [a,b,*], Yun Zhu [c,*], Yani Liu [a,b], Hongmei Chen [a,b], Ping Li [a,b], Chuan Peng [a,b], Bibo Xu [a,b], Caiting Li [a,b], Guangming Zeng [a,b]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control, Hunan University, Ministry of Education, Changsha 410082, PR China
[c] Office of Scientific R&D, Hunan University, Changsha 410082, PR China

HIGHLIGHTS

- Size-segregated APM was collected using an 8 Stage Non-Viable Cascade Impactor.
- Concentrations of size-segregated APM and HMs in size-segregated APM were measured.
- Health risk of HMs in APM was assessed by hazard quotient and cancer risk.
- Non-carcinogenic health effect existed in the APM.
- Cancer risks of Cd, Ni and Cr were all below the safe level.

ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form 13 February 2015
Accepted 19 February 2015
Available online 27 February 2015

Editor: P. Kassomenos

Keywords:
Size-segregated airborne particulate matter
Heavy metal
Health risk assessment

ABSTRACT

This study was performed to investigate the concentration and the health risk of heavy metals (HMs: Zn, Pb, Cd, Ni, Fe, Mn, Cr and Cu) in size-segregated airborne particulate matter (APM). APM samples were collected into 9 size fractions (>9.0 μm, 5.8–9.0 μm, 4.7–5.8 μm, 3.3–4.7 μm, 2.1–3.3 μm, 1.1–2.1 μm, 0.7–1.1 μm, 0.4–0.7 μm, <0.4 μm) by an 8 Stage Non-Viable Cascade Impactor in the campus of Hunan University in Changsha. And then 9 fractions of APM were analyzed for HMs by ICP–OES. The total size-segregated APM concentration in the campus of Hunan University ranged from 120.24 to 271.15 μg/m^3, and the concentration of HMs in APM was in the range of 38.08–13955.14 ng/m^3. The health risk of HMs in APM was evaluated by hazard quotient (HQ) and hazard index (HI) and the results showed that dermal contact and ingestion of APM were the major exposure pathways to human health. The HI values of Cd, Mn, Pb and Cr for children and Cd, Mn and Pb for adults exhibited to be higher than 1 indicating that a non-carcinogenic health effect existed in the APM of the campus of Hunan University. The carcinogenic risks of Cd, Ni and Cr were all bellow the safe value.

1. Introduction

According to China's environmental bulletin in 2013, the days with an air quality level of "excellent" take only 40% of the total in Changsha in the first season of 2014 and the primary pollutant is $PM_{2.5}$. The main pollution sources of airborne particulate matter (APM) in Changsha are automobile exhaust, industrial production, reentrainment of dust, coal burning, cooking oil fume, biomass burning and other unknown sources (Zhai et al., 2014). APM is a key marker of air quality which highly relates to human health. As it is known, the adverse influences of APM on the human body and environment usually associate with their sizes (Donaldson and MacNee, 2001; Kappos et al., 2004; Martins et al., 2004). Fine particles are easy to penetrate into lungs and stay there for a long time and then enter the blood circulation system. APM is associated with cardiovascular deaths, myocardial infarctions, ventricular fibrillation and autonomic function of the heart (Mohanraj and Azeez, 2004). The presence of chemical and biological contaminants of indoor dust might pose health effects, such as some HMs in dust including lead, cadmium, mercury and arsenic may pose carcinogenic effects (Järup, 2003; Kurt-Karakus, 2012). Otherwise the APM could exert ecological effects on vegetation and ecosystems by light absorption (Horvath, 1995) virtue of the mass loading of its chemical constituents (Grantz et al., 2003).

* Correspondence to: Y. Zhai, College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China.
* Corresponding authors.
E-mail addresses: ybzhai@hnu.edu.cn (Y. Zhai), zhuyun@hnu.edu.cn (Y. Zhu).

http://dx.doi.org/10.1016/j.scitotenv.2015.02.066
0048-9697/

Literatures about the size-segregated APM and HMs in the size-segregated APM are mainly from European countries (Brüggemann et al., 2009; Chuersuwan et al., 2008; Contini et al., 2014; Filippo et al., 2010; Pennanen et al., 2007; Scheinhardt et al., 2013) and a few from China which are all about the chemical composition of size-segregated APM (Li et al., 2012; Sun et al., 2013). Investigations about the health risk assessment of APM are even less and few of them are about the health risk assessment of size-segregated APM. Greene and Morris (2006) investigated that $PM_{2.5}$ in the Washington, DC area posed notable deleterious health risk to subpopulations. Bartoš et al. (2009) studied that polyaromatic hydrocarbons (PAHs) in the atmosphere contributed most to human health risk at the urban sites. Cao et al. (2012) found that the particle size had a significant influence on human exposure risk assessment. Du et al. (2013) assessed the health risk of Cr, Ni, Cu, Zn, Cd and Pb in road dust.

In this study, mass concentrations of size-segregated APM and HMs in the size-segregated APM were measured. Moreover, the assessment of human health risks associated with HMs in size-segregated APM was performed. The size distribution of APM is useful for controlling strategy and policy making of government department. The study results described the air quality of the campus of Hunan University Changsha city and could help the physicians, public health officials and the general public to get a better understanding about the health risks of HMs in size-segregated APM via ingestion, dermal contact and inhalation exposure. This study also provides useful information as a basis for further research on risk assessment of APM and it suggests that effective measures should be taken to control the discharge of pollutants.

2. Experiment

2.1. Sampling

Changsha is located in the south central of China and northeastern of Hunan Province (Fig. 1). It is surrounded by mountains in the south, east and west. Changsha has a subtropical humid monsoon climate. The sampling site is situated in the campus of Hunan University in Changsha (28.12° N latitude, 112.59° E longitude). It is a tourist and educational area, where it has little industrial emission but a large amount of automobiles. Additionally the sampling site is close to a bus station (about 10 m away) and there are some scattered small restaurants and construction sites around the sampling site. The sampling site is close to a four-lane road with a traffic density of approximately 5000 vehicles/day and it increases on weekends due to the large number of tourists.

Size-segregated APM was collected by an 8 Stage Non-Viable Cascade Impactor (*Westech Instrument Services Ltd*) in a building of Hunan University. Ambient gases enter the inlet cone and through the succeeding orifice stages with successively higher velocities from Stage 0 to Stage 7. And whether a particle is impacted on any given stage depends on the jet velocity of the stage and the cut-off of the previous stage. Each sampling period was performed uninterruptedly for 48 h with 9 glass-fiber filters (diameter of 81 mm, first two have open centers of 7/8 in.) on sunny days during April 13th to May 6th of 2014. 36 samples were collected during the total four periods. The sampler was operated at a constant flow rate of 28.3 l/min, and APM size ranges were: >9.0 μm, 5.8–9.0 μm, 4.7–5.8 μm, 3.3–4.7 μm, 2.1–3.3 μm, 1.1–2.1 μm, 0.7–1.1 μm, 0.4–0.7 μm, and <0.4 μm.

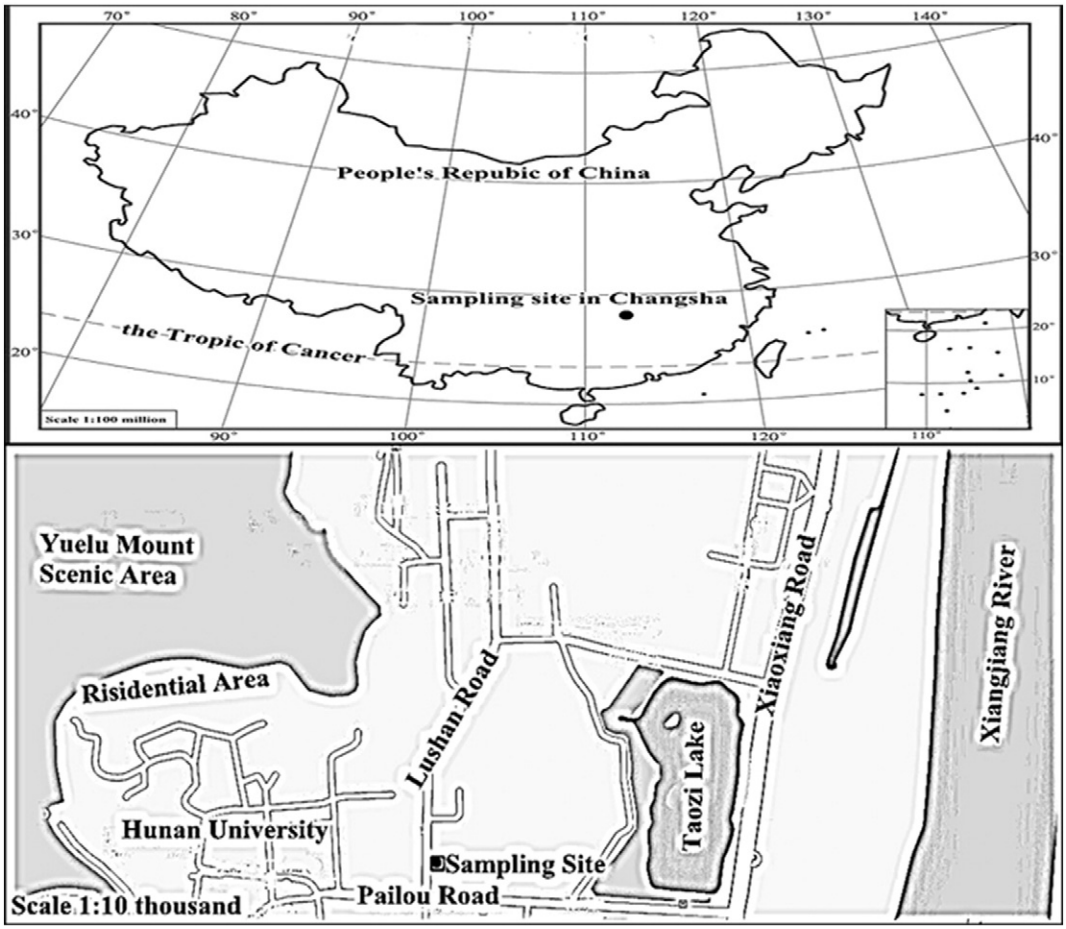

Fig. 1. The sampling site location.

Table 1
Recommended values in equations of the daily exposure dose of HMs in APM.

Parameter	Definition	Value	Reference
C	Average concentration of HMs in APM (mg/kg)		Hu et al. (2012)
IngR	Ingestion rate (mg/day)	30 (adults), 60 (children)	US EPA (2007)
EV	Events frequency (events/day)	1	US EPA (2004)
EF	Exposure frequency (days/year)	180	US EPA (2004)
ED	Exposure duration (years)	24 (adults), 6 (children)	US EPA (2004)
CF	Conversion factor	10^{-6} (kg/mg)	US EPA (2004)
BW	Body weight (kg)	70 (adults), 15 (children)	US EPA (2004)
AT	Averaging time (days)	Non-carcinogens, AT = ED * 365 days/year	US EPA (2004)
		Carcinogens, AT = 70 year * 365 days/year	Du et al. (2013)
SA	Skin surface area parameter (cm^2)	5700 (adults), 2800 (children)	US EPA (2004)
AF	Adherence factor of soil to skin (mg/cm^2/event)	0.07 (adults), 0.2 (children)	US EPA (2004)
ABS	Dermal absorption fraction	0.001	US EPA (2004)
InhR	Inhalation rate (m^3/day)	7.63 (adults), 20 (children)	US EPA (2009)
PEF	Particle emission factor (m^3/kg)	$1.36 * 10^9$	US EPA (2009)

2.2. Sample preparation

Filters were weighed before and after sampling and conditioned in a desiccator at a constant temperature (25 ± 0.5 °C) and relative humidity (50 ± 5%) for 24 h. After sampling, each filter was cut into fragments and put into an Erlenmeyer Flask with 10 ml HCl (v:v = 1:1). The mixture was heated for 30 min under the low temperature (30–50 °C). Then the HCl solution was poured into a clean flask, and the membrane filters were leached for 3 times with ultrapure water. The HCl solution and the filtrate were merged and the mixture solution was evaporated to near dryness. 10 ml HCl (v:v = 1:1) and 10 drops HNO_3 (v:v = 1:1) were added to dissolve again. The solution was transferred to a volumetric flask and the volume set to 50 ml. Solutions were subsequently stored in the centrifuge tube at 4 °C until instrumental analysis. Procedural blank only consisted of acids used for digestion of samples and was treated with the same method as APM filter samples by digesting, and then setting the volume to 50 ml with ultra pure water. The field blank was measure by a blank filter which was exposed to the same air condition for 48 h and processed simultaneously with sampling filters. And these values were subtracted from the measured sample concentration. Zn, Pb, Cd, Ni, Fe, Mn, Cr and Cu were measured using an inductively coupled plasma optical emission spectrometer (*PE ICP–OES DV2100*).

2.3. Human exposure and health risk assessment

The exposure health effect of HMs in APM to the human body is applied by the US Environmental Protection Agency (EPA) human health evaluation method (US EPA, 2001). There are three potential exposure pathways of HMs in APM: (a) ingestion, (b) dermal contact, and (c) inhalation (Ferreira-Baptista and Miguel, 2005; Kurt-Karakus, 2012; Wcisło et al., 2002). The exposure assessment evaluates the type and magnitude of potential exposures to pollutants. Besides it also provides a basic framework for health risk assessment at a site (US EPA, 1989, 2004). The average daily exposure dose of HMs in APM through ingestion (ADD_{ing}, mg/kg/day), average daily exposure dose of HMs in APM through dermal contact (ADD_{derm}, mg/kg/day) and average daily exposure dose of HMs in APM through inhalation (ADD_{inh}, mg/kg/day) were defined as follows:

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

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

$$ADD_{inh} = \frac{C \times InhR \times EF \times ED}{PEF \times BW \times AT}. \quad (3)$$

The definitions and values of parameters used in Eqs. (1)–(3) were listed in Table 1.

The hazard quotient (HQ) is used to estimate the non-carcinogenic effect of HMs in APM. A hazard index (HI) is equal to the sum of multiple-chemical or multiple-route HQ (US EPA, 2009). If the HI value greater than 1 shows that there was a chance that non-carcinogenic effects may occur, then, the greater the HI value, the higher the probability of non-carcinogenic effects (USEPA, 2001). Similarly, the exposure estimation of carcinogens is by cancer risk (CR). CR value below 1E−06 to 1E−04 typically has been judged to be acceptable or tolerable for regulatory purposes (Hu et al., 2012). Health risk characterization can be quantified by the following equations:

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

$$HI = \sum_{1}^{n} HQ_i \quad (5)$$

$$CR = ADD_{inh} \times CSF_{inh} \quad (6)$$

where ADD is the average daily exposure dose of HMs in APM through the ingestion, dermal contact and inhalation pathways (mg/kg/day), RfD is the reference dose, and CSF is the cancer slope factor $(mg/kg/day)^{-1}$. And the values of RfD and CSF used in this study were tabulated in Table 2. All the equations used in this research referred to

Table 2
Recommended values in equations of the health risk characterization of HMs in APM.

	Zn	Pb	Cd	Ni	Fe	Mn	Cr	Cu
$RfD–ADD_{ing}$	3.00E−01	3.50E−03	1.00E−03	2.00E−02	–	4.60E−02	3.00E−03	4.00E−02
$RfD–ADD_{derm}$	6.00E−02	5.25E−04	1.00E−05	2.06E−02	–	1.43E−05	2.86E−05	4.02E−02
$RfD–ADD_{inh}$	3.01E−01	3.52E−03	1.00E−03	5.40E−03	–	1.84E−03	6.00E−05	1.20E−02
$RfD–CSF_{inh}$	–	–	6.30E+00	8.40E−01	–	–	4.20E+01	–

Table 3
Size segregated APM concentration and mass percentage of each APM fraction.

Size (μm)	<0.4	0.4–0.7	0.7–1.1	1.1–2.1	2.1–3.3	3.3–4.7	4.7–5.8	5.8–9.0	>9.0	Total
April 13th	2.45	6.13	22.08	44.17	18.4	8.59	8.59	1.23	8.59	120.24
April 15th	3.68	12.27	28.22	58.89	29.45	18.4	14.72	8.59	15.95	190.17
April 28th	3.68	15.95	47.85	68.71	13.5	34.35	24.54	25.77	36.81	271.15
May 6th	20.86	25.77	41.72	57.67	24.54	20.86	17.18	8.59	17.18	234.35
Average value (μg/m^3)	7.67 ± 12.06	15.03 ± 10.41	34.97 ± 6.6	57.36 ± 10.62	21.47 ± 6.98	20.55 ± 10.09	16.26 ± 11.87	11.04 ± 8.22	19.63 ± 8.81	203.9 ± 64.9
Percentage (%)	3.56	7.11	17.16	29.41	11.56	9.6	7.82	4.68	9.11	

Table 4
Size segregated APM concentration and mass percentage of each APM fraction.

	Zn	Pb	Cd	Ni	Fe	Mn	Cr	Cu
ng/m^3	918.67 ± 411.96	385.87 ± 189.39	209.81 ± 80.75	38.08 ± 12.60	13955.14 ± 6933.79	482.49 ± 132.25	254.44 ± 201.73	164.26 ± 21.08
%	0.45	0.21	0.1	0.02	6.84	0.24	0.12	0.08

USEPA methods and other documents (Čupr et al., 2013; Lee et al., 2006; US EPA, 2011; Wcisło et al., 2002).

3. Results and discussion

3.1. APM concentrations

As it was shown in Table 3, the total APM concentration ranged from 120.24 μg/m^3 to 271.15 μg/m^3, and the average APM concentration was 203.9 ± 64.90 μg/m^3 which was higher than the previously measured value in literature (Zhai et al., 2014) and exceeded the limit level in the National Ambient Air Quality Standards (75 μg/m^3 for total suspended particles). This was mainly because of APM in this work including both the coarse particles (diameter > 2.1 μm) and fine particles (diameter < 2.1 μm). And the relatively high mass concentration of total APM was related to the topography of Changsha which was bad for transferring and diffusing of air pollutants. Besides, the high frequency of static wind and temperature inversion in Changsha caused the pollutants hard to be diluted.

In fine particles, particularly the average $PM_{1.1–2.1}$ concentration of 57.36 ± 10.62 μg/m^3 was the highest concentration of APM that appeared in all size fractions, approximately 30% of the total APM mass as given in Table 3. The APM fraction in the size range < 2.1 μm was the dominant one in the APM mass concentration, and it accounted

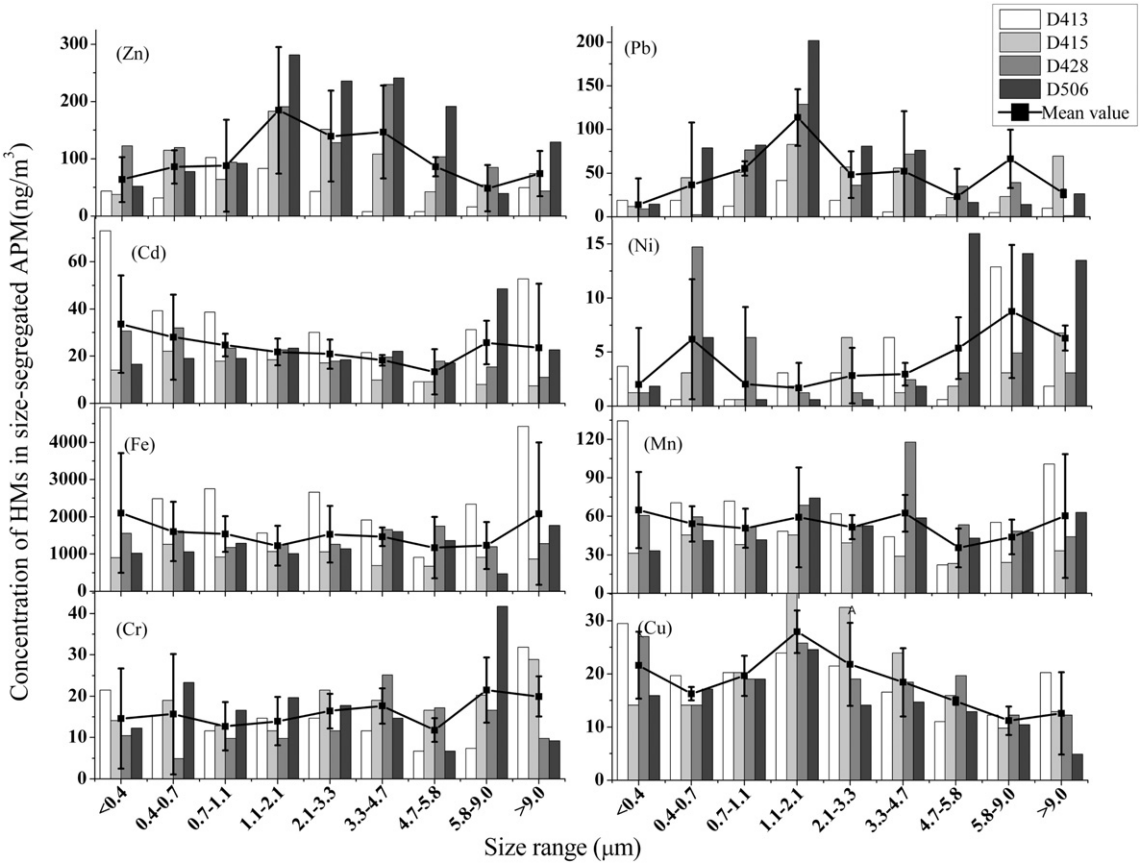

Fig. 2. Mass concentration and average concentration of HMs in size-segregated APM during sampling days.

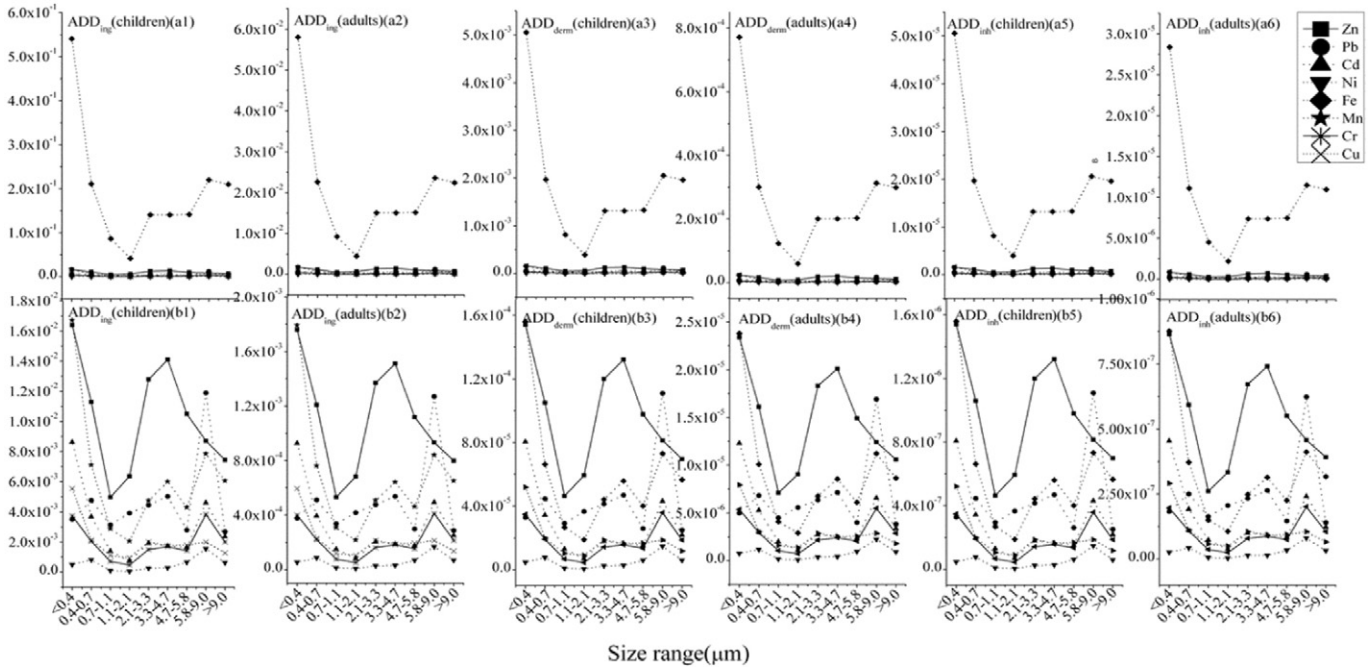

Fig. 3. (a1–a6) Complete curve chart of health risk of Fe, Zn, Mn, Pb, Cd, Cu, Cr and Ni via three exposure pathways for children and adults. (b1–b6) The magnification of health risk of Zn, Mn, Pb, Cd, Cu, Cr and Ni via three exposure pathways for children and adults.

for almost 60% of the total APM. This result was in agreement with Balachandran et al. (2000), Duarte et al. (2008) and Gnauk et al. (2008). The relatively high concentration of APM, especially the high percentage of fine particles in Changsha is about to have a greater harm to human health.

3.2. Concentrations of HMs in size-segregated APM

As shown in Table 4, mass proportion of investigated HMs accounted for about 8% of total APM during this sampling period. The concentration of HMs in size-segregated APM was relatively higher than that in previous literature (Rizzio et al., 2001) especially the concentration of Fe. Therefore, the order of total concentrations of HMs in APM was Fe > Zn > Mn > Pb > Cr > Cd > Cu > Ni. As it was presented in Table 4, the most abundant HM was Fe. The same result came from Ntziachristos et al. (2007) and Shah and Shaheen (2007), almost accounting for 85% of the measured elements in the study.

As it was presented in Fig. 2, the size distribution for Pb and Cu, they were concentrated in fine particles <2.1 μm. These HMs mainly originated from anthropogenic sources such as coal combustion and traffic emissions such as mechanical abrasion of engine, brakes and tires (Pio et al., 2013). And concentrations of Ni and Cr were higher in the coarse particles. Cd, Fe, Mn and Cr were presented a uniform distribution in both fine and coarse particles which indicated that they were contributed by anthropogenic emissions and natural sources including soil dust re-suspension and second aerosol aggregation (Brüggemann et al., 2009; Hu et al., 2008; Li et al., 2012; Samara and Voutsa, 2005). From the description of Fig. 2, the size distribution pattern varied a little with the sampling date, since the sampling location and sampling time were constant and the difference of meteorological parameters was small during the entire sampling campaign.

3.3. Average daily exposure doses and health risk assessment of HMs in size-segregated APM through ingestion, dermal contact and inhalation exposure

The average daily exposure doses of HMs in size-segregated APM via ingestion, dermal contact and inhalation exposure were shown in Fig. 3. The average daily exposure doses of HMs in APM through the three exposure pathways for both children and adults followed the variation pattern of Fe > Zn > Mn > Pb > Cd > Cu > Cr > Ni. As it was shown in Fig. 3(a1–a6), the ADD value of Fe via the three exposure pathways was much higher than other elements. And in Fig. 3(b1–b6), the ADD value of Ni was the smallest among all the elements. Comparing the ordinate value of Fig. 3(a1–a2), (a3–a4) and (a5–a6), the average daily exposure doses of HMs through ingestion, dermal contact and inhalation exposure were greater for children than for adults. And the average daily exposure doses of HMs in APM were in the following order: ingestion > dermal contact > inhalation. However, the health risks of HMs in size-segregated APM were in the order of dermal contact > ingestion > inhalation as presented in Table 4. HI_{ing}, HI_{derm}

Table 5
HI of HMs in size-segregated APM via ingestion, dermal contact and inhalation exposure.

Size range (μm)	HI_{ing} (children)	HI_{ing} (adults)	HI_{derm} (children)	HI_{derm} (adults)	HI_{inh} (children)	HI_{inh} (adults)
<0.4	1.03E+01	1.11E+00	2.03E+01	3.09E+00	2.39E−03	1.34E−03
0.4–0.7	5.38E+00	5.77E−01	8.84E+00	1.35E+00	1.19E−03	6.66E−04
0.7–1.1	2.42E+00	2.59E−01	3.46E+00	5.28E−01	4.83E−04	2.71E−04
1.1–2.1	1.97E+00	2.11E−01	2.26E+00	3.45E−01	3.63E−04	2.04E−04
2.1–3.3	3.43E+00	3.68E−01	5.46E+00	8.33E−01	7.97E−04	4.48E−04
3.3–4.7	3.46E+00	3.71E−01	6.19E+00	9.46E−01	8.88E−04	4.99E−04
4.7–5.8	2.66E+00	2.85E−01	4.83E+00	7.38E−01	6.96E−04	3.91E−04
5.8–9.0	8.42E+00	9.02E−01	1.09E+01	1.66E+00	1.79E−03	1.01E−03
>9.0	3.39E+00	3.64E−01	6.85E+00	1.05E+00	9.34E−04	5.25E−04

Table 6
Risk characterization of HMs in total APM.

	Zn	Pb	Cd	Ni	Fe	Mn	Cr	Cu
HQ_{ing} (children)	3.09E−01	1.20E+01	2.67E+01	2.44E−01	–	1.25E+00	4.37E−01	4.65E−01
HQ_{ing} (adults)	3.31E−02	1.29E+00	2.86E+00	2.62E−02	–	1.34E−01	4.68E−02	4.98E−02
HQ_{derm} (children)	1.44E−02	7.49E−01	2.49E+01	2.22E−03	–	3.76E+01	5.71E+00	4.32E−03
HQ_{derm} (adults)	2.20E−03	1.14E−01	3.81E+00	3.38E−04	–	5.74E+00	8.71E−01	6.59E−04
HQ_{inh} (children)	2.88E−05	1.12E−03	2.50E−03	8.46E−05	–	2.93E−03	2.72E−03	1.45E−04
HQ_{inh} (adults)	1.62E−05	6.29E−04	1.40E−03	4.75E−05	–	1.64E−03	1.53E−03	8.14E−05
HI (children)	3.23E−01	1.28E+01	5.17E+01	2.47E−01	–	3.89E+01	6.15E+00	4.69E−01
HI (adults)	3.53E−02	1.40E+00	6.67E+00	2.66E−02	–	5.88E+00	9.19E−01	5.06E−02
CR (children)	–	–	1.35E−06	3.29E−08	–	–	5.88E−06	–
CR (adults)	–	–	3.03E−06	7.39E−08	–	–	1.32E−05	–

and HI_{inh} in Table 5 were the sums of calculated HQs of all the elements in each size. As it was shown in Fig. 3 and Table 5, the smallest size possessed the greatest ADD value for all the elements which meant that the fine particles could present a greater health hazard. This result indicated that exposure health risk mainly came from dermal contact and ingestion for both children and adults (Chang et al., 2009). HIs of HMs through ingestion and dermal contact of children were all greater than 1 which means that the health risk of these HMs in APM had a non-carcinogenic effect to the health of children. In general, the health risk of the HMs in size-segregated APM increased when the size of APM decreased in the size range <2.1 μm. We can conclude that in fine particles the smaller the particle size, the greater the harm to human health.

The US EPA has not established a RfD for the element Fe so that the HQ and HI values for Fe were not available in this study as it was provided in Table 6. HQ_{ing}, HQ_{derm} and HQ_{ing} here were the sums of calculated HQs in all size ranges. HI was the sum of HQ_{ing}, HQ_{derm} and HQ_{ing} and meant the total non-carcinogenic effects for a single element (Du et al., 2013). HQ_{ing} and HQ_{derm} values for adults and children were following the order of Cd > Pb > Mn > Cr > Cu > Zn > Ni and Mn > Cd > Cr > Pb > Zn > Cu > Ni. HQ_{inh} values for adults and children were in the order of Mn > Cr > Cd > Pb > Cu > Ni > Zn and they were all lower than 3.00E−03. Therefore, the major contributions for the HI value were HQ_{ing} and HQ_{derm}. In terms of the HI value for both the children and adults, it decreased in the order of Cd > Mn > Pb > Cr > Cu > Zn > Ni. The HI values of Cd, Mn, Pb and Cr for children and Cd, Mn and Pb for adults exhibited to be higher than 1 which indicated that there may be concern for potential non-carcinogenic effects. The HI values of Cu, Zn and Ni for children and Cr, Cu, Zn and Ni for adults were less than 1 showing that no chronic risks are likely to occur.

The cancer risk for Cd, Ni and Cr was calculated by the average daily exposure doses of the inhalation pathway for these elements were known human carcinogens and there was a lack of CSFs for the ingestion and dermal contact exposure pathways. Cancer risks of the analyzed three elements were in Table 6 and followed the order of Cr > Cd > Ni. And the cancer risks of Cr, Cd and Ni were all below the acceptable level (10^{-6}–10^{-4}), indicating that carcinogenic risks of Cd, Ni and Cr in size-segregated APM can be negligible in Changsha.

4. Conclusions

Size-segregated APM samples were collected by an 8 Stage Non-Viable Cascade Impactor in the campus of Hunan University in Changsha. The mass concentration of size-segregated APM and HMs in size-segregated APM were measured. These were significant information for research of air condition in a suburb area in Changsha. Otherwise, the health risk of HMs in size-segregated APM was investigated by calculating the HQ and CR values of HMs which indicated that the potential non-carcinogenic risk existed in the size-segregated APM and the carcinogenic effect of Cd, Ni and Cr in size-segregated APM could be negligible.

The limitations of this paper are the small number of APM samples and simplex analysis of elemental compositions of APM. Growing concern of the public on the health risk of APM makes it necessary to get a more overall research on APM composition such as organic carbon (OC), elemental carbon (EC), PAHs and water soluble ions in size-segregated APM. Besides, the research of heath risk assessment of HMs in APM should be improved in the future.

Acknowledgments

This work was supported by the Program for New Century Excellent Talents in University (NCET-12-0169), the Scientific and Technological Project of Hunan Province in China (2013FJ4040), the Scientific Research Foundation for Returned Scholars and the Students Innovation Training Project (SIT) of Hunan University.

References

Balachandran, S., Meena, B.R., Khillare, P.S., 2000. Particle size distribution and its elemental composition in the ambient air of Delhi. Environ. Int. 26, 49–54.
Bartoš, T., Čupr, P., Klánová, J., Holoubek, I., 2009. Which compounds contribute most to elevated airborne exposure and corresponding health risk s in the Western Balkans? Environ. Int. 35, 1066–1071.
Brüggemann, E., Gerwig, H., Gnauk, T., Müller, K., Herrmann, H., 2009. Influence of seasons, air mass origin and day of the week on size-segregated chemical composition of aerosol particles at a kerbside. Atmos. Environ. 43, 2456–2463.
Cao, Z.G., Yu, G., Chen, Y.S., Cao, Q.M., Fiedler, H., Deng, S.B., Huang, J., Wang, B., 2012. Particle size: a missing factor in risk assessment of human exposure to toxic chemicals in settled indoor dust. Environ. Int. 49, 24–30.
Chang, J., Liu, M., Li, X.H., Lin, X., Wang, L.L., Gao, L., 2009. Primary research on health risk assessment of heavy metals in road dust of Shanghai China. Environ. Sci. 29 (5), 548–554.
Chuersuwan, N., Nimrat, S., Lekphet, S., Kerdkumrai, T., 2008. Levels and major sources of $PM_{2.5}$ and PM_{10} in Bangkok Metropolitan Region. Environ. Int. 34, 671–677.
Contini, D., Cesari, D., Genga, A., Siciliano, M., Ielpo, P., Guascito, M.R., Conte, M., 2014. Source apportionment of size-segregated atmospheric particles based on the major water-soluble components in Lecce (Italy). Sci. Total Environ. 472, 248–261.
Čupr, P., Flegrová, Z., Franců, J., Landlová, L., Klánová, J., 2013. Mineralogical, chemical and toxicological characterization of urban air particles. Environ. Int. 54, 26–34.
Donaldson, K., MacNee, W., 2001. Mini-review: potential mechanisms of adverse pulmonary and cardiovascular effects of particulate air pollution (PM_{10}). Int. J. Hyg. Environ. Health 203, 411–415.
Du, Y.R., Gao, B., Zhou, H.D., Ju, X.X., Hao, H., Yin, S.H., 2013. Health risk assessment of heavy metals in road dusts in urban parks of Beijing, China. Procedia Environ. Sci. 18, 299–309.
Duarte, R.M.B.O., Mieiro, C.L., Penetra, A., Pio, C.A., Duarte, A.C., 2008. Carbonaceous materials in size-segregated atmospheric aerosols from urban and coastal-rural areas at the Western European Coast. Atmos. Res. 90, 253–263.
Ferreira-Baptista, L., Miguel, E.D., 2005. Geochemistry and risk assessment of street dust in Luanda, Angola: a tropical urban environment. Atmos. Environ. 39, 4501–4512.
Filippo, P.D., Riccardi, C., Pomata, D., Buiarelli, F., 2010. Concentrations of PAHs, and nitro- and methyl-derivatives associated with a size-segregated urban aerosol. Atmos. Environ. 44, 2742–2749.
Gnauk, T., Müller, K., Pinxteren, D., He, L.Y., Niu, Y.W., Hu, M., Herrmann, H., 2008. Size-segregated particulate chemical composition in Xinken, Pearl River Delta, China: OC/EC and organic compounds. Atmos. Environ. 42, 6296–6309.
Grantz, D.A., Garner, J.H.B., Johnson, D.W., 2003. Ecological effects of particulate matter. Environ. Int. 29, 213–239.
Greene, N.A., Morris, V.R., 2006. Assessment of public health risks associated with atmospheric exposure to $PM_{2.5}$ in Washington, DC, USA. Int. J. Environ. Res. Public Health 3 (1), 86–97.
Horvath, H., 1995. Size segregated light absorption coefficient of the atmospheric aerosol. Atmos. Environ. 29 (8), 875–883.
Hu, X.M., Wang, L.P., Bi, J.H., 2008. Research on the heavy metal pollution in city atmosphere. J. Anhui Agric. Sci. 36 (1), 302–303.

Hu, X., Zhang, Y., Ding, Z.H., Wang, T.J., Lian, H.Z., Sun, Y.Y., Wu, J.C., 2012. Bioaccessibility and health risk of arsenic and heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn and Mn) in TSP and PM2.5 in Nanjing, China. Atmos. Environ. 57, 146–152.
Järup, L., 2003. Hazards of heavy metal contamination. Br. Med. Bull. 68, 167–182.
Kappos, A.D., Bruckmann, P., Eikmann, T., Englert, N., Heinrich, U., Höppe, P., Koch, E., Krause, G.H.M., Kreyling, W., Rauchfuss, K., Schulz-Klemp, P.R.V., Thiel, W.R., Wichmann, H.E., 2004. Report: the German view: health effects of particles in ambient air. Int. J. Hyg. Environ. Health 203, 399–407.
Kurt-Karakus, P.B., 2012. Determination of heavy metals in indoor dust from Istanbul, Turkey: estimation of the health risk. Environ. Int. 50, 47–55.
Lee, S.W., Lee, B.T., Kim, J.Y., Kim, K.W., Lee, J.S., 2006. Human risk assessment for heavy metals and as contamination in the abandoned metal mine areas, Korea. Environ. Monit. Assess. 119, 233–244.
Li, X.R., Wang, L.L., Wang, Y.S., Wen, T.X., Yang, Y.J., Zhao, Y.N., Wang, Y.F., 2012. Chemical composition and size distribution of airborne particulate matters in Beijing during the 2008 Olympics. Atmos. Environ. 50, 278–286.
Martins, M.C.H., Fatigati, F.L., Véspoli, T.C., Martins, L.C., Pereira, L.A.A., Martins, M.A., Saldiva, P.H.N., Braga, A.L.F., 2004. Research report: influence of socioeconomic conditions on air pollution adverse health effects in elderly people: an analysis of six regions in São Paulo, Brazil. J. Epidemiol. Community Health 58, 41–46.
Mohanraj, R., Azeez, P.A., 2004. Health effects of airborne particulate matter and the Indian scenario. Curr. Sci. India 87 (6), 741–748.
Ntziachristos, L., Ning, Z., Geller, M.D., Sheesley, R.J., Schauer, J.J., Sioutas, C., 2007. Fine, ultrafine and nanoparticle trace element compositions near a major freeway with a high heavy-duty diesel fraction. Atmos. Environ. 41, 5684–5696.
Pennanen, A.S., Sillanpää, M., Hillamo, R., Quass, U., John, A.C., Branis, M., Hůnová, I., Meliefste, K., Janssen, N.A.H., Koskentalo, T., Castaño-Vinyals, G., Bouso, L., Chalbot, M.C., Kavouras, I.G., Salonen, R.O., 2007. Performance of a high-volume cascade impactor in six European urban environments: mass measurement and chemical characterization of size-segregated particulate samples. Sci. Total Environ. 374, 297–310.
Pio, C., Mirante, F., Oliveira, C., Matos, M., Caseiro, A., Oliveira, C., Querol, X., Alves, C., Martins, N., Cerqueira, M., Camões, F., Silva, H., Plana, F., 2013. Size-segregated chemical composition of aerosol emissions in an urban road tunnel in Portugal. Atmos. Environ. 71, 15–25.
Rizzio, E., Bergamaschi, L., Valcuvia, M.G., Profumo, A., Gallorini, M., 2001. Trace elements determination in lichens and in the airborne particulate matter for the evaluation of the atmospheric pollution in a region of northern Italy. Environ. Int. 26, 543–549.
Samara, C., Voutsa, D., 2005. Size distribution of airborne particulate matter and associated heavy metals in the roadside environment. Chemosphere 59, 1197–1206.
Scheinhardt, S., Müller, K., Spindler, G., Herrmann, H., 2013. Complexation of trace metals in size-segregated aerosol particles at nine sites in Germany. Atmos. Environ. 74, 102–109.
Shah, M.H., Shaheen, N., 2007. Statistical analysis of atmospheric trace metals and particulate fractions in Islamabad, Pakistan. J. Hazard. Mater. 147, 759–767.
Sun, Z.Q., Mu, Y.J., Liu, Y.J., Shao, L.Y., 2013. A comparison study on airborne particles during haze days and non-haze days in Beijing. Sci. Total Environ. 456–7, 1–8.
U.S. Environmental Protection Agency, 1989. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual. Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington, D.C., p. 20450.
U.S. Environmental Protection Agency, 2001. Risk Assessment Guidance for Superfund: Volume III — Part A, Process for Conducting Probabilistic Risk Assessment Office of Emergency and Remedial Response. U.S. Environmental Protection Agency, Washington, D.C., p. 20460.
U.S. Environmental Protection Agency, 2004. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment). Office of Superfund Remediation and Technology Innovation, Washington, D.C.
U.S. Environmental Protection Agency, 2007. Guidance for Evaluating the Oral Bioavailability of Metals in Soils for Use in Human Health Risk Assessment.
U.S. Environmental Protection Agency, 2009. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part F, Supplemental Guidance for Inhalation Risk Assessment). Office of Superfund Remediation and Technology Innovation, Washington, D.C.
U.S. Environmental Protection Agency, 2011. Exposure Factors Handbook: 2011 Edition. National Center for Environmental Assessment, Washington, D.C. (EPA/600/R-09/052F. Available from the National Technical Information Service, Springfield, VA, and online at http://www.epa.gov/ncea/efh).
Wcisło, E., Ioven, D., Kucharski, R., Szdzuj, J., 2002. Human health risk assessment case study: an abandoned metal smelter site in Poland. Chemosphere 47, 507–515.
Zhai, Y.B., Liu, X.T., Chen, H.M., Xu, B.B., Zhu, L., Li, C.T., Zeng, G.M., 2014. Source identification and potential ecological risk assessment of heavy metals in $PM_{2.5}$ from Changsha. Sci. Total Environ. 493, 109–115.